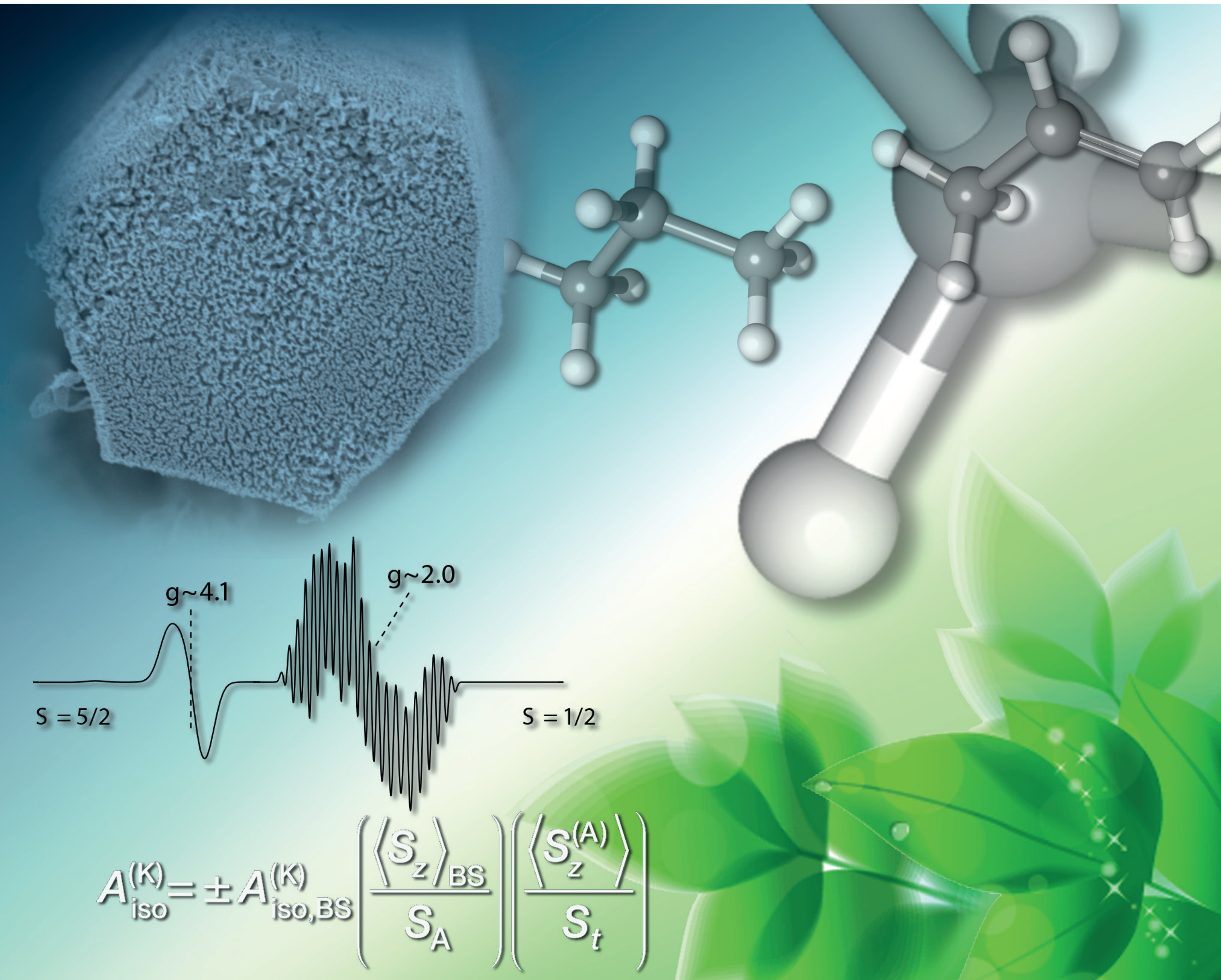
MAX PLANCK SOCIETY

MAX-PLANCK-INSTITUT FÜR CHEMISCHE ENERGIEKONVERSION

Scientific Report 2010 – 2013



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Scientific Report 2010 – 2013

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Historical background

The MPI CEC is being developed out of the *MPI für Bioanorganische Chemie* that followed the *MPI für Strahlenchemie*. The formal re-dedication of the *MPI für Bioanorganische Chemie* into the *MPI für Chemische Energiekonversion* (MPI CEC) was the consequence of two lines of decisions with their own history. Following decisions in 2003 about the future of the *MPI für Bioanorganische Chemie* a structure commission was put in action to find a new dedication. This dedication should strengthen chemistry within the MPG and should avoid duplications of activities typical for chemistry departments at German universities. The other line of decisions began in 2007 with a commission looking into the engagement of the MPG in energy science. After an initial critical view on this issue with its many applied and political implications it was decided in 2011 that the collaborative effort of Max Planck Institutes which had been initiated in 2007 would be insufficient to cope with the substantial fundamental challenges of chemical energy conversion as pre-requisite for post-fossil energy systems. Complementing the activities in the physics of energy science culminating in the Max Planck Institute for Plasma Physics (IPP) for fusion science it was decided to engage also in the chemical aspects of energy science with an MPI for chemical energy conversion. The substantial commitment of the State of North Rhine-Westphalia (NRW) made it possible to join the two lines of decisions and to transform the *MPI für Bioanorganische Chemie* in July 2012 into the *MPI for chemical energy conversion (MPI CEC).*

Definition of the field of activity

Chemical energy conversion designates a family of large-scale chemical reactions that are carried out not to obtain a specific product of the reaction but rather to store or retrieve free energy. Three families of reactions may be considered:

a) Oxidation reactions of energy carriers with molecular oxygen are used to obtain free energy usually as thermal energy that may be converted into mechanical and electrical energy. Burning of fossil fuels or of biomass are the prototypical examples.
b) Hydrogenation of molecules such as N_2 and CO_2 can be used to store free energy via molecular hydrogen as primary energy carrier. Ammonia synthesis, power-to-gas and methanol synthesis are examples of such reactions.
c) Reversible redox reactions of an energy carrier can be used in accumulators (often called wrongly batteries) to store and retrieve electrical energy.

Chemical energy conversion can be done in sequences of reactions or may be combined with physical processes of charge separation using solar energy. The photo-electrochemical conversion of CO_2 and water to solar fuels in artificial leaf systems is a prototypical example of a combined process. Such approaches would be close to the scientific heritage of the MPI CEC where understanding of biological energy conversion in real leaves was a key activity. Due to its model function the understanding of structure and functions in biological energy conversion processes is still an ongoing activity in the MPI CEC.

Mission of the MPI CEC

The mission of the new institute is to generate the basic understanding of chemical energy conversion processes. This comprises mechanistic and kinetic understanding of individual reactions, the generation and use of adequate theoretical and experimental methodologies ("toolboxes") and the identification of synthetic pathways to models and materials required for these reactions.

The common scientific concept of all energy conversion reactions is catalysis as the science of controlling energy barriers and reaction pathways. Catalysis is a widely practiced group of methods in chemical industry as well as in biological objects. Despite its common function catalysis has divided itself into three disciplines of chemistry namely homogeneous, biological and heterogeneous catalysis. In each area the insight and predictive understanding and the ability to synthesize suitable catalysts are developed with different foci and methodologies. Given the enormous scale at which chemical energy conversion has to be carried out as a basis of post-fossil energy supply systems it is essential that we rejoin the concepts of the different forms of catalysis and find a suite of best solutions for different applications in differing systemic environments of such energy systems. It is thus a core objective of the MPI CEC to unify the concepts in catalysis. This shall be done by learning the key insights and operation principles in each branch of catalysis in order to arrive at a common understanding of how active sites are generated and work in a given reaction. The MPI CEC will thus retain activities from the bioinorganic past and combine it with new aspects of molecular and interfacial catalysis.

In all disciplines of catalysis it became clear over the last decades that the interplay of theory with dedicated functional analysis and with target synthesis is the required path to move forward the empirical catalyst development into a rational knowledge-based approach respecting the unity between reactants, catalyst and reactor. The MPI CEC will thus practice a close cooperation between theory and experiment both for molecular and interfacial catalysis. The inherited strength of the *MPI für Bioanorganische Chemie* in inventing and building dedicated in-situ analytical instrumentation will be continued and complemented by other methodical competencies. Synchrotron-based spectroscopy at low and high energies, advanced electron microscopy including electron energy loss spectroscopy for chemical reactions ("chemical electron microscopy") and additional methods of spectro-electrochemistry dedicated to molecular and interfacial systems are currently implemented and practiced.

Initial field of activity and structure of the MPI CEC

In order to generate visible impact of the new MPI it is essential to focus the activities to a small number of energy conversion reactions. This is not without challenges in the broader mission of the Max Planck Society that is fully dedicated to the advancement of basic science and requires thus utmost flexibility in the activities of their institutes. The area of activity is initially set to a strong focus in order to ascertain the necessary depth of analysis essential for understanding key reactions of energy conversion. These reactions are "conceptually simple" but are far from being mastered at a level of performance that they could be put into world-scale operation.

For chemical energy conversion reactions it is essential also for an institute working in fundamentals that its activities are scaled to an extent that the validity of the concepts can be verified. For energy conversion reactions this requires the dimension of technology transfer: we need a mechanistic understanding that is cast into micro-kinetic models requiring verification in macro-kinetics. For that we need concepts of synthesizing model systems as well as performance catalysts and we need reactor designs and operation schemes. Finally we need to demonstrate operation at a scale where material and energy streams are closed in order to verify that the reaction and feedback network is adequately described.

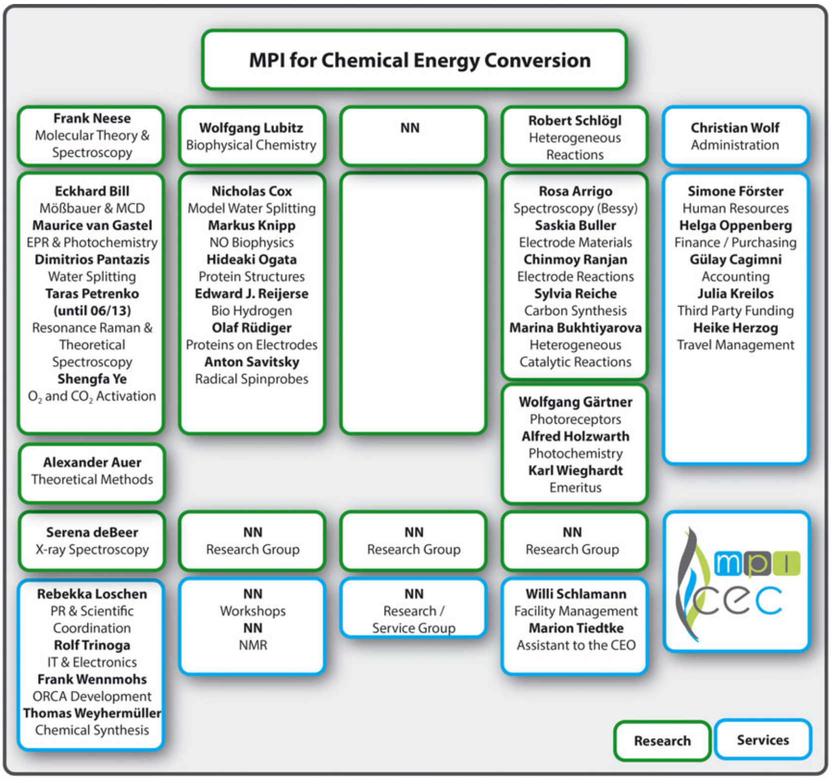

Figure 1. Organisational structure of the MPI CEC in its foundation period. The dual structure of research departments and of supporting competence groups can be seen. The institute organizes all scientific activities under the supervision of a scientific director.

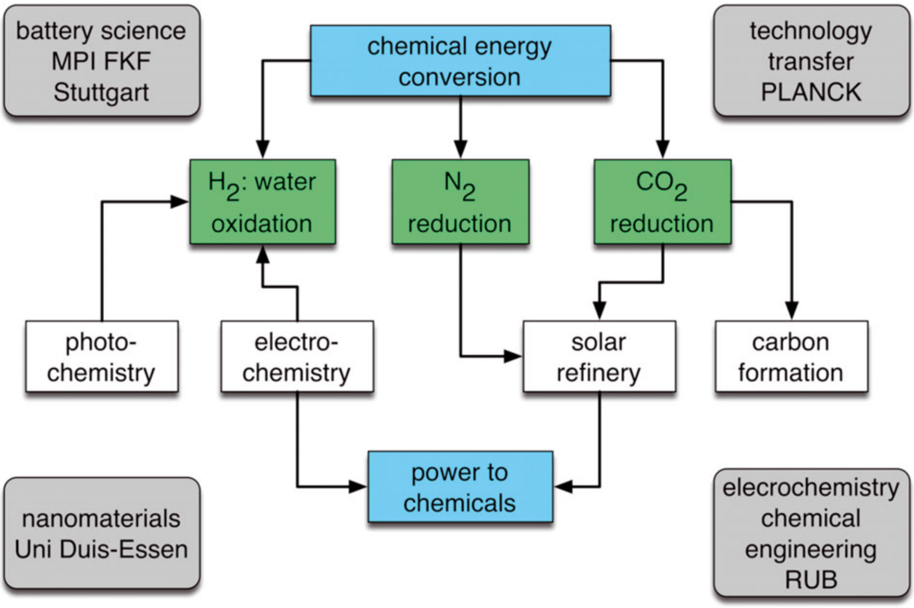

Figure 2. Key research areas of the MPI CEC and important external collaborations.

As the MPI CEC cannot perform all these tasks within its own competence we implement elements of collaboration as a functional necessity rather than as add-on activity. Such a concept is common in many areas of science but not frequently practiced in chemistry. The associated binding of activities to targets is clearly seen and requires careful planning as well as clear exit scenarios in the project definitions in order to maintain the "Max Planck flexibility". This holds not for core competences in the methodical area where we aim for long-term commitments in order to achieve and maintain leadership positions. For that reason the MPI has adopted an internal structure where competence and service groups support the activities of the departments. The Institute considers this organisational flexibility as a major advantage that it will use to its advantage in attracting leading scientists in this highly competitive field. The present organisation is indicated in Figure 1.

The figure reveals that the MPI CEC will have four departments being active in aspects of chemical energy conversion. We aim at two departments dealing with molecular chemistry and possibly photochemistry, one department for electrochemistry and one department for interfacial reactions. The biological research activities will be phased out, whereas research on molecular catalysis will remain and strengthened in the future development. The research areas pursued in the present initiation phase of the MPI CEC are illustrated in Figure 2.

The three departments operating at present have initiated substantial collaborative efforts along the path of unifying concepts and disciplines in catalysis for energy conversion. All departments are active in building the methodical infrastructure required. Details can be found in the individual reports of the departments.

It is pointed out that the *Kollegium* acts in a joint collaborative spirit and constantly builds upon measures to initiate and strengthen the inter-departmental scientific contacts. Selected important external collaborations are indicated and will be described below.

The desired target structure of the MPI CEC can only be realized once sufficient space will be available for this operation exceeding substantially the size of the former *MPI für Bioanorganische Chemie*. Substantial efforts have been made to buy sufficient land in the immediate vicinity of the present building of the MPI CEC and to initiate the building up of some 5000 m^2 new laboratory and office space to create the institute. The building operation is currently at the stage of architectural concepts and simultaneously in the process of obtaining the building permit on land dedicated for housing purposes. As a matter of course the new buildings will be erected using highest established standard of energy conservation and that experiments can be carried out for operating novel energy technologies. We have actively chosen the immediate neighbourhood to the *Max Planck Institute für Kohlenforschung (MPI KOFO)* to exploit scientific and operational synergies. In this way a "Mülheim Chemistry Campus" (MCC) will form once the MPI CEC is fully operational. We have initiated efforts for collaboration both on the level of departments and on the operational level. Initial results can be found in the reports of the departments.

The extension of the *Kollegium* is planned in the following way: In the coming two years we wish to appoint a director for electrochemistry. To this end preparatory measures have been taken. *F. Neese* and this person will carry the core responsibility to appoint two additional directors in the following 3 years replacing *W. Lubitz* and the founding director *R. Schlögl*. One precondition is that the building operation has reached a stage that the new directors can have a reliable perspective about the availability of their infrastructure. The resources necessary for the extension of the activities of the institute are allocated within the 5 year planning of the Max Planck Society. We expect this appointment process to take place in about 2016-2018.

Scientific scope of MPI CEC

The MPI CEC has analyzed [1] the basic design of post-fossil energy supply systems and finds that the interface between electrical and chemical energy is the most critical bottleneck. Figure 3 shows one realization of one network of energy supply with key components.

This simple flow chart visualizes the interface between electricity and chemical energy carriers omitting thermo-mechanical storage concepts. The primary energy carrier available from electricity is hydrogen through water splitting. This can be done by electrolysis or by combinations of electro-catalytic with photochemical or thermal methods (SOEC). Hydrogen should not be distributed to end-users.

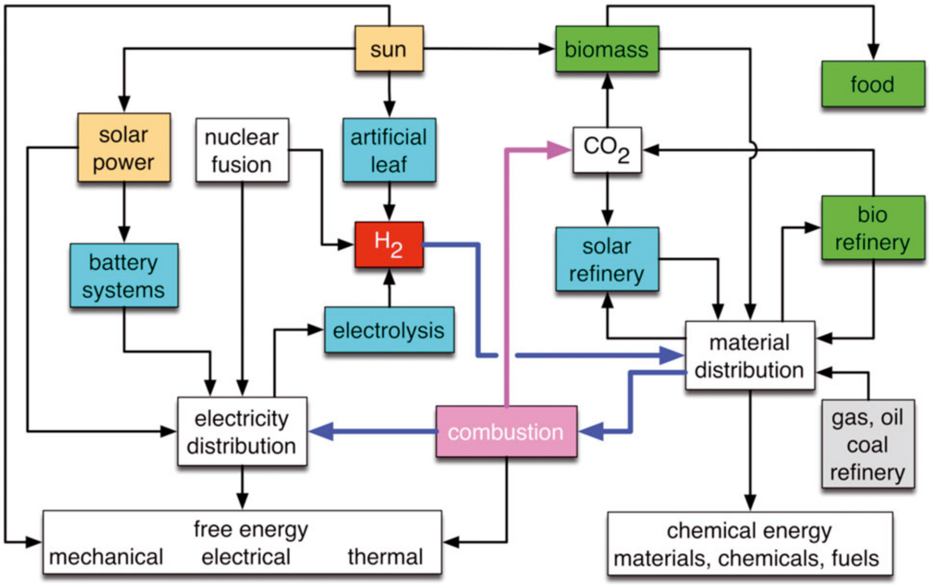

Figure 3. Network of energy supply combining renewable and fossil sources. The coloured arrows indicate the critical interface between electrical energy (left) and material energy carriers (right).

It should be used either to buffer volatile electricity generation or, together with CO_2 or N_2, as "solar fuel" produced in a solar refinery operating a set of catalytic processes for producing energy carriers that can be used by conventional end user applications. The CO_2 cycle is closed by collecting stationary large-scale sources directly or by using biomass as solar-operated CO_2 collectors.

The MPI CEC in its initial period of activity will focus on the areas indicated in blue in Figure 3. They all require chemical solutions that are not available today considering world-scale applications. Origins of shortcomings are the lack of understanding of the underlying elementary reactions as well as the lack of suitable materials that are sufficiently stable and sustainable in their supply. To this end the MPI puts a strong focus on utilizing earth-abundant elements in its material solutions. Noble metals are studied for fundamental reasons and to gain connection to many parallel activities. The substitution of noble metals in the relevant catalytic reactions is a generic key task of the institute, as this much-desired process requires deep and verified functional understanding of the role of noble metals for a rational substitution strategy. This strategy will most likely not be a "drop-in" into an existing process but will require a complete redesign of the process. For batteries where we seek understanding of the elementary interfacial reactions associated with charge separation at the electrodes we will rely on close collaboration with the department *J. Maier* in Stuttgart (see Figure 2) and on collaboration with the *Juelich Research Centre* of the *Helmholtz Association*. The artificial leaf topic representing a combination of electro-catalysis with the charge carrier separation process driven by solar light absorption will be followed with reduced priority, as many of its critical elementary reactions are identical in electrolysis and in the conversion of N_2 and

CO_2 to solar fuels in the "solar refinery". At present we prefer to establish the electrochemical competence with top priority as it forms the common basis for hydrogen generation by all chemical means representing the critical bottleneck in all renewable energy scenarios with low or zero fossil backup supply.

Collaborations

The MPI CEC sees scientific collaboration within the institute and with external partners as a key ingredient of its research strategy. This originates from the interdisciplinary character of its mission aiming at a verified understanding of processes and materials necessary for chemical energy conversion. The core internal collaboration along generic tasks is indicated in Figure 4.

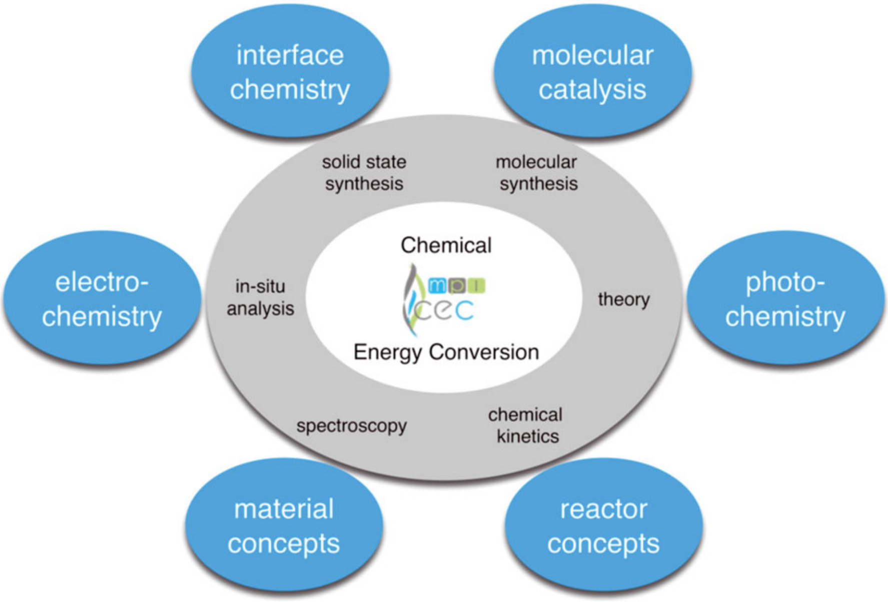

Figure 4. Research areas and competence fields within the MPI CEC in its foreseen structure. The initial team covers already several fields and is active in setting up the necessary tools and competences. The interdisciplinary research begins to bear fruits in first projects described in the departmental reports.

A second level of collaborations concerns the Max Planck Society. The origin of the MPI CEC was partly a preceding research network "ENERCHEM" targeting material science issues in chemical energy conversion. This network between several Max Planck Institutes will be re-established as MAXNET ENERGY in 2014 under the coordination of the MPI CEC. The research focus was placed on material science and process issues arising from water splitting. The neighbouring *MPI KOFO* is part of the MAXNET ENERGY (*F. Schueth*), additional collaborations exist between several departments in both institutes.

Collaboration was further initiated with the neighbouring universities. At the *Ruhr University Bochum* multiple research activities including a centre for electrochemistry initiated by the *MPI für Eisenforschung* by *M. Stratmann* and the Centre of Excellence RESOLV exist in chemical sciences with close relation to the focus of the MPI CEC. At the *University Duisburg-Essen* the research centres NETZ and ZBT deal with material and process challenges of electrochemistry and of nanoparticles for photochemical, chemical and thermoelectric applications. The MPI CEC is installing a Max-Planck research group at each university dealing with synthetic aspects of the work at the MPI CEC. In this way a close collaboration including exchange of researchers is created and the MPI CEC can extend its activities into the critically needed synthetic activities for which at present only very limited space is available. These two research groups act as anchors for multiple other collaborations in DFG-funded activities many of which originate from earlier relations with members of the universities to *W. Lubitz*, and *R. Schlögl*. *F. Neese* is connected with his former *University of Bonn*.

The MPI CEC is preparing for joint laboratories with the *Helmholtz Zentrum Berlin* and with the *Juelich Research Centre* both from the *Helmholtz Association*. With HZB we plan a laboratory for the use of synchrotron-based spectroscopy in energy science. This activity includes collaboration with universities and encompasses a total of five end stations and four beam lines all dedicated to chemical applications of NAP XPS in different sample environments. A framework agreement between Helmholtz and Max Planck Society is in place with the respective annexe being in negotiation. Details are described in the report of *R. Schlögl* for the Fritz-Haber-Institute (FHI) Berlin. The Joint Laboratory with Juelich is being negotiated around the application of solid state NMR as in-situ analytical tool. Magnetic resonance complements in an excellent fashion the in-house EPR activities. This was planned initially in the foundation concept of the MPI as competence centre to be installed. As the new institute for fundamental electrochemistry in Juelich has already started to set up infrastructure and has experienced personnel for this technique it seems adequate to combine our chemical insight and complementary in-situ capabilities with the NMR activity at Juelich to which we will contribute human resources.

In addition, a large number of bilateral collaborations exist with many research places in academia and in industry. Presently active collaborations include BASF, Bayer, University of Stanford and SLAC.

Additional activities

We are actively transferring our results into technology by initiating an open platform for technology transfer. The scientific reason for this is the feedback we obtain from partner practicing concepts and solutions at scales that are beyond the capabilities of a fundamental research institute. The MPI CEC is founding a company

(*PLANCK GmbH)* jointly with the *Fraunhofer Society* and the *State of NRW* to pursue technology transfer with industry. Major players from chemical, utility, steelmaking and electrical industry sectors have joined the activity and substantial funding is projected from the federal ministry of research for a period of 10 years. This structure was chosen to free the MPI CEC from obligations and influences coming with large industrial application projects and to get access to the application knowledge gained. Through this platform we also fulfil an obligation to make available the results of fundamental science as directly as possible to industrial path finding applications.

The MPI is further engaged in leading function in a project of the National Academies of Germany (*Leopoldina*, *acatech* and *Union der Akademien*) aiming at developing options of how to transform the German energy system into a sustainable future. In the project *ESYS* (*Energiesysteme der Zukunft*) are about 100 leading scientists from scientific disciplines as well as economists. Law experts and social sciences collaborate in eight coordinated working parties. The aim is to develop an understanding of the systemic properties of energy supply, to identify target functions and to consider external influences on the temporal evolution of energy supply.
Details can be found at: *http://www.acatech.de/de/projekte/laufende-projekte/energiesysteme-der-zukunft.html.*

The MPI CEC actively pursues the information and documentation of important developments in Germany relating to the transformation of the energy system. As competence centre we are frequently asked by scientific and societal bodies to comment on relevant issues. We wish to contribute channelling unbiased information on the transformation process into the public and to manage public expectations. To this end, the institute operates a website edited by *G. Hofmann* documenting and sometime commenting the relevant activities in politics and economy. The website SOLARIFY.eu can be found via the website of the Institute.

Supporting structures

The operating scientific support structures were activated in short time thanks to excellent scientific co-workers who were willing to take on the challenge of collaborating with other groups and departments. From the *MPI für Bioanorganische Chemie* came *R. Trinoga*, *T. Weyhermüller* and *F. Wennmohs*. From the Fritz-Haber-Institute (FHI) in Berlin came *R. Arrigo* and *M. Schuster*. The dimension of these competence groups will increase partly by an additional group for chemical reactor testing and by extension of the activities in electron microscopy and synchrotron spectroscopy involving also the transfer of infrastructure and personnel from the department of Inorganic Chemistry at FHI (see also report of FHI). This ensures together with the groups being active in the department of *W. Lubitz* the continuity of critical competence in the generic analytical methodologies required for molecular and interfacial catalysis indicated in the table.

Table: Competence groups in the MPI CEC

Group Name	Group Leader	Competence
Nanostructure	M. Willinger* (M. Schuster)	TEM, SEM, EELS, ETEM, EDX
Synchrotron Spectroscopy	A. Knop-Gericke* (R. Arrigo), S. DeBeer	NAP-XPS, NEXAFS, XAS, XES
Synthesis	T. Weyhermüller	Inorganic and metal-organic synthesis
Chemical Reactors	N.N	Heterogeneous catalysis, homogeneous catalysis
NMR	N.N	In-situ solid state NMR
Mössbauer Spectroscopy	E. Bill	Mössbauer, EPR, MCD, SQUID, Spin-Hamiltonian theory
ORCA	F. Wennmohs	Software design, High performance computing
Resonance Raman	M. van Gastel	Vibrational and magnetic resonance spectroscopy
EPR	E. Reijerse	Pulse and High-field EPR

* presently at FHI Berlin

In this way the previously developed analytical in-situ competencies originating from the *MPI für Bioanorganische Chemie*, from *MPI KOFO* and from the *FHI* will be joined forming a strong basis for future knowledge-based catalysis science. The resulting cluster of functional analysis represents a central element of the *Muelheim Chemistry Campus* supplemented by a suite of collaborations between the two MPI dealing with synthesis concepts and catalytic reactions.

The administration carrying the load of supporting the whole initiation process is most actively involved in all aspects of supporting the increasing operation of the Institute. We installed early a position for research coordination inside and outside of the new institute: *R. Loschen* is instrumental in bringing together research between different partners on the operational level. *J. Mayrhofer* coordinates the science communication to the general public. *Ch. Wolf* in addition to his function as head of administration carries responsibilities in creating a trustful and effective operational collaboration with the MPI KOFO in many technical and scientific areas including unification of the libraries, joint energy supply, analytical support, media supply. The technical operation of the building under *W. Schlamann* had to support the extensive building operations ongoing during the last years in preparation for the restructuring of the building and the installation of the departments *F. Neese* and *R. Schlögl* completed in 2013. Their excellent support is acknowledged as well as their creativity in the beginning planning process for the new buildings. It is emphasized that the workers council of the MPI CEC proactively supports the changes and gives constructive support to the multiple measures within all fields of co-operation.

References

[1] a) R. Schlögl, in *Chemical Energy Storage* (Ed.: R. Schlögl), DeGruyter, **2012**;
b) R. Schlögl, *Angew. Chem. Int. Ed.* **2011**, *50*, 6424–6426.

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Scientific Research Reports 2010 – 2013

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Director
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(since 2000)

Department of Biophysical Chemistry

The department of Biophysical Chemistry was founded in 2000 by Prof. Wolfgang Lubitz following his appointment as a director of the Max Planck Institute for Bioinorganic Chemistry, formerly Radiation Chemistry, which in 2012 was re-established as the Max Planck Institute for Chemical Energy Conversion (MPI CEC). At present there are approximately 50 scientists, technicians and administrative staff working in the department.

The department's main research objective is the characterization of metalloproteins and related biomimetic molecular models, which catalyze reactions relevant for chemical energy conversion and storage, i.e. small molecule chemistry. Two specific biological systems are of significant importance for future energy supply: i) the water oxidizing complex (WOC) of oxygenic photosynthesis; and ii) the hydrogenases that produce or convert hydrogen (Figure 1), which are briefly discussed below. We use a variety of different physical techniques to study these systems, including electrochemistry, X-ray crystallography, magnetic resonance (EPR/NMR), Mößbauer as well as optical and vibrational spectroscopy. As these systems contain transition metals a particular emphasis is placed on characterizing their magnetic properties as studied by advanced electron paramagnetic resonance (EPR) techniques. Most of the investigated systems are prepared in-house, which allows sample optimization and modification to be performed in an efficient way.

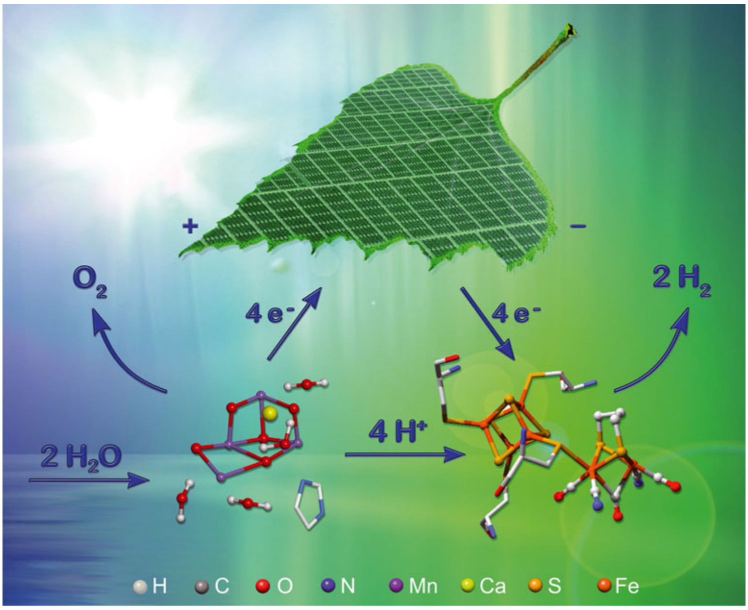


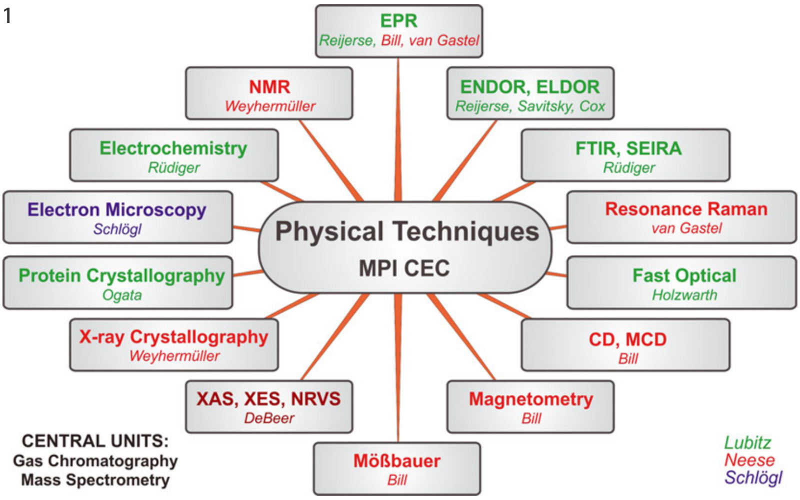
Figure 1. The artificial leaf, facilitating the light driven splitting of water into O_2 and H_2, performed by the enzymes wateroxidase and [FeFe] hydrogenase; shown are the structures of the catalytically active metal clusters determined by X-ray crystallography (PDB files 3ARC and 1HFE).

The information obtained from such spectroscopies can be combined using modern quantum chemical approaches, with the aim of resolving catalytic function at the atomic scale (co-operation with the Molecular Theory and Spectroscopy Department of Prof. Neese). In this way, insight into enzymatic water splitting and (bio)hydrogen production/consumption has been developed, providing new and important design criteria for synthetic bioinspired catalysts for energy conversion (Department Schlögl, Heterogeneous Catalysis). A summary of our recent work can be found in "Chemical Energy Storage", edited by Prof. Robert Schlögl [1], which was selected for publication in the De Gruyter 'Green' journal [1].

New Methodologies and Instrumentation

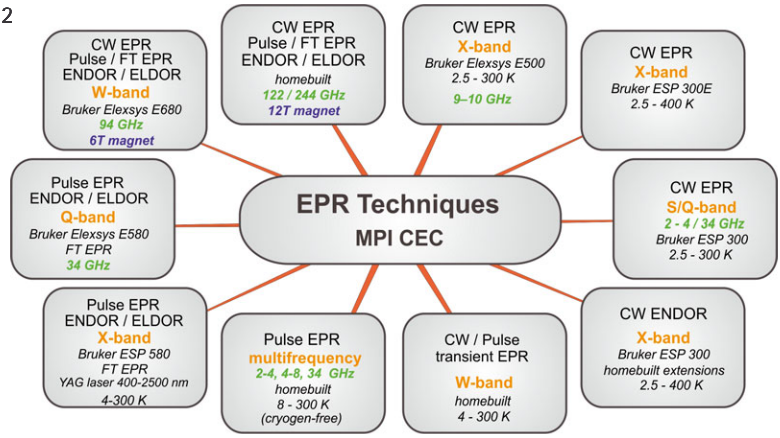
One of the central targets of our department is the development of instrumentation and its extension to new chemical systems. An overview of the techniques currently available at the institute, and used by researchers from all departments, is given in Scheme 1. We are recognized as an international center for the development of multi-frequency EPR and related spectroscopies (Scheme 2). The 10 EPR instruments currently available span the microwave frequency range from 2 to 244 GHz at fields between 0 and 12 T, and at temperatures from below 2 K to above room temperature, operating in both CW and pulse configurations. This unique EPR facility has allowed a variety of systems to be studied, far beyond the range typically accessible using standard instrumentation. As an example, modifications allowing light access for *in situ* illumination using dedicated tunable laser systems, has extended the number of light-active systems (e.g. in photosynthesis) that can be characterized using EPR techniques.

Scheme 1



In recent years several microwave resonators have been designed and developed on campus (see reports by Dr. Savitsky and Dr. Reijerse), which together with improvements in related microwave technology and data acquisition have led to a substantial increase in the sensitivity and stability of EPR measurements.

Scheme 2



This has dramatically expanded the number of chemical systems that can be characterized using magnetic resonance techniques to included: i) large protein supercomplexes with multiple paramagnetic centers; ii) fast relaxing spin systems such as transition metal complexes/materials and trappable higher spin organic radical intermediates; and iii) samples of constrained dimensions e.g. small single crystals. EPR experiments on single crystals are of particular importance; in the department we are therefore running a crystal growth laboratory (see report by H. Ogata). Specific technological improvements include:

1. Microresonators that have allowed for the first time investigations of protein single crystals with a volume consisting of only a few nanoliters.
2. High pressure equipment which allows EPR experiments to be performed at high field (W-band) up to 2.5 kbar (4 kbar peak).

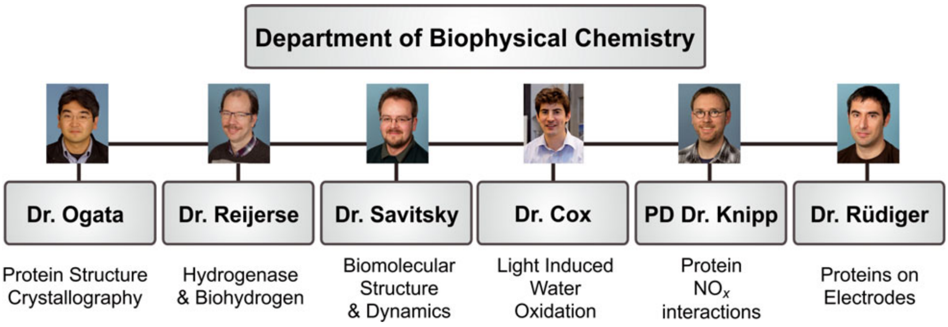
3. Chemical reactors engineered inside an EPR resonator, allowing the monitoring of heterogeneous catalysis *in situ* and in real time.

A particular emphasis has been placed on the use of double resonance techniques such as electron-nuclear double resonance (ENDOR) and electron-electron double resonance (ELDOR) at a range of microwave frequencies. These methods provide a unique window into paramagnetic systems allowing nuclear (NMR) transitions to be obtained, even for high spin magnetic nuclei including ^{55}Mn and ^{17}O, both key components of the water oxidizing complex of PSII [2]. For fast trapping of intermediate states, e.g. in water splitting catalysis, freeze-quench trapping is also being developed. During the last 2-3 years protein electrochemistry has also been substantially extended in our department (see report by Dr. O. Rüdiger). Next to cyclic voltammetry and spectroelectrochemistry, protein film electrochemistry (PFE) has been set up performed under controlled environmental conditions in a glove box using a gas mixer. Very recently this technique has been combined with surface enhanced IR absorption spectroscopy, SEIRA.

In close collaboration with the Molecular Theory and Spectroscopy Department of Prof. Neese, DFT and *ab initio* calculations are being performed to combine measured spectroscopic parameters and obtain reliable, unified electronic and geometrical structural models, e. g. of key catalytic intermediates, to elucidate reaction mechanisms. The computing facilities at the institute to perform such calculations have been dramatically expanded in recent years.

Group Structure: Focus and Organization

At present the Biophysical Chemistry Department contains six independent research groups; an additional subgroup ([NiFe] hydrogenase) is directly supervised by Prof. Wolfgang Lubitz. Each independent research group is headed by a group leader shown in Scheme 3 along with their main research objectives. PD Dr. Markus Knipp who is heading the group on NO_x-binding and conversion has recently accepted a position at the Ruhr University Bochum within the Cluster of Excellence RESOLV. He is still working and supervising his group at MPI CEC having guest scientist status within our department.



Scheme 3

Former group leaders of the department who worked mostly in photobiology/photochemistry have either retired as is the case for Dr. Helmut Görner (1/2011), or are now assigned to the Department of the Managing Director, Prof. Schlögl as is the case for Professor Alfred Holzwarth and Professor Wolfgang Gärtner. Alfred Holzwarth is working on photosynthetic problems using fast optical techniques and will retire in 2014. Wolfgang Gärtner's research field is biological photoreceptors (retirement 2016).

Collaboration within the Max Planck Institute for Chemical Energy Conversion and the Mülheim Chemistry Campus

An intensive collaboration exists between the Biophysical Chemistry Department and the Molecular Theory and Spectroscopy Department of Frank Neese. In particular the Water Oxidizing Complex (WOC) is studied both with advanced spectroscopic techniques (Dr. N. Cox) and theoretical methods (Dr. D. Pantazis). The joint effort of these two research groups across the two departments has, in recent years, led to a molecular/atomic level understanding of the structure and structural changes of the WOC. Our WOC models now assign the oxidation and spin states of the individual manganese ions in each of the metastable, transition states of the catalyst, locate the sites of substrate water binding, and have almost resolved the mechanism of O–O bond formation and O_2 release (for a recent review see ref. [3]).

In the field of hydrogenase, a collaboration with Dr. M. van Gastel [4] has led to a significant advancement in the understanding of the structure and function of the catalytic site in [NiFe] hydrogenases, and together with Dr. E. Bill, who uses Mößbauer spectroscopy, new important information regarding the enzyme's oxygen tolerance has been obtained [5]. This work has been complimented by measurements on NiFe model systems with Prof. S. DeBeer using XES, which have already generated exciting results on the structure and properties of the catalytic Ni site. Similarly, with Dr. T. Weyhermüller, new biomimetic models of the active NiFe site have been structurally characterized, revealing important information on the site of H^+/H_2 binding [6]. These combined results, together with the recent crystallographic and spectroscopic data, provide a near complete understanding of the [NiFe] hydrogenase catalytic cycle [7].

With the Department Schlögl we have initiated projects on the application of EPR techniques to detect reactive carbon species (radicals) in modified carbon nanostructures (with Dr. S. Reiche). In a joint BMBF project, in which members of all three departments (S. Buller, D. Pantazis, N. Cox) are collaborating on "biomimetic water splitting", a spectroscopic characterization of the constructs (i. e. Mn-Ca-oxides on functionalized carbon nanotubes as support) is planned.

With the neighboring Max Planck Institute for Coal Research we have initiated research projects with Prof. F. Schüth on *in situ* EPR detection of catalytically active component of heterogeneous Copper/Cerium materials and with Prof. B. List on radical intermediates in homogeneous catalytic reactions (see report of Dr. A. Savitsky).

Within the Cluster of Excellence at the Ruhr University Bochum (RUB) we are collaborating with Prof. W. Thiel on protein dynamics including the solvent shell (QM/MM).

Hydrogenases

The structure and function of the enzyme hydrogenase is of central importance for a future biologically based hydrogen production technology and for the design and synthesis of bioinspired model systems for hydrogen conversion catalysis. In our department both the [NiFe] and the [FeFe] hydrogenases are studied together with appropriate model systems [7] by applying a broad range of selected techniques.

[NiFe] Hydrogenase: As described above, the comprehensive spectroscopic characterization of the intermediate states of the activation/deactivation, inhibition and the catalytic cycle, and structural studies helped significantly to unravel the mechanism of these enzymes. For the reduced state of a standard [NiFe] hydrogenase a crystal structure of 0.89Å resolution has recently been obtained in which hydrogen atoms are visible (Ogata et al., unpublished). In particular, the products of the catalytic splitting of molecular hydrogen (into a hydride and a proton) at the catalytic NiFe site could be detected for the first time, yielding immediate information about the mechanism (see report by Dr. H. Ogata).

For the practical application of hydrogenases in (bio)fuel cells or water electrolysis devices the oxygen sensitivity of these enzymes must be addressed. Nature has already solved this problem for a group of [NiFe] hydrogenases, found for example in Knallgas bacteria. We could show that the O_2 tolerance of these systems is due to the FeS cluster of the ET chain proximal to the active NiFe site that is able to undergo two redox steps in a narrow potential range, which has never been observed before for 4Fe-clusters [5]. Subsequent structural work has shown that this cluster is not a [4Fe-4S]-4Cys but a novel [4Fe-3S]-6Cys cluster which exists in different structural conformations.

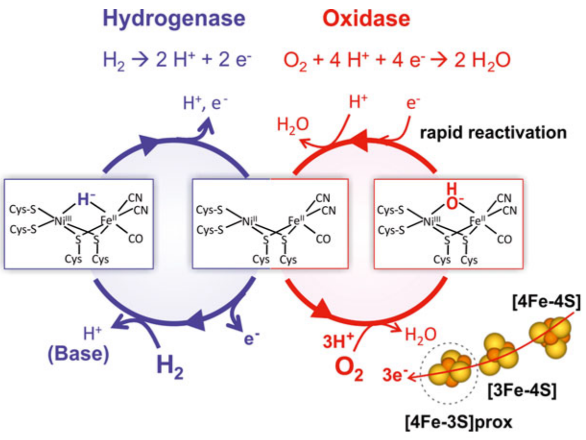


Figure 2. Scheme of O_2 tolerant hydrogenase that can also act as oxygen reductase (oxidase) under attack of molecular oxygen. Electrons are delivered via the chain of FeS clusters, in particular via the proximal [4Fe-3S]-6Cys cluster [8].

Our current model is that under O_2 attack, [NiFe] hydrogenase can avoid deactivation by reducing oxygen to water. The [4Fe]-cluster proximal to the catalytic site is instrumental in this reaction by delivering two of the four electrons required to reduce O_2, with the other two provided by the nickel center and [3Fe-4S] cluster (Figure 2). Intensive research is being performed to better understand the mechanism of this reaction; our current model postulates that the enzyme can act both as *hydrogenase* and also as an *oxidase* when exposed to O_2.

In an attempt to shield hydrogenases from the attack of O_2 our group – together with the group of Prof. W. Schuhmann (RUB) – has designed a protective matrix (a methylviologen-based polymer/hydrogel) in which the hydrogenase can be embedded. It is shown in electrochemical experiments that this matrix not only shields the hydrogenase from the deleterious effect of oxygen but also prevents deactivation of the hydrogenase at high potentials (Figure 3). This approach therefore eliminates the two major problems that have so far prevented the use of hydrogenases in biotechnological devices (see report of Dr. O. Rüdiger).

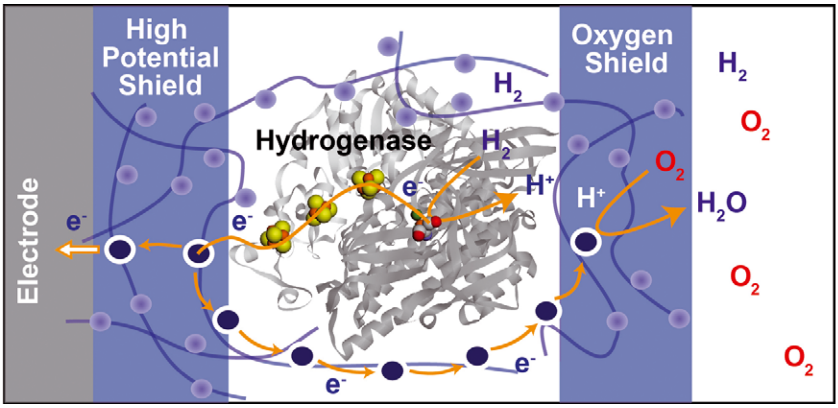


Figure 3. [NiFe] hydrogenase embedded in a viologen-modified polymer applied to an electrode. The polymer shields the hydrogenase against high potential deactivation and inhibition by oxygen.

[FeFe] Hydrogenase: Whereas in [NiFe] hydrogenases the catalytic H_2 splitting and formation is performed by a nickel ion aided by a sulfur of a terminal cysteine ligand acting as a base [7], the [FeFe] hydrogenases instead uses one of the Fe ion of its dimetal cofactor and a special azadithiolate ligand bridging the two iron sites, in which the nitrogen acts as a base. The presence of a nitrogen has recently been confirmed by measurements performed in Mülheim in collaboration with the groups of Fontecave/Artero (Grenoble) and Happe (Bochum), see report by Dr. E. Reijerse. In these experiments, completely synthetic biomimetic [2Fe] complexes were inserted into the apo-protein of bacterial and algal hydrogenases – either with the help of a chaperone (HydF) or via direct incorporation [9] (see Figure 4). The only catalytically active system obtained was the hydrogenase reconstituted with the azadithiolate bridge motif. These experiments on the artificial maturation of [FeFe] hydrogenases have far-reaching consequences for hydrogenase research.

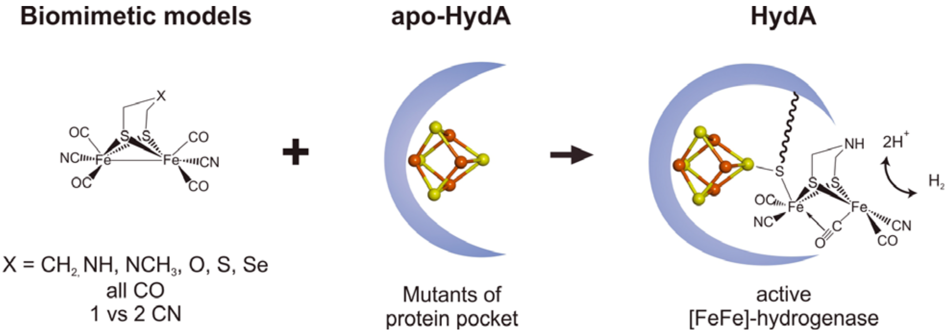


Figure 4. Synthetic biology of hydrogenases: direct incorporation of an inorganic [2Fe] cluster into the apo form of an [FeFe] hydrogenase to yield the active enzyme [9b]. This offers the possibility to both change the substitution pattern or even the type of the [2Fe] model and/or the protein (e.g. by mutagenesis) to obtain an improved enzyme.

Spontaneous cluster assembly, without chemical maturation, provides a means to develop artificial enzymes of potentially higher efficiency and robustness (e.g. oxygen tolerance) than the native system and may further our understanding of geobiochemical evolution of the hydrogenases and other related metallocofactor enzymes.

Wateroxidase

An understanding of the water oxidation in photosynthesis performed by the Mn_4O_5Ca cluster in PS II requires both knowledge of the geometrical and electronic structure and the dynamic changes of the protein-bound catalytic site in all steps of the catalytic (S-state) cycle. In this cycle the cluster passes through five intermediate states S_0 to S_4, where the subscript denotes the number of transiently stored oxidizing equivalents. For many years, a lack of structural data and the intrinsic complexity of the water splitting reaction, led to slow scientific progress in this important research field. With the advent of an atomic level X-ray structure from Japan in 2011, recent progress in XAS/XES and time-resolved X-ray diffraction in USA, and with the development of novel techniques in magnetic resonance here in Mülheim, this field has witnessed an explosion of research activity. Together with theoretical calculations an understanding of the process of water splitting in Nature is now within reach (see reports by Drs. N. Cox and D. Pantazis).

Magnetic resonance is unique amongst molecular spectroscopic techniques in that it allows the site oxidation states and electronic structure of magnetically coupled transition metal complexes, to be readily obtained, specifically using EPR and ^{55}Mn ENDOR. This has been used to great effect for the Mn_4O_5Ca cluster, where now the site oxidation and spin states of the individual manganese ions and their interactions with each other have been determined for all intermediate states of the complex, reviewed in ref. 3. Furthermore, the binding of the first substrate water and its incorporation into the Mn-cluster has been assessed by using magnetically labeled water ($H_2{}^{17}O$) and detection via a double resonance technique ^{17}O EDNMR at high magnetic fields [10].

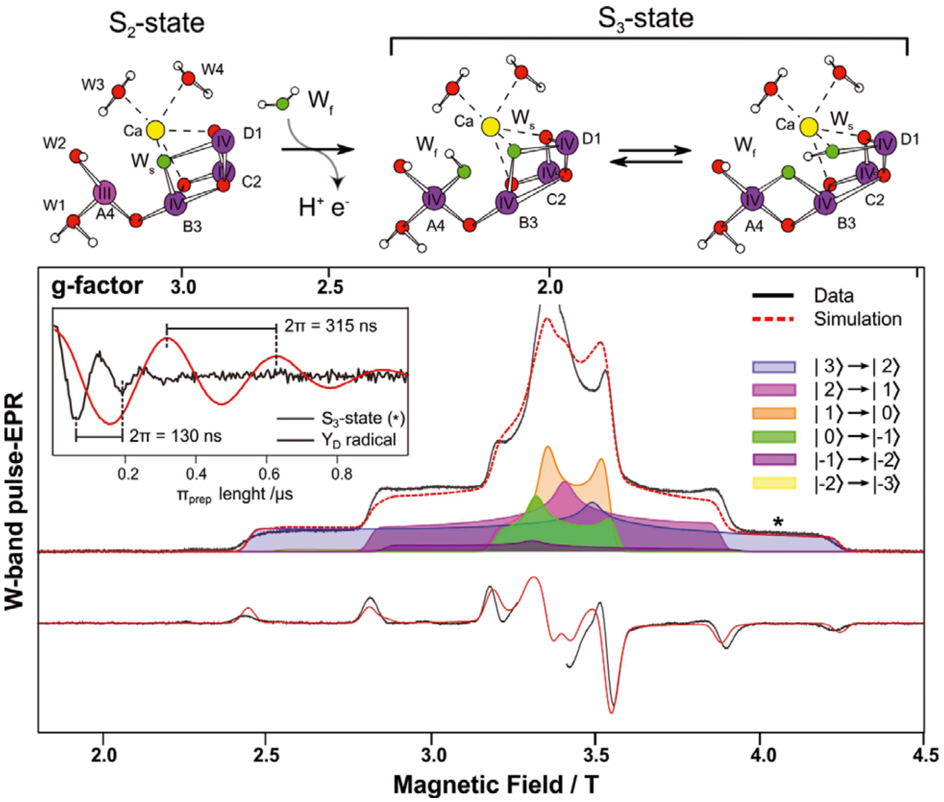


Figure 5. The EPR spectrum of the wateroxidase of PS II in the S_3 state. The simulation (coloured lines) demonstrates that the complex has an S=3 spin ground state (via the coupling of four Mn^{IV} ions). Insert: Electron spin nutation curve corroborating this assignment. On top a model for the water binding (green) in the S_2 to S_3 transition is shown.

Very recently the S_3 state, which represents the last metastable intermediate of the complex prior to O-O bond formation (in the S_4 state), has been characterized by our group (Figure 5). This state is shown to have an S=3 ground state (6 unpaired electrons) arising from coupling of four structurally and electronically similar Mn^{IV} ions. That is to say, all four Mn^{IV} ions are six coordinate, with coordinately saturated (octahedral) site geometries. This result strongly suggests that the second water is incorporated into the complex during the $S_2 \rightarrow S_3$ transition, binding to the only remaining manganese coordination site; the analogy in heterogeneous catalysis would be the binding of a substrate water to a defect site of the transition metal/metal oxide surface. Thus in the S_3 state, the two substrate oxygens are ideally located, bound between two Mn sites (Figure 5), allowing efficient O-O bond formation in the final S_4 state. This supports an oxo-oxyl coupling model originally proposed by Siegbahn (Stockholm) and expanded by Pantazis and Neese (Mülheim).

Our work on the S_3 state (Cox et al., in preparation) clearly resolves any remaining questions as to the net oxidation state assignments of the WOC and for the first time addresses the spin state(s) of the transition state, driving O-O bond formation.

References

1. Cox, N., Lubitz, W. Molecular concepts of water splitting: Nature's approach. In *Chemical Energy Storage*; Schlögl, R., Ed.; Walter de Gruyter GmbH: Berlin/Boston, 2013, 185-224; de Gruyter Bookshelf, *Green* **2013**, *3,* 235-263
2. Cox, N., Lubitz, W., Savitsky, A. W-band ELDOR-detected NMR (EDNMR) spectroscopy as a versatile technique for the characterization of transition metal-ligand interactions, *Mol. Phys.* **2013**, *111*, 2788-2808
3. Cox, N., Pantazis, D. A., Neese, F., Lubitz, W. Biological water oxidation, *Acc. Chem. Res.* **2013**, *46*, 1588-1596
4. (a) Kampa, M., Pandelia, M. E., Lubitz, W., van Gastel, M., Neese, F. A metal-metal bond in the light-induced state of [NiFe] hydrogenases with relevance to hydrogen evolution, *J. Am. Chem. Soc.* **2013**, *135*, 3915-3925 (b) Krämer, T., Kampa, M., Lubitz, W., van Gastel, M., Neese, F. Theoretical spectroscopy of the Ni(II) intermediate states in the catalytic cycle and the activation of [NiFe] hydrogenase, *Chem. Bio. Chem.* **2013**, *14*, 1898-1905
5. (a) Pandelia, M. E., Nitschke, W., Infossi, P., Giudici-Orticoni, M. T., Bill, E., Lubitz, W. Characterization of a unique [FeS] cluster in the electron transfer chain of the oxygen tolerant [NiFe] hydrogenase from *Aquifex aeolicus*, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 6097-6102 (b) Pandelia, M. E., Bykov, D., Izsak, R., Infossi, P., Giudici-Orticoni, M. T., Bill, E., Neese, F., Lubitz, W. Electronic structure of the unique [4Fe-3S] cluster in O_2-tolerant hydrogenases characterized by ^{57}Fe Mössbauer and EPR spectroscopy, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 483-488
6. (a) Weber, K., Krämer, T., Shafaat, H. S., Weyhermüller, T., Bill, E., van Gastel, M., Neese, F., Lubitz, W. A functional [NiFe]-hydrogenase model compound that undergoes biologically relevant reversible thiolate protonation, *J. Am. Chem. Soc.* **2012**, *134*, 20745-20755 (b) Weber, K., Heise, I., Weyhermüller, T., Lubitz, W. Synthesis and Characterization of Nickel Compounds with Tetradentate Thiolate–Thioether Ligands as Precursors for [NiFe]–Hydrogenase Models, *Eur. J. Inorg. Chem* **2014**, 148-155
7. Lubitz, W., Ogata, H., Rüdiger, O., Reijerse, E. *Chem. Rev.* **2014**, in press (invited review)
8. Shafaat, H. S., Rüdiger, O., Ogata, H., Lubitz, W. [NiFe] hydrogenases: a common active site for hydrogen metabolism under diverse conditions, *Biochim. Biophys. Acta Bioenerg.* **2013**, *1827*, 986-1002
9. (a) Berggren, G., Adamska, A., Lambertz, C., Simmons, T. R., Esselborn, J., Atta, M., Gambarelli, S., Mouesca, J. M., Reijerse, E., Lubitz, W., Happe, T., Artero, V., Fontecave, M. Biomimetic assembly and activation of [FeFe]-hydrogenases, *Nature* **2013**, *499*, 66-69 (b) Esselborn, J., Lambertz, C., Adamska-Venkatesh, A., Simmons, T., Berggren, G., Noth, J., Siebel, J., Hemschemeier, A., Artero, V., Reijerse, E., Fontecave, M., Lubitz, W., Happe, T. Spontaneous activation of the [FeFe]-hydrogenases by an inorganic [2Fe] active site mimic, *Nat. Chem. Biol.* **2013**, *9*, 607-609
10. Rapatskiy, L., Cox, N., Savitsky, A., Ames, W., Sander, J., Nowaczyk, M., Rögner, M., Boussac, A., Neese, F., Messinger, J., Lubitz, W. Detection of the water binding sites of the oxygen-evolving complex of photosystem II using W-band ^{17}O ELDOR-detected NMR spectroscopy, *J. Am. Chem. Soc.* **2012**, *134*, 16619-16634

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Light-Induced Water Oxidation

My research is primarily focused on the study of biological enzymes using both magneto-optical spectroscopy and magnetic resonance techniques. The motivation for my research is to understand how biological systems use earth-abundant metals especially manganese, to perform difficult oxidative/reductive chemistry of small molecules such as water and oxygen. The techniques we are developing for these systems are in principle transferable to metal oxide materials, which should in the future allow molecular level characterization of heterogeneous catalysis. Three topics currently being studied in my group include:

i. The development of magnetic resonance spectroscopic techniques for the study of transition metal complexes and heterogeneous materials in collaboration with the group of A. Savitsky;
ii. The oxygen-evolving complex (OEC) of photosystem II (PSII) – its structure and function. The mechanism of water splitting in collaboration with the group of D. Pantazis;
iii. Biological manganese catalysis - including ribonucleotide reductase (RNR), manganese catalase and a newly isolated heterobimetallic (Mn/Fe) lipid oxidase/desaturatase with the groups of H. Ogata/D. Pantazis.

i. The development and application of magnetic resonance and magneto-optical techniques for the characterization of transition metal materials (with AG Savitsky).

We are currently attempting to extend the application of multifrequency pulse electron paramagnetic resonance (EPR) spectroscopy for the characterization of materials with fast magnetic relaxation properties, such as transition metal ions, with future applications for heterogeneous metal oxides. With regard to transition metal catalysis, EPR can be used to monitor oxidation states, transient/intermediate states, substrate binding and conversion as well as product formation and release. Thus, EPR can provide important complementary information to static spectroscopic and diffraction methods [1].

We are developing a new high-field pulse EPR method for characterizing such transition metal systems, such as ELDOR-detected NMR (ED-NMR) [1]. Fig. 1 shows the ED-NMR spectrum of a simple model system, the solvated Mn^{II} ion. In a single acquisition, all nuclear transition frequencies of the complex are obtained, allowing the simultaneous characterization of the metal center and its solvation sphere. The same broad-band detection and high sensitivity cannot be achieved with conventional EPR techniques. The application of EDNMR to monitor substrate binding (H_2O) to the tetramanganese cluster of the OEC is shown in section (ii) [2].

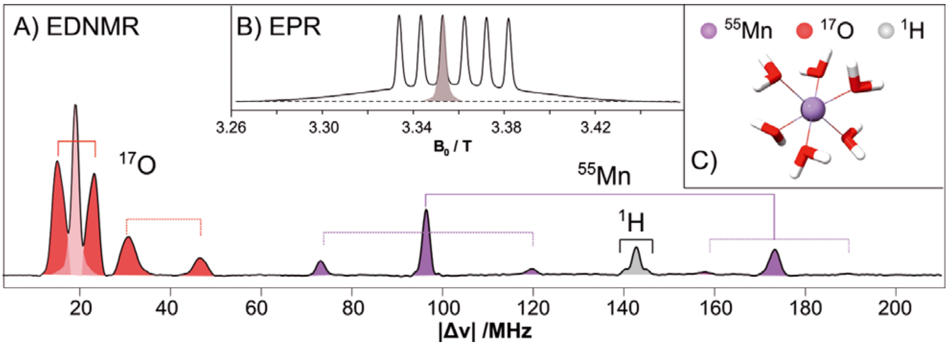

Figure 1. A) W-band ELDOR-detected NMR (ED-NMR spectrum) of $Mn^{II}(H_2{}^{17}O)_6$ at 20 K, modified from ref.[1]. **B)** The W-band EPR spectrum of $Mn^{II}(H_2{}^{17}O)_6$ indicating the position where the ED-NMR experiment was performed. **C)** The structure of the solvated Mn^{II} ion in aqueous solution. The transitions from all three magnetic nuclei of the complex, ^{17}O, ^{55}Mn and ^{1}H, are marked by red, magenta and grey color, respectively. Both single- (solid) and double-quantum (dotted) transitions of the three magnetic nuclei of the complex are observed.

ii. The Oxygen-Evolving Complex (OEC) of Photosystem II (with AG Pantazis).

Oxygenic photosynthesis uses a single enzyme for water splitting, the water-oxidizing complex (WOC) – or oxygen-evolving complex (OEC) – in PSII. The water splitting half reaction is [3]:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

Thus far, only very minor differences between photosynthetic organisms have been found at the level of the OEC. This feature is unique within biology and highlights the high level of complexity that is required to perform this chemically challenging reaction with earth-abundant metals. Our research on the structure and mechanism of the OEC is a close collaborative effort involving Dr. D. A. Pantazis's research group. As described in Dr. D. A. Pantazis's report, we have now merged information from X-ray crystallography, magnetic resonance and high level theory to develop an elaborate picture of the OEC. Importantly, this work begins to unravel the structural changes that occur during the catalytic cycle and the position(s) of the substrate water sites, both of which are critical to resolving the mechanism of O-O bond formation.

Recently we have directly examined substrate (water) binding to the OEC in the publication of Rapatskiy et al. [2] using EDNMR as described above [1]. Here we monitored the uptake of magnetic labeled water ($H_2{}^{17}O$) by the OEC. Three water binding site are observed in the S_2 state, midway through the catalytic cycle (Fig. 2A): i) water weakly associated with the OEC, i.e. bound to the Ca^{2+} ion; ii) water bound to the outer Mn ion (Mn_{A4}, W1 and W2) and; iii) water taken up as a μ-oxo bridge between two Mn ions (Fig. 2C). The binding of ammonia (NH_3), a water analogue, to Mn_{A4}, displacing W1, together with theoretical modeling, allows the exchangeable μ-oxo bridge to be assigned to O5 (Fig. 2B) [4], the μ-oxo-bridge *trans* to the W1 position i.e. O5 [4] (Fig. 2C). It is noted that the unusually fast rate of exchange of O5 makes it unique, as all other oxygen bridges of the complex do not readily exchange with $H_2{}^{17}O$ labeled water, in agreement with results from synthetic model complexes. The fast exchange of O5 is likely due to the unique flexibility of the metal coordination of O5, acting as a ligand to either Mn_{A4} or Mn_{D1}, and supports its assignment as one of the two substrate waters [3]. A mechanism for O-O bond formation involving the bridging μ-oxo (O5) and a second substrate that binds to the open coordination site on Mn_{D1} is shown in Fig. 2D [3,4]. Resolution of the mechanism of O-O bond formation forms ongoing work of our laboratory. The binding of the second substrate (water) in the S_3 state, the state immediately prior to O-O bond formation (S4), is discussed in Prof. Lubitz's section.

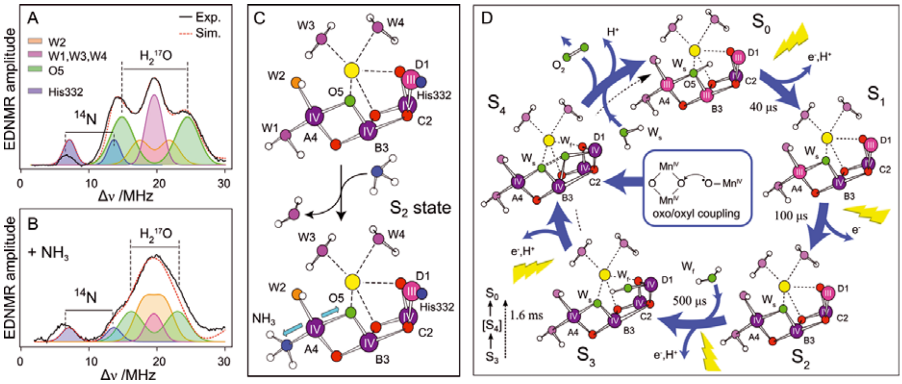

Figure 2. A) ^{17}O EDNMR spectra (94 GHz) of the OEC exchanged in $H_2{}^{17}O$ and poised in the S_2 state, modified from ref. [2] **B)** the same as A with NH_3 bound to the OEC [4]; **C)** the structure of the Mn_4O_5Ca cluster showing the exchanged water ligands, i.e. the μ-oxo bridge (O5), the terminal Mn_{A4} water ligands (W1, W2) and the terminal Ca^{2+} water ligands (W3, W4). Mn – purple; Ca – yellow; N – blue; H – white; O (non-exchangeable) – red; O (exchangeable) – pink/orange/green). **D)** Suggested mechanism for O-O bond formation involving O5 via an oxo-oxyl coupling mechanism see [2-4].

iii. Biological manganese catalysis (with AG Ogata/Pantazis).

The ferritin-like super-family of proteins catalyzes a diverse number of biological reactions. Until recently it was assumed that all proteins of this class contain an active diiron cofactor. However, two new subfamilies have recently emerged harboring either a homodinuclear Mn/Mn [5] or heterodinuclear Mn/Fe [6] cofactor. We are using a combination of X-ray crystallography and multifrequency EPR spectroscopy to structurally characterize such Mn-containing metallocofactors, to deduce *in vivo* chemical activity, cofactor assembly and the mechanism of cofactor activation, see Fig. 3. As cofactor activation occurs via its reaction with O_2, i.e. O-O bond cleavage, these enzymes can be considered as performing the water-splitting reaction in reverse. O_2 reduction is another important industrial reaction with applications in fuel cells.

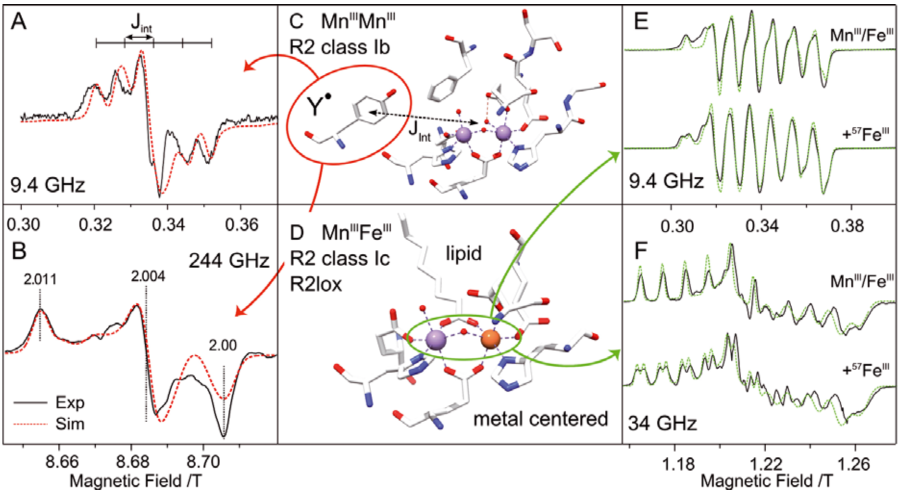

Figure 3. A,B Multifrequency EPR measurements of the homodinuclear $Mn^{III}Mn^{III}Y^{\bullet}$ Mn-RNR metallocofactor, shown in panel C [5]. In this system, the Mn/Mn cofactor is not directly observed. It can however be characterized by examining its magnetic interaction (J_{int}) with a nearby oxidized tyrosine residue, which is critical for enzymatic function. The tyrosine radical's interaction with the $Mn^{III}Mn^{III}$ cofactor leads to a splitting of the EPR signal. **E,F** Multifrequency EPR measurements of the heterodinuclear $Mn^{III}Fe^{III}$ R2lox metallocofactor, shown in panel D [6]. In this system, the Mn/Fe cofactor is directly observed by EPR. The structure of its EPR signal(s) is derived from the hyperfine interaction and is characteristic of metal complexes containing Mn and Fe.

References

1. Cox, N., Lubitz, W., Savitsky, A. W-band ELDOR-detected NMR (EDNMR) spectroscopy as a versatile technique for the characterization of transition metal-ligand interactions. *Mol. Phys.* **2013**, *111*, 2788-2808

2. Rapatskiy, L., Cox, N., Savitsky, A., Ames, W. M., Sander, J., Nowaczyk, M. M., Rogner, M., Boussac, A., Neese, F., Messinger, J., Lubitz, W. Detection of the Water Binding Sites of the Oxygen-evolving Complex of Photosystem II using W-band ^{17}O ELDOR-detected NMR Spectroscopy. *J. Am. Chem. Soc.* **2012**, *134*, 16619-16634

3. Cox, N., Pantazis, D. A., Neese, F., Lubitz, W. Biological Water Oxidation. *Acc. Chem. Res.* **2013**, *46*, 1588-1596

4. Pérez Navarro, M., Ames, W. M., Nilsson, H., Lohmiller, T., Pantazis, D. A., Rapatskiy, L., Nowaczyk, M. M., Neese, F., Boussac, A., Messinger, J., Lubitz, W., Cox, N. Ammonia binding to the oxygen-evolving complex of photosystem II identifies the solvent-exchangeable oxygen bridge (μ-oxo) the manganese tetramer. *Proc. Natl. Acad. Sci. U.S.A* **2013**, *110*, 15561-15566

5. Cox, N., Ogata, H., Stolle, P., Reijerse, E., Auling, G., Lubitz, W. A Tyrosyl-Dimanganese Coupled Spin System is the Native Metalloradical Cofactor of the R2F Subunit of the Ribonucleotide Reductase of *Corynebacterium ammoniagenes. J. Am. Chem. Soc.* **2010**, *132*, 11197-11213

6. Griese, J. J., Roos, K., Cox, N., Shafaat, H. S., Branca, R. M. M., Lehtiö, J., Gräslund, A., Lubitz, W., Siegbahn, P. E. M., Högbom, M. Structurally Encoded Metal Discrimination and Ether Bond Formation in a Heterodinuclear Metalloprotein. *Proc. Natl. Acad. Sci. U.S.A* **2013**, *110*, 17189-17194

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NO_x Binding and Conversion at Protein Metal Sites

Nitrophorins – Insect Proteins in Vertebrate Blood

Nitric oxide carrying proteins from blood feeding insects. The lipocalins represent a large group of proteins that are characterized by the formation of an 8-standed antiparallel β-barrel. The nitrophorins (NPs) represent a particularly interesting class of lipocalins because they accomodate a heme inside their β-barrel. NPs are found in the saliva of the blood feeding insect *Rhodnius prolixus* and are used by this animal to store the small gaseous radical molecule NO bound to the iron atom of the heme cofactor. During a blood meal the animal injects the saliva into a victim's tissue where NO is then released. NO is a well-known signaling molecule which promotes vaso-dilatation and inhibition of blood coagulation in the human body. Thus, the transportation of NO by NPs during feeding helps the insect to obtain a sufficient blood meal.

Structure of NP7. Vasodilatation and inhibition of blood coagulation are pharmacologically desired drug properties. Synthetic compounds are currently being developed that contain NO for release at a specific target site. We are studying NPs as natively occurring NO donors in molecular detail. Five isoforms of NPs are currently known, termed NP1, 2, 3, 4, and 7. However, where NP1-4 have been extensively investigated in the past, we are focusing on the novel isoform NP7, which is the only one able to attach to cell surfaces. Using robot assisted protein crystallization screening in collaboration with the group of H. Ogata (MPI CEC), crystals of NP7 were obtained (Fig. 1a) and the crystal structure was solved (Fig. 1b).

As expected the overall structure is very similar to those of the NP1-4; however, it is an important prerequisite for further dynamic studies. Thus, in collaboration with the group of F.J. Luque (University of Barcelona) molecular dynamics (MD) simulations were performed that revealed three interconnected inner gas binding cavities in

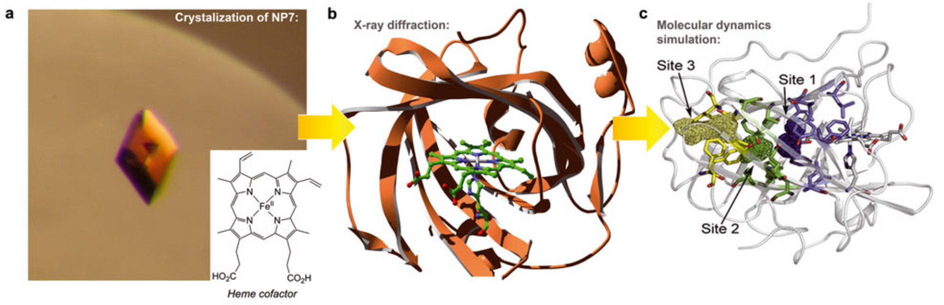

Figure 1. Structure of the membrane binding NP7 from *R. prolixus*. (a) NP7 was recombinantly expressed in *E. coli* cells, then purified and reconstituted with the heme cofactor (inset). Conditions for crystallization were obtained from crystallization screens. (b) From the X-ray diffraction pattern recorded at the synchrotron BESSY II, Berlin, a structural model was obtained at 1.8 Å resolution. (c) The crystal structure was used for molecular dynamics (MD) simulations carried out by the Bioinformatics group of F. Javier, Luque (University of Barcelona) to obtain information about the protein dynamics. Calculations in the presence of a sphere resembling an NO molecule revealed the presence of a gas channel. This is comprised of three interconnected cavities (site 1-3) leading from the heme pocket to the membrane attaching surface.

NP7 which allow the escape of the gas molecule through the back of the protein, *i.e.*, toward the membrane attaching surface (Fig. 1c) [1]. This result strongly supports our hypothesis that NP7 represents an unprecedented NO injection system upon cell surface binding.

Dynamics of the NO release. To experimentally support the MD simulations, the mechanism of binding and release of the gaseous ligand was studied by nanosecond laser-flash photolysis (LFP) [2]. In these experiments performed in collaboration with the group of C. Viappiani (University of Parma) NO was substituted by CO. The Fe–C bond is broken by the laser pulse at 532 nm and the difference in the absorbance of CO bound and unbound NP can be used for the detection of the CO binding kinetics by transient absorbance spectroscopy. The resulting kinetic traces were fitted with the simplest kinetic model that sufficiently describes the kinetic trace. Most importantly, the model obtained from the experimental values suggests the presence of three inner gas hosting cavities, which agrees well with the results obtained from MD simulations (Fig. 1c) [1]. In conclusion, both experimental and theoretical results support the hypothesis that NP7 represents an efficient biological NO delivery system.

"Nitrite-only" NO generation. The current model of NP action implies that one NP molecule (~20 kDa) provides a single diatomic NO molecule. However, this process seems to be very inefficient. In vertebrate blood NO_2^- occurs as a substrate for NO production via 1-electron reduction. While this reaction is carried out by ferrohemes, ferrihemes typically simply bind NO_2^-. In contrast, we found that ferriheme NPs converge NO_2^- to NO and NO_3^- by the nitrite disproportionation reaction at neutral pH.

$$3NO_2^- + 2H^+ \rightarrow 2NO + H_2O + NO_3^- \quad (1)$$

The NPs are, therefore, the first example of a nitrite dismutase and were classified by the IUBMB as EC 1.7.6.1. The structure of the complex was solved by X-ray crystallography in collaboration with H. Ogata (MPI CEC) demonstrating that the NO_2^- ligand is bound to the iron via the N atom [3]. EPR spectra and resonance Raman (RR) spectra revealed that the complex is low-spin (S = $^1/_2$). The X-ray structure demonstrates that close to the NO_2^- an interesting arrangement Asp30···water···water··· Asp35 is located that is a potential source for the H^+ required for the reaction (Eq.1), which is in good agreement with the previously proposed high pK_a value of Asp30 of up to ~8.5. Accordingly, the mutant NP4(D30N) has a significantly decreased nitrite dismutase activity demonstrating that Asp30 is indeed crucial for the reaction [4].

Nitrophorins as protein models. The chemistry of the NO_2^- and heme proteins is an emerging field due to its occurrence with heme nitrite reductases (NiR) that are involved in the global nitrogen cycle. Furthermore, NO_2^- interaction with the human heme proteins hemoglobin (Hb) and myoglobin (Mb) awoke recent interest because NO_2^- has been recognized as an important cardiovascular metabolite. However, ferriheme-nitrite chemistry is poorly understood, not the least because the preparation of model hemes is difficult due to the low affinity of NO_2^- and the necessity of structural shielding to prevent the formation of heme–NO_2^-–heme intermediates. With the advent of the Hb–NO_2^- and Mb–NO_2^- structures, the first examples of stable O-coordinated heme–NO_2^- complexes were reported (Fig. 2).

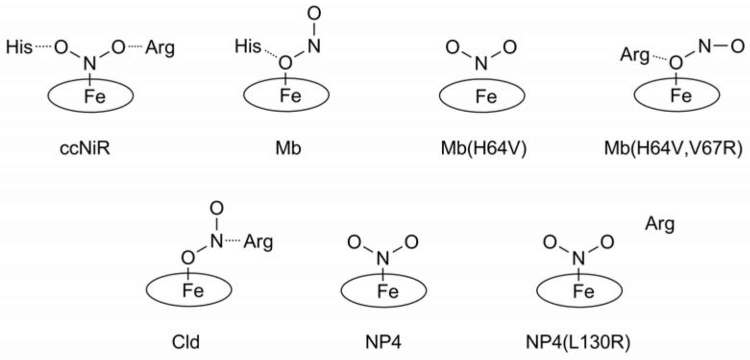

Figure 2. Comparison of the NO_2^- coordination of NP4 with those found in other crystal structures of heme proteins. In case of the cytochrome *c* nitrite reductases (c*c*NiR) NO_2^- is N-bound and H-bonded by a His and an Arg residue. In case of chlorite dismutase (Cld) and myoglobin (Mb) NO_2^- was found in the O-bound form held in position by H-bonding with an Arg or a His residue. When His64 in Mb was displaced (Mb(H64V)) NO_2^- was found N-oriented. (The long Fe↔N distance of 2.6 Å does not support the formation of a bond.) Reinsertion of another H-bonding residue into the heme pocket (Mb(H64V,V67R)) resulted in the O-bound form. As shown in Fig. 3, NO_2^- is N-bound in NP4. Insertion of an H-bonding residue into the NP4 heme pocket (NP4(L130R)) did neither affect the structure of the protein nor of the NO_2^- coordination.

Thus, the question emerges which factors determine ligand orientation and reactivity. Previous studies demonstrated that the removal of the H-bonding His64 residue in Mb leads to the disruption of the η^1-O complex while reinsertion of an Arg residue reestablishes it, suggesting that an H-bonding residue in the heme pocket determines the NO_2^- orientation (Fig. 2). In contrast to all other examples, NO_2^- in NP4 is not bound by an H-donor residue. Therefore, the heme pocket mutant NP4(L130R) was generated which otherwise presents the same structure as the wild-type. Interestingly, NO_2^- remained N-bound, thus demonstrating that the presence of an H-donating residue is not sufficient for the determination of NO_2^- coordination (Fig. 2) [4,5]. However, it also demonstrates that NPs represent an ideal model system for the detailed study of heme–nitrite chemistry.

α_1-Microglobulin – Toward the Function of a Well-Known Human Blood Protein

α_1-Microglobulin is a novel heme-lipocalin. α_1-Microglobulin (α_1m) is a human lipocalin type of protein occuring in blood plasma that has been known for a long time. However, the function of this protein is not understood. Some reports mentioned the interaction of α_1m with heme, which is a toxic compound in blood. Yet, a stable α_1m–heme complex could not be obtained. α_1m has, in contrast to the NPs, a free Cys34 residue that was previously demonstrated to be particularly reactive. For this purpose, we converted Cys34 into a thioester using 2-iodoacetamide (IAM). Afterwards the protein was titrated with heme so that a stable α_1m–heme complex was obtained [6]. Moreover, heme uptake resulted in the formation of a stable α_1m trimer. In addition, the quantification of α_1m compared to heme revealed a ratio of 1:2 demonstrating that a $(\alpha_1\text{m[heme]}_2)_3$ complex was obtained. The heme center was further characterized by RR and EPR spectroscopy demonstrating that the iron centers of the heme molecules appear in a quantum mechanically admixed spin state with $S = {}^5/_2, {}^3/_2$. This is a rare case in heme proteins but corresponding model hemes are well established. Based on this information in combination with the apo-protein structure it can be concluded that the iron coordination inside the protein is likely accomplished by a tyrosinate, a Lys or a Met side-chain.

Nitroxide spin-labeling of α_1-microglobulin. However, a structure of the holo-protein is currently not known and attempts to crystallize the protein have failed so far. To gain deeper insight into the mode of this unusual heme binding, in collaboration with the group of Savitsky (MPI CEC) a nitroxide spin label was attached to Cys34 sing the same nucleophilic reaction as that of the IAM modification (Fig. 3a).

The computational model of the spin-labeled α_1m shows that the fold is principally not affected (Fig. 3b), which was also confirmed by UV CD spectroscopy. EPR spectra of the labeled protein demonstrated that the dynamics of the attached spin-label is strongly hindered compared to the free nitroxide, indicating that the spin-label is well adopted by the protein structure (Fig. 3c). This system will be used to determine the distances between the unpaired electrons of the nitroxides of each α_1m in the trimer upon heme binding using pulsed electron-electron double resonance (PELDOR) spectroscopy. It will be further used to determine nitroxide metal distances.

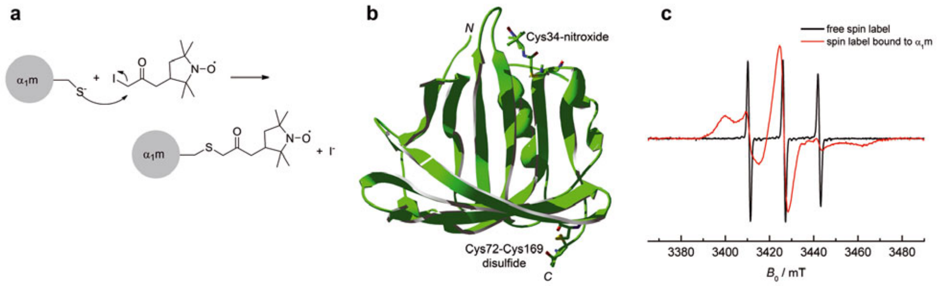

Figure 3. Nitroxide spin-labeling of α_1-microglobulin (α_1m). (a) The nitroxide spin label 3-(2-iodoacetamido)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy was inserted into α_1m by nucleophilic substitution at Cys34. The yield of the reaction was 90%. (b) Model of the spin-labeled α_1m based on the α_1m(C34S) crystal structure (PDB code 3QKG). The presence of the spin label does not affect the overall protein structure which is also supported by UV circular dichroism (CD) spectroscopy. (c) EPR spectra of free spin label (black) and of the spin labeled α_1m (red) recorded at X-band at room temperature. The largely increase anisotropy of the spectrum reveals a strongly inhibited mobility of the nitroxide inside the α_1m structure.

The distances will be used as constrains for the construction of an advanced structural model of the $(\alpha_1\text{m[heme]}_2)_3$ complex. These studies will shed light on the biological function of this poorly understood human blood protein.

Coupling of Solvent Dynamics with Protein Function in Metalloproteins

In case of metalloproteins the active site is easily assessable by spectroscopy, which allows the determination of kinetic data, for example, during enzymatic reactions. In conjunction with the Cluster of Excellence RESOLV (University of Bochum) a project was launched to apply certain metalloproteins for the study of solvent dynamics using the novel technology of THz detection (M. Havenith, University of Bochum) in combination with the time-resolved monitoring of the metal ligand sphere throughout protein function. For this purpose, the absorbance detected laser-induced kinetic measurements of NP–CO complexes will now be expanded to detection by THz absorbance. In another project, the pharmacologically important class of matrix metalloproteinases (MMPs) will be examined. These proteins are extracellular zinc peptidases and we recently managed to exchange the active site Zn(II) by Co(II), which retains the enzymatic activity. However, in contrast to Zn(II) the d^7 electron configuration of Co(II) allows to detect changes in the metal coordination sphere by absorbance, magnetic circular dichroism (MCD), and EPR spectroscopy. In summary, the combination of time-resolved water dynamics (Havenith, Bochum), active site–ligand interaction (Knipp, Mülheim), enzymatic activity (fluorescence detection, Knipp, Mülheim and I. Sagi, Weizmann Institute, Rehovot), and MD simulation (W. Thiel, MPI for Coal Research) will provide an extremely detailed description of the protein dynamics and the coupling of this process with the solvent. The results are of fundamental importance for the understanding of protein function and engineering.

References

1. Oliveira, A., Allegri, A., Bidon-Chanal, A., Knipp, M., Roitberg, A. E., Abbruzzetti, S., Viappiani, C., Luque, F. J., Kinetics and computational studies of ligand migration in nitrophorin 7 and its Δ1-3 mutant, *Biochim. Biophys. Acta – Prot. Proteom.* **2013**, *1834*, 1711-1721

2. Abbruzzetti, S., He, C., Ogata, H., Bruno, S., Viappiani, C., Knipp, M., Heterogeneous kinetics of the carbon monoxide association and dissociation reaction of nitrophorin 4 and 7 coincide with structural heterogeneity of the gate-loop, *J. Am. Chem. Soc.* **2012**, *134*, 9986-9998

3. He, C., Ogata, H. Knipp, M., Formation of the complex of nitrite with the ferriheme *b* β-barrel proteins nitrophorin 4 and nitrophorin 7, *Biochemistry* **2010**, *49*, 5841-5851

4. He, C., Ogata, H., Knipp, M., Insertion of an H-bonding residue into the distal pocket of the ferriheme protein nitrophorin 4: Effect on nitrite–iron coordination and nitrite disproportionation, *Chem. Biodiv.* **2012**, *9*, 1761-1775

5. He, C., Fuchs, M. R., Ogata, H., Knipp, M., Guanidine–ferroheme coordination in the mutant protein nitrophorin 4(L130R), *Angew. Chem. Int. Ed.* **2012**, *51*, 4470-4473

6. Siebel, J.F., Kosinsky, R.L., Åkerström, B., Knipp, M., Insertion of heme *b* into the structure of the Cys34–carbamidomethylated human lipocalin α_1-microglobulin: Formation of a $[(\text{heme})_2(\alpha_1\text{-microglobulin})]_3$ complex, *ChemBioChem* **2012**, *13*, 879-887

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Protein Structure - Crystallography

Protein crystallography is a potent method to understand structure, function and reaction mechanisms of proteins in nature. As examples, in our group the crystal structures of the metalloproteins ([NiFe] hydrogenases, ribonucleotide reductase (R2F subunit), nitrophorin 4 and nitrophorin 7, dissimilatory APS reductase, dissimilatory sulfite reductase, and membrane type-1 matrix metalloproteinase have been determined at high resolution, which gives detailed insight into the function of these enzymes.

1. [NiFe] hydrogenases

Hydrogenases catalyze the reversible splitting of molecular hydrogen. The [NiFe] active site is located in the large subunit of a heterodimer and possesses three diatomic non-protein ligands coordinated to the Fe (2 CN^-, 1 CO). Ni is bound to the protein backbone via four cysteines, two of them bridging the two metals. In the inactive form, a third bridging ligand, e. g. OH^-, is found between the metals. Once the enzyme is activated, the bridging position is supposed to be vacant or bridged by a hydride. A previous X-ray crystallographic study at 1.4 Å resolution revealed that the bridging ligand (OH^-) is removed upon H_2 reduction. EPR spectroscopy showed that a hydride is located in the bridge between the metals, which is lost upon illumination at cryogenic temperature (< 100 K). We have investigated the fully reduced (Ni-R) state of [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F at 0.89 Å resolution. The ultra-high resolution analysis revealed the presence of the hydride bridge at the [NiFe] active site in the catalytic active Ni-R state (Figure 1). Furthermore the CO and CN^- ligands could be identified and a protonated thiolate sulfur ligand (Cys546) of the Ni is postulated based on the electron density. Furthermore, a spectroscopic study of ^{57}Fe-labeled [NiFe] hydrogenase by NRVS (Nuclear Resonance Vibrational Spectroscopy) was performed with the group of Prof. S.P. Cramer (University of California Davis, USA). Thereby the Fe-CO and Fe-CN^- bending and stretching vibrations could be identified [1].

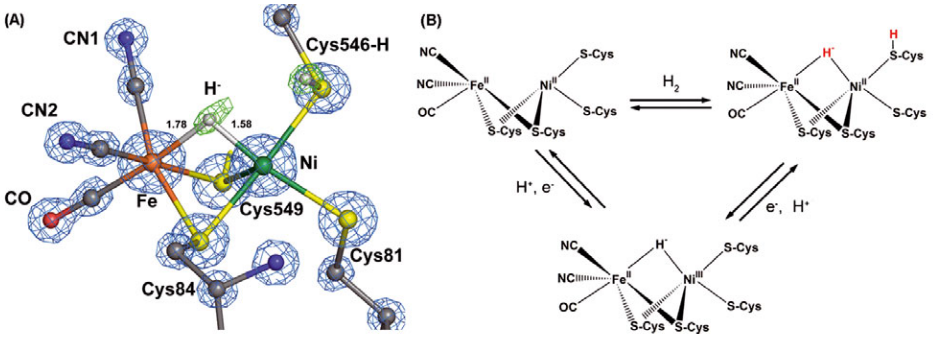

Figure 1. (A) Electron density map and ball and stick representation of the [NiFe] active site in the Ni-R state at 0.89 Å resolution ($2F_o$-F_c map, blue; F_o-F_c map, green) (B) The proposed catalytic reaction of the [NiFe] hydrogenase (Ogata et al., manuscript in preparation).

The crystal structure of the membrane-associated [NiFe] hydrogenase from the photosynthetic purple-sulfur bacterium *Allochromatium vinosum* (*A. vinosum*) has been determined to 2.1 Å resolution [2]. EPR and FTIR spectra on dissolved crystals showed that it is present in the inactive Ni-A state (> 90 %). The structure of the *A. vinosum* [NiFe] hydrogenase reveals significant similarities with [NiFe] hydrogenase structures derived from *Desulfovibrio* hydrogenases (Figure 2A). One of the bridging cysteines exhibits a modified thiolate in part of the sample. A mono-oxo bridging ligand was assigned between nickel and iron (Figure 2B). This is in contrast to a proposal for *Desulfovibrio* hydrogenases that show a di-oxo species in this position for the Ni-A state. The anomalous Fourier map indicates a distorted proximal iron-sulfur cluster. The altered proximal cluster is supposed to be paramagnetic and is exchange coupled to the Ni^{3+} ion and the medial [3Fe-4S]$^{+}$ cluster that are both EPR active (S = 1/2 species).

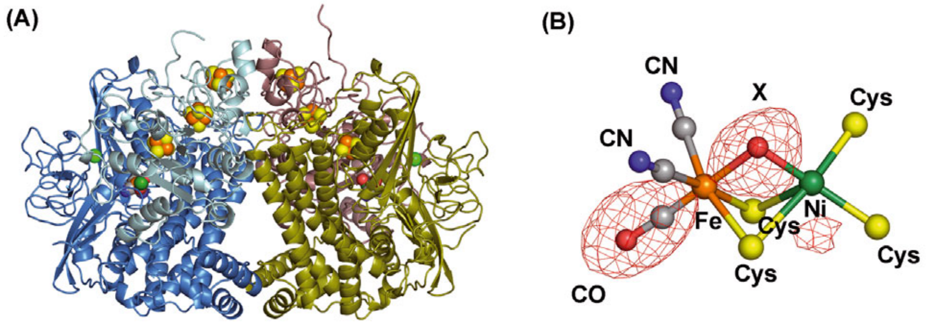

Figure 2. (A) The crystal structure of [NiFe] hydrogenase from *A. vinosum*. (B) The electron density omit map depicted only the bridging ligand and the CO ligand of the [NiFe] active site. The sphere shape of the electron density of the bridging ligand indicated that it is a monatomic, not a diatomic ligand [2].

Single crystal EPR and ENDOR spectroscopies are ideally suited methods to study the paramagnetic species in metalloenzymes. We performed single crystal EPR and ENDOR on the Ni-A state of *D. vulgaris* [NiFe] hydrogenase in H_2O and D_2O buffer [3].

This revealed the presence of a hydroxyl ligand at the bridging position in the inactive Ni-A state. Recently a single crystal EPR study with a microresonator, which requires a smaller size of the crystals, was performed [4]. This newly developed method can be applied to most metalloenzyme single crystals (typically nanoliter size). (Collaboration with groups of Dr. A. Savitsky, Dr. E. Reijerse, and Prof. D. Suter, University Dortmund).

2. Ribonucleotide reductase

Ribonucleotide reduction, the unique step of DNA precursor biosynthesis, involves radical-dependent redox chemistry and diverse metallo-cofactors. The crystal structure of the native R2F subunit of the ribonucleotide reductase (RNR) of *Corynebacterium ammoniagenes* ATCC 6872 has been determined at a resolution of 1.36 Å [5]. The metal site contains an oxo/hydroxo-bridged manganese dimer, spatially located close to a tyrosine residue (Tyr115). The Mn sites have been identified by the anomalous dispersion method using synchrotron radiation (Figure 3A). The coordination of the manganese dimer and its distance to a nearby tyrosine residue resemble the di-iron metalloradical cofactor of class I RNR from *Escherichia coli* (Figure 3B). This showed for the first time that in some RNRs the two Fe ions can be replaced by manganese (Collaboration with the group of Dr. N. Cox)

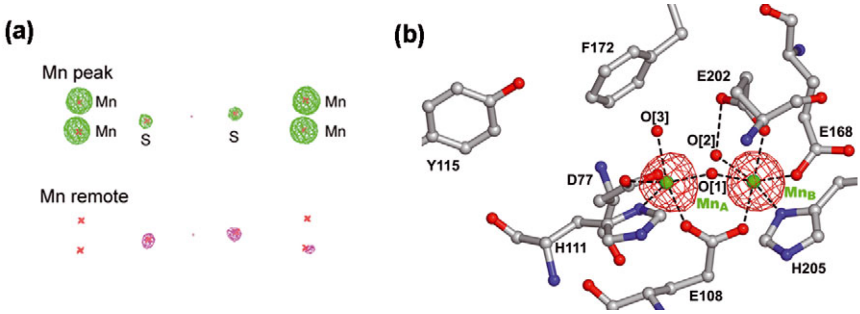

Figure 3. (A) The electron density calculated by the anomalous dispersion method. The strong electron densities, which were measured at the X-ray wavelength of 1.890 Å (Mn-peak), were assigned to the Mn ions. (B) Structure of the Mn cluster sites with amino acid ligands and Tyr115 [5].

3. Nitrophorin 4

Nitrophorins comprise a unique class of ferriheme proteins originating from the saliva of the blood feeding insect *Rhodnius prolixus*. The major biological function of these proteins is the transport and delivery of NO from the insect saliva to the blood vessels of a host species where it acts as a vasodilator and blood-coagulation inhibitor. The various ligand-bound forms (Nitrite, NO, Histidine, and L-Cysteine, 2-mercaptoethanol, L-homocysteine and Na_2S) and different mutants, such as D30N, D70A, L130R, have been investigated by X-ray crystallography at high-resolution (1.3-1.4 Å) [6,7]. It represented the first structural characterization of a ferriheme protein in complex with L-cysteine, L-homocysteine. (Collaboration with the group of Dr. M. Knipp.)

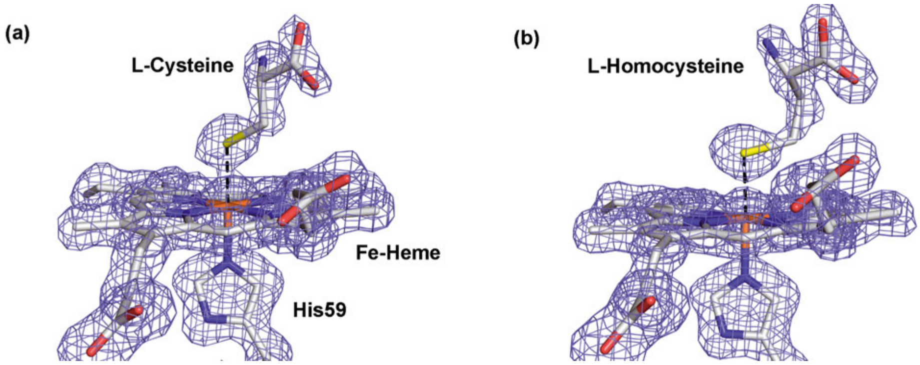

Figure 4. (A) Heme centers of the crystal structures of nitrophorin 4 with (A) L-Cysteine, and (B) L-homocysteine as ligands [6].

4. Photosystem II

Photosynthesis is one of the most essential processes for energy storage and conversion in nature. To understand the mechanism – e.g. of water oxidation – detailed structural information is essentially required. Crystallization of PSII from a thermophilic cyanobacterium, *Thermosynechococcus elongatus,* and a red algae, *Cyanidioschyzon merolae*, are done in collaboration with Prof. M. Rögner (Ruhr-Universität Bochum) and Prof. J.M. Kargul (Warsaw University, Poland). *C. merolae* has a very small genome of only 8 Mbp, which makes it one of the most basal representatives of its group. *C. merolae* is an intermediate between cyanobacteria and higher plants. Another PSII from a higher plant, *Spinacia oleracea* (spinach), was purified in our institute and crystallized. Preliminary X-ray diffraction experiments on PSII single crystals from *C. merolae* and spinach were performed using synchrotron radiation yielding a resolution of ~11 to 15 Å. We obtained small crystals (0.1 – 0.5 mm), and these are suitable for single crystal EPR studies (collaboration with Prof. Lubitz and Dr. Cox).

External collaborations

Prof. S. P. Cramer (University of California, Davis, USA): NRVS for [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F.

Dr. O. Lenz (Technische Universität Berlin, Germany): Regulatory [NiFe] hydrogenase from *Ralstonia eutropha* H16.

Prof. M. Rögner and Dr. M. Nowaczyk (Ruhr-Universität Bochum, Germany):
Photosystem II from *Thermosynechococcus elongatus.*

Prof. J. M. Kargul (University of Warsaw, Poland): Photosystem II from *Cyanidioschyzon merolae.*

References

1. Kamali, S., Wang, H., Mitra, D., Ogata, H., Lubitz, W., Manor, B.C., Rauchfuss, T.B., Byrne, D., Bonnefoy, V., Jenney Jr., F.E., Adams, M.W.W., Yoda, Y., Alp, E., Zhao, J., Cramer, S.P., Observation of the Fe-CN and Fe-CO Vibrations in the Active Site of [NiFe] Hydrogenase by Nuclear Resonance Vibrational Spectroscopy. *Angew. Chem. Int. Ed.* **2013**, *52*, 724-728
2. Ogata, H., Kellers, P. and Lubitz, W., The crystal structure of the [NiFe] hydrogenase from photosynthetic bacterium *Allochromatium vinosum:* Characterization of the oxidized enzyme (Ni-A state). *Journal of Molecular Biology* **2010**, *402*, 428-444
3. Pandelia, M.E., Ogata, H., Lubitz, W., Intermediates in the Catalytic Cycle of [NiFe] Hydrogenase: Functional Spectroscopy of the Active Site. *ChemPhysChem* **2010**, *11*, 1127-1140
4. Narkowicz, R., Ogata, H., Reijerse, E., Suter, D., A cryogenic receiver for EPR. *Journal of Magnetic Resonance*, **2013**, *237*, 79-84
5. Cox, N., Ogata, H., Stolle, P., Reijerse, E., Auling, G., Lubitz, W., A Tyrosyl-Dimanganese Coupled Spin System is the Native Metalloradical Cofactor of the R2F Subunit of the Ribonucleotide Reductase of *Corynebacterium ammoniagenes*. *J. Am. Chem. Soc.* **2010**, *132*, 11197-11213
6. He, C., Nishikawa, K., Erdem, Ö. F., Reijerse, E., Ogata, H., Lubitz, W., Knipp, M., Complexes of Ferriheme Nitrophorin 4 with Low-Molecular Weight Thiol(ate)s Occurring in Blood Plasma. *J. Inorg. Biochem.* **2013**, *122*, 38-48
7. He, C., Fuchs, M. R., Ogata, H. and Knipp, M., Guanidine–Ferroheme Coordination in the Mutant Protein Nitrophorin 4(130R). *Angew. Chem. Int. Ed.* **2012**, *51*, 4470-4473

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Hydrogenase and Biohydrogen

The mission of our institute is to explore sustainable energy systems of the future. The ultimate goal is to design energy converting catalysts which are based on cheap and clean materials. An obvious and viable strategy is to study energy converting systems in nature and unveil the mechanisms by which biocatalysts e.g. convert sunlight and secondary energy sources into biofuels. Hydrogenases are champions in the production of molecular hydrogen from protons and electrons. In particular [FeFe] hydrogenases show extraordinary activity for this reaction. The study of this process using spectroscopic techniques is one of the major themes in our group. In this research we are collaborating both with biologists (study of enzymes) and chemists (study of model systems and inorganic catalysts).

1. [FeFe] Hydrogenase

The active site of [FeFe] hydrogenases, i.e. the “H-cluster”, contains a binuclear Fe-Fe cluster coordinated by CO and CN^- ligands as well as a dithiolate bridging ligand. This di-iron subsite is connected through a bridging cysteine to a cubane cluster which is linked to the electron transport chain of the enzyme. Our group has contributed significantly to the understanding of the structure and function of the H-cluster. In 2009 we already provided spectroscopic evidence for the presence of an amine in the dithiolate bridge (Silakov et al. PCCP 2009). It is generally assumed that this amine moiety is responsible for shuttling protons to and from the open coordination site at the distal iron of the bi-nuclear subsite where the hydrogen species is binding. The assignment of the amine group was further supported by studies of inorganic model systems with a similar azadithiolate (ADT) bridge [1,2]. Unequivocal evidence for the identity of the ADT bridge was finally provided by our group together with collaborators in Bochum and Grenoble [3]. In these studies it was demonstrated that the maturation pathway of the H-cluster, which in vivo requires three helper proteins or “maturases” could be cut short by simply adding a synthetic analogue of the binuclear subsite to the apo-hydrogenase protein in which this part is lacking. Using FTIR and EPR it was shown that three bi-nuclear analogues containing a carbon, oxygen or nitrogen atom at the center of the dithiolate bridge could be inserted into the apo-protein. But only the nitrogen containing analogue (ADT) afforded a fully active enzyme [3]. This artificial maturation procedure is assumed to be functional for all [FeFe] hydrogenases (Figure 1).

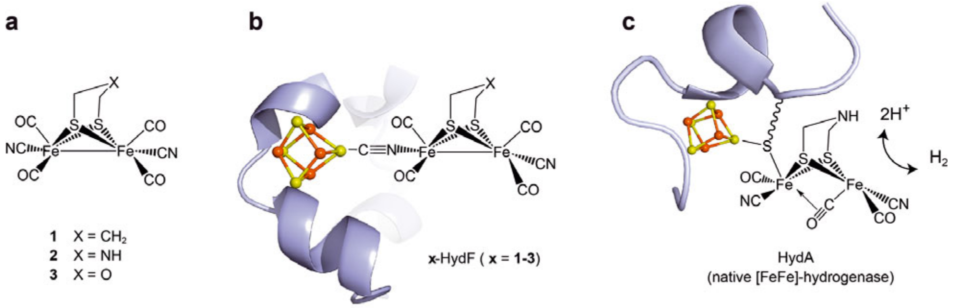

Figure 1. Structures of the di-iron clusters. a, The synthetic mimics. b, Proposed structure for the x–HydF hybrid proteins. c, The H-cluster (active site) of [FeFe]-hydrogenase. The protein ribbon and the [4Fe-4S] clusters (shown as balls and sticks with Fe shown as white spheres) are shown only schematically.

The H-cluster passes through several redox states during its catalytic cycle. The elucidation and characterization of these redox intermediates is crucial to understanding the hydrogenase reaction mechanism. In addition to the already known active states, i.e. H_{ox} and H_{red}, using FTIR spectro-electrochemistry, our group identified an additional reduced state already in 2009 (Silakov et al. 2009 Biochemistry). The exact electronic configuration of this so-called super-reduced state, H_{sred}, was elucidated a few years later using combined FTIR and EPR spectroscopy [4]. It turned out the H_{sred} is characterized by a reduction of the $[4Fe\text{-}4S]_H$ cluster thus enabling the storage of a total of two reduction equivalents relative to H_{ox}. In the same study, using protein film electrochemistry in collaboration with the group of Dr. Rüdiger, we also showed that H_{sred} most probably is part of the reaction cycle of all [FeFe] hydrogenases. Based on our data a new reaction cycle was formulated [4] (Figure 2).

The "discovery" of the H_{sred} state showed that the $[4Fe\text{-}4S]_H$ cluster is an integral part of the H-cluster taking part in the catalysis by shifting electron to and from the bi-nuclear subsite. The electronic configuration of the complete iron core is therefore a key property to understand the catalytic mechanism.

From the structure of the H-cluster it is apparent that both the dithiol bridge and the open coordination site at the distal iron (induced by the so-called "rotated conformation" are key elements in the catalytic cycle (see Figure 1). In collaboration with synthetic chemists in Urbana (USA), Texas A&M (USA), and Uppsala (Sweden), these structural motives have been studied in detail [1, 2, 5, 6].

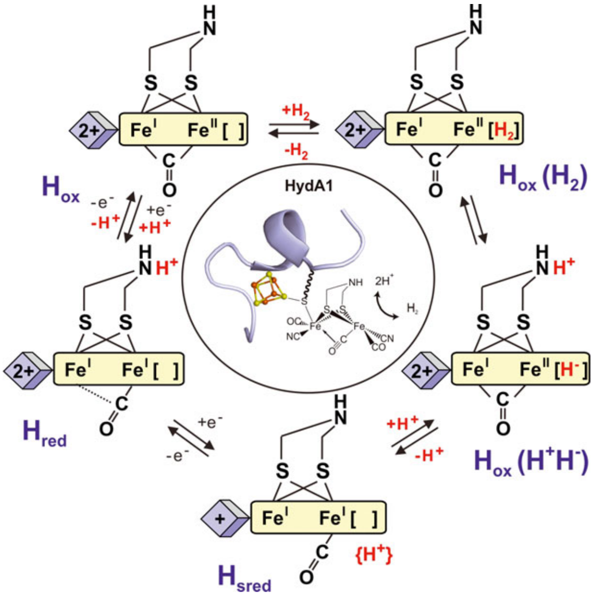

Figure 2. Proposed catalytic cycle for [FeFe] hydrogenase including the H_{sred} state. $\{H^+\}$ in H_{sred} indicates that the proton is believed to be associated with the H-cluster and possibly bound to a nearby amino acid residue.

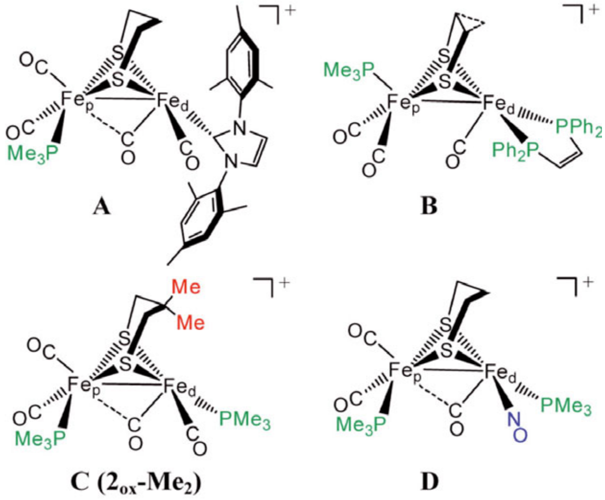

Figure 3. Studied $[2Fe]_H$ mimics with a "rotated conformation" at Fe_d similar to that in the native H-cluster.

While in the native H-cluster the rotated conformation is stabilized by a lysine H-bond, synthetic mimics in solution require bulky ligands either in the bridge or at the distal iron [2, 5] (see Figure 3).

Using ^{57}Fe 2D-Mims-ENDOR, HYSCORE, and Mößbauer spectroscopy in combination with DFT calculations our group has demonstrated that the rotated conformation has a strong effect on the localization of the spin density in the $[2Fe]_H$ subcluster [2, 6]. In the native H-cluster, this behavior is, however, additionally influenced by the presence of the $[4Fe\text{-}4S]_H$ subcluster. Through the study of the ^{1}H, ^{2}H, $C^{14}N$, $C^{15}N$, ^{31}P, and ^{13}CO interactions it was shown that the lack of the protein surrounding

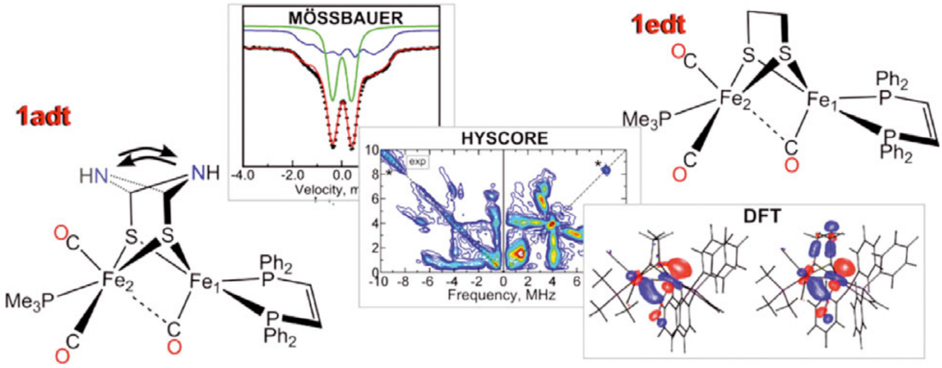

Figure 4. Overview of the studied 1adt and 1edt $[2Fe]_H$ mimics together with their Mössbauer and HYSCORE spectra as well as the DFT estimated spin-density plots.

causes significant differences in the primary coordination sphere of the bi-nuclear cluster [2, 6]. In particular it was shown that the ADT bridge can show conformational flexibility which, in the native system may be of importance for the catalytic mechanism (Figure 4) [2].

2. Instrumental developments

The Q-band pulsed EPR experiments performed in our institute strongly rely on the properties of a homebuilt 34 GHz resonator probehead with large sample volume and high power ENDOR capabilities. This resonator was carefully characterized and compared with the commercial Bruker dielectric resonator. It turns out that for applications where sensitivity is more important than bandwidth, the homebuilt TE011 resonator clearly wins [7]. In addition a new coupling scheme was developed to enable strong overcoupling of the TE011 resonator in order to increase its bandwidth (Savitsky et al 2013 Rev. Sci. Instrum.). In collaboration with the group of Dr. Savitsky (CEC) we submitted a successful proposal in the DFG priority program SPP1601 for the development of micro-resonators (spp1601.de). The envisaged main application of these structures would be the study of tiny proteins single crystals and thin film samples.

3. External collaborations

In collaboration with Prof. Reetz (MPI for Coal Research) and Dr. Bill (MPI CEC) an artificial Cu enzyme was studied using EPR and HYSCORE spectroscopy. It was demonstrated that a catalytic Cu histidine coordinated site could be engineered into a thermostable protein [8].

In collaboration with the group of Dr. Cox (MPI CEC), Dr. Ogata (MPI CEC) and Prof. Auling (University Hannover) a new type of Ribonucleotide Reductase was characterized using multifrequency EPR (9, 34, and 244 GHz). This RNR utilizes a binuclear $Mn(III)_2$ cluster instead of $Fe(III)_2$ to initiate the radical reaction [9].

In collaboration with the groups of Dr. Schneider (University Göttingen) and Dr. de Bruin (University Amsterdam) a stable nitrido Ir complex was characterized using EPR and ^{14}N pulsed ENDOR. This complex showed a remarkable nitridyl (Ir=N) character in which the radical is strongly localized on the nitrido ligand [10].

References

1. Erdem, Ö. F., Schwartz, L., Stein, M., Silakov, A., Kaur-Ghumaan, S., Huang, P., Ott, S., Reijerse, E. J., Lubitz, W. A model of the [FeFe] hydrogenase active site with a biologically relevant azadithiolate bridge: a spectroscopic and theoretical investigation *Angew. Chem. Int. Ed.* **2011**, *50*, 1439-1443
2. Silakov, A., Olsen, M. T., Sproules, S., Reijerse, E. J., Rauchfuss, T. B., Lubitz, W. EPR/ENDOR, Mössbauer, and quantum-chemical investigations of diiron complexes mimicking the active oxidized state of [FeFe] hydrogenase, *Inorg. Chem.* **2012**, *51*, 8617-8628
3. (a) Berggren, G., Adamska, A., Lambertz, C., Simmons, T. R., Esselborn, J., Atta, M., Gambarelli, S., Mouesca, J. M., Reijerse, E., Lubitz, W., Happe, T., Artero, V., Fontecave, M. Biomimetic assembly and activation of [FeFe]-hydrogenases, *Nature* **2013**, 499, 66-69. (b) Esselborn, J., Lambertz, C., Adamska-Venkatesh, A., Simmons, T., Berggren, G., Noth, J., Siebel, J., Hemschemeier, A., Artero, V., Reijerse, E., Fontecave, M., Lubitz, W., Happe, T. Spontaneous activation of the [FeFe]-hydrogenases by an inorganic [2Fe] active site mimic, *Nat. Chem. Biol.* **2013**, 9, 607-609.
4. Adamska, A., Silakov, A., Lambertz, C., Rüdiger, O., Happe, T., Reijerse, E., Lubitz, W. Identification and characterization of the 'super-reduced' state of the H-cluster in [FeFe] hydrogenase: a new building block for the catalytic cycle? *Angew. Chem. Int. Ed.* **2012**, *51*, 11458-11462
5. Hsieh, C.-H., Erdem, Ö. F., Harman, S. D., Singleton, M. L., Reijerse, E., Lubitz, W., Popescu, C. V., Reibenspies, J. H., Brothers, S. M., Hall, M. B., Darensbourg, M. Y. An iron-nitoryl paradigm for base metal proton reduction electrocatalysis, *J. Am. Chem. Soc.* **2012**, *134,* 13089-13102
6. Silakov, A., Shaw, J. L., Reijerse, E. J., Lubitz, W. Advanced electron paramagnetic resonance and density functional theory study of a {2Fe3S} cluster mimicking the active site of [FeFe] hydrogenase, *J. Am. Chem. Soc.* **2010**, *132*, 17578-17587
7. Reijerse, E., Lendzian, F., Isaacson, R., Lubitz, W. A tunable general purpose Q-band resonator for CW and pulse EPR/ENDOR experiments with large sample access and optical excitation, *J. Magn. Resonan.* **2012**, *214*, 237-243
8. Podtetenieff, J., Taglieber, A., Bill, E., Reijerse, E. J., Reetz, M. T. An artificial metalloenzyme: Creation of a designed copper binding site in a thermostable protein *Angew. Chem. Int. Ed.* **2010**, *49*, 5151-5155
9. Cox, N., Ogata, H., Stolle, P., Reijerse, E., Auling, G., Lubitz, W. A tyrosyl-dimanganese coupled spin system is the native metalloradical cofactor of the R2F subunit of the ribonucleotide reductase of *Corynebacterium ammoniagenes*, *J. Am. Chem. Soc.* **2010**, *132*, 11197-11213
10. Scheibel, M. G., Askevold, B., Heinemann, F. W., Reijerse, E. J., de Bruin, B., Schneider, S. Closed-shell and open-shell square-planar iridium nitrido complexes *Nature Chemistry* **2012**, *4*, 552-558

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Proteins on electrodes

Our research is focused on the electrochemical study of hydrogenases. Hydrogenases are the enzymes that catalyze in a very efficient reversible way the H_2 oxidation/evolution. These enzymes use earth abundant atoms in the active site (as Ni or Fe). Understanding their properties and learning how to use them in energy conversion devices could help to solve the energy problems of our society.

As electrons are part of the catalytic reaction of hydrogenases, electrochemistry is the method of choice for studying their activity. In protein film electrochemistry (Figure 1A) a monolayer of enzyme is immobilized with the right orientation on top

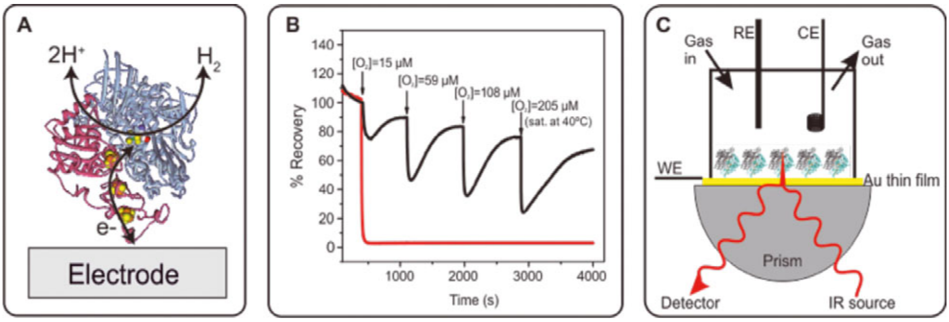

Figure 1. (A) In protein film electrochemistry experiments the hydrogenase has to be immobilized on the electrode with the distal [4Fe-4S] cluster facing the electrode surface. With such orientation direct electron transfer can be measured between protein and the electrode. **(B)** Chronoamperometry experiments at +150 mV (vs. SHE) to measure hydrogen oxidation catalytic current of *Desulfovibrio vulgaris* MF [NiFe] hydrogenase (red) and *Aquifex aeolicus* Hase I (black) immobilized on a pyrolytic graphite electrode. Additions of aliquots of oxygen-saturated buffer are indicated. The cell is flushed continuously by a stream of hydrogen, at pH 7.0 and 40 °C and 2500 rpm electrode rotation rate. Only the O_2 tolerant hydrogenase maintains H_2 oxidation catalysis upon O_2 exposure. **(C)** Spectroelectrochemical cell employed for SEIRA spectroscopy. A nanostructured gold thin film is grown on top of a silicon prism. The protein is immobilized on the Au electrode using a self-assembled monolayer. A standard gas-tight three electrode electrochemical cell is assembled on top of the prism, using the Au surface as working electrode.

of an electrode and the catalytic current is directly measured as a function of the electrode potential under different experimental conditions that we can accurately control during the measurement (pH, temperature, H_2 concentration). Inhibition of the enzyme by small molecules like O_2, CO or oxidizing potentials imposed by the electrode can be determined very accurately using this technique. Measurement of the enzyme's activity in the presence of O_2 is not possible using the traditional methods based on redox mediators, therefore PFE is the best technique to test O_2 tolerance of hydrogenases (Figure 1B). Covalent immobilization of the hydrogenase allows more accurate electrochemical studies due to enhanced long-term stability of the catalytic current (Rüdiger et al. *JACS*, 2005; Alonso-Lomillo et al. *Nano Letters*, 2007). But more importantly, this stability over time is a requirement for using hydrogenases in energy converting devices for water splitting or in fuel cells.

FTIR spectroscopy has proven to be a very useful technique for studying the rich redox chemistry of hydrogenases. This has been established at the MPI and is now used routinely together with a spectroelectrochemical cell for redox titrations. Combination of IR spectroscopy with PFE can be achieved using surface-enhanced infrared absorption spectroscopy (**SEIRA**). This technique provides a good potential control over the active site of the enzyme in the presence of substrate and/or inhibitors and IR spectra can be recorded while the enzyme is under turnover conditions (Figure 1C).

Protein Film Electrochemistry (PFE)

PFE has been set-up at the MPI during the last 3 years and is now used to electrochemically study enzymes on electrodes. For example, in collaboration with the group of Dr. E. Reijerse, we have employed PFE to determine if the spectroscopically detected H_{sred} state from [FeFe] hydrogenases is an active state which participates in the catalytic cycle of the enzyme.[1] For this purpose, the [FeFe] hydrogenases from *Desulfovibrio desulfuricans* (*Dd*), *Chlamydomonas reinhardtii* (*Cr*) and *Clostridium acetobutylicum* (*Ca*) were immobilized on carbon rotating disc electrodes and the catalytic currents at negative potentials were analyzed (Figure 2). The cyclic voltammograms showed an increase of the catalytic H^+ reduction currents with negative potentials. Chronoamperometry experiments at negative potentials confirmed that the catalytic activity was sustained over the time at potentials where H_{sred} should be formed, a clear indication that this state should be part of the catalytic cycle.

PFE was also used to study the [NiFeSe] hydrogenase from *Dv*MF [2]. This hydrogenase was purified by the group of Prof. W. Gärtner. In this case the hydrogenase was covalently immobilized on a gold rotating disc electrode modified with an amino-terminated self-assembled monolayer. The CV showed that this enzyme is biased towards H_2 production rather than H_2 oxidation. An inactivation process at high potentials was also described, as it was also found for the [NiFeSe] hydrogenase from *Desulfovibrio baculatum*. Using a chronoamperometry experiment the enzyme was shown to be capable of producing H_2 in the presence of small amounts of O_2.

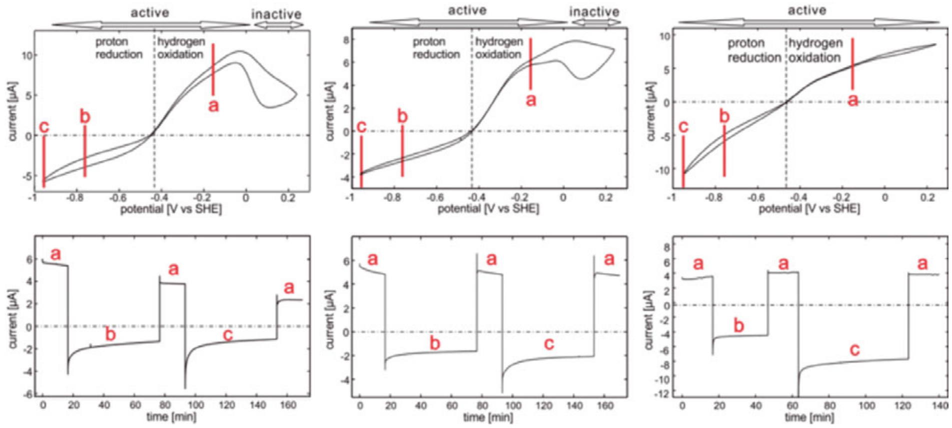

Figure 2. From left to right: cyclic voltammetry (upper part) and chronoamperometric experiments (lower part) on *Chlamydomonas reinhardtii* adsorbed on and *Desulfovibrio desulfuricans* and *Clostridium acetobutylicum* covalently attached to a pyrolytic graphite edge electrode. Perpendicular markings and letters on the cyclic voltammograms indicate the potentials used in the chronoamperometric measurements (a=-209 mV, b=-759 mV, c=-959 mV) [1].

While determining the O_2 tolerance of the [NiFeSe] hydrogenase, we decided to compare it with a standard [NiFe] hydrogenase. When the same experiment was repeated with the [NiFe] hydrogenase from *Dv*MF, it showed that also standard O_2 sensitive hydrogenases can maintain H_2 production in the presence of O_2 [3]. This finding suggests that standard hydrogenases could be also used for water splitting devices, which is an important feature, because standard hydrogenases are better H_2 producers than O_2 tolerant hydrogenases.

Another way to improve the O_2 tolerance is to take advantage of the immobilization method. In collaboration with the group of Prof. W. Schuhmann from the Ruhr Universität in Bochum, we designed a polymer modified with viologen (V^{++}) molecules, which have the adequate potential to exchange electrons directly with the hydrogenase. Using PFE and FTIR we showed that when the electrons are transferred to or from the enzyme through the V^{++} the active enzyme cannot be oxidized back to the inactive states by high potentials applied on the electrode (Figure 3A). When using hydrogenases in fuel cells, under operating conditions, the hydrogenase anode suffers positive potentials from the fuel cell cathode that inactivates the hydrogenase. The V^{++} polymer is therefore protecting the enzyme from this high potential inactivation. But the V^{++} not only shields the enzyme against high potential inactivation, we also demonstrated that the redox polymer can use the electrons generated by the hydrogenase H_2 oxidation to catalytically reduce O_2 on the surface of the polymer (Figures 3B and 3C). This second protection mechanism confers an O_2 sensitive hydrogenase the ability to maintain H_2 oxidation in the presence of O_2, a characteristic that was exclusive of O_2 tolerant hydrogenases. The double protection allowed us to test the electrode in a single compartment bio-fuel cell which showed better performance than that reported for fuel cells using oxygen tolerant hydrogenases [4].

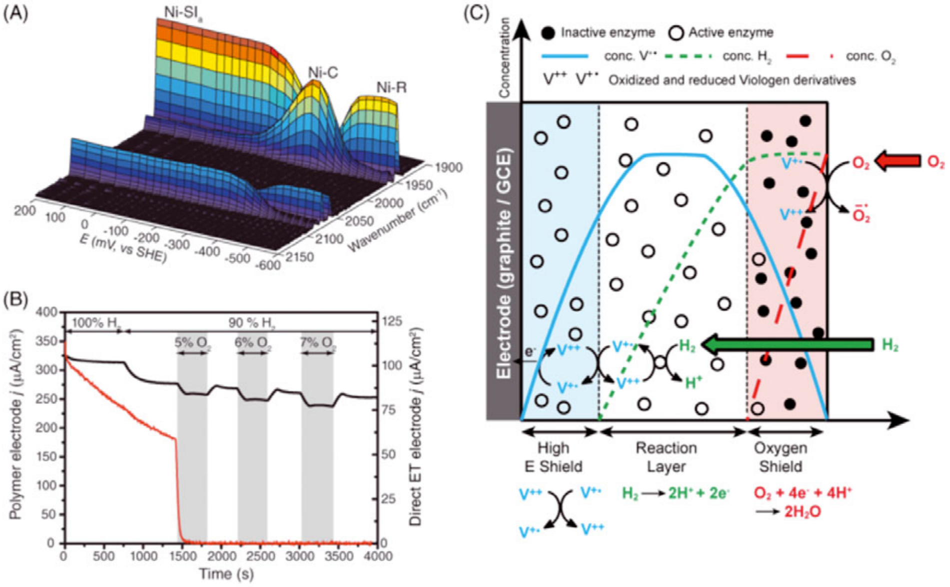

Figure 3. (A) Three dimensional representation of a spectroelectrochemical FTIR titration of the *Desulfovibrio vulgaris* MF [NiFe] hydrogenase in a hydrogel film. Measurements done in the oxidative direction showing that the most oxidized state accessible to the protein in the redox polymer is the active Ni-SI$_a$. (B) Chronoamperometry at +141 mV for evaluation of oxygen tolerance. Black trace: glassy carbon electrode (GCE) drop-coated with *Dv*MF [NiFe] hydrogenase/polymer, red trace: electrode with the same enzyme in direct ET regime. During O_2 exposure the concentration of H_2 was kept constant at 90% and N_2 was used as an inert gas to complete the mixture. When the protein is not inside the redox polymer, the catalytic current vanishes rapidly upon O_2 exposure, while when the redox polymer is shielding the enzyme, the behavior resembles that of an O_2 tolerant hydrogenase (Figure 1B). **(C)** Scheme of the viologen-modified polymer with embedded hydrogenase applied to the electrode explaining the shielding mechanism [4].

SEIRA

One of the limitations of PFE of hydrogenases is that it measures only catalytic currents; it tells us if the enzyme is active, and how active it is, but it does not provide any evidence about the redox states participating in the measured activity. SEIRA is a technique that combines PFE with FTIR spectroscopy. The protein is immobilized on a nanostructured gold electrode which enhances IR absorption by molecules in the proximity of the gold surface. The gold electrode can be covered with buffer and used as a working electrode in a standard three electrode electrochemical cell, so that we can record spectra while we measure catalytic currents as we do in PFE (Figure 1C).

In another study in collaboration with Dr. A. De Lacey (CSIC Instituto de Catálisis and Petroleoquímica, Madrid) and Dr. I.A.C. Pereira (Universidade Nova de Lisboa) we used SEIRA to follow the incorporation of the membrane bound [NiFeSe] hydrogenase from *Desulfovibrio vulgaris* Hildenborough to an artificial lipid bi-layer [5]. In a single experiment we could determine the protein orientation on the membrane and distinguish between different electrode configurations by following the intensity of the FTIR bands assigned to the amide vibrations from the protein or the CH_2/CH_3

vibration modes from the alkyl part of the lipid bi-layer. For an optimum electrode configuration, it was possible to measure DET between enzyme and electrode and also record the CO/CN$^-$ absorption bands of the hydrogenase active site by FTIR. Therefore SEIRA proved to be an ideal technique to study membrane bound hydrogenases.

External collaborations

We collaborate with Dr. O. Lenz (TU Berlin) to study the Actinobacterial type hydrogenase from *Ralstonia eutropha*.

We are working with Dr. Vidakovic-Koch (MPI for Dynamics of Complex Technical Systems, Magdeburg) in a project to obtain information of the catalytic mechanism of hydrogenases by simulating the steady state cyclic voltammograms and impedance spectroscopy of covalently attached hydrogenases on electrodes.

An intensive collaborative work exists with the groups of Prof. W. Schuhmann and Dr. N. Plumere (Ruhr University in Bochum) to further develop redox polymers for [FeFe] hydrogenases and biomimetic compounds, as well as for application to photocatalytic water splitting devices.

References

1. Adamska, A., Silakov, A., Lambertz, C., Rüdiger, O., Happe, T., Reijerse, E., Lubitz, W. Identification and characterization of the 'super-reduced' state of the H-cluster in [FeFe] hydrogenase: a new building block for the catalytic cycle? *Angew. Chem. Int. Ed.* **2012**, *51*, 11458-11462
2. Riethausen, J., Rüdiger, O., Gärtner, W., Lubitz, W., Shafaat, H. S. Spectroscopic and electrochemical characterization of the [NiFeSe] hydrogenase from *Desulfovibrio vulgaris Miyazaki F:* reversible redox behavior and interactions between electron tranfer centers, *Chem. Bio. Chem.* **2013**, *14*, 1714-1719
3. Shafaat, H. S., Rüdiger, O., Ogata, H., Lubitz, W. [NiFe] hydrogenases: a common active site for hydrogen metabolism under diverse conditions, *Biochim. Biophys. Acta Bioenerg.* **2013**, *1827*, 986-1002
4. Plumeré N., Rüdiger O., Alsheikh Oughli, A., Williams, R., Vivekananthan, J., Pöller, S., Schuhmann, W., Lubitz, W. *Nature Chemistry* (under review)
5. Gutiérrez-Sanz, O., Marques, M., Pereira, I. A. C., de Lacey, A. L., Lubitz, W., Rüdiger, O. Orientation and function of a membrane bound enzyme monitored by electrochemical surface enhanced infrared absorption spectroscopy, *J. Phys. Chem. Lett.* **2013**, *4*, 2794-2798

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Biomolecular Structure and Dynamics

During the past two decades, high-field EPR (HFEPR) has become an increasingly valuable technique and offers significant advantages, including both an increase in detection sensitivity, and gain in spectral and time resolution, which are crucial for the investigation of biological and chemical systems.

(1) The research of our group is preliminary focused on methodological and instrumental developments and improvements of new EPR techniques.
(2) The application of these new spectroscopic techniques is dedicated to a number of topics which include:
(2.1) electron-transfer;
(2.2) structure and dynamics;
(2.3) solvation;
(2.4) homogeneous/heterogeneous catalysis.

1 Instrumental and methodological development of advanced multifrequency multiresonance EPR spectroscopy. Advanced EPR methodologies allow for detailed characterisation of the electronic structure and the microenvironment of paramagnetic systems. We are currently working on the development of high-field ELDOR-detected NMR (EDNMR) and orientation resolving dipolar high-field EPR methods. EDNMR in particular is suited for investigations of materials with fast magnetic relaxation, such as transition metal ions [1], with future applications for heterogeneous metal oxide catalysis (in cooperation with AG Cox, MPI CEC). Orientation resolving dipolar EPR methods such as RIDME (relaxation-induced dipolar modulation enhancement) and PELDOR (pulsed electron-electron double resonance) in conjunction with elaborate data-analysis procedures allow the determination of structural constrains within proteins [2, 3].

These new EPR methods require an increase of stability, sensitivity, resolution and bandwidth. To this end we are developing microwave bridges and EPR probeheads: this includes both modification of commercial spectrometers and home-build EPR equipment. We have already developed and built several W-band (95 GHz) cavities which fulfil a variety of requirements, for instance large bandwidth [1], see Figure 1A. Additional projects include (a) development of EPR probeheads based on planar microresonator structures for EPR experiments on protein single crystals, Fig. 1B (DFG SA 2471/1-1 in the framework of priority program SPP 1601); (b) development of high-pressure high-field EPR for the investigation of protein conformational dynamics under very high pressures up to 4000 bar, Fig. 1C, and (c) the development of Fabry-Perot based resonators for matrix isolation Q-band EPR spectroscopy, see Fig 1D and section 2.3.

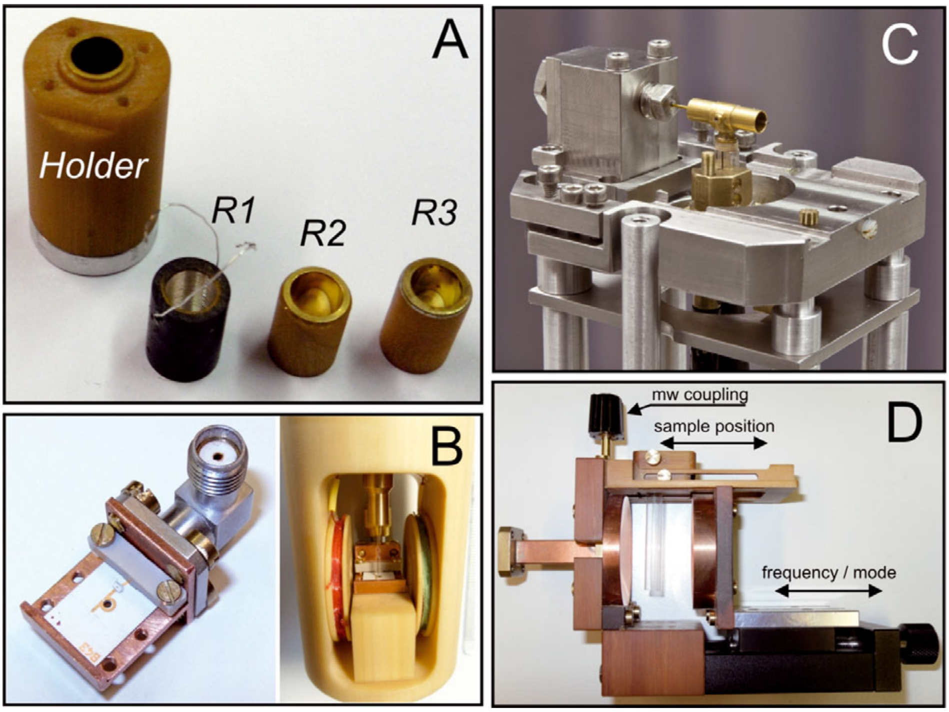

Figure 1. (A) W-band (94 GHz) TE011 resonators developed for the commercial EPR probehead (Bruker Corporation) (R1) 1H-ENDOR broad band (low-Q) cavity, (R2) narrow band (very high Q) cavity manufactured from 99.999% Au and (R3) moderate band width multipurpose cavity. (B) Planar X-band (9.5 GHz) W-type microresonator structure with 1mm sample diameter mounted on holder and the lower part of EPR probehead. (C) W-band high-pressure high-field probehead. (D) Fabry-Perot type resonator for inert gas matrix isolation Q-band (34GHz) EPR spectroscopy.

2 Applications

2.1 Investigations of natural photosynthetic systems by means of EPR spectroscopy.

The primary reactions of photosynthesis provide a "Garden of Eden" for EPR spectroscopists. We are applying multifrequency, as well as multiresonance (ENDOR, ELDOR) EPR techniques in order to obtain three-dimensional geometrical information about the electron-transfer cofactors and to probe the structural dynamics occurring in photosynthetic reaction centers upon charge-separation and charge-recombination processes [2, 4]. Our present results are summarized in Progress of Nuclear Magnetic Resonance Spectroscopy [5]. The influence of the matrix on the photosynthetic reaction center function, as modelled for instance by trehalose, as well as the properties of such matrixes themselves are also a topic of interest [6, 7].

2.2 EPR investigation of biologically relevant systems using nitroxide spin-probe and side-directed spin-labeling methods. We are applying well established nitroxide spin-probe and SDSL methods to probe the structure and dynamics of macromolecular complexes of biological relevance. Some selected SDSL projects include (a) investigation of conformational changes of the Hmd hydrogenase during catalysis (cooperation AG. Dr. S. Shima, MPI for Terrestrial Microbiology, Marburg), (b) EPR investigation of the conformational change of DNA 'tweezers' (cooperation AG Prof. I. Willner, Hebrew University Jerusalem), (c) investigation of spin labeled human alpha(1)-microglobulin (cooperation AG Knipp, MPI CEC). Spin-probe methods are being applied to investigate bulk, heterogeneous systems such as sugar matrixes [6]. The investigation of hydrogen bonded complexes of nitroxide radicals with organic donors is also in the focus of our research, see Fig. 2.

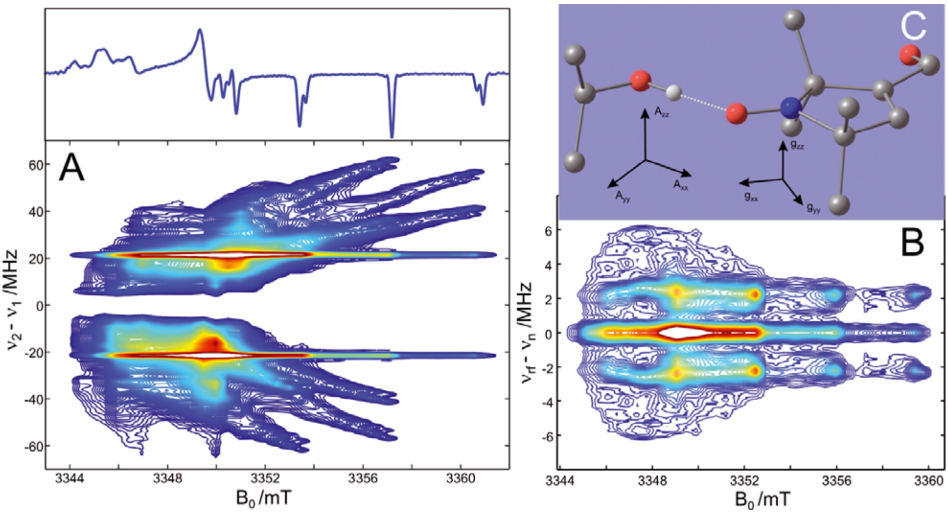

Figure 2. (A) Contour plot of the field-frequency dependence of W-band EDNMR intensities of a perdeuterated nitroxide radical in 2-propanol-D_8 glass at 50 K. (B) Contour plot of field-frequency dependence of W-band ^{1}H-ENDOR intensities of a perdeuterated nitroxide radical in 2-propanol-D_7 glass at 50 K. (C) Structure of hydrogen bonded complex of a nitroxide with 2-propanol evaluated from EPR experimental results.

2.3 Solvent effects on the structure and low temperature reactivity of high-spin carbenes. The lifetimes of paramagnetic organic intermediates such as radicals, diradicals and transient triplet state molecules are determined by intramolecular processes, for instance rearrangements or deactivations of the excited states, and by intermolecular processes, such as bimolecular reactions with other reactants or with solvent molecules. An understanding how the reactivity depends on the solvation is of particular importance not only for organic synthesis, but also for many other areas, such as atmospheric chemistry and biological chemistry. In this project we are studing the influence of the solvation on structure and reactivity of triplet ground state carbenes (cooperation with AG Prof. W. Sander, University of Bochum, within the Cluster of Excellence RESOLV). Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valence shell. The carbene carbon is linked to two adjacent groups by covalent bonds and possesses two non-bonding electrons which may have antiparallel (closed shell and open shell singlet state) or parallel (triplet state) spin conformations. The ground state spin multiplicity of the carbene dictates its reactivity. Matrix isolation FTIR in combination with advanced EPR techniques are used to gain unprecedented insight into carbene-solvent interactions. Complete resolution of electron-nuclear interaction patterns requires EPR experiments to be performed at higher microwave frequencies. Our experiments show that Q-band EPR (35 GHz, 1.16 cm^{-1}) is required to obtain proton hyperfine patterns that are necessary to reconstruct the geometrical structure of carbene molecules, see Fig 3. For probing electron-deuteron interaction even higher microwave frequencies, for instance W-band (95 GHz, 3.15 cm^{-1}), are required, see Fig. 3A.

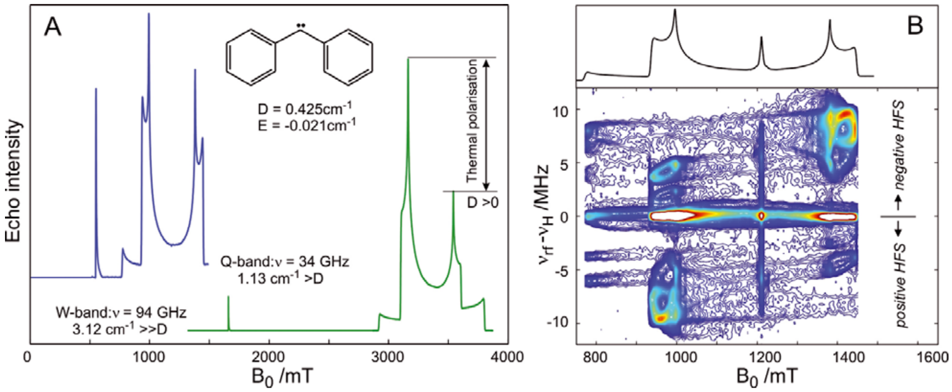

Figure 3. (A) Field-swept echo-detected EPR spectra of diphenyl carbene in frozen 2-methyl THF solution, 5K, acquired at Q- and W-band microwave frequencies. (B) Contour plot of field-frequency dependence of Q-band ^{1}H-ENDOR intensities of diphenyl carbene in frozen 2-methyl THF solution (Savitsky et al., unpubl.).

2.4 Homogeneous and heterogeneous catalytic systems. Our group is involved in the several newly established cooperation projects with the neighboring MPI for Coal Research dealing with heterogeneous and homogeneous catalytic systems. In cooperation with the AG of Prof. F. Schüth we have initiated collaborations to investigate Cu-based surface catalysts for gaseous preferential oxidation reactions. Up to now, the gas reactor was constructed which allows for simultaneous in-situ EPR experiments and gas analysis of working catalysts at temperatures up to 250°C. The preliminary results reveal the high potential of both techniques to get quantitative and mechanistic characterizations of catalytically active Cu-centers. The second on-going project (cooperation with the group of Prof. B. List) deals with EPR investigations of transient paramagnetic states in enantioselective organocatalysis. The EPR experiments should lead to a deeper understanding of the catalytic mechanisms in the various homogenous catalytic systems.

References

1. Cox, N., Lubitz, W., Savitsky, A., W-band ELDOR-detected NMR (EDNMR) spectroscopy as a versatile technique for the characterization of transition metal-ligand interactions, *Mol. Phys.* **2013**, *111*, 2788-2808
2. Savitsky, A., Niklas, J., Golbeck, J. H., Möbius, K., Lubitz, W., Orientation Resolving Dipolar High-Field EPR Spectroscopy on Disordered Solids: II. Structure of Spin-Correlated Radical Pairs in Photosystem I. *J. Phys. Chem. B* **2013**, *117*, 11184-11199
3. Savitsky, A., Dubinskii, A. A., Zimmermann, H., Lubitz, W., Möbius, K., High-Field Dipolar Electron Paramagnetic Resonance (EPR) Spectroscopy of Nitroxide Biradicals for Determining Three-Dimensional Structures of Biomacromolecules in Disordered Solids, *J. Phys. Chem. B* **2011**, *115*, 11950-11963
4. Mula, S., Savitsky, A., Möbius, K., Lubitz, W., Golbeck, J. H., Mamedov, M. D., Semenov, A. Y., van der Est, A., Incorporation of a high potential quinone reveals that electron transfer in Photosystem I becomes highly asymmetric at low temperature. *Photochem. Photobiol. Sci.* **2012**, *11*, 946-956
5. Möbius, K., Lubitz, W., Savitsky, A., High-field EPR on Membrane Proteins - Crossing the Gap to NMR. *Progr. NMR Spectr.* **2013**, *75*, 1-49
6. Malferrari, M., Nalepa, A., Francia, F., Lubitz, W., Möbius, K., Venturoli, G., Savitsky, A., Structural and dynamical characteristics of trehalose and sucrose matrices at different hydration levels as probed by high-field EPR and FTIR, *Phys. Chem. Chem. Phys.* **2014**, DOI:10.1039/C3CP54043J
7. Savitsky, A., Malferrari, M., Francia, F., Venturoli, G., Möbius, K., Bacterial Photosynthetic Reaction Centers in Trehalose Glasses: Coupling between Protein Conformational Dynamics and Electron-Transfer Kinetics as Studied by Laser-Flash and High-Field EPR Spectroscopies. *J. Phys. Chem. B* **2010**, *114*, 12729-12743

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Department of Molecular Theory and Spectroscopy

Introduction

The department of molecular theory and spectroscopy has been newly established in July 2011. The department is constituted from previous members of the department of Prof. Wieghardt, the previous chair of theoretical chemistry at the university of Bonn (Prof. Neese) as well as from Cornell university (Prof. DeBeer) and the Max Planck Institute for Iron Research (Prof. Auer). Altogether there are about 70 scientists, technicians and administrative staff working in the department. The mission of the department at the MPI CEC is to perform excellent basic research in the field of molecule based energy conversion.

Thus, the department is strongly engaged in research concerning the catalytic mechanisms of small molecule activation by transition metals. A particular focus of the department is the combination of experimental and theoretical techniques. To this end new spectroscopic methods and protocols are developed alongside intense efforts in the development of quantum chemical techniques (ORCA program, see section 3) as well as large-scale computational chemistry applications. The department is also engaged in chemical synthesis in order to produce new catalytic systems as well as to synthesize known catalysts in order to make them amenable to detailed physico-chemical and theoretical characterization.

Our vision on molecular energy research has been summarized in a recent book chapter [1]. This chapter was written as a joint effort between the group leaders of the department. In a nutshell, the efficient and reversible storage and release of energy in chemical bonds is the essential task in molecular energy research. Ideally such energy conserving chemistry follows the capture of photon energy provided by sunlight. In this respect, the most impressive chemistry of renewable energy occurs in green plants, algae and photosynthetic bacteria, all of which convert CO_2 and H_2O into O_2 and energy rich sugar molecules under the action of sunlight.

The essence: Activation of small molecules

The relevant processes all involve the activation of small, largely inert, molecules. The most important elementary processes are summarized by the following six reactions.

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (1)$$
$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^- \qquad (2)$$
$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O \qquad (3)$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad (4)$$
$$CH_4 + {}^1/_2\,O_2 \rightarrow H_3COH \qquad (5)$$
$$N_2 + 6H^+ + 6e^- \rightarrow 2\,NH_3 \qquad (6)$$

Reaction (1) is one of the most elementary chemical reactions and is of central importance for energy research as it provides H_2, which either serves as a fuel by itself or acts as precursor for further reduction reactions, e.g. in the activation of O_2, CO_2, and N_2 (reactions 3, 4, and 6). Ideally, the protons and electrons required for reaction (1) are provided by reaction (2), the oxidation of water. The latter process has been found to be very difficult to achieve in chemical catalysis and its technological realization by homogenous, heterogeneous or electrochemical means is of fundamental importance for energy research. The oxidation chemistry of methane (or higher reduced hydrocarbons, reaction (5)) is a paradigm for the conversion of biomass to fuel. It involves the activation of non-activated C-H bonds in a controlled manner, again a process that is exceedingly difficult to achieve in catalysis. Finally, the activation of the triple bond of dinitrogen (reaction (6)) is a pivotal step of fundamental importance for the large-scale production of fertilizer and consequently feedstock, and thus is also an integral part of energy research.

Focus and Organization of the Group

The Department of Molecular Theory and Spectroscopy is organized according to the guiding principles explained above. The focus of the department and the guiding idea behind all of our efforts is that mechanistic understanding will eventually lead to rational design. Mechanistic understanding requires deep analysis, which in turn requires advanced tools for analysis. Hence, the groups working in the department are all involved in the development and application of advanced spectroscopic and theoretical methods. At the same time each of the groups is focusing on the analysis of at least one of the fundamental reactions (1)-(6) (Figure 1).

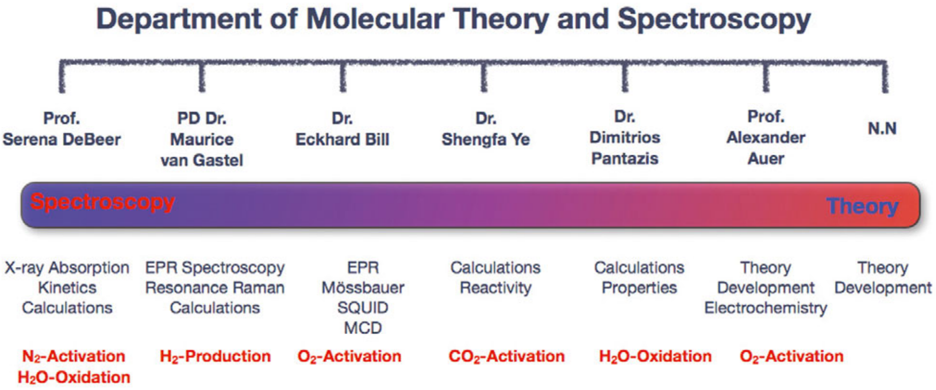


Figure 1. Structure of the department for molecular theory and spectroscopy. The group N.N. will focus on theoretical method development and is envisioned to perform computational applications in one of the relevant fields of molecular energy conservation.

The group has intensely pursued all these subjects and more detailed documentation of the results will be found in the individual sections for each group leader. Below a few important results will be briefly mentioned. In addition to our own activities, we have started to pursue joint projects with the departments of Prof. Lubitz and Prof. Schlögl (see below).

Selected Results

Significant progress has been made in elucidating the structural basis for nitrogen fixation by the enzyme Nitrogenase. Driven by the group of Prof. DeBeer, our joint efforts have led to the discovery of the first carbide group (C^{4-}) at the iron-molybdenum active site (Figure 2) [2].

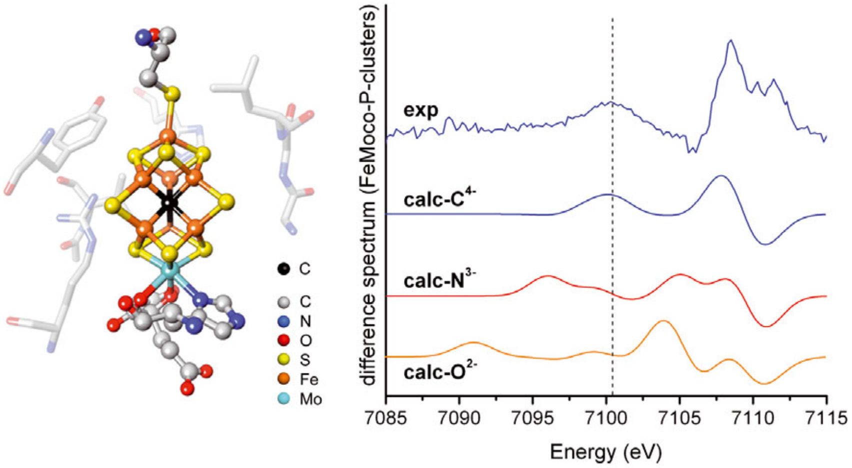


Figure 2. A combination of X-ray emission spectroscopy and quantum chemical calculations were used in order to arrive at the conclusion that the 'magic' central atom in the nitrogenase active site (shown in black on the left) is a carbide ion (C^{4-}) thus providing an important structural framework for dinitrogen activation in nature.

Furthermore, joint X-ray spectroscopic and quantum chemical studies led to the assignment of the molybdenum oxidation state in resting nitrogenase to be Mo(III), thus revising several decades of literature and paving the way for an electronic structure level understanding of nitrogen activation chemistry by transition metals (see report of Prof. DeBeer). Parallel studies have been pursued on molecular systems by Dr. Bill in collaboration with the group of Prof. Pat Holland (now at Yale university; see report of Dr. Bill) [3]. Efforts are now underway to extend and apply our spectroscopic and theoretical protocols towards heterogeneous systems (Haber-Bosch process). Most recently, we have been able to demonstrate the reverse process (N-N bond formation) on the basis of high-valent Fe(V)-nitrido complexes (see report of Dr. Bill).

The group of Prof. Auer has pursued the theoretical study of oxygen activation reactions at platinum surfaces and nanoparticles [4]. These studies are facing enormously complex questions of theoretical electrochemistry and will be extended in the future (see report of Prof. Auer).

Collaboration with the Biophysical Chemistry Department

In collaboration with Prof. Lubitz's department for Biophysical Chemistry, detailed combined experimental and theoretical studies have been performed on the oxygen evolving complex in photosystem II of higher plants. The results give strong hints at the most likely mechanism for water oxidation and provides invaluable hints at how to possibly pursue water oxidation catalysis in artificial photosynthetic systems. A number of high profile papers have been published [5] and prominently featured at major international conferences. (Figure 3, see report of Dr. Pantazis).

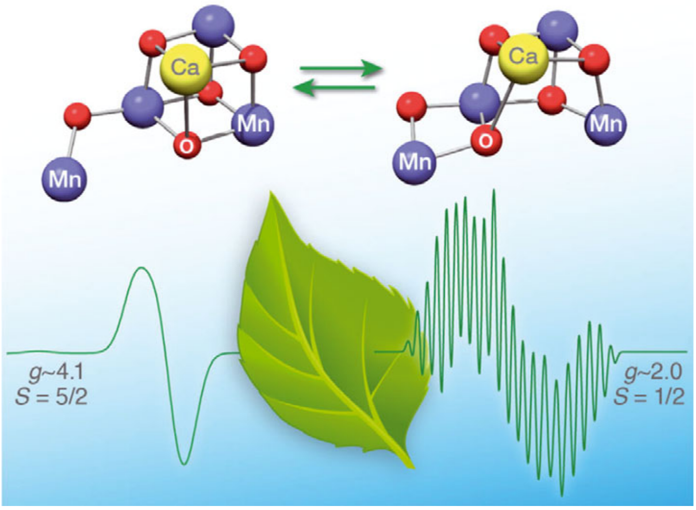


Figure 3. The combination of high-resolution EPR spectroscopy with quantum chemical calculations have revealed a number of structural and electronic features of the oxygen evolving complex (OEC) in photosystem II of higher plants which provide key clues to the mechanism of water oxidation in nature.

Much progress has also been made by jointly studying the enzyme hydrogenase which leads to insights concerning the mechanism for hydrogen formation [6]. Presently molecular catalysts are being synthesized in the hope to immobilize them on electrode surfaces in collaboration with Prof. Schlögl's department (see report of Dr. van Gastel).

In all of our experimental studies the highly-effective molecular synthesis group, led by Dr. Weyhermüller, has been instrumental in providing tailor-made molecules. It is evident that these activities must be intensified in the future.

Collaboration with the Heterogeneous Catalysis Department

Together with Prof. Schlögl's department for Heterogeneous Reactions in Mülheim as well as his group at the Fritz Haber Institute in Berlin, we have started to extend our activities towards heterogeneous systems. Coming from a molecular and biochemical background, the group needed to acquire some familiarity with experimental and theoretical issues to study solids and surfaces. However, good progress has been made. We have been able to develop a radically new theoretical approach for the calculation of X-ray absorption spectra at the metal L-edges (The DFT/ROCIS method) and have demonstrated that it can be applied to large cluster models of solids [7]. This approach allowed, for the first time, to successfully calculate the spectra of V_2O_5 (Figure 4)

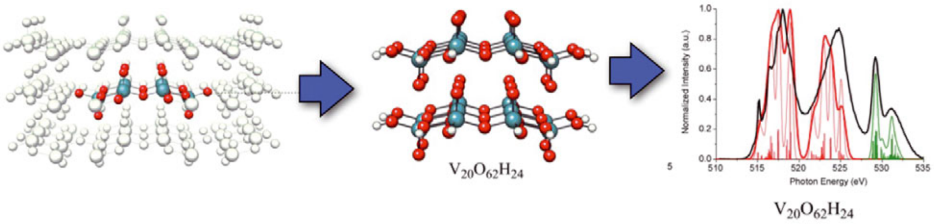


Figure 4. The ROCIS/DFT method allowed, for the first time, an accurate prediction of the vanadium L-edge X-ray absorption spectra of V_2O_5 (experimental spectra in black on the right side, calculated spectra at the vanadium L-edge in red and the oxygen K-edge in green). The ability to accurately predict these spectra is a prerequisite for identifying catalytic intermediates in heterogeneous reactions.

Having well calibrated methodology available is of paramount importance for studying reaction mechanisms at surfaces. Our studies are being extended towards industrially important oxidation catalysis by vanadium oxide species in close collaboration with the experimental efforts of Prof. Schlögl's department [8]. We plan to significantly extend these activities in the future.

References

1. DeBeer, S., van Gastel, M., Bill, E., Ye, S., Petrenko, T., Pantazis, D. A., Neese, F., in *Chemical Energy Storage* (Ed.: R. Schlögl), DeGruyter, Berlin, **2012**

2. Lancaster, K. M., Roemelt, M., Ettenhuber, P., Hu, Y. L., Ribbe, M. W., Neese, F., Bergmann, U., DeBeer, S., X-Ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor, *Science* **2011**, *334*, 974-977

3. Rodriguez, M. M., Bill, E., Brennessel, W. W., Holland, P. L., N_2 Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex, *Science* **2011**, *334*, 780-783

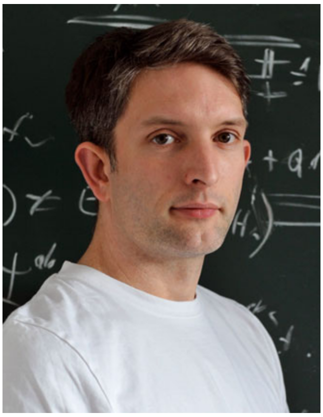
4. a) Katsounaros, I., Schneider, W. B., Meier, J. C., Benedikt, U., Biedermann, P. U., Cuesta, A., Auer, A. A., Mayrhofer, K. J. J., The impact of spectator species on the interaction of H_2O_2 with platinum – implications for the oxygen reduction reaction pathways, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8058-8068; b) Benedikt, U., Schneider, W. B., Auer, A. A., Modelling electrified interfaces in quantum chemistry: constant charge vs. constant potential, *Phys. Chem. Chem. Phys.* **2013**, *15*, 2712-2724

5. a) Krewald, V., Neese, F., Pantazis, D. A., On the magnetic and spectroscopic properties of high-valent Mn_3CaO_4 cubanes as structural units of natural and artificial water oxidizing catalysts, *J. Am. Chem. Soc.* **2013**, *135*, 5726-5739; b) Pantazis, D. A., Ames, W., Cox, N., Lubitz, W., Neese, F., Two Interconvertible Structures that Explain the Spectroscopic Properties of the Oxygen-Evolving Complex of Photosystem II in the S_2 State, *Ang. Chem. Int. Ed.* **2012**, *51*, 9935-9940; c) Su, J. H., Cox, N., Ames, W., Pantazis, D. A., Rapatskiy, L., Lohmiller, T., Kulik, L. V., Dorlet, P., Rutherford, A. W., Neese, F., Boussac, A., Lubitz, W., Messinger, J., The electronic structures of the S(2) states of the oxygen-evolving complexes of photosystem II in plants and cyanobacteria in the presence and absence of methanol, *Biochimica Et Biophysica Acta-Bioenergetics* **2011**, *1807*, 829-840

6. a) Kampa, M., Pandelia, M. E., Lubitz, W., van Gastel, M., Neese, F., A Metal–Metal Bond in the Light-Induced State of [NiFe] Hydrogenases with Relevance to Hydrogen Evolution, *J. Am. Chem. Soc.* **2013**, *135*, 3915-3925; b) Weber, K., Krämer, T., Shafaat, H. S., Weyhermuller, T., Bill, E., van Gastel, M., Neese, F., Lubitz, W., A Functional [NiFe]-Hydrogenase Model Compound That Undergoes Biologically Relevant Reversible Thiolate Protonation, *J. Am. Chem. Soc.* **2012**, *134*, 20745-20755

7. a) Roemelt, M., Neese, F., Excited States of Large Open-Shell Molecules: An Efficient, General, and Spin-Adapted Approach Based on a Restricted Open-Shell Ground State Wave function, *J. Phys. Chem. A* **2013**, *117*, 3069-3083; b) Roemelt, M., Maganas, D., DeBeer, S., Neese, F., A combined DFT and restricted open-shell configuration interaction method including spin-orbit coupling: Application to transition metal L-edge X-ray absorption spectroscopy, *J. Chem. Phys.* **2013**, *138*, 204101-204122

8. Maganas, D., Roemelt, M., Havecker, M., Trunschke, A., Knop-Gericke, A., Schlögl, R., Neese, F., First principles calculations of the structure and V L-edge X-ray absorption spectra of V_2O_5 using local pair natural orbital coupled cluster theory and spin–orbit coupled configuration interaction approaches, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7260-7276



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Quantum chemical methods, simulation of electrochemical processes

Methods and Materials Group

Research in our group is driven by a very broad interest that ranges from very basic method development for electron correlation problems up to application of quantum chemistry to systems from electrocatalysts or polymer chemistry. This diverse profile stems from the deep interest in fundamental electronic structure theory but is strongly influenced by the motivation to cooperate with experimentalists in fields where theory can aid in the interpretation of results and design of new experiments. Coming from a background in Coupled Cluster theory and code development, I have spend several years of my scientific career in materials related institutes like the MPIE in Düsseldorf, which resulted in this diverse profile.

Method Development – new approximations for accurate solutions

In methodological developments we focus on finding novel approximations that allow to solve the n-electron problem more efficiently. While the numerical solution of Schrödinger's equation for an n-electron system is possible in principle, namely via the Full Configuration Interaction (FCI) method, its exponential scaling of computational effort with number of electrons does not allow the application to problems other then small benchmark examples. However, FCI is still a vital component of common multi-reference methods (like CASSCF) that are widely used to calculate structures and properties of transition metal complexes or bond-breaking processes in chemical reactions, for example.

While several novel and extremely successful approximations have been devised in recent years to overcome the steep scaling of electron correlation methods with system size, reducing the exponential scaling while approaching the exact n-electron solution is still an open task. Approaches like DMRG, QMC or the novel QMC-FCI schemes appear promising, but so far no breakthrough has been reported and the search for alternative approaches goes on.

In our work we focus on an approximation scheme that is based on tensor decomposition/representation techniques which have been developed in applied mathematics over the recent decades. The basic idea is to break the curse of dimensionality by approximating high dimensional tensors using objects of lower dimensionality.

In recent work we have shown that if an appropriate tensor representation is used, solving any n-electron method would require in the order of $O(N^4)$ to $O(N^6)$ complexity *in principle*. This can be achieved if classical post-HF-methods like Coupled Cluster or CI are approximated by casting all wavefunction parameters into the Canonical Polyadic (CP) product form (see Fig. 1). However, whether this is beneficial in practice is determined by the expansion length (called „rank“ in this case) of the approximation. We have been able to demonstrate that for example for doubles amplitudes in Coupled Cluster theory the rank scales between N and N^2 proving that the scheme is indeed very promising [7]. However, the overhead of the representation algorithm and the additional steps that are introduced have an extremely high pre-factor. Current work is directed towards improvements of the efficiency and the extention to higher order methods like FCI. Furthermore, the application of different representation formats offers a broad field for investigations that might even yield a different perspective on the electron correlation problem as a whole [2].

$$r_{ij}^{ab} \leftarrow t_{ij}^{ef} v_{ef}^{ab} = \sum_{e=1} \sum_{f=1} t_{ij}^{ef} v_{ef}^{ab}$$

all tensors in decomposed representation

$$t_{ij}^{ef} v_{ef}^{ab} = \sum_{l'=1}^{k} \sum_{l=1}^{r} \sum_{e=1} \sum_{f=1} \left[(t^e)_{l'} (t^f)_{l'} (t_i)_{l'} (t_j)_{l'} \right] \left[(v^a)_l (v^b)_l (v_e)_l (v_f)_l \right]$$

$$= \sum_{l'=1}^{k} \sum_{l=1}^{r} \left(\sum_{e=1} (t^e)_{l'} (v_e)_l \right) \left(\sum_{f=1} (t^f)_{l'} (v_f)_l \right) (v^a)_l \, (v^b)_l \, (t_i)_{l'} \, (t_j)_{l'}$$

complexity is reduced from $occ^2 virt^4$ to $\sim k \cdot r \cdot N$
benefit if product of ranks is smaller than N^5

Figure 1. Example for tensor decomposition in the CP format for a term from the Coupled Cluster doubles equations. If all tensors are cast into the CP format, the expression reduces to a series of scalar products and copy operations.

Materials Science – simulation of systems with relevance in electrocatalysis

While the group is intensively involved in work in the Forschergruppe FOR 1497 „Organisch-Anorganische Nanokomposite durch Zwillingspolymerisation“ („organic-inorganic nanocomposites by twin polymerization“) [6], which is located at the TU

Chemnitz, the focus of our work in materials science has shifted towards electrocatalytic systems in recent years. Through the close collaboration with experimental groups that work in the area of electrocatalysis, our group is interested in the simulation of catalytic reactions that include nanoparticles, possibly in contact with a supporting electrode material, as for example used for the oxygen reduction reaction (ORR) in PEM fuel cells.

Using standard DFT Methodology, we have been able to investigate the role of peroxide in the ORR [4, 1] or the segregation behavior of Pt-Co Nanoparticles in the presence of adsorbates [3]. While these studies directly addressed questions raised by the experimentalists at a very qualitative level, a recent study has focused on the application of novel dispersion interaction corrected DFT methods to investigate the basic adhesion mechanism of metal nanoparticles on graphitic carbon support materials (see Fig. 2 [8]).

While for problems from homogenous or even heterogeneous catalysis, the toolbox of quantum chemists includes almost everything that is needed - from cost effective methods like DFT, corrections for dispersion interactions, embedding methods or implicit treatment of solvation - an important ingredient for electrocatalysis is missing. This is the explicit inclusion of the electrochemical potential in the electronic structure of the system. While several approximate schemes have been suggested, especially a-posteriori corrections motivated from thermodynamics, a satisfactory routine protocol for treating the electrochemical potential in quantum chemical approaches has yet to be devised. This is especially important if one aims at simulating supported nanoparticles in electrocatalysis, which are very common in current electrocatalytic processes. For this reason, we are actively developing grand canonical DFT schemes, in which, rather then working with a fixed number of electrons, the chemical potential of the electrons is fixed while the number of electrons is varied within the SCF cycles [2].

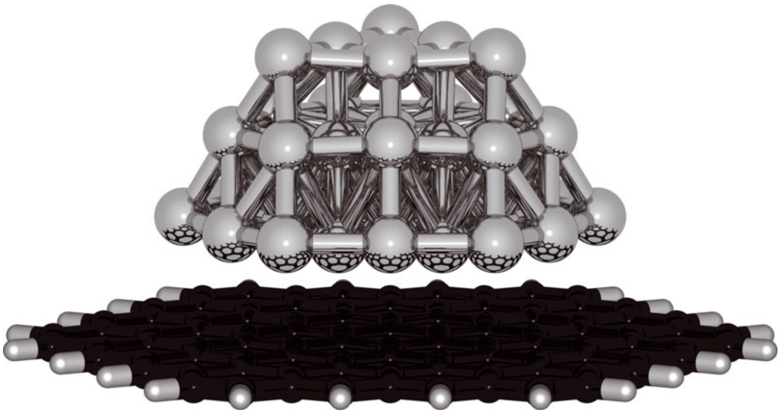
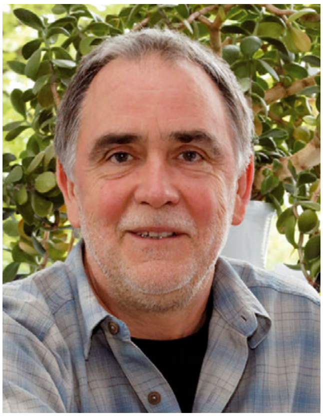


Figure 2. Computational model for Pt-Nanoparticle consisting of 37 Pt atoms and a graphitic carbon support modeled by a patch of graphene. If conventional DFT methods are applied, no interaction is observed while novel DFT-D approximations allow the quantification of bonding interactions in these systems.

References

1. Katsounaros, I., Schneider, W. B., Meier, J. C., Benedikt, U., Biedermann, U. P., Cuesta, A., Auer, A. A., Mayrhofer, K. J. J., The impact of spectator species on the interaction of H_2O_2 with platinum - implications for the oxygen reduction reaction pathways, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8058-8068, DOI: 10.1039/c3cp50649e
2. Benedikt, U., Schneider, Wolfgang B., Auer, Alexander A., Modelling electrified interfaces in quantum chemistry: constant charge vs. constant potential, *Phys. Chem. Chem. Phys.* **2013**, *15*, 2712-2724, DOI: 10.1039/c2cp42675g
3. Kettner, M., Schneider, W. B., Auer, A. A., Computational Study of Pt/Co Core-Shell Nanoparticles: Segregation, Adsorbates and Catalyst Activity, *J. Phys. Chem. C,* **2012**, *116*, 15432-15438, DOI: 10.1021/jp303773y
4. Katsounaros, I., Schneider, W. B., Meier, J. C., Benedikt, U., Biedermann, P. U., Auer, A. A., Mayrhofer, K. J. J., Hydrogen peroxide electrochemistry on platinum: towards understanding the oxygen reduction reaction mechanism, *Phys. Chem. Chem. Phys.*, **2012**, *14*, 7384-7391, DOI: 10.1039/c2cp40616k
5. Benedikt, U., Auer, A. A., Espig, M., Hackbusch, W., Tensor decomposition in post-Hartree-Fock methods. I. Two-electron integrals and MP2, *J. Chem. Phys.* **2011**, *134*, 054118, DOI: 10.1063/1.3514201
6. Auer, A. A., Richter, A., Berezkin, A. V., Guseva, D. V., Spange, S., Theoretical Study of Twin Polymerization - From Chemical Reactivity to Structure Formation, *Macromolecular Theory and Simulations* **2012**, *21*, 615-628
7. Benedikt, U., Auer, H., Espig, M., Hackbusch, W., Auer, A. A., Tensor representation techniques in post-Hartree–Fock methods: matrix product state tensor format, *Molecular Physics* **2013**, DOI: 10.1080/00268976.2013.798433
8. Schneider, Wolfgang B., Benedikt, Udo; Auer, Alexander A., Interaction of platinum nanoparticles with graphitic carbon structures: a computational study, *ChemPhysChem.* **2013**, *14*, 13, 2984-2989



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Inorganic Spectroscopy of Molecular Transition Metal Complexes

We studied the electronic structure of molecular transition metal complexes, relevant for the activation of small molecules like oxygen, nitrogen, or hydrogen, or other electron-transfer processes, or showing otherwise interesting catalytic, electronic or magnetic properties. The work was performed in collaboration with a number of top groups in inorganic synthetic or biochemistry. The physical techniques used were ^{57}Fe-Mössbauer spectroscopy, multi-frequency cw-EPR spectroscopy (S-, X-, and Q-band), magnetic susceptibility measurements and vis/NIR MCD spectroscopy. Some of the projects will be cursorily highlighted in the following.

Low-Valent, Low-Coordinated Iron Compounds

Together with the group of Pat Holland, Yale University (previously Rochester) we studied the electronic structure and catalytic function of low-valent iron and cobalt compounds with unusual three- and four-coordination. The Holland group is leading in synthesizing electron-rich, low coordinated transition metal compounds suitable as catalysts, e.g. for the activation of nitrogen or C-H activation. The metal ligands are mostly two-coordinating β-diketiminate derivatives, and one or two small molecules or atoms. We mainly focused on the investigation of iron in the oxidation states (I), (II), and (III). In this program it was found that reduction of the dinuclear iron(II) compound (**1**) in nitrogen atmosphere yielded the tetranuclear bis-nitride complex (**2**) (Figure 1A) [1]. Three iron centers are surrounding two bridging nitrogen atoms with an unprecedented long N-N distance of 2.8 Å, indicating that the N-N bond is broken (free N_2 has 1.1 Å). Hence, N_2 must have been reduced with six electrons, giving two nitrides (N^{3-}) that are ready for further reactions. The compound provides a molecular model for dinitrogen activation, similar to the key step in the Haber-Bosch process. In fact, compound (**2**) produces ammonia at 25°C upon treatment with H_2.

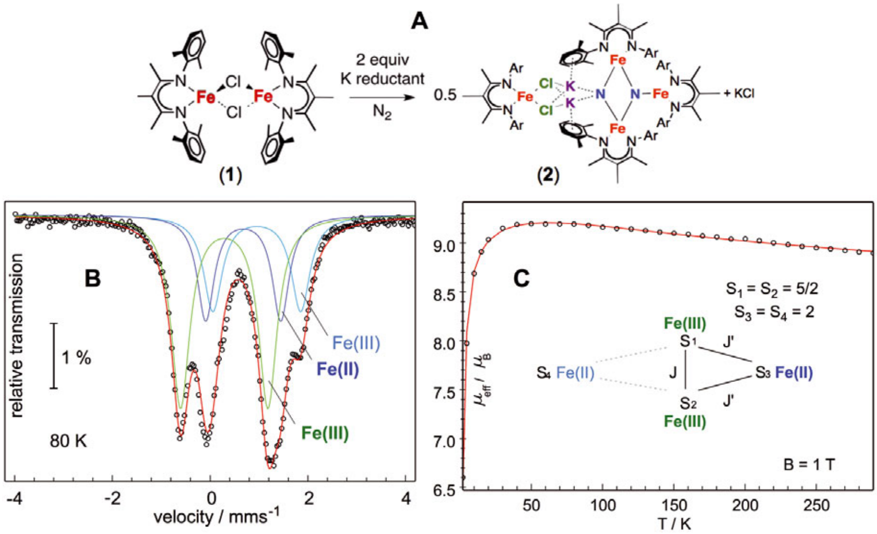

Figure 1. (A) Schematic view of the reduction of compound (**1**) forming the bis-nitride complex (**2**). (B) Zero-field Mössbauer spectrum of (**2**). (C) Temperature dependence of the effective magnetic moment of (**2**) and spin-coupling scheme of the four iron sites (inset).

Zero-field Mössbauer spectra revealed the presence of two identical iron ions in oxidation state (III) and two different iron(II) (Figure 1B). Assignment of the oxidation states to the individual metal sites, however, could be derived only from the temperature dependence of the magnetic susceptibility (Figure 1C). The high effective moments revealed parallel spin alignment of the ferric ions (S=5/2) due to dominating antiparallel coupling to the weaker spin of one ferrous iron (S=2; J'>J), whereas the second ferrous ion is magnetically isolated. The features allowed unambiguous mapping of the Mössbauer data to the molecular structure via the spin coupling scheme as sketched in the inset of Figure 1C.

Low-Valent Iron Complex with Short Metal-Metal Bond

Inorganic complexes with electron-rich metal-metal bonds are presently investigated because of the large number of possible metal pairings and electronic interactions, providing a wide range of electronic properties and chemical reactivity. In particular, one sought-after application is the cooperative coupling of metals in multi-electron catalysis. With the group of Connie Lu, Minneapolis, we explored the electronic structure of established as well as new iron and cobalt complexes with metal-metal bonds, showing paramagnetic ground states with high spin up to S=7/2. So far this is rather unusual for metal-metal bonds in general.

Iron-Sulfur Clusters with Unusual Properties

Fe:S centers are biological electron-transfer units involved in a wide range of (bio) inorganic redox reactions, including the function of hydrogenases. An increasing number of enzymes is found now using Fe:S clusters also for catalysis. Our spectroscopic work was focused on their versatile electronic properties, which we could extend to new model systems from the group of Franc Meyer, Göttingen.

They synthesized and crystallized a series of dinuclear systems in three oxidation states, which allowed us to address the phenomena of double exchange in new detail, potentially relevant for the understanding of redox potentials. The work was complemented with biochemical projects.

Oxygen-tolerant [NiFe]Hydrogenase

The most challenging investigation of Fe:S clusters was performed in collaboration with the group of Prof. Lubitz on the role of the Fe:S clusters in the electron-transfer chain of the oxygen-tolerant hydrogenase from Aquifex aeolicus with twelve iron sites in four different centers. Extensive Mössbauer measurements on three different oxidation states at different temperatures and applied magnetic fields, in conjunction with the EPR investigations of the Lubitz group enabled us to unravel the fundamental distribution pattern of iron oxidation states in the multi-center system. With the help of additional systematic, spectroscopy-oriented DFT calculations in the Neese group we finally achieved a consistent description of the electronic structure of the new so-called [4Fe-3S] cluster, positioned closest to the catalytic [NiFe] center [2]. The cluster has an unprecedented molecular structure undergoing redox-dependent changes in order to support three different oxidation states, whereas only one redox pair is found by all other Fe:S centers. Transition of the cluster to its super-oxidized state provides the basis of oxygen tolerance in this system.

A Textbook Project

In 2009 I accepted an invitation from Ph. Gütlich and A.X. Trautwein to join their initiate for a revised edition of their textbook on Mössbauer spectroscopy from 1978. Until publication in 2011 I added a comprehensive revision of the fundamental chapters on physical concepts, experiments and methods, and hyperfine interactions, including new parts on paramagnetic systems and spin Hamiltonian analyses (chap. 2-4), as well as new applications from modern inorganic chemistry (chap. 8). The contributions are based on my in-house teaching experience with mainly chemistry students. The book [3] is well accepted as a new standard reference for teaching and chemical applications of Mössbauer spectroscopy.

References

1. Rodriguez, M. M., Bill, E., Brennessel, W. W. and Holland, P. L., N_2 Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex, *Science* **2011**, 334, 780-783
2. Pandelia, M.-E., Bykov, D., Izsak, R., Infossi, P., Giudici-Orticoni, M.-T., Bill, E., Neese, F. and Lubitz, W., Electronic structure of the unique [4Fe-3S] cluster in O_2-tolerant hydrogenases characterized by ^{57}Fe Mössbauer and EPR spectroscopy, *Proc. Nat. Acad. Sci.* **2013**, *110*, 483-488
3. Gütlich, P., Bill, E. and Trautwein, A. X. **2011**. Mössbauer Spectroscopy and Transition Metal Chemistry. Berlin Heidelberg, Springer Verlag

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X-Ray Spectroscopy

This progress report summarizes research in the DeBeer group since moving to the MPI in Muelheim in July 2011. Our research focuses on the development and application of X-ray spectroscopic methods as tools to understand electronic structure and catalytic function. Herein, our recent advances in methodological developments and their applications to small molecule model systems, as well as biological catalysts are briefly summarized.

Methodological Developments.
V2C XES. The valence-to-core region of an X-ray emission spectrum (V2C XES), results from the fluorescent photon that is produced when a valence electron refills the 1s core hole of an absorbing atom. Over the last several years, my group and I have been interested in developing the full chemical information content of these spectra. We have shown that V2C XES spectra provide a sensitive probe of ligand identity, ionization potential and protonation state. The experimental spectra can be readily modeled within a one-electron DFT approach, furthering the quantitative information that one can extract from experiment. From the correlation of experimental data to theory, we have been able to rigorously show that spectral energies primarily reflect ligand identities, while spectral intensities primarily reflect metal-ligand bond lengths. Detailed calibration studies for both Fe and Mn complexes have recently been completed [1, 2], building upon previous work from our group.

In addition, we have recently shown that V2C XES can be used as a probe of small molecule bond activation. Using a series of iron model complexes in which the N-N bond varies from a formal triple bond to a fully cleaved bis-nitride species, we have shown that the experimental V2C XES energies can be directly correlated to the N-N bond strength (Figure 1) [3].

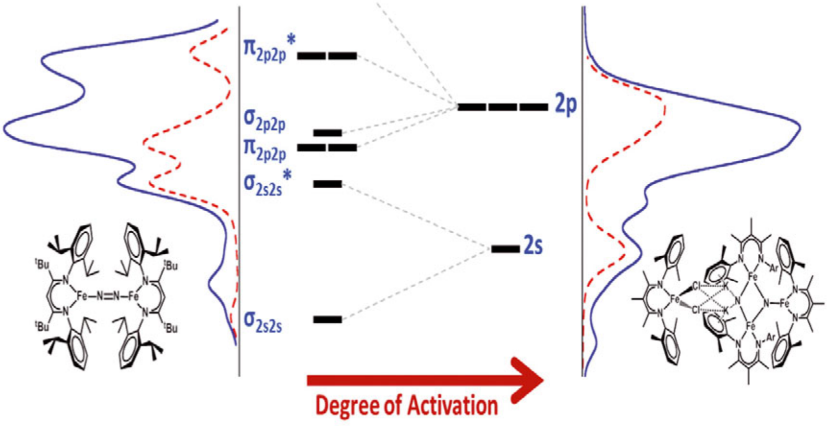

Figure 1. Qualitative molecular orbital diagram showing the change in the N_2 contribution to the V2C XES spectrum as the N-N bond is elongated.

Specifically an experimental peak, which corresponds to the N-N 2s-2s sigma antibonding molecular orbital, shows ~2 eV shift to lower energy upon N-N bond cleavage. The correlation between V2C XES peak energies and N-N vibrational frequencies is linear. This indicates that V2C XES may be of utility as a time-resolved probe of small molecule activation.

HERFD XAS. High-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) is a means to obtain XAS spectra with resolution better than the core hole lifetime. This is achieved using a high-resolution fluorescence analyzer to set a narrow window on the K-alpha (2p-1s) emission line. The approach has the potential for great impact on our understanding of heavy metal XAS spectra, which due to the short core hole lifetimes, suffer from a large intrinsic broadening. Recently we have reported the first Mo HERFD data for a series of model complexes [4]. We have shown that the resolution is improved by a factor of ~2 relative to conventional measurements, greatly increasing the quantitative information that can be extracted from the data. Further, we have shown that the data can be readily calculated within a time-dependent density functional theory (TDDFT) approach. Linear correlations between theory and experiment have been obtained for both the transition energies and intensities. These studies thus indicate that Mo HERFD spectra can be used to obtain quantitative information about the electronic structure of unknown systems. A recent application to the nitrogenase enzyme system is highlighted below.

Applications

Nitrogenase. The conversion of dinitrogen to ammonia is a process of fundamental biological and economic importance. Biologically, this transformation is enabled by free diazotrophs, containing the enzyme nitrogenase. The catalytic active site of nitrogenase is a 1Mo-7Fe-9S core with a previously unidentified atom X at the center (the so called FeMoco active site). The presence of a light atom (C, N or O) at the center of FeMoco was first revealed by protein crystallography, however, its exact

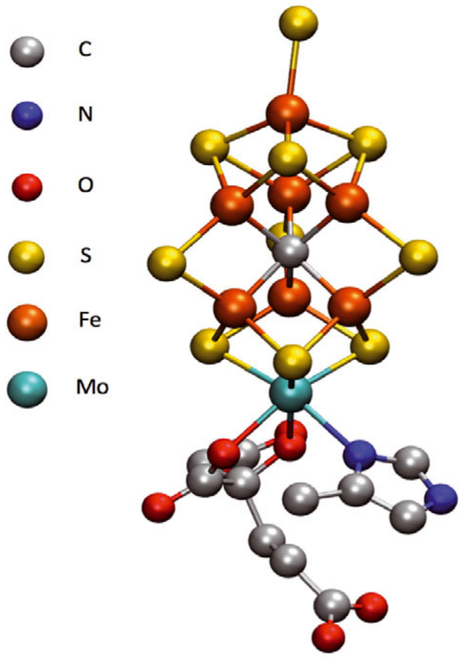

Figure 2. The FeMoco factor in nitrogenase. V2C XES studies revealed the presence of a central carbon atom.

identity had eluded spectroscopic characterization for nearly a decade. Using the V2C XES methodology described above, we were able to unambiguously identify the presence of a central mu6 carbon at the heart of the nitrogenase catalytic active site (Figure 2) [5].

Further, we were able to use this same approach to interrogate earlier gene products, and show that insertion of the carbon occurs on NifB, a radical SAM enzyme, which is capable of methyl insertion [6]. The presence of this central carbon atom raises many important questions about why it is there and how it tunes the catalytic cluster for optimal activity. These questions are being actively investigated in our research group.

Beyond the identity of the central atom in FeMoco, there are also many fundamental questions about the electronic structure of the active site. Presently the total charge on the cluster and the oxidation state distribution within the cluster are unknown. In general it has been assumed that the Mo atom in the cluster is a diamagnetic Mo(IV) species. However, recently, using the Mo HERFD methodology described above, we have shown that the active site contains a Mo(III) center. Further, by correlation of the nitrogenase data to theory, we have been able to show that the Mo(III) ion is in an unusual non-Hund configuration which arises due to coupling with the neighboring Fe atoms. A similar situation also was shown to be present in a small molecule (Bu_4N) [$[(Tp)MoFe_3S_4Cl_3]_2$ $(\mu\text{-S})$] cluster. These results raise interesting parallels between FeMoco and the known catalytic Mo model complexes for N_2 reduction. Further, our result demonstrate the first example of Mo(III) in biology.

Photosystem II Model Complexes. Photosynthetic water oxidation is enabled by the Mn_4CaO_5 cluster of photosystem II. The active site is well known to cycle through five S-states, successively accumulating the four oxidizing equivalents, which allow for formation of an O-O bond. A key question in understanding the mechanism of the O-O bond formation involves determination of the proton inventory during the catalytic cycle. One would like to identify whether O^{2-}, OH^- or H_2O are coordinated to Mn. This requires selective tools to interrogate the Mn ligation sphere.

Recently we have used V2C XES to examine a series of dimeric Mn model complexes in which the bridging motif is systematically varied from O^{2-}/O^{2-} to O^{2-}/OH^- to OH^-/OH^-. Our results show that single protonation events can be readily determined. Extension of these studies to the Mn_4CaO_5 cluster of PSII are currently underway.

References

1. Chandrasekaran, P., Chiang, K. P., Nordlund, D., Bergmann, U., Holland, P. L., DeBeer, S., On the Sensitivity of X-ray Core Spectroscopy to Changes in Metal Ligation: A Systematic Study of High-Spin Ferrous Complexes, *Inorg. Chem.*, **2013**, *52*, 6286-6298
2. Beckwith, M. A., Roemelt, M., Collomb, M.-N., DuBoc, C., Weng, T.-C., Bergmann, U., Glatzel, P., Neese, F. and DeBeer, S., Manganese K X-ray Emission Spectroscopy as a Probe of Metal-Ligand Interactions, *Inorg. Chem*, **2011**, *50*, 8397-8409
3. Pollock, C. J., Grubel, K., Holland, P. L., DeBeer, S., Experimentally Quantifying Small Molecule Bond Activation Using Valence-to-Core X-ray Emission Spectroscopy, *J. Am. Chem. Soc.*, **2013**, *135*, 11803-11808
4. Lima, F. A., Bjornsson, R., Weyhermüller, T., Chandrasekaran, P., Glatzel, P., Neese, F., DeBeer, S., High-Resolution Molybdenum K-edge X-ray Absorption Spectroscopy Analyzed with Time-Dependent Density Functional Theory , *Phys. Chem. Chem. Phys*, **2013**, *15*, 20911-20920
5. Lancaster, K. M., Roemelt, M., Ettenhuber, P., Hu, Y., Ribbe, M. W., Neese, F., Bergmann, U., DeBeer, S., X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor, *Science*, **2011**, *334*, 974-977
6. Lancaster, K. M., Hu, Y., Bergmann, U., Ribbe, M. W., DeBeer, S., X-ray Spectroscopic Observation of an Interstitial Carbide in NifEN-bound FeMoco Precursor, *J. Am. Chem. Soc.* **2013**, *135*, 610-612

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Multiscale modeling of natural and artificial photosynthesis

The main focus of research in the Pantazis group in the past two years has been the detailed understanding of the electronic and geometric structure of the oxygen evolving complex (OEC) of Photosystem II (PSII) as the archetypical water oxidizing system. The OEC contains the Mn_4CaO_5 cluster that, driven by sunlight-induced charge separation at the reaction center of PSII, cycles through five oxidation states (S_0–S_4), accumulating the oxidizing equivalents required to catalyze the oxidation of two water molecules into O_2. Our group develops quantum chemical methods and computational models for the prediction of experimental observables in order to correlate structural features with spectroscopic properties. This overcomes limitations of experimental data interpretation, and allows exploration of otherwise inaccessible aspects of the OEC. The synergy of theory and experiment (this work involves close collaboration with the group of Dr. Nicholas Cox) has enhanced our understanding of the natural system in terms of both structure and mechanism [1]. Parallel research efforts are directed towards synthetic analogues of the OEC, as well as in heterogeneous catalytic Co, Mn and Mn/Ca oxide materials.

Multiscale modeling of Photosystem II.

The latest crystal structure of PSII at a resolution of 1.9 Å has greatly limited the structural possibilities for the OEC. However, owing to X-ray induced reduction of the Mn_4CaO_5 cluster, the crystallographic structure represents a superposition of non-physiological states and thus is not an accurate structural model for the catalyst. A major line of research for our group was to establish the correct structure of the OEC by refining the X-ray model, and to explain the spectroscopic properties of the experimentally most well-studied S_2 state.

Using quantum mechanical (QM) models of the OEC, the artifacts of the crystallographic model with respect to the Mn_4CaO_5 were identified and a screening of protonation states and patterns was carried out.[2] Comparison with experimental data confirmed that all oxo-bridges of the cluster are unprotonated in the S_2 state, and that of the two "water" ligands of the terminal Mn, one binds as H_2O and the other as OH^-.

Subsequent investigations addressed the intrinsic structural heterogeneity of the OEC, which manifests in the S_2 state as two distinct EPR signals, a multiline signal centered around $g \approx 2.0$ and arising from a spin $S=1/2$ state, and a broad signal at $g \geq 4.1$ arising from an $S=5/2$ state. Using QM models of approximately 230 atoms it was shown that two distinct but essentially isoenergetic minima exist in the S_2 state: one with an "open cubane" topology and an $S=1/2$ ground state, and one with a "closed cubane" topology that displays a $S=5/2$ ground state as a result of dominant ferromagnetic interactions within the cuboidal Mn_3CaO_4 subunit. Spectral simulations proved that the two species give rise to the two observed types of EPR signal, while the two species were found to be interconvertible over a low barrier, in line with experiment (Figure 1) [3]. The concept of two structures corresponding to the observed signals of the S_2 state now forms the basis for interpretation of a wide range of observations and provides a framework for mechanistic considerations. Moreover, this work has highlighted structural flexibility as a fundamental feature of the OEC, critical for second substrate binding [1].

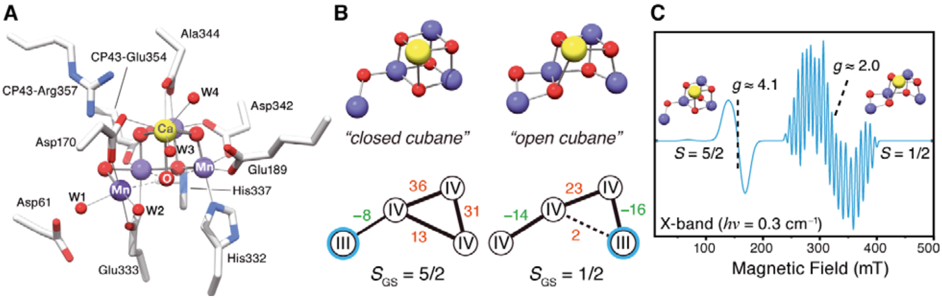

Figure 1. A: The oxygen evolving complex. B: The two interconvertible forms of the Mn_4CaO_5 core along with computed exchange couplings constants (in cm^{-1}). C: Simulated EPR spectra of the S_2 state.

Despite the level of elaboration achieved with the above approach, models that only include the first and fragments of the second coordination sphere of the OEC are not sufficient to address all questions related to the complex phenomenology of the system. To investigate how the protein environment affects the properties of the OEC and how it, in turn, responds to changes in the electronic and geometric structure of the Mn_4CaO_5 cluster, as well as to chemical events such as deprotonations, substrate binding and interaction with inhibitors, our group has developed hybrid quantum mechanics/molecular mechanics (QM/MM) models with more than 8000 atoms (Figure 2). In these models the QM description of the Mn_4CaO_5 cluster and its immediate environment is retained so all methods for the calculation of spectroscopic properties remain applicable, while the force-field modeling of the surrounding protein enables the efficient exploration of the conformational space.

The QM/MM models were validated by investigating the convergence of magnetic and spectroscopic properties with respect to the size of the QM region and the MM point charge treatment [4]. This study defined the minimum requirements for achieving a satisfactory level of accuracy for spectroscopic parameters, and revealed important effects of charged residues and hydrogen-bond networks that originate beyond the second ligand sphere, and hence are absent in pure QM models.

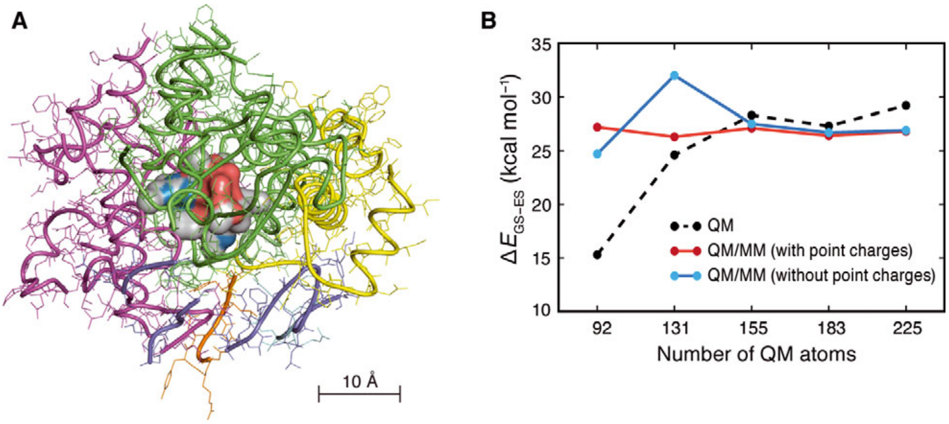

Figure 2. A: The QM/MM model of the OEC. B: Convergence of the ground-state to first excited energy gap with increasing size of QM region.

The multi-scale approach outlined above was recently advanced to a complete MM model of the PSII monomer that includes all protein subunits and is embedded in an atomistic representation of the membrane and the water environment. This model, consisting of nearly 400 000 atoms, provides a unique platform for molecular dynamics simulations to explore large-scale features of the enzyme and investigate phenomena beyond the reach of other computational approaches. Current efforts are directed towards establishing the architecture of channels for substrate delivery, proton removal and dioxygen release. Progress has also been made in studying the effect of point mutations and in predicting differences between the bacterial PSII and the PSII of higher plants, for which no crystal structures are yet available.

Synthetic Mn/Ca oxide models.

The highly connected Mn/Ca oxide topology of the OEC has only very recently been partly replicated in synthetic systems at the oxidation states found in PSII. A detailed study of two synthetic complexes that incorporate the motif of the high-valent Mn_3CaO_4 cubane was undertaken, combined with the study of prototypical model systems, with the aim to identify the structural and electronic determinants of their magnetic properties.[5] This work established that an $Mn(IV)_3CaO_4$ cubane is an intrinsically ferromagnetically coupled high-spin unit (S=9/2), in agreement with the conclusions regarding the "closed cubane" form of the S_2 state of the OEC [3], and that the ground state is unlikely to be altered upon reduction and protonation (Figure 3). Additionally, it was shown that the lack of coordinative flexibility for any of the oxo-bridges inhibited the opening of the cubane upon reduction, unlike in the OEC. Since the Mn_3CaO_4 cubane motif is found in mixed Mn/Ca oxide materials employed in the electrocatalytic oxidation of water, this work prepared the ground for the quantum mechanical treatment of such subunits as parts of a larger system and forms the basis for ongoing embedded-cluster simulations of catalytic Mn/Ca oxide materials.

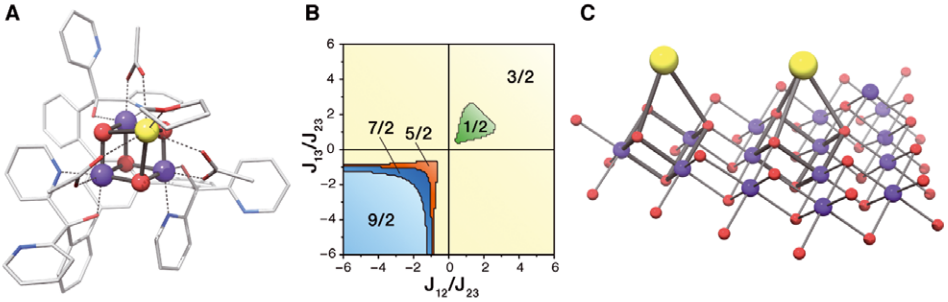

Figure 3. A: A synthetic model containing the $Mn(IV)_3CaO_4$ cubane core. B: Spin map showing the correlation between exchange coupling constant ratios and the total spin of the ground state for three Mn(IV) sites. C: A model of a Ca-doped manganese oxide water oxidizing catalyst.

All-electron scalar relativistic basis sets.

In terms of methodological advances, a line of research followed in the Pantazis group deals with the development of all-electron basis sets that allow efficient calculations with the popular zero-order regular approximation (ZORA) and the Douglas–Kroll–Hess scalar relativistic Hamiltonians. The family of segmented all-electron relativistically contracted (SARC) basis sets that initially included the third-row transition metals and the lanthanides was extended to include the actinides and, most recently, the 6p elements [6]. The SARC basis sets enjoy a rapidly increasing use by the computational chemistry community because they enable the user to avoid the limitations of effective core potentials and to obtain physically realistic descriptions of heavy-element containing systems for predicting molecular properties.

References

1. Cox, N., Pantazis, D. A., Neese, F., Lubitz, W., Biological water oxidation, *Accounts of Chemical Research* **2013**, *46*, 1588-1596
2. Ames, W., Pantazis, D. A., Krewald, V., Cox, N., Messinger, J., Lubitz, W., Neese, F., Theoretical evaluation of structural models of the S_2 state in the oxygen evolving complex of photosystem II: protonation states and magnetic interactions, *J. Am. Chem. Soc.* **2011**, *133*, 19743-19757
3. Pantazis, D. A., Ames, W., Cox, N., Lubitz, W., Neese, F., Two interconvertible structures that explain the spectroscopic properties of the oxygen-evolving complex of photosystem II in the S_2 state, *Ang. Chem. Int. Ed.* **2012**, *51*, 9935-9940
4. Retegan, M., Neese, F., Pantazis, D. A., Convergence of QM/MM and cluster models for the spectroscopic properties of the oxygen-evolving complex in photosystem II, *Journal of Chemical Theory and Computation* **2013**, *9*, 3832-3842
5. Krewald, V., Neese, F., Pantazis, D. A., On the magnetic and spectroscopic properties of high-valent Mn_3CaO_4 cubanes as structural units of natural and artificial water oxidizing catalysts. *J. Am. Chem. Soc.* **2013**, *135*, 5726-5739
6. Pantazis, D. A., Neese, F., All-electron scalar relativistic basis sets for the 6p elements, *Theoretical Chemistry Accounts* **2012**, *131*, 1292

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Molecular hydrogen research

The hydrogen economy represents a way of fulfilling our need for energy by using molecular hydrogen as an energy carrier and using reactions in which polluting products like greenhouse gases are avoided. The prospects of such an economy require the development of clean and efficient ways of producing and storing molecular hydrogen, or, in an extended sense, of molecules by which energy is stored in their chemical bonds.

Presently, the most common methods for the production of molecular hydrogen on an industrial basis concern firstly, steam reforming, a process in which steam is allowed to react with fossil fuels at high temperatures. The energy required (*i.e.*, the enthalpy change *DH*), for, e.g., methane steam reforming

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \qquad (1)$$

amounts to +49 kcal/mol. Secondly, a well-established and widely applied method for hydrogen production, introduced during the early days of electrochemistry in 1800, and which has recently become commercially available, concerns electrolysis of water,

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \qquad (2)$$

which requires +116 kcal/mol. For comparison, the bond dissociation energy of H_2 amounts to +104 kcal/mol. Thus to split hydrogen into two hydrogen atoms costs double its production in energy by electrolysis of water. These numbers indicate that the production of molecular hydrogen, the key ingredient of the hydrogen economy, is by no means a trivial task. Moreover, the mechanisms of catalytic hydrogen production are generally unknown at the microscopic level, even for platinum.

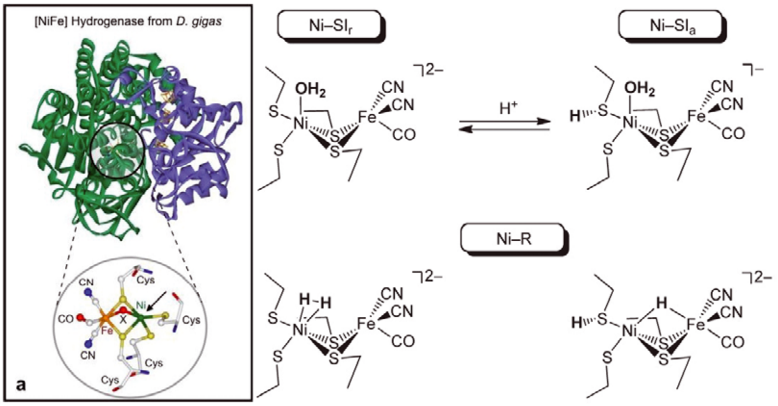

Figure 1. (left) Structure of [NiFe] hydrogenase from *D. gigas* (PDB 1FRV). The two subunits are indicated in blue (small subunit) and green (large subunit). The structure of the active site is shown enlarged at the bottom (see text). The arrow indicates the 6th coordination site at Ni which is found to be unoccupied. The figure is reproduced from reference 1. (right) Structural models of the Ni-SI$_r$, Ni-SI$_a$ and Ni-R redox states. For the Ni-R state, the structures with a side-on coordinated hydrogen molecule or with a bridging hydride and protonated cysteine residue were found to be almost isoenergetic and in agreement with the CO and CN stretching frequencies, indicating the minimum requirement of reorganization upon hydrogen splitting [2].

In our group, we are especially interested in unraveling reaction mechanisms of catalytically active molecules. We study three systems by a combination of spectroscopy, electrochemistry and quantum chemistry. First, we examine the proteins that evolve hydrogen, which are called hydrogenases. These proteins they catalyze both the formation and the decomposition of molecular hydrogen.

$$H_2 \rightleftharpoons 2\,H^+ + 2e^- \qquad (3)$$

In the family of [NiFe] hydrogenases, the catalytic center includes inorganic CO and CN ligands and four cysteine residues. During the catalytic cycle, the active site cycles through multiple redox states that can be investigated by FTIR spectroscopy. In particular the stretching frequencies of the CO and CN ligands contain information about the composition of the active site and can be accessed even for EPR-silent states. We have performed extensive calculations of these frequencies with available quantum chemical methods. For two very important catalytically active states, Ni-SI$_a$ and Ni-R [2], we succeeded for the first time, by a combination of FTIR spectroscopy and theory to obtain the structure of these redox states, providing a detailed picture of the catalytic mechanism that is validated both by theory and spectroscopy. Detailed information, e.g., tables with stretching frequencies can be found in reference 2. Moreover, in the light-induced Ni-L state, we found that a direct bond between Ni and Fe is present, which can be protonated, giving a formal Ni(III)-H$^-$ species in Ni-C [3, 4], similar to the case in batteries.

The active sites of hydrogenases have been a focal point for inorganic chemists with the aim to prepare biomimetic inorganic molecules that possess catalytic activity.

In our group, we study a molecule from the group of DuBois et al. [6] that is essentially made up of a bis(diphosphine)nickel core. By tuning the ligand periphery, this molecule is active towards hydrogen production with an activity of up to 2300 s^{-1} and an overpotential of about 350 mV. This nickel complex is presently the most active molecular catalyst for hydrogen production that also features a relatively low overpotential and stability towards H_2O in the millimolar region [5]. The catalyst can undergo two reversible one-electron reductions and the Ni^{II}, Ni^{I} and Ni^{0} redox states are all spectroscopically accessible. We resynthesized the molecule and recorded EPR and ENDOR spectra for the Ni^{I} state that indicate that as opposed to the crystal structure, the molecule attains a non-symmetric structure in solution. Moreover, in contrast to data reported in literature, which favor the Ni^{0} state as the oxidation state in which hydrogen is produced, our data is in addition compatible with a comproportionation of two Ni^{I} species.

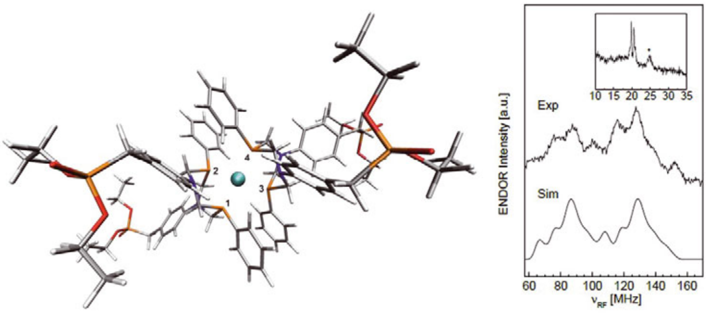

Figure 2. (left) Optimized structure of the "DuBois" bis(diphosphine)nickel complex. (right) Q-band Davies ^{31}P ENDOR spectra and simulations of the phosphorus atoms 1-4 and simulations based on DFT data, indicating the inequivalence of the ^{31}P atoms. In the inset, the signals of the ^{31}P atoms of the remote phosphate groups are shown. Analysis of the data is in progress [6].

The third system under investigation concerns a cobalt-salen complex. In our group, we have been able to show for the first time that this complex displays catalytic activity towards hydrogen production. Our observation establishes the family of Co (salen) complexes as interesting candidates for mechanistic investigations, although the activity and overpotential of the first investigated complex presently cannot compete with the DuBois catalyst. Still the spectroscopic, electrochemical and theoretical studies tell an interesting story. In protonated form, ENDOR spectroscopy and DFT calculations tell that the anilido groups are in a staggered conformation. This means, firstly, that the complex is apparently flexible enough to adapt the staggered conformation, and at room temperature may even undergo dynamic changes in which the distortion moves back and forth between both anilino moieties. Secondly, the staggering gives rise to symmetry-inequivalent protons that thus have different acidities. DFT calculations confirm that the proton that is moved maximally out of the equatorial plane is most acidic, which indicates that this proton is the most probable candidate to take the role of the hydride in a putative Co(III)-hydride transition state upon further reduction of the complex.

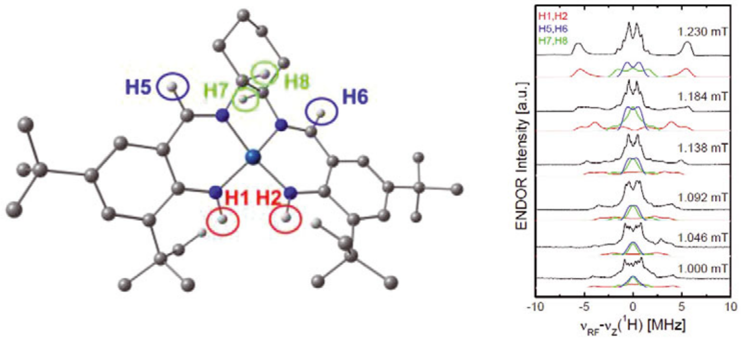

Figure 3. (left) structure of the catalytically active Co(salen) complex. The nitrogen atoms at H1 and H2 can become doubly protonated, after which the two NH2 groups attain a staggered conformation with one N-H bond approximately parallel to the molecular z axis of the ligand field. (right) ^1H Davies ENDOR spectra and simulations based on DFT parameters. Analysis of the data is in progress.[7]

Future research directions include functionalizing the ligands such that coupling of these molecules to surfaces, for example electrode surfaces, becomes possible. This will establish whether the catalyst molecules are catalytically active in a heterogeneous environment as well. Spectroscopic studies can then be performed, e.g., with surface enhanced vibrational spectroscopy.

References

1. Lubitz, W., Reijerse, E.R., van Gastel, M., [NiFe] and [FeFe] Hydrogenase Studied by Advanced Magnetic Resonance Techniques, *Chem. Rev.* **2007**, *107*, 4331-4365
2. Krämer, T., Kampa, M., Lubitz, W., van Gastel, M., Neese, F., Theoretical Spectroscopy of the Ni^{II} Intermediate States in the Catalytic Cycle and the Activation of [NiFe] Hydrogenases, *ChemBioChem* **2013**, in press
3. Kampa, M., Lubitz, W., van Gastel, M., Neese, F., Computational study of the electronic structure and magnetic properties of the Ni-C state in [NiFe] hydrogenases including the second coordination sphere, *J. Inorg. Biol. Chem.* **2012**, *17*, 1269-1281
4. Kampa, M., Pandelia, M.E., Lubitz, W., van Gastel, M., Neese, F., A metal-metal bond in the light-induced state of [NiFe] hydrogenases with relevance to hydrogen evolution, *J. Am. Chem. Soc.* **2013**, *135*, 3915-3925
5. (a) Rakowski DuBois, M., DuBois D. L., The roles of the first and second coordination spheres in the design of molecular catalysts for H_2 production and oxidation, *Chem. Soc. Rev.* **2009**, *38*, 62-72; (b) Kilgore, U.J., Roberts, J. A. S., Pool, D. H., Appel, A. M., Stewart, M. P., Rakowski DuBois, M., Dougherty, W. G., Kassel, W. S., Bullock, R. M., DuBois, D. L., $[Ni(PPh_2NC_6H_4X_2)_2]_2$ Complexes as Electrocatalysts for H_2 Production: Effect of Substituents, Acids, and Water on Catalytic Rates, *J. Am. Chem. Soc.* **2011**, *133*, 5861-5872
6. Kochem, A., Neese, F., van Gastel, M., A Spectroscopic and Quantum Chemical Study of the “DuBois” $Ni(P^{Ph}{}_2N^{C6H4CH2P(O)(OEt)2}{}_2)_2$ Electrocatalyst for Hydrogen Production, accepted for publication in J. Phys. Chem. C.
7. Kochem, A., Thomas, F., Jarjayes, O., Gellon, G., Philouze, C., Weyhermüller, T., Neese, F., van Gastel, M., Hydrogen Generation by an Anilinosalen Cobalt Complex containing Proton Relays in the First Coordination Sphere, *Inorg. Chem.* **2013**, *52*, 14428-14438

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Spectroscopic model complexes

Chemical activation of small molecules is a key step in energy research. A considerable amount of the world's energy is invested in the reduction of dinitrogen to ammonia or the conversion of methane to hydrogen and other carbon-containing compounds. In the future, it is likely that small molecule activation will consume even more energy due to the development of technologies for production of hydrogen from water and the reduction of carbon dioxide. It is the goal of this institute to study such reactions in detail and gain insights that will allow the efficiency of these energy demanding reactions to be increased. This will require that high activation barriers be overcome. In both industrial processes and in living cells transition metal-containing catalysts serve this function. It is therefore imperative to investigate and understand structure and function of such catalytic systems.

Model Complexes – Why?

Experimentally, in catalytic reactions, spectroscopic methods are the probes of choice to obtain information about reaction intermediates, structure, redox state etc. Quantum chemical calculations can help with interpretation of spectroscopic data and to support or exclude models for the reaction cycle.

Our approach to assist interpretation of spectroscopic data, and development of quantum chemical methods for calculation of spectroscopic properties is to prepare well-defined model compounds. These compounds, with known structure and electronic properties, provide a base of reliable spectroscopic data. Directed variation of structural and electronic parameters in a series of model compounds allows systematic study of their spectroscopic response and to calibrate methods.

Spectroscopic model complexes

In order to support development of new methods in quantum chemistry (department Prof. Neese) and to aid interpretation of data from spectroscopic measurements (departments of Prof. Schlögl and Prof. Lubitz), series of coordination compounds with systematically diversified structures and electronic ground states are required. They allow for comparison and calibration of experimentally measured data with theoretically calculated parameters.

Tools invaluable for study of catalytically active systems include EPR, X-ray absorption (XAS) and X-ray emission (XES) spectroscopy. These methods can directly address issues concerning electronic structure, and identification of the type and properties of donor atoms coordinated to a metal site.

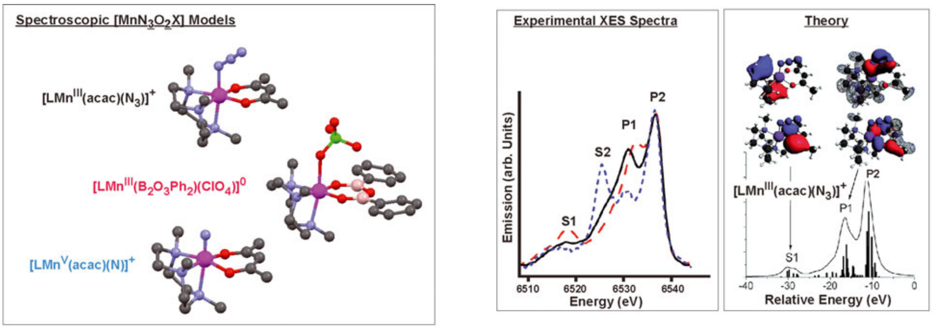


Figure 1. A series of manganese model complexes (top), their XES-spectra (bottom left), and interpretation and simulation of spectrum of the azido complex [Mn(III)(acac)(N$_3$)] by density functional theory (bottom right).

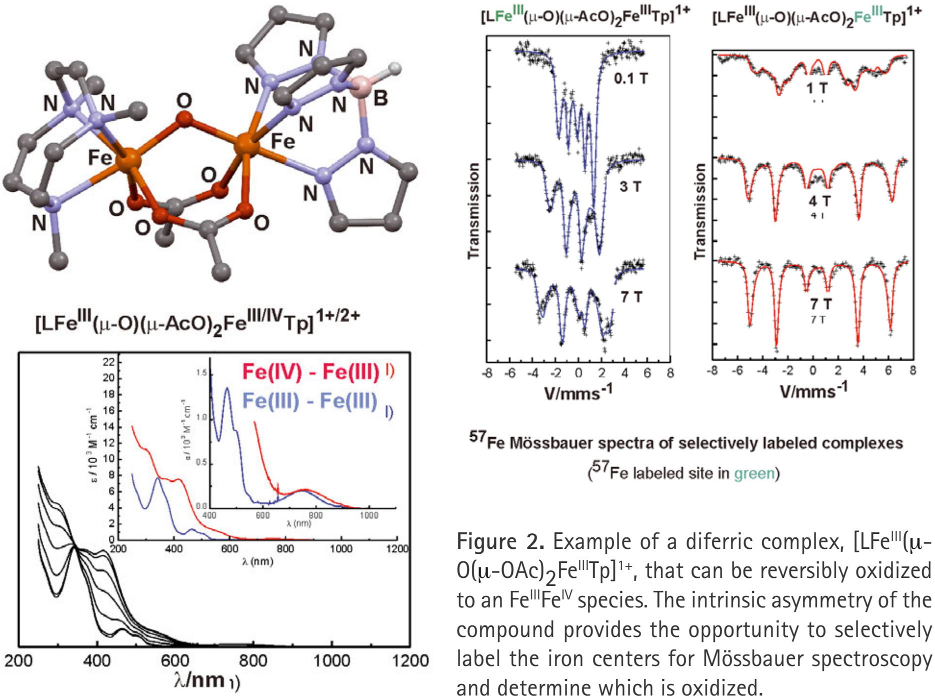
Figure 1 summarizes some results from a study in which we demonstrate how XES in combination with DFT theory can help provide information about donor atom type, binding properties of ligand and the electronic structure of the metal core. The top part of figure 1 shows this for a series of three simple mononuclear octahedral manganese complexes possessing a N3O2X donor set [1]. Valence-to-core XES spectra (bottom left) of the three compounds show significant differences, which reflects slight variations in the chemical environments and oxidation states of the central manganese ions. These spectra can be nicely reproduced by density functional theory (DFT) calculations, as illustrated for the complex [Mn(III)(acac)(N$_3$)] (bottom right). In a recent collaboration with the DeBeer group, we prepared series of mono and dinuclear molybdenum complexes in various oxidation states, and a row of [MoFe 3S4]-complexes. The compounds were extensively investigated by XAS spectroscopy and DFT. The XAS spectra display rich near-edge features and it is our aim to understand these spectra in detail. This data can be used help to deduce electronic structures on molybdenum-containing enzyme active sites, such as nitrogenases [2].

Mimicking active sites

Catalytically active sites of metalloproteins represent an important source of information for small molecule activation chemistry, and are designed by nature to perform highly specific reactions under mild conditions. For example, nature manages to convert nitrogen from air to ammonia or water to oxygen under ambient conditions, but chemists require drastic conditions to perform such reactions.

A vast amount of spectroscopic and structural data has been collected in an effort to elucidate how these systems work, but due to their complexity these data are often incomplete or not well understood. It is, therefore, helpful to synthetically model structural features of active sites, and to compare their spectroscopic and structural properties with data from enzymes. Additionally, DFT calculations on synthetic metal complexes and truncated models of enzyme active sites allow us to refine our perceptions of how catalytic reactions proceed.

In this context, high-valent oxoiron complexes are of great interest. Various iron proteins like methane monoxygenase, cytochrome P450 and ribonucleotide reductase promote redox reactions of organic substrates by hydrogen abstraction reactions. We investigated models of oxo- and carboxylato-bridged dinuclear iron enzymes and found that one-electron oxidation of these diferric complexes yields a Fe(IV)-oxo-Fe(III) unit capable of performing hydrogen abstraction reactions with certain substrates. Synthesis of the derivative $[\mathrm{LFe^{III}}(\mu\text{-O})(\mu\text{-OAc})_2\mathrm{Fe^{III}Tp}]^{1+}$ containing two different macrocyclic ligands allowed selective oxidation of one of the two iron sites [3]. Some results for this system are summarized in Figure 2. The X-ray structure of this monocationic complex clearly shows that the iron(III) centers are asymmetrically ligated. Spectroelectrochemical measurements indicate that the complex can be reversibly oxidized. Due to the asymmetric ligation, it is possible to selectively label the iron sites by ^{57}Fe, and the Mössbauer spectra of both isotopomers are displayed at the bottom of Figure 2.



^{57}Fe Mössbauer spectra of selectively labeled complexes
(^{57}Fe labeled site in green)

Figure 2. Example of a diferric complex, $[\mathrm{LFe^{III}}(\mu\text{-O})(\mu\text{-OAc})_2\mathrm{Fe^{III}Tp}]^{1+}$, that can be reversibly oxidized to an $\mathrm{Fe^{III}Fe^{IV}}$ species. The intrinsic asymmetry of the compound provides the opportunity to selectively label the iron centers for Mössbauer spectroscopy and determine which is oxidized.

The EXAFS and Mössbauer data of the oxidized species unambiguously demonstrate that only the Fe center ligated by the trispyrazolyl ligand is oxidized.

Structure Determination

In coordination chemistry structural determination is an absolute prerequisite to understanding properties of transition metal complexes. Furthermore, structure determination by single crystal X-ray diffraction is obligatory in coordination chemistry because our ability to obtain a target compound is limited and unexpected self-assembly phenomena sometimes prevail. X-ray structure analysis delivers highly precise information about the three-dimensional arrangement of atoms, thereby providing bond length and bond angles, which are of enormous importance in understanding chemical properties. Since it is our aim to correlate spectroscopic features and functional properties with structure, X-ray structure analysis is vital to this area of research. Figure 3 shows a crystal structure from a recent publication in which we studied protonation properties of hydrogenase model complexes [4]. Structures of both, unprotonated and protonated species could be determined and the protonation site could be clearly located.

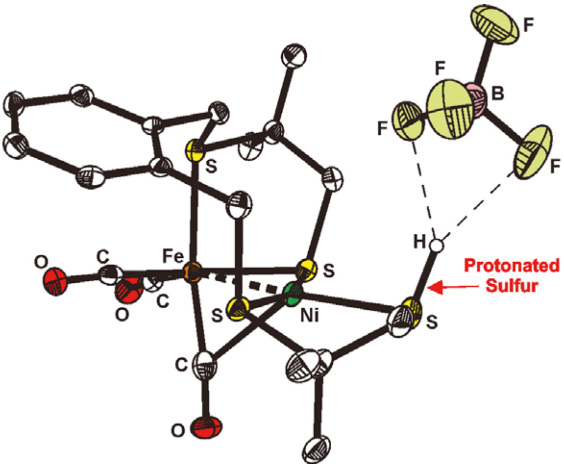


Figure 3. X-ray structure of a hetero-binuclear iron-nickel hydrogenase model complex. The structure clearly shows that a coordinating thiolate has been protonated.

References

1. Smolentsev, G., Soldatov, A.V., Messinger, J., Merz, K., Weyhermüller, T., Bergmann, U., Pushkar, Y., Yano, J., Yachandra, V. K., Glatzel, P., X-ray Emission Spectroscopy to Study Ligand Valence Orbitals in Mn Coordination Compounds, *J. Am. Chem. Soc.* **2009**, *131*, 13161-13167

2. Lima, F.A., Bjornsson, R., Weyhermüller, T., Chandraskaran, P., Glatzel, P., Neese, F., DeBeer, S., High-Resolution Molybdenum K-edge X-ray Absorption Spectroscopy Analyzed with Time-Dependent Density Functional Theory. *Phys. Chem. Chem. Phys.* **2013**, *15,* 20911-20920

3. Slep, L.D. , Weyhermüller, T., Bill, E., Neese, F., Bothe, E., Wieghardt, K., The mixed-valent [Fe^{IV}(μ-O)(μ-carboxylato)$_2$Fe^{III}]$^{3+}$ core. *J. Am. Chem. Soc.* **2003** ,125, 15554-15570

4. Weber, K., Krämer, T., Shafaat, H., Weyhermüller, T., Bill, E., van Gastel, M., Neese, F., Lubitz, W., A functional [NiFe]-hydrogenase model compound that undergoes biologically relevant reversible thiolate protonation, *J. Am. Chem. Soc.* **2012**, 134, 20745-20755

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CO_2 and O_2 activation

CO_2 is a cheap, nontoxic, and abundant C1 feedstock. However, it is difficult to use in chemical synthesis due to its thermodynamic stability and non-polar nature. To date, CO_2 functionalization typically requires highly reactive nucleophiles or electrochemical reductions. Thus, efficient CO_2 transformation poses a challenge to chemists. O_2 activation by non-heme iron enzymes is the second focus of my group. Nature couples O_2 reduction to generate high-valent ferryl species to selective modification of unactivated C-H bonds. More importantly, such processes are carried out under ambient conditions with high efficiency. Therefore, understanding the mechanisms of both reactions at the atomic level will enhance our knowledge for further design and synthesis of novel environmentally friendly catalysts.

1. Electrochemical CO_2 reduction

Homogeneous CO_2 reduction can be electrochemically catalyzed by Ni(cyclam) (cyclam = 1,4,8,11-tetraazacyclotetradecane) system with high efficiency and selectivity. We have carried out a detailed computational investigation to elucidate the reaction mechanism (Figure 1a). As CO_2 reduction is most likely to proceed via inner sphere electron transfer, several feasible coordination modes for CO_2 binding to the

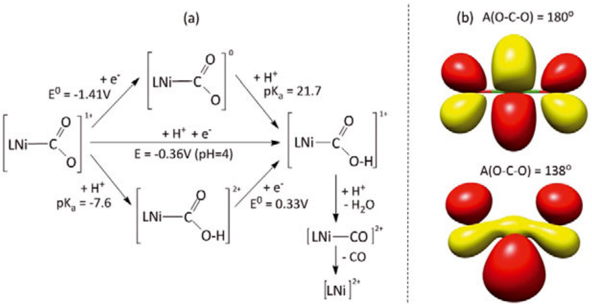

Figure 1. (a). Mechanism of CO_2 reduction catalyzed by Ni(cyclam)$^+$; (b). π*-orbitals of linear and bent CO_2.

low-valent Ni^I center, namely, η^1 C-, η^1 O-, and η^2 C,O-bound, have been taken into account in our calculations. We found that η^1 C-bound is energetically favored by at least 20 kcal/mol compared with the other two modes. This can be readily rationalized by the fact that the π^*-orbital of CO_2, functioning as the electron accepting orbital in the reaction, has a larger lobe on the central C-atom relative to those on the two terminal O-atoms, especially for a bent CO_2 molecule (Figure 1b). After the CO_2 binding, CO and formate can be easily formed from the η^1 C- and η^1 O-bound CO_2 adducts, respectively. Thus, the energetically preferable CO_2 binding mode dictates the chemical selectivity. More importantly, our results suggested that the C-O bond cleavage required for the CO formation is concerted with a proton coupled electron transfer process. The η^1-CO_2 adduct $[Ni(CO_2)(cyclam)]^+$ first simultaneously couples to a proton and an electron to yield $[Ni(C(O)OH)(cyclam)]^+$. Then, this carboxyl intermediate may undergo a spontaneous C-O bond cleavage in the presence of a proton to generate CO due to the exceedingly large driven force (~ -38 kcal/mol).

2. CO_2 hydrogenation

Metal-hydride complexes have been established to be very active and productive for catalytic hydrogenation of CO_2. However, most of the catalysts contain expensive noble metals such as Ru, Rh and Ir. Recent experiments showed that an iron complex, $[Fe(\eta^2\text{-}H_2)H(PP_3)]^+$ (PP_3 = tris(2-(diphenylphosphino)phenyl)phosphino), exhibits rather high catalytic reactivity for CO_2 reduction to produce formic acid. The catalytically active species was experimentally analyzed to be an iron-dihydride, $[FeH_2(PP_3)]$, that is generated via a heterolytic cleavage of H_2 in the presence of NEt_3. In the proposed mechanism, this complex carries out CO_2 insertion to afford an iron-formate intermediate, followed by product release to complete the catalytic circle

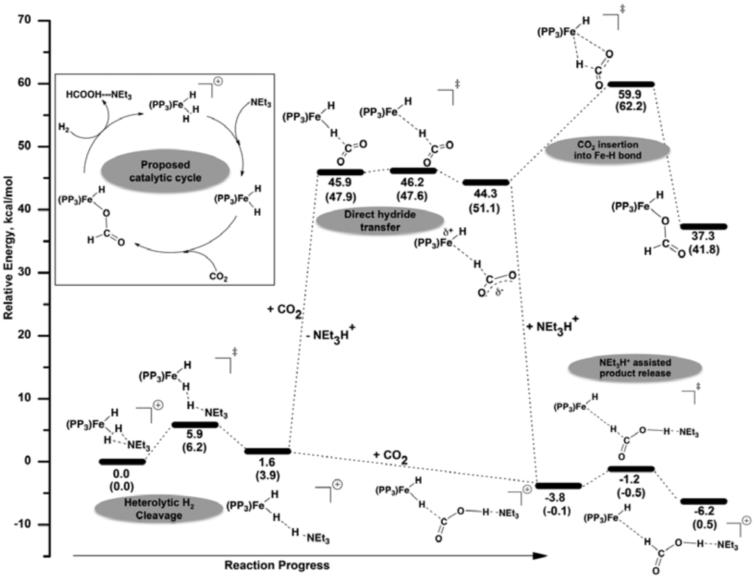

Figure 2. Potential energy surface of CO_2 hydrogenation by $[Fe(\eta^2\text{-}H_2)H(PP_3)]^+$ along with the proposed catalytic cycle (inset). Relative enthalpies (ΔH) are presented in parentheses together with relative energies (ΔE).

(Figure 2). Our calculations confirmed the proposed mechanism and revealed that the rate-determining step is the H_2 heterolytic cleavage (ΔH = 6.2 kcal/mol) rather than the hydride transfer step (ΔH = –0.3 kcal/mol) (Figure 2). However, the previous computational studies on the related systems suggested that the product release is the rate-determining step. In line with this, the direct product release from the metal-formate complex, the intermediate ADD generated from CO_2 insertion into Fe-H bond, was calculated to involve a high activation barrier of 20.4 kcal/mol. By contrast, with the assistance of $HNEt_3^+$ formed from the heterolytic scission of the H-H bond, this step can be significantly accelerated with an activation barrier of -0.4 kcal/mol. Thus, our calculation highlighted the role played by NEt_3 in modulating the reaction barriers. Moreover, in the rate-determining step, NEt_3 can stabilize the proton derived from the H_2 ligand, and hence promotes the heterolytic H-H bond breaking.

3. Spectroscopic and computational investigations of Fe^{IV}=O intermediates

In collaboration with Prof. Que (University of Minnesota) and Dr. Bill, we have undertaken a systematic study of a mononuclear Fe^{IV}=O and a dinuclear OH-Fe^{IV}-O-Fe^{IV}=O species using a combined experimental and theoretical approach. By careful analysis of the temperature dependent MCD *C*-term intensity variation and the signs thereof of the key electronic transitions for both complexes, we could reach an unambiguous assignment for each feature. This provided the fingerprint information about their electronic structures. In fact, bonding of the Fe^{IV}=O unit to the second metal center in OH-Fe^{IV}-O-Fe^{IV}=O does not substantially change its electronic structure. This is consistent with the experimental observation that this dinuclear species exhibits the similar H-atom transfer (HAT) reactivity to the mononuclear complex, because the common Fe^{IV}=O moieties serve as the reactive sites in both cases [1].

In addition, we have explored how hydrogen bonding modulates the HAT reactivity of two mixed-valent X-Fe^{III}-O-Fe^{IV}=O (X = F, OH) complexes [2]. The two species share similar core structures. However, in the case of X = OH, a hydrogen bond is formed between the terminal hydroxo and oxo groups. Interestingly, it is 10-fold less reactive relative to the F derivative, which has no hydrogen bonding interaction. Our calculations suggested that the lower reactivity of OH congener results from the additional activation barrier required for breaking the hydrogen bond in the course of HAT by the Fe^{IV}oxo motif.

References

1. Ye, S., Geng, C.-Y., Shaik, S., Neese, F., Electronic structure analysis of multistate reactivity in transition metal catalyzed reactions: the case of C–H bond activation by non-heme iron(IV)–oxo cores, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8017–8030
2. Xue, G., Geng, C.-Y., Ye, S., Fiedler, A. T., Neese, F., Que, L., Jr., Hydrogen-Bonding Effects on the Reactivity of [X–Fe^{III}–O–Fe^{IV}–O] (X = OH,F) Complexes toward C–H Bond Cleavage, *Inorg. Chem.* **2013**, *52*, 3976–3984

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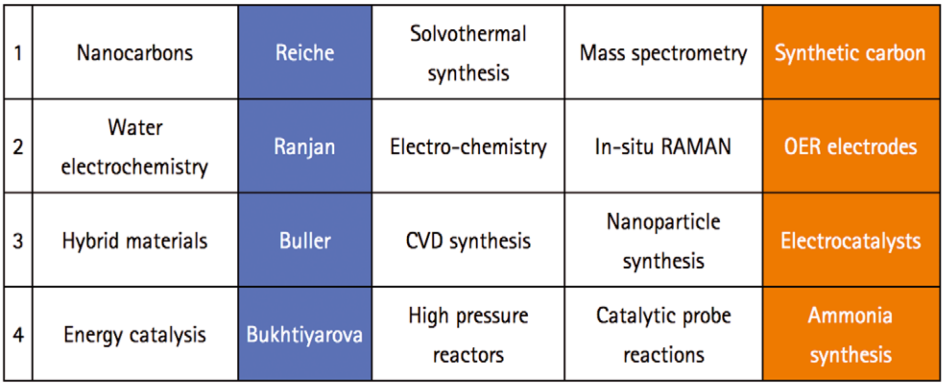
Department of Heterogeneous Reactions

General Development

The department was founded in 2012 as a "fractional department" with the mission to support the new orientation of the MPI CEC in the direction of heterogeneous reactions. The department has the obligation to dissolve itself with the return of the founding director to the FHI Berlin. It is not excluded that some of the present activities remain with the MPI CEC but this decision is left to the new *Kollegium.* The department started "from scratch" with no pre-existing personnel or infrastructure. The general administration and a lot of other people supported the installation of the department. Without their help we would not be operational today.

The department organized itself into groups dealing with essential aspects of the oxygen evolution reaction in water splitting and with the catalytic hydrogenation of CO_2 to methanol and of N_2 to ammonia. Important analytical techniques (nanostructural analysis, in-situ electron spectroscopy) and synthetic competencies are transferred to competence and service groups belonging to the entire MPI CEC. These groups are described in the report of the Managing Director and represent generic assets of competence that are required for research in heterogeneous energy science in line with the mission of the MPI CEC.

The department started scientific activities in the second half of 2013 and is operational with its equipment in a stable situation of lab and office space since the end of 2013. The following text describes the concept of the department and first results. Its structure can be seen from the table 1. More details can be found in the individual reports of the groups.



1	Nanocarbons	Reiche	Solvothermal synthesis	Mass spectrometry	Synthetic carbon
2	Water electrochemistry	Ranjan	Electro-chemistry	In-situ RAMAN	OER electrodes
3	Hybrid materials	Buller	CVD synthesis	Nanoparticle synthesis	Electrocatalysts
4	Energy catalysis	Bukhtiyarova	High pressure reactors	Catalytic probe reactions	Ammonia synthesis

Table 1. Concept of the department Heterogeneous Reactions.

The work of the department should be understood in the context of collaborations within the MPI CEC, within the relation to the FHI Berlin (Department Inorganic Chemistry) and within external collaborations described also in the general report. A typical element of collaboration with the FHI in Berlin is the use of electron microscopy facilities (*M. Schuster*) necessitated by the fact that first the building for electron microscopy needs to be constructed in Mülheim before high-level microscopy is possible and a provisional installation is hardly possible at acceptable cost. This strong element of collaboration is untypical for a MPG research department but is the consequence of the particular mission in the founding situation of the MPI CEC. It is expected that this will normalize with the end of the founding period. By then the interdisciplinary research within the MPI CEC should be normal and the competence groups should be fully active. To support the collaborative activity the department has organized four workshops in 2013 with partners (*F. Schueth*, *F. Neese*, FHI-AC, *W. Lubitz + F. Neese*). The program that initiates contacts at the level of co-workers will be repeated in 2014. The department has activated the MAXNET energy starting from 2014 with seven partnering MPS departments all active in chemical energy conversion. The systemic approach towards water splitting was chosen as first joint topic. The department also organized a round table discussion on the use of manganese compounds in water splitting that should result in a national funding activity between 15 partners from universities, MPG and Helmholtz foundation to be supported by the Ministry of Research directly (application submitted).

The collaboration requires special attention to create continuity in science and communication. This is taken care of by the positions of a science coordinator closely related to the position of communication. Both positions and supporting staff were transferred after an initial period with *R. Schlögl* to the responsibility of *F. Neese*.

Strategy of Research

The department heterogeneous reactions develops a strategy aiming at identification of rational design parameters for heterogeneous catalysts to be applied in energy-related chemical conversions [1] of CO_2 and di-nitrogen. The relevant entity is the active site forming in several processes of chemical dynamics [2] during start-up and operation of the catalyst. It is essential to identify the structural criteria discriminating active sites from other surface sites in order to design and find these entities in analytical studies of working catalysts. The option that molecular catalysis may reach the operational performances of heterogeneous systems is taken into consideration but the primary aim is to use homogeneous systems as models where in contrast to heterogeneous systems the chemistry of a central atom can be determined and controlled with verifiable precision.

Past experience has shown that a combination of properties of "central" metal species with its often-neglected "environment" is essential for catalytic function. This is evident in molecular catalysis with its ligand systems or protein structures but not so obvious in heterogeneous catalysis where surface defects, supports, co-adsorbates or deposits from reactants form the "environment" that is hardly present in model studies and under conditions of very low conversion.

The approach taken in the department conceptually divides the active site in the central sphere of metal species and the surrounding sphere of ligands, supports and adsorbates. The system of central and peripheral species is gradually made more complex from metal-organic complexes to supported performance catalysts. A coarse approximation on the gradual increase in complexity of the system is shown in Figure 1.

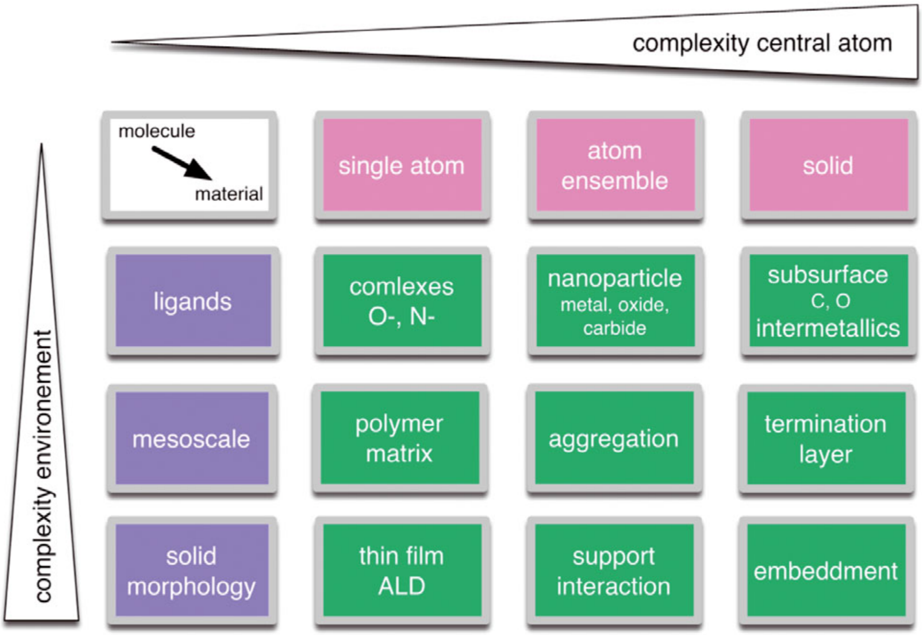


Figure 1. Strategy matrix for the department. The dimensions of the central atom (red) and the environment (blue) are indicated in three levels of complexity each.

The figure illustrates the transition from molecules to materials with an emphasis on the aspects of nano-structuring. The diagonal elements in the matrix indicate the gradual increase in system size, the off-diagonal elements describe synthetic approaches. Multiple layers of complexity within the molecular domain are omitted here as partners and collaborating groups cover them. The relation to energy applications of the reduction of small molecules dictates the selection of ligand systems. For the second focus of the departmental activities namely the oxygen evolution reaction we use metal hydroxides as molecular starting systems exhibiting in their pure form only moderately defined molecular environments due to the inherent tendency towards condensation.

Basis of this strategy is the hypothesis that the chemical activity of aggregates of metal atoms are not determined by their geometric size but by the local properties of a sub-set of surface atoms [2a, 3] being present in environments differing from translational order of the respective bulk phase. Such surface atoms ("Taylor sites") are located in distances to their neighbors differing from the bulk equilibrium distance by geometric reasons ("roughness") or by hetero-atoms [4]. Additional factors such as strain, alloy formation or bulk defects may cause the same effect of non-equilibrium geometric situations. Nano-size is thus a proxy [5] for the complete local and non-local electronic structure of the ensemble of an active site.

An essential pre-requisite for the successful application of the concept of Figure 1 is the verification of a particular synthesis by in-situ structural and functional analysis. Origin of this necessity is the decisive role of the chemical potential created by reaction conditions (reagents, products, deposits, pressure, temperature, concentration gradients). A suite of in-situ methods ranging from NAP-XPS and ambient pressure XAS over in-situ optical and vibrational spectroscopy (RAMAN, FT-IR, UV-VIS) to in-situ X-ray diffraction and EXAFS and to chemical electron microscopy serves as the methodical basis. Methodical additions in the arsenal of in-situ probes are being established with Mössbauer spectroscopy and EPR.

This basis is provided by the work of the *Schlögl* department in Berlin and by the activities of the departments of *F. Neese* and *W. Lubitz*. The joint use of these methods for molecular and heterogeneous catalytic systems is a critical element in the strategy of the Institute of how interdisciplinarity will be realized in practical projects.

The synthesis competence of the department concentrates on inorganic nanostructures and composite structures. Collaborating groups also within the MPI CEC are generating molecular species. Synthetic approaches cover precipitation as co-precipitation or deposition-precipitation, hydrothermal reactions under in-situ control of reactant gradients and controlled gas-solid thermal processes. Thin films are available by ALD, CVD and electro-deposition. Reaction products are characterized by BET, SEM, EDX, XRF, TG-DTA, TPR.

Reaction Targets

The department focuses in chemical catalysis on the reduction of CO_2 and N_2 with hydrogen generated by water splitting. The combined process of photo-electrochemical synthesis ("artificial leaf") is considered as too complex a target for a knowledge-based development approach. This view stems largely from the activities of the *Lubitz* department showing in great detail the chemical and operational complexity of the energy conversion reactions in the natural photosynthesis process. This knowledge is taken, however as invaluable input for developing strategies how to conduct the water splitting reaction as technical process. The results and insights generated in the course of following the individual reactions shown in Figure 2 may serve as basis for the artificial leaf approach by returning the knowledge from individual heterogeneous reactions back into this integrated approach.

The rationale in the choices of Figure 2 is that carbon capture and conversion to chemicals (C^3) is a powerful method of integrating renewable electricity in complete energy systems at situations where fossil energy carriers are still in competition. The activation of nitrogen to ammonia is the prototypical heterogeneous reaction for testing the understanding of catalysis as a whole and it is relevant for biomass use as fertilizers and for chemical synthesis. In addition, an ammonia-based cycle for energy storage[6] is an option allowing to release hydrogen without global warming effects.

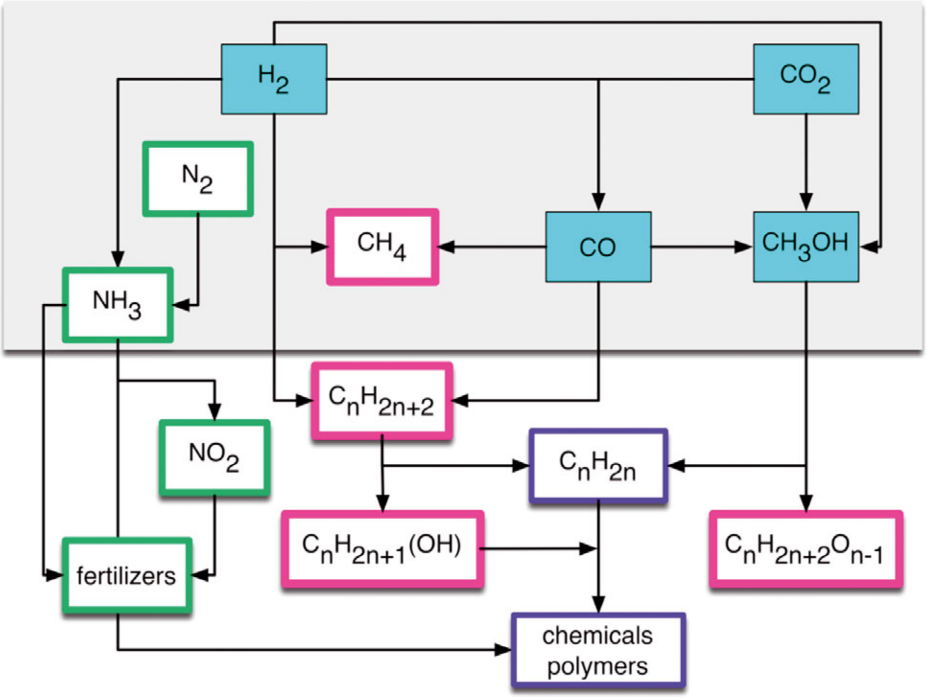


Figure 2. A simplified view of a solar refinery using renewable hydrogen and the greenhouse gas CO_2. It describes the research area of the department Heterogeneous Reactions.

The department focuses presently on the initial reactions indicated by the grey area in Figure 2. Collaborating partners and the FHI Berlin consider some of the downstream reactions.

The department can look back on extensive experience collected already with methanol [7] and ammonia synthesis [8] both being now considered under the rather special conditions of chemical energy conversion applications differing substantially from the realm of petrochemical industrial applications.

For studying molecular reactions in this context, the reduction of CO_2 to formic acid is a substitute for the methanol synthesis and the decomposition of ammonia may replace the high-pressure Haber-Bosch synthesis. Both reactions can be related to gas phase processes and have relevance in energy applications in their own right.

It is in the logic of the approach that the nature of the central atom can be chosen adequately. The core study question is the modification of its reactivity upon enhancing its complexity by adding more metal atoms of the same kind or by alloying. The environment that can be adapted for molecular systems by ligand molecules and for heterogeneous systems by reactants and supports gives the handles of fine-tuning the reactivity. We choose base metal systems, as the intended energy applications would not permit noble metals as world scale application and their substitution in energy conversion reactions is a critical task of knowledge-based energy chemistry.

The elements iron and copper are pragmatic choices based upon existing knowledge. In addition they represent typical open shell and closed shell systems and thus allow studying the role of oxidation states and spin states. Besides the reactions indicated in Figure 2 the generation of formiates and the decomposition of ammonia are catalyzed by both elements (to different extents) both in the gas phase and in liquid phase at least to measurable performances. With these two reactions and the two elements of choice a system of observations of chemical reactivity can be established allowing studying systematic effects of the modification of the electronic structure of the central species with their environment.

At present we have started with the group of *M. Bukhtiyarova* to study the direct hydrogenation of CO_2 and N_2 under relevant high-pressure operation conditions. Such experiments produce benchmark data and allow identifying research challenges that are not seen by typical academic low-load testing conditions. With this activity we are independent on scarce literature data obtained under not well-described conditions with often insufficiently characterized systems. The activity forms the nucleus of the intended reactor service group as the ability to test catalytic systems under performance conditions is seen as invaluable resource for basic research focusing on relevant problems. In addition, the real performance test of a self-synthesized catalyst is the ultimate verification for having understood synthesis and operation. No other method can deliver this unequivocal information. Only the limited lab resources prevent us to expand the scope of reaction testing that we try to organize in collaboration until the new building (*Reaktorhalle*) will be available.

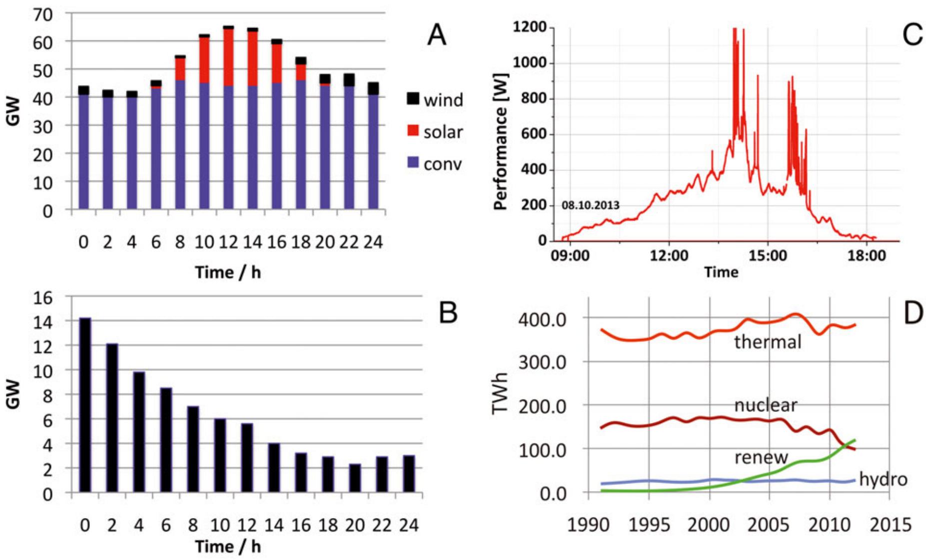


Figure 3. Examples of integration issues of renewable electricity into the German grid system. (A) Generation of electricity from renewable and fossil sources can favorably combine (data of 16. August 2013). (B) This can also fail during e.g a winter storm (data 9. January 2013). (C) The MPI CEC solar power test field reveals with high temporal resolution the volatility of electricity also during "sunny" days. (D) The dimension of the integration issue becomes clear when we observe the contribution of renewable energy to the total national power consumption.

These reactions of chemical energy conversion are not possible without a source of cheap renewable hydrogen that can only come from water splitting. We respect the enormous investments in generating regenerative electricity with its volatility that is indicated in Figure 3 and conclude that electrolysis as compensation for intermittent load is the first key requirement for energy integration in real mixed grid situations that will prevail in the next decades.

In the absence of reliable open information on the technological status of water electrolysis under practical conditions and at relevant pricing we conclude that the lack of basic understanding of the electrolysis process under conditions of production (not in the limit of very low conversion) is a critical stumbling block in chemical energy conversion and designed the integrated research portfolio shown in Figure 4.

This portfolio is embedded in a greater context of the MPI research network MAXNET Energy. We focus on the oxygen evolution reaction in full recognition that an electrolyzer is a system of reactions and materials and there are still many issues with the systemic functional description. We suppose on the other hand that the severity of the issues with oxygen evolution in terms of stability and energy efficiency (overpotential) are critical so that here a limited effort of basic science is applied best.

We study (group of *Ch. Ranjan* in collaboration with the nanostructure and electronic structure groups at the FHI Berlin) noble metal systems of Ir and Pt as benchmark systems that work well under conditions of investigation.

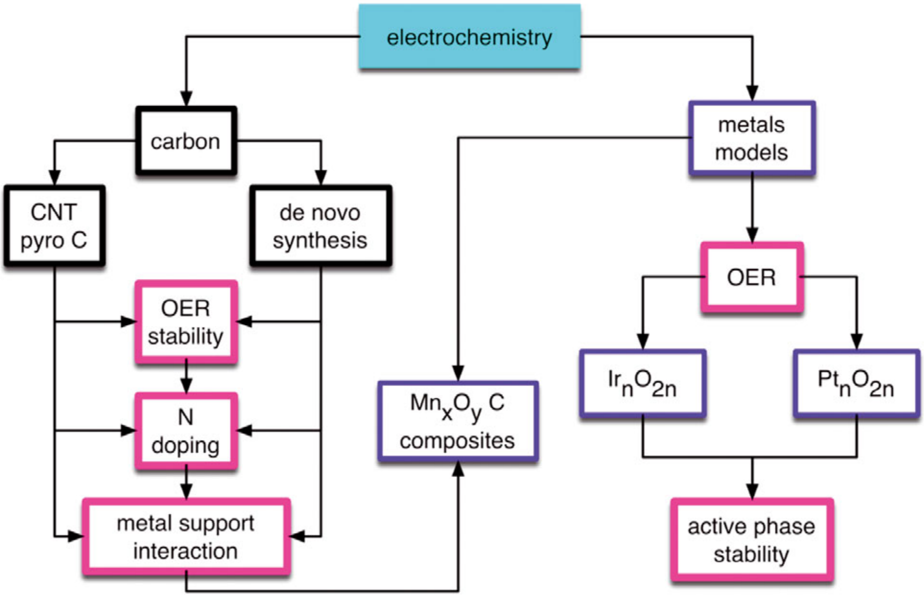


Figure 4. Research portfolio of the department for water electrolysis. The activity focuses fully on the oxygen evolution reaction.

The direct electrochemical measurements are supported by in-situ RAMAN spectroscopy. NAP XPS [9] and supporting surface analytical work in Berlin and at BESSY (conducted by *R. Arrigo* in collaboration with *D. Teschner* in Berlin). So we can learn functional details, about the chemical nature of active sites and about their dynamics under load conditions. We think that future practical solutions will need to avoid noble metals. We favor as radical approach the use of tailor-made carbon materials as their even limited stability will include a "self-repair" function by the evolution of defective sites as CO_2. *S. Reiche* studies the controlled synthesis of carbon materials indicated in Figure 4. The work includes several synthetic approaches and attempts to control the electronic structure of carbon by nitrogen functionalization. We try to do all work under in-situ control and always verify the effect of synthetic measures on properties. Electrochemical parameters are studied in collaboration with the *Ranjan* group.

As we cannot be sure that this approach is successful we study also options of anchoring individual metal atoms or nano-particles into carbon as indicated in Figure 1. The group of *S. Buller* conducts this activity. We chose Mn as active element as we can use the experience and methodical portfolio of the departments of *W. Lubitz* and *F. Neese*: we assume further that single atoms will not be sufficient as active sites and thus focus of clusters of Mn species in close electrical contact to a conductive carbon matrix that further provide the essential meso-structure for controlling the transport of molecules and liquid to the active surface.

In summary, the department wishes to contribute to several critical aspects of chemical energy conversion. These aspects that all relate to the science of catalysis were chosen on the basis of a detailed analysis of hypothetical development pathways of realistic energy systems. Many other groups worldwide also cover the issues chosen. We discriminate our approach by using and developing dedicated in-situ analytical control methods in close contact to synthetic efforts. This enables us to study the nature and dynamics of catalytic active sites under relevant operation conditions and without having to use poorly functional model systems such as single crystals. Results on homogeneous and heterogeneous models are considered as valuable input (and are also performed by us and in collaborations) into our work. Model studies need however, validation under conditions of high performance with the resulting driving forces of dynamical material response to avoid the well-known “gaps in catalysis science”. This can only be done with catalysts performing at high levels of conversion requiring thus real-world systems synthesized by using the knowledge from model systems. The results of our work will be conceptual insight into modes of operation and into critical material properties of energy conversion reactions. Material synthesis strategies towards scalable amounts of products are additional expected results. The transfer into practical systems and technology will be done however, in collaborations as described in the report of the Managing Director.

Selected Results from the Department

Carbon Synthesis

Carbon with its infinite structural variability [10] is a key component in our material strategy for connecting electrical energy with chemical energy. It can transport electrons with properties ranging from semiconducting to semi-metallic. It is inert under many relevant reaction conditions. It can be functionalized to accommodate acid-base surface reactivity and to tailor its electronic properties. This dual function can be executed jointly during synthesis or can be decoupled between surface and bulk functionalization by post-synthesis treatments.

We use in a dual approach multi-walled carbon nano-tubes of commercial grade and the de novo synthesis from presently glucose as basic ingredients to arrive at electrochemically stable functional carbons for oxygen evolution. A critical step in this endeavor is the correct formulation for electrochemical testing. The practice from literature to form inks with organic binders or nafion was found to be inappropriate as multiple reactions between the material of interest and the auxiliary species prevent a meaningful derivation of structure-function relations. We currently develop a technology of tempering mechanical green bodies as disks into conducting self-supported samples. Optimization is still required for controlling kinetic limitations within the bulk of the sample. This work is not only essential for obtaining generic sample-related property data but also for possible applications of the carbon in structures that can be scaled to real applications where inks or loose powders are inacceptable.

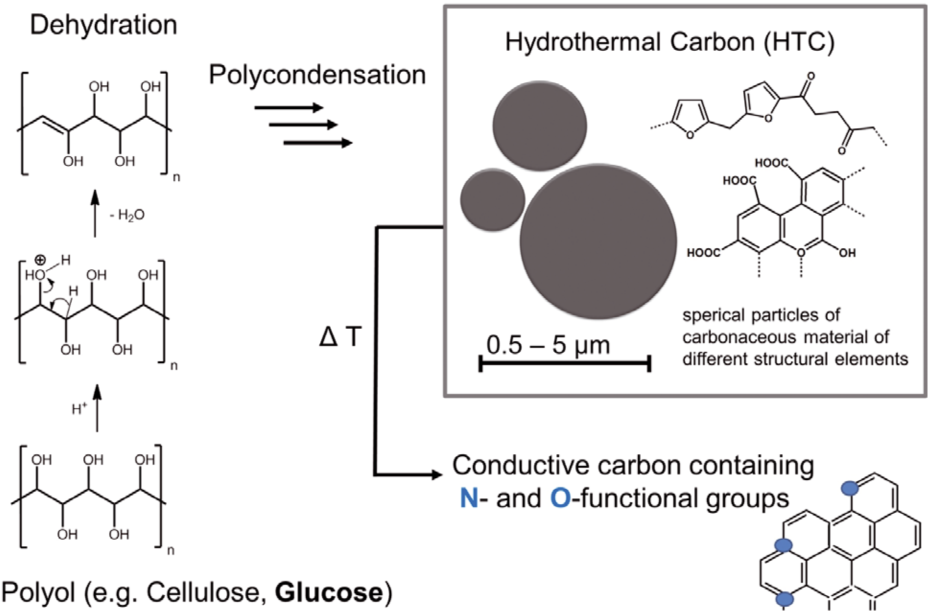


Figure 5. Reaction scheme for generating via reactive intermediates that are selected by reaction pH a pre-carbon that can be condensed or co-condensed by thermal treatment to a variety of functional carbons.

Figure 5 shows the general strategy of the de-novo approach. The reaction proceeds in an analytical or synthetic autoclave under hydrothermal conditions with the possibility of controlling the pH during reaction. We use the primary aggregates of carbon with large amounts of functional groups for either thermal product formation in a peat-condensation reaction under liberation of CO_x or for nitrogen functionalization [11] by co-condensation with a nitrogen source such as urea. Other processes using these reactive pre-carbons are under development. The reactive properties of the pre-carbon can be controlled by choosing the pH of the initial dehydrogenation reactions:

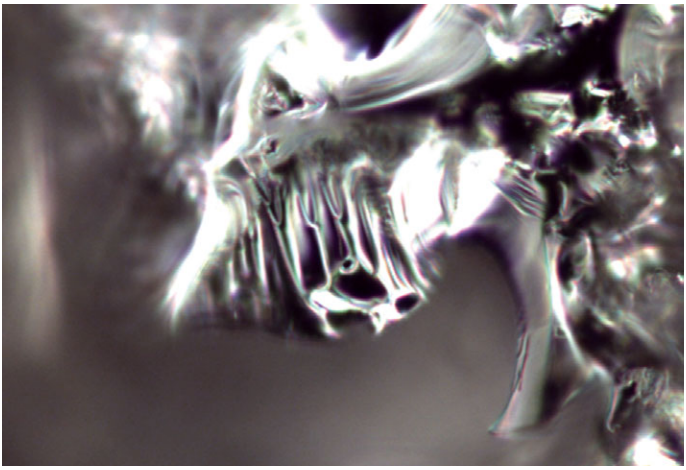


Figure 6. Optical micrograph (x 100) of the peat intermediate phase obtained from condensing glucose at acidic pH before thermal curing.

We can either co-condense HMF molecules to oligomers as detected by MALDI TOF analysis or we can decarboxylate the initial molecules forming small organic carboxylic acids and polycyclic aromatic residues with still substantial amounts of reactive sites (hetero-atoms) on them. The optical micrograph in Figure 6 obtained during RAMAN analysis gives an impression of the peat stage intermediate before thermal curing.

Post-synthetic nitrogen doping is studied in a systemic fashion using three electrochemical-grade nanocarbons of technical origin. From the study we show as example a material that was treated with ammonia at 750 °C. This treatment has two consequences: It removes debris from the carbon ribbons obtained in the industrial synthesis process and it incorporates substantial amounts of nitrogen. The EELS analysis shows that nitrogen species are part of the electronic p system of the sp^2 carbon as indicated by the identical splitting of resonances between π^* and σ^* in the carbon K edge and nitrogen K edge spectra. Such an analysis is local and can be quantified. It complements XPS data providing more integral information about the multitude of N functional groups. Carbons that are modified in such a way seem to exhibit superior properties for binding metal nanoparticles under aggressive conditions as it was tested with H_2O_2 synthesis [12] being a severe chemical probe reaction for metal-carbon binding schemes relevant for electrochemical water splitting (the direct testing facility is under construction).

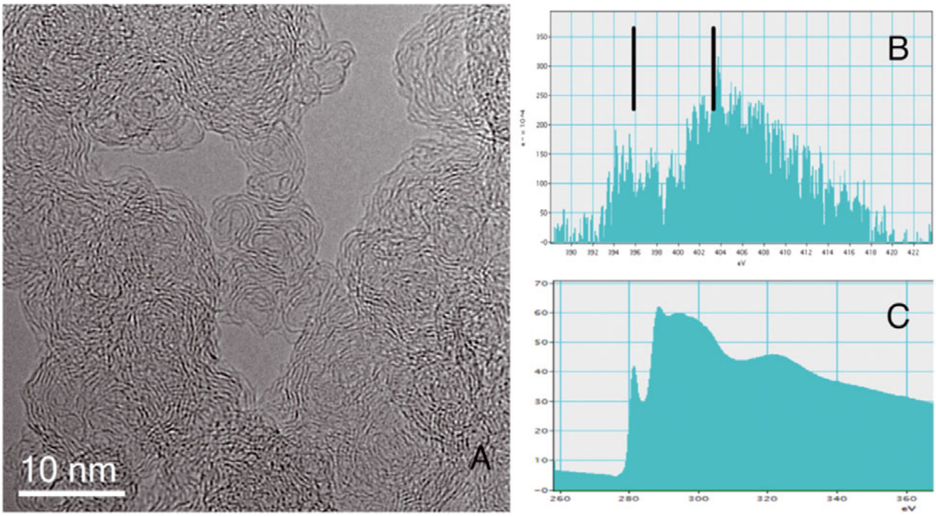


Figure 7. TEM image of technical electro-grade soot after ammonia functionalization. The BF image reveals the very homogeneous nature of twisted sp^2 carbon ribbons in the basic structural units. The EELS data (B: NK, C: CK) can locally characterize the electronic structure. The two lines in spectrum (B) indicate the splitting between π^* and σ^* states. The overall shape of spectrum C indicates multiple C-H terminations and structural defects with significant deviations from sp^2 hybridization as also seen by the multiple bends in the TEM image.

MnO_y on carbon nanotubes

Following previous studies of synthesizing composites of Mn oxides with CNT for OER application [13] it was attempted to use technical MWCNT and functionalize them with sulfuric acid to generate multiple oxophilic sites. Then a con-proportionation-deposition of Mn oxide was performed with the idea to generate small particles of tetravalent Mn oxide anchored onto the CNT. If this con-proportionation is carried out without CNT then a solid is obtained that is so insulating that no electrochemical activity occurs other than weak dissolution.

This is not the case for the composite as can be seen from Figure 8. In contrast to conventional rapid cycling of the potential we apply a time-resolved procedure to separate the charging current of the electrode from electro-chemical processes. This is necessary for such composites as they act as supercapacitor with quite appreciable charge storage functions and not only as electro-catalyst. The integrated electrochemical current implies function of the system in OER but the temporal profiles and their dependence on potential let us conclude that additional reactions than oxygen evolution are involved. This is frequently found with OER systems consisting of novel active materials. We thus construct presently a DEMS device to determine the nature of the electro-catalytic reaction product. We investigate the electrode dissolution kinetics in collaboration with the group of *K. Mayrhofer* at MPI Düsseldorf.

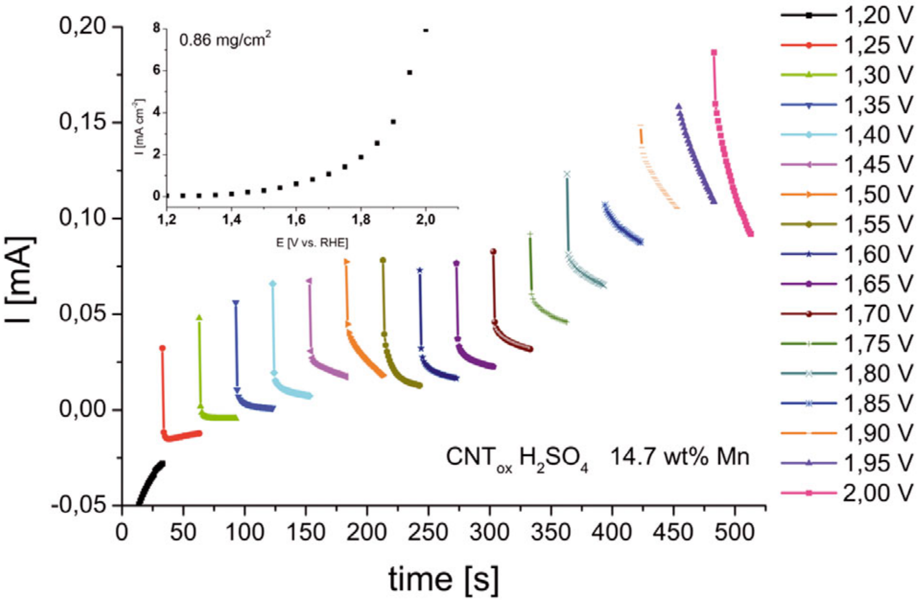


Figure 8. Electrochemical behavior of a MnOy CNT composite electrode. The time-resolved scanning of the working potential was applied to separate the electrode charging (rapid) from the electrocatalytic (slow) processes. The latter traces are a superposition of several reactions with complex dependencies on potential. The inset shows the integrated current of the electrocatalytic reactions.

The complex behavior suggests the presence of several species or size distributions of the oxide component. This was substantiated by TEM revealing a thin film of MnO_y on some CNT and aggregates of particulates intermixed.

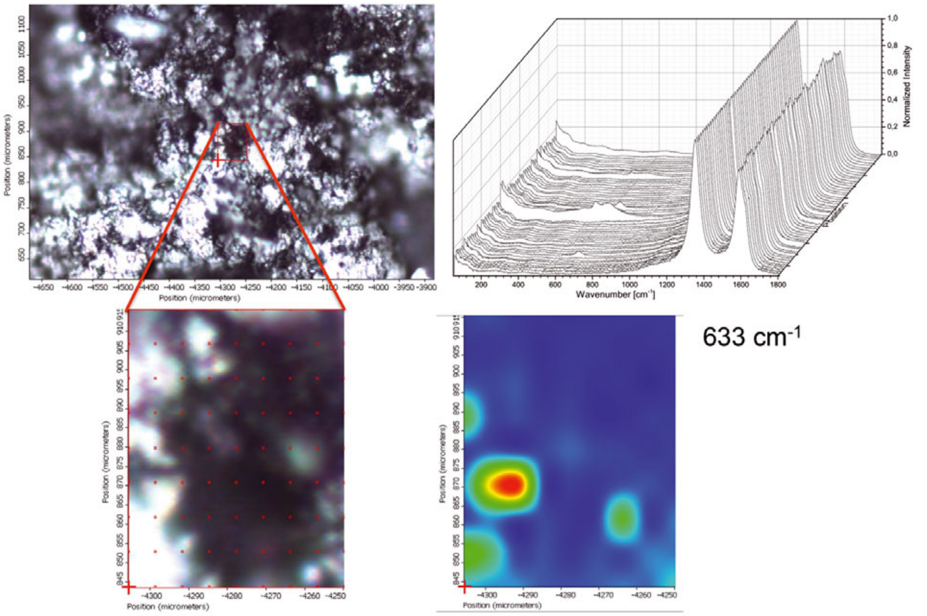


Figure 9. RAMAN mapping of the CNT-MnOy composite used for the experiment in Figure 8. From the top survey micrograph the small section shown at the bottom was selected for a raster scan with 64 pixel spectra displayed in the top right box. Localization of the Mn oxide revealed the distribution image showing particles and faint structures of disperse species. It is obvious that the optical contrast of such a working electrode alone is insufficient for analysis.

To complement this information with an integral method we applied chemical analysis ($y = 1.7$-1.9 depending on loading) and RAMAN mapping searching for particle aggregates and for the extent of coverage of the CNT. Figure 9 shows a typical result confirming the existence of oxide aggregates with vibrations of Mn-O-Mn bridges. The strong contrasts in the distribution image designate particle aggregates, the weak contrast locales bundles of CNT with MnO_y thin films.

The approach that is also used for studying electronically doped Mn-oxides without carbon conductors is suited to identify samples and synthesis procedures for truly OER-active systems with a meaningful stability. Such systems will then be investigated with the in-situ analysis tools in order to get insight into their mode of operation. The results further show the urgent need to improve the fixation strategy for electroactive species and may give an impression as to why nature constructed in the photosystem 2 such a complicated surrounding for the active oxide cluster that requires internal dynamics for operation. We conclude that simple ion-exchange adsorption of Mn-species on oxo-functionalized carbon is insufficient for stabilization as well as attached crystals with little internal structural dynamics may only serve with their surfaces as capacitors rather than as OER catalysts.

IrO_x reference systems

Ir oxide electrodes are commercially available as OER systems but suffer from stability issues and from the enormous price. For us they represent the working benchmark system. Even these electrodes exhibit substantial over-potentials in excess of 350 meV. They accept, however the technically relevant current densities of up to 1000 mA/cm^2. In initial work we found strong evidence that the working phase is not IrO_2 but a mixed-valent system with a high oxidation potential capable of oxidizing CO at 100K. In further work we found a strong dependence of the performance on nano-structuring indicating that some of the over-potential may arise from transport limitations. Some other part may be due to internal losses associated with the transformation of the initial oxide into the active phase that may be facilitated through nano-structuring.

We currently concentrate on the identification of the chemical nature of the active phase. In Figure 10 a series is shown of variable high-energy XPS scans through the Ir 4f lines with high resolution. Whereas under the conditions of UHV the dominant phase is a tetravalent species one can see that the outer surface contains some Ir metal as extended phase (sharp line at low B.E) and the sub-surface regime seems to be disproportionated into a species with intermittent valence and a species exhibiting extensive core-hole coupling and a high shift.

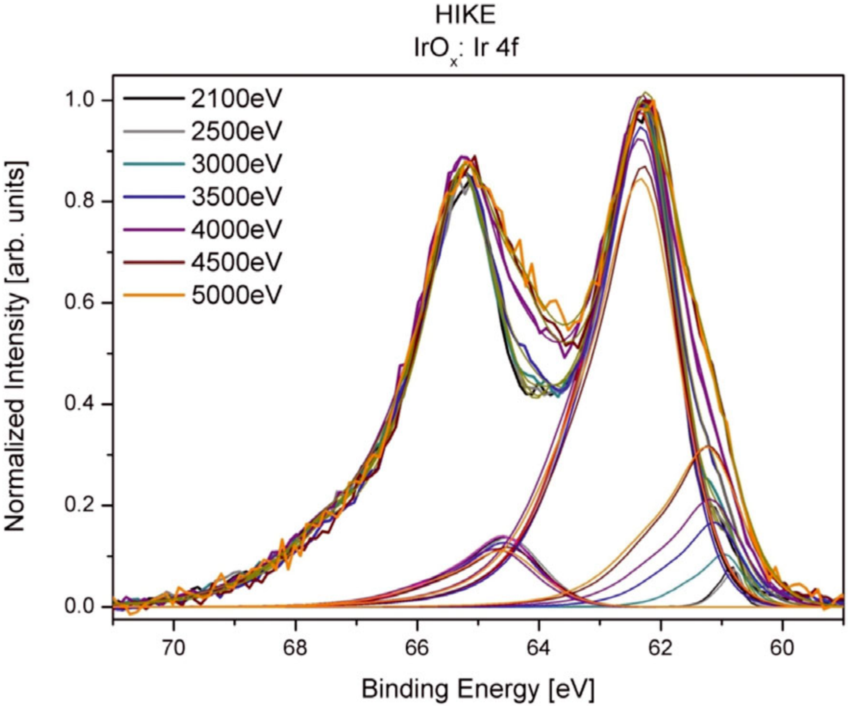


Figure 10. Variable energy XPS (HIKE) of an IrO_2 electrode after cycling in acidic electrolyte. The spectra cover a depth resolution of ca. 10 nm with the most surface-sensitive spectrum integrating over about 1.5 nm depth. Data were recorded at KMC1 at BESSY.

The line shape of the signal which was proven not to be a satellite structure of the main species is compatible with a isolated molecular species such as a hydroxoperoxide that could explain the enormous oxidation potential of the used electrode against CO.

The identification of a hydroxylated oxide species as active phase is corroborated by in-situ surface enhanced RAMAN spectroscopy (SERS). Several characteristic Ir-OH and Ir-O-Ir vibrations were identified and assigned by using quantum chemical calculations of vibrations on model compounds in collaboration with the department of *F. Neese*. In addition it was possible to show that if the Ir compound is synthesized from solution by electrodeposition one can obtain active surfaces with over-potentials as low as 30 meV disproving the conjecture that high over-potentials in OER are intrinsic to the reaction. This finding is further consistent with earlier results on the active phase of Pt oxides in OER [9] where a metallic sub-oxide-hydroxide was found through in-situ NAP XPS.

In summary it seems likely that active OER catalysts are thin films of semiconducting oxi-hydroxide structures without a crystal structure. They are capable of easily dissociating water. It is conceivable that metal-oxo species act after reduction into oxyl species as co-reactants with OH and form first an oxygen-oxygen bond prior to deprotonation in contrast to the idea that two oxyl species combine as it is conventionally assumed in mechanistic concepts of heterogeneous OER. This idea of participation of a surface species in addition to an adsorbate in the OER reaction will be substantiated with isotope labeling in-situ studies currently in preparation.

Performance Data of Catalysts for the Reduction of CO_2 and N_2

The reduction of small molecules is the scientific basis of chemical energy storage. It provides the most effective form of storing primary electricity in transportable and storable fuels that can be generated in world-scale quantities. The reduction of large amounts of CO_2 would further contribute to the reduction of greenhouse gases in the scheme of carbon capture and conversion into chemicals. In a first stage it is desirable to use primary electricity to produce through hydrogenation bulk chemicals that are otherwise generated from fossil sources. This produces substantial economic value much greater than achievable by combustion into secondary electricity. Such a mode (power to gas) comes only into play when fossil sources cannot be used anymore.

In view of this scenario it is of utmost relevance to optimize the performance of the processes. This is even more relevant when we consider that a substantial effort in present technologies is put into the preparation of suitable feed gas purities allowing continuous operation of plants. Ideally we need catalysts that operate on impure feed gasses in intermittent operation avoiding the need to store large amounts of primary hydrogen. In any artificial leaf operation these requirements are mandatory.

The department has thus initiated the development of test facilities allowing to determine the performance of existing catalysts under application-near conditions meaning at high pressures and with catalyst amounts allowing to simulate transport limitations and intermittent operation. We use off-line detection of products for high-quality quantitative data and we need to test catalysts for months rather than for days.

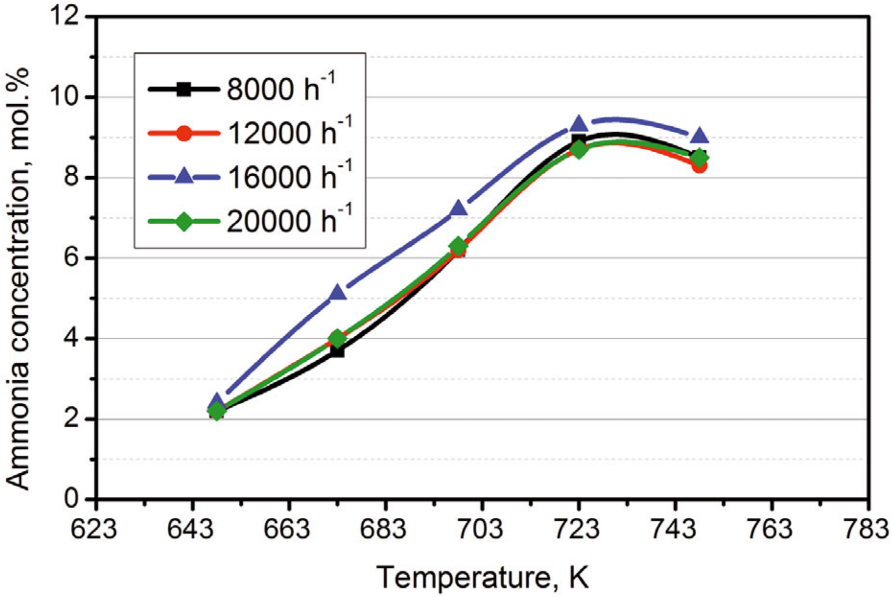


Figure 11. Precision data of ammonia synthesis over a commercial iron catalyst at 90 bar pressure. The typical general curve of an equilibrium-limited reaction can be seen. The loss of activity towards lower reaction temperatures is a direct measure of the quality of the catalyst.

With this concept we have set-up devices for high-pressure synthesis of methanol from either CO_2, or conventional synthesis gas and contaminated feed gases. In addition we can perform ammonia synthesis at pressures up to 100 bar. We will extend the facilities by a methanation unit and by multi-purpose reactors capable of performing catalyst test reactions for identifying active sites on carbon materials. The oxidation of CO [14] and selective oxidation of alkanes [15] are suitable test reactions. An advanced analytical infrastructure for precision off-line analysis of reactants and products complements the reactor equipment.

The example data set of Figure 11 shows the relevance of optimization of catalyst activation in iron-based ammonia synthesis. The system was started according to prescriptions of the supplier. During operation of about 40 days the catalyst begins self-activation from a rather poorly performing state indicated by the insensitivity of the production on space velocity. The data set for 16.000 h^{-1} SV was recorded after a steady state operation period of two weeks and shows an enhanced performance. This indicates that the start-up procedure needs detailed investigation and that the catalytic performance of such a well-studied system is still far from understood in terms of its material chemistry. As such data are not available in the open literature it would be hard to assess the research agenda for ammonia synthesis (in direction of lower temperature and/or lower feed gas purity) catalysts based on iron.

The underlying question behind such data is the identification of the formation and number and ultimately the structure of active sites. This is being answered in collaboration with *S. DeBeer* and by using the analytical arsenal of the FHI AC department. First results indicate that the anisotropy of iron required for effective ammonia synthesis [8] is generated by the reduction of Fe_3O_4 through a maximum concentration of intermittent FeO. The reduction kinetics and with it a low content of reduction water seems to be of decisive relevance for avoiding the formation of a stable isotropic iron. As the final iron metal cannot be formed into an anisotropic form at the temperatures available in catalysis, the activity of the catalyst is lost as soon as isotropic iron metal nuclei begin to form. This is decided in early stages of the catalyst activation procedure. We plan to synthesize adequate precursors allowing to better control the anisotropy of the final iron than by minimizing the reduction kinetics.

References

1. Schlögl, R., Chemistry's Role in Regenerative Energy, *Angew. Chem. Int. Ed.* **2011**, *50*, 6424–6426
2. a) Shao, L., Zhang, B., Zhang, W., Hong, S. Y., Schlögl, R., Su, D. S., The Role of Palladium Dynamics in the Surface Catalysis of Coupling Reactions, *Angew. Chem. Int. Ed.* **2013**, *52*, 2114-2117; b) Rocha, T. C. R., Oesterreich, A., Demidov, D. V., Hävecker, M., Zafeiratos, S., Weinberg, G., Bukhtiyarov, V. I., Knop-Gericke, A., Schlögl, R., The silver–oxygen system in catalysis: new insights by near ambient pressure X-ray photoelectron spectroscopy, *Phys. Chem. Chem. Phys.* **2012**, *14*, 4554-4564
3. a) Wowsnick, G., Teschner, D., Kasatkin, I., Girgsdies, F., Armbrüster, M., Zhang, A., Grin, Y., Schlögl, R., Behrens, M., Surface dynamics of the intermetallic catalyst Pd2Ga, Part I – Structural stability in UHV and different gas atmospheres, *J. Catal.* **2014**, *309*, 209-220; b) Frank, B., Cotter, T. P., Schuster, M. E., Schlögl, R., Trunschke, A., Carbon Dynamics on the Molybdenum Carbide Surface during Catalytic Propane Dehydrogenation, *Chem. Eur. J.* **2013**, *19*, 16938-16945; c) Zhang, B., Wang, D., Zhang, W., Su, D. S., Schlögl, R., Structural Dynamics of Low-Symmetry Au Nanoparticles Stimulated by Electron Irradiation, *Chemistry-A European Journal* **2011**, *17*, 12877-12881
4. a) Papaefthimiou, V., Dintzer, T., Lebedeva, M., Teschner, D., Hävecker, M., Knop-Gericke, A., Schlögl, R., Pierron-Bohnes, V., Savinova, E., Zafeiratos, S., Probing Metal–Support Interaction in Reactive Environments: An in Situ Study of PtCo Bimetallic Nanoparticles Supported on TiO_2, *J. Phys. Chem. C* **2012**, *116*, 14342-14349; b) Bauer, M., Schoch, R., Shao, L., Zhang, B., Knop-Gericke, A., Willinger, M., Schlögl, R., Teschner, D., Structure–Activity Studies on Highly Active Palladium Hydrogenation Catalysts by X-ray Absorption Spectroscopy, *J. Phys. Chem. C* **2012**, *116*, 22375-22385; c) Teschner, D., Borsodi, J., Kis, Z., Szentmiklósi, L., Révay, Z., Knop-Gericke, A., Schlögl, R., Scheffler, M., Torres, D., Sautet, P., Role of Hydrogen Species in Palladium-Catalyzed Alkyne Hydrogenation, *J. Phys. Chem. C* **2010**, *114*, 2293-2299; d) Teschner, D., Borsodi, J., Wootsch, A., Révay, Z., Hävecker, M., Knop-Gericke, A., Jackson, S. D., Schlögl, R., The Roles of Subsurface Carbon and Hydrogen in Palladium-Catalyzed Alkyne Hydrogenation, *Science* **2008**, *320*, 86-89
5. Schlögl, R., Abd Hamid, S. B., Nanocatalysis: Mature Science Revisited or Something Really New? *Angew. Chem. Int. Ed.* **2004**, *43*, 1628-1637
6. a) Schüth, F., Palkovits, R., Schlögl, R., Su, D. S., Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition, *Energy Environ. Sci.* **2012**, *5*, 6278-6289; b) Schlögl, R. Ammonia Synthesis in *Handbook of Heterogeneous Catalysis, Vol. Vol. 5* (Eds.: Ertl, G., Knözinger, H., Schüth, F., Weitkamp, J.), Wiley VCH Verlag, Weinheim, **2008**, pp. 2501-2575
7. Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., Zander, S., Girgsdies, F., Kurr, P., Kniep, B.-L., Tovar, M., Fischer, R. W., Nørskov, J. K., Schlögl, R., The Active Site of Methanol Synthesis over $Cu/ZnO/Al_2O_3$ Industrial Catalysts, *Science* **2012**, *336*, 893-897

8. Kandemir, T., Schuster, M. E., Senyshyn, A., Behrens, M., Schlögl, R., The Haber–Bosch Process Revisited: On the Real Structure and Stability of "Ammonia Iron" under Working Conditions, *Angew. Chem. Int. Ed.* **2013**, *52*, 12723-12726

9. Arrigo, R., Hävecker, M., Schuster, M. E., Ranjan, C., Stotz, E., Knop-Gericke, A., Schlögl, R., In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, *Angew. Chem. Int. Ed.* **2013**, *52*, 11660-11664

10. Schlögl, R., Carbon in Catalysis in *Advances in Catalysis* (Eds.: B. C. Gates, F. C. Jentoft), Elsevier Inc., **2013**, *56*, 103-185

11. a) Artyushkova, K., Kiefer, B., Halevi, B., Knop-Gericke, A., Schlögl, R., Atanassov, P., Density functional theory calculations of XPS binding energy shift for nitrogen-containing graphene-like structures, *Chem. Commun.* **2013**, *49*, 2539-2641; b) Arrigo, R., Wrabetz, S., Schuster, M. E., Wang, D., Villa, A., Rosenthal, D., Schlögl, R., Su, D. S., Tailoring the morphology of Pd nanoparticles on CNTs by nitrogen and oxygen functionalization, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10523-10532

12. Arrigo, R., Schuster, M. E., Abate, S., Wrabetz, S., Amakawa, K., Teschner, D., Freni, M., Centi, G., Perathoner, S., Hävecker, M., Schlögl, R., Dynamics of Palladium on Nanocarbon in the Direct Synthesis of H_2O_2, *ChemSusChem* **2013**, *Early View*

13. Mette, K., Bergmann, A., Tessonnier, J.-P., Hävecker, M., Yao, L., Ressler, T., Schlögl, R., Strasser, P., Behrens, M., Nanostructured Manganese Oxide Supported on Carbon Nanotubes for Electrocatalytic Water Splitting, *ChemCatChem* **2012**, *4*, 851-862

14. a) Vogel, D., Spiel, C., Schmid, M., Stöger-Pollach, M., Schlögl, R., Suchorski, Y., Rupprechter, G., The Role of Defects in the Local Reaction Kinetics of CO Oxidation on Low-Index Pd Surfaces, *J. Phys. Chem. C* **2013**, *117*, 12054-12060; b) Freund, H.-J., Meijer, G., Scheffler, M., Schlögl, R., Wolf, M., CO Oxidation as a Prototypical Reaction for Heterogeneous Processes, *Angew. Chem. Int. Ed.* **2011**, *50*, 10064-10094

15. Frank, B., Blume, R., Rinaldi, A., Trunschke, A., Schlögl, R., Oxygen Insertion Catalysis by sp^2 Carbon, *Angew. Chem. Int. Ed.* **2011**, *50*, 10226-10230

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Oxygen evolution reaction (OER) over Platinum: a study using near ambient pressure X-ray photoemission spectroscopy (NAP-XPS)

Introduction

Knowledge of the structural transformation of the electrocatalyst surface upon OER is essential to design a better electrode material. Our research activity aims to study the chemical modification of the electrode surface and sub-surface occurring in the dynamic interaction with the reactant molecules for low temperature gas-phase electrolysis using the NAP-XPS end-station at the ISISS beamline in collaboration with the Inorganic Chemistry Department of the Fritz-Haber-Institut der Max-Planck-Gesellschaft.

The first study undertaken here focuses on Pt as electrode for OER. Pt is one of the most used materials for PEM fuel cells and has been considered as model system to study the structural transformation upon polarization. However, convincing description of the structure of the Pt electrode-electrolyte boundary layer is still lacking. In this work, chronoamperometry (CA) is applied to the electrode system in combination with in situ XPS investigation. The gas composition is continuously monitored by online mass spectrometry (MS).

The system under investigation is a Pt/Nafion-based electrode. The Nafion membrane electrolyte is sputter-coated on both sides by the electro-active element (Pt), functioning as cathode on one side and anode on the other.

The cell designed for in-situ investigation is sketched in Fig. 1. The cell has a reservoir for liquid sealed through the coated Nafion membrane. Liquid water in the reservoir serves two purposes: on one hand it supplies the reactant molecules to both the

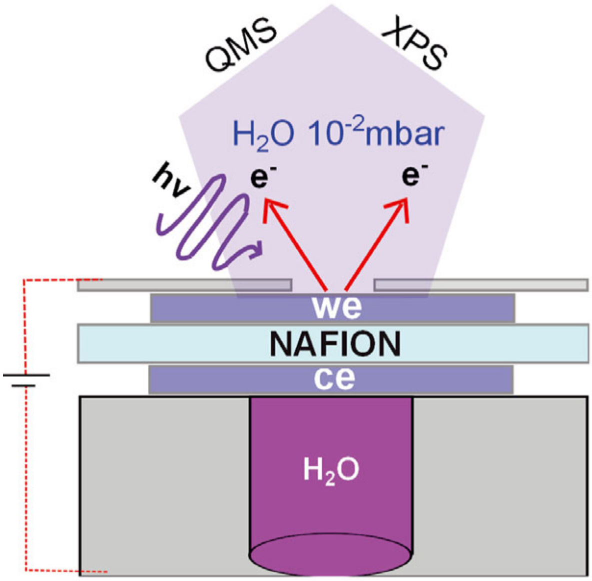

Figure 1: A cell for in-situ investigation with a liquid reservoir is represented. Due to the pressure difference, the water in the liquid reservoir diffuses through the membrane and generates a water pressure in the XPS chamber in the range of mbar. The porosity of the Pt film allows the water transport. The electrode exposed to X-rays is the WE.

electrodes due to the permeability of the Nafion membrane and the porosity of the Pt film; on the other hand it guarantees a good hydration of the membrane which is fundamental for achieving good ion conductivity. The electrode directly in contact with the liquid water functions as counter electrode (CE), while the electrode exposed to photons is the working electrode (WE).

The MS traces of H_2 and O_2 in Fig. 2 show the response of the system to the applied potentials.

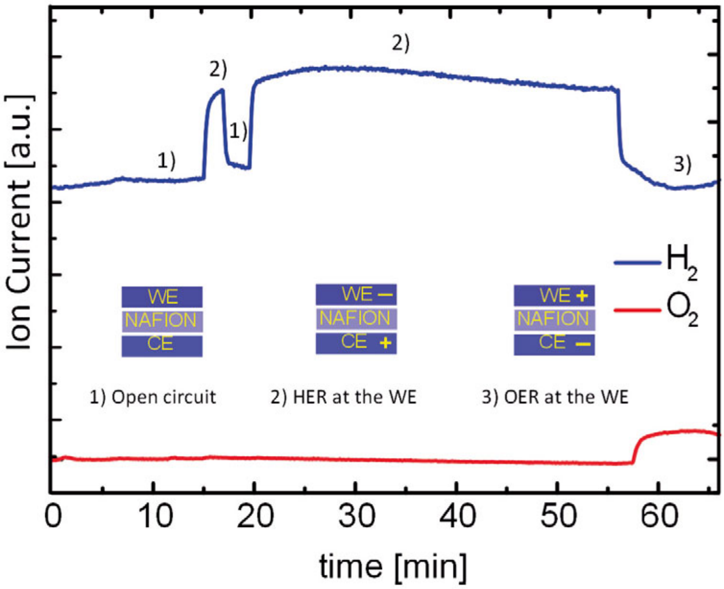

Figure 2. MS during NAP-XPS study. Depending on the potential applied at the WE, OER (+2V), or HER (-2V) occurs and the m/z 2 for H_2 or m/z 32 for O_2 are detected.

When the WE acts as cathode, the H_2 trace increases, whereas when the WE acts as anode, the O_2 trace increases. These results indicate that the in-situ cell/electrode assembly works as functional water splitting device.

Chemical surface state of Pt upon OER [1]

The nature of the active Pt surface upon OER - whether a surface PtO_2 Pt_3O_4 and PtO oxide or hydroxide phase, or a combination of them - is still a matter of debate. To investigate the electronic structure of Pt in the active state for OER and the nature of the oxygen species, we have compared the OER rate at constant potential for Pt electrode with different chemical oxidation state. Thus, a sputtered Pt film was subjected to O_3 treatment with the purpose to increase its oxidation state. The current generated due to OER at constant anodic polarization is representative of the OER rate. The measured current and the corresponding Pt4f spectra are reported in Fig. 3.

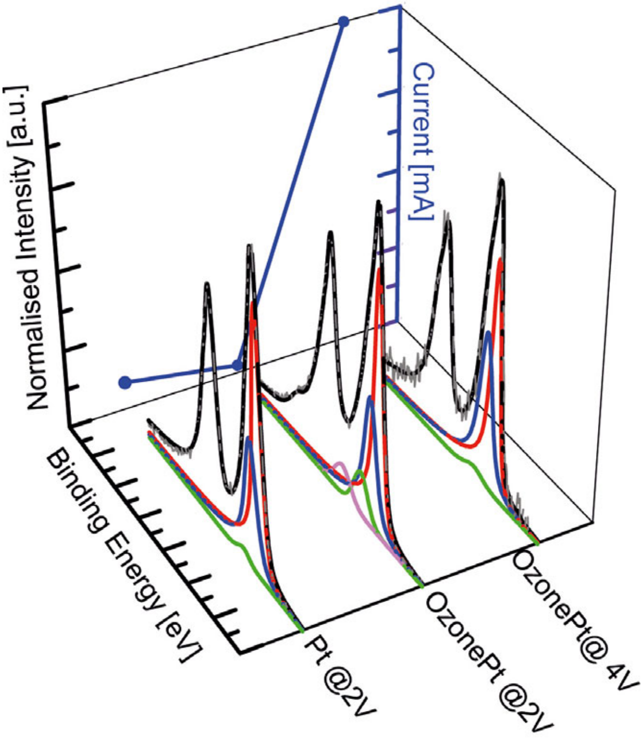

Figure 3. Pt4f spectra with KE=150eV during constant anodic polarization and the corresponding measured current for the sputtered Pt film WE at 2V, and at 2V and 4V after a pretreatment in 1 bar O_3: the order indicates chronological sequence of the experiments.

The Pt4f spectrum for a sputtered Pt film is described by three components, Pt1 (binding energy (BE) 71 eV), Pt2 (71.6 eV) and Pt3 (72.3 eV), corresponding to metallic Pt, electronically modified metallic Pt^{+} by oxygen in the near-surface region and Pt^{2+} species, respectively. The O_3 treatment induces an enhancement of the Pt3 species and an additional component Pt4 (73.7 eV) corresponding to Pt in higher oxidation state.

The higher abundance of the Pt3 as well as Pt4 in the Pt4f spectrum of the O_3 treated Pt film correspond to a reduction of the current at 2V with respect to the case of the Pt film before the O_3 pretreatment. Another interesting discovery is that increasing the potential to 4V favors the Pt reduction to a chemical composition similar to the fresh film and correspondingly the current is significantly increased.

Conclusion and outlook

On the basis of these results, the active Pt surface for OER is described as an electronically modified metallic surface with oxygen in the surface and near-surface region forming nanoclusters with O-Pt-O trilayer structure. This species is required for water dissociation. Together with this state, a divalent hydrated Pt species also occurs with the OER activity. In contrary, stronger Pt-O bonds in stable oxidic phase induce overpotential. Structural modifications on bare Pt may prevent the formation of unnecessary oxide over layers during OER. In future, this investigation will be extended to IrOx electro-catalyst for OER. A continuous flow cell for long-term experiments is under development for this purpose.

References

1. Arrigo, R., Hävecker, M., Schuster, M. E., Ranjan, C., Stotz, E., Knop-Gericke, A., Schlögl, R., In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, *Angew. Chem. Int. Ed.* **2013**, *52*, 11660-11664

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Methanol synthesis and ammonia synthesis over an industrial catalyst

Introduction

Many important industrial processes rely on heterogeneous catalytic reactions, in which the catalyst is in a different phase than the substrate. Usually the catalyst is a solid and the reactants are gases. Reactions proceed on the active sites of the catalyst surface. Our group investigates three industrial processes: methanol synthesis, ammonia synthesis, and oxidative dehydrogenation of ethylbenzene.

1) Methanol synthesis

Nowadays, solar, wind and hydro energy sources are often touted as a solution of the energy problem. However, it is difficult to transport this energy. The liquid transportation fuel can be methanol produced from atmospheric CO_2 and H_2 generated by water electrolysis, which could provide a convenient storage of energy. This would provide capture of CO_2 from the atmosphere to decrease the global warming effect. Hydrogenation of CO_2 is a known process to produce methanol.

Experimental part

The reaction was carried out in a fixed-bed catalytic reactor system which is equipped with a liquid storage vessel to collect the mixture of methanol and water. We used a commercial catalyst, $Cu/ZnO/Al_2O_3$, provided by Süd-Chemie. Prior to all experiments the fresh catalyst was reduced at 573 K (1 K/min) for 3 hours in 20 % H_2 in N_2. The catalyst testing was carried out at the following conditions: 463 – 533K, 30 – 50 bars, and feed of 800 – 1200 ml/min with molar ratio $H_2:CO_2 = 3:1$ [1].

Reaction products were collected for 18 hours of continuous synthesis. The liquid samples were characterized by Agilent 6890 GC with two detectors TCD for quantification of CH_3OH, H_2O and FID for quantification by-products (methyl formate).

Results and discussion

The CO_2 hydrogenation activities data are present in terms of CO_2 conversion and methanol selectivity values, indicating that the activity depends on temperature, pressure and space velocity.

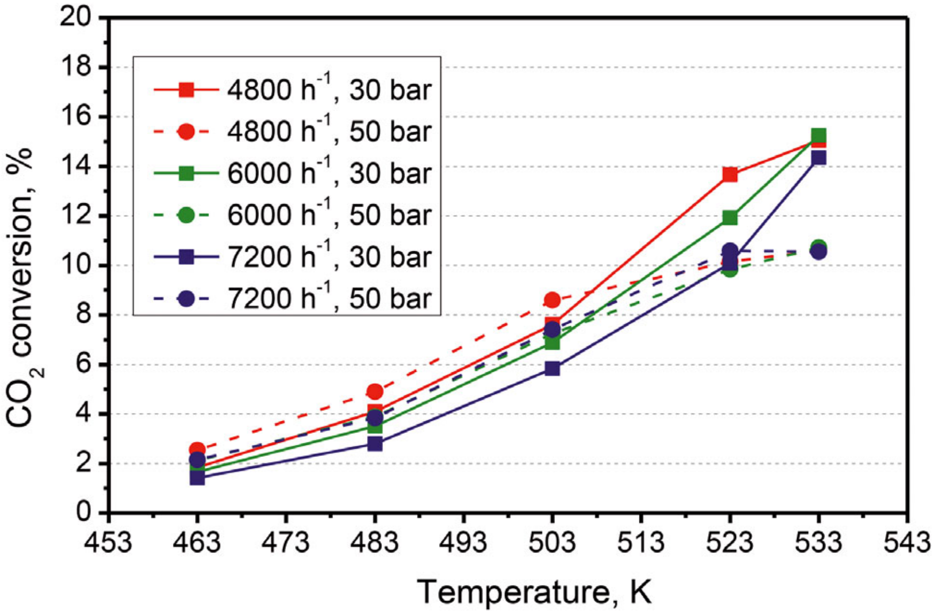

Figure 1. CO_2 conversion versus temperature.

Figure 1 shows the influence of the reaction temperature on the CO_2 conversion at different pressures and flows. As it is seen, the CO_2 conversion increases monotonously with increasing reaction temperature. On the other hand, activity decreases with increasing space velocity because of smaller contact time of gas mixture with the catalyst. However, the conversion is practically the same at 260°C regardless of space velocity. It is worth to note that activity is higher for higher pressure up to 230°C at the same space velocity and then increase of temperature results in changing this tendency. The higher the pressure, the lower the CO_2 conversion.

Figure 2 shows that at 30 bar methanol selectivity monotonously decreases with temperature and lies in the ranges of 58.3% – 34.5% at 4800 h^{-1} and from 64.8 to 32.2% at 7200 h^{-1}. This behavior can be caused by passing the competitive reverse water gas shift reaction which is more preferable at higher temperature due to its endothermic character.

$$CO_2 + H_2 \rightarrow CO + H_2O$$
$$\Delta H \rightarrow 41.2 \text{ kJ/mole}$$

Thus, the higher amount of CO is produced during the experiment at higher temperature, and methanol selectivity decreases. However, increase of pressure up to 50 bar results in obtaining practically constant selectivity for certain GHSV.

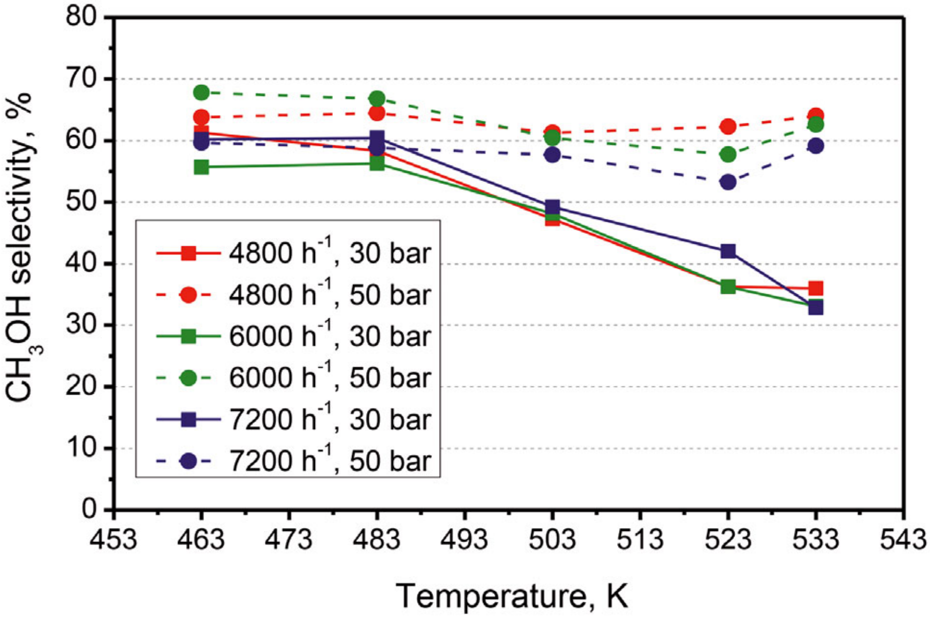

Figure 2. CH_3OH selectivity versus temperature.

Activation energies for methanol formation were measured at different pressure and space velocities. Activation energy for methanol production is nearly constant at different conditions and lies in the range of 44.9 – 50.0 kJ/mole.

2) Ammonia synthesis

The main industrial route for production of ammonia is the reaction of hydrogen and nitrogen via the Haber-Bosch process. A hydrogen-nitrogen mixture reacts on the double-promoted iron catalysts at elevated temperature in the range (300 – 550°C) and operating pressure above 100 bars. The iron catalyst is promoted by Al_2O_3 and K_2O. Al_2O_3 is a structural promoter of the catalyst; its function is to prevent sintering of the catalyst particles. K_2O is an electronic promoter.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

We built up a setup for producing ammonia. The setup consists of purification and synthesis reactors. The first one is intended to remove impurities in the feed gas before the synthesis reactor since the ammonia catalyst is very sensitive to any oxygen species in the feed gas. The highest pressure value which we can use for this setup is 100 bar. Reaction products can be taken from gas-sampling port and analyzed by NDIR.

Prior to the experiment the catalyst is reduced by the specific procedure in the gas mixture of H_2:N_2 = 3:1. Pretesting experiments were done for this setup at a pressure of 90 bar and a temperature of 400°C.

3) Oxidative dehydrogenation (ODH)

For styrene synthesis, ODH is an energy-saving candidate for an industrial process.

$$C_6H_5CH_2CH_3 + {}^1/_2\,0_2 \rightarrow C_6H_5CH = CH_2 + H_2O$$

This reaction is important for producing styrene which is used as a starting monomer for polystyrene. ODH of ethylbenzene in the presence of oxygen allows one to operate at relatively low temperatures (300 – 400°C).

Our group designed a setup for oxidative dehydrogenation of ethylbenzene or propane. This setup has two reactors. Gases with different components can pass through both reactors by switching valve. Two reactors at the outlet are connected to one GC, and gas product composition can be determined in parallel by GC using a special valve. This setup allows us to run two different reactions in parallel or use different reaction conditions in two reactors for the same reaction.

Recently studies revealed that different carbon materials with graphitic structure are as efficient as metal catalysts [2]. The aim of our research is to study catalytic properties of carbon materials with different functional groups on the surface.

References

1. Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., Zander, S., Girgsdies, F., Kurr, P., Kniep, B.-L., Tovar, M., Fischer, R. W., Nørskov, J. K., Schlögl, R., The Active Site of Methanol Synthesis over Cu/ZnO/Al_2O_3 Industrial Catalysts, *Science* **2012**, 336, 893 – 897
2. Delgado, J.J., Chen, X.-W., Frank, B., Su, D. S., Schlögl, R., Activation Processes of Highly Ordered Carbon Nanofibers in the Oxidative Dehydrogenation of Ethylbenzene, *Catal.Today*, **2012**, *186*, 93 – 98

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Electrode Materials

Introduction

Sustainable energy production is nowadays often performed by wind, solar or hydrogen techniques. The major problem is to store and to transport the energy safely and efficiently. In our working group we develop electrode materials for electrocatalytic water splitting. For a global application the expensive electrodes, which often consist out of rare elements like platinum or iridium oxides have to be replaced by cheap alternatives. The general idea is to generate electrodes out of conductive carbon supports, which are functionalized with metal oxides as catalytic active species. The main challenge is to end up with a highly efficient material with long-term stability.

Setup

Within the last year a setup for gas phase syntheses was built. The schematic of the facility for atomic layer deposition is shown in Figure 1. Evacuation of the facility can be realized with a turbo molecular pump connected to a rotary vane pump. All connections are grease free, so that a contamination can be excluded. The system is equipped with a mass spectrometer (HPA 220, Pfeiffer) and several pressure sensors and thermocouples, due to this an in-situ control of the process is ensured. It is possible to apply continuous gas flows of H_2, O_2, N_2, Ar, He and one further exchangeable process gas (X). Constant mixtures of the gases can be implemented to achieve selective oxidative or reductive gas atmospheres. There are three connections for glass flasks, where precursors, solvents, acids or other substances can be introduced to the reaction chamber. Big diameters of about 60 mm of the glass and metal tubes fulfill the demand for a fast and efficient work with high amounts of material. Several grams of support material can be functionalized in the ALD setup. The big dimensions guarantee a characterization of the same batch.

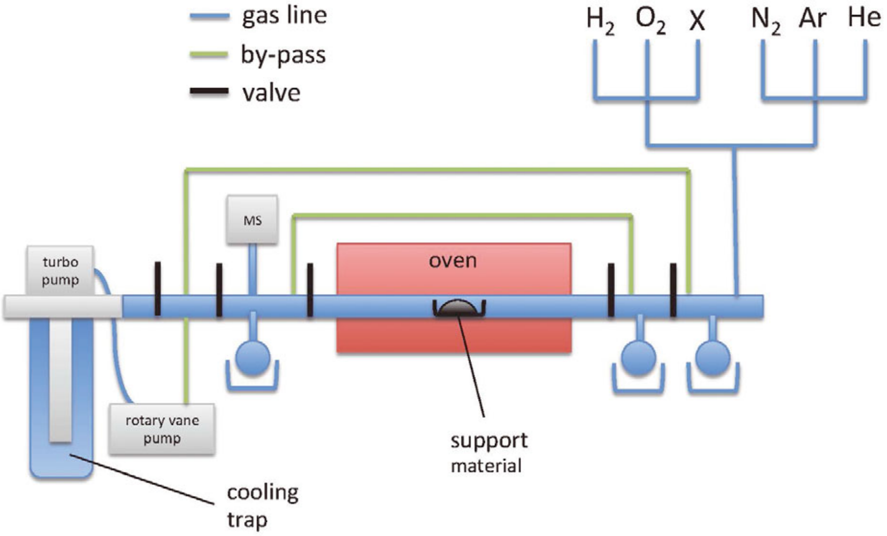

Figure 1. Sketch of the system for gas phase syntheses.

Atomic layer deposition

First experiments were realized with carbon nanotubes. They were pre-functionalized in the ALD setup and characterized by elemental analysis, Titration, TG-MS and IR.

Different process parameters were used to remove amorphous carbon and to anchor functional groups on the surface of carbon nanotubes. Process parameters have to be chosen in a way to introduce specific functional groups and to prevent thermal decomposition of the carbon materials. Temperature, pressure and duration times are the main factors. Characterization of the support materials before and after manganese is deposited is essential for a basic understanding and will be performed by TEM, thermal methods, UV and Raman spectroscopy. It is planned to perform manganese oxide particles in different oxidation states, different particle sizes and distributions. A homogeneous distribution of small particles of the metal oxides is achieved.

Wet chemistry

Carbon nanotubes were pre-functionalized with nitric acid or sulfuric acid and further treated with $Mn(NO_3)_2 \cdot H_2O$ in an incipient wetness impregnation or symproportionation deposition-precipitation reaction as described by Mette et al. [1]. The weight percentage of manganese was adjusted from 1 % to 60 %. Characterization of the samples was performed by elemental analysis, Titration, TG-MS, IR, Raman, temperature programmed reduction (TPR), XRD, N_2 sorption measurements and cyclic voltammetry (CV).

TPR measurements (Figure 2) exhibit a clear trend between the loading of manganese and the oxidation state of the reducible species. With increasing amount of manganese the composition conform the ideal compound of MnO_2, which correlates to an increase of the oxidation state with increasing manganese.

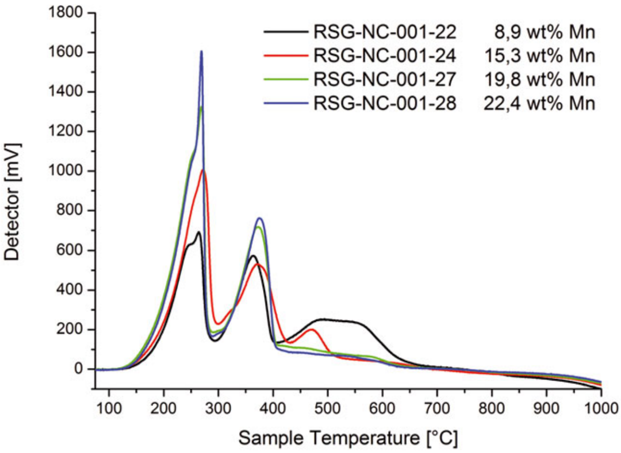

Figure 2. TPR measurements of functionalized samples with different amounts of manganese.

Multiple heating rate programs have been used to evaluate kinetic data of the reaction. First results show reduction process independent from heating rate.

Electrodes had to be prepared for the electrocatalytic characterization. Several techniques were performed to develop mechanically stable tablets that do not fall apart in electrolyte. A specific holder for the tablets was created to guarantee reproducible measurements. Samples show high capacities, so that an application as supercapacitors is also conceivable. Chronoamperometric measurements were also performed to identify the electrochemical activity under static conditions. The tested materials seem to be promising candidates for electrocatalytic water splitting.

Matrix isolation setup

A matrix isolation setup with in-situ Raman and in-situ IR spectrometer was used to investigate manganese and manganese oxide particles. The compounds and their spectra serve as models for the materials prepared by wet chemistry and ALD.

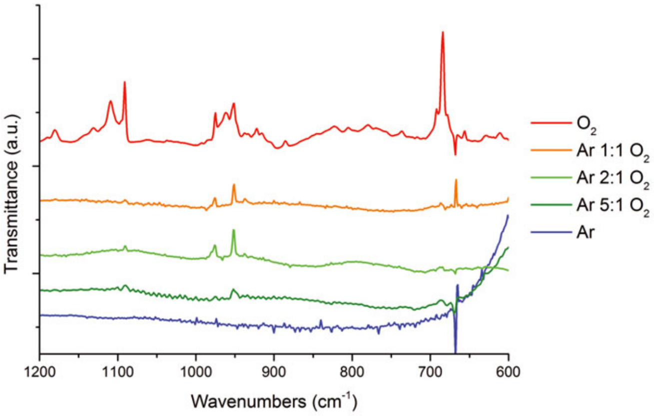

Figure 3. IR spectra of MnO_x particles in different gas matrices.

Manganese was thermally evaporated and deposited on a potassium chloride window in an argon or argon-oxygen matrix at 8 K. Deposition rates and argon to oxygen ratios were varied to perform different manganese oxides (Figure 3). Mobilization of the particles in the matrix was realized by radiation with UV light or by thermal heating. Deposition of the particles directly on a TEM grid revealed that clusters of small particles of about 2-3 nm are formed during the process.

Outlook

In cooperation with members of the university Duisburg-Essen a SFB application was handed in. It is called SFB 1099 *Eigenschaftsgetriebene Herstellung nanostrukturierter Funktionsmaterialien: Von den elementaren Vorgängen zu Prozessen*. The project was peer-reviewed and is now submitted for financial support. Two PhD positions will be paid within the project. The aim of the project is to understand the correlation between the structure and the electrocatalytic behavior fundamentally.

A second application was written for a project called BmBF Verbundprojekt „Biomimetische Wasserspaltung". This project has to be peer-reviewed.

References

1. Mette, K., Bergmann, A., Tessonnier, J.-P., Haevecker, M., Yao, L., Ressler, T., Schloegl, R., Strasser, P., Behrens, M., Nanostructured Manganese Oxide Supported on Carbon Nanotubes for Electrocatalytic Water Splitting, *ChemCatChem* **2012**, *4*, 851

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Biological Photoreceptors – Novel Tools in Optogenetics and Superresolution Microscopy

Introduction

This research group is studying biological photoreceptors that function as important, light-sensing chromoproteins. We are mainly studying the role of light as an information medium and only partly follow its fundamental role as energy source on earth (our research on light as an energy source is a collaborative project with LIMLA, CONyCET group in Tucuman, Argentina). For our photosensory activities, we concentrate in particular on proteins that employ FMN (flavin mononucleotide) or bilins (open-chain tetrapyrroles) as chromophores. FMN-binding photoreceptors show blue light (BL) sensitivity, bilin-binding proteins are (classically, *see below*) red light sensing. Study on a new class of bilin-binding photoreceptors with highly variable spectral sensitivity (extending from near-UV into the far red range) has just started (in 2013). Research on both classes, red- and blue sensing, is performed in parallel, as, despite their spectral variance and photochemical reactivity, their physiological (signaling) function often follows similar pathways. Our contributions to chromophore-protein interaction in phytochromes have been summarized [1], and research on BL sensing photo-receptors, including functional principles and novel applications are summarized in two recent reviews [2,3]. For a detailed understanding of flavin-based photoreceptors we have teamed up with two theoretician's groups, Prof. C. M. Marian, University Düsseldorf, and Prof. W. Thiel, MPI Kohlenforschung. Our biochemical expertise helped in the preparation of hydrogenases (collaboration with the Dept of Prof. Lubitz, coworking with O. Rüdiger and H. Shafaat) that allowed detailed FTIR-, EPR-, and electrochemical characterization of the [NiFeSe]-hydrogenase from

Desulfovibrio vulgaris Miyazaki F, for details see contribution from O. Rüdiger (this work was performed as part of the Ph.D. work of J. Riethausen). Our photochemical expertise will help studying photochemical reactivity of catalyst material (Ge-doped ZnON) provided by C. Giordano, MPI Golm.

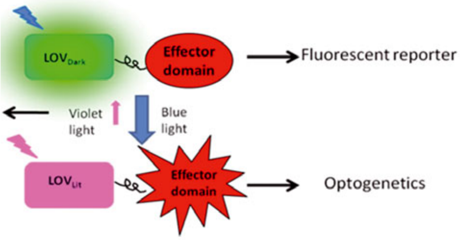
Red light sensing photoreceptors

(i) Classical phytochromes. The sensing domain of canonical phytochromes is composed of three protein domains, PAS, GAF, PHY that bind the bilin chromophore and determine the light induced double bond isomerization of the chromophore. We could characterize the entire photochemistry from the sub-ps into the long ms time domain for various phytochromes from plant and cyanobacteria. In collaboration with a solid-state NMR research group (Matysik, University Leipzig, funded by Volkswagen-Foundation) we identified conformational motions of the bilin chromophore at the atomic level, and identified by first time-application of a MELODI-HETCOR pulse sequence (to a protein of this size) motions of close-by located amino acid side chains in response to the chromophore movements [4]. (ii) A novel class of bilin-binding photoreceptors. These proteins exhibit a repetitive arrangement of GAF domains, in contrast to the classical PAS-GAF-PHY structure of phytochromes. Here, already the isolated GAF domains show the capability to bind the bilin chromophore and to undergo the photochromic photochemistry akin classical phytochromes, i.e., double bond photoisomerization, yet, with a much wider spectral range (expanding from near UV-A into the far red range). Furthermore, these proteins modify the incorporated bilin chromophore by chemical reactions (converting initially adopted phycocyanobilin into either phycoviolobilin or into rubinoid-type tetrapyrroles). Study of these proteins has just started (collaboration with University Wuhan, China). The properties of these proteins, i.e., their small size, great stability, and outstanding photochemical parameters (high extinction coefficient, significant and switchable fluorescence) make them excellent tools for modern biotechnological and optogenetics applications (to be performed as *below, Applications*).

Blue light sensing photoreceptors

Research on BL sensing receptors is performed since many years in a close collaboration with Prof. Aba Losi, the Physics Dept. of University of Parma, Italy. Our studies deal mainly with flavin-binding LOV-domain proteins. Here, chemical synthesis of modified flavins and assembly into the protein has triggered theoretical calculations on the reactivity of these chromophores in a hydrogen bond-rich protein pocket [5]. With these photoreceptors much more studies on the physiological relevance of BL sensing could be performed, including investigations of bacterial communities isolated from extremely UV-exposed environments in the Argentinian Andes [6].

This work was accomplished in my group by V. Albarracin from Tucuman, Argentina, funded by a Marie-Curie Grant. Also, the signaling function of BL sensing proteins, i.e., the regulation of the “output”-signal in either the dark or the lit state could be clearly documented for several proteins. Signaling in most cases is based on a photo-



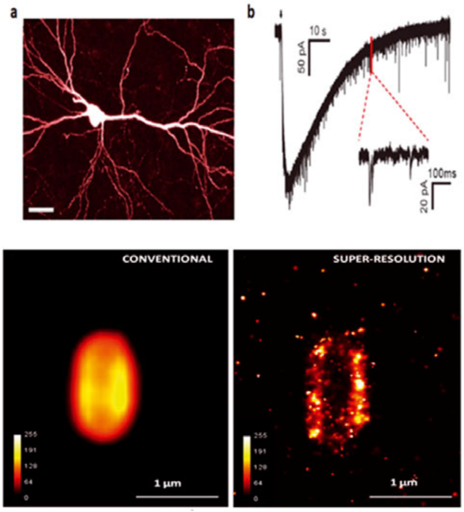


Figure 1. Left, function of BL-sensing photoreceptor YtvA with two states, physiologically silent, fluo-active and physiologically active, fluo-silent. Right, top (a) neuronal cell, (b) light-induced neuronal activity upon PAC expression; bottom, left, conventional fluorescence microscopy of bacterial cell, right, FPALM superresolution.

regulation of an enzyme function in a second, fused protein domain. Demonstrated examples are the light-regulated enzymatic activity of histidine kinases or of cyclic-di-GMP phosphodiesterases. This finding has enabled optogenetics studies in living cells (*see following paragraph, Applications*).

Applications

Biotechnological and optogenetics applications of photoreceptors have preferentially been demonstrated by us so far for the BL sensing receptors. Flavin-based LOV-domain receptors show a dual functionality: in their physiologically active LIT state (enzyme activity control) they do not show any fluorescence, whereas in their physiological silent state they show a strong fluorescence (Fig. 1, left). Both properties could be demonstrated by us in recent experiments. Fig.1, right top shows a light-activated enzyme activity in a BL sensing receptor with signaling function that is based on the formation of cAMP. cAMP is a very important "second messenger" that among other functions opens membrane channels. In vitro proof of the light regulation was successful, thus, this protein was expressed in neuronal cells.

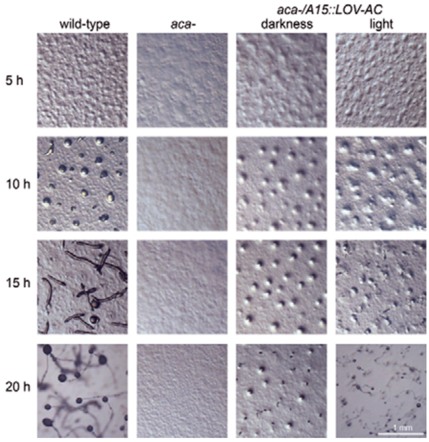


Figure 2. 20 h-time course of life cycles of *Dictyostelium discoideum* wild type cells. From left to right: Wild-type cells; second panel from left: null mutants in adenylyl cyclase ACA (*aca*-). ACA being the essential enzyme for the formation of cAMP as a signal for development. Third and fourth panel: *aca*-cells transformed with mPAC (*aca-/A15::LOV-AC*) and incubated in darkness (p.3) or under irradiation (p.4). Irradiation was performed with white light. After 20 h the wild-type, but not the aca-cells had formed fruiting bodies. mPAC restored formation of smaller fruiting bodies in the *aca*-mutant, when stimulated with light, but was much less effective in darkness.

Here, irradiation of the cells now causes channel opening, resulting in a intracellular potential change and thereby in neuronal activity [7]. A follow-up application of light-activated adenylyl cyclases could be demonstrated by expressing another PAC (photoactivated Adenylyl-cyclase) in the slime mold *Dictyostelium discoideum*. This organism lives unicellular, until, under certain life conditions, enzymatic cAMP generation causes the aggregation of cells and differentiation into a fruiting body that excretes spores for the next generation. Also in this experiment, light induced cAMP by a PAC led to cell aggregation and fruiting body formation (collaboration P. Schaap, University Dundee, G. Nagel, University Würzburg, Fig. 2).

The most recent application is based on the above mentioned possibility to switch on and off the fluorescence of BL photoreceptors. If a situation of stochastic "blinking" is generated, so-called FPALM protocols allow overcoming the picture-resolution in microscopy (then called "nanoscopy") by nearly one order of magnitude. This could be demonstrated for the BL-sensing receptor YtvA (collaboration University Parma and IIT, Genova, Italy). Fig. 1, bottom, right shows the difference. Normal fluorescence microscopy shows the fully fluorescent bacterial cell expressing the fluorescent photoreceptor; structural details under FPALM conditions could be resolved down to ca. 30 nm [8].

References

1. Gärtner, W. and Bongards, C., The Role of the Chromophore in the Biological Photoreceptor Phytochrome: An Approach Using Chemically Synthesized Tetrapyrroles. *Accounts Chem. Res.* **2010**, *43*, 485-495
2. Losi, A. and Gärtner, W., Old chromophores, new photoactivation paradigms, trendy applications: flavins in LOV and BLUF photoreceptors. *Photochem. Photobiol.* **2011**, *87,* 491-510
3. Losi, A. and Gärtner, W., The evolution of flavin-binding photoreceptors: an ancient chromophore serving trendy blue-light sensors. *Annu. Rev. Plant Biol.* **2012**, *63,* 49-72
4. Song, C., Psakis, G., Lang, C., Mailliet, J., Gärtner, W., Hughes, J., and Matysik, J., Two ground state isoforms and a chromophore D-ring photoflip triggering extensive intramolecular changes in a canonical phytochrome. *Proc. Natl. Acad. Sci. USA* **2011**, *108,* 3842-3847
5. Silva-Junior, M.R., Mansurova, M., Gärtner, W. and Thiel, W., Photophysics of structurally modified flavin derivatives in the blue light photoreceptor YtvA: A combined experimental and theoretical study. *ChemBioChem* **2013**, *14,* 1648-1661
6. Albarracín, V.H., Pathak, G.P., Douki, T., Cadet, J., Borsarelli, C.D., Gärtner, W., and Farias, M.E., Extremophilic *Acinetobacter* strains from High-Altitude Lakes in Argentinean Puna: Remarkable UV-B resistance and efficient DNA repair. Origins of Life and Evolution of Biospheres **2012**, *42,* 201-221
7. Stierl, M., Stumpf, P., Udwari, D., Gueta, R., Hagedorn, R., Losi, A., Gärtner, W., Petereit, L., Efetova, M., Schwarel, Oertner, T., Nagel, G. and Hegemann,, P. *J. Biol. Chem.* **2011**, *286,* 1181-1188
8. Losi, A., Gärtner, W., Raffelberg, S., Cella Zanacchi, F., Bianchini, P., Diaspro, A., Mandalari, C., Abbruzzetti, S. and Viappiani, C., A photochromic bacterial photoreceptor with potential for super-resolution microscopy. *Photochem. Photobiol. Sci.* **2013**, *12,* 231-235

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Photophysics of energy and electron transfer systems and of artificial light-harvesting devices

The group's research activities over the last 3 years concentrated on three main subjects: i) Molecular mechanisms of non-photochemical quenching (NPQ) and state transitions in higher plants, cyanobacteria, and a variety of other photosynthetic microorganisms (supported by an EU Marie Curie network, and a DFG joint grant with Prof. Jahns, University Düsseldorf), ii) the development and structural/functional characterization of supramolecular self-assembled chlorophyll (Chl) nano-structures serving as natural and artificial photonic units for solar-to-fuels conversion within the EUROCORES network SolarFuelTandem, and iii) characterization of the excited states dynamics of carotenoids by ultrafast spectroscopy. We published 18 papers in refereed journals in these fields since 2011, with several additional manuscripts submitted.

NPQ and state transitions

Photosynthetic organisms require photoprotection against severe photodamage in rapidly varying illumination conditions producing excessive light input that cannot be handled by the electron flow in the reaction centers. This photoprotection is provided by a range of regulation mechanism(s) summarized under the term NPQ. Likewise unequal excitation of the two photosystems of oxygenic photosynthesis, PSI and PSII, is balanced by a mechanism called "state transitions". Both types of regulation mechanism affect the non-radiative deactivation rates in the antenna system of the PS II supercomplex. According to generally accepted models the NPQ regulation involves a small protein, PsbS, and the activation of the "xanthophyll cycle", converting violaxanthin to zeaxanthin. The molecular mechanisms of all these regulations are hardly understood and are discussed highly controversially in the literature. On the one hand we exploited in our studies the vast potential of ultrafast time-resolved fluorescence and transient absorption spectroscopy on both isolated antenna complexes as well as intact organisms (intact leaves of higher plants, intact microalgae, intact photosymbiotic systems like lichens and corals). A particular highlight has been the development of a femtosecond transient absorption system capable of following the development of high-light-induced NPQ in real time, thus resolving the kinetics and spectra of the femto/picosecond quenching intermediates involved in NPQ. On the other hand we performed theoretical and partly experimental studies that give rise to a better general functional description of NPQ effects, thus helping to avoid some pitfalls and erroneous conclusions when employing the existing traditional definitions for NPQ [1]. The ultrafast fluorescence studies on intact leaves of *Arabidopsis* (combined with some antenna mutants), *Monstera deliciosa*, as well as intact cells or photosymbionts of photosynthetic microalgae in lichen, corals and green algae, further strengthened and generalized our mechanistic model (see Fig. 1) [2, 3].

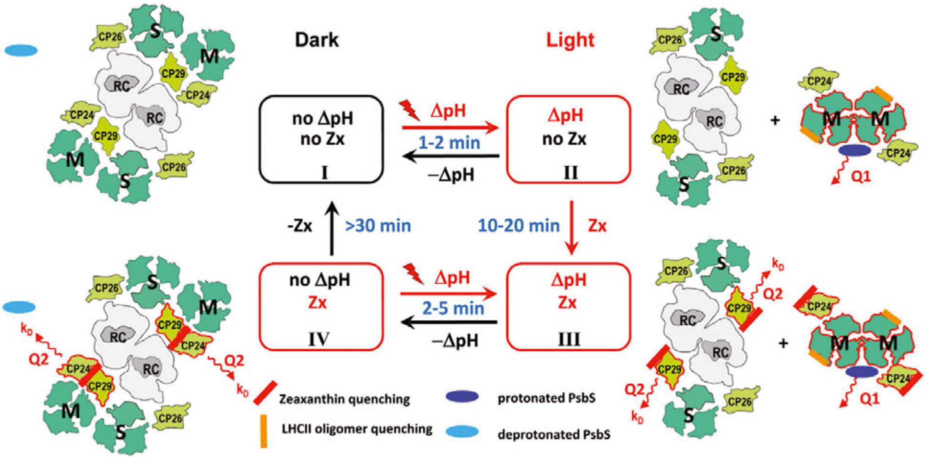

Figure 1. 4-state-2 site quenching model for in vivo-quenching in higher plants. Left part: Dark-adapted state (top) and slowly-relaxing state (bottom) Right part: States appearing upon actinic light adaptation or NPQ induction. Four states are indicated in boxes by roman numbers along with the different quenching conditions. The wavy arrows indicate the quenching processes at sites Q1 and Q2. The red and orange bars indicate the quenching locations in the various antenna parts. Right-hand side: The blue oval represents protonated PsbS. The model shown indicates that protonated PsbS may be associated with the detached and quenched LHCII aggregate. This is actually an unproven hypothesis since no direct association of PsbS with detached LHCII has been demonstrated thus far. The detached LHCII aggregate also is associated with CP24, which may be enhancing (or modulating) quenching in this site if Z is present.

These studies also extended the validity of the model to seemingly unrelated quenching cases like heat-induced quenching (in corals and isolated dinoflagellates) and drying-induced quenching (in lichen). The basic feature of our NPQ model consists of two independently operating quenching sites, one activated by the action of PsbS (or equivalent) which leads to the detachment and strong quenching of the major antenna complex (LHCII) from the PSII supercomplex in high light, as well as a quenching induced in the minor PSII antenna complexes (mainly CP29) by the violaxanthin cycle product Zea. The Zea molecule produced in this cycle indirectly enables quenching within the minor antenna complexes. The common molecular mechanism proposed by us for both quenching sites is the formation of Chl-Chl charge transfer (CT) states, essentially creating a reaction-center like situation in the antenna complexes by inducing fast electron transfer. We thus explicitly rule out the direct involvement of carotenoids in the quenching mechanisms. Structural differences between quenched and unquenched LHCII were revealed by solid-state NMR studies, and a well-defined *in vitro* PsbS-induced quenching system (artificial liposomes) has been developed by us for LHCII which is essentially mimicking exactly the process in the intact thylakoid membrane. In addition in these studies a novel – third – and highly efficient quenching mechanism was discovered, operating in extreme quenching cases, like light-induced quenching in high-light-grown *Monstera* [2], drying-induced quenching in lichen [3], and heat-induced quenching in coral. The common mechanistic denominator in these extreme quenching cases lies in the loss of thylakoid membrane appression followed by complete mixing of PSII and PSI units, which gives rise to a pronounced energy spillover effect from PSII to PSI, thus strongly quenching PSII [2]. A very similar effect was actually found to be responsible for state transitions in higher plants (*Arabidopsis and mutants*), thus contradicting the present canonical model of state transitions according to which LHCII detaches from the PSII supercomplex upon overexcitation of PSII and attaches to PSI. In contrast, our data rule out a pronounced increase in PSI antenna cross-section, but favor a spillover model.

Supramolecular self-assembled chlorophyll (Chl) nano-structures

Green bacteria contain a highly unusual huge photosynthetic antenna complex, the so-called chlorosome, which contains up to 250.000 Chls per chlorosome of self-assembled Chl aggregates, forming a concentric multi-tubular nano-structure, devoid of interaction with proteins. These self-assembled nano-structures of Chls have great potential for applications in self-assembled photonic nano-devices suitable as artificial antennae for solar-to-fuels conversion units. The basic structure, a multi-lamellar concentric tube arrangement, was resolved by us a few years ago (Fig. 2).

We continued to study the details of these self-assembled structures in various chlorosome mutants of *C. tepidum* as well as in *in vitro* assemblies by solid-state NMR [4], by optical spectroscopic methods in *in vitro* nanostructures on chemically modified Chls [5], and in template-strengthened macroscopic structures based on self-assembly of these special Chls in the nano-channels of inorganic membranes. In a further study we demonstrated the exceptionally high charge conduction properties of these Chl nanostructures – higher than of good conducting polymers and the highest detected so far for molecular aggregates - employing both direct conduction measurements by contacting of self-assembled nano-rods in a conducting AFM arrangement, as well as the characterization of bulk charge conduction properties [6]. The low degree of organizational disorder in the intact chlorosomes was characterized by single-chlorosome fluorescence polarization measurements [7].

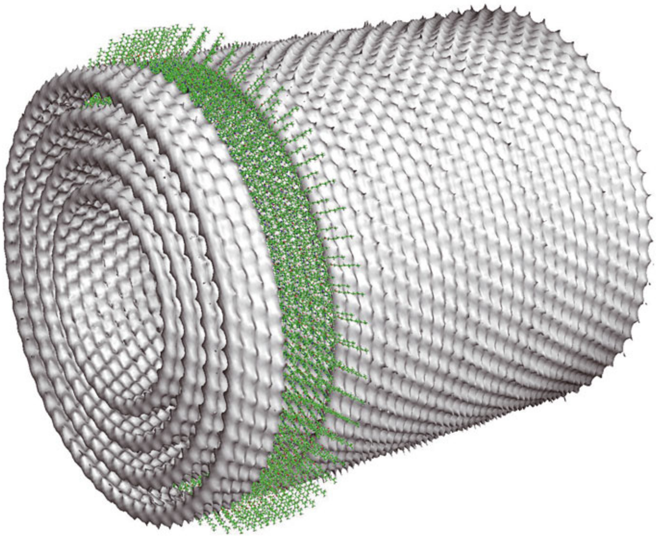

Figure 2. Concentric tube structure of chlorosomes from the green bacterium *C. tepidum* as determined by a combination of solid-state NMR spectroscopy, high-resolution cryo-electron microscopy, and optical spectroscopic data. The structure is formed by supramolecular self-organization of bacteriochlorophylls without the interaction of proteins. The diameter of the outer tubes is up to 50 nm. The whole multi-tube structures combines up to ca. 250.000 BChls and represents the largest and most efficient antenna structure known in nature.

This low disorder forms the basis for the highly exceptional energy transport properties within chlorosomes. We have recently obtained evidence that the chlorosome as a whole acts as a huge light-harvesting unit that operates highly efficiently on the basis of quantum-coherent long range energy transfer.

Dynamics of carotenoid excited states

Carotenoids play a key role in many biological processes, owing to their highly unusual excited state properties which are only poorly understood. Following up on our previous studies we were able to clarify several hitherto unexplained excited state properties, in particular the so-called dark-state S_X, and the S^* state [8]. These studies led to the development of an interaction scheme of three different excited states with crossing potential curves in a narrow energy region (three state conical intersection description) for which a theoretical description within a modified Redfield model was developed. This scheme provides a basic advancement in our insights into the dynamics of excited state relaxation in carotenoids.

References

1. Holzwarth, A. R., Lenk, D., Jahns, P., On the analysis of non-photochemical chlorophyll fluorescence quenching curves. I. Theoretical considerations, *Biochim. Biophys. Acta,Bioenerg.* **2013**, *1827*, 786-792; Schansker, G., Toth, S. Z., Holzwarth, A. R., Garab, G., Chlorophyll *a* fluorescence: beyond the limits of the Q_A-model, *Photosynth. Res.* **2013**, DOI 10.1007/s11120-013-9806-5; Jahns, P. and Holzwarth, A. R., The role of the xanthophyll cycle and of lutein in photoprotection of photosystem II, *Biochim. Biophys. Acta, Bioenerg.* **2012**, *1817*,182-193; Lambrev, P.H., Miloslavina, Y., Jahns, P., Holzwarth, A. R., On the relationship between non-photochemical quenching and photoprotection of photosystem II, *Biochim. Biophys. Acta, Bioenerg.* **2012**, *1817,* 760-769; Schansker, G., Toth, S. Z., Kovacs, L., Holzwarth, A. R., Garab, G., Evidence for a fluorescence yield change driven by a light-induced conformational change within photosystem II during the fast chlorophyll a fluorescence rise, *Biochim. Biophys. Acta, Bioenerget*. **2011**, *1807*, 1032-1043

2. Holzwarth, A. R. and Jahns, P., NPQ mechanisms in intact organisms as derived from ultrafast fluorescence kinetics studies **2014**, In: *Non-Photochemical Quenching and Thermal Energy Dissipation In Plants, Algae and Cyanobacteria*, Editors: B. Demmig-Adams, W. W. Adams III, G. Garab, Govindjee, Springer Science, Dordrecht, in print.

3. Slavov, C., Reus, M., Holzwarth, A. R., Two different mechanisms cooperate in the desiccation-induced excited state quenching in *Parmelia* lichen, *J. Phys. Chem. B* **2013**, 117, (38), 11326-11336; Miloslavina, Y., DeBianchi, S., Dall'Osto, L., Bassi, R., Holzwarth, A. R., Quenching in *Arabidopsis thaliana* mutants lacking monomeric antenna proteins of photosystem II, *J. Biol. Chem.* **2011**, *286,* 36830-36840

4. Pandit, A., Ocakoglu, K., Buda, F., van Marle, T., Holzwarth, A. R., de Groot, H. J. M., Structure determination of a bio-inspired self-assembled light-harvesting antenna by solid-state NMR and molecular modeling, *J. Phys. Chem. B* **2013**, 117 (38), 11292-11298; Ganapathy, S., Oostergetel, G., Reus, M., Tsukatani, Y., Gomez Maqueo Chew, A., Buda, F., Bryant, D. A., Holzwarth, A. R., de Groot, H. J. M., Structural variability in wild-type and *bchQ bchR* mutant chlorosomes of the green sulfur bacterium *Chlorobaculum tepidum* , *Biochemistry* **2012**, *51*, 4488-4498

5. Jesorka, A., Holzwarth, A. R., Eichhöfer, A., Reddy, C.M. , Kinoshita, D., Tamiaki, H., Katterle, M., Naubron, J. V., Balaban, T. S., Water coordinated zinc dioxo-chlorin and porphyrin self-assemblies as chlorosomal mimics: Variability of supramolecular interactions, *Photochem. Photobiol. Sci.* **2012**, *11*,1069-1080

6. Sengupta, S., Ebeling, D., Patwardhan, S., Zhang, X., von Berlepsch, H., Böttcher, C., Stepanenko, V., Uemura, S., Hentschel, C., Fuchs, H., Grozema, F.C., Siebbeles, L.D.A., Holzwarth, A.R., Chi, L., Würthner, F., Biosupramolecular nanowires from chlorophyll dyes with exceptional charge-transport properties, *Angew. Chem. Int. Ed.* **2012**, *51,* 6378-6382

7. Tian, Y., Camacho, R., Thomsson, D., Reus, M., Holzwarth, A.R., Scheblykin, I.G., Organization of bacteriochlorophylls in individual chlorosomes from *Chlorobaculum tepidum* studied by 2-dimensional polarization fluorescence microscopy, *J. Am. Chem. Soc.* **2011**, *133*,17192-17199

8. Ostroumov, E.E., Müller, M., Reus, M., Holzwarth, A.R., On the nature of the „dark S*" excited state of b-carotene, *J. Phys. Chem. A* **2011**, *115,* 3698-3712

9. Pandit, A., Reus, M., Morosinotto, T., Bassi, R., Holzwarth, A. R., deGroot, H.J.M., An NMR comparison of the light-harvesting complex (LHCII) in active and photoprotective states reveals subtle changes in the chlorophyll *a* ground-state electronic structures, *Biochim. Biophys. Acta, Bioenerg.* **2013**, *1827*, 738-744; Müller, M.G., Jahns, P., Holzwarth, A.R., Femtosecond transient absorption spectroscopy on the light-adaptation of living plants, *EPJ Web Conf.* **2013**, *41*, 8006; Thapper, A., Styring, S., Saracco, G., Rutherford, A.W., Robert, B., Magnuson, A., Lubitz, W., Llobet, A., Kurz, P., Holzwarth, A.R., Fiechter, S., de Groot, H., Campagna, S., Braun, A., Bercegol, H., Artero, V., Artificial photosynthesis for Solar Fuels-an Evolving Research Field within AMPEA, a Joint Programme of the European Energy Research Alliance, *Green* **2013**, *3*, 43-57; Pandit, A., Morosinotto, T., Reus, M., Holzwarth, A.R., Bassi, R., deGroot, H.J.M., First solid-state NMR analysis of uniformly ^{13}C-enriched major light-harvesting complexes from *Chlamydomonas reinhardtii* and identification of protein and cofactor spin clusters, *Biochim. Biophys. Acta Bioenergetics* **2011**, *1807*, 437-443

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Electrochemical Reactions

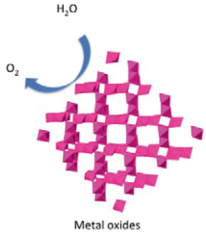
The electrode reactions group was started in August 2012, with the founding of the new institute. The group focuses on electrochemical reactions of fundamental importance towards energy storage and usage. Water electrolysis is a central technology for achieving the goal of sustainable energy economy [1]. Slow kinetics and corrosion of the oxygen electrode form the biggest hurdles in large scale implementation of this technology. Our group works towards understanding the boundary conditions of the oxygen electrode reaction. Besides this we explore the possibility of Liquid Organic Hydrogen Carriers as fuels for applications in fuel cells instead of pure hydrogen.

We collaborate extensively with groups of Dr. Malte Behrens (FHI Berlin), Dr. Axel-Knop Gericke (FHI Berlin), Dr. Marc Willinger (FHI Berlin), Dr. Sylvia Reiche, Dr. Saskia Buller, Dr. Maurice van Gastel towards developing a better understanding of the materials we investigate. We work with institutions such as *Jülich Research Center* and industrial partners such as *Solvicore*, *FUMA-Tech* and *Gräbener Maschinentechnik* to translate the fundamental research done in the group towards applications in the German industry as a part of the EKOLYSER project (funded by BMWi).

We primarily use electrochemical methods such as voltammetry, chronoamperometry, impedance spectroscopy combined with *in situ* Surface Enhanced Raman Spectroscopy (SERS) and electrochemical product detection to study various noble and non-noble metal catalysts for water splitting reaction.

Bridging the gap between nominal and real catalysts: study of noble metal benchmarks

We studied Pt as a model electrocatalyst for water oxidation reaction. Pt was studied as single crystals, foils and *in situ* as sputtered films. Single crystals showed a strong tendency to degrade after a certain critical potential was reached.



The resulting surface showed electrochemical activity that was remnant of their initial surface structure [2]. Under high applied potentials (> 2.5V) in acidic conditions the Pt surface was found to develop metastable highvalent Pt oxo-hydroxo species that impeded the charge transfer [3]. Electronic structure and stability of this material was studied using XPS.

IrO_2 is well known for oxygen evolution under acidic conditions. Literature is replete with catalysts based on IrO_2 with a large degree of variation based on synthesis and pretreatment history. Improving this catalyst needs systematic understanding of catalyst behavior under operational conditions. It is not unusual for catalysts to undergo physiochemical modifications during the actual catalytic event. Understanding the active form of catalyst is critical to understanding its real nature and limitations. In literature [4] it is believed that the active form of iridium/iridium oxide anode catalyst is a form of hydrous iridium oxide. Hydrous oxides are common occurrence but are a less studied part of electrochemical literature. The exact structure of hydrous oxide, its catalytic properties and its stability are very critical to understanding the nature of the real catalyst. This knowledge will allow us to develop better catalysts based on iridium.

We have studied electrodeposited iridium oxide as model catalyst for electrochemical oxygen evolution using SERS. SERS allows us to study M-O interactions using vibrational spectroscopy *in situ*. M-OH peaks can be easily seen (450 - 650cm^{-1}). If we follow the peak (520 cm^{-1}) over potentials ranging from 0.4 to 1.8 V the peak shows expected tuning in response to applied electric field. The shifting of this peak to higher values (stronger bonds) can be linked to higher charge on the Iridium center. The peak at 780 cm^{-1} appears at 1.4V and grows in intensity till 1.8V (beyond which the potential was turned off). This peak exists only under applied potential regime of oxygen evolution and goes away as soon as the applied potential is removed and open circuit (OCP) is established. This experiment reiterates the importance of *in situ* studies in the context of electrocatalysis.

Non noble metal catalysts for oxygen evolution reaction

Non noble metal „*earth abundant*" electrocatalysts will significantly reduce the costs and make it possible to use electrochemical water splitting on a very large scale. Non noble metal catalysts can be an effective replacement even if their electrochemical activities are a fraction of their noble metal counterparts. If these catalysts can be developed to an extent where their operational lifetime would become comparable to their noble metal counterparts, a large part of the problem would be solved.

Whether in acidic, alkaline or neutral media, catalyst corrosion remains a significant challenge to oxygen evolution. MnO_2 is earth abundant and well known for catalyzing oxygen evolution. A form of MnO_x cluster is known to catalyze water oxidation in photosynthesis. The problem is that the catalyst comes with a significant corrosion problem.

$$MnO_2 + 2H_2O \rightarrow MnO_4^- + 4H^+ + 3e^- \; E_0 = 1.69V \text{ vs. NHE}$$

Besides that MnO_{2-x} naturally exists in various polymorphs, with various amounts of defects each of which is known to have a different electrocatalytic performance. Poor ballistic electronic conduction (important for good electrode materials) is also a prevalent issue with these oxides. These catalysts although with immense potential remain a long way from successful implementation within electrolysers. We study MnO_x-MO_x, MnO_x/CNT (M is another component such as Sn) class of catalysts synthesized using "*electrodeposition*" and "*solvothermal*" methods. Besides studying electrochemical activity and stability, the *in situ* SERS allows us to study the M-O environment directly. The effect of applied potential on corrosion can be directly observed. These studies will be combined with evolved gas analysis and direct corrosion measurements to establish the fundamental limiting conditions of electrocatalysis with MnO_x based materials.

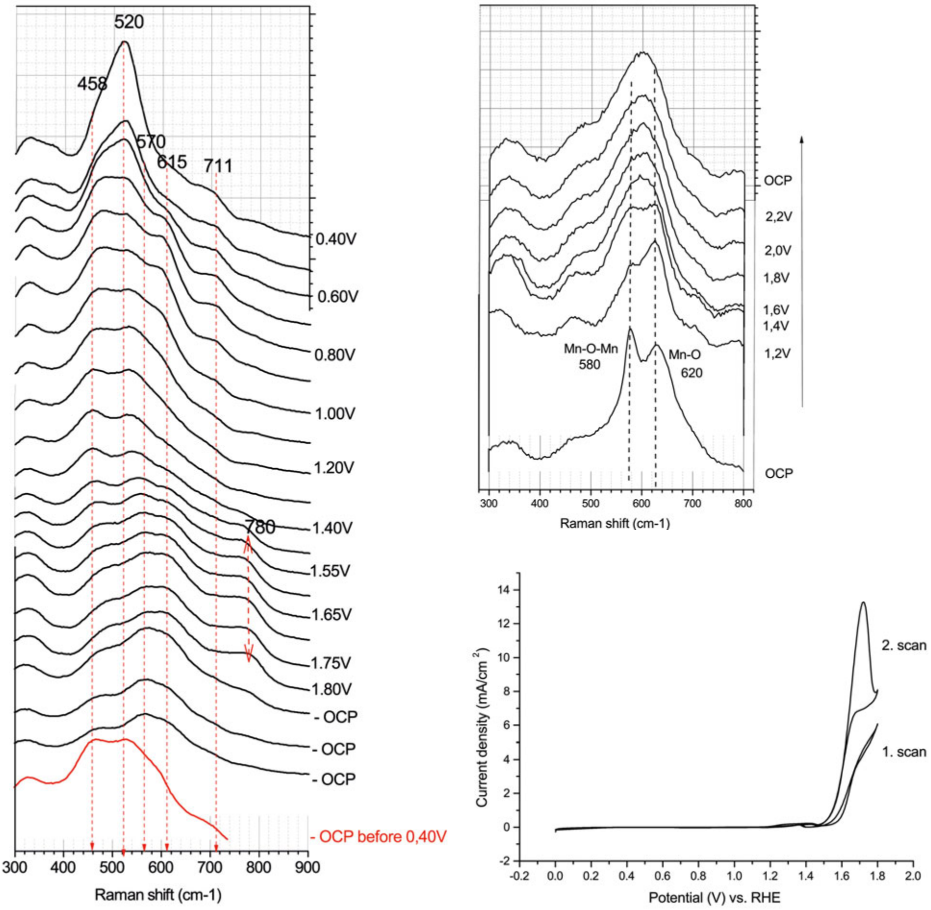


Figure 1. (Left) SERS study of electrodeposited $IrO_x(OH)_y(H_2O)_z$ thin film on Au conducted in alkaline medium. (Top Right) Electrodeposited MnO_x/Au studied was studied using in situ SERS in acidic media (0.1 M $HClO_4$). (Bottom right) Oxygen evolution using a sol of IrOx nanoparticles.

Solution based evaluation of electrocatalytic activity of nanoparticular catalysts
IrOx nanoparticles were synthesized and a sol of these nanoparticles was tested using external electrodes such as glassy carbon and Au. The nanoparticles were found to be highly active for water oxidation. The oxygen evolving properties of these materials are significantly dependent on pH and window of potential scanning. These electrocatalytic materials show high promise and are being explored systematically.

References

1. Schlögl, R., The Role of Chemistry in the Energy Challenge. *ChemSusChem* **2010,** *3*, 209-222
2. Ranjan, C., Arrigo, R., Schuster, M. E., Schlögl, R., Eiswirth, M., Johnson, B., Girgsdies, F., Weinberg, G., Knop-Gericke, A., Electrochemical oxidation of Pt: From single crystal degradation to anodically grown oxides, *submitted* **2013**
3. Arrigo, R., Hävecker, M., Schuster, M. E., Ranjan, C., Stotz, E., Knop-Gericke, A., Schlögl, R., In-situ study of gas phase water electrolysis on Pt by NAP-XPS. *Angew. Chem. Int. Edit.* **2013**
4. Kotz, R., Neff, H., Stucki, S., Anodic Iridium Oxide-Films - Xps-Studies of Oxidation-State Changes and O_2-Evolution. *J. Electrochem. Soc.* **1984,** *131* (1), 72-77

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Bottom-up Synthesis of Nitrogen-functionalized Carbon Electrodes on a Sustainable Basis

The central challenge on our way towards sustainable energy supply lies in overcoming the daily fluctuations of the energy feed from renewable sources. In order to buffer the oscillations in energy supply, the development of suitable storage solutions is essential [1]. Chemical energy storage by hydrogen production in the water splitting process offers one possibility of efficient storage potential. For efficient water splitting on a global scale, the development of innovative and sustainable electrode materials is required. Functional carbon materials, synthesized by hydro-thermal carbonization (HTC), offer a sustainable material basis from biomass feedstocks [2]. Another major advantage of such bottom up synthesis approach is specific introduction of nitrogen-functional groups, even in large quantities. N-functionalized carbon materials have been shown to provide higher conductivity, higher stability towards oxidative degradation, as well as positive effects on the anchoring ability of catalyst nanoparticles [3].

As basis of controlled functionalization strategies of the hydrothermal carbon, structural dependences on synthesis procedures and important synthesis parameters have been investigated. The structural variation depending on the initial synthesis pH has been found to be the major influencing factor. In varying the initial synthesis pH systematically from pH 0 to pH 6 by HNO_3, first differences between the samples can be observed macroscopically. The materials synthesized at lower pH showed a linear decrease of powder density till pH 3 (Figure 1 a). For samples synthesized at pH>3 similar powder densities of 0.6-0.7 g/ml were determined. Together with the decrease in powder density, the color of the solid material changes from black to brown. Also here, the major transition can be observed at pH 3 (Figure 1 b).

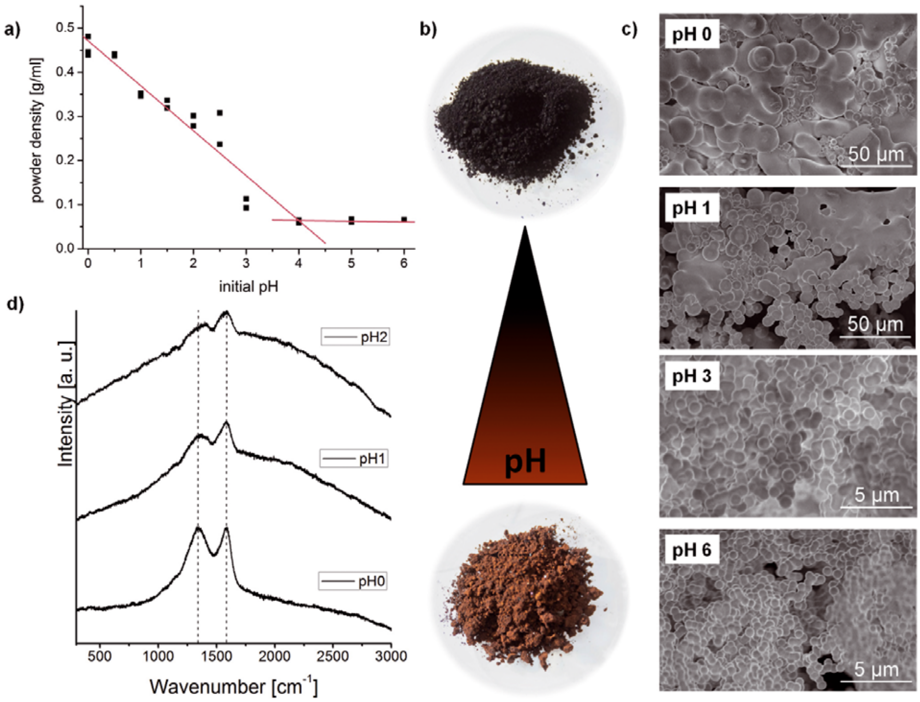


Figure 1. a) Powder density of hydrothermal carbon of initial synthesis pH, b) color variation with synthesis pH, c) SEM of hydrothermal carbons, d) comparison in Raman spectroscopy

The reasons for the macroscopic differences mentioned, were found in the microscopic structure of the materials as analyzed by SEM (Figure 1 c). The particle size of the carbon shrinks gradually with increasing synthesis pH. Furthermore, regions of "sintered" particles were found for materials synthesized at pH 0 and pH 1, whereas the homogeneity in morphology of the samples improves with synthesis pH. Typical particle sizes for the samples synthesized at pH 6 and pH 3 are 500 nm and 1 µm, respectively. In both cases the spherical particles form loosely packed agglomerates which correspond to the fluffy macroscopic appearance of the low density materials. The particles synthesized at pH 1 are of broader size distribution of 4-15 µm. Regions of particle aggregates can be found as well as films without defined structural features. The latter determine the majority of structural morphology of the sample synthesized at pH 0.

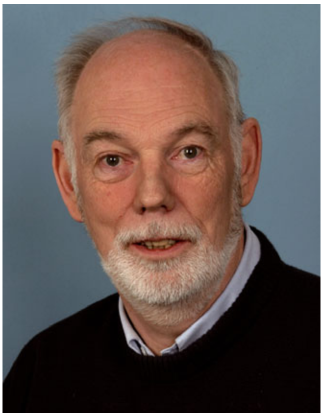
The observations clearly show differences in the kinetics of nucleation and growth in the particle formation process for different initial synthesis pH. The particle formation occurs due to a phase segregation of water insoluble polymeric phase from the aqueous solvent, in the early stages of the reaction. The hydrophobic polymeric phase forms spherical particles in order to thermodynamically minimize the surface tensions. Such emulsion formation has been discussed before by Baccile et al. [4] as possible explanation of the spherical character of the final particles. The pH dependence, however, has not been discussed in this regard before. Since the reaction is proton catalyzed, generally a faster formation of the spherical polymeric phase is expected. In the formation of metallic nanoparticles the faster particle formation would lead to smaller particle. In the case of HTC the opposite behavior was observed. The results points to a formation process that also involves aggregation of polymer fragments in the particle formation process. By MALDI analysis of the reaction mixture we could observe the majority of polymeric fragments between 600-800 m/z, and none over 1150 m/z. This result supports the idea of an aggregation mechanism.

Furthermore, we have evidence of different chemical structures of the hydrothermal carbon synthesized at different initial synthesis pH. The TG-MS analysis showed a higher fraction of oxygen functional groups of lower thermal stability for the materials synthesized at lower pH. The IR data point to higher content of carbonyl functional groups. And Raman measurements showed the intensity decrease of the characteristic D- and G-bands at around 1360 and 1580 cm-1, respectively, with increasing synthesis pH (Figure 1 d). For materials synthesized at pH 0 and 1 the existence of a carbonaceous structure could be confirmed. Due to the broad signals it can be concluded that rather amorphous structures have been formed during the hydrothermal synthesis. Furthermore, significant beam damage and fluorescence was observed for the materials synthesized above pH 2. For this reason we concluded rather polymeric, not carbonaceous structures are abundant in hydrothermal carbon synthesized at higher initial pH.

As conclusion of our studies on structural dependencies of hydrothermal carbon on synthesis parameters, we decided to use the more homogeneous, rather polymeric hydrothermal product from higher pH synthesis for N-functionalization post treatment. The post treatment in 1 mol/l nitric acid resulted in 5 wt% N-containing carbon material. The spherical basis shape was maintained while significant surface roughness could be introduced by the treatment. Another class of N-functionalized carbon materials was synthesized by addition of N-containing precursors. Here, imidazol and urea could successful introduce N-functional groups into the hydrothermal carbon structure, with 5 wt% and 15 wt% N-content respectively. First electrochemical tests successfully qualified the N-containing carbon materials as conductive electrode basis. The TG-MS analysis of the different N-functionalized carbon materials showed characteristic abundance of different types of N-functional groups for the different functionalization techniques. The observed characteristics can now be used for specific binding of the different metal or metal oxide nanoparticles during the synthesis of (electro)catalysts. The nature of the metal support interaction and its influence on the performance and the stability of the final catalyst will be the future focus of our studies.

References

1. Schlögl, R., The Role of Chemistry in the Energy Challenge, *ChemSusChem.* **2010**, *3,* 209 – 222
2. Titirici, M.-M., Antonietti, M., Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, *Chemical Society Reviews* **2010**, *39* (1), 103-116
3. Zhao, L., Fan, L.-Z., Zhou, M.-Q., Guan, H., Qiao, S., Antonietti, M., Titirici, M.-M., Nitrogen-Containing Hydrothermal Carbons with Superior Performance in Supercapacitors, *Adv. Mater.* **2010**, *22*, 5202-5206; Koós, A. A., Dillon, F., Obraztsova, E. A., Crossley, A., Grobert, N., Comparison of structural changes in nitrogen and boron-doped multi-walled carbon nanotubes, *Carbon* **2010**, *48*, 3033 – 3041; Arrigo, R., Schlögl, R., Su, D. S., Tailoring the morphology of Pd nanoparticles on CNTs by nitrogen and oxygen functionalization, *Phys. Chem. Chem. Phys*. **2012**, *14*, 10523 – 10532
4. Titirici, M.-M., Antonietti, M., Baccile, N., Hydrothermal carbon from biomass: a comparison of the local structure from poly- to monosaccharides and pentose/hexoses, *Green Chemistry* **2008**, *10*, 1204-1212



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We have in the past four years continued to study in depth the molecular and electronic structures of transition metal ions with redox-active 2,2'-bipyridine (bpy) and 2,2':6,'2''-terpyridine (tpy) ligands.

In particular, the electron transfer series $[M(bpy)_3]^n$ (n = 3+, 2+, 1+,0, 1-, 2-, 3-) and $[M(tpy)_2]^m$ (m = 2+, 1+, 0, 1-) have been investigated by spectroscopy(UV-vis, EPR, XAS, magnetochemistry) and computationally by density functional theory. We have discovered methodology to determine independently the oxidation level of the ligands by using cryogenic X-ray crystallography and the oxidation state of the central metal ion by X-ray absorption spectroscopy in collaboration with Professor Serena DeBeer's group.

We have shown that all so called "low valent", neutral, and mononanionic complexes $[M(bpy)_3]^0$, $[M(bpy)_3]^{1-}$ and their (tpy) analogs contain in fact transition metal ions with oxidation states >2. They are not "low valent" species but contain highly reduced ligands as for example in $[Ta(bpy)_3]^{1-}$ which possesses a high valent central Ta(V) ion and three dianionic $(bpy^{2-})^{2-}$ ligands. These compounds turn out to be classic Werner-type species.

MPI CEC in Scientific Dialogue

ORCA – a Powerful Tool for Quantum Chemistry

A major activity in the department is the development of the ORCA quantum chemistry project [1]. Following the move from the university of Bonn to the MPI CEC, it was possible to found an ORCA development team (led by Dr. Wennmohs). Excellent progress has been made and due to the efforts of the team, ORCA has been continuing to gain popularity in the computational chemistry community with an estimated 10,000-15,000 users worldwide. In September 2013 the long awaited ORCA version 3.0 was released and almost 2000 downloads have been witnessed within the first two days after the release. In Version 3.0 significant overall performance and parallelization efficiency gains have been realized in addition to major new functionalities such as analytic second derivatives for Hartree-Fock, DFT and MP2 energies, explicitly correlated wavefunction methods, density matrix renormalization group approaches among many others.

In terms of theoretical method development substantial progress has been made during the evaluation period. These developments, lead and supervised by Prof. Neese, have been made available to the ORCA user community free of charge and have significantly contributed to the visibility of the MPI CEC.

Perhaps the most spectacular development was the so called ‘domain-based pair natural orbital coupled cluster’ (DLPNO-CCSD(T)) method (Figure 1) [2]. This method scales nearly linear with system size and allows, for the first time, to treat truly large molecules on the basis of an accurate, wave-function based *ab initio* method. As a result we have been able to report the first CCSD(T) level calculation on an entire protein (Crambin). Our results have been widely recognized at international conferences and have been prominently featured in a Physics Today article [3].

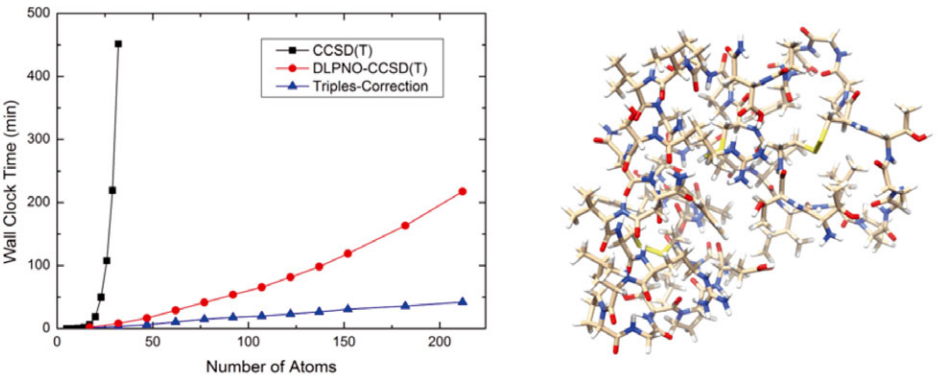

Figure 1. The domain based local pair natural orbital coupled cluster method (DLPNO-CCSD(T) allows for giant wavefunction based ab initio calculation with near linear scaling computational effort (left). The largest system treated was the entire Crambin protein (right).

We believe that this method has the potential to have a significant impact on the way quantum chemical calculations will be pursued in the future and will put major efforts towards its further development. Dr. Riplinger was awarded the Otto-Hahn medal of the Max-Planck Society in recognition of his outstanding contributions to this project.

A very significant development has been the Restricted Open-Shell Configuration Interaction with Single Excitations/DFT (ROCIS/DFT) method. This method has been formulated for general ground state spin S and exactly preserves spin-symmetry even in complicated spin-coupled states. The purpose of the development was to be able to treat high-resolution soft X-ray absorption (XAS) and double-resonance (RIXS) spectra at the transition metal L-edge [4]. The method indeed allow, for the first time, a realistic modeling of these very complicated spectra and is applicable to molecules and cluster models with more than 100 atoms [5].

A second major activity in the method development realm is the treatment of difficult electronic structures in combination with spin-dependent relativistic effects. The group is well known for its contribution to magnetic spectroscopy. In the evaluation period, we have applied a method that we have made applicable to large molecules (the CASSCF/NEVPT2) to a number of problems in molecular magnetic material, which has led to a number of high-profile publications (these studies have been driven by Prof. Atanasov) [6]. Much progress towards more accurate multireference methods has been made during the very enjoyable sabbatical visit of Prof. Marcel Nooijen at the department (2012-2013).

In collaboration with the group of Prof. Chan at Princeton, we were able to obtain the first near-full-CI quality results on oligonuclear iron-sulfur transition metal clusters on the basis of the density matrix renormalization group (DMRG) formalism. The results have led to the revision of the approaches that have been used for decades in the description of such systems. In a similar realm and mindset are the efforts of Prof. Auers group who has pursued advanced tensor decomposition method [7]. In the evaluation period Prof. Auer's group has shown that the full CI problem can be approached in this way with much reduced scaling. Thus, we expect tensor decomposition techniques will be highly promising as alternatives for DMRG in the future.

References

1. Neese, F. *Wiley Interdisciplinary Reviews-Computational Molecular Science* **2012**, *2*, 73-78
2. a) Riplinger, C., Neese, F. *Journal of Chemical Physics* **2013**, *138*; b) Riplinger, C., Sandhöfer, B., Hansen, A., Neese, F. *J. Chem. Phys.* **2013**, *139*
3. J. Miller, **2013**. *http://www.physicstoday.org/daily_edition/physics_update/coupled_cluster_theory_tackles_a_protein*
4. a) Roemelt, M., Neese, F. *Journal of Physical Chemistry A* **2013**, *117*, 3069-3083; b) Roemelt, M., Maganas, D., DeBeer, S., Neese, F. *Journal of Chemical Physics* **2013**, *138*
5. Maganas, D., Roemelt, M., Havecker, M., Trunschke, A., Knop-Gericke, A., Schlogl, R., Neese, F. *Physical Chemistry Chemical Physics* **2013**, *15*, 7260-7276
6. a) Zadrozny, J. M., Xiao, D. J., Atanasov, M., Long, G. J., Grandjean, F., Neese, F., Long, J. R., *Nature Chemistry* **2013**, *5*, 577-581; b) Zadrozny, J. M., Atanasov, M., Bryan, A. M., Lin, C. Y., Rekken, B. D., Power, P. P., Neese, F., Long, J. R. *Chemical Science* **2013**, *4*, 125-138; c) Atanasov, M., Zadrozny, J. M., Long, J. R., Neese, F. *Chemical Science* **2013**, *4*, 139-156; d) Atanasov, M., Ganyushin, D., Sivalingam, K., Neese, F. in *Molecular Electronic Structures of Transition Metal Complexes Ii, Vol. 143* (Eds.: Mingos, D. M. P., Day, P., Dahl, J. P.), Springer, New York, **2012**, pp. 149-220
7. Benedikt, U., Auer, A. A., Espig, M., Hackbusch, W. *Journal of Chemical Physics* **2011**, *134*

The Institute in Public

The Team Research Communication publish the activities of the MPI CEC to the international community of scientists, to national and international journals, magazines and newspapers, and to the general public. The department also tries to create awareness for the important role of basic research in the filed of chemical energy conversion. To realize this, the department initiates several internal and external communication measures. The aim is to provide an independent and positive image and confidence and to build a bridge from the research facility to the public. We promote the perception of our research among the community, the press, government, corporate partners, prospective students, alumni and our own internal public. Therefore we inform journalists with press releases and background knowledge, and we also invite them to visit the institute.

Figure 1. The CEC series in the local newspaper NRZ: Behind the scene.

With the foundation of the MPI CEC a new website with a clear structure was launched. Visitors can navigate through the research groups on the one hand, and on the other hand they receive general information about energy topics. Additionally a media area was installed.

The Public Relations Team published more than 30 press releases since its inception. In addition to current press releases a PR highlight in 2013 was an exclusive co-operation with Neue Ruhr Zeitung (NRZ). The MPI CEC opened the doors and the readers got the opportunity to look behind the scenes of the institute. A fourteen-part series was published in the local press (see Figure 1).

Another task of the department is the organization of conferences, seminars and other big events. In addition to numerous workshops and in-house events the Team organized a one-week Summer School in collaboration with the Department Molecular Theory and Spectroscopy (see teaching activities).

This event was followed by a one-week conference. The "International Conference on Carbon for energy Storage/Conversion and Environment Protection" (CESEP) was organized in collaboration with the Department Heterogeneous Reactions in the city hall – Mülheim.

Welcome

5th International Conference on
Carbon for Energy Storage/Conversion
and Environment Protection

September 23th to 26th 2013
Mülheim a.d. Ruhr - Germany

We are inviting to the 5th International Conference on Carbon for Energy Storage/Conversion and Environment Protection (CESEP´13).

In September 2013 the first "Klimawoche" took place in NRW. In collaboration with the city of Mülheim the MPI CEC invited interested pupils to the institute.

In October 2013 a delegation of scientific journalists visited the MPI CEC. They were informed in detail about the research in the field of chemical energy conversion.

As in previous years, the institute organized a Girls' Day in collaboration with the MPI KOFO. The aim of this event is to interest girls in scientific and technical professions. Furthermore tours through the institutes for School and Organizations are organized throughout the whole year.

To form its own identity, the MPI CEC implemented its own logo and corporate design in addition to the Minerva Logo of the Max-Planck-Society in 2012. The shape of the leaf or the flame is representative for energy. The different colours represent the topic of energy conversion and storage. Green represents sustainability, blue stands for water and water splitting, grey represents the connection to carbon materials.

The aim for upcoming years is to expand the communication efforts in terms of scientific community, press and the general public.

Teaching Activities

Several members of the department "Molecular Theory & Spectroscopy" are affiliated with German universities (Prof. Neese – Bonn, Prof. Auer – Chemnitz, Prof. DeBeer – Bochum, PD Dr. van Gastel – Bonn) and have taught courses there to various degrees.

In addition to their regular university teaching, members of the department have been active in teaching activities beyond their university appointments. Specifically members of the department have taught in various summer and winter schools (Stockholm – 'Theoretical Chemistry', Prof. Neese, 2012, Sicily – 'European Summer School in Quantum Chemistry', Prof. Neese 2011, 2013, Trieste – 'Hands on DFT Workshop', Prof. Neese, 2013, Louvain la Neuve – 'Chemistry of transition metal ions in biological system'. Dr. Bill, Prof. Neese, 2011, 2013, Penn State University, USA 'Transition Metals in Biological Systems', Prof. DeBeer, Prof. Neese, 2011).

The department has organized a summer school on 'Physical and theoretical methods in molecular energy research' in September 2013 (Essen, Germany) that was attended by more than 100 students from all over the world. The school received excellent feedback and is envisioned to become a regular event in the future.

Participants of the Summer School on Physical and Theoretical Methods in Molecular Energy Research 2013

Teaching Activities at the University of Düsseldorf

The institute is involved in the teaching of biochemistry students at the master level (1st semester) as part of the compulsory module "Biophysical Chemistry" during winter semesters. The module consists of four main parts covering X-ray crystallography, NMR spectroscopy, fluorescence spectroscopy, and EPR spectroscopy, the latter is performed by the institute. Each of the four parts is taught for two weeks full day and includes lectures, exercises, and laboratory training. Dr. Bill, Dr. Cox, PD Dr. Knipp, Dr. Reijerse, and Dr. Savitsky participate in the EPR part. In addition to the four main parts of the module, PD Dr. Knipp provides the lecture "Additional Methods in Structural Biology" which gives an overview about spectroscopic methods used in biochemistry. The students have to pass a written exam that covers all aspects of the module.

Another teaching activity, carried out by Prof. Gärtner during winter semesters, is provided for "Advanced Protein Biochemistry", a combined experimental and teaching module within the Master Studies in Biochemistry (1st semester). Attendance is compulsory for the students. Contribution to this module is two weeks-full day. Further educational activities were given by Prof. Gärtner during the collaborative research initiative "Biostruct" of the University of Düsseldorf and during experimental modules on "photobiology" that are selected by the students (duration four to six weeks). These modules combine teaching and experimental work.

During summer semesters, PD Dr. Knipp is also involved in the teaching of Chemistry and Biochemistry students in the compulsory bachelor module "Basics in Physical Chemistry II", which includes lectures and exercises. The content of the module involves thermodynamics, which is lectured by Prof. Peter Gilch (University of Düsseldorf), and reaction kinetics, which is held by PD Dr. Knipp.

List of Teaching activities

2010

Bill, E.: In-house training course for Ph.D. students and post-docs on 'Molecular Magnetism and Magnetochemistry', 2h per week. 2010-01 to 2010-02.

Braslavsky, S. E.: Biological Photoreceptors, Univ. Nacional of Rio Cuarto, 2010.

Knipp, M.: EPR-Spektroskopie, Universität Düsseldorf, WS 2010/2011.

Knipp, M.: Spektroskopische Methoden der Strukturbiologie, Universität Düsseldorf, WS 2010/2011.

Lubitz / Savitsky / Knipp / Reijerse / Möbius: “Biophysical Chemistry and BioStruct Course“ (lectures, excersise and practical training) together with Heinrich-Heine-Universität, Düsseldorf, 2010.

Neese, F.: Electronic Structure Methods and Spin Hamiltonian Parameters and hands-on course on using ORCA. Summer school on ‘EPR Spectroscopy’. Konstanz, Germany, 2010.

Neese, F.: Ligand Field Theory. FEBS Advanced Course ‘Metals in Biology’. 2010.

Van Gastel, M.: Ruhr-Universität Bochum: Magnetic Properties of Matter, WS 2010.

2011

Braslavsky, S.E.: Biological Photoreceptors, Univ. Nacional of Santiago del Estero, 2011.

Knipp, M.: EPR-Spektroskopie, Universität Düsseldorf, WS 2011/2012.

Knipp, M.: Spektroskopische Methoden der Strukturbiologie, Universität Düsseldorf, WS 2011/2012.
Lubitz / Savitsky / Knipp / Reijerse / Möbius: “Biophysical Chemistry and BioStruct Course“ (lectures, excersise and practical training) together with Heinrich-Heine-Universität, Düsseldorf, 2011.

Neese, F.: European Summer school in Quantum Chemistry, University of Palermo, Italy, 2011.

Van Gastel, M.: Ruhr-Universität Bochum: Magnetic Properties of Matter, WS 2011.

2012

Bill, E.: In-house training course for Ph.D. students and post-docs on ‘Electron Paramagnetic Resonance for Chemists’, 2h per week. 2012-07 to 2012-09.

Braslavsky, S. E.: Biological Photoreceptors, INTECH, Chascomús, 2012.

Cox, N.: EPR – theoretical background, Heinrich-Heine-Universität Düsseldorf, Germany, 2012-10 to 2012-11.

DeBeer, S.: Master’s Level Bioinorganic Chemistry, Ruhr University Bochum, WS 2012/2013.

Lubitz / Savitsky / Knipp / Reijerse / Möbius : "Biophysical Chemistry and BioStruct Course" (lectures, excersise and practical training) together with Heinrich-Heine-Universität, Düsseldorf, 2012.

Neese, F.: 2nd Penn State Bioinorganic Workshop, Penn State University, USA, 2012-05-31 to 2012-06-09.

Neese, F.: Energy Seminar, Essen, Germany, 2012.

Neese, F.: KCSE Winter School in Multiscale Modelling, Stockholm, Sweden, 2012.

2013

Auer, A.: TU Chemnitz: Quantenchemie in der Katalyse, SS 2013.

Braslavsky, S.E.: Biological Photoreceptors, Univ. Nacional of Córdoba, 2013.

Braslavsky, S.E.: Biological Photoreceptors, Univ. Santiago de Chile, 2013.

Cox, N.: EPR – theoretical background, Heinrich-Heine-Universität Düsseldorf, Germany, 2013-10 to 2013-11.

DeBeer, S.: Master's Level Bioinorganic Chemistry, Ruhr University Bochum, SS 2013.

DeBeer, S X-ray Spectroscopy Lecture Series, Holland Research School of Molecular Chemistry, Physical Methods in Inorganic Chemistry, University of Amsterdam, Science Park 2013-02.

DeBeer, S.: X-ray Spectroscopy Training Module, Cornell University, Ithaca, NY, USA, 2013-09.

Knipp, M.: Grundlagen der Physikalischen Chemie II, Universität Düsseldorf, SS 2013.

Knipp, M.: EPR-Spektroskopie, Universität Düsseldorf, WS 2013/2014.

Knipp, M.: Spektroskopische Methoden der Strukturbiologie, Universität Düsseldorf, WS 2013/2014.

Lubitz / Savitsky / Knipp / Reijerse / Möbius: "Biophysical Chemistry and BioStruct Course" (lectures, excersise and practical training) together with Heinrich-Heine-Universität, Düsseldorf, 2013.

Neese, F.: Ligand Field Theory. FEBS Advanced Course ‘Metals in Biology’. 2013.

Neese, F.: Advanced EPR school of EFEPR, Weizmann Institute of Science, Rehovot, Israel, 2013.

Neese, F.: Density functional theory and beyond: Computational materials science for real materials, Trieste, Italy, 2013.

Neese, F.: European Summer School in Quantum Chemistry, University of Palermo, Italy, 2013.

Neese, F.: Theory and Spectroscopy of Transition Metal Complexes, Summer School: Methods in Molecular Energy Research, Essen, Germany, 2013.

Schlögl, R.: Katalyse für die Energieumwandlung, MPI Lecture, Universität Duisburg-Essen, Germany, 2013-01 to 2013-02.

Van Gastel, M.: ORCA Workshop, 6th EFEPR Winter School on Advanced EPR Spectroscopy“, Rehovot, Israel, 2013.

Van Gastel, M.: Summerschool, Method in Molecular Energy Research: Theory and Spectroscopy of Transition Metal Complexes“, Essen, 2013.

Scientific Output and Statistics

List of Publications

2010

Aliaga-Alcalde, N., Marques-Gallego, P., Kraaijkamp, M., Herranz-Lancho, C., den Dulk, H., Görner, H., Roubeau, O., Teat, S.J., Weyhermüller, T. and Reedijk, J., 2010: *Copper curcuminoids containing anthracene groups: Fluorescent molecules with cytotoxic activity*, Inorganic Chemistry, 49, 9655.

Baitalik, S., Dutta, S., Biswas, P., Florke, U., Bothe, E. and Nag, K., 2010: *Structural, Spectroscopic, and Proton-Coupled Electron-transfer Behavior of Pyrazolyl-3,5-bis(benzimidazole)-Bridged Homo- and Heterochiral Ru^{II}Ru^{II}, Os^{II}Os^{II}, and Os^{II}Ru^{II} 2,2 - Bipyridine Complexes*, European Journal of Inorganic Chemistry, 570.

Biswas, B., Salunke-Gawali, S., Weyhermüller, T., Bachler, V., Bill, E. and Chaudhuri, P., 2010: *Metal-Complexes As Ligands to Generate Asymmetric Homo- and Hetero-dinuclear* $M_A^{III}M_B^{II}$ *Species: a Magneto-Structural and Spectroscopic Comparison of Imidazole-N versus Pyridine-N*, Inorganic Chemistry, 49, 626.

Bongards, C. and Gärtner, W., 2010: *The role of the chromophore in the biological photoreceptor phytochrome: An approach using chemically synthesized tetrapyrroles*, Accounts of Chemical Research, 43, 485.

Bordignon, E., Brutlach, H., Urban, L., Hideg, K., Savitsky, A., Schnegg, A., Gast, P., Engelhard, M., Groenen, E., Möbius, K. and Steinhoff, H.J., 2010: *Heterogeneity in the nitroxide micro-environment: Polarity and proticity effects in spin-labeled proteins studied by multi-frequency EPR*, Applied Magnetic Resonance, 37, 391.

Bowman, A.C., Milsmann, C., Atienza, C.C.H., Lobkovsky, E., Wieghardt, K. and Chirik, P.J., 2010: *Synthesis and molecular and electronic structures of reduced bis(imino)-pyridine cobalt dinitrogen complexes: Ligand versus metal reduction*, Journal of the American Chemical Society, 132, 1676.

Bowman, A.C., Milsmann, C., Bill, E., Lobkovsky, E., Weyhermüller, T., Wieghardt, K. and Chirik, P.J., 2010: *Reduced N-alkyl substituted bis(imino)pyridine cobalt complexes: Molecular and electronic structures for compounds varying by three oxidation states*, Inorganic Chemistry, 49, 6110.

Cao, Z., Livoti, E., Losi, A. and Gärtner, W., 2010: *A blue light-inducible phosphodiesterase activity in the cyanobacterium Synechococcus elongatus*, Photochemistry and Photobiology, 86, 606.

Casazza, A.P., Szczepaniak, M., Müller, M.G., Zucchelli, G. and Holzwarth, A.R., 2010: *Energy transfer processes in the isolated core antenna complexes CP43 and CP47 of photosystem II*, Biochimica et Biophysica Acta-Bioenergetics, 1797,1606.

Chaudhuri, P., Wagner, R. and Weyhermüller, T., 2010: *An Oximate-Free Ferromagnetically Coupled Triangular* $[Mn^{III}_3(\mu_3\text{-}O)]^{7+}$ *Core*, European Journal of Inorganic Chemistry, 1339.

Chibisov, A.K., Slavnova, T.D. and Görner, H., 2010: *J-aggregation of N-sulfobutyl oxacarbocyanine in binary mixtures of organic solvents*, Chemical Physics Letters, 498, 63.

Chirik, P.J. and Wieghardt, K., 2010: *Radical ligands confer nobility on base-metal catalysts*, Science, 327, 794.

Cowley, R.E., DeYonker, N.J., Eckert, N.A., Cundari, T.R., DeBeer, S., Bill, E., Ottenwaelder, X., Flaschenriem, C. and Holland, P.L., 2010: *Three-coordinate terminal imidoiron(III) complexes: Structure, spectroscopy, and mechanism of formation*, Inorganic Chemistry, 49, 6172.

Cox, N., Ogata, H., Stolle, P., Reijerse, E., Auling, G. and Lubitz, W., 2010: *A Tyrosyl-dimanganese coupled spin system is the native metalloradical cofactor of the R2F subunit of the ribonucleotide reductase of Corynebacterium ammoniagenes*, Journal of the American Chemical Society, 132, 11197.

Cramer, S.P., Yan, L., Wang, H., Mitra, D., Guo, Y., Dapper, C., Newton, W.E., Fujita, Y., Ogata, H., Lubitz, W., Kuchenreuther, J.M., Swartz, J.R., Yoda, Y., 2010: *Nuclear resonance vibrational spectroscopy (NRVS) of iron-sulfur enzymes for hydrogen metabolism, nitrogen fixation, & photosynthesis*, SPring-8 Information, 15, 157.

Czech, I., Silakov, A., Lubitz, W. and Happe, T., 2010: *The [FeFe]-hydrogenase maturase HydF from Clostridium acetobutylicum contains a CO and* CN^- *ligated iron cofactor*, FEBS Letters, 584, 638.

Daviso, E., Diller, A., Gast, P., Alia, A., Lugtenburg, J., Müller, M.G. and Matysik, J., 2010: *Action spectroscopy on dense samples of photosynthetic reaction centers of Rhodobacter sphaeroides WT based on nanosecond laser-flash* ^{13}*C photo-CIDNP MAS NMR*, Applied Magnetic Resonance, 38, 105.

Drew, S.C., Baldas, J. and Boas, J.F., 2010: *Theoretical calculation of the magnetic resonance parameters of trigonal-prismatic tris(o-aminobenzenethiol)technetium and -rhenium complexes*, Inorganic Chemistry, 49, 6799.

Duboc, C., Ganyushin, D., Sivalingam, K., Collomb, M.N. and Neese, F., 2010: *Systematic theoretical study of the zero-field splitting in coordination complexes of Mn(III). Density functional theory versus multireference wave function approaches*, Journal of Physical Chemistry A, 114, 10750.

Flores, M., Savitsky, A., Paddock, M.L., Abresch, E.C., Dubinskii, A.A., Okamura, M.Y., Lubitz, W. and Möbius, K., 2010: *Electron-nuclear and electron-electron double resonance spectroscopies show that the primary quinone acceptor* Q_A *in reaction centers from photosynthetic bacteria Rhodobacter sphaeroides remains in the same orientation upon light-induced reduction*, Journal of Physical Chemistry B, 114, 16894.

Gärtner, W., 2010: *Lights on: A switchable fluorescent biliprotein*, ChemBioChem, 11, 1649.

Ghosh, M., Weyhermüller, T. and Wieghardt, K., 2010: *Electronic structure of the members of the electron transfer series* $[NiL]^z$ *(z = 3+, 2+, 1+, 0) and* $[NiL(X)]^n$ *(X = Cl, CO,* $P(OCH_3)_3$*) species containing a tetradentate, redox-noninnocent, Schiff base macrocyclic ligand L: an experimental and density functional theoretical study*, Dalton Transactions, 39, 1996.

Görner, H., 2010: *Reduction of 4,4 '-stilbenequinone and 4,4 '-diphenoquinone upon reaction with photogenerated radicals*, Photochemistry and Photobiology, 86, 1202.

Görner, H., 2010: *Nitro group photoreduction of 4-(2-nitrophenyl)- and 4-(3-nitrophenyl)-1,4-dihydropyridines*, Chemical Physics, 373, 153.

Görner, H., 2010: *Photocyclization of 2,6-dichlorodiphenylamines in solution*, Journal of Photochemistry and Photobiology A-Chemistry, 211, 1.

Görner, H. and Gruen, H., 2010: *Direct and ketone-sensitized photoconversion of 1-nitro-9,10-anthraquinone to 1-amino-9,10-anthraquinone mediated by donor radicals*, Chemical Physics, 368, 20.

Görner, H., Megyesi, M., Miskolczy, Z. and Biczok, L., 2010: *Photoproducts and triplet reactivity of 4 '-nitro- and 2 ',4 '-dinitro-substituted 4-hydroxystilbenes*, Journal of Photochemistry and Photobiology A-Chemistry, 214, 188.

Görner, H., Slavnova, T.D. and Chibisov, A.K., 2010: *Kinetics of spontaneous formation of chiral j-aggregate of n-sulfobutyl oxacarbocyanine*, Journal of Physical Chemistry B, 114, 9330.

Gruen, H. and Görner, H., 2010: *Properties of 16,17-disubstituted dihydroviolanthrones formed by reaction of violanthrones with photogenerated radicals*, Photochemical & Photobiological Sciences, 9, 1088.

Grzyb, J., Xu, F., Weiner, L., Reijerse, E.J., Lubitz, W., Nanda, V. and Noy, D., 2010: *De novo design of a non-natural fold for an iron-sulfur protein: Alpha-helical coiled-coil with a four-iron four-sulfur cluster binding site in its central core*, Biochimica et Biophysica Acta-Bioenergetics, 1797, 406.

Gutiérrez-Sánchez, C., Rüdiger, O., Fernández, V. M., de Lacey, A. L., Marques, M., Pereira, I. A. C., 2010: *Interaction of the Active Site of the Ni-Fe-Se Hydrogenase from Desulfovibrio vulgaris Hildenborough With Carbon Monoxide and Oxygen Inhibitors*, Journal of Biological Inorganic Chemistry 15, 1285.

He, C., Ogata, H. and Knipp, M.: *The interaction between the ferriheme protein nitrophorin and nitrite*. In: D. Kessissoglou and T. Salifoglou (eds.), 10th European Biological Inorganic Chemistry Conference. MEDIMOND, Thessaloniki, Greece, 2010, pp. 53.

He, C., Ogata, H. and Knipp, M., 2010: *Formation of the complex of nitrite with the ferriheme b ß-barrel proteins nitrophorin 4 and nitrophorin 7*, Biochemistry, 49, 5841.

Herrero, C., Hughes, J.L., Quaranta, A., Cox, N., Rutherford, A.W., Leibl, W. and Aukauloo, A., 2010: *Intramolecular light induced activation of a salen-Mn^{III} complex by a ruthenium photosensitizer*, Chemical Communications, 46, 7605.

Hess, C.R., Weyhermüller, T., Bill, E. and Wieghardt, K., 2010: *Influence of the redox active ligand on the reactivity and electronic structure of a series of Fe(TIM) complexes*, Inorganic Chemistry, 49, 5686.

Hughes, J., Cox, N., Rutherford, A.W., Krausz, E., Lai, T.L., Boussac, A. and Sugiura, M., 2010: *D1 protein variants in photosystem II from Thermosynechococcus elongatus studied by low temperature optical spectroscopy*, Biochimica et Biophysica Acta - Bioenergetics, 1797, 11.

Indumathy, R., Weyhermüller, T. and Nair, B.U., 2010: *Biimidazole containing cobalt-(III) mixed ligand complexes: Crystal structure and photonuclease activity*, Dalton Transactions, 39, 2087.

Jana, A., Majumder, S., Carrella, L., Nayak, M., Weyhermüller, T., Dutta, S., Schollmeyer, D., Rentschler, E., Koner, R. and Mohanta, S., 2010: *Syntheses, Structures, and Magnetic Properties of Diphenoxo-Bridged Cu^{II}Ln^{III} and Ni^{II}(Low-Spin)Ln^{III} Compounds Derived from a Compartmental Ligand (Ln = Ce–Yb)*, Inorganic Chemistry, 49, 9012.

Jurk, M., Dorn, M., Kikhney, A., Svergun, D., Gärtner, W. and Schmieder, P., 2010: *The switch that does not flip: The blue-light receptor YtvA from Bacillus subtilis adopts an elongated dimer conformation independent of the activation state as revealed by a combined AUC and SAXS Study*, Journal of Molecular Biology, 403, 78.

Kapre, R.R., Roy, N., Sproules, S., Weyhermüller, T. and Wieghardt K., 2010: *The Molecular and Electronic Structures of Some Cobalt Complexes Containing Redox Noninnocent o-Aminobenzothiolate Ligands. An Experimental and Density Functional Theoretical Study*, Inorganica Chimica Acta, 363, 2702.

Karmakar, S., Das, O., Ghosh, S., Zangrando, E., Johann, M., Rentschler, E., Weyhermüller, T., Khanra, S. and Paine, T.K., 2010: *Hexanuclear copper(II) cage with* $\{Cu_3O{\bullet}{\bullet}{\bullet}H{\bullet}{\bullet}{\bullet}OCu_3\}$ *core supported by a dicompartmental oxime ligand with m-xylyl spacer: synthesis, molecular structure and magnetic studies*, Dalton Transactions, 39, 10920.

Kossmann, S. and Neese, F., 2010: *Correlated ab initio spin densities for larger molecules: Orbital-optimized spin-component-scaled MP2 method*, Journal of Physical Chemistry A, 114, 11768.

Kossmann, S. and Neese, F., 2010: *Efficient structure optimization with second-order many-body perturbation theory: The RIJCOSX-MP2 method*, Journal of Chemical Theory and Computation, 6, 2325.

Kulon, K., Lubitz, W. and Antonkine, M.L.: *Modelling the binding site of a linear [3Fe-4S] cluster*. In: D. Kessissoglou and T. Salifoglou (eds.), 10th European Biological Inorganic Chemistry Conference, Thessaloniki, Greece. Medimond s.r.l., Pianoro (Bologna), Italy, 2010, 39.

Lambrev, P.H., Nilkens, M., Miloslavina, Y., Jahns, P. and Holzwarth, A.R., 2010: *Kinetic and spectral resolution of multiple nonphotochemical quenching components in arabidopsis leaves*, Plant Physiology, 152, 1611.

Lancaster, K.M., Sproules, S., Palmer, J.H., Richards, J.H. and Gray, H.B., 2010: *Outer-sphere effects on reduction potentials of copper sites in proteins: The Curious case of high potential type 2 C112D/M121E Pseudomonas aeruginosa azurin*, Journal of the American Chemical Society, 132, 14590.

Lassalle-Kaiser, B., Hureau, C., Pantazis, D.A., Pushkar, Y., Guillot, R., Yachandra, V.K., Yano, J., Neese, F. and Anxolabehere-Mallart, E., 2010: *Activation of a water molecule using a mononuclear Mn complex: from Mn-aquo, to Mn-hydroxo, to Mn-oxyl via charge compensation*, Energy & Environmental Science, 3, 924.

Marchanka, A., Savitsky, A., Lubitz, W., Möbius, K. and van Gastel, M., 2010: *B-branch electron transfer in the photosynthetic reaction center of a Rhodobacter sphaeroides quadruple mutant Q- and W-band electron paramagnetic resonance studies of triplet and radical-pair cofactor states*, Journal of Physical Chemistry B, 114, 14364.

Megyesi, M., Biczok, L., Görner, H. and Miskolczy, Z., 2010: *Effects of solvent polarity and hydrogen bonding on the fluorescence properties of trans-4-hydroxy-4 '-nitro-stilbenes*, Chemical Physics Letters, 489, 59.

Merenyi, G., Lind, J., Naumov, S. and von Sonntag, C., 2010: *Reaction of ozone with hydrogen peroxide (peroxone process): A revision of current mechanistic concepts based on thermokinetic and quantum-chemical considerations*, Environmental Science & Technology, 44, 3505.

Merenyi, G., Lind, J., Naumov, S. and von Sonntag, C., 2010: *The reaction of ozone with the hydroxide ion: Mechanistic considerations based on thermokinetic and quantum chemical calculations and the role of* HO_4^- *in superoxide dismutation*, Chemistry-A European Journal, 16, 1372.

Milsmann, C., Sproules, S., Bill, E., Weyhermüller, T., George, S.D. and Wieghardt, K., 2010: *Stabilization of High-Valent* $Fe^{IV}S_6$*-Cores by Dithiocarbamate(1–) and 1,2-Dithiolate(2–) Ligands in Octahedral* $[Fe^{IV}(Et_2dtc)_{3}\_n(mnt)n]^{(n-1)-}$ *Complexes (n=0, 1, 2, 3): A Spectroscopic and Density Functional Theory Computational Study*, Chemistry - A European Journal, 16, 3628.

Müller, M.G., Lambrev, P., Reus, M., Wientjes, E., Croce, R. and Holzwarth, A.R., 2010: *Singlet energy dissipation in the photosystem II light-harvesting complex does not involve energy transfer to carotenoids*, ChemPhysChem, 11, 1289.

Müller, M.G., Slavov, C., Luthra, R., Redding, K.E. and Holzwarth, A.R., 2010: *Independent initiation of primary electron transfer in the two branches of the photosystem I reaction center*, Proceedings of the National Academy of Sciences of the United States of America, 107, 4123.

Naumov, S., Mark, G., Jarocki, A. and von Sonntag, C., 2010: *The reactions of nitrite ion with ozone in aqueous solution - new experimental data and quantum-chemical considerations*, Ozone-Science & Engineering, 32, 430.

Naumov, S. and von Sonntag, C., 2010: *Quantum chemical studies on the formation of ozone adducts to aromatic compounds in aqueous solution*, Ozone-Science & Engineering, 32, 61.

Niklas, J., Gopta, O., Epel, B., Lubitz, W. and Antonkine, M.L., 2010: *Investigation of the stationary and transient* $A_1^{\bullet-}$ *radical in Trp → Phe mutants of photosystem I*, Applied Magnetic Resonance, 38, 187.

Nilkens, M., Kress, E., Lambrev, P., Miloslavina, Y., Müller, M., Holzwarth, A.R. and Jahns, P., 2010: *Identification of a slowly inducible zeaxanthin-dependent component of non-photochemical quenching of chlorophyll fluorescence generated under steady-state conditions in Arabidopsis*, Biochimica et Biophysica Acta-Bioenergetics, 1797, 466.

Nippe, M., Wang, J.F., Bill, E., Hope, H., Dalal, N.S. and Berry, J.F., 2010: *Crystals in which some metal atoms are more equal than others: Inequalities from crystal packing and their spectroscopic/magnetic consequences*, Journal of the American Chemical Society, 132, 14261.

Nohr, R.S., McCallum, C.M. and Schuchmann, H.P., 2010: *The elimination of molecular chlorine catalyzed by* BCl_3 *an aspect of chloroboron subphthalocyanine formation*, Journal of Porphyrins and Phthalocyanines, 14, 271.

Nöthe, T., Launer, M., von Sonntag, C. and Fahlenkamp, H., 2010: *Computer-assisted determination of reaction parameters for the simulation of micropollutant abatement in wastewater ozonation*, Ozone-Science & Engineering, 32, 424.

Nowaczyk, M.M., Sander, J., Grasse, N., Cormann, K.U., Rexroth, D., Bernat, G. and Rögner, M., 2010: *Dynamics of the cyanobacterial photosynthetic network: Communication and modification of membrane protein complexes*, European Journal of Cell Biology, 89, 974.

Ocakoglu, K. and Okur, S., 2010: *Humidity sensing properties of novel ruthenium polypyridyl complex*, Sensors and Actuators B-Chemical, 151, 223.

Ogata, H., Kellers, P. and Lubitz, W., 2010: *The crystal structure of the [NiFe] hydrogenase from the photosynthetic bacterium Allochromatium vinosum: Characterization of the oxidized enzyme (Ni-A State)*, Journal of Molecular Biology, 402, 428.

Ogata, H., Shomura, Y., Goenka Agrawal, A., Pal Kaur, A., Gärtner, W., Higuchi, Y. and Lubitz, W., 2010: *Purification, crystallization and preliminary X-ray analysis of the dissimilatory sulfite reductase from Desulfovibrio vulgaris Miyazaki F*, Acta Crystallographica Section, F66, 1470.

Özbolat-Schön, A., Bode, M., Schnakenburg, G., van Gastel, M., Neese, F., Streubel, R., 2010: *First insights into the chemistry of P-functional phosphanyl complexes*, Angewandte Chemie International Edition, 49, 6894.

Ostroumov, E.E., Müller, M.G., Hundsdörfer, C., Stahl, W., Marian, C.M. and Holzwarth, A.R., 2010: *Excited state relaxation dynamics and electronic properties of a quinoid carotenoid*, Chemical Physics, 373, 137.

Paddock, M.L., Flores, M., Isaacson, J.N., Shepherd, J.N. and Okamura, M.Y., 2010: *EPR and ENDOR Investigation of rhodosemiquinone in bacterial reaction centers formed by B-branch electron transfer*, Applied Magnetic Resonance, 37, 39.

Pandelia, M.E., Fourmond, V., Tron-Infossi, P., Lojou, E., Bertrand, P., Léger, C., Giudici-Orticoni, M.T. and Lubitz, W., 2010: *Membrane-bound hydrogenase I from the hyper-thermophilic bacterium Aquifex aeolicus: Enzyme activation, redox intermediates and oxygen tolerance*, Journal of the American Chemical Society, 132, 6991.

Pandelia, M.E., Infossi, P., Giudici-Orticoni, M.T. and Lubitz, W., 2010: *The oxygen-tolerant hydrogenase I from Aquifex aeolicus weakly interacts with carbon monoxide: An electrochemical and time-resolved FTIR study*, Biochemistry, 49, 8873.

Pandelia, M.E., Ogata, H., Currell, L.J., Flores, M. and Lubitz, W., 2010: *Inhibition of the [NiFe] hydrogenase from Desulfovibrio vulgaris Miyazaki F by carbon monoxide: An FTIR and EPR spectroscopic study*, Biochimica et Biophysica Acta-Bioenergetics, 1797, 304.

Pandelia, M.E., Ogata, H. and Lubitz, W., 2010: *Intermediates in the catalytic cycle of [NiFe] hydrogenase: Functional spectroscopy of the active site*, ChemPhysChem, 11, 1127.

Pantazis, D.A., Krewald, V., Orio, M. and Neese, F., 2010: *Theoretical magnetochemistry of dinuclear manganese complexes: broken symmetry density functional theory investigation on the influence of bridging motifs on structure and magnetism*, Dalton Transactions, 39, 4959.

Pathak, G.P. and Gärtner, W.: *Detection and isolation of selected genes of interest from metagenomic libraries by a DNA microarray approach.* In: W. R. Streit and Media (eds.), Methods in Molecular Biology, Springer, Berlin, 2010, 299.

Pfirrmann, S., Limberg, C., Herwig, C., Knispel, C., Braun, B., Bill, E. and Stosser, R., 2010: *A reduced β-diketiminato-ligated Ni_3H_4 unit catalyzing H/D exchange*, Journal of the American Chemical Society, 132, 13684.

Pocostales, J.P., Sein, M.M., Knolle, W., von Sonntag, C. and Schmidt, T.C., 2010: *Degradation of ozone-refractory organic phosphates in wastewater by ozone and ozone/hydrogen peroxide (peroxone): The role of ozone consumption by dissolved organic matter*, Environmental Science & Technology, 44, 8248.

Podtetenieff, J., Taglieber, A., Bill, E., Reijerse, E.J. and Reetz, M.T., 2010: *An artificial metalloenzyme: Creation of a designed copper binding site in a thermostable protein*, Angewandte Chemie-International Edition, 49, 5151.

Prinz, M., Kuepper, K., Taubitz, C., Raekers, M., Khanra, S., Biswas, B., Weyhermüller, T., Uhlarz, M., Wosnitza, J., Schnack, J., Postnikov, A.V., Schröder, C., George, S.J., Neumann, M. and Chaudhuri, P., 2010: *A star-shaped heteronuclear* $Cr^{III}Mn^{II}_3$ *species and its precise electronic and magnetic structure: Spin frustration studied by X-ray spectroscopic, magnetic, and theoretical methods*, Inorganic Chemistry, 49, 2093.

Reijerse, E., 2010: *High-frequency EPR instrumentation*, Applied Magnetic Resonance, 37, 795.

Rohmer, T., Lang, C., Bongards, C., Gupta, K.B.S.S., Neugebauer, J., Hughes, J., Gärtner, W. and Matysik, J., 2010: *Phytochrome as molecular machine: Revealing chromophore action during the Pfr -> Pr photoconversion by magic angle spinning NMR spectroscopy*, Journal of the American Chemical Society, 132, 4431.

Rohmer, T., Lang, C., Gärtner, W., Hughes, J. and Matysik, J., 2010: *Role of the protein cavity in phytochrome chromoprotein assembly and double-bond isomerization: A comparison with model compounds*, Photochemistry and Photobiology, 86, 856.

Roy, A.S., Biswas, M.K., Weyhermüller, T. and Ghosh, P., 2010: *Stereoselective non-equivalent bis-diimine coordination to Co(II) ion: Structure, luminescence and density functional theory calculations*, Inorganica Chimica Acta, 363, 2874.

Rubin, M.B. and Braslavsky, S.E., 2010: *Quantum yield: the term and the symbol. A historical search*, Photochemical & Photobiological Sciences, 9, 670.

Rüdiger, O., Gutiérrez-Sánchez, C., Olea, D., Pereira, I.A.C., Velez, M., Fernández, V.M. and de Lacey, A.L., 2010: *Enzymatic anodes for hydrogen fuel cells based on covalent attachment of Ni-Fe hydrogenases and direct electron transfer to SAM-modified gold electrodes*, Electroanalysis, 22, 776.

Safaei, E., Wojtczak, A., Bill, E. and Hamidi, H., 2010: *Synthesis, crystal structure, magnetic and redox properties of Cu(II)-Cu(II) binuclear complexes of bis(phenol) amine ligands*, Polyhedron, 29, 2769.

Saggu, M., Teutloff, C., Ludwig, M., Brecht, M., Pandelia, M.E., Lenz, O., Friedrich, B., Lubitz, W., Hildebrandt, P., Lendzian, F. and Bittl, R., 2010: *Comparison of the membrane-bound [NiFe] hydrogenases from R. eutropha H16 and D. vulgaris Miyazaki F in the oxidized ready state by pulsed EPR*, Physical Chemistry Chemical Physics, 12, 2139.

Sander, J., Nowaczyk, M., Buchta, J., Dau, H., Vass, I., Deak, Z., Dorogi, M., Iwai, M. and Rögner, M., 2010: *Functional characterization and quantification of the alternative PsbA copies in thermosynechococcus elongatus and their role in photoprotection*, Journal of Biological Chemistry, 285, 29851.

Sathyaraj, G., Weyhermüller, T. and Nair, B.U., 2010: *Synthesis, characterization and DNA binding studies of new ruthenium(II)bisterpyridine complexes*, European Journal of Medicinal Chemistry, 45, 284.

Savitsky, A., Gopta, O., Mamedov, M., Golbeck, J., Tikhonov, A., Möbius, K. and Semenov, A., 2010: *Alteration of the Axial Met Ligand to Electron Acceptor* A_0 *in Photosystem I: Effect on the Generationof* $P_{700}^{\bullet +}$ $A_1^{\bullet -}$ *Radical Pairs as Studied by W-band Transient EPR*, Applied Magnetic Resonance, 37, 85.

Savitsky, A., Malferrari, M., Francia, F., Venturoli, G. and Möbius, K., 2010: *Bacterial photosynthetic reaction centers in trehalose glasses: Coupling between protein conformational dynamics and electron-transfer kinetics as studied by laser-flash and high-field EPR spectroscopies*, Journal of Physical Chemistry B, 114, 12729.

Savitsky, A., Plato, M. and Möbius, K., 2010: *The temperature dependence of nitroxide spin-label interaction parameters: a high-field EPR study of intramolecular motional contributions*, Applied Magnetic Resonance, 37, 415.

Schwenkert, S., Netz, D.J.A., Frazzon, J., Pierik, A.J., Bill, E., Gross, J., Lill, R. and Meurer, J., 2010: *Chloroplast HCF101 is a scaffold protein for [4Fe-4S] cluster assembly*, Biochemical Journal, 425, 207.

Silakov, A., Shaw, J.L., Reijerse, E.J. and Lubitz, W., 2010: *Advanced electron paramagnetic resonance and density functional theory study of a {2Fe3S} cluster mimicking the active site of [FeFe] hydrogenase*, Journal of the American Chemical Society, 132, 17578.

Slavov, C., Mansurova, M., Holzwarth, A.R. and Gärtner, W., 2010: *Excited state processes in 1-deazariboflavin studied by ultrafast fluorescence kinetics*, Photochemistry and Photobiology, 86, 31.

Sproules, S., Kapre, R.R., Roy, N., Weyhermüller, T. and Wieghardt, K., 2010: *The molecular and electronic structures of monomeric cobalt complexes containing redox noninnocent o-aminobenzenethiolate ligands*, Inorganica Chimica Acta, 363, 2702.

Sproules, S., Weyhermüller, T., DeBeer, S. and Wieghardt, K., 2010: *Six-membered electron transfer series* $[V(dithiolene_3)]^z$ *(z=1+, 0, 1-, 2-, 3-, 4-). An X-ray absorption spectroscopic and density functional theoretical study*, Inorganic Chemistry, 49, 5241.

Sproules, S. and Wieghardt, K., 2010: *o-Dithiolene and o-aminothiolate chemistry of iron: Synthesis, structure and reactivity*, Coordination Chemistry Reviews, 254, 1358.

Steenken, S. and Reynisson, J., 2010: *DFT calculations on the deprotonation site of the one-electron oxidised guanine-cytosine base pair*, Physical Chemistry Chemical Physics, 12, 9089.

Stolle, P., Barckhausen, O., Oehlmann, W., Knobbe, N., Vogt, C., Pierik, A.J., Cox, N., Schmidt, P.P., Reijerse, E.J., Lubitz, W. and Auling, G., 2010: *Homologous expression of the nrdF gene of Corynebacterium ammoniagenes strain ATCC 6872 generates a manganese-metallocofactor (R2F) and a stable tyrosyl radical (*$Y^\bullet$*) involved in ribonucleotide reduction*, FEBS Journal, 277, 4849.

Su, J.H. and Messinger, J., 2010: *Is Mn-bound substrate water protonated in the* S_2 *state of Photosystem II?* Applied Magnetic Resonance, 37, 123.

Tang, Y.F., Cao, Z., Livoti, E., Krauss, U., Jaeger, K.E., Gärtner, W. and Losi, A., 2010: *Interdomain signalling in the blue-light sensing and GTP-binding protein YtvA: A mutagenesis study uncovering the importance of specific protein sites*, Photochemical & Photobiological Sciences, 9, 47.

Tondreau, A.M., Milsmann, C., Patrick, A.D., Hoyt, H.M., Lobkovsky, E., Wieghardt, K. and Chirik, P.J., 2010: *Synthesis and electronic structure of cationic, neutral, and anionic bis(imino)pyridine iron alkyl complexes: Evaluation of redox activity in single-component ethylene polymerization catalysts*, Journal of the American Chemical Society, 132, 15046.

Van der Est, A., Pushkar, Y., Karyagina, I., Fonovic, B., Dudding, T., Niklas, J., Lubitz, W. and Golbeck, J.H., 2010: *Incorporation of 2,3-disubstituted-1,4-naphthoquinones into the* A_1 *binding site of photosytem I studied by EPR and ENDOR spectroscopy*, Applied Magnetic Resonance, 37, 65.

Van Gastel, M., 2010: *Structural features of the unready Ni-A state of [NiFe] hydrogenase revealed by x-ray cryastallography and EPR spectroscopy*, Applied Magnetic Resonance, 37, 207.

Van Gastel, M., 2010: *Zero-field splitting of the lowest excited triplet states of C60, C70 and benzene*, Journal of Physical Chemistry A, 114, 10864.

Van Slageren, J., Piligkos, S. and Neese, F., 2010: *Magnetic circular dichroism spectroscopy on the* Cr_8 *antiferromagnetic ring*, Dalton Transactions, 39, 4999.

Von Sonntag, C. (2010). Radiation-induced DNA damage: Indirect Effects. In Recent Trends in Radiation Cemistry, J. F. Wishart, B. S. M. Rao, J. F. Wishart and B. S. M. Rao, eds. (London, Covent Garden: World Scientific), pp. 543.

Woertink, J.S., Tian, L., Maiti, D., Lucas, H.R., Himes, R.A., Karlin, K.D., Neese, F., Wurtele, C., Holthausen, M.C., Bill, E., Sundermeyer, J., Schindler, S. and Solomon, E.I., 2010: *Spectroscopic and computational studies of an end-on bound superoxo-Cu(II) complex: Geometric and electronic factors that determine the ground state*, Inorganic Chemistry, 49, 9450.

Wolff, T. and Görner, H., 2010: *Photocleavage of dimers of coumarin and 6-alkylcoumarins*, Journal of Photochemistry and Photobiology A-Chemistry, 209, 219.

Yao, S.L., Herwig, C., Xiong, Y., Company, A., Bill, E., Limberg, C. and Driess, M., 2010: *Monooxygenase-like reactivity of an unprecedented heterobimetallic* $\{FeO_2Ni\}$ *moiety*, Angewandte Chemie-International Edition, 49, 7054.

Yao, S.L., Xiong, Y., Milsmann, C., Bill, E., Pfirrmann, S., Limberg, C. and Driess, M., 2010: *Reversible* P_4 *activation with nickel(I) and an* ^{3}*-coordinated tetraphosphorus ligand between Two* Ni^{I} *centers*, Chemistry-A European Journal, 16, 436

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2011

Abe, C., Dietrich, F., Gajula, P., Benz, M., Vogel, K.P., van Gastel, M., Illenberger, S., Ziegler, W.H. and Steinhoff, H.J., 2011: *Monomeric and Dimeric Conformation of the Vinculin Tail Five-Helix Bundle in Solution Studied by EPR Spectroscopy*, Biophysical Journal, 101, 1772.

Albers, A., Demeshko, S., Dechert, S., Bill, E., Bothe, E. and Meyer, F., 2011: *The Complete Characterization of a Reduced Biomimetic [2Fe-2S] Cluster*, Angewandte Chemie-International Edition, 50, 9191.

Albers, A., Demeshko, S., Dechert, S., Bill, E., Bothe, E. and Meyer, F., 2011: *Die vollständige Charakterisierung eines reduzierten biomimetischen [2-Fe-2S]-Clusters*, Angewandte Chemie, 123, 9357.

Ames, W., Pantazis, D.A., Krewald, V., Cox, N., Messinger, J., Lubitz, W. and Neese, F., 2011: *Theoretical evaluation of structural models of the* S_2 *state in the oxygen evolving complex of Photosystem II: Protonation states and magnetic interactions*, Journal of the American Chemical Society, 133, 19743.

Arumugam, K., Shaw, M.C., Mague, J.T., Bill, E., Sproules, S. and Donahue, J.P., 2011: *Long-Range Spin Coupling: A Tetraphosphine-Bridged Palladium Dimer*, Inorganic Chemistry, 50, 2995.

Atanasov, M., Ganyushin, D., Pantazis, D.A., Sivalingam, K. and Neese, F., 2011: *Detailed Ab Initio First-Principles Study of the Magnetic Anisotropy in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes*, Inorganic Chemistry, 50, 7460.

Beckwith, M.A., Roemelt, M., Collomb, M.N., DuBoc, C., Weng, T.C., Bergmann, U., Glatzel, P., Neese, F. and DeBeer, S., 2011: *Manganese K ßX-ray Emission Spectroscopy As a Probe of Metal-Ligand Interactions*, Inorganic Chemistry, 50, 8397.

Berliner, L.J., Görner, H. and Schuchmann, H.P., 2011: *Evaluation of EPR monitoring of singlet oxygen production using the photosensitizer chloroboron subphthalocyanine*, Journal of Porphyrins and Phthalocyanines,15, 118.

Birk, T., Schau-Magnussen, M., Weyhermüller, T. and Bendix, J., 2011: *cyclo-Tetra-μ-fluorido-1:2*κ^2*F;2:3*κ^2*F;3:4*κ^2*F;1:4*κ^2*F-octanitrato-1*κ^8*O,O′;3*κ^8*O,O′-tetrakis (1,10-phenanthroline)-2*κ^4*N,N′;4*κ^4*N,N′-2,4-dichromium(III)-1,3-dineodymium(III) methanol tetrasolvate monohydrate*, Acta Crystallographica Section E-Structure Reports Online, 67, M1561.

Bowman, A.C., Milsmann, C., Bill, E., Turner, Z.R., Lobkovsky, E., DeBeer, S., Wieghardt, K. and Chirik, P.J., 2011: *Synthesis and Electronic Structure Determination of N-Alkyl-Substituted Bis(imino)pyridine Iron Imides Exhibiting Spin Crossover Behavior*, Journal of the American Chemical Society, 133, 17353.

Braslavsky, S.E., Braun, A.M., Cassano, A.E., Emeline, A.V., Litter, M.I., Palmisano, L., Parmon, V.N., Serpone, N., Alfano, O.M., Anpo, M., Augugliaro, V., Bohne, C., Esplugas, S., Oliveros, E., von Sonntag, C., Weiss, R.G. and Schiavello, M., 2011: *Glossary of terms used in photocatalysis and radiation catalysis (IUPAC Recommendations 2011)*, Pure and Applied Chemistry, 83, 931.

Braslavsky, S.E. and Rubin, M.B., 2011: *The history of ozone Part VIII. Photochemical formation of ozone*, Photochemical & Photobiological Sciences, 10, 1515.

Busch, A.W.U., Reijerse, E.J., Lubitz, W., Frankenberg-Dinkel, N. and Hofmann, E., 2011: *Structural and mechanistic insight into the ferredoxin-mediated two-electron reduction of bilins*, Biochemical Journal, 439, 257.

Busch, A.W.U., Reijerse, E.J., Lubitz, W., Hofmann, E. and Frankenberg-Dinkel, N., 2011: *Radical mechanism of cyanophage phycoerythrobilin synthase (PebS)*, Biochemical Journal, 433, 469.

Castro, M.A., Rusjan, M., Vega, D., Pena, O., Weyhermüller, T., Cukiernik, F.D. and Slep, L.D., 2011: *An unexpected carboxylato-bridged-only hexanuclear copper compound*, Inorganica Chimica Acta, 374, 499.

Chandrasekaran, P., Stieber, S.C.E., Collins, T.J., Que, L., Neese, F. and DeBeer, S., 2011: *Prediction of high-valent iron K-edge absorption spectra by time-dependent Density Functional Theory*, Dalton Transactions, 40, 11070.

Chiang, K.P., Ding, K., Dugan, T.R., Sadique, A., Bill, E., Scarborough, C.C., Wieghardt, K., Brennessel, W.W. and Holland, P.L., 2011: *Synthesis and characterization of novel three-coordinate iron(I)-hydride complexes*, Abstracts of Papers of the American Chemical Society, 241,1027.

Cohen-Ofri, I., van Gastel, M., Grzyb, J., Brandis, A., Pinkas, I., Lubitz, W. and Noy, D., 2011: *Zinc-bacteriochlorophyllide dimers in de novo designed four-helix bundle proteins. A model system for natural light energy harvesting and dissipation*, Journal of the American Chemical Society, 133, 9526.

Cox, N., Ames, W., Epel, B., Kulik, L.V., Rapatskiy, L., Neese, F., Messinger, J., Wieghardt, K. and Lubitz, W., 2011: *Electronic structure of a weakly antiferromagnetically coupled* $Mn^{II}Mn^{III}$ *model relevant to manganese proteins: A combined EPR,* ^{55}*Mn-ENDOR, and DFT study*, Inorganic Chemistry, 50, 8238.

Cox, N., Rapatskiy, L., Su, J.H., Pantazis, D.A., Sugiura, M., Kulik, L., Dorlet, P., Rutherford, A.W., Neese, F., Boussac, A., Lubitz, W. and Messinger, J., 2011: *Effect of* Ca^{2+}/Sr^{2+} *substitution on the electronic structure of the oxygen-evolving complex of Photosystem II: A combined multifrequency EPR,* ^{55}*Mn-ENDOR, and DFT study of the* S_2 *state, Journal of the American Chemical Society, 133, 3635. Addition published:* Journal of the American Chemical Society, 133, 14149.

Crimmin, M.R., Rosebrugh, L.E., Tomson, N.C., Weyhermüller, T., Bergman, R.G., Toste, F.D. and Wieghardt, K., 2011: $[(TMEDA)Co(NO)_2][BPh_4]$*: A versatile synthetic entry point to four and five coordinate* $\{Co(NO)_2\}^{10}$ *complexes*, Journal of Organometallic Chemistry, 696, 3974.

DeBeer, S.: *X-ray Absorption Spectroscopy*. In: Ribbe, M. (ed.), Nitrogen Fixation: Methods and Protocols, Humana Press, New York, 2011.

Delgado-Jaime, M.U., Dible, B.R., Chiang, K.P., Brennessel, W.W., Bergmann, U., Holland, P.L. and DeBeer, S., 2011: *Identification of a Single Light Atom within a Multinuclear Metal Cluster Using Valence-to-Core X-ray Emission Spectroscopy*, Inorganic Chemistry, 50, 10709.

Drew, S.C., Baldas, J. and Boas, J.F., 2011: *The Unusual Magnetic Resonance Properties of Trigonal Prismatic Tc and Re Complexes*, Applied Magnetic Resonance, 40, 427.

Drew, S.C. and Barnham, K.J., 2011: *The Heterogeneous Nature of* Cu^{2+} *Interactions with Alzheimer's Amyloid- Peptide*, Accounts of Chemical Research, 44, 1146.

Drew, S.C., Reijerse, E., Quentmeier, A., Rother, D., Friedrich, C.G. and Lubitz, W., 2011: *Spectroscopic characterization of the molybdenum cofactor of the sulfane dehydrogenase SoxCD from Paracoccus pantotrophus*, Inorganic Chemistry, 50, 409.

Erdem, Ö.F., Schwartz, L., Stein, M., Silakov, A., Kaur-Ghumaan, S., Huang, P., Ott, S., Reijerse, E.J. and Lubitz, W., 2011: *A model of the [FeFe] hydrogenase active site with a biologically relevant azadithiolate bridge: a spectroscopic and theoretical investigation*, Angewandte Chemie International Edition, 50, 1439. German translation published: *Ein Modell des aktiven Zentrums der [FeFe]-Hydrogenasen mit biologisch relevanter Azadithiolat-Brücke: Eine spektroskopische und theoretische Untersuchung*, Angewandte Chemie, 123, 1475.

Gansäuer, A., Knebel, K., Kube, C., van Gastel, M., Cangönül, A., Daasbjerg, K., Hangele, T., Hülsen, M., Dolg, M., Friedrich, J., 2011: *Radical 4-exo Cyclizations via Template Catalysis*, Chemistry. A European Journal, 18, 2591.

Gass, I.A., Gartshore, C.J., Lupton, D.W., Moubaraki, B., Nafady, A., Bond, A.M., Boas, J.F., Cashion, J.D., Milsmann, C., Wieghard, K. and Murray, K.S., 2011: *Anion Dependent Redox Changes in Iron Bis-terdentate Nitroxide {NNO} Chelates*, Inorganic Chemistry, 50, 3052.

Gennari, M., Orio, M., Pecaut, J., Bothe, E., Neese, F., Collomb, M.N. and Duboc, C., 2011: *Influence of Mixed Thiolate/Thioether versus Dithiolate Coordination on the Accessibility of the Uncommon +I and +III Oxidation States for the Nickel Ion: An Experimental and Computational Study*, Inorganic Chemistry, 50, 3707.

Gennari, M., Pecaut, J., DeBeer, S., Neese, F., Collomb, M.N. and Duboc, C., 2011: *A Fully Delocalized Mixed-Valence Bis- (Thiolato) Dicopper Complex: A Structural and Functional Model of the Biological* Cu_A *Center*, Angewandte Chemie-International Edition, 50, 5662.

Gennari, M., Retegan, M., DeBeer, S., Pecaut, J., Neese, F., Collomb, M.N. and Duboc, C., 2011: *Experimental and Computational Investigation of Thiolate Alkylation in* Ni^{II} *and* Zn^{II} *Complexes: Role of the Metal on the Sulfur Nucleophilicity*, Inorganic Chemistry, 50,10047.

Görner, H., 2011: *Photoreduction of nitro-1,4-naphthoquinones in solution*, Journal of Photochemistry and Photobiology A-Chemistry, 224,135.

Görner, H., 2011: *Direct Photoreduction and Ketone-Sensitized Reduction of Nitrospirobenzopyranindolines by Aliphatic Amines*, Journal of Physical Chemistry A, 115, 8208.

Görner, H., 2011: *Charge transfer fluorescence of trans-stryrylpyridinium iodides*, Journal of Photochemistry and Photobiology A-Chemistry, 218, 199.

Görner, H., Miskolczy, Z., Megyesi, M. and Biczok, L., 2011: *Photooxidation of Alkaloids: Considerable Quantum Yield Enhancement by Rose Bengal-sensitized Singlet Molecular Oxygen Generation*, Photochemistry and Photobiology, 87, 1315.

Görner, H., Miskolczy, Z., Megyesi, M. and Biczok, L., 2011: *Photoreduction and Ketone-sensitized Reduction of Alkaloids*, Photochemistry and Photobiology, 87, 284.

Greco, C., Silakov, A., Bruschi, M., Ryde, U., De Gioia, L. and Lubitz, W., 2011: *Magnetic properties of [FeFe]-hydrogenases: A theoretical investigation based on extended QM and QM/MM models of the H-cluster and its surroundings*, European Journal of Inorganic Chemistry, 1043.

Gruen, H. and Görner, H., 2011: *Reduction of isoviolanthrone by reaction with photogenerated radicals*, Photochemical & Photobiological Sciences, 10, 1527.

Hansen, A., Liakos, D.G. and Neese, F., 2011: *Efficient and accurate local single reference correlation methods for high-spin open-shell molecules using pair natural orbitals*, Journal of Chemical Physics, 135, 214102.

Hazra, S., Sasmal, S., Fleck, M., Grandjean, F., Sougrati, M.T., Ghosh, M., Harris, T.D., Bonville, P., Long, G.J. and Mohanta, S., 2011: *Slow magnetic relaxation and electron delocalization in an S=9/2 iron(II/III) complex with two crystallographically inequivalent iron sites*, Journal of Chemical Physics, 134, 174507.

He, C., Neya, S. and Knipp, M., 2011: *Breaking the proximal* $Fe^{II}N_{His}$ *bond in heme proteins through local structural tension: Lessons from the beme b proteins nitrophorin 4, nitrophorin 7, and related site-directed mutant proteins*, Biochemistry, 50, 8559.

Holzwarth, A.R., 2011: *Chlorophyll-chlorophyll charge transfer quenching is the main mechanism of non-photochemical quenching in higher plants*, European Biophysics Journal with Biophysics Letters, 40, S176.

Hoppe, A., Pandelia, M.E., Gärtner, W. and Lubitz, W., 2011: *[Fe_4S_4]- and [Fe_3S_4]-cluster formation in synthetic peptides*, Biochimica et Biophysica Acta-Bioenergetics, 1807, 1414.

Hoyle, M.A.M., Pantazis, D.A., Burton, H.M., McDonald, R. and Rosenberg, L., 2011: *Benzonitrile Adducts of Terminal Diarylphosphido Complexes: Preparative Sources of „$Ru=PR_2$“*, Organometallics, 30, 6458.

Izsak, R. and Neese, F., 2011: *An overlap fitted chain of spheres exchange method*, Journal of Chemical Physics, 135, 144105.

Jana, A., Koner, R., Weyhermüller, T., Lemoine, P., Ghosh, M. and Mohanta, S., 2011: *Syntheses, crystal structures and magnetic properties of [2 x 1+1 x 2] heterotetrametallic and [1 x 1+1 x 1] heterodimetallic cocrystals of copper(II) and iron(II/III)*, Inorganica Chimica Acta, 375, 263.

Kajiwara, T., Wagner R., Bill E., Weyhermüller, T., and Chaudhuri, P., 2011: Nonoxo 5-coordinate and 6-coordinate Vanadium(IV) Complexes with Their Precursor $[LV^{III}(CH_3OH)]^0$, where L = A Trianionic Aminetris(phenolate)-[N,O,O,O] Donor Ligand. A Magnetostructural and EPR Study, Dalton Transactions, 40, 12719.

Khusniyarov, M.M., Bill, E., Weyhermüller, T., Bothe, E. and Wieghardt, K., 2011: *Hidden Noninnocence: Theoretical and Experimental Evidence for Redox Activity of a beta-Diketiminate(1-) Ligand*, Angewandte Chemie-International Edition, 50, 1652.

Knipp, M. and He, C., 2011: *Nitrophorins: Nitrite disproportionation reaction and other novel functionalities of insect heme-based nitric oxide transport proteins*, IUBMB Life, 63, 304.

Knipp, M., He, C. and Ogata, H., 2011: *Nitrite disproportionation reaction: Investigations on the mechanism of the conversion of nitrite into nitric oxide at the ferriheme center of nitrophorins at blood plasma pH*, Nitric Oxide-Biology and Chemistry, 24, S33.

Knipp, M., Taing, J.J. and He, C., 2011: *Reduction of the lipocalin type heme containing protein nitrophorin - Sensitivity of the fold-stabilizing cysteine disulfides toward routine heme-iron reduction*, Journal of Inorganic Biochemistry, 105, 1405.

Lancaster, K.M., Roemelt, M., Ettenhuber, P., Hu, Y.L., Ribbe, M.W., Neese, F., Bergmann, U. and DeBeer, S., 2011: *X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor*, Science, 334, 974.

Losi, A. and Gärtner, W., 2011: *Old Chromophores, New Photoactivation Paradigms, Trendy Applications: Flavins in Blue Light-Sensing Photoreceptors*, Photochemistry and Photobiology, 87, 491.

Manikandamathavan, V.M., Parameswari, R.P., Weyhermüller, T., Vasanthi, H.R. and Nair, B.U., 2011: *Cytotoxic copper (II) mixed ligand complexes: Crystal structure and DNA cleavage activity*, European Journal of Medicinal Chemistry, 46, 4537.

Mansurova, M., Scheercousse, P., Simon, J., Kluth, M. and Gärtner, W., 2011: *Chromophore Exchange in the Blue Light-Sensitive Photoreceptor YtvA from Bacillus subtilis*, ChemBioChem, 12, 641.

Marchanka, A., Maier, S.K., Höger, S. and van Gastel, M., 2011: *Photoinduced Charge Separation in an Organic Donor-Acceptor Hybrid Molecule*, Journal of Physical Chemistry B, 115, 13526.

Mark, G., Naumov, S. and von Sonntag, C., 2011: *The Reaction of Ozone with Bisulfide (*HS^-*) in Aqueous Solution - Mechanistic Aspects*, Ozone-Science & Engineering, 33, 37.

Meyer, A., van Gastel, M., 2011: *An EPR and ENDOR Study of the Frozen Ammoniated Electron at Low Alkali-Metal Concentrations*, Journal of Physical Chemistry A, 115, 1939.

Millo, D., Hildebrandt, P., Pandelia, M.E., Lubitz, W. and Zebger, I., 2011: *SEIRA spectroscopy of the electrochemical activation of an immobilized [NiFe] hydrogenase under turnover and non-turnover conditions*, Angewandte Chemie-International Edition, 50, 2632. German translation published: *SEIRA-spektroskopische Untersuchung der elektrochemischen Aktivierung einer immobilisierten [NiFe]-Hydrogenase unter Turnover- und Non-Turnover-Bedingungen*, Angewandte Chemie, 123, 2690.

Miloslavina, Y., de Bianchi, S., Dall'Osto, L., Bassi, R. and Holzwarth, A.R., 2011: *Quenching in Arabidopsis thaliana Mutants Lacking Monomeric Antenna Proteins of Photosystem II*, Journal of Biological Chemistry, 286, 36830.

Miskolczy, Z., Megyesi, M., Biczok, L. and Görner, H., 2011: *Effect of electrolytes, nucleotides and DNA on the fluorescence of flavopereirine natural alkaloid*, Photochemical & Photobiological Sciences, 10, 592.

Misra, S.K., Buckmaster, H.A., Reijerse, E., Subramanian, S. and Krishna, M.C.: *Spectrometers*. In: Misra, S.K. (ed.), Multifrequency Electron Paramagnetic Resonance: Theory and Applications. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, 115.

Misra, S.K., Möbius, K. and Savitsky, A.: *Multifrequency EPR on photosynthetic systems*. In: Misra, S.K. (ed.), Multifrequency Electron Paramagnetic Resonance: Theory and Applications. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, 875.

Möbius, K., Lubitz, W. and Savitsky, A., 2011: *Photo-induced electron spin polarization in chemical and biological reactions: Probing structure and dynamics of transient intermediates by multifrequency EPR spectroscopy*, Applied Magentic Resonance, 41, 113.

Mroginski, M.A., Kaminski, S., von Stetten, D., Ringsdorf, S., Gärtner, W., Essen, L.O. and Hildebrandt, P., 2011: *Structure of the Chromophore Binding Pocket in the Pr State of Plant Phytochrome phyA*, Journal of Physical Chemistry B, 115, 1220.

Nakayama, K., Heise, I., Görner, H. and Gärtner, W., 2011: *Peptide Release upon Photoconversion of 2-Nitrobenzyl Compounds into Nitroso Derivatives*, Photochemistry and Photobiology, 87, 1031.

Naumov, S. and von Sonntag, C., 2011: *Standard Gibbs Free Energies of Reactions of Ozone with Free Radicals in Aqueous Solution: Quantum-Chemical Calculations*, Environmental Science & Technology, 45, 9195.

Naumov, S. and von Sonntag, C., 2011: *The reaction of $^{\bullet}OH$ with O_2, the decay of $O_3^{\bullet}$ and the pK_a of $HO_3^{\bullet}$- interrelated questions in aqueous free-radical chemistry*, Journal of Physical Organic Chemistry, 24, 600.

Neese, F.: *First principles approach to Spin-Hamiltonian parameters*. In: Misra, S.K. (ed.), Multifrequency Electron Paramagnetic Resonance: Theory and Applications. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, 295.

Neese, F. and Pantazis, D.A., 2011: *What is not required to make a single molecule magnet*, Faraday Discussions, 148, 229.

Neuba, A., Florke, U., Meyer-Klaucke, W., Salomone-Stagni, M., Bill, E., Bothe, E., Hofer, P. and Henkel, G., 2011: *The Trinuclear Copper(I) Thiolate Complexes$[Cu_3(NGuaS)_3]^{0/1+}$ and their Dimeric Variants $[Cu_6(NGuaS)_6]^{1+/2+/3+}$ with Biomimetic Redox Properties*, Angewandte Chemie-International Edition, 50, 4503.

Neuba, A., Flörke, U., Meyer-Klaucke, W., Salomone-Stagni, M., Bill, E., Bothe, E., Höfer, P. and Henkel, G., 2011: *Die dreikernigen Kupfer(I)-Thiolat-Komplexe $[Cu_3(NGuaS)_3]^{0/1+}$ und ihre dimeren Varianten $[Cu_6(NGuaS)_6]^{1+/2+/3+}$ mit biomimetischen Redoxeigenschaften*, Angewandte Chemie, 123, 4596.

Nippe, M., Bill, E. and Berry, J.F., 2011: *Group 6 Complexes with Iron and Zinc Heterometals: Understanding the Structural, Spectroscopic, and Electrochemical Properties of a Complete Series of M≡M•••M’ Compounds*, Inorganic Chemistry, 50, 7650.

Ocakoglu, K., Bayrak, E., Onursal, M., Yilmaz, O., Lambrecht, F.Y. and Holzwarth, A.R., 2011: *Evaluation of ^{99m}Tc-Pheophorbide-a use in infection imaging: A rat model*, Applied Radiation and Isotopes, 69, 1165.

Oelgemöller, M., Mattay, J. and Görner, H., 2011: *Direct Photooxidation and Xanthene-Sensitized Oxidation of Naphthols: Quantum Yields and Mechanism*, Journal of Physical Chemistry A, 115, 280.

Ostroumov, E.E., Müller, M.G., Reus, M. and Holzwarth, A.R., 2011: *On the Nature of the „Dark S*" Excited State of β-Carotene*, Journal of Physical Chemistry A, 115, 3698.

Paine, T.K., Sheet, D., Weyhermüller, T. and Chaudhuri, P., 2011: *Iron(II)-Mediated Reductive Cleavage of Disulfide and Diselenide Bonds: Iron(III) Complexes of Mixed O,X,O and O,X (X = S, Se) Donor Ligands*, European Journal of Inorganic Chemistry, 5250.

Pandelia, M.E., Nitschke, W., Infossi, P., Giudici-Orticoni, M.T., Bill, E. and Lubitz, W., 2011: *Characterization of a unique [FeS] cluster in the electron transfer chain of the oxygen tolerant [NiFe] hydrogenase from Aquifex aeolicus*, Proceedings of the National Academy of Sciences of the United States of America, 108, 6097.

Pandit, A., Morosinotto, T., Reus, M., Holzwarth, A.R., Bassi, R. and de Groot, H.J.M., 2011: *First solid-state NMR analysis of uniformly ^{13}C-enriched major light-harvesting complexes from Chlamydomonas reinhardtii and identification of protein and cofactor spin clusters*, Biochimica et Biophysica Acta-Bioenergetics, 1807, 437.

Pantazis, D.A. and Neese, F., 2011: *All-Electron Scalar Relativistic Basis Sets for the Actinides*, Journal of Chemical Theory and Computation, 7, 677.

Pedrolli, D.B., Nakanishi, S., Barile, M., Mansurova, M., Carmona, E.C., Lux, A., Gärtner, W. and Mack, M., 2011: *The antibiotics roseoflavin and 8-demethyl-8-amino-riboflavin from Streptomyces davawensis are metabolized by human flavokinase and human FAD synthetase*, Biochemical Pharmacology, 82, 1853.

Petrenko, T., Kossmann, S. and Neese, F., 2011: *Efficient time-dependent density functional theory approximations for hybrid density functionals: Analytical gradients and parallelization*, Journal of Chemical Physics, 134, 054116.

Pfaff, F.F., Kundu, S., Risch, M., Pandian, S., Heims, F., Pryjomska-Ray, I., Haack, P., Metzinger, R., Bill, E., Dau, H., Comba, P. and Ray, K., 2011: *An Oxocobalt(IV) Complex Stabilized by Lewis Acid Interactions with Scandium(III) Ions*, Angewandte Chemie-International Edition, 50, 1711.

Presow, S.R., Ghosh, M., Bill, E., Weyhermüller, T. and Wieghardt, K., 2011: *Molecular and electronic structures of new iron complexes containing N,S-coordinated o-iminothionebenzosemiquinonate(1-) π radical ligands: An experimental and density functional theoretical study*, Inorganica Chimica Acta, 374, 226.

Raffelberg, S., Mansurova, M., Gärtner, W. and Losi, A., 2011: *Modulation of the Photocycle of a LOV Domain Photoreceptor by the Hydrogen-Bonding Network*, Journal of the American Chemical Society, 133, 5346.

Rajalakshmi, S., Weyhermüller, T., Freddy, A.J., Vasanthi, H.R. and Nair, B.U., 2011: *Anomalous behavior of pentacoordinate copper complexes of dimethylphenanthroline and derivatives of terpyridine ligands: Studies on DNA binding, cleavage and apoptotic activity*, European Journal of Medicinal Chemistry, 46, 608.

Rather, L.J., Bill, E., Ismail, W. and Fuchs, G., 2011: *The reducing component BoxA of benzoyl-coenzyme A epoxidase from Azoarcus evansii is a [4Fe-4S] protein*, Biochimica et Biophysica Acta-Proteins and Proteomics, 1814, 1609.

Rather, L.J., Weinert, T., Demmer, U., Bill, E., Ismail, W., Fuchs, G. and Ermler, U., 2011: *Structure and Mechanism of the Diiron Benzoyl-Coenzyme A Epoxidase BoxB*, The Journal of Biological Chemistry, 286, 29241.

Riplinger, C. and Neese, F., 2011: *The Reaction Mechanism of Cytochrome P450 NO Reductase: A Detailed Quantum Mechanics/Molecular Mechanics Study*, ChemPhys Chem, 12, 3192.

Rodriguez, M.M., Bill, E., Brennessel, W.W. and Holland, P.L., 2011: *N_2 Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex*, Science, 334, 780.

Rohmer, T., Matysik, J. and Mark, F., 2011: *Solvation and Crystal Effects in Bilirubin Studied by NMR Spectroscopy and Density Functional Theory*, Journal of Physical Chemistry A, 115, 11696.

Roy, A.S., Biswas, M.K., Weyhermüller, T. and Ghosh, P., 2011: *Unsymmetrical diimine complexes of iron(II) and manganese(II): synthesis, structure and photoluminescence of an isomer*, Dalton Transactions, 40, 146.

Russell, S.K., Milsmann, C., Lobkovsky, E., Weyhermüller, T. and Chirik, P.J., 2011: *Synthesis, Electronic Structure, and Catalytic Activity of Reduced Bis(aldimino)pyridine Iron Compounds: Experimental Evidence for Ligand Participation*, Inorganic Chemistry, 50, 3159.

Safaei, E., Rasouli, M., Weyhermüller, T. and Bill, E., 2011: *Synthesis and characterization of binuclear [ONXO]-type amine-bis(phenolate) copper(II) complexes*, Inorganica Chimica Acta, 375, 158.

Sathyaraj, G., Weyhermüller, T. and Nair, B.U., 2011: *Crystal Structure and Thermal Studies of Ruthenium(II) Bisimidazolylterpyridine Hexafluorophosphate Complex*, Journal of Chemical Crystallography, 41, 353.

Savitsky, A., Dubinskii, A.A., Zimmermann, H., Lubitz, W. and Möbius, K., 2011: *High-field dipolar electron paramagnetic resonance (EPR) spectroscopy of nitroxide biradicals for determining three-dimensional structures of biomacromolecules in disordered solids*, Journal of Physical Chemistry B, 115, 11950.

Scarborough, C.C., Sproules, S., Weyhermüller, T., DeBeer, S. and Wieghardt, K., 2011: *Electronic and Molecular Structures of the Members of the Electron Transfer Series* $[Cr(^{t}bpy)(3)]^{n}$ *(n=3+, 2+, 1+, 0): An X-ray Absorption Spectroscopic and Density Functional Theoretical Study*, Inorganic Chemistry, 50, 12446.

Scarborough, C.C. and Wieghardt, K., 2011: *Electronic Structure of 2,2 '-Bipyridine Organotransition-Metal Complexes. Establishing the Ligand Oxidation Level by Density Functional Theoretical Calculations*, Inorganic Chemistry, 50, 9773.

Schansker, G., Toth, S.Z., Kovacs, L., Holzwarth, A.R. and Garab, G., 2011: *Evidence for a fluorescence yield change driven by a light-induced conformational change within photosystem II during the fast chlorophyll a fluorescence rise*, Biochimica et Biophysica Acta-Bioenergetics, 1807, 1032.

Schansker, G., Toth, S.Z., Kovacs, L., Holzwarth, A.R. and Garab, G., 2011: *Variable chlorophyll fluorescence: in part a yield change due to light-induced conformational change*, European Biophysics Journal with Biophysics Letters, 40, S179.

Sedoud, A., Cox, N., Sugiura, M., Lubitz, W., Boussac, A. and Rutherford, A.W., 2011: *Semiquinone-iron complex of photosystem II: EPR signals assigned to the low-field edge of the ground state doublet of* $Q_A^{\cdot -}\ Fe^{2+}$ *and* $Q_B^{\cdot -}\ Fe^{2+}$, Biochemistry, 50, 6012.

Sedoud, A., Kastner, L., Cox, N., El-Alaoui, S., Kirilovsky, D. and Rutherford, A.W., 2011: *Effects of formate binding on the quinone-iron electron acceptor complex of photosystem II*, Biochimica et Biophysica Acta-Bioenergetics, 1807, 216.

Shevela, D., Beckmann, K., Clausen, J., Junge, W. and Messinger, J., 2011: *Membrane-inlet mass spectrometry reveals a high driving force for oxygen production by photosystem II*, Proceedings of the National Academy of Sciences of the United States of America, 108, 3602.

Silakov, A., Reijerse, E.J. and Lubitz, W., 2011: *Unraveling the electronic properties of the photoinduced states of the H-cluster in the [FeFe] hydrogenase from D. desulfuricans*, European Journal of Inorganic Chemistry, 1056.

Slavnova, T.D., Görner, H. and Chibisov, A.K., 2011: *Cyanine-Based J-Aggregates as a Chirality-Sensing Supramolecular System*, Journal of Physical Chemistry B, 115, 3379.

Song, C., Psakis, G., Lang, C., Mailliet, J., Gärtner, W., Hughes, J. and Matysik, J., 2011: *Two ground state isoforms and a chromophore D-ring photoflip triggering extensive intramolecular changes in a canonical phytochrome*, Proceedings of the National Academy of Sciences of the United States of America, 108, 3842.

Song, C., Psakis, G., Lang, C., Mailliet, J., Zaanen, J., Gärtner, W., Hughes, J. and Matysik, J., 2011: *On the Collective Nature of Phytochrome Photoactivation*, Biochemistry, 50, 10987.

Sproules, S., Banerjee, P., Weyhermüller, T., Yan, Y., Donahue, J.P. and Wieghardt, K., 2011: *Monoanionic Molybdenum and Tungsten Tris(dithiolene) Complexes: A Multifrequency EPR Study*, Inorganic Chemistry, 50, 7106.

Sproules, S., Weyhermüller, T., Goddard, R. and Wieghardt, K., 2011: *The Rhenium Tris(dithiolene) Electron Transfer Series: Calibrating Covalency*, Inorganic Chemistry, 50, 12623.

Sproules, S. and Wieghardt, K., 2011: *Dithiolene radicals: Sulfur K-edge X-ray absorption spectroscopy and Harry's intuition*, Coordination Chemistry Reviews, 255, 837.

Stierl, M., Stumpf, P., Udwari, D., Gueta, R., Hagedorn, R., Losi, A., Gärtner, W., Petereit, L., Efetova, M., Schwarzel, M., Oertner, T.G., Nagel, G. and Hegemann, P., 2011: *Light Modulation of Cellular cAMP by a Small Bacterial Photoactivated Adenylyl Cyclase, bPAC, of the Soil Bacterium Beggiatoa*, Journal of Biological Chemistry, 286, 1181.

Strautmann, J.B.H., von Richthofen, C.G.F., Heinze-Bruckner, G., DeBeer, S., Bothe, E., Bill, E., Weyhermüller, T., Stammler, A., Bogge, H. and Glaser, T., 2011: *Molecular and Electronic Structures of Dinuclear Iron Complexes Incorporating Strongly Electron-Donating Ligands: Implications for the Generation of the One- and Two-Electron Oxidized Forms*, Inorganic Chemistry, 50, 155.

Su, J.-H., Lubitz, W. and Messinger, J., 2011: *Addition/ Correction : Probing mode and site of substrate water binding to the oxygen-evolving complex in the S_2 state of photosystem II by ^{17}O-HYSCORE Spectroscopy*, Journal of the American Chemical Society, 133, 12317.

Su, J.H., Cox, N., Ames, W., Pantazis, D.A., Rapatskiy, L., Lohmiller, T., Kulik, L.V., Dorlet, P., Rutherford, A.W., Neese, F., Boussac, A., Lubitz, W. and Messinger, J., 2011: *The electronic structures of the S_2 states of the oxygen-evolving complexes of photosystem II in plants and cyanobacteria in the presence and absence of methanol*, Biochimica et Biophysica Acta-Bioenergetics, 1807, 829.

Surawatanawong, P., Sproules, S., Neese, F. and Wieghardt, K., 2011: *Electronic Structures and Spectroscopy of the Electron Transfer Series* $[Fe(NO)L_2]^z$ *(z=1+, 0, 1-, 2 ,3-; L = Dithiolene)*, Inorganic Chemistry, 50, 12064.

Tian, Y.X., Camacho, R., Thomsson, D., Reus, M., Holzwarth, A.R. and Scheblykin, I.G., 2011: *Organization of Bacteriochlorophylls in Individual Chlorosomes from Chlorobaculum tepidum Studied by 2-Dimensional Polarization Fluorescence Microscopy*, Journal of the American Chemical Society, 133, 17192.

Tomson, N.C., Crimmin, M.R., Petrenko, T., Rosebrugh, L.E., Sproules, S., Boyd, W.C., Bergman, R.G., DeBeer, S., Toste, F.D. and Wieghardt, K., 2011: *A Step beyond the Feltham-Enennark Notation: Spectroscopic and Correlated ab Initio Computational Support for an Antiferromagnetically Coupled M(II)-*$(NO)^-$ *Description of Tp*M(NO) (M = Co, Ni)*, Journal of the American Chemical Society, 133, 18785.

Tomson, N.C., Labios, L.A., Weyhermüller, T., Figueroa, J.S. and Wieghardt, K., 2011: *Redox Noninnocence of Nitrosoarene Ligands in Transition Metal Complexes*, Inorganic Chemistry, 50, 5763.

Veber, S.L., Fedin, M.V., Maryunina, K.Y., Potapov, A., Goldfarb, D., Reijerse, E., Lubitz, W., Sagdeev, R.Z., Ovcharenko, V.I. and Bagryanskaya, E.G., 2011: *Temperature-dependent exchange interaction in molecular magnets* $Cu(hfac)_2L^R$ *studied by EPR: Methodology and Interpretations*, Inorganic Chemistry, 50, 10204.

Von Sonntag, C. and Schmidt, T.C.: *Sauberes Wasser mit Ozon*, In: Zellner, R. and Zellner, R. (eds.), Chemie über den Wolken …und darunter, Wiley-VCH, Weinheim, 2011, pp. 101.

Weyhermüller, T., Wagner, R., Biswas, B. and Chaudhuri, P., 2011: *A non-linear (2,2,2) alkoxo-bridging in a* $Fe^{III}{}_4O_6$ *core potentially relevant to iron-tunicates*, Inorganica Chimica Acta, 374, 140.

Weyhermüller, T., Wagner, R. and Chaudhuri, P., 2011: *Asymmetrically Dibridged Diiron(III) Complexes with Aminebis(phenoxide)-Based Ligands for a Magnetostructural Study*, European Journal of Inorganic Chemistry, 2547.

Zhang, Y.Z. and Görner, H., 2011: *Photooxidation of lysozyme or serum albumin bound to meso-tetra-arylporphyrins*, Dyes and Pigments, 90, 163.

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2012

Abbruzzetti, S., He, C., Ogata, H., Bruno, S., Viappiani, C. and Knipp, M., 2012: *Heterogeneous kinetics of the carbon monoxide association and dissociation reaction to nitrophorin 4 and 7 coincide with structural heterogeneity of the gate-loop*, Journal of the American Chemical Society, 134, 9986.

Adamska, A., Silakov, A., Lambertz, C., Rüdiger, O., Happe, T., Reijerse, E. and Lubitz, W., 2012: *Identification and characterization of the „super-reduced" state of the H-cluster in [FeFe] hydrogenase: A new building block for the catalytic cycle?*, Angewandte Chemie-International Edition, 51, 11458. German translation published: *Identifizierung und Charakterisierung des "super-reduzierten" Zustands des H-Clusters von [FeFe]-Hydrogenasen: Ein neuer Baustein im katalytischen Zyklus?*, Angewandte Chemie, 124, 11624.

Albarracin, V.H., Pathak, G.P., Douki, T., Cadet, J., Borsarelli, C.D., Gärtner, W. and Farias, M.E., 2012: *Extremophilic Acinetobacter Strains from High-Altitude Lakes in Argentinean Puna: Remarkable UV-B Resistance and Efficient DNA Damage Repair*, Origins of Life and Evolution of Biospheres, 42, 201.

Albrecht, C., Shi, L.L., Perez, J.M., van Gastel, M., Schwieger, S., Neese, F. and Streubel, R., 2012: *Deoxygenation of Coordinated Oxaphosphiranes: A New Route to P=C Double-Bond Systems*, Chemistry-A European Journal, 18, 9780.

Aliaga-Alcalde, N., Rodriguez, L., Ferbinteanu, M., Höfer, P. and Weyhermüller, T., 2012: *Crystal Structure, Fluorescence, and Nanostructuration Studies of the First* Zn^{II} *Anthracene-Based Curcuminoid*, Inorganic Chemistry, 51, 864.

Argirevic, T., Riplinger, C., Stubbe, J., Neese, F. and Bennati, M., 2012: *ENDOR Spectroscopy and DFT Calculations: Evidence for the Hydrogen-Bond Network Within* $\alpha 2$ *in the PCET of E. coli Ribonucleotide Reductase*, Journal of the American Chemical Society, 134, 17661.

Atanasov, M., Comba, P. and Helmle, S., 2012: *Cyanide-Bridged* Fe^{III}-Cu^{II} *Complexes: Jahn-Teller Isomerism and Its Influence on the Magnetic Properties*, Inorganic Chemistry, 51, 9357.

Atanasov, M., Comba, P., Helmle, S., Müller, D. and Neese, F., 2012: *Zero-Field Splitting in a Series of Structurally Related Mononuclear* Ni^{II} *-Bispidine Complexes*, Inorganic Chemistry, 51, 12324.

Atanasov, M., Ganyushin, D., Sivalingam, K. and Neese, F.: *Modern first principles view on Ligand Field Theory Through the Eyes of Correlated Multireference Wavefunctions*. In: Mingos, D.M.P., Day, P. and Dahl, J.P. (eds.), Molecular Electronic Structures of Transition Metal Complexes II. Springer, Berlin, pp. 149.

Auer, A.A., Richter, A., Berezkin, A.V., Guseva, D.V. and Spange, S., 2012: *Theoretical Study of Twin Polymerization - From Chemical Reactivity to Structure Formation*, Macromolecular Theory and Simulations, 21, 615.

Bachler, V., 2012: *A quantum chemical calculation on* $Fe(CO)_5$ *revealing the operation of the Dewar-Chatt-Duncanson model*, Journal of Computational Chemistry, 33, 1936.

Bauer, D., Montforts, F.P., Losi, A. and Görner, H., 2012: *Photoprocesses of chlorin e6 glucose derivatives*, Photochemical & Photobiological Sciences, 11, 925.

Benkhäuser-Schunk, C., Wezisla, B., Urbahn, K., Kiehne, U., Daniels, J., Schnakenburg, G., Neese, F. and Lutzen, A., 2012: *Synthesis, Chiral Resolution, and Absolute Configuration of Functionalized Tröger's Base Derivatives: Part II*, Chempluschem, 77, 396.

Biczok, L. and Görner, H., 2012: *Photophysical properties and photoreduction of N-acetyl- and N-benzoylphthalimides*, Chemical Physics, 392, 10.

Birk, T., Pedersen, K.S., Thuesen, C.A., Weyhermüller, T., Schau-Magnussen, M., Piligkos, S., Weihe, H., Mossin, S., Evangelisti, M. and Bendix, J., 2012: *Fluoride Bridges as Structure-Directing Motifs in 3d-4f Cluster Chemistry*, Inorganic Chemistry, 51, 5435.

Bowman, A.C., Sproules, S. and Wieghardt, K., 2012: *Electronic Structures of the* $[V(tbpy)_3]z$ *(z = 3+, 2+, 0, 1–) Electron Transfer Series*, Inorganic Chemistry, 51, 3707.

Braslavsky, S.E., Cosa, G., Sherman, B. and Thomas, A.H., 2012: *Introduction to the Symposium-in-Print: 21st Conference of the Inter-American Photochemical Society, Mendoza, Argentina, May 2011*, Photochemistry and Photobiology, 88, 761.

Braslavsky, S.E. and Holzwarth, A.R., 2012: *Role of Carotenoids in Photosystem II (PSII) Reaction Centers*, International Journal of Thermophysics, 33, 2021.

Bridges, H.R., Bill, E. and Hirst, J., 2012: *Mössbauer Spectroscopy on Respiratory Complex I: The Iron-Sulfur Cluster Ensemble in the NADH-Reduced Enzyme Is Partially Oxidized*, Biochemistry, 51, 149.

Burger, B., Demeshko, S., Bill, E., Dechert, S. and Meyer, F., 2012: *The Carboxylate Twist: Hysteretic Bistability of a High-Spin Diiron(II) Complex Identified by Mössbauer Spectroscopy*, Angewandte Chemie-International Edition, 51, 10045.

Bykov, D. and Neese, F., 2012: *Reductive activation of the heme iron-nitrosyl intermediate in the reaction mechanism of cytochrome c nitrite reductase: a theoretical study*, Journal of Biological Inorganic Chemistry, 17, 741.

Cardona, T., Sedoud, A., Cox, N. and Rutherford, A.W., 2012: *Charge separation in Photosystem II: A comparative and evolutionary overview*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 26.

Chiang, K.P., Scarborough, C.C., Horitani, M., Lees, N.S., Ding, K.Y., Dugan, T.R., Brennessel, W.W., Bill, E., Hoffman, B.M. and Holland, P.L., 2012: *Characterization of the Fe-H Bond in a Three-Coordinate Terminal Hydride Complex of Iron(I)*, Angewandte Chemie-International Edition, 51, 3658.

Cho, K., Leeladee, P., McGown, A.J., DeBeer, S. and Goldberg, D.P., 2012: *A High-Valent Iron-Oxo Corrolazine Activates C-H Bonds via Hydrogen-Atom Transfer*, Journal of the American Chemical Society, 134, 7392.

Christian, G.J., Ye, S.F. and Neese, F., 2012: *Oxygen activation in extradiol catecholate dioxygenases - a density functional study*, Chemical Science, 3, 1600.

Codesido, N.O., De Candia, A.G., Weyhermüller, T., Olabe, J.A. and Slep, L.D., 2012: *An Electron-Rich* $\{RuNO\}^6$ *Complex: trans-*$[Ru(DMAP)_4(NO)(OH)]^{2+}$ *- Structure and Reactivity*, European Journal of Inorganic Chemistry, 4301.

Cowley, R.E., Christian, G.J., Brennessel, W.W., Neese, F. and Holland, P.L., 2012: *A Reduced (ß-Diketiminato)iron Complex with End-On and Side-On Nitriles: Strong Backbonding or Ligand Non-Innocence?*, European Journal of Inorganic Chemistry, 479.

Darmon, J.M., Stieber, S.C.E., Sylvester, K.T., Fernandez, I., Lobkovsky, E., Semproni, S.P., Bill, E., Wieghardt, K., DeBeer, S. and Chirik, P.J., 2012: *Oxidative Addition of Carbon-Carbon Bonds with a Redox-Active Bis(imino)pyridine Iron Complex*, Journal of the American Chemical Society, 134, 17125.

Delgado-Jaime, M.U. and DeBeer, S., 2012: *Expedited analysis of DFT outputs: Introducing moanalyzer*, Journal of Computational Chemistry, 33, 2180.

Desrochers, P.J., Sutton, C.A., Abrams, M.L., Ye, S.F., Neese, F., Telser, J., Ozarowski, A. and Krzystek, J., 2012: *Electronic Structure of Nickel(II) and Zinc(II) Borohydrides from Spectroscopic Measurements and Computational Modeling*, Inorganic Chemistry, 51 2793.

Domingo, A., Carvajal, M.A., de Graaf, C., Sivalingam, K., Neese, F. and Angeli, C., 2012: *Metal-to-metal charge-transfer transitions: reliable excitation energies from ab initio calculations*, Theoretical Chemistry Accounts, 131, 1264.

Dreiser, J., Pedersen, K.S., Birk, T., Schau-Magnussen, M., Piamonteze, C., Rusponi, S., Weyhermüller, T., Brune, H., Nolting, F. and Bendix, J., 2012: *X-ray Magnetic Circular Dichroism (XMCD) Study of a Methoxide-Bridged* Dy^{III}*-*Cr^{III} *Cluster Obtained by Fluoride Abstraction from cis-*$[(Cr^{III}sF_2(phen)_2]^+$, Journal of Physical Chemistry A, 116, 7842.

Dugan, T.R., Bill, E., MacLeod, K.C., Christian, G.J., Cowley, R.E., Brennessel, W.W., Ye, S.F., Neese, F. and Holland, P.L., 2012: *Reversible C-C Bond Formation between Redox-Active Pyridine Ligands in Iron Complexes*, Journal of the American Chemical Society, 134, 20352.

Ebrahimi, K.H., Bill, E., Hagedoorn, P.L. and Hagen, W.R., 2012: *The catalytic center of ferritin regulates iron storage via Fe(II)-Fe(III) displacement*, Nature Chemical Biology, 8, 941.

England, J., Scarborough, C.C., Weyhermüller, T., Sproules, S. and Wieghardt, K., 2012: *Electronic Structures of the Electron Transfer Series* $[M(bpy)_3]^n$, $[M(terpy)_2]^n$*, and* $Fe[^t(bpy)_3]^n$ *(M=Fe,Ru;n=3+,2+,1+,0,1-): A Mössbauer Spectroscopic and DFT Study*, European Journal of Inorganic Chemistry, 4605.

Filippou, A. C., Barandov, A., Schnakenburg, G., Lewall, B., van Gastel, M., Marchanka, A., 2012: *Open shell germylidyne complexes of group 6 metals*, Angewandte Chemie International Edition, 51, 789.

Flores, M., Okamura, M.Y., Niklas, J., Pandelia, M.E. and Lubitz, W., 2012: *Pulse Q-band EPR and ENDOR spectroscopies of the photochemically generated monoprotonated benzosemiquinone radical in frozen alcoholic solution*, Journal of Physical Chemistry B, 116, 8890.

Ganapathy, S., Oostergetel, G.T., Reus, M., Tsukatani, Y., Chew, A.G.M., Buda, F., Bryant, D.A., Holzwarth, A.R. and de Groot, H.J.M., 2012: *Structural Variability in Wild-Type and bchQ bchR Mutant Chlorosomes of the Green Sulfur Bacterium Chlorobaculum tepidum*, Biochemistry, 51, 4488.

Gansäuer, A., Cangönül, A., Behlendorf, M., Kube, C., Cuerva, J. M., Friedrich, J., van Gastel, M., 2012: H_2O *Activation for Hydrogen-Atom Transfer: Correct Structures and Revised Mechanisms Advanced EPR-Spectroscopy*, Angewandte Chemie International Edition, 51, 3266.

Gärtner, W., 2012: *Kurt Schaffner: from organic photochemistry to photobiology*, Photochemical & Photobiological Sciences, 11, 872.

Gemma, J.C., Ye, S. and Neese, F., 2012: *Oxygen activation in extradiol catecholate dioxygenases – a density functional study*, Chemical Sciences, 3, 1600.

Gopal, S., Mathiyalagan, K., Weyhermüller, T. and Nair, B.U., 2012: *Oxidative Cleavage of DNA by Ruthenium(II) Complexes Containing Ferrocene/Non-Ferrocene Conjugated Imidazole Phenol Ligand*, Organometallics, 31, 6980.

Griesbeck, A.G., Hinze, O., Görner, H., Huchel, U., Kropf, C., Sundermeier, U. and Gerke, T., 2012: *Aromatic aldols and 1,5-diketones as optimized fragrance photocages*, Photochemical & Photobiological Sciences, 11, 587.

Grzyb, J., Xu, F., Nanda, V., Luczkowska, R., Reijerse, E., Lubitz, W. and Noy, D., 2012: *Empirical and computational design of iron-sulfur cluster proteins*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 1256.

He, C., Fuchs, M.R., Ogata, H. and Knipp, M., 2012: *Guanidine–ferroheme coordination in the mutant protein nitrophorin 4(L130R)*, Angewandte Chemie-International Edition, 51, 4470. German translation published: *Guanidin–Ferrohäm-Koordination in der Proteinmutante Nitrophorin-4(L130R),* Angewandte Chemie, 124, 4546.

He, C., Ogata, H. and Knipp, M., 2012: *Insertion of an H-Bonding residue into the distal pocket of the ferriheme protein nitrophorin 4: Effect on nitrite–iron coordination and nitrite disproportionation*, Chemistry & Biodiversity, 9, 1761.

Hilberg, M., Pierik, A.J., Bill, E., Friedrich, T., Lippert, M.L. and Heider, J., 2012: *Identification of FeS clusters in the glycyl-radical enzyme benzylsuccinate synthase via EPR and Mössbauer spectroscopy*, Journal of Biological Inorganic Chemistry, 17, 49.

Hsieh, C.H., Erdem, Ö.F., Harman, S.D., Singleton, M.L., Reijerse, E., Lubitz, W., Popescu, C.V., Reibenspies, J.H., Brothers, S.M., Hall, M.B. and Darensbourg, M.Y., 2012: *Structural and spectroscopic features of mixed valent* $Fe^{II}Fe^{I}$ *complexes and factors related to the rotated configuration of diiron hydrogenase*, Journal of the American Chemical Society, 134, 13089.

Huntington, L.M.J., Hansen, A., Neese, F. and Nooijen, M., 2012: *Accurate thermochemistry from a parameterized coupled-cluster singles and doubles model and a local pair natural orbital based implementation for applications to larger systems*, Journal of Chemical Physics, 136, 064101.

Indumathy, R., Weyhermüller, T., Rajapandian, V., Subramanian, V. and Nair, B.U., 2012: *An unusual oxidation of the imidazolyl ring in a cobalt terpyridyl complex: Crystal structure and photonuclease activity of the transformed cobalt terpyridyl complex*, Polyhedron, 43, 159.

Izsak, R., Hansen, A. and Neese, F., 2012: *The resolution of identity and chain of spheres approximations for the LPNO-CCSD singles Fock term*, Molecular Physics, 110, 2413.

Jahns, P. and Holzwarth, A.R., 2012: *The role of the xanthophyll cycle and of lutein in photoprotection of photosystem II*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 182.

Jesorka, A., Holzwarth, A.R., Eichhofer, A., Reddy, C.M., Kinoshita, Y., Tamiaki, H., Katterle, M., Naubron, J.V. and Balaban, T.S., 2012: *Water coordinated zinc dioxo-chlorin and porphyrin self-assemblies as chlorosomal mimics: variability of supramolecular interactions*, Photochemical & Photobiological Sciences, 11, 1069.

Kammler, L., van Gastel, M., 2012: *Electronic structure of the lowest triplet state of flavin mononucleotide*, Journal of Physical Chemistry A, 116, 10090.

Kampa, M., Lubitz, W., van Gastel, M. and Neese, F., 2012: *Computational study of the electronic structure and magnetic properties of the Ni-C state in [NiFe] hydrogenases including the second coordination sphere*, Journal of Biological Inorganic Chemistry, 17, 1269.

Karnahl, M., Tschierlei, S., Erdem, Ö.F., Pullen, S., Santoni, M.P., Reijerse, E.J., Lubitz, W. and Ott, S., 2012: *Mixed-valence [Fe(I)Fe(II)] hydrogenase active site model complexes stabilized by a bidentate carborane bis-phosphine ligand*, Dalton Transactions, 41, 12468.

Kettner, M., Schneider, W.B. and Auer, A.A., 2012: *Computational Study of Pt/Co Core-Shell Nanoparticles: Segregation, Adsorbates and Catalyst Activity*, Journal of Physical Chemistry C, 116, 15432.

Knipp, M., Soares, R.P. and Pereira, M.H., 2012: *Identification of the native N-terminus of the membrane attaching ferriheme protein nitrophorin 7 from Rhodnius prolixus*, Analytical Biochemistry, 424, 79.

Knipp, M., Taing, J.J., He, C. and Viappiani, C., 2012: *A caged cyanide*, Photochemical & Photobiological Sciences, 11, 620.

Knörzer, P., Silakov, A., Foster, C.E., Armstrong, F.A., Lubitz, W. and Happe, T., 2012: *Importance of the Protein Framework for Catalytic Activity of [FeFe]-Hydrogenases*, Journal of Biological Chemistry, 287, 1489.

Kropp, H., King, A.E., Khusniyarov, M.M., Heinemann, F.W., Lancaster, K.M., DeBeer, S., Bill, E. and Meyer, K., 2012: *Manganese Nitride Complexes in Oxidation States III, IV, and V: Synthesis and Electronic Structure*, Journal of the American Chemical Society, 134, 15538.

Kruk, M.M. and Braslavsky, S.E., 2012: *Structural volume changes upon triplet formation of water-soluble porphyrins depend on the resonant effect of the substituents*, Photochemical & Photobiological Sciences, 11, 972.

Lambrev, P.H., Miloslavina, Y., Jahns, P. and Holzwarth, A.R., 2012: *On the relationship between non-photochemical quenching and photoprotection of Photosystem II*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 760.

Lancaster, K.M., Zaballa, M.E., Sproules, S., Sundararajan, M., DeBeer, S., Richards, J.H., Vila, A.J., Neese, F. and Gray, H.B., 2012: *Outer-Sphere Contributions to the Electronic Structure of Type Zero Copper Proteins*, Journal of the American Chemical Society, 134, 8241.

Liakos, D.G. and Neese, F., 2012: *Improved Correlation Energy Extrapolation Schemes Based on Local Pair Natural Orbital Methods*, Journal of Physical Chemistry A, 116, 4801.

Lohmiller, T., Cox, N., Su, J.H., Messinger, J. and Lubitz, W., 2012: *The basic properties of the electronic structure of the oxygen-evolving complex of photosystem II are not perturbed by* Ca^{2+} *removal*, Journal of Biological Chemistry, 287, 24721.

Lohmiller, T., Cox, N., Su, J.H., Messinger, J. and Lubitz, W. 2012: *An EPR and ENDOR spectroscopic investigation of the* Ca^{2+}*-depleted oxygen-evolving complex of photosystem II*. In: Kuang, T., Lu, C. and Zhang, L. (eds.), Photosynthesis: Research for Food, Fuel and Future-15th International Conference on Photosynthesis, Springer, Berlin, 2012, pp. 239.

Losi, A. and Gärtner, W., 2012: *The Evolution of Flavin-Binding Photoreceptors: An Ancient Chromophore Serving Trendy Blue-Light Sensors*, Annual Review of Plant Biology, 63, 49.

Losi, A. and Gärtner, W.: *Blue light regulation in plants and microorganisms.* In: Griesbeck, A., Oelgemöller, M., and Ghetti, F. (eds.) CRC Handbook of Organic Photochemistry and Photobiology, 3rd edn. Vol. II, chapter 53, 2012, 1237. ISBN 978-1-4398-9936.

Lubitz, W., Ogata, H., Reijerse, E. and Higuchi, Y.: *Structure and function of hydrogenase enzymes*. In: Wydrzynski, T., and Hillier, W. (eds.), RSC Energy and Environment Series No. 5. Molecular Solar Fuels, RSC Publishing, Cambridge, 2012, pp. 288.

Maekawa, M., Roemelt, M., Daniliuc, C.G., Jones, P.G., White, P.S., Neese, F. and Walter, M.D., 2012: *Reactivity studies on* $[Cp'MnX(thf)]_2$*: manganese amide and polyhydride synthesis*, Chemical Science, 3, 2972.

Maganas, D., Krzystek, J., Ferentinos, E., Whyte, A.M., Robertson, N., Psycharis, V., Terzis, A., Neese, F. and Kyritsis, P., 2012: *Investigating Magnetostructural Correlations in the Pseudooctahedral trans-*$[Ni^{II}\{(OPPh_2)(EPPh_2)N\}_2(sol)_2]$ *Complexes (E = S, Se; sol = DMF, THF) by Magnetometry, HFEPR, and ab Initio Quantum Chemistry*, Inorganic Chemistry, 51, 7218.

Manikandamathavan, V.M., Rajapandian, V., Freddy, A.J., Weyhermüller, T., Subramanian, V. and Nair, B.U., 2012: *Effect of coordinated ligands on antiproliferative activity and DNA cleavage property of three mononuclear Cu(II)-terpyridine complexes*, European Journal of Medicinal Chemistry, 57, 449.

Marchanka, A. and van Gastel, M., 2012: *Reversed Freeze Quench Method near the Solvent Phase Transition*, Journal of Physical Chemistry A, 116, 3899.

Martire, D.O., Russell, S., Dietrich, H.J., Cobos, C.J. and Braslavsky, S.E., 2012: *Photophysics of novel 22p porphyrinoids*, Journal of Porphyrins and Phthalocyanines, 16, 499.

McLaughlin, M.P., Retegan, M., Bill, E., Payne, T.M., Shafaat, H.S., Pena, S., Sudhamsu, J., Ensign, A.A., Crane, B.R., Neese, F. and Holland, P.L., 2012: *Azurin as a Protein Scaffold for a Low-coordinate Nonheme Iron Site with a Small-molecule Binding Pocket*, Journal of the American Chemical Society, 134, 19746.

Molter, A., Bill, E. and Mohr, F., 2012: *Synthesis, structures and reactivity of two oxidovanadium(IV) and dioxidovanadium(V) selenosemicarbazonato complexes*, Inorganic Chemistry Communications, 17, 124.

Mula, S., Savitsky, A., Möbius, K., Lubitz, W., Golbeck, J.H., Mamedov, M.D., Semenov, A.Y. and van der Est, A., 2012: *Incorporation of a high potential quinone reveals that electron transfer in photosystem I becomes highly asymmetric at low temperature*, Photochemical & Photobiological Sciences, 11, 946.

Nesterov, V., Özbolat-Schön, A., Schnakenburg, G., Shi, L.L., Cangönül, A., van Gastel, M., Neese, F. and Streubel, R., 2012: *An Unusal Case of Facile Non-Degenerate P-C Bond Making and Breaking*, Chemistry-an Asian Journal, 7, 1708.

Netz, D.J.A., Pierik, A.J., Stümpfig, M., Bill, E., Sharma, A.K., Pallesen, L.J., Walden, W.E. and Lill, R., 2012: *A Bridging [4Fe-4S] Cluster and Nucleotide Binding Are Essential for Function of the* $Cfd1\text{-}Nb_{p35}$ *Complex as a Scaffold in Iron-Sulfur Protein Maturation*, Journal of Biological Chemistry, 287, 12365.

Ogata, H. and Knipp, M., 2012: *Crystallization and preliminary X-ray crystallographic analysis of the membrane-binding haemprotein nitrophorin 7 from Rhodnius prolixus*, Acta Crystallographica Section F-Structural Biology and Crystallization Communications, 68, 37.

Pandelia, M.E., Infossi, P., Stein, M., Giudici-Orticoni, M.T. and Lubitz, W., 2012: *Spectroscopic characterization of the key catalytic intermediate Ni-C in the* O_2 *-tolerant [NiFe] hydrogenase I from Aquifex aeolicus: evidence of a weakly bound hydride*, Chemical Communications, 48, 823.

Pandelia, M.E., Lubitz, W. and Nitschke, W., 2012: *Evolution and diversification of Group 1 [NiFe] hydrogenases. Is there a phylogenetic marker for* O_2*-tolerance?*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 1565.

Pantazis, D.A., Ames, W., Cox, N., Lubitz, W. and Neese, F., 2012: *Two interconvertible structures that explain the spectroscopic properties of the oxygen-evolving complex of photosystem II in the* S_2 *state*, Angewandte Chemie-International Edition, 51, 9935. German translation published: *Zwei ineinander umwandelbare Strukturen erklären die spektroskopischen Eigenschaften des Wasser oxidierenden Enzyms des Photosystems II im* S_2*-Zustand*, Angewandte Chemie, 124, 10074.

Pantazis, D.A. and Neese, F., 2012: *All-electron scalar relativistic basis sets for the 6p elements*, Theoretical Chemistry Accounts, 131, 1292.

Pathak, G.P., Losi, A. and Gärtner, W., 2012: *Metagenome-based Screening Reveals Worldwide Distribution of LOV-Domain Proteins*, Photochemistry and Photobiology, 88, 107.

Rajalakshmi, S., Weyhermüller, T., Dinesh, M. and Nair, B.U., 2012: *Copper(II) complexes of terpyridine derivatives: A footstep towards development of antiproliferative agent for breast cancer*, Journal of Inorganic Biochemistry, 117, 48.

Rapatskiy, L., Cox, N., Savitsky, A., Ames, W.M., Sander, J., Nowaczyk, M.M., Rögner, M., Boussac, A., Neese, F., Messinger, J. and Lubitz, W., 2012: *Detection of the water-binding sites of the oxygen-evolving complex of photosystem II using W-band* ^{17}O *electron-electron double resonance-detected NMR spectroscopy*, Journal of the American Chemical Society, 134, 16619.

Reijerse, E., Lendzian, F., Isaacson, R. and Lubitz, W., 2012: *A tunable general purpose Q-band resonator for CW and pulse EPR/ENDOR experiments with large sample access and optical excitation*, Journal of Magnetic Resonance, 214, 237.

Rodriguez, M.M., Stubbert, B.D., Scarborough, C.C., Brennessel, W.W., Bill, E. and Holland, P.L., 2012: *Isolation and Characterization of Stable Iron(I) Sulfide Complexes*, Angewandte Chemie-International Edition, 51, 8247.

Roemelt, M., Beckwith, M.A., Duboc, C., Collomb, M.N., Neese, F. and DeBeer, S., 2012: *Manganese K-Edge X-Ray Absorption Spectroscopy as a Probe of the Metal-Ligand Interactions in Coordination Compounds*, Inorganic Chemistry, 51, 680.

Roveri, O.A. and Braslavsky, S.E., 2012: *π-Cation interactions as the origin of the weak absorption at 532 nm observed in tryptophan-containing polypeptides*, Photochemical & Photobiological Sciences, 11, 962.

Russell, S.K., Bowman, A.C., Lobkovsky, E., Wieghardt, K. and Chirik, P.J., 2012: *Synthesis and Electronic Structure of Reduced Bis(imino)pyridine Manganese Compounds*, European Journal of Inorganic Chemistry, 535.

Safaei, E., Sheykhi, H., Weyhermüller, T. and Bill, E., 2012: *A magnetostructural study of three novel iron(III) complexes of tripodal amine phenolate ligands*, Inorganica Chimica Acta, 384, 69.

Salunke-Gawali, S., Kathawate, L., Shinde, Y., Puranik, V.G. and Weyhermüller, T., 2012: *Single crystal X-ray structure of Lawsone anion: Evidence for coordination of alkali metal ions and formation of naphthosemiquinone radical in basic media*, Journal of Molecular Structure, 1010, 38.

Sameera, W.M.C. and Pantazis, D.A., 2012: *A Hierarchy of Methods for the Energetically Accurate Modeling of Isomerism in Monosaccharides*, Journal of Chemical Theory and Computation, 8, 2630.

Sandhöfer, B. and Neese, F., 2012: *One-electron contributions to the g-tensor for second-order Douglas-Kroll-Hess theory*, Journal of Chemical Physics, 137, 094102.

Sathyaraj, G., Kiruthika, M., Weyhermüller, T. and Nair, B.U., 2012: *Ruthenium(II) [3+2+1] mixed ligand complexes: substituent effect on photolability, photooxidation of bases, photocytotoxicity and photonuclease activity*, Dalton Transactions, 41, 8460.

Sathyaraj, G., Muthamilselvan, D., Kiruthika, M., Weyhermüller, T. and Nair, B.U., 2012: *Ferrocene conjugated imidazolephenols as multichannel ditopic chemosensor for biologically active cations and anions*, Journal of Organometallic Chemistry, 716, 150.

Scarborough, C.C., Lancaster, K.M., DeBeer, S., Weyhermüller, T., Sproules, S. and Wieghardt, K., 2012: *Experimental Fingerprints for Redox-Active Terpyridine in* $[Cr(tpy)_2](PF_6)_n$ *(n=3-0), and the Remarkable Electronic Structure of* $[Cr(tpy)_2]^{1-}$, Inorganic Chemistry, 51, 3718.

Scarborough, C.C., Sproules, S., Doonan, C.J., Hagen, K.S., Weyhermüller, T. and Wieghardt, K., 2012: *Scrutinizing Low-Spin Cr(II) Complexes*, Inorganic Chemistry, 51, 6969.

Scheibel, M.G., Askevold, B., Heinemann, F.W., Reijerse, E.J., de Bruin, B. and Schneider, S., 2012: *Closed-shell and open-shell square-planar iridium nitrido complexes*, Nature Chemistry, 4, 552.

Sengupta, S., Ebeling, D., Patwardhan, S., Zhang, X., von Berlepsch, H., Böttcher, C., Stepanenko, V., Uemura, S., Hentschel, C., Fuchs, H., Grozema, F.C., Siebbeles, L.D.A., Holzwarth, A.R., Chi, L.F. and Würthner, F., 2012: *Biosupramolecular Nanowires from Chlorophyll Dyes with Exceptional Charge-Transport Properties*, Angewandte Chemie -International Edition, 51, 6378.

Shafaat, H.S., Weber, K., Petrenko, T., Neese, F. and Lubitz, W., 2012: *Key hydride vibrational modes in [NiFe] hydrogenase model compounds studied by resonance raman spectroscopy and density functional Calculations*, Inorganic Chemistry, 51, 11787.

Shah, R., Schwach, J., Frankenberg-Dinkel, N. and Gärtner, W., 2012: *Complex formation between heme oxygenase and phytochrome during biosynthesis in Pseudomonas syringae pv. tomato*, Photochemical & Photobiological Sciences, 11, 1026.

Shongwe, M.S., Al-Zaabi, U.A., Al-Mjeni, F., Eribal, C.S., Sinn, E., Al-Omari, I.A., Hamdeh, H.H., Matoga, D., Adams, H., Morris, M.J., Rheingold, A.L., Bill, E. and Sellmyer, D.J., 2012: *Accessibility and Selective Stabilization of the Principal Spin States of Iron by Pyridyl versus Phenolic Ketimines: Modulation of the* $^6A_1$ *<->* $^2T_2$ *Ground-State Transformation of the* $[FeN_4O_2]^+$ *Chromophore*, Inorganic Chemistry, 51, 8241.

Siebel, J.F., Kosinsky, R.L., Åkerström, B. and Knipp, M., 2012: *Insertion of heme b into the structure of the Cys34–carbamidomethylated human lipocalin* α_1*-microglobulin: Formation of a* $[(heme)_2(\alpha_1$ *-microglobulin*$)]_3$ *complex*, ChemBioChem, 13, 879.

Silakov, A., Olsen, M.T., Sproules, S., Reijerse, E.J., Rauchfuss, T.B. and Lubitz, W., 2012: *EPR/ENDOR, Mössbauer, and quantum-chemical investigations of diiron complexes mimicking the active oxidized state of [FeFe] hydrogenase*, Inorganic Chemistry, 51, 8617.

Song, C., Essen, L.O., Gärtner, W., Hughes, J. and Matysik, J., 2012: *Solid-State NMR Spectroscopic Study of Chromophore-Protein Interactions in the Pr Ground State of Plant Phytochrome A*, Molecular Plant, 5, 698.

Song, C., Lang, C., Mailliet, J., Hughes, J., Gärtner, W. and Matysik, J., 2012: *Exploring Chromophore-Binding Pocket: High-Resolution Solid-State* ^1H*-*^{13}C *Interfacial Correlation NMR Spectra with Windowed PMLG Scheme*, Applied Magnetic Resonance, 42, 79.

Stieber, S.C.E., Milsmann, C., Hoyt, J.M., Turner, Z.R., Finkelstein, K.D., Wieghardt, K., DeBeer, S. and Chirik, P.J., 2012: *Bis(imino)pyridine Iron Dinitrogen Compounds Revisited: Differences in Electronic Structure Between Four- and Five-Coordinate Derivatives*, Inorganic Chemistry, 51, 3770.

Sundararajan, M. and Neese, F., 2012: *Detailed QM/MM study of the Electron Paramagnetic Resonance Parameters of Nitrosyl Myoglobin*, Journal of Chemical Theory and Computation, 8, 563.

Sylvester, K.T., Stieber, S.C.E., Darmon, J.M., Fernandez, I., Lobkovsky, E., Semproni, S.P., Bill, E., Wieghardt, K., DeBeer, S. and Chirik, P.J., 2012: *Oxidative Addition of Carbon-Carbon Bonds with a Redox-Active Bis(imino)pyridine Iron Complex*, Journal of the American Chemical Society, 134, 17125.

Thiessen, A., Wettach, H., Meerholz, K., Neese, F., Höger, S. and Hertel, D., 2012: *Control of electronic properties of triphenylene by substitution*, Organic Electronics, 13, 71.

Tomasini, E.P., Braslavsky, S.E. and San Roman, E., 2012: *Triplet quantum yields in light-scattering powder samples measured by laser-induced optoacoustic spectroscopy (LIOAS)*, Photochemical & Photobiological Sciences, 11, 1010.

Torres-Alacan, J., Krahe, O., Filippou, A.C., Neese, F., Schwarzer, D. and Vöhringer, P., 2012: *The Photochemistry of* $[Fe^{III}N_3(cyclam\text{-}ac)]PF_6$ *at 266 nm*, Chemistry - A European Journal, 18, 3043.

Tretyakov, E.V., Tolstikov, S.E., Suvorova, A.O., Polushkin, A.V., Romanenko, G.V., Bogomyakov, A.S., Veber, S.L., Fedin, M.V., Stass, D.V., Reijerse, E., Lubitz, W., Zueva, E.M. and Ovcharenko, V.I., 2012: *Crucial role of paramagnetic ligands for magnetostructural anomalies in breathing crystals*, Inorganic Chemistry, 51, 9385.

Tuysuz, H., Salabas, E.L., Bill, E., Bongard, H., Spliethoff, B., Lehmann, C.W. and Schüth, F., 2012: *Synthesis of Hard Magnetic Ordered Mesoporous* $Co_3O_4/CoFe_2O_4$ *Nanocomposites*, Chemistry of Materials, 24, 2493.

Wallner, T., Hagiwara, Y., Bernat, G., Sobotka, R., Reijerse, E.J., Frankenberg-Dinkel, N. and Wilde, A., 2012: *Inactivation of the conserved open reading frame ycf34 of Synechocystis sp PCC 6803 interferes with the photosynthetic electron transport chain*, Biochimica et Biophysica Acta-Bioenergetics, 1817, 2016.

Weber, K., Krämer, T., Shafaat, H.S., Weyhermüller, T., Bill, E., van Gastel, M., Neese, F. and Lubitz, W., 2012: *A functional [NiFe]-hydrogenase model compound that undergoes biologically relevant reversible thiolate protonation*, Journal of the American Chemical Society, 134, 20745.

Westphal, A., Broda, H., Kurz, P., Neese, F. and Tuczek, F., 2012: *Magnetic Circular Dichroism Spectrum of the Molybdenum(V) Complex* $(Mo(O)Cl_3dppe)$*: C-Term Signs and Intensities for Multideterminant Excited Doublet States*, Inorganic Chemistry, 51, 5748.

Yan, Y., Chandrasekaran, P., Mague, J.T., DeBeer, S., Sproules, S. and Donahue, J.P., 2012: *Redox-Controlled Interconversion between Trigonal Prismatic and Octahedral Geometries in a Monodithiolene Tetracarbonyl Complex of Tungsten*, Inorganic Chemistry, 51, 346.

Yao, S.A., Lancaster, K.M., Götz, A.W., DeBeer, S. and Berry, J.F., 2012: *X-ray Absorption Spectroscopic, Crystallographic, Theoretical (DFT) and Chemical Evidence for a Chalcogen-Chalcogen Two-Center/Three-Electron Half Bond in an Unprecedented „Subselenide“* Se_2^{3-} *Ligand*, Chemistry-A European Journal, 18, 9179.

Ye, S.F. and Neese, F., 2012: *How Do Heavier Halide Ligands Affect the Signs and Magnitudes of the Zero-Field Splittings in Halogenonickel(II) Scorpionate Complexes? A Theoretical Investigation Coupled to Ligand-Field Analysis*, Journal of Chemical Theory and Computation, 8, 2344.

Ye, S.F., Riplinger, C., Hansen, A., Krebs, C., Bollinger, J.M. and Neese, F., 2012: *Electronic Structure Analysis of the Oxygen-Activation Mechanism by* Fe^{II}*- and* α*-Ketoglutarate (*α *KG)-Dependent Dioxygenases*, Chemistry-A European Journal, 18, 6555.

Zall, C.M., Zherebetskyy, D., Dzubak, A.L., Bill, E., Gagliardi, L. and Lu, C.C., 2012: *A Combined Spectroscopic and Computational Study of a High-Spin S=7/2 Diiron Complex with a Short Iron-Iron Bond*, Inorganic Chemistry, 51, 728.

Zhang, Y.Z. and Görner, H., 2012: *Photoprocesses of merocyanine 540 bound to serum albumin and lysozyme*, Journal of Molecular Structure, 1011, 94.

127 publications in 2012

2013

Alarcon, E.I., Aspee, A., Aliaga, C. and Braslavsky, S.E., 2013: *Special Issue Dedicated to the Memory of Elsa Beatriz Abuin Saccomano (1942-2012) Introduction*, Photochemistry and Photobiology, 89, 1270.

Albers, A., Demeshko, S., Propper, K., Dechert, S., Bill, E. and Meyer, F., 2013: *A Super-Reduced Diferrous 2Fe-2S Cluster*, Journal of the American Chemical Society, 135, 1704.

Ali, M.A., Bernhardt, P.V., Brax, M.A.H., England, J., Farlow, A.J., Hanson, G.R., Yeng, L.L., Mirza, A.H. and Wieghardt, K., 2013: *The Trivalent Copper Complex of a Conjugated Bis-dithiocarbazate Schiff Base: Stabilization of Cu in Three Different Oxidation States*, Inorganic Chemistry, 52, 1650.

Amakawa, K., Kolen'ko, Y.V., Villa, A., Schuster, M.E., Csepei, L.-I., Weinberg, G., Wrabetz, S., d'Alnoncourt, R.N., Girgsdies, F., Prati, L., Schlögl, R. and Trunschke, A., 2013: *Multifunctionality of Crystalline MoV(TeNb) M1 Oxide Catalysts in Selective Oxidation of Propane and Benzyl Alcohol*, Acs Catalysis, 3, 1103.

Arpita, J., Weyhermüller, T. and Mohanta, S., 2013: *Metal complex analogues of crown ethers as the preorganized motif to stabilize aquated proton in solid state*, Crystengcomm, 15, 4099.

Arrigo, R., Schuster, M. E., Abate, S., Wrabetz, S., Amakawa, K., Teschner, D., Freni, M., Centi, G., Perathoner, S., Hävecker, M. and Schlögl, R. 2013: *Dynamics of Palladium on nanocarbon in the direct synthesis of* H_2O_2.ChemSusChem: chemistry & sustainability, energy & materials. doi:10.1002/cssc.201300616

Arrigo, R., Haevecker, M., Schuster, M. E., Ranjan, C., Stotz, E., Knop-Gericke, A. and Schlögl, R., 2013: *In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS.* Angewandte Chemie International Edition: a journal of the Gesellschaft Deutscher Chemiker, 52 (44), 11660-11664. doi:10.1002/anie.201304765.

Arrigo, R., Haevecker, M., Schuster, M. E., Ranjan, C., Stotz, E., Knop-Gericke, A. and Schlögl, R., 2013: *In Situ-Studie der Gasphasen Wasserelektrolyse auf Platin mittels NAP-XPS.* Angewandte Chemie: Eine Zeitschrift der Gesellschaft Deutscher Chemiker, 125 (44),11660-11664. doi:10.1002/anie.201304765.

Artyushkova, K., Kiefer, B., Halevi, B., Knop-Gericke, A., Schlögl, R. and Atanassov, P., 2013: *Density functional theory calculations of XPS binding energy shift for nitrogen-containing graphene-like structures*, Chemical Communications, 49, 2539.

Atanasov, M., Surawatanawong, P., Wieghardt, K. and Neese, F., 2013: *A theoretical study of zero-field splitting in Fe(IV)S-6 (S=1) and Fe(III)S-6 (S=1/2) core complexes, Fe-IV(Et(2)dtc)(3-n)(mnt)(n) ((n-1)-) and Fe-III(Et(2)dtc)(3-n)(mnt)(n) (n-) (n=0, 1, 2, 3): The origin of the magnetic anisotropy*, Coordination Chemistry Reviews, 257, 27.

Atanasov, M., Zadrozny, J.M., Long, J.R. and Neese, F., 2013: *A theoretical analysis of chemical bonding, vibronic coupling, and magnetic anisotropy in linear iron(II) complexes with single-molecule magnet behavior*, Chemical Science, 4, 139.

Banci, L., Ciofi-Baffoni, S., Mikolajczyk, M., Winkelmann, J., Bill, E. and Pandelia, M.E., 2013: *Human anamorsin binds 2Fe-2S clusters with unique electronic properties*, Journal of Biological Inorganic Chemistry, 18, 883.

Barbosa, R.L., Papaefthimiou, V., Law, Y.T., Teschner, D., Hävecker, M., Knop-Gericke, A., Zapf, R., Kolb, G., Schlögl, R. and Zafeiratos, S., 2013: *Methanol Steam Reforming over Indium-Promoted* Pt/Al_2O_3 *Catalyst: Nature of the Active Surface*, Journal of Physical Chemistry C, 117, 6143.

Bayer, B.C., Castellarin-Cudia, C., Blume, R., Steiner, S.A., III, Ducati, C., Chu, D., Goldoni, A., Knop-Gericke, A., Schlögl, R., Cepek, C., Robertson, J. and Hofmann, S., 2013: *Tantalum-oxide catalysed chemical vapour deposition of single- and multi-walled carbon nanotubes*, Rsc Advances, 3, 4086.

Behrens, M., Lolli, G., Muratova, N., Kasatkin, I., Hävecker, M., d'Alnoncourt, R.N., Storcheva, O., Köhler, K., Muhler, M. and Schlögl, R., 2013: *The effect of Al-doping on ZnO nanoparticles applied as catalyst support*, Physical Chemistry Chemical Physics, 15, 1374.

Behrens, M., Zander, S., Kurr, P., Jacobsen, N., Senker, J., Koch, G., Ressler, T., Fischer, R.W. and Schlögl, R., 2013: *Performance Improvement of Nanocatalysts by Promoter-Induced Defects in the Support Material: Methanol Synthesis over Cu/ZnO:Al*, Journal of the American Chemical Society, 135, 6061.

Benedikt, U., Schneider, W.B. and Auer, A.A., 2013: *Modelling electrified interfaces in quantum chemistry: constant charge vs. constant potential*, Physical Chemistry Chemical Physics, 15, 2712.

Berggren, G., Adamska, A., Lambertz, C., Simmons, T.R., Esselborn, J., Atta, M., Gambarelli, S., Mouesca, J.M., Reijerse, E., Lubitz, W., Happe, T., Artero, V. and Fontecave, M., 2013: *Biomimetic assembly and activation of [FeFe]-hydrogenases*, Nature, 499, 66.

Bill, E., 2013: *Single-molecule magnets: Iron lines up*, Nature Chemistry, 5, 556.

Biswas, M.K., Patra, S.C., Maity, A.N., Ke, S.C., Weyhermüller, T. and Ghosh, P., 2013: *Asymmetric cleavage of 2,2 '-pyridil to a picolinic acid anion radical coordinated to ruthenium(II): splitting of water to hydrogen*, Chemical Communications, 49, 4522.

Bowman, A.C., England, J., Sproules, S., Weyhermüller, T. and Wieghardt, K., 2013: *Electronic Structures of Homoleptic Tris(2,2 '-bipyridine)M (n) Complexes of the Early Transition Metals (M = Sc, Y, Ti, Zr, Hf, V, Nb, Ta; n=1+, 0, 1-, 2-, 3-): An Experimental and Density Functional Theoretical Study*, Inorganic Chemistry, 52, 2242.

Brautigam, L., Johansson, C., Kubsch, B., McDonough, M.A., Bill, E., Holmgren, A. and Berndt, C., 2013: *An unusual mode of iron-sulfur-cluster coordination in a teleost glutaredoxin*, Biochemical and Biophysical Research Communications, 436, 491.

Cangonul, A., Behlendorf, M., Gansauer, A. and van Gastel, M., 2013: *Radical-Based Epoxide Opening by Titanocenes*, Inorganic Chemistry, 52, 11859.

Chan, S.C., England, J., Lee, W.C., Wieghardt, K. and Wong, C.Y., 2013: *Noninnocent Behavior of NitrosoarenePyridine Hybrid Ligands: Ruthenium Complexes Bearing a 2-(2-Nitrosoaryl)Pyridine Monoanion Radical*, Chempluschem, 78, 214.

Chandrasekaran, P., Chiang, K.P., Nordlund, D., Bergmann, U., Holland, P.L. and DeBeer, S., 2013: *Sensitivity of X-ray Core Spectroscopy to Changes in Metal Ligation: A Systematic Study of Low-Coordinate, High-Spin Ferrous Complexes*, Inorganic Chemistry, 52, 6286.

Chandrasekaran, P., Mague, J.T., DeBeer, S. and Donahue, J.P., 2013: *Investigation of phophine induced metal to ligand electron transfer in platinum bis(dithiolene) complexes*, Abstracts of Papers of the American Chemical Society, 245.

Chaudhuri, S., Patra, S.C., Saha, P., Roy, A.S., Maity, S., Bera, S., Sardar, P.S., Ghosh, S., Weyhermüller, T. and Ghosh, P., 2013: *Zinc(II), iron(II/III) and ruthenium(II) complexes of o-phenylenediamine derivatives: oxidative dehydrogenation and photoluminescence*, Dalton Transactions, 42, 15028.

Chizhov, I., Zorn, B., Manstein, D.J. and Gärtner, W., 2013: *Kinetic and Thermodynamic Analysis of the Light-induced Processes in Plant and Cyanobacterial Phytochromes*, Biophysical Journal, 105, 2210.

Chung, L.H., Cho, K.S., England, J., Chan, S.C., Wieghardt, K. and Wong, C.Y., 2013: *Ruthenium(II) and Osmium(II) Complexes Bearing Bipyridine and the N-Heterocyclic Carbene-Based (CNC)-N-boolean AND-C-boolean AND Pincer Ligand: An Experimental and Density Functional Theory Study*, Inorganic Chemistry, 52, 9885.

Coggins, M.K., Martin-Diaconescu, V., DeBeer, S. and Kovacs, J.A., 2013: *Correlation Between Structural, Spectroscopic, and Reactivity Properties Within a Series of Structurally Analogous Metastable Manganese(III)-Alkylperoxo Complexes*, Journal of the American Chemical Society, 135, 4260.

Cotter, T., Frank, B., Zhang, W., Schlögl, R. and Trunschke, A., 2013: *The Impact of V Doping on the Carbothermal Synthesis of Mesoporous Mo Carbides*, Chemistry of Materials, 25, 3124.

Cox, N., Lubitz, W.: *Molecular concepts of water splitting: Nature's approach*. In: Schlögl, R. (ed.), Chemical Energy Storage, Walter de Gruyter GmbH, Berlin, 2013, pp. 185.

Cox, N., Lubitz, W., 2013: *Molecular concepts of water splitting: Nature's approach*. De Gruyter Bookshelf. Green, 3, 235.

Cox, N., Lubitz, W. and Savitsky, A., 2013: *W-band ELDOR-detected NMR (EDNMR) spectroscopy as a versatile technique for the characterisation of transition metal-ligand interactions*, Molecular Physics, 111, 2788.

Cox, N. and Messinger, J., 2013: *Reflections on substrate water and dioxygen formation*, Biochimica Et Biophysica Acta-Bioenergetics, 1827, 1020.

Cox, N., Pantazis, D.A., Neese, F. and Lubitz, W., 2013: *Biological water oxidation*, Accounts of Chemical Research, 46, 1588.

Danovich, D., Shaik, S., Neese, F., Echeverria, J., Aullon, G. and Alvarez, S., 2013: *Understanding the Nature of the CH center dot center dot center dot HC Interactions in Alkanes*, Journal of Chemical Theory and Computation, 9, 1977.

Davydov, R.M., McLaughlin, M.P., Bill, E., Hoffman, B.M. and Holland, P.L., 2013: *Generation of High-Spin Iron(1) in a Protein Environment Using Cryoreduction*, Inorganic Chemistry, 52, 7323.

DeBeer, S., van Gastel, M., Bill, E., Ye, S., Petrenko, T., Pantazis, D.A. and Neese F.: Challenges in molecular energy research. In: Schlögl, R. (ed.), Chemical Energy Storage. De Gruyter, Berlin, 2013, 353.

DeBeer S., Neese, F.: *X-ray Spectroscopy*. In: Reedijk & Poeppelmeier (eds.), Comprehensive Inorganic Chemistry, Elsevier, 2013.

Delgado-Jaime, M.U., DeBeer, S. and Bauer, M., 2013: *Valence-to-Core X-Ray Emission Spectroscopy of Iron-Carbonyl Complexes: Implications for the Examination of Catalytic Intermediates*, Chemistry-a European Journal, 19, 15888.

Dinse, A., Wolfram, T., Carrero, C., Schlögl, R., Schomaecker, R. and Dinse, K.P., 2013: *Exploring the Structure of Paramagnetic Centers in SBA-15 Supported Vanadia Catalysts with Pulsed One- and Two-Dimensional Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR)*, Journal of Physical Chemistry C, 117, 16921.

Eichelbaum, M., Glaum, R., Hävecker, M., Wittich, K., Heine, C., Schwarz, H., Dobner, C.-K., Welker-Nieuwoudt, C., Trunschke, A. and Schlögl, R., 2013: *Towards Physical Descriptors of Active and Selective Catalysts for the Oxidation of n-Butane to Maleic Anhydride*, Chemcatchem, 5, 2318.

Engelhard, C., Raffelberg, S., Tang, Y.F., Diensthuber, R.P., Möglich, A., Losi, A., Gärtner, W. and Bittl, R., 2013: *A structural model for the full-length blue light-sensing protein YtvA from Bacillus subtilis, based on EPR spectroscopy*, Photochemical & Photobiological Sciences, 12, 1855.

England, J. and Wieghardt, K., 2013: *2,2 '-Bipyridine Compounds of Group 14 Elements: A Density Functional Theory Study*, Inorganic Chemistry, 52, 10067.

Erdem, Ö.F., Reijerse, E., Ott, S., Darensbourg, M.Y. and Lubitz, W., 2013: *EPR/ENDOR and DFT investigations of bioinspired FeFe hydrogenase model compounds*, Abstracts of Papers of the American Chemical Society, 245.

Erdem, Ö.F., Stein, M., Kaur-Ghumaan, S., Reijerse, E.J., Ott, S., Lubitz, W. 2013: *Effect of cyanide ligands on the electronic structure of [FeFe] hydrogenase active site model complexes with an azadithiolate ligand*, Chemistry – A European Journal, 19, 14566.

Escobar, F.V., Utesch, T., Narikawa, R., Ikeuchi, M., Mroginski, M.A., Gärtner, W. and Hildebrandt, P., 2013: *Photoconversion Mechanism of the Second GAF Domain of Cyanobacteriochrome AnPixJ and the Cofactor Structure of Its Green-Absorbing State*, Biochemistry, 52, 4871.

Esselborn, J., Lambertz, C., Adamska-Venkatesh, A., Simmons, T., Berggren, G., Nothl, J., Siebel, J., Hemschemeier, A., Artero, V., Reijerse, E., Fontecave, M., Lubitz, W. and Happe, T., 2013: *Spontaneous activation of [FeFe]-hydrogenases by an inorganic [2Fe] active site mimic*, Nature Chemical Biology, 9, 607.

Farias, M.E., Rascovan, N., Toneatti, D.M., Albarracin, V.H., Flores, M.R., Poire, D.G., Collavino, M.M., Aguilar, O.M., Vazquez, M.P. and Polerecky, L., 2013: *The Discovery of Stromatolites Developing at 3570 m above Sea Level in a High-Altitude Volcanic Lake Socompa, Argentinean Andes*, Plos One, 8.

Farra, R., Eichelbaum, M., Schlögl, R., Szentmiklosi, L., Schmidt, T., Amrute, A.P., Mondelli, C., Perez-Ramirez, J. and Teschner, D., 2013: *Do observations on surface coverage-reactivity correlations always describe the true catalytic process? A case study on ceria*, Journal of Catalysis, 297, 119.

Farra, R., Girgsdies, F., Frandsen, W., Hashagen, M., Schlögl, R. and Teschner, D., 2013: *Synthesis and Catalytic Performance of CeOCl in Deacon Reaction*, Catalysis Letters, 143, 1012.

Faunce, T.A., Lubitz, W., Rutherford, A.W., MacFarlane, D.R., Moore, G.F., Yang, P.D., Nocera, D.G., Moore, T.A., Gregory, D.H., Fukuzumi, S., Yoon, K.B., Armstrong, F.A., Wasielewski, M.R. and Styring, S., 2013: *Energy and environment policy case for a global project on artificial photosynthesis*, Energy & Environmental Science, 6, 695.

Frank, B., Cotter, T.P., Schuster, M.E., Schlögl, R. and Trunschke, A., 2013: *Carbon Dynamics on the Molybdenum Carbide Surface during Catalytic Propane Dehydrogenation*, Chemistry-a European Journal, 19, 16938.

Frank, B., Friedel, K., Girgsdies, F., Huang, X., Schlögl, R. and Trunschke, A., 2013: *CNT-Supported MoxC Catalysts: Effect of Loading and Carburization Parameters*, Chemcatchem, 5, 2296.

Frank, B., Schlögl, R. and Su, D.S., 2013: *Diesel Soot Toxification*, Environmental Science & Technology, 47, 3026.

Frank, B., Schuster, M.E., Schlögl, R. and Su, D.S., 2013: *Emission of Highly Activated Soot Particulate - The Other Side of the Coin with Modern Diesel Engines*, Angewandte Chemie-International Edition, 52, 2673.

Gallo, E., Bonino, F., Swarbrick, J.C., Petrenko, T., Piovano, A., Bordiga, S., Gianolio, D., Groppo, E., Neese, F., Lamberti, C. and Glatzel, P., 2013: *Preference towards Five-Coordination in Ti Silicalite-1 upon Molecular Adsorption*, ChemPhysChem, 14, 79.

Ganyushin, D. and Neese, F., 2013: *A fully variational spin-orbit coupled complete active space self-consistent field approach: Application to electron paramagnetic resonance g-tensors*, Journal of Chemical Physics, 138.

Gonidec, M., Krivokapic, I., Vidal-Gancedo, J., Davies, E.S., McMaster, J., Gorun, S.M. and Veciana, J., 2013: *Highly Reduced Double-Decker Single-Molecule Magnets Exhibiting Slow Magnetic Relaxation*, Inorganic Chemistry, 52, 4464.

Ghosh, P., Biswas, M.K., Weyhermüller, T., Patra, S.C., Maity, A.N. and Ke, S.C., 2013: *9,10-Phenanthrenesemiquinone radical complexes of ruthenium(III), osmium(III) and rhodium(III) and redox series*, Dalton Transactions, 42, 6538.

Griese, J.J., Roos, K., Cox, N., Shafaat, H.S., Branca, R.M.M., Lehtiö, J., Gräslund, A., Lubitz, W., Siegbahn, P.E.M. and Högbom, M., 2013: *Direct observation of structurally encoded metal discrimination and ether bond formation in a heterodinuclear metalloprotein*, Proceedings of the National Academy of Sciences of the United States of America, 110, 17189.

Grigoropoulos, A., Maganas, D., Symeonidis, D., Giastas, P., Cowley, A.R., Kyritsis, P. and Pneumatikakis, G., 2013: *Synthesis of Chalcogenidoimidodiphosphinato-Rh-I Complexes and DFT Investigation of Their Catalytic Activation in Olefin Hydroformylation*, European Journal of Inorganic Chemistry, 1170.

Gutiérrez-Sanz, O., Marques, M., Pereira, I.A.C., De Lacey, A.L., Lubitz, W. and Rüdiger, O., 2013: *Orientation and function of a membrane-bound enzyme monitored by electrochemical surface-enhanced infrared absorption spectroscopy*, Journal of Physical Chemistry Letters, 4, 2794.

Hall, E.R., Pollock, C.J., Glatzel, P., Bendix, J., Collins, T., Neese, F. and DeBeer, S., 2013: *Valence-to-core detected X-ray absorption spectroscopy: Progress toward ligand selectivity using resonant detection*, Abstracts of Papers of the American Chemical Society, 245.

Hazra, S., Bhattacharya, S., Singh, M.K., Carrella, L., Rentschler, E., Weyhermüller, T., Rajaraman, G. and Mohanta, S., 2013: *Syntheses, Structures, Magnetic Properties, and Density Functional Theory Magneto-Structural Correlations of Bis(mu-phenoxo) and Bis(mu-phenoxo)-mu-acetate/Bis(mu-phenoxo)-bis(mu-acetate) Dinuclear (FeNiII)-Ni-III Compounds*, Inorganic Chemistry, 52, 12881.

He, C., Nishikawa, K., Erdem, Ö.F., Reijerse, E., Ogata, H., Lubitz, W. and Knipp, M., 2013: *Complexes of ferriheme nitrophorin 4 with low-molecular weight thiol(ate)s occurring in blood plasma*, Journal of Inorganic Biochemistry, 122, 38.

Heine, C., Girgsdies, F., Trunschke, A., Schlögl, R. and Eichelbaum, M., 2013: *The model oxidation catalyst alpha-*V_2O_5*: insights from contactless in situ microwave permittivity and conductivity measurements*, Applied Physics a-Materials Science & Processing, 112, 289.

Hoeke, V., Krickemeyer, E., Heidemeier, M., Theil, H., Stammler, A., Bogge, H., Weyhermüller, T., Schnack, J. and Glaser, T., 2013: *A Comprehensive Study on Triplesalen-Based (Mn6FeIII)-Fe-III (3+) and (Mn6FeII)-Fe-III (2+) Complexes: Redox-Induced Variation of Molecular Magnetic Properties*, European Journal of Inorganic Chemistry, 2013, 4398.

Holzwarth, A.R., Lenk, D. and Jahns, P., 2013: *On the analysis of non-photochemical chlorophyll fluorescence quenching curves I. Theoretical considerations*, Biochimica Et Biophysica Acta-Bioenergetics, 1827, 786.

Hsieh, C.H., Erdem, Ö.F., Harman, S., Singleton, M., Reijerse, E., Lubitz, W., Popescu, C., Reibenspies, J., Brothers, S., Hall, M. and Darensbourg, M., 2013: *Structural and spectroscopic features of mixed valent Fe(I)Fe(II) complexes and factors related to the rotated configuration of diiron hydrogenase*, Abstracts of Papers of the American Chemical Society, 245.

Izsak, R. and Neese, F., 2013: *Speeding up spin-component-scaled third-order pertubation theory with the chain of spheres approximation: the COSX-SCS-MP3 method*, Molecular Physics, 111, 1190.

Izsak, R., Neese, F. and Klopper, W., 2013: *Robust fitting techniques in the chain of spheres approximation to the Fock exchange: The role of the complementary space*, Journal of Chemical Physics, 139.

Johnson, B., Girgsdies, F., Weinberg, G., Rosenthal, D., Knop-Gericke, A., Schlögl, R., Reier, T. and Strasser, P., 2013: *Suitability of Simplified (Ir,Ti)O-x Films for Characterization during Electrocatalytic Oxygen Evolution Reaction*, Journal of Physical Chemistry C, 117, 25443.

Joya, K.S. and de Groot, H.J.M., 2013: *Electrochemical in situ surface enhanced Raman spectroscopic characterization of a trinuclear ruthenium complex, Ru-red*, Journal of Raman Spectroscopy, 44, 1195.

Joya, K.S., Joya, Y.F., Ocakoglu, K. and van de Krol, R., 2013: *Water-Splitting Catalysis and Solar Fuel Devices: Artificial Leaves on the Move*, Angewandte Chemie-International Edition, 52, 10426.

Joya, K.S., Valles-Pardo, J.L., Joya, Y.F., Eisenmayer, T., Thomas, B., Buda, F. and de Groot, H.J.M., 2013: *Molecular Catalytic Assemblies for Electrodriven Water Splitting*, Chempluschem, 78, 35.

Kaichev, V.V., Gladky, A.Y., Prosvirin, I.P., Saraev, A.A., Hävecker, M., Knop-Gericke, A., Schlögl, R. and Bukhtiyarov, V.I., 2013: *In situ XPS study of self-sustained oscillations in catalytic oxidation of propane over nickel*, Surface Science, 609, 113.

Kamali, S., Wang, H., Mitra, D., Ogata, H., Lubitz, W., Manor, B.C., Rauchfuss, T.B., Byrne, D., Bonnefoy, V., Jenney, F.E., Adams, M.W.W., Yoda, Y., Alp, E., Zhao, J.Y. and Cramer, S.P., 2013: *Observation of the Fe-CN and Fe-CO vibrations in the active site of [NiFe] hydrogenase by nuclear resonance vibrational spectroscopy*, Angewandte Chemie-International Edition, 52, 724. German translation published: *Detektion von Fe-CN- und Fe-CO-Schwingungen im aktiven Zentrum der [NiFe]-Hydrogenase durch inelastische kernresonante Streuung*, Angewandte Chemie, 125, 752.

Kampa, M., Pandelia, M.E., Lubitz, W., van Gastel, M. and Neese, F., 2013: *A metal-metal bond in the light-induced state of [NiFe] hydrogenases with relevance to hydrogen evolution*, Journal of the American Chemical Society, 135, 3915.

Kandemir, T., Girgsdies, F., Hansen, T.C., Liss, K.-D., Kasatkin, I., Kunkes, E.L., Wowsnick, G., Jacobsen, N., Schlögl, R. and Behrens, M., 2013: *InSitu Study of Catalytic Processes: Neutron Diffraction of a Methanol Synthesis Catalyst at Industrially Relevant Pressure*, Angewandte Chemie-International Edition, 52, 5166.

Kandemir, T., Schuster, M.E., Senyshyn, A., Behrens, M. and Schlögl, R., 2013: *The Haber-Bosch Process Revisited: On the Real Structure and Stability of „Ammonia Iron" under Working Conditions*, Angewandte Chemie-International Edition, 52, 12723.

Katsounaros, I., Schneider, W.B., Meier, J.C., Benedikt, U., Biedermann, P.U., Cuesta, A., Auer, A.A. and Mayrhofer, K.J.J., 2013: *The impact of spectator species on the interaction of* H_2O_2 *with platinum - implications for the oxygen reduction reaction pathways*, Physical Chemistry Chemical Physics, 15, 8058.

Khavryuchenko, O.V., Frank, B., Trunschke, A., Hermann, K. and Schlögl, R., 2013: *Quantum-Chemical Investigation of Hydrocarbon Oxidative Dehydrogenation over Spin-Active Carbon Catalyst Clusters*, Journal of Physical Chemistry C, 117, 6225.

Kidambi, P.R., Bayer, B.C., Blume, R., Wang, Z.-J., Baehtz, C., Weatherup, R.S., Willinger, M.-G., Schlögl, R. and Hofmann, S., 2013: *Observing Graphene Grow: Catalyst-Graphene Interactions during Scalable Graphene Growth on Polycrystalline Copper*, Nano Letters, 13, 4769.

Knipp, M., He, C. and Ogata, H., 2013: *Nitrite dismutase - A „nitrite-only" source for NO*, Nitric Oxide-Biology and Chemistry, 31, S36.

Kochem, A., Thomas, F., Jarjayes, O., Gelon, G., Philouze, C., Weyhermüller, T., Neese, F. and van Gastel, M., 2013: *Structural and Spectroscopic Investigation of an Anilinosalen Cobalt Complex with Relevance to Hydrogen Production,* Inorganic Chemistry, 52, 14428.

Korup, O., Goldsmith, C.F., Weinberg, G., Geske, M., Kandemir, T., Schlögl, R. and Horn, R., 2013: *Catalytic partial oxidation of methane on platinum investigated by spatial reactor profiles, spatially resolved spectroscopy, and microkinetic modeling*, Journal of Catalysis, 297, 1.

Kozlowski, J.T., Behrens, M., Schlögl, R. and Davis, R.J., 2013: *Influence of the Precipitation Method on Acid-Base-Catalyzed Reactions over Mg-Zr Mixed Oxides*, Chemcatchem, 5, 1989.

Krahe, O., Neese, F. and Engeser, M., 2013: *Iron Azides with Cyclam-Derived Ligands: Are They Precursors for High-Valent Iron Nitrides in the Gas Phase?*, Chempluschem, 78, 1053.

Krämer, T., Kampa, M., Lubitz, W., van Gastel, M. and Neese, F., 2013: *Theoretical spectroscopy of the Ni(II) intermediate states in the catalytic cycle and the activation of [NiFe] hydrogenases*, ChemBioChem, 14, 1898.

Kreikemeyer-Lorenzo, D., Unterberger, W., Blume, R., Hävecker, M., Rocha, T.C.R., Knop-Gericke, A., Schlögl, R., Lerotholi, T.J., Duncan, D.A. and Woodruff, D.P., 2013: *Quantitative adsorbate structure determination under catalytic reaction conditions*, Physical Review B, 87.

Krewald, V., Lassalle-Kaiser, B., Boron, T.T., Pollock, C.J., Kern, J., Beckwith, M.A., Yachandra, V.K., Pecoraro, V.L., Yano, J., Neese, F. and DeBeer, S., 2013: *The Protonation States of Oxo-Bridged Mn-IV Dimers Resolved by Experimental and Computational Mn K Pre-Edge X-ray Absorption Spectroscopy*, Inorganic Chemistry, 52, 12904.

Krewald, V., Neese, F. and Pantazis, D.A., 2013: *On the Magnetic and Spectroscopic Properties of High-Valent* Mn_3CaO_4 *Cubanes as Structural Units of Natural and Artificial Water-Oxidizing Catalysts*, Journal of the American Chemical Society, 135, 5726.

Kundu, S., Maity, S., Weyhermüller, T. and Ghosh, P., 2013: *Oxidovanadium Catechol Complexes: Radical versus Non-Radical States and Redox Series*, Inorganic Chemistry, 52, 7417.

Kundu, S., Pfaff, F.F., Miceli, E., Zaharieva, I., Herwig, C., Yao, S.L., Farquhar, E.R., Kuhlmann, U., Bill, E., Hildebrandt, P., Dau, H., Driess, M., Limberg, C. and Ray, K., 2013: *A High-Valent Heterobimetallic Cu-III(mu-O)(2)Ni-III (2+) Core with Nucleophilic Oxo Groups*, Angewandte Chemie-International Edition, 52, 5622.

Kveder, M., Rakvin, B., Jokic, M. and Reijerse, E., 2013: *Frozen-in disorder probed by electron spin relaxation*, Solid State Communications, 167, 23.

Lancaster, K.M., Hu, Y.L., Bergmann, U., Ribbe, M.W. and DeBeer, S., 2013: *X-ray Spectroscopic Observation of an Interstitial Carbide in NifEN-Bound FeMoco Precursor*, Journal of the American Chemical Society, 135, 610.

Lassalle-Kaiser, B., Boron, T.T., Krewald, V., Kern, J., Beckwith, M.A., Delgado-Jaime, M.U., Schroeder, H., Alonso-Mori, R., Nordlund, D., Weng, T.C., Sokaras, D., Neese, F., Bergmann, U., Yachandra, V.K., DeBeer, S., Pecoraro, V.L. and Yano, J., 2013: *Experimental and Computational X-ray Emission Spectroscopy as a Direct Probe of Protonation States in Oxo-Bridged Mn-IV Dimers Relevant to Redox-Active Metalloproteins*, Inorganic Chemistry, 52, 12915.

Lima, F.A., Bjornsson, R., Weyhermüller, T., Chandrasekaran, P., Glatzel, P., Neese, F. and DeBeer, S., 2013: *High-resolution molybdenum K-edge X-ray absorption spectroscopy analyzed with time-dependent density functional theory*, Physical Chemistry Chemical Physics, 15, 20911.

Lindsay, S., Lo, S.K., Maguire, O.R., Bill, E., Probert, M.R., Sproules, S. and Hess, C.R., 2013: *Syntheses and Electronic Structure of Bimetallic Complexes Containing a Flexible Redox-Active Bridging Ligand*, Inorganic Chemistry, 52, 898.

Lohmiller, T., Ames, W., Lubitz, W., Cox, N. and Misra, S.K., 2013: *EPR spectroscopy and the electronic structure of the oxygen-evolving complex of photosystem II*, Applied Magnetic Resonance, 44, 691.

Losi, A., Gärtner, W., Raffelberg, S., Zanacchi, F.C., Bianchini, P., Diaspro, A., Mandalari, C., Abbruzzetti, S. and Viappiani, C., 2013: *A Photochromic Bacterial Photoreceptor with Potential for Super-Resolution Microscopy*, Biophysical Journal, 104, 672A.

Losi, A., Gärtner, W., Raffelberg, S., Zanacchi, F.C., Bianchini, P., Diaspro, A., Mandalari, C., Abbruzzetti, S. and Viappiani, C., 2013: *A photochromic bacterial photoreceptor with potential for super-resolution microscopy.* Photochem. Photobiol. Sci., 12, 231.

Lubitz, W. and Cox, N. 2013: *Wie Pflanzen Wasser spalten*, Spektrum der Wissenschaften, 9, 34.

Lubitz, W. and Ogata, H.: *Hydrogenases, structure and function*. In: Lennarz, W.J. and Lane, M.D. (eds) The Encyclopedia of Biological Chemistry, Academic Press, Waltham, 2013, pp. 562

Lundberg, M, Kroll, T., DeBeer, S., Bergmann, U., Wilson, S.A., Glatzel, P., Nordlund, D., Hedman, B., Hodgson, K.O., Solomon, E.I., 2013: *Metal-ligand Covalency of Iron Complexes from High-Resolution Resonant Inelastic Xray Scattering*, Journal of the American Chemical Society, 135, 17121.

Ma, M.Y., Noei, H., Mienert, B., Niesel, J., Bill, E., Muhler, M., Fischer, R.A., Wang, Y.M., Schatzschneider, U. and Metzler-Nolte, N., 2013: *Iron MetalOrganic Frameworks MIL-88B and NH2-MIL-88B for the Loading and Delivery of the Gasotransmitter Carbon Monoxide*, Chemistry-a European Journal, 19, 6785.

Maganas, D., Roemelt, M., Hävecker, M., Trunschke, A., Knop-Gericke, A., Schlögl, R. and Neese, F., 2013: *First principles calculations of the structure and V L-edge X-ray absorption spectra of* V_2O_5 *using local pair natural orbital coupled cluster theory and spin-orbit coupled configuration interaction approaches*, Physical Chemistry Chemical Physics, 15, 7260.

Mandalari, C., Losi, A. and Gärtner, W., 2013: *Distance-tree analysis, distribution and co-presence of bilin- and flavin-binding prokaryotic photoreceptors for visible light*, Photochemical & Photobiological Sciences, 12, 1144.

Mansurova, M., Simon, J., Salzmann, S., Marian, C.M. and Gärtner, W., 2013: *Spectroscopic and Theoretical Study on Electronically Modified Chromophores in LOV Domains: 8-Bromo- and 8-Trifluoromethyl-Substituted Flavins*, Chembiochem, 14, 645.

Menelaou, M., Weyhermüller, T., Soler, M. and Aliaga-Alcalde, N., 2013: *Novel paramagnetic-luminescent building blocks containing manganese(II) and anthracene-based curcuminoids*, Polyhedron, 52, 398.

Meyer, S., Klawitter, I., Demeshko, S., Bill, E. and Meyer, F., 2013: *A Tetracarbene-Oxoiron(IV) Complex*, Angewandte Chemie-International Edition, 52, 901.

Möbius, K., Lubitz, W. and Savitsky, A., 2013: *High-field EPR on membrane proteins - Crossing the gap to NMR*, Progress in Nuclear Magnetic Resonance Spectroscopy, 75, 1.

Molitor, B., Stassen, M., Modi, A., El-Mashtoly, S.F., Laurich, C., Lubitz, W., Dawson, J.H., Rother, M. and Frankenberg-Dinkel, N., 2013: *A heme-based redox sensor in the methanogenic archaeon Methanosarcina acetivorans*, Journal of Biological Chemistry, 288, 18458.

Morgenstern, B., Neis, C., Zaschka, A., Romba, J., Weyhermüller, T. and Hegetschweiler, K., 2013: *Formation and Base Hydrolysis of Oxidimethaneamine Bridges in Co-III-Amine Complexes*, Inorganic Chemistry, 52, 12080.

Moriconi, V., Sellaro, R., Ayub, N., Soto, G., Rugnone, M., Shah, R., Pathak, G., Gärtner, W. and Casal, J.J., 2013: *LOV-domain photoreceptor, encoded in a genomic island, attenuates the virulence of Pseudomonas syringae in light-exposed Arabidopsis leaves*, Plant Journal, 76, 322.

Nalepa, A.I., Taing, J.J., Savitsky, A. and Knipp, M., 2013: *Preparation of cysteine-34-nitro-xide spin labeled human* α_1*-microglobulin*, Protein Expression and Purification, 88, 33.

Narkowicz, R., Ogata, H., Reijerse, E., Suter, D., 2013: *A cryogenic receiver for EPR*, Journal of Magnetic Resonance, 237, 79.

Oliveira, A., Allegri, A., Bidon-Chanal, A., Knipp, M., Roitberg, A.E., Abbruzzetti, S., Viappiani, C. and Luque, F.J., 2013: *Kinetics and computational studies of ligand migration in nitrophorin 7 and its* Δ*1-3 mutant*, Biochimica et Biophysica Acta-Proteins and Proteomics, 1834, 1711.

Pal, S., Jadhav, M., Weyhermüller, T., Patil, Y., Nethaji, M., Kasabe, U., Kathawate, L., Konkimalla, V.B. and Salunke-Gawali, S., 2013: *Molecular structures and antiproliferative activity of side-chain saturated and homologated analogs of 2-chloro-3-(n-alkylamino)-1,4-napthoquinone*, Journal of Molecular Structure, 1049, 355.

Pandelia, M.E., Bykov, D., Izsak, R., Infossi, P., Giudici-Orticoni, M.T., Bill, E., Neese, F. and Lubitz, W., 2013: *Electronic structure of the unique [4Fe-3S] cluster in O_2-tolerant hydrogenases characterized by ^{57}Fe Mössbauer and EPR spectroscopy*, Proceedings of the National Academy of Sciences of the United States of America, 110, 483.

Pandelia, M.E., Bykov, D., Izsak, R., Infossi, P., Giudici-Orticoni, M.T., Bill, E., Neese, F. and Lubitz, W., 2013: *Reply to Mouesca et al.: Electronic structure of the proximal [4Fe-3S] cluster of O_2-tolerant NiFe hydrogenases*, Proceedings of the National Academy of Sciences of the United States of America, 110, E2539.

Pandit, A., Reus, M., Morosinotto, T., Bassi, R., Holzwarth, A.R. and de Groot, H.J.M., 2013: *An NMR comparison of the light-harvesting complex II (LHCII) in active and photoprotective states reveals subtle changes in the chlorophyll a ground-state electronic structures*, Biochimica Et Biophysica Acta-Bioenergetics, 1827, 738.

Papaefthimiou, V., Shishkin, M., Niakolas, D.K., Athanasiou, M., Law, Y.T., Arrigo, R., Teschner, D., Hävecker, M., Knop-Gericke, A., Schlögl, R., Ziegler, T., Neophytides, S.G. and Zafeiratos, S., 2013: *On the Active Surface State of Nickel-Ceria Solid Oxide Fuel Cell Anodes During Methane Electrooxidation*, Advanced Energy Materials, 3, 762.

Pérez Navarro, M., Ames, W.M., Nilsson, H., Lohmiller, T., Pantazis, D.A., Rapatskiy, L., Nowaczyk, M.M., Neese, F., Boussac, A., Messinger, J., Lubitz, W. and Cox, N., 2013: *Ammonia binding to the oxygen-evolving complex of photosystem II identifies the solvent-exchangeable μ-oxo of the manganese tetramer*, Proceedings of the National Academy of Sciences of the United States of America, 110, 15561.

Plois, M., Hujo, W., Grimme, S., Schwickert, C., Bill, E., de Bruin, B., Pottgen, R. and Wolf, R., 2013: *Open-Shell First-Row Transition-Metal Polyhydride Complexes Based on the fac - RuH3(PR3)3 - Building Block*, Angewandte Chemie-International Edition, 52, 1314.

Pollock, C.J., Grubel, K., Holland, P.L. and DeBeer, S., 2013: *Experimentally Quantifying Small-Molecule Bond Activation Using Valence-to-Core X-ray Emission Spectroscopy*, Journal of the American Chemical Society, 135, 11803.

Pollock, C.J., Grubel, K., Holland, P.L., Neese, F. and DeBeer, S., 2013: *Experimentally quantifying small molecule bond activation using Kb X-ray emission spectroscopy*, Abstracts of Papers of the American Chemical Society, 245.

Raffelberg, S., Gutt, A., Gärtner, W., Mandalari, C., Abbruzzetti, S., Viappiani, C. and Losi, A., 2013: *The amino acids surrounding the flavin 7a-methyl group determine the UVA spectral features of a LOV protein*, Biological Chemistry, 394, 1517.

Raffelberg, S., Wang, L.Z., Gao, S.Q., Losi, A., Gärtner, W. and Nagel, G., 2013: *A LOV-domain-mediated blue-light-activated adenylate (adenylyl) cyclase from the cyanobacterium Microcoleus chthonoplastes PCC 7420*, Biochemical Journal, 455, 359.

Retegan, M., Collomb, M.N., Neese, F. and Duboc, C., 2013: *A combined high-field EPR and quantum chemical study on a weakly ferromagnetically coupled dinuclear Mn(III) complex. A complete analysis of the EPR spectrum beyond the strong coupling limit*, Physical Chemistry Chemical Physics, 15, 223.

Retegan, M., Neese, F. and Pantazis, D.A., 2013: *Convergence of QM/MM and Cluster Models for the Spectroscopic Properties of the Oxygen-Evolving Complex in Photosystem II*, Journal of Chemical Theory and Computation, 9, 3832.

Riethausen, J., Rüdiger, O., Gärtner, W., Lubitz, W. and Shafaat, H.S., 2013: *Spectroscopic and electrochemical Ccharacterization of the [NiFeSe] hydrogenase from Desulfovibrio vulgaris Miyazaki F: Reversible redox behavior and interactions between electron transfer centers*, ChemBioChem, 14, 1714.

Riplinger, C. and Neese, F., 2013: *An efficient and near linear scaling pair natural orbital based local coupled cluster method*, Journal of Chemical Physics, 138.

Riplinger, C., Sandhöfer, B., Hansen, A. and Neese, F., 2013: *Natural triple excitations in local coupled cluster calculations with pair natural orbitals*, Journal of Chemical Physics, 139.

Roemelt, M., Maganas, D., DeBeer, S. and Neese, F., 2013: *A combined DFT and restricted open-shell configuration interaction method including spin-orbit coupling: Application to transition metal L-edge X-ray absorption spectroscopy*, Journal of Chemical Physics, 138.

Roemelt, M. and Neese, F., 2013: *Excited States of Large Open-Shell Molecules: An Efficient, General, and Spin-Adapted Approach Based on a Restricted Open-Shell Ground State Wave function*, Journal of Physical Chemistry A, 117, 3069.

Rudd, P.A., Liu, S.S., Planas, N., Bill, E., Gagliardi, L. and Lu, C.C., 2013: *Multiple Metal-Metal Bonds in Iron-Chromium Complexes*, Angewandte Chemie-International Edition, 52, 4449.

Salewski, J., Escobar, F.V., Kaminski, S., von Stetten, D., Keidel, A., Rippers, Y., Michael, N., Scheerer, P., Piwowarski, P., Bartl, F., Frankenberg-Dinkel, N., Ringsdorf, S., Gärtner, W., Lamparter, T., Mroginski, M.A. and Hildebrandt, P., 2013: *Structure of the Biliverdin Cofactor in the Pfr State of Bathy and Prototypical Phytochromes*, Journal of Biological Chemistry, 288, 16800.

Sandhöfer, B., Kossmann, S. and Neese, F., 2013: *Derivation and assessment of relativistic hyperfine-coupling tensors on the basis of orbital-optimized second-order Moller-Plesset perturbation theory and the second-order Douglas-Kroll-Hess transformation*, Journal of Chemical Physics, 138.

Savitsky, A., Grishin, Y., Rakhmatullin, R., Reijerse, E. and Lubitz, W., 2013: *An improved coupling design for high-frequency TE011 electron paramagnetic resonance cavities*, Review of Scientific Instruments, 84, 014704.

Savitsky, A., Niklas, J., Golbeck, J.H., Möbius, K., Lubitz, W. 2013: *Orientation resolving dipolar high-field EPR spectroscopy on disordered solids: II. Structure of spin-correlated radical pairs in photosystem I*, The Journal of Physical Chemistry B, 117, 11184.

Schapiro, I., Sivalingam, K. and Neese, F., 2013: *Assessment of n-Electron Valence State Perturbation Theory for Vertical Excitation Energies*, Journal of Chemical Theory and Computation, 9, 3567.

Schneider, W.B., Benedikt, U. and Auer, A.A., 2013: *Interaction of Platinum Nanoparticles with Graphitic Carbon Structures: A Computational Study*, Chemphyschem, 14, 2984.

Schuchmann, H.P., Adhikary, A., O'Neill, P. and Cadet, J., 2013: *Professor Clemens von Sonntag (1936-2013) OBITUARY*, International Journal of Radiation Biology, 89, 590.

Schweinfurth, D., Krzystek, J., Schapiro, I., Demeshko, S., Klein, J., Telser, J., Ozarowski, A., Su, C.Y., Meyer, F., Atanasov, M., Neese, F. and Sarkar, B., 2013: *Electronic Structures of Octahedral Ni(II) Complexes with „Click" Derived Triazole Ligands: A Combined Structural, Magnetometric, Spectroscopic, and Theoretical Study*, Inorganic Chemistry, 52, 6880.

Selvaraj, B., Pierik, A.J., Bill, E. and Martins, B.M., 2013: *4-Hydroxyphenylacetate decarboxylase activating enzyme catalyses a classical S-adenosylmethionine reductive cleavage reaction*, Journal of Biological Inorganic Chemistry, 18, 633.

Shafaat, H.S., Rüdiger, O., Ogata, H. and Lubitz, W., 2013: *[NiFe] hydrogenases: A common active site for hydrogen metabolism under diverse conditions*, Biochimica Et Biophysica Acta-Bioenergetics, 1827, 986.

Shao, L., Zhang, B., Zhang, W., Hong, S.Y., Schlögl, R. and Su, D.S., 2013: *The Role of Palladium Dynamics in the Surface Catalysis of Coupling Reactions*, Angewandte Chemie-International Edition, 52, 2114.

Shevela, D., Noering, B., Koroidov, S., Shutova, T., Samuelsson, G. and Messinger, J., 2013: *Efficiency of photosynthetic water oxidation at ambient and depleted levels of inorganic carbon*, Photosynthesis Research, 117, 401.

Silva, M.R., Mansurova, M., Gärtner, W. and Thiel, W., 2013: *Photophysics of Structurally Modified Flavin Derivatives in the Blue-Light Photoreceptor YtvA: A Combined Experimental and Theoretical Study*, Chembiochem, 14, 1648.

Simandiras, E.D. and Liakos, D.G., 2013: *Theoretical prediction of new Kubas four centre H-2 complexes involving dimolybdate clusters*, Chemical Physics Letters, 583, 18.

Soras, G., Psaroudakis, N., Manos, M.J., Tasiopoulos, A.J., Liakos, D.G. and Mousdis, G.A., 2013: *Synthesis, experimental and theoretical investigation of a new type nickel dithiolene complex*, Polyhedron, 62, 208.

Sparta, M., Jensen, V.R. and Borve, K.J., 2013: *Accurate metal-ligand bond energies in the (2)-C2H4 and (2)-C-60 complexes of Pt(PH3)(2), with application to their Bis(triphenylphosphine) analogues*, Molecular Physics, 111, 1599.

Thapper, A., Styring, S., Saracco, G., Rutherford, A.W., Robert, B., Magnuson, A., Lubitz, W., Llobet, A., Kurz, P., Holzwarth, A.R., Fiechter,S., de Groot, H. Campagna, S. Braun, A. Bergecol, H. and Vincent, A. 2013: *Artificial photosynthesis for solar fuels - an evolving research field within AMPEA, a Joint Programme of the European Energy Research Alliance*, Green, 3, 43.

Tondreau, A.M., Stieber, S.C.E., Milsmann, C., Lobkovsky, E., Weyhermüller, T., Semproni, S.P. and Chirik, P.J., 2013: *Oxidation and Reduction of Bis(imino)pyridine Iron Dinitrogen Complexes: Evidence for Formation of a Chelate Trianion*, Inorganic Chemistry, 52, 635.

Urbano, S.B., Albarracin, V., Ordonez, O.F., Farias, M.E. and Alvarez, H.M., 2013: *Lipid storage in high-altitude Andean Lakes extremophiles and its mobilization under stress conditions in Rhodococcus sp A5, a UV-resistant actinobacterium*, Extremophiles, 17, 217.

Varghese, S., Yang, F., Pacheco, V., Wrede, K., Medvedev, A., Ogata, H., Knipp, M. and Heise, H., 2013: *Expression, purification, and solid-state NMR characterization of the membrane binding heme protein nitrophorin 7 in two electronic spin states*, Biochemistry, 52, 7031.

Velazquez Escobar, F., Utesch, T., Narikawa, R., Ikeuchi, M., Mroginski, M.-A., Gärtner, W. and Hildebrandt, P., 2013: *Photoconversion mechanism of the second GAF domain of cyanobacteriochrome AnPixJ and the cofactor structure of its green-absorbing state*, Biochemistry, 52, 4871.

Vogel, D., Budinska, Z., Spiel, C., Schlögl, R., Suchorski, Y. and Rupprechter, G., 2013: *Silicon Oxide Surface Segregation in CO Oxidation on Pd: An in situ PEEM, MS and XPS Study*, Catalysis Letters, 143, 235.

Vogel, D., Spiel, C., Schmid, M., Stoeger-Pollach, M., Schlögl, R., Suchorski, Y. and Rupprechter, G., 2013: *The Role of Defects in the Local Reaction Kinetics of CO Oxidation on Low-Index Pd Surfaces*, Journal of Physical Chemistry C, 117, 12054.

Wang, D., Villa, A., Su, D., Prati, L. and Schlögl, R., 2013: *Carbon-Supported Gold Nanocatalysts: Shape Effect in the Selective Glycerol Oxidation*, Chemcatchem, 5, 2717.

Wang, M., England, J., Weyhermüller, T., Kokatam, S.L., Pollock, C.J., DeBeer, S., Shen, J.M., Yap, G.P.A., Theopold, K.H. and Wieghardt, K., 2013: *New Complexes of Chromium(III) Containing Organic pi-Radical Ligands: An Experimental and Density Functional Theory Study*, Inorganic Chemistry, 52, 4472.

Wang, H., Ogata, H., Lubitz, W. and Cramer, S.P. 2013: *A dynamic view of [NiFe] hydrogenase by means of nuclear resonance vibrational spectroscopy*, SPring-8 Research Frontiers 2012, 80.

Wang, M., Weyhermüller, T., England, J. and Wieghardt, K., 2013: *Molecular and Electronic Structures of Six-Coordinate „Low-Valent" M((Me)bpy)(3) (0) (M = Ti, V. Cr, Mo) and M(tpy)(2) (0) (M = Ti, V, Cr), and Seven-Coordinate MoF((Me)bpy)(3) (PF6) and MX(tpy)(2) (PF6) (M = Mo, X = Cl and M = W, X = F)*, Inorganic Chemistry, 52, 12763.

Weatherup, R.S., Bähtz, C., Dlubak, B., Bayer, B.C., Kidambi, P.R., Blume, R., Schlögl, R. and Hofmann, S., 2013: *Introducing Carbon Diffusion Barriers for Uniform, High-Quality Graphene Growth from Solid Sources*, Nano Letters, 13, 4624.

Xue, G.Q., Geng, C.Y., Ye, S.F., Fiedler, A.T., Neese, F. and Que, L., 2013: *Hydrogen-Bonding Effects on the Reactivity of X-Fe-III-O-Fe-IV = O (X = OH, F) Complexes toward C-H Bond Cleavage*, Inorganic Chemistry, 52, 3976.

Yan, Y., Keating, C., Chandrasekaran, P., Jayarathne, U., Mague, J.T., DeBeer, S., Lancaster, K.M., Sproules, S., Rubtsov, I.V. and Donahue, J.P., 2013: *Ancillary Ligand Effects upon Dithiolene Redox Noninnocence in Tungsten Bis(dithiolene) Complexes*, Inorganic Chemistry, 52, 6743.

Yao, S.L., Hrobarik, P., Meier, F., Rudolph, R., Bill, E., Irran, E., Kaupp, M. and Driess, M., 2013: *A Heterobimetallic Approach To Stabilize the Elusive Disulfur Radical Trianion („Subsulfide") S-2(center dot 3-)*, Chemistry-a European Journal, 19, 1246.

Ye, S.F., Geng, C.Y., Shaik, S. and Neese, F., 2013: *Electronic structure analysis of multistate reactivity in transition metal catalyzed reactions: the case of C-H bond activation by non-heme iron(IV)-oxo cores*, Physical Chemistry Chemical Physics, 15, 8017.

Zadrozny, J.M., Atanasov, M., Bryan, A.M., Lin, C.Y., Rekken, B.D., Power, P.P., Neese, F. and Long, J.R., 2013: *Slow magnetization dynamics in a series of two-coordinate iron(II) complexes*, Chemical Science, 4, 125.

Zadrozny, J.M., Xiao, D.J., Atanasov, M., Long, G.J., Grandjean, F., Neese, F. and Long, J.R., 2013: *Magnetic blocking in a linear iron(I) complex*, Nature Chemistry, 5, 577.

Zadrozny, J.M., Xiao, D.J., Long, J.R., Atanasov, M., Neese, F., Grandjean, F. and Long, G.J., 2013: *Mössbauer Spectroscopy as a Probe of Magnetization Dynamics in the Linear Iron(I) and Iron(II) Complexes* $[Fe(C(SiMe_3)_3)_2]^{1-/0}$, Inorganic Chemistry, 52, 13123.

Zall, C.M., Clouston, L.J., Young, V.G., Ding, K.Y., Kim, H.J., Zherebetskyy, D., Chen, Y.S., Bill, E., Gagliardi, L. and Lu, C.C., 2013: *Mixed-Valent Dicobalt and Iron-Cobalt Complexes with High-Spin Configurations and Short Metal-Metal Bonds*, Inorganic Chemistry, 52, 9216.

Zander, S., Kunkes, E.L., Schuster, M.E., Schumann, J., Weinberg, G., Teschner, D., Jacobsen, N., Schlögl, R. and Behrens, M., 2013: *The Role of the Oxide Component in the Development of Copper Composite Catalysts for Methanol Synthesis*, Angewandte Chemie-International Edition, 52, 6536.

Zemlyanov, D., Klötzer, B., Gabasch, H., Smeltz, A., Ribeiro, F.H., Zafeiratos, S., Teschner, D., Schnoerch, P., Vass, E., Hävecker, M., Knop-Gericke, A. and Schlögl, R., 2013: *Kinetics of Palladium Oxidation in the mbar Pressure Range: Ambient Pressure XPS Study*, Topics in Catalysis, 56, 885.

Zheng, W., Cotter, T.P., Kaghazchi, P., Jacob, T., Frank, B., Schlichte, K., Zhang, W., Su, D.S., Schüth, F. and Schlögl, R., 2013: *Experimental and Theoretical Investigation of Molybdenum Carbide and Nitride as Catalysts for Ammonia Decomposition*, Journal of the American Chemical Society, 135, 3458.

178 publications in 2013, total 540 publications in 2010 – 2013

Invited and Plenary Lectures at Conferences

2010

Cox, N.: EPR/ENDOR Studies of Manganese-containing Enzymes: The Ribonucleotide reductase and Photosystem II (Award Lecture, IX. Asia-Pacific EPR/ESR Symposium. Jeju, South Korea, 2010)

Gärtner, W.: Blue Light-Sensing Photoreceptors – A Progress Report (DFG Research Initiative, Chiemsee, Germany, 2010-03)

Gärtner, W.: Novel Blue Light-Sensing Photoreceptors from a Metagenomic Approach (Gordon Conference, Il Ciocco, Italy, 2010-04)

Gärtner, W.: Effect of Chromophore Modification on the Photochemistry of Phytochromes (ICPP Congress Albuquerque, USA, 2010-07)

Knipp, M.: The formation of nitric oxide from nitrite happens at the heme center of nitrophorins. (XVIth International Conference on Oxygen Binding and Sensing Proteins, Antwerp, Belgium, 2010)

Knipp, M.: The ferriheme protein nitrophorin 7 forms nitric oxide from nitrite (Sixth International Conference on Porphyrins and Phthalocyanins (ICPP-6), Albuquerque, New Mexico, 2010)

Knipp, M.: Interaction of nitrophorin with liposomes. (Inter-work group meeting "Cellular radical stress and related biomarkers", COST action CM0603, Athens, Greece, 2010)

Lubitz, W.: Light-Induced Water Splitting in Oxygenic Photosynthesis: EPR Studies of the Wateroxidase in Photosystem II. Umeå (Renewable Energy Workshop. From Structures and Mechanisms of Biological Enzymes to Biomass Production and Utilization, University of UMEÅ; Sweden, 2010)

Lubitz, W.: Structure and Function of [NiFe] and [FeFe] Hydrogenases: Blueprints for Catalytic Model Systems (Umeå Renewable Energy Workshop. From Structures and Mechanisms of Biological Enzymes to Biomass Production and Utilization, University of UMEÅ, Sweden, 2010)

Lubitz, W.: A Tyrosyl-Dimanganese Coupled Spin System in Ribonucleotide Reductase of *C. ammoniagenes* Studied by Multifrequency EPR Spectroscopy and X-ray Crystallography (Multi-Frequency Electron Paramagnetic Resonance: A Perspective for the Biosciences, Lorentz Center International Center for Workshops in the Sciences, Leiden, The Netherlands, 2010)

Lubitz, W.: Structure and Function of [NiFe] Hydrogenases: Insights from FTIR, EPR and Electrochemical Techniques (Internationales Graduiertenkollegs 1422 „Metal Sites in Biomolecules“, Institut für Anorganische Chemie der Universität Göttingen, Germany, 2010)

Lubitz, W.: The Hydrogen Converting FeS Cluster in [FeFe] Hydrogenase: Insight from Magnetic Resonance and Vibrational Spectroscopy (Gordon Research Conference on Iron-Sulfur Enzymes, New London, New Hampshire, USA, 2010)

Lubitz, W.: Intermediates in Hydrogenase Catalysis Studied by Advanced EPR Techniques (Joint EUROMAR 2010 and 17th ISMAR Conference, World Wide Magnetic Conference, Florence, Italy 2010)

Lubitz, W.: Metalloenzymes Studied by Multifrequency EPR and Related Techniques (Joint NMR/EPR 33rd International EPR Symposium/52nd Rocky Mountain Conference on Analytical Chemistry, Snowmass, USA, 2010)

Lubitz, W.: Metalloproteins Studied by Pulse EMR Techniques - Wateroxidase and Hydrogenase (XXIVth ICMRBS International Conference on Magnetic Resonance in Biological Systems, Cairns, Australia, 2010)

Lubitz, W.: Application of Multifrequency Pulsed Electron Spin Resonance Techniques to Biological Questions (School of Physics Colloquia 2010, ARC Australian Research Fellow School of Physics, Faculty of Science, University of Sydney, Australia, 2010)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: The Enzymes Wateroxidase and Hydrogenase (Nanyang Technological University, Singapur, 2010)

Lubitz, W.: Multifrequency EPR Spectroscopy of Tyrosyl-Dimanganese Coupled Spin System in Ribonucleotide Reductase of *C. ammoniagenes* (DFG-Rundgespräch „New Frontiers in Electron Spin Resonance Methodology“, Hirschegg, Austria, 2010)

Lubitz, W.: Pulse EPR Techniques Applied to the Metalloenzyme Hydrogenase: Hydrogen Production and Conversion in Nature (32nd Discussion Meeting and Joint Benelux/German MR Conference, Development and Applications of Modern Magnetic Resonance Techniques in Chemistry, Life Sciences and Material Research, Gesellschaft Deutscher Chemiker, Fachgruppe Magnetische Resonanzspektroskopie, Münster, Germany, 2010)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: Structure and Function of the Enzymes Wateroxidase and Hydrogenase (4th International IMBG Meeting on Metals and Bioenergetics, Institute of Metals in Biology of Grenoble, Autrans, France, 2010)

Lubitz, W.: Recent Advances in Spectroscopic Techniques to Study Metalloproteins: Electron Magnetic Resonance (EMR) Methods (IMBG advanced courses on Metals and Bioenergetics; Institute of Metals in Biology of Grenoble, Autrans, France, 2010)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: EPR Studies of the Enzymes Wateroxidase and Hydrogenase (VIIIth International Workshop on EPR (ESR) in Biology and Medicine, Kraków, Poland, 2010)

Lubitz, W.: Biological Catalysts Involved in Biosolar Hydrogen Production (Leopoldina Workshop Biofuels and Bioconversion, Deutsche Akademie der Naturforscher Leopoldina – Nationale Akademie der Wissenschaften, Greifswald, Germany, 2010)

Lubitz, W.: The Metalloradical-Cofactor in Ribonucleotide Reductase: Can Iron be Substituted by Manganese? (GDCh-Lecture, University of Hannover, Germany, 2010)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Conversion in Nature (GDCh-Lecture, University of Paderborn, Germany, 2010)

Neese, F.: The reaction mechanism of cytochrome P450 NO reductase. Spectroscopy and QM/MM calculations (Pacifichem, Honolulu, USA, 2010)

Neese, F.: Magnetic spectroscopy of transition metal complexes with strong spin-orbit coupling (Aussois, France. Club de Metalloproteins et Modelles, 2010)

Neese, F.: Magnetic spectroscopy of transition metal complexes with strong spin-orbit coupling (International Symposium on Molecular Coordination Chemistry. Mülheim, Germany, on occasion of Karl Wieghardts retirement, 2010)

Neese, F.: The electron spin in chemistry: from subtle reactivity issues to distance measurements (GdCH Kolloquium, Aachen, Germany, 2010)

Neese, F.: The electron spin in chemistry: from subtle reactivity issues to distance measurements (GdCH Kolloquium, Bielefeld, Germany, 2010)

Neese, F.: From the design of theoretical methods to insights about the water oxidizing manganese cluster in photosystem II (Cornell University, Ithaca, USA, 2010)

Neese, F.: Subtleties of the electron spin in chemistry: reactivity and molecular properties (Princeton University, USA, 2010)

Neese, F.: On the importance of trace elements for life (Martin Niemöller Gymnasium, Wiesbaden, Germany, 2010)

Neese, F.: Electronic Structure and Spectroscopy of systems with strong Spin-Orbit Coupling (Gordon conference for computational chemistry, Les Diableres, Switzerland, 2010)

Neese, F.: Symposium on "Electronic Structure and Spectroscopy of systems with strong Spin-Orbit Coupling (American Chemical Society Meeting, Boston, USA, 2010)

Neese, F.: Reaction Mechanisms of Nonheme Iron Enzymes (EUROBIC, Tessaloniki, Greece, 2010)

Neese, F.: C-H Bond Activation by Nonheme Iron Centers (Penn State University. Frontiers in Bioinorganic Chemistry, 2010)

Neese, F.: Recent Developments in Local Coupled Cluster Methods (Berkeley University, Berkely, CA, USA. Symposium in honour of Prof. Henry F. Schaefer III., 2010)

Neese, F.: Theory and applications of magnetic circular dichroism spectroscopy (University of Mainz, Physical and Theoretical Chemistry, Germany, 2010)

Neese, F.: Recent developments in local pair natural orbital based coupled cluster methods (Meeting on first principles quantum chemistry. From elementary reactions to enzymes in honour of H.-J. Werner, Bad Herrenalb, Germany, 2010)

Neese, F.: Mössbauer Spectroscopy and Quantum Chemistry (American Chemical Society Meeting, San Francisco, USA, 2010)

Neese, F.: Spin dependent effects in Chemistry. From Reaction Mechanisms to Distance Measurements (University of Barcelona, Spain, 2010)

Neese, F.: Introduction, Multireference Approaches, Single Reference Approaches (University of Tarragona, Spain, 2010)

Neese, F.: Spin Dependent Effects in Chemistry (University of Groningen, The Netherlands, 2010)

Neese, F.: International Symposium on Theoretical and Computational Chemistry, Mülheim an der Ruhr, Germany. Invited Lecture "Uses of Theoretical Spectroscopy"

Neese, F.: Perspectives for Theoretical Spectroscopy in Bioinorganic Chemistry (Gordon Conference on Metals in Biology, Ventura, CA, USA, 2010)

Neese, F.: Recent Developments in Quantum Chemical Approaches: From Reaction Mechanisms to Distance Measurements (McElvain Lecture, University of Wisconsin, Madison, USA, 2010)

Neese, F.: Transition Metals, Spectra and Quanta: A Powerful Combination (Evaluation of the Max-Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr, Germany, 2010) "

Neese, F.: Recent Developments in Pair Natural Orbital Coupled Cluster Calculations (RAMET10; Kalkotta, India, 2010)

Reijerse E.: Multi-frequency Pulsed EPRcharacterization of the active site of [FeFe] Hydrogenases and related model systems. (Asia Pacific EPR conference, Jeju, South Korea, 2010-10-10 to 2010-01-14)

Reijerse E. and Silkov, A.: Structural and Mechanistic investigations of *[NiFe]* and *[FeFe] hydrogenases*; Nature's guide to artificial hydrogen production. (9th International Hydrogenase Conference, Uppsalla, Sweden, 2010-06)

Wieghardt, K.: Invited Lectures (Gordon Research Conference Ventura, USA; R. Siedle Lectureship, Bloomington, USA; Tulane University, New Orleans, USA; GDCh, Erlangen; Penn State University, USA, Cornell University, USA; Universität Göttingen; Schweizer Che. Ges., Zürich; University of Minneapolis, USA; Pacifichem, USA, 2010)

2011

Bill, E.: Iron Sulfur Clusters – New Features in Hydrogenases and Synthetic Models. (International Conference on the Application of the Mössbauer Effect' (ICAME 2011), Kobe, Japan, 2011-09-27)

Bill, E.: Eisenschwefel-Cluster - neue Strukturen und Funktionen. (Chemie Seminar, Georg-August Universität Göttingen, Germany, 2011-12-20)

DeBeer, S.: Iron Kb X-ray emission spectroscopy as a probe of biological and chemical catalysis (University of Bonn, Department of Inorganic Chemistry, Bonn, Germany, 2011-01)

DeBeer, S.: Valence to Core X-ray Emission as a Probe of Biological and Chemical Catalysis (Fritz-Haber Institute, Berlin, Germany, 2011-04)

DeBeer, S.: Valence to Core X-ray Emission Spectroscopy: A Novel Probe of Metal-Ligand Interactions (Max Planck Institute for Bioinorganic Chemistry, Mülheim, Germany, 2011-04)

DeBeer, S.: Probing Biological and Chemical Catalysis with Metal K-Beta X-ray Emission Spectroscopy (Ruhr-Universität Bochum, Bochum, Germany, 2011-04)

DeBeer, S.: Probing Biological and Chemical Catalysis with Metal K-Beta X-ray Emission Spectroscopy (Third Georgian Bay International Conference on Bioinorganic Chemistry (CanBIC), Parry Sound, Canada, 2011-06)

DeBeer, S.: K-Beta X-ray Emission Spectroscopy as a Probe of Biological Catalysis: New Insights into the FeMoco Cluster of Nitrogenase (94th Canadian Chemistry Conference, Montreal, Canada, 2011-06)

DeBeer, S.: Valence to Core X-ray Emission as a Novel Probe of Metal-Ligand Interactions in Biological Catalysis (CECAM Workshop on X-ray Spectroscopy, Zurich, Switzerland, 2011-07)

DeBeer, S.: Probing Biological Catalysis using K-Beta X-ray Emission Spectroscopy: New Insights into Nitrogenase (American Chemical Society Meeting, Denver, CO, 2011-08)

DeBeer, S.: Iron and Manganese K-Beta X-ray Emission Spectroscopy as a Probe of Biological and Chemical Catalysis (Third Erlangen SFB-Symposium on Redoxactive Metal Complexes – Control of Reactivity via Molecular Architecture, 2011-10)

DeBeer, S.: Introduction to X-ray Spectroscopy: Mainly (X-ray) absorption and a bit of emission (Stanford Synchrotron Radiation Lightsource, SLAC, Workshop on Demystifying the Synchrotron Experience, 2011-10)

DeBeer, S.: X-ray Emission Spectroscopy as a Probe of Biological and Chemical Catalysis (Stanford Synchrotron Radiation Lightsource, SLAC, Workshop on Synchrotron Applications in Chemical Catalysis, 2011-10)

DeBeer, S.: On the Nature of X: K-Beta X-ray Emission of Nitrogenase (Stanford Synchrotron Radiation Lightsource, SLAC, Annual Users' Meeting, 2011-10)

Gärtner, W.: Red- and Blue Light-Sensing Biological Photoreceptors: Functional Principles and Potential Biotechnological Applications + Biological Photoreceptors (Summerschool, Wuhan, China, 2011-05)

Gärtner, W.: Opening Lecture (International Congress on Tetrapyrrole Photoreceptors from Photosynthetic Organisms, Berlin, Germany, 2011-07)

Gärtner, W.: Novel Biological Photoreceptors from Genome Database Mining (Congress Eur. Soc. Photobiology, Geneva, Switzerland, 2011-09)

Gärtner, W.: Biotechnological Applications of Flavin-Binding Biological Photoreceptors (Plant Biochemistry, Univ. Freiburg, 2011-09)

Gärtner, W.: Flavin-Binding Photoreceptors in Microscopy (MPI Biophys. Chemistry, Göttingen, Germany, 2011-12)

Knipp, M.: Nitrophorins, a lipocalin type of ferriheme proteins, produce nitric oxide from nitrite. (GDCh-Wissenschaftsforum Chemie, Bremen, Germany, 2011)

Lubitz, W.: Biological Catalysts involved in Hydrogen Conversion and Production: Enzyme Activation, Inhibition, Oxygen Tolerance and the Catalytic Cycle (Gordon Research Conference on Metals in Biology, Ventura, CA, USA, 2011)

Lubitz, W.: Structure and Function of the Enzymes Wateroxidase and Hydrogenase: Blueprints for Catalytic Model Systems? Structural Quantitative Biology Seminar, Department of Chemistry, University of California Berkeley, USA, 2011)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: Spectroscopic Studies of the Enzymes Wateroxidase and Hydrogenase (Department of Chemistry, Stanford University, USA, 2011)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: Wateroxidase and Hydrogenase Studied by Advanced EPR Techniques (4th North America - Greece - Cyprus Workshop on Paramagnetic Materials (NAGC 2011), Patras, Greece, 2011)

Lubitz, W.: A [NiFe] Hydrogenase Utilizing a Novel Iron-Sulfur Cluster with Unique Redox Properties to Cope with Attack of Molecular Oxygen (ICBIC 2011, Vancouver, Canada, 2011)

Lubitz, W.: Multifrequency EPR Studies of Oxygen-Tolerant Hydrogenases (33rd Discussion Meeting of the MR Spectroscopy Division of the GDCh and 8th European Federation for EPR Groups Meeting EUROMAR 2011, Frankfurt, Germany, 2011)

Lubitz, W.: Hydrogen Conversion in Nature: Structure and Function of [NiFe] and [FeFe] Hydrogenases (EBSA Course on Solar Energy – Biological and Biomimetic Solutions, Biological Research Center of the Hungarian Academy of Sciences, Szeged, Hungary, 2011)

Lubitz, W.: „Biological Catalysts Involved in Biosolar Water Splitting and Hydrogen Production" 4th Conference on Chemistry for Life Sciences (ECCLS), Budapest, Hungary (2011)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: Structure and Function of the Enzymes Wateroxidase and Hydrogenase (International Year of Chemistry (IYC) 2011, the Campus of Caparica, Faculty of Sciences and Technology (Department of Chemistry), Universidade Nova de Lisboa, Portugal, 2011)

Lubitz, W.: EPR Methods and Selected Applications to Solar Fuels Research (Network Meeting Solarfuels Tandem, Max-Planck-Institute für Bioanorganische Chemie, Mülheim, Germany, 2011)

Lubitz, W.: Structure and Function of Hydrogenases: A Summary of Recent Spectroscopic Results (Stenbjörn Styring 60th Anniversary Symposium, Ångström Laboratory, Uppsala, Sweden, 2011)

Lubitz, W.: In Search of Renewable Energy Resources: Mechanisms of Light-Induced Water Splitting and Hydrogen Production Studied by Advanced EPR Techniques (Spin physics, spin chemistry and spin technology, Kazan, Russia, 2011)

Lubitz, W.: Structure and Function of Hydrogenases: A Summary of Recent Spectroscopic Results (Solar H_2 Workshop, Uppsala, Sweden, 2011)

Neese, F.: From Radiation Chemistry to Energy: Past, Present and Future of (80th Birthday Colloquim of Prof. Schaffner, Mülheim, Germany, 2011)

Neese, F.: A New First Principles Method to Calculate Transition Metal X-Ray Absorption and Emission Spectra (Graduiertenkolleg, Heidelberg, Germany, 2011)

Neese, F.: New Insights into the Structure of Photosystem II from a Combination of Spectroscopy and Quantum Chemistry (Sonderforschungsbereich, Erlangen, Germany, 2011)

Neese, F.: Recent Developments in Efficient Multireference Correlation Methods for Larger Molecules (CECAM Workshop on Advances in Many Body Methods, Bremen, Germany, 2011)

Neese, F.: The Electron Spin In Chemistry: Properties and Reactivity (Colorado State University, USA, 2011)

Neese, F.: New Insights into the Structure of Photosystem II from a Combination of Spectroscopy and Quantum Chemistry (American Chemical Society Meeting, Denver, USA, 2011)

Neese, F.: Theoretical Spectroscopy of Systems with Strong Spin-Orbit Coupling (European Magnetic Resonance Meeting, Frankfurt, Germany, 2011)

Neese, F.: New Developments in Single Reference Local Correlation Methods based on Pair Natural Orbitals (World Association of Theoretically Oriented Chemists, WATOC, Santiago De Compostella, Spain, 2011)

Neese, F.: A New First Principles Method for the Calculation of transition Metal L-Edge Spectra (CECAM Workshop on Advances in X-Ray Spectroscopy, Zürich, Switzerland, 2011)

Neese, F.: New Developments in Single Reference Local Correlation Methods based on Pair Natural Orbitals (European Seminar on Quantum Chemistry, Oscarsborg, Norway, 2011)

Neese, F.: New Insights into the Structure of Photosystem II from a Combination of Spectroscopy and Quantum Chemistry (Canadian Chemical Society Meeting, Montreal, Canada, 2011)

Neese, F.: Theoretical Spectroscopy of Nitrogenase mimicking catalysts (Canadian Bioinorganic Chemistry Meeting, CanBIC, Perry Sound, Canada, 2011)

Neese, F.: Ligand Field Theory (FEBS Advanced Course "Metal Ions in Biological Systems", Louvain La Neuve, Belgium, 2011)

Neese, F.: Theoretical Spectroscopy of Systems with strong Spin-Orbit Coupling (American Chemical Society Meeting, Anaheim, CA, USA, 2011)

Neese, F.: Insight into the active site of Nitrogenase and Photosystem II from a combination of theory and spectroscopy (Final colloquium of the SFB 546, activation of small molecules, 2011)

Neese, F.: Modeling metalloproteins with quantum mechanics/molecular mechanics techniques (46th Biophysical seminar, Klosters, Switzerland, 2011)"

Reijerse E.: The inner workings of [FeFe] hydrogenase as seen by spectroscopy and theory. (BMBF Meeting Berlin, Germany, 2011-10)

Wieghardt, K.: Invited Lectures (University of Amsterdam, The Netherlands; Universität Mainz, Germany; UniCat, Universität Berlin, Germany; University of Hong Kong, China; Princeton University, USA; University of Miami, USA; EUCHEM, Louvain-la-Neuve, Switzerland; 25. National Chem. Congr., Erzurum, Türkei; Universität Kaiserslautern, Germany; ICBIC Vancouver, Canada; University of Copenhagen, Denmark; Zing Conference, Cancun, Mexico, 2011).

2012

Auer, A.: Modeling Electrochemistry - a Challenge for Quantum Chemistry. (Workshop „SIMULATIONS OF/AT ELECTRODE INTERFACES"

The AIT Austrian Institute of Technology and CEST Centre of Electrochemical Surface Technology, Wiener Neustadt, Austria, 2012-06-25 to 2012-06-26)

Auer, A.: Post-HF Methods in the canonical polyadic product format. (246th National ACS Meeting, Quantum Mechanics in many Dimensions, Indianapolis, Indiana, USA, 2012-09-08 to 2012-09-11)

Auer, A.: Modelling ORR on Pt-Nanoparticles. (Elementary reaction steps in electrocatalysis: Theory meets Experiment, DFG Research Unit FOR1376 Workshop, Reisenburg, Germany, 2012-10-28 to 2012-10-31)

Braslavsky, S.E.: Electron-Transfer Reactions in Aqueous Media and in Photosynthesis Reaction Centers - Laser-Induced Optoacoustic Studies (TRR 61 Colloquium, Center for Nanotechnology, University of Münster, Germany, 2012-06-29)

DeBeer, S.: K-Beta X-ray Emission Spectroscopy as a Probe of Biological Catalysis: New Insights into the FeMoco Cluster of Nitrogenase (Metals in Biology, Gordon Research Conference, Ventura, CA, 2012-01)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction (Swiss Light Source, Paul Scherrer Institute, Switzerland, 2012-02)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction (Hemholtz Zentrum Berlin, Berlin, Germany, 2012-03)

DeBeer, S.: On the Nature of X: X-ray Spectroscopic Studies of Nitrogenase and Related Models (American Chemical Society Meeting, San Diego, CA, 2012-03)

DeBeer, S.: X-ray Spectroscopic Studies of Biological Dinitrogen Reduction (95th Canadian Chemistry Conference, Calgary, Canada, 2012-05)

DeBeer, S.: Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES... (2nd Penn State Bioinorganic Workshop, State College, PA, 2012-06)

DeBeer, S.: X-ray Spectroscopic Studies of Biological Dinitrogen Reduction (GDCh Seminar, University of Freiburg, Germany, 2012-06)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen (DESY Photon Science Colloquium, Hamburg, Germany, 2012-09)

DeBeer, S.: X-ray Spectroscopic Studies of Biological Nitrogen Reduction (Wöhler-Vereinigung für Anorganische Chemie, Göttingen, Germany, 2012-09)

DeBeer, S.: How to Write a 'Good' Proposal (Stanford Synchrotron Radiation Laboratory and the Linac Coherent Light Source Users' Meeting, Workshop on Demystifying the Light Source Experience, 2012-09)

DeBeer, S.: X-ray Spectroscopic Studies of Biological Dinitrogen Reduction (Princeton University, Department of Chemistry, Princeton, NJ, USA, 2012-10)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen (Ruhr-Universität Bochum, Bochum, Germany, 2012-11)

Gärtner, W.: Phytochromes as Tools in Biotechnology (MPI Biophys. Chemistry, Göttingen, Germany, 2012-02)

Gärtner, W.: Biological Photoreceptors (Summerschool, Wuhan, China, 2012-05)

Gärtner, W.: Optogenetics Applications using Biological Photoreceptors (Congress American Soc. Photobiology, Montreal, Canada, 2012-06)

Gärtner, W.: Applications of Biological Photoreceptors in Biotechnology and Optogenetics (MPI Biophysics, Frankfurt, Germany, 2012-10)

Gärtner, W.: Biological Photoreceptors – An Overview (Summer School Photoreceptors, Tucuman, Argentina, 2012-12)

Gärtner, W.: Biological Photoreceptors – Details on Function and Potential Biotechnological Applications (Annu. Meeting Biophys Soc Argentina, Tucuman, Argentina, 2012-12)

Knipp, M.: Association and dissociation kinetics of CO to nitrophorin 4 and 7. (XVIIth International Conference on Oxygen Binding and Sensing Proteins (O_2BIP), Parma, Italy, 2012)

Knipp, M.: Iron-porphyrin coordinates an arginine guanidine side-chain in a protein pocket – Insights from microspectrophotometry and crystallography. (3rd Workshop on Simultaneous Combination of Spectroscopies with X-ray Absorption, Scattering and Diffraction Techniques (CSX2012), ETH Zürich, Switzerland, 2012)

Lubitz, W.: Einsatz physikalischer Techniken zum Studium von Struktur und Funktion von Wasserstoff erzeugenden Enzymen (Vortrag Förderverein Erneuerbare Energien, Ruhr Universität, Bochum, 2012)

Lubitz, W.: Hydrogenase and Wateroxidase. Some Recent Results from the MPI in Mülheim, EuroSolarFuels Meeting, University of Glasgow, Glasgow, UK, 2012)

Lubitz, W.: Hydride Binding in Oxygen Tolerant and Oxygen Sensitive [NiFe] Hydrogenases (‘Metal Hydrides in Biology’ Experts Workshop, Exploring the Roles of Metal-Hydrides in Reductive Metalloenzyme Catalysis, Oxford, UK, 2012)

Lubitz, W.: Water Binding and water splitting in photosystem II probed by high frequency multinuclear EPR, ENDOR and ELDOR-detected NMR (Alfred Bader Award in Bioinorganic Chemistry: Symposium in Honour of Brian M. Hoffman, ACS Meeting, San Diego, USA, 2012)

Lubitz, W.: Hydrogen Conversion in Nature in the Presence of Oxygen: The [NiFe] Hydrogenase from *Aquifex aeolicus (*Hydrogen Production and Applications, National Meeting of the American Chemical Society, San Diego, USA, 2012)

Lubitz, W.: Water Binding and Water Splitting at the MnCa Cluster in Photosystem II Probed by Advanced Magnetic Resonance Methods (SolarFuelsTandem Meeting, Bologna, Italy, 2012)

Lubitz, W.: Water Binding and Water Oxidation in Photosystem II: Insight from Novel EPR Experiments (H_2 Designzellen Projektmeeting (BMBF), Köln, Germany, 2012)

Lubitz, W.: Lichtinduzierte Wasserspaltung und Wasserstoffproduktion: Die Natur als Vorbild (Physikalisches Kolloquium, Fakultät für Physik, Universität Duisburg-Essen, Germany, 2012)

Lubitz, W.: High Field ELDOR-detected NMR Studies of the Water Oxidizing Complex in Photosystem II: Water Binding and Water Splitting in Photosynthesis (12th Chianti/INSTRUCT Workshop on BioNMR, Montecatini Terme (Pistoia), Italy, (2012)

Lubitz, W.: Unravelling Structure and Function of the Water Oxidizing Complex in Photosynthesis by High Field EPR, ENDOR and ELDOR-Detected NMR (2nd International Symposium on Electron Spin Science (ISESS2012), Matsushima, Japan, 2012)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature: Structure and Function of the Enzymes Wateroxidase and Hydrogenase (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan, 2012)

Lubitz, W.: Hydrogen Formation: Design Principles of Molecular Catalysts Based on Structure and Function of [NiFe] and [FeFe] Hydrogenases (Telluride Science Research Center workshop Solar Fuels Institute (SOFI), Telluride, USA, 2012)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature (3rd International Symposium on Solar Cells & Solar Fuels, Dalian, Dalian Technical Institute, China, 2012)

Lubitz, W.: Water Splitting and Hydrogen Production in Nature: Blueprints for Photoelectrocatalytic Processes (Electrochemistry 2012, Fundamental and Engineering Needs for Sustainable Development, Technical University, Munich, Germany, 2012)

Lubitz, W.: The Water Oxidizing Manganese Cluster in Oxygenic Photosynthesis Studied by Pulse EPR, ENDOR and ELDOR-detected NMR Techniques (34. Diskussionstagung der GDCh-Fachgruppe Magnetresonanz, Halle an der Saale, Germany, 2012)

Lubitz, W.: Research from the Max Planck Institute (First EuroSolarFuels Meeting, Buchanan Arms, Drymen, UK, 2012)

Lubitz, W.: Light-Induced Water Oxidation in Photosynthesis: Learning from Nature (Chemistry Colloquium, Weizmann Institute of Science, Rehovot, Israel, 2012). Technical Developments for Biophysical Studies in Energy Research (Hebrew University, Jersualem, Israel, 2012)

Lubitz, W.: Lichtinduzierte Wasserspaltung und Wasserstoffproduktion in der Natur: Funktionsprinzipien von Metallkatalysatoren zur Erzeugung regenerativer Energieträger (Hans Fischer Symposium 2012, Technische Universität München, Germany, 2012)

Neese, F.: Correlated Methods (Lecture at KCSE Winter School in Multiscale, Stockholm, Sweden, 2012)

Neese, F.: Theoretical Spectroscopy of Open Shell Transition Metals in Enzymes and Coordination Complexes (48th Symposium on Theoretical Chemistry, Karlsruhe, Germany, 2012)

Neese, F.: A Perspective on Chemical Computing (Max Planck Seminar on the “A bold look into the future of Chemistry”, Berlin, Germany, 2012)

Neese, F.: Insight Into the Structure and Mechanism of Metalloenzymes from Spectroscopy and Theory (International Conference on Reactive Intermediates and Unusual Molecules (ISRIUM), Ascona, Switzerland, 2012)

Neese, F.: Combined quantum mechanics/molecular mechanics and theoretical spectroscopy studies on the mechanism of Cytochrome P450 NO reductase (X. Girona Seminar on Theoretical and Computational Chemistry for the Modeling of Biochemical Systems, Girona, Spain, 2012)

Neese, F.: Efficient Coupled Cluster Calculations on Large Molecules Using Pair Natural Orbitals (8th Congress on Electronic Structure: Principles and Applications (ESPA), Barcelona, Spain, 2012)

Neese, F.: Insight into Structure and Mechanisms of Photosystem II from a combination of spectroscopy and quantum chemistry (Gordon Conference on Renewable Energy: Solar Fuel, Il Ciocco Lucca, Italy, 2012)

Neese, F.: Developments in double hybrid density functional theory and beyond (Symposium 'Challenges in Density Matrix and Density Functional Theory' Ghent, Brussels, 2012)

Neese, F.: First principles view on ligand field theory – Recent combined theoretical and experimental studies on nitrogenase and nitrogenase model complexes (ACS National Meeting 2012, San Diego, USA, 2012)

Ogata, H.: Hydrogenase: Structure and Function (OCARINA Annual Meeting, Osaka, Japan, 2012-03-05 to -03-06)

Schlögl, R.: The Impact of Catalysis on the Energy Challenge (7th International Green Energy Conference & The 1st DNL Conference on Clean Energy, Dalian, China, 2012-05-30)

Schlögl, R.: Keine Energiewende ohne Katalyse (Besichtigungsprogramm der Physikalischen Gesellschaft zu Berlin (PGzB), Berlin, Germany, 2012-06-20)

Schlögl, R.: Material dynamics of OER electrodes (2nd Ertl Symposium on Surface and Interface Chemistry) Stuttgart, Germany, 2012-06-24)

Schlögl, R.: Speicherung in sekundären Energieträgern wie z.B. H_2, CH_4, CH_3OH (DECHEMA Infotag "Kleine Moleküle als Energieträger") Frankfurt a. Main, Germany, 2012-12-05)

Schlögl, R.: Energiesysteme der Zukunft (Acatech Portfolio-Konferenz, München, Germany, 2012-11-23)

Schlögl, R.: Offene technische Herausforderungen von Power to Gas – The role of catalysis in Power to Gas (6. Biomasse-Forum, Bad Hersfeld, Germany, 2012-11-22)

Schlögl, R.: Catalyst characterization: a challenge in functional material science (Basic Lecture Program – Berlin International Graduate School of Natural Sciences and Engineering, TU Berlin, Berlin, Germany, 2012-11-20)

Schlögl, R.: Advanced Synchrotron Technology for Energy Research and Catalysis International Symposium on Advanced Synchrotron Techniques for Energy and Catalysis Applications, Shanghai, China, 2012-11-13)

Schlögl, R.: The role of size effects in catalysis (Shell Technology Center Amsterdam (STAC), Amsterdam, The Netherlands, 2012-11-08)

Schlögl, R.: Elektrochemie und Speicher (VW Wolfsburg, Wolfsburg, Germany, 2012-10-21)

Schlögl, R.: Why do we need in-situ studies on catalysis? (Symposium "The Future of Catalysis", SLAC at Stanford University, Menlo Park CA, USA, 2012-09-27)

Schlögl, R.: From static model systems to dynamical high performance catalysts UOP LLC, a Honeywell Company, Des Plaines IL, USA, 2012-09-25)

Schlögl, R.: Heterogeneous catalysts: from black magic to design strategies (BASF Research Seminar 2012, St. Martin, Germany, 2012-09-24)

Schlögl, R.: Energie ist Chemie – Katalyse als Schlüsseltechnik. Energie von Morgen: Eine Momentaufnahme (126. Versammlung der Gesellschaft deutscher Naturforscher und Ärzte (GDNÄ), Dresden, Germany, 2012-09-17)

Schlögl, R.: Teller oder Tank: Warum wir chemische Energiespeicherung brauchen (Herbstschule für Teilchenphysik, Kloster Maria Laach, Laach, Germany, 2012-09-11)

Schlögl, R.: Grenzflächenprozesse bei elektrochemischen Oxidationsreaktionen (GDCh-Vortrag Bayer, Leverkusen, Germany, 2012-09-06)

Schlögl, R.: Energieversorgung 2050 – wie lösen wir das Speicherproblem? (2. Kooperationsveranstaltung des Forums ElektroMobilität e.V. und CMS Hasche Sigle, Berlin, Germany, 2012-09-05)

Schlögl, R.: Functional Groups on Nanocarbons (Topsøe Catalysis Forum – Microscopy in catalysis, Gilleleje, Denmark, 2012-08-23)

Schlögl, R.: Functional Groups on Nanocarbons (CARBOCAT-V, Bressanone, Italy, 2012-06-29)

Wieghardt, K.: Invited Lectures (Am. Chem. Soc. San Diego, USA; Emory University, Atlanta, USA; Canadian Chem. Conf. Calgary, Canada; University of Nottingham; Brazilian National Meeting, Florianopolis, Brazil, 2012)

Ye, S.: Elucidation of the Reaction Mechanism of Nonheme Iron Enzymes by a Combined Theoretical and Experimental Approach ("Iron: mother earth's favorite metal for synthesis, catalysis & energy supply", a thematic mini symposium, Regensburg, Germany, 2012-06-04 to 2012-06-05)

2013

Bill, E.: Magnetochemistry, EPR and Mössbauer Spectroscopy. (Methods Course of the 'International Research Training Group' (IRTG) Göttingen – Lund, Göttingen, Germany, 2013-12-19 to 2013-12-20)

Bill, E.: New Iron-Sulfur Centers in Enzymes and Model Compounds. (GDCH Kolloqium, TU Braunschweig, Braunschweig, Germany, 2013-04-08)

Bill, E.: Mössbauerspektroskopie mit Eisen-Schwefel-Cluster. (Biophysik – Workshop „Molekulare Prozesse und Dynamik in biologischen Systemen", TU Kaiserslautern, Kaiserslautern, Germany, 2013-09-12)

Bill, E.: Molecular Iron Complexes at the Limits of Classical Valence Assignments. (Award Lecture at 'International Conference on the Application of the Mössbauer Effect' (ICAME 2013), Opatija, Croatia, 2013-09-02)

Cox, N.: The Oxygen Evolving Complex of Photosystem II: Water Binding and Water Splitting in Photosynthesis (IXth International workshop on EPR in Biology and Medicine. Krakow, Poland, 2013)

Cox, N.: The Oxygen Evolving Complex of Photosystem II: Water Binding and Water Splitting in Photosynthesis (16th International Congress of Photosynthesis. St Louis, U.S.A, 2013)

Cox, N.: The Water Oxidizing Complex in Photosystem II: Water Binding and Water Splitting in Photosynthesis (Umeå Renewable Energy Meeting. Umeå University, Umeå, Sweden, 2013)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen: Insights from X-ray Spectroscopy (Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel, 2013-01)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen: Insights from X-ray Spectroscopy (Hebrew University of Jerusalem, Institute of Chemistry, Jerusalem, Israel, 2013-01)

DeBeer, S.: Introduction to X-ray Spectroscopy (Holland Research School of Molecular Chemistry, Physical Methods in Inorganic Chemistry, University of Amsterdam, Science Park, The Netherlands, 2013-02)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen: Insights from X-ray Spectroscopy (Universiteit van Amsterdam, van't Hoff Institute for Molecular Sciences, The Netherlands, 2013-02)

DeBeer, S.: Recent Applications of Resonant and Non-Resonant Valence to Core X-ray Emission Spectroscopy (Workshop of Fundamental Aspects of X-ray Spectroscopies – Utrecht, The Netherlands, 2013-02)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen: Insights from X-ray Spectroscopy (Laboratório Nacional de Luz Síncrotron, LNLS, CNPEM, Campinas, Brazil, 2013-05)

DeBeer, S.: Nature's Machinery for Splitting Nitrogen: Insights from X-ray Spectroscopy (University of Hamburg, Institut für Anorganische und Angewandte Chemie, Hamburg, Germany, 2013-05)

DeBeer, S.: X-ray Emission Spectroscopy as a Probe of Catalysis (British Petroleum, Workshop on Advanced Catalyst Characterization, Naperville, IL, USA, 2013-06)

DeBeer, S.: New Insights into the Electronic Structure of the FeMo Cofactor of Nitrogenase (International Conference on Biological Inorganic Chemistry (ICBIC), Grenoble, France, 2013-07)

DeBeer, S.: Introduction to X-ray Spectroscopy (Methods in Molecular Energy Research: Theory and Spectroscopy Summer School, Essen, Germany, 2013-09)

DeBeer, S.: New Insights into the Electronic Structure of the FeMo Cofactor of Nitrogenase (Coordination Chemistry Conference, Xcaret, Mexico, 2013)

DeBeer, S.: X-ray spectroscopic studies of biological catalysis (ACS Symposium: Non-Precious Metal Catalysis: Opportunities and Impacts, Indianapolis, IN, USA, 2013-09)

DeBeer, S.: Spectroscopy in Catalysis (NSF SusChem Workshop: Base Metal Catalysis, Indianapolis, IN, USA, 2013-09)

DeBeer, S.: "X-ray Spectroscopy" lecture series (IGERT Graduate Training Module, Cornell University, Ithaca, NY, USA, 2013-09)

Gärtner, W.: Blue- and Red-Light Sensing Photoreceptors: Novel Applications in Microscopy and Optogenetics (Sfb Meeting, Berlin, Germany 2013-06)

Gärtner, W.: Blue- and Red-Light Sensing Photoreceptors (Progress report, Universität Giessen, Germany, 2013-08)

Gärtner, W.: Kinetic and Spectroscopic Characterization of Isolated GAF Domains from Cyanobacteriochromes (ICTPPO 2104, Wuhan, China, 2013-09)

Gärtner, W.: Biological Photoreceptors – An Overview (Summerschool Photoreceptors, Wuhan, China, 2013-09)

Gärtner, W.: Fundamentals and Applications of Biological Photoreceptors (IMPRS, Düsseldorf, Germany 2013-12)

Knipp, M.: Nitrite dismutase – A "nitrite-only" source for NO. (Fifth International Meeting on the Role of Nitrite and Nitrate in Physiology, Pathophysiology, and Therapeutics, Pittsburgh (PA), 2013)

Lubitz, W.: Hydrogenase: Structure and Function (XVII International School of Pure and Applied Biophysics International School of Pure and Applied Biophysics on "Renewable Energy and Biofuels: A Biophysical and Biochemical Approach, Istituto Veneto di Scienze, Lettere ed Arti, Venice, Italy, 2013)

Lubitz, W.: Water Splitting in Photosynthesis: Learning from Nature (XVII International School of Pure and Applied Biophysics International School of Pure and Applied Biophysics on "Renewable Energy and Biofuels: A Biophysical and Biochemical Approach, Istituto Veneto di Scienze, Lettere ed Arti, Venice, Italy, 2013)

Lubitz, W.: Magnetic Resonance applied to PS Systems (The Dead Sea Winter School on Exciton Dynamics in Natural and Man Made Systems, Ein-Gedi Institute of Chemistry, Fritz Haber Research Center for Molecular Dynamics & Farkas Center for Light-Induced Processes, Israel, 2013)

Lubitz, W.: Light-induced Water Oxidation in Photosynthesis (The Dead Sea Winter Workshop on Exciton Dynamics in Natural and Man Made Systems, Ein-Gedi Institute of Chemistry, Fritz Haber Research Center for Molecular Dynamics & Farkas Center for Light-Induced Processes, Israel, 2013)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Production in Nature (Joint Grand Technion Energy Program/Chemistry Seminar, Technion – Israel Institute of Technology, Schulich Faculty of Chemistry, Haifa, Israel, 2013)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Production in Nature: Blueprints for the Design of Chemical Catalysts (Alternative Energy Research Seminar, Weizmann Institute of Science, Rehovot, Israel, 2013)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production: Learning from Nature (OCARINA Conference Annual Meeting 2013, Osaka City University, Osaka, Japan, 2013)

Lubitz, W.: Photosynthesis – A Garden of Eden for EPR Spectroscopists (Workshop, DFG-Schwerpunktprogramm 1601 „New frontiers in sensitivity for EPR spectroscopy: from biological cells to nano materials“, Free University of Berlin, Germany, 2013)

Lubitz, W.: The Spin as Functional Probe in Biological Energy Conversion and Storage (Spins as Functional Probes in Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany, 2013)

Lubitz, W.: Magnetic Resonance Studies of Photosynthetic Systems (Humboldt-Kolleg, Novosibirsk, Russia, 2013)

Lubitz, W.: Molecular Catalysts and Devices for Water Oxidation and Hydrogen Production" EERA JP-AMPEA Cross Linking Workshop on Artificial Photosynthesis, Wageningen, The Netherlands, 2013)

Lubitz, W.: Characterization of Intermediates in the Reaction Cycle of [FeFe] and [NiFe] Hydrogenases (10th International Hydrogenase Conference, Biological Research Center, Hungarian Academy of Sciences and the Department of Biotechnology, University of Szeged, Szeged, Hungary, 2013)

Lubitz, W.: [NiFe] and [FeFe] Hydrogenases: Active Site Structures and Catalytic Mechanisms (16th International Conference on BioInorganic Chemistry (ICBIC16), Grenoble, France, 2013)

Lubitz, W.: The Water Splitting Machine of Photosynthesis Studied by EPR Techniques (Modern Development of Magnetic Resonance 2013 and Zavoisky Award 2013 Ceremony, Zavoisky Physical-Technical Institute, Russian Academy of Sciences, Kazan, Russia, 2013)

Lubitz, W.: Insight into Water Splitting and Hydrogen Conversion in Nature: Basis for artificial photosynthesis (Università degli Studi di Padova, Padua, Italy, 2013)

Lubitz, W.: Hydrogen as a Fuel: Learning from the Native Enzyme Hydrogenase (University of Milano-Bicocca, Milano, Italy, 2013)

Lubitz, W.: Artificial Photosynthesis (acatech-interne Informationsveranstaltung Künstliche Fotosynthese, Berlin, 2013)

Lubitz, W.: Effect of the Protein Matrix on Hydrogenase Maturation, Structure and Functional Properties (Responsive Material for Solar Fuels, Lorentz Workshop, Leiden, The Netherlands, 2013)

Lubitz, W.: Light-Induced Water Splitting and Hydrogen Production in Nature (Center for Nanosystems Chemistry, CNC-Lecture, Universität Würzburg, 2013)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Production in Nature: Blueprints for the Design of Chemical Catalysts? (Institutskolloqium, Institut für Theoretische und Physikalische Chemie, Universität Bonn, Germany, 2013)

Lubitz, W.: Lichtinduzierte Wasserspaltung – die Natur als Vorbild (Jubilarfeier der Fakultät – Mathematik und Naturwissenschaften der TU Berlin, Technische Universität, Berlin, Germany, 2013

Neese, F.: Insight into energy conserving reactions in nature (2nd International Symposium on Chemistry for Energy Conversion and Storage, Berlin, Germany, 2013-02)

Neese, F.: Neue Einblicke in biologische Stickstoffaktivierung und Wasseroxidation durch eine Kombination von Spektroskopie und Quantenchemie (GDCh Vortrag, Göttingen, Germany, 2013)

Neese, F.: Insights into the Structure and Function of Complex Metallproteins from a Combinations of Spectroscopy and Quantum Chemistry: Photosystem II and Nitrogenase (Physical Chemistry Seminar, Technion, Haifa, Israel, 2013)

Neese, F.: Pushing the frontiers of wavefunction based ab initio quantum chemistry (Colloquium, Technion, Haifa, Israel, 2013)

Neese, F.: A new first principles method for the calculation of transition metal L-edge spectra: theory and application (Science with Photons, Helmholtz Zentrum Berlin, Germany, 2013)

Neese, F.: Pushing the frontiers of wavefunction based ab initio quantum chemistry (Colloquium for Theory, Modelling & Informatics Research Interest Group, Dep. of Chemistry, University of Cambridge, UK, 2013)

Neese, F.: A configuration interaction based method for the calculation of transition metal L-edge absorption pectra. Theory and application (Workshop on fundamental Aspects of X-ray Spectrosocpies: the role of the 2p core in XAS and RIXS, Utrecht, The Netherlands, 2013-02-21)

Neese, F.: Combination of High-Level Spectroscopy and Quantum Chemistry: A Strong Partnership in (Bio)chemistry and Material Sciences (Eröffnung BeJEL, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany, 2013-04-11)

Neese, F.: Insights into transition metal catalysis from combination of spectroscopy and quantum chemistry (Bunsentagung 2013, Karlsruhe, Germany, 2013-05-09 to 2013-05-11)

Neese, F.: Ligand Field Theory (2013 Chemistry of Metals in Biological Systems Summer School, Louvin-la-Neuve, Belgium, 2013-05-12 to 2013-05-09)

Neese, F.: Theoretical EPR Spectroscopy of Open-Shell Transition Metal Complexes with Strong Spin Orbit Coupling (18th ISMAR Meeting, Rio de Janeiro, Brazil, 2013-05-19 to 2013-05-24)

Neese, F.: Recent Development in Pair Natural Orbital Based Local Coupled Cluster Methods (7th Molecular Quantum Mechanics, Lugano, Switzerland, 2013-06-02 to 2013-06-07)

Neese, F.: Spektroskopie und Quantenchemie: Eine starke Partnerschaft in (Bio)chemie und Materialwissenschaften (Computational Chemistry, Physics and Biology, Ulm, Germany, 2013-06-17)

Neese, F.: Spektroskopie und Quantenchemie: Eine starke Partnerschaft in (Bio)chemie und Materialwissenschaften (Tag der Chemie und Biochemie, Bochum, Germany, 2013-06-28)

Neese, F.: Theoretical EPR spectroscopy of open-shell transition metal complexes (EUROMAR 2013, Hersonissos, Crete, Greece, 2013-06-30 to 2013-07-05)

Neese, F.: Theoretical Spectroscopy of Open Shell Transition Metals in Enzymes and Model Complexes (International Conference on BioInorganic Chemistry ICBIC16, Grenoble, France, 2013-07-20 to 2013-07-27)

Neese, F.: Wavefunction Correlation Methods: From the Basics to the Frontiers (Workshop on Density functional theory and beyond: Computional materials science for real materials, Trieste, Italy, 2013-08-06 to 2013-08-15)

Neese, F.: Recent development in pair natural orbital based local coupled cluster methods (The VIIIth Congress of the International Society of Theoretical Chemical Physics, ISTCP-VIII, Budapest, Hungary, 2013-08-215 to 2013-08-31)

Neese, F.: Quantum Chemistry at Work (European Summerschool in Quantum Chemistry, ESQC13, Sicily, Italy, 2013-09-08 to 2013-09-21)

Neese, F.: Insights into the Chemistry of Biological Energy Conversion from a Combination of Spectroscopy and Quantum Chemistry (Universität Zürich, Zürich, Switzerland, 2013-10-01)

Neese, F.: Molecular Magnetism and Quantum Chemistry (The 4th European Conference on Molecular Magnetism (ECMM-2013), Karlsruhe, Germany, 2013-10-06 to 2013-10-10)

Neese, F.: Unravelling Nature's Chemistry of Clean Energy (Les 14èmes Journées Francophones des Jeunes Physico-Chimistes (JFJPC 14), Fréjus, France, 2013-10-14 to 2013-10-18)

Neese, F.: Pushing the frontiers of wavefunction based ab initio quantum chemistry (Colloquium on the occasion of the 80th birthday of Professor Werner Kutzelnigg, Ruhr-Universität Bochum, 2013-10-24)

Neese, F.: Insights into Biological Conversion from a Combination of Spectroscopy and Quantum Chemistry (GDCh Seminar, TU-München, Germany, 2013-11-19)

Neese, F.: Neue Einblicke in die Struktur und Mechanismus des "Oxygen-Evolving-Complex" in Photosystem II durch eine Kombination von Spektroskopie und Quantenchemie (GDCh Seminar, TU-Braunschweig, Germany, 2013-11-25)

Reijerse E.: The inner workings of [FeFe] hydrogenase as seen by spectroscopy and theory. (National Renewable Energy Lab (NREL) Goldon Colorador, 2013-08)

Reijerse E.: EPR investigations onf the active site of [FeFe] hydrogenases and related biomimetic model complexes. (IXth International workshop on EPR in Biology and Medicine, Krakow, Poland 2013-10-07 to 2013-10-10)

Schlögl, R.: Heterogene Katalyse (Grundvorlesung, Technische Universität Berlin, Berlin, Germany, 2013-01-17)

Schlögl, R.: Ausbaustand und Rolle der Photovoltaik im Energiemix der Zukunft (Branchendialog "Die Photovoltaikbranche in Sachsen-Anhalt – Entwicklung, Trends und Ausblick", Bitterfeld-Wolfen, Germany, 2013-10-14)

Schlögl, R.: Ingenieure, Impulse, Innovation - Die Schnittstelle von Elektrizität und Chemie als strategische Aufgabe für nachhaltige Energiesysteme (52.gat – Gasfachliche Aussprachetagung, Nürnberg, Germany, 2013-10-01)

Schlögl, R.: Dynamics in Heterogeneous Catalysis – A Buzzword or a Fundamental Concept? – A Look from the Side of the Catalyst (Lecture: IMPRS, Berlin, Germany, 2013-09-30)

Schlögl, R.: NAP-XPS: A Critical Tool in the Energy Challenge (5th ANKA/KNMF Users' Meeting 2013, Bruchsal, Germany, 2013-09-26)

Schlögl, R.: Why Carbon Materials for Energy Application? (5th International Conference on Carbon for Energy Storage/Conversion, and Environment Protection, Mülheim a.d. Ruhr, Germany, 2013-09-23 to 2013-09-26)

Schlögl, R.: The role of Chemistry in the Energy Challenge (246th ACS National Meeting and Exposition, "Frontiers in Energy Conversion and Fuel Production", Indianapolis, Indiana, USA, 2013-09-13)

Schlögl, R.: Systemic Approach towards the Energy System: the Critical Role of Chemistry (Rotary Club Berlin, Berlin, Germany, 2013-09-06)

Schlögl, R.: Energiesysteme der Zukunft (Vollversammlung des Akademienprojektes "Energiesysteme der Zukunft, Berlin, Germany, 2013-09-05)

Schlögl, R.: Wie wir große Mengen Energie in kleinen Molekülen speichern können: Ein Statusbericht (GDCh-Wissenschaftsforum CHEMIE 2013, Darmstadt, Germany, 2013-09-04)

Schlögl, R.: Active Sites in Heterogeneous Catalysis (SUNCAT Summer Institute 2013, SLAC (National Accelerator Laboratory), Menlo Park, CA, USA, 2013-08-26)

Schlögl, R.: Pt Nanoparticles as Electrocatalysts for Water Splitting: Atomistic Insights into Functions and Stability and In-situ Studies of Working Catalysts at the Mesascopic Level (2013 Microscopy & Microanalysis Annual Meeting, Indianapolis, IN, USA, 2013-08-04 to 2013-08-06)

Schlögl, R.: Dynamics in Heterogeneous Catalysis (Telluride Meeting "Theory and Practice of Catalysis",Telluride, Collorado, USA, 2013-08-02)

Schlögl, R.: On the Mode of Operation of OCM over MgO-based (OCM Meeting, Gerhard Ertl Center, Technische Universität Berlin, Berlin, Germany, 2013-07-25)

Schlögl, R.: Chemical Energy Storage – Status and Perspectives (2. BHC-Symposium, Kloster Banz, Bad Staffelstein, Germany, 2013-07-22)

Schlögl, R.: Systems Approach as a Key for a Sustainable Energy Supply (Workshop "The Future of Energy Technology", Max-Planck-Haus, München, Germany, 2013-07-09)

Schlögl, R.: On the Relation between Bulk Crystal Structure and Catalytic Function in the Selective Oxidation Catalysis (Advances in Selective Oxidation Catalysis and Electrocatalysis (Irsee VI Symposium), Kloster Irsee, Irsee, Germany, 2013-07-05)

Schlögl, R.: Nanocarbon: Surface Analysis Strategies (Institute of Metal Research Chinese Academy of Sciences, Shenyang, China, 2013-06-27)

Schlögl, R.: Was wir über heterogene Katalysatoren heute verstehen (GDCh-Kolloquium, Chemische Institute Bonn-Enderich, Bonn, Germany, 2013-05-28)

Schlögl, R.: Energiewende – wohin? (Wissenschaftliches Kolloquium, DLR Oberpfaffenhofen, Weßling, Germany, 2013-05-27)

Schlögl, R.: How to rationally design heterogeneous catalysts (University of Malaya, Kuala Lumpur, Malaysia, 2013-05-10)

Schlögl, R.: The role of chemistry in the energy challenge – Systemic view (Ministry Of Science, Technology and Innovation (MOSTI), Putrajaya, Malaysia, 2013-05-09)

Schlögl, R.: Chemistry enables sustainable energy – Keine Energiewende ohne Chemie (Forschungspressekonferenz BASF "Chemistry powers energy – Regenerativ erzeugen, sicher speichern, effizient übertragen und nutzen", Ludwigshafen, Germany, 2013-05-06)

Schlögl, R.: Mobilität in der Energiewende: Betrachtungen eines Chemikers zu Ausrichtungen über längere Zeiträume? (34. Internationales Wiener Motorensymposium, Wien, Austria, 2013-04-25)

Schlögl, R.: In-situ analysis of working catalyst surfaces: can we understand heterogeneous processes without a-priori models? (Netherlands' Catalysis and Chemistry Conference NCCC-14, Noordwijkerhout, The Netherlands, 2013-03-12)

Schlögl, R.: Chemistry and Energy (Festsymposium 125 Jahre Angewandte Chemie, Berlin, Germany, 2013-03-12)

Schlögl, R.: Energiesysteme der Zukunft (BDEW/BMBF-Forschungssymposium, Berlin, Germany, 2013-03-12)

Schlögl, R.: Design and Dynamics of Heterogeneous Catalysts? (6th IDECAT/ERIC-JCAT Conference (IEJCat-6) "Design advanced multifunctional catalysts for sustainable processes", Bressannone/Brixen, Italy, 2013-03-03)

Schlögl, R.: Energiewende? Wunsch und Wirklichkeit (Klassensitzung Berlin-Brandenburgische Akademie der Wissenschaften, Berlin, Germany, 2013-02-22)

Schlögl, R.: Kleine Teilchen für große Aufgaben (Einweihung des NanoEnergieTechnik Zentrums NETZ, Duisburg, Germany, 2013-02-21)

Schlögl, R.: Energiewende – Wunsch und Wirklichkeit ("Physik am Samstagvormittag 2013" Universität Bayreuth, Bayreuth, Germany, 2013-01-26)

Schlögl, R.: Kohlenstoff (GDCh Vortrag Ruhr-Universität Bochum, Bochum, Germany, 2013-01-24)

Schlögl, R.: Active Sites in Heterogeneous Catalysis (Physikalisches Kolloquium der Universität Duisburg-Esssen, Duisburg, Germany, 2013-01-23)

Schlögl, R.: Grundlagen der heterogenen Katalyse ("MPI-Lectures" Universität Duisburg-Essen, Essen, Germany, 2013-01-16 to 2013-01-30)

Schlögl, R.: Die Energiewende - wohin? (Industrie-Club e. V. Düsseldorf, Düsseldorf, Germany, 2013-01-16)

Schlögl, R.: Katalysatoren auf die Finger geschaut: Wie wir heute heterogene Katalyse verstehen (Kolloquium der Gesellschaft Österr. Chemiker, Leopold-Franzens-Universität Innsbruck, Austria, 2013-01-14)

Wieghardt, K.: Invited Lectures (Ludwig-Maximilian-Universiät, München, Germany; American Chem. Soc., Indianapolis, USA, 2013)

Ye, S.: Elucidation of the Reaction Mechanism of Nonheme Iron Enzymes by a Combined Theoretical and Experimental Approach (International Conference on Theoretical and High Performance Computational Chemistry, Dalian, China, 2013-07-21 to 2013-07-25)

Awards, Honours and Memberships of the CEC Staff

2010

Y. Brandenburger and M. Dunsch were awarded with the Ernst Haage-Preis for apprentices (award ceremony on 2010-12-07).

Dr. N. Cox was awarded with the APES Young Scientist Award 2010 of the Asia-Pacific EPR/ESR Society, Jeju, South Korea, 2010.

Prof. Dr. Dr. h.c. Wolfgang Lubitz has been elected a Fellow of the International Society of Magnetic Resonance (ISMAR) in recognition of distinction in contributing to the field of magnetic resonance, 2010.

Dr. C. He: Chinese Government Scholarship for Outstanding Self-Financed Students Studying Abroad, Berlin, 2010-05.

The Max-Planck-Institut für Bioanorganische Chemie was awarded with the certificate "Ökoprofit-Betrieb", 2010-09-04.

Dr. D. Pantazis was awarded with the Ernst Haage-Preis for Ph.D. students, award ceremony on 2010-12-07.

Dr. M. Pandelia was awarded with the Otto-Hahn-Medal 2009 of the Max Planck Society „für die Arbeiten zur Charakterisierung und zur Sauerstofftoleranz einer aus [NiFe]-Hydrogenase aus dem hyperthermophilen Bakterium *Aquifex aeolius*", award ceremony in Hannover on 2010-06-16.

Prof. Dr. Frank Neese was awarded with McElvain Lecture, University of Wisconsin, Madison, 2010.

Prof. Dr. Frank Neese was awarded with the Gottfried-Wilhelm Leibniz Award of the German Science Foundation, 2010.

J. Taing and Y. Brandenburger were awarded with MPG Azubi-Preis, 2010-09-14.

2011

Dr. N. Cox was awarded with the Ernst Haage-Preis for Ph.D. students, award ceremony on 2011-12-06.

Dr. A. Silakov was awarded with the IES Young Investigator Award 2011 of the International ESR (EPR) Society.

Prof. Dr. Silvia Braslavsky was awarded with the Raices Prize by the Minister of Science, Technology and Applied Research in Argentina (MINCYT) to honor the efforts made for the scientific collaboration between Germany and Argentina, 2011-10-06.

Prof. Dr. Serena DeBeer: Alfred P. Sloan Research Fellow, 2011.

N. Kowalew was awarded with the Ernst Haage-Preis for apprentices, award ceremony on 2011-12-06.

Prof. Dr. Klaus Möbius, IES Fellow 2011 of the International ESR (EPR) Society

2012

Prof. S.E. Braslavsky, Dedicated Session, XI ELAFOT (Latin-American Encounter on Photochemistry), Córdoba, Argentina, 2012.

Prof. Dr. Serena DeBeer received the Kavli Fellowship of the U.S. National Academy of Sciences, 2012.

Prof. Dr. Serena DeBeer: Chair of the Stanford Synchrotron Radiation Lightsource Users' Executive Committee (2011-2012)

Prof. Dr. Serena DeBeer: Chair of the Biological Spectroscopy, Scattering and Imaging Proposal Review Panel for the Linac Cohernet Light Source, SLAC, Stanford University (2012-present)

Dr. A. Hansen was awarded with the Ernst Haage-Preis for Ph.D. students, award ceremony on 2012-12-07.

Dr. C. He received the FEBS Short-Term Fellowship, "The Mechanism of the Release of Carbon Monoxide from Ferroheme Nitrophorins: Dynamical Aspects and the Role of Water", 2012-02-06

N. Kowalew was awarded with MPG Azubi-Preis 2012, 2012-07.

Prof. Dr. Dr. h.c. Wolfgang Lubitz had been elected as a Foreign Fellow of the Tatarstan Academy of Sciences for the Division of Physics, Power Engineering and Earth Sciences (2012-06-20)

Dr. L. Rapatskiy was awarded with the APES 2012 Young Scientist Award of the Asia Pacific EPR/ESR Society (2012-07-31)

Prof. Dr. Frank Neese was elected to the International Academy of Quantum Molecular Sciences, 2012.

Dr. K. Ray was awarded with the first National Ernst Haage-Preis for young academics, award ceremony on 2012-12-07.

Prof. Dr. Robert Schlögl was appointed Honorary Professorship at Universität Duisburg-Essen, 2012.

A. Steinbach was awarded with the Ernst Haage-Preis for apprentices, award ceremony on 2012-12-07.

2013

Dr. E. Bill was given the 'IBAME Science Award' ('International Board on the Application of the Mössbauer Effect') at the ICAME 2013, Opatja, Croatia, 2013-09-02.

Prof. S.E. Braslavsky was appointed Honorary Professor at the Universidad Nacional de La Plata, Argentina, 2013.

Prof. Dr. Serena DeBeer: Member of the DW-XAS beam line advisory team for NSLSII, Brookhaven National Laboratory (-present).

PD Dr. M. Knipp received the Award for Outstanding Research, Fifth International Meeting on the Role of Nitrite and Nitrate in Physiology, Pathophysiology, and Therapeutics, Pittsburgh USA, 2013-05-05.

Prof. Dr. Frank Neese was elected to the Leopoldina Society (Germany National Academy of Sciences), 2013.

Prof. Dr. Frank Neese was elected "Jean Perrin Reader" for the year 2013.

Prof. Dr. Frank Neese was appointed honorary professor (Theoretical Chemistry) at the University of Bonn, 2013.

Prof. Dr. Frank Neese was elected a honorary member of the Israelian Society of Chemistry, 2013.

Prof. Dr. Robert Schlögl was awarded with the Max-Planck-Communitas-Preis of the Max Planck Society, 2013.

Theses

Master and Diploma Theses

Klaßen, S.: Spektroskopische Charakterisierung von Mutationen des bakteriellen Blaulichtrezeptors YtvA. Hochschule Niederrhein, Krefeld, 2010-08.

Zimmermann, S.: Stationäre und kinetische Untersuchungen zur Assemblierung des Phytochroms. Univ. Düsseldorf, 2010-09.

Neubert, D.: Chemical synthesis of 5-thiariboflavin as a potential chromophore in blue light-sensitive photoreceptors. Hochschule Niederrhein, Krefeld, 2011-02.

Schwarzbach, K.: Untersuchungen zur Interaktion des NO-transportierenden Ferrihäm-Proteins Nitrophorin 7 mit Phosphatidylserin-haltigen Liposomen und niedermolekularen Di- und Polyanionen. Fakultät für Chemie der Universität Essen, 2011.

Stieber, S. C. E.: A Systematic Spectroscopic and Computational Examination of the Electronic Structures of Bis(Imino)Pyridine Iron Alkyl and Halide Compounds, Cornell University, USA, 2011.

Gutt, A.: Aminosäuren-Chromophor-Interaktionen im Blaulicht-sensitiven Photorezeptor YtvA aus Bacillus subtilis. Hochschule Niederrhein, Krefeld, 2012-09.

Hong, K.: Maturation of [FeFe]-Hydrogenases: Isolation and Characterization of HydG from *Shewanella oneidensis*. Heinrich-Heine-Universität, Düsseldorf, 2012.

Sardella, A.: Studies of the biological photoreceptors from the plant pathogen Pseudomanas syringae pv. tomato and their possible role in infectivity. Univ. Parma, Italy, 2012-06.

Simon, J.: Herstellung und Charakterisierung neuartiger Photolyasen des extremophilen γ-Proteobakteriums *Acinetobacter sp.* Ver3. Hochschule Niederrhein, Krefeld, 2012-09.

Doctoral Theses

2010

Cao, Z.: Structural and functional characterization of bacterial LOV domain-containing blue-light photoreceptors. Heinrich-Heine-Universität, Düsseldorf, 2010.

Hoppe, A.: Funktionsuntersuchung an artifiziellen [Fe-S]-Cluster bindenden Peptiden. Heinrich-Heine-Universität, Düsseldorf, 2010.

Khuzeeva, L.: Investigation of the Light-Induced Intermediate States in Type I Photosynthetic Reaction Centers. Heinrich-Heine-Universität, Düsseldorf, 2010.

Ostroumov, E.E.: Ultrafast relaxation dynamics of carotenoid excited states. Heinrich Heine Universität, Düsseldorf, 2010.

Pathak, G.P: A metagenomic approach towards novel LOV domail containing blue light photoreceptors. Heinrich-Heine Universität, Düsseldorf, 2010.

Ringsdorf, S.: Synthese gezielt isotopenmarkierter und strukturell modifizierter Tetrapyrrole. Heinrich-Heine Universität, Düsseldorf, 2010.

Sharda, S.: Structural-functional reciprocal affiliations between the phytochrome two-component signal transduction system and intra-domain crosstalk in *Calothrix* PCC7601. Heinrich-Heine Universität, Düsseldorf, 2010.

Wenk, B.: Die periplasmatische [FeFe]-Hydrogenase aus Desulfovibrio desulfuricans ATCC 7757: Aufreinigung, Kristallisation, spektroskopische und elektronische Charakterisierung. Heinrich-Heine Universität Düsseldorf, 2010.

2011

He, C.: Spectroscopic and Functional Characterization of the Heme Proteins Nitrophorin 4, Nitrophorin 7, and Selected Site-Directed Mutants: Studies of Their Nitrite Reactivity and of the Ferroheme Forms. Heinrich-Heine-Universität, Düsseldorf, 2011.

Rangadurai, P.: Spectroscopic Investigation of Chlorophyll Model Systems in a Myoglobin Matrix. Heinrich-Heine-Universität, Düsseldorf, 2011.

Sha, R.: The importance of the integrity of phytochromes for their biochemical and physiological function. Heinrich-Heine Universität, Düsseldorf, 2011.

Stieber, S. C. E.: A Systematic Spectroscopic and Computational Examination of the Electronic Structures of Bis(Imino)Pyridine Iron Alkyl and Halide Compounds, Princeton University, USA, 2013.

2012

Beckwith, M.A.: X-ray Absorption and Emission Spectroscopy of Manganese Complexes Relevant to Photosystem II, Cornell University, USA, 2012.

Geng, C.: Theoretical Study of C H Bond Activation by Mononuclear and Dinuclear High-Valent Iron Complexes. University of Bonn, 2012.

Rapatskiy, L.: The Structure of the Water Oxidizing Complex of Photosystem II and the Sites of Substrate Binding as Investigated by Pulse EPR Spectroscopy. Heinrich-Heine-Universität, Düsseldorf, 2012.

2013

Benedikt, U.: Low-Rank Tensor Approximation in post Hartree-Fock Methods, TU Chemnitz, 2013.

Cangönül, A.: Investigation of Metal-Catalyzed Epoxide Polymerisation and Phosphanyl Transition-Metal Complexes by Electron Paramagnetic Resonance. Universität Bonn, 2013.

Gandor, S.: Sha, R.: The importance of the integrity of phytochromes for their biochemical and physiological function. Heinrich-Heine Universität, Düsseldorf, 2013.

Kammler, L.: Physicochemical Analysis of Bacterial and Firefly Bioluminescence. Universität Bonn, 2013.

Raffelberg, S.: Blue light photoreceptors - From mechanisms to applications. Heinrich-Heine Universität, Düsseldorf, 2013.

Riethausen, J.: Isolierung und funktionelle Charakterisierung neuartiger Hydrogenasen sowie synthetischer [FeS] Cluster Proteine. Heinrich-Heine-Universität, Düsseldorf, 2013.

Stieber, S. C. E.: Methods for Determining the Electronic Structure and Mechanism of Bis(Imino)Pyridine Iron Pre-catalysts, Princeton University, USA, 2013.

Habilitation Theses

PD Dr. van Gastel, M.: Spin Centers in Biochemistry and Catalysis. Investigations by Magnetic Resonance Spectroscopy and Quantum Chemistry. Universität Bonn, 2012.

PD Dr. Knipp, M.: Heme-based Nitric Oxide Carrier Proteins: Structural and Functional Investigations of Nitrophorins. Heinrich-Heine-Universität, Düsseldorf, 2013.

Conferences and Workshops organized by the institute

2010

International Symposium on Molecular Coordination Chemistry (Emeritierung Prof. Wieghardt), Mülheim an der Ruhr (from 2010-11-07 to 2010-11-09)

H_2-Designcells Meeting 2010, Mülheim an der Ruhr, organized by Prof. Lubitz and Prof. Dr. Matthias Rögner, Ruhr-Universität, Bochum (from 2010-09-22 to 2010-09-23)

International conference on 'Chemistry at Spin Centers', Bad Honeff, Germany, organized by Prof. Neese (2010)

Verwaltungsleitertagung, Mülheim an der Ruhr (from 2010 05-05 to 2010-05-07)

SOLAR-H_2 Workshop 2010, Harnack-Haus Berlin, organized by Prof. Lubitz together with Prof. Bärbel Friedrich and Dr. Oliver Lenz, Humboldt University of Berlin (from 2010-03-21 to 2010-03-25)

Award Lectures Series „Frontiers in Biological Chemistry 2009", Mülheim an der Ruhr, Awardee: Prof. Dr. Bärbel Friedrich, Humboldt-Universität (Berlin).

60th Lindau Nobel Laureate Meeting, 3rd Interdisciplinary Meeting, Prof. Lubitz is member of the Council for the Lindau Nobel Laureate Meetings and was Scientific Chairperson for this meeting (from 2010-06-27 to 2010-07-02)

2011

Scientific Congress ICTPPO2011 (Intl. Congress Tetrapyrrole Photoreceptors of Photosynthetic Organisms), Berlin, organized by Prof. Gärtner (2011)

Symposium (Festkolloquium) on occasion of the 80th Birthday of Prof. Dr. Kurt Schaffner, Mülheim an der Ruhr (2011-09-24)

Symposium on "Advanced EPR Spectroscopy on Biomolecules" on occasion of the 75th Birthday of Prof. Dr. Klaus Möbius, Mülheim an der Ruhr (from 2011-06-20 to 2011-06-22)

International Workshop „Mechanisms of Non-photochemical Quenching“, An International Workshop on the subject of „Mechanisms of Non-photochemical Quenching“ will be organized by the EU Marie Curie Network „HARVEST“, Mülheim an der Ruhr (Prof. Holzwarth)

Gordon Research Conferences on Renewable Energy: Solar Fuels Ventura, CA (USA) (Prof. Lubitz/Vice Chair) (from 2011-01-16 to 2011-01-21)

2012

Symposium on occasion of the 70th Birthday of Prof. Dr. Karl Wieghardt (2012-10-24)

Gordon Research Conference on Renewable Energy: Solar Fuels, Il Ciocco, Italy (Prof. Lubitz/Chair) (from 2012-05-12 to 2012-05-13)

Gordon Research Seminar on Renewable Energy: Solar Fuels, Il Ciocco, Italy (Dr. Pandelia/Chair) (from 2012-05-13 to 2012-05-18)

Award Lectures Series „Frontiers in Biological Chemistry 2012", Awardee: Prof. Dr. Sason Shaik, (from 2012-04-23 to 2012-04-27)

Recent trends in chemical energy conversion - Research opportunities and challenges, Sondierungsgespräch Energie, organized by Prof. Schlögl (2012-09-12)

Symposium on "Integrating advanced spectroscopic tools for structure and dynamics of biological macromolecular complexes in vitro and in vivo", Schloss Ringberg, Kreuth, jointly organized by Prof. Lubitz (MPI); Prof. Steinhoff (University of Osnabrück) and Prof. MacMillan (School of Chemistry University of East Anglia, UK) (from 2012-12-12 to 2010-12-15)

2013

63th Lindau Nobel Laureate Meeting dedicated to Chemistry, organizer and scientific leader Prof. Lubitz together with Prof. Dr. Astrid Gräslund (University of Stockholm) (from 2013-06-30 to 2013-07-05)

IXth International Workshop on EPR in Biology and Medicine, Kraków, Poland, jointly organized by Prof. Lubitz, Prof. Balaraman Kalynaraman, Medical College of Wisconsin (USA) and Prof. Tadeusz Sarna, Jagiellonian University (Poland) (from 2013-10-07 to 2013-10-10)

Third Russian-German Seminar on Catalysis “Bridging the Gap between Model and Real Catalysis”, Burduguz village, Lake Baikal, Russia, jointly organized by Prof. Schlögl and Prof. Bukthiyarov, Boreskov Institute of Catalysis, SB RAS, Novosibirsk, Russia (from 2013-06-24 to 2013-06-27)

Summer School 2013 „Methods in Molecular Energy Research: Theory and Spectroscopy“, Essen, Germany, organized by Prof. Neese and Prof. DeBeer (from 2013-09-02 to 2013-09-06)

„5th International Conference on Carbon for Energy Storage/Conversion and Environment Protection“, Mülheim an der Ruhr, Germany, jointly organized by Prof. Schlögl and Prof. D.S. Su, Catalysis and Material Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research (IMR), CAS (China) (from 2013-09-23 to 2013-09-26)

Joint Schüth – Schlögl Seminar, MPI CEC and MPI for Kohleforschung, (2013-11-06)

Copper Catalysis Workshop, MPI CEC and MPI for Kohlenforschung (2013-12-16)

Joint Neese – Schlögl Seminar, MPI CEC and FHI Berlin, (2013-12-17)

Award Lectures Series „Frontiers in Chemical Energy Science 2013“, Mülheim an der Ruhr, Awardee: Prof. Dr. Gabriele Centi, University of Messina, Italy, (from 2014-01-08 to 2014-01-10)

SCIENCE IS INTERNATIONAL

Scientists from all these countries worked at the Institute from 2010 – 2013

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