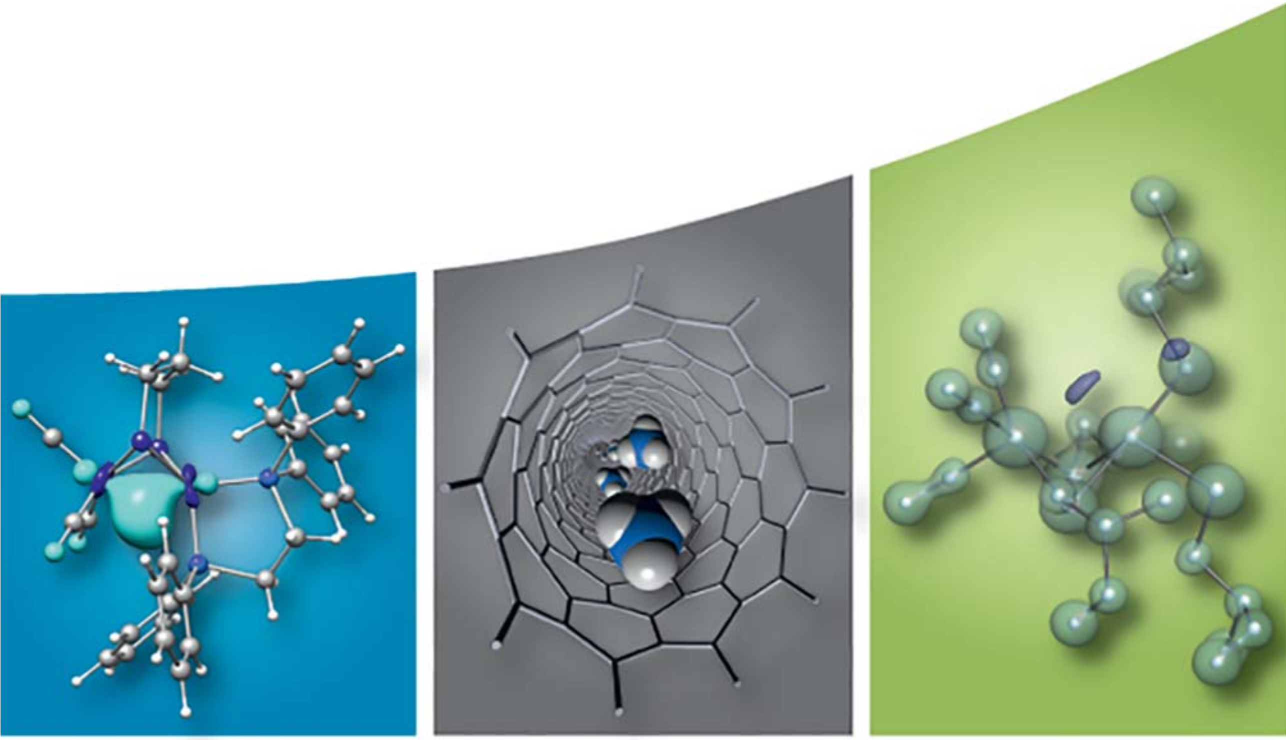
# Scientific Report

## *2014-2016*



MAX-PLANCK-INSTITUT FÜR
CHEMISCHE ENERGIEKONVERSION

# Scientific Report

## *2014-2016*

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CHEMISCHE ENERGIEKONVERSION

Mülheim an der Ruhr, February 2017
www.cec.mpg.de

## Report of the Managing Director

## Scientific Research Reports 2014-2016

### Department of Biophysical Chemistry

### Department of Molecular Theory and Spectroscopy

## Department of Heterogeneous Reactions

## MPI CEC in Scientific Dialogue

## Scientific Output and Statistics

# Report of the Managing Director

The MPI CEC is an institute in foundation. It originates from the former MPI of Bioinorganic Chemistry. In its foundation concept it was given the task to work on the scientific basis of chemical energy conversion understood as an indispensable part of transformation of energy systems towards sustainability. This dedication leads to the identification of catalysis as the cross-sectional strategic science underpinning every step of chemical energy conversion be it energy liberation through combustion or energy storage through water splitting and hydrogenation of $CO_2$ or $N_2$ to name prominent examples of simple substrates. Chemical energy conversion encompasses also transformations of biomass and the science of fossil energy carriers. From all these options the foundation collegium consisting of F. Neese, W. Lubitz and R. Schlögl decided to concentrate on the transformation of the small substrates. We wish to understand at the molecular level the options of how transformations can be achieved in molecular and interfacial catalysis and use this insight to arrive at generic strategies for finding and optimizing catalytic reactions. The practical conditions of executing these reactions are relevant in the context of the known unity between reactor and catalyst. Technological realization and engineering are outside the scope of the institute. Translating our insight into technological areas and informing decision makers about the possibilities of chemical energy conversion are, however, tasks of the institute.

The foundation process was planned as creating the necessary space for the institute and then in time start with an appointment process of 4 directors working in the complementary fields of experimentation in molecular and interfacial catalysis and in theory addressing molecular details and possibly micro kinetic processes. This concept turns out to be more slowly as originally planned due to the complexity of the building process. It was thus argued at the past meeting of the Fachbeirat that a change of the plan should enable a faster creation of the whole institute becoming visible by the accelerated appointment of new directors.

We first explored options to move the location of the MPI CEC to speed up the building process. This option was finally discarded on grounds of not leaving out the potential of a joint action with the neighboring MPI KOFO to erect the Mülheim Chemistry Campus (MCC) offering the chance to form a strong activity in fundamental science covering almost all fields of chemical catalysis. We concentrate thus on creating the foundations of MCC and move forward with the building activity. In addition, we moved forward with involving the institute in collaborative projects within the limits set by the spatial situation.

## New Buildings

The planning situation is now much advanced. We have a clear structure of the buildings comprising the final MPI CEC. The planning is advanced to the state that we have entered the process of seeking permissions from the local authorities and from the national bodies approving such investment. We successfully acquired the land needed. We kept the budget with an uncertainty of 10% mainly due to changing prices with respect to the price basis of 2011 where the budget was granted. Nonetheless, we are still facing issues with getting the necessary permissions that should be in our hands at the time of the meeting of the Fachbeirat. We still hope to begin building in July 2017 (exactly 5 years after the official foundation of the Institute) and to finish in 4 years from now. We perform the building in two stages due to the different legal situation of the land on which we build. In Figure 1 an overview is shown. The functions of the buildings are now clearly structured with dedicated buildings for chemical experiments (E) and for physics experiments (D). Building (C) will house the operando electron microscopy center and building (B) a multi-purpose hall for performing reactor experiments requiring special infrastructure. Office space will be located in buildings (A) and (D), all buildings will be connected by walkways.

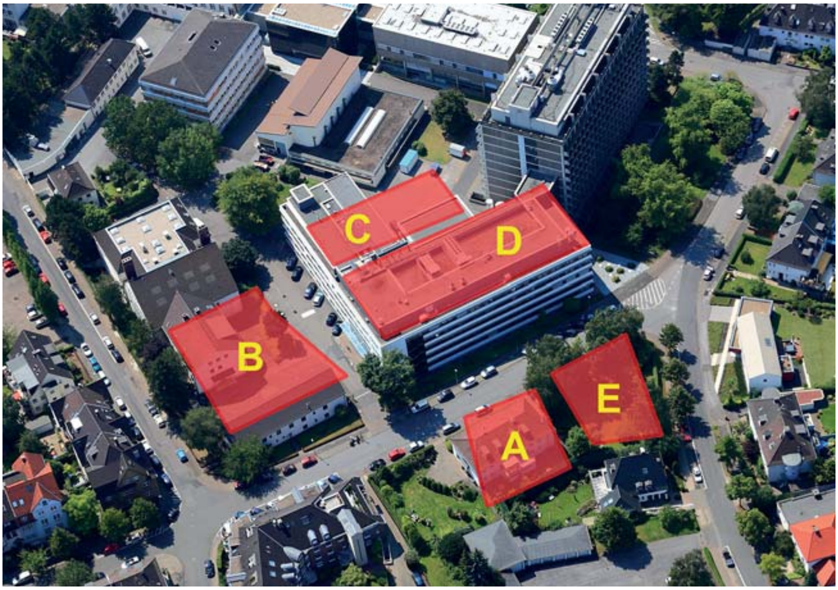

**Figure 1.** Aerial view of the CEC campus and the MPI KOFO campus (rear). The red areas designate the location and size of the buildings of MPI CEC. The street between (A,E) and (B,D) also belongs to the campus and will be closed for car traffic.

Usable at present is only building (D). Buildings (B) and (C) will be erected first as we have the permit to do so already in our hands. Buildings (A) and (E) across the street (that we need to close) stand on land dedicated for other purposes and for this we are in a process for obtaining the building permit. We expect building (B) to be ready by late 2018, which will be most relevant for our present appointment planning. The planning work was conducted with high priority and much support from the General Administration. Our building coordinator W. Schlamann invested enormous efforts and social competence in the process. Nonetheless, multiple delays including those created by a change of planning contractors were not exactly accelerating the process.

### The Present Structure

The MPI CEC consisted during the review period for the Fachbeirat of two and a half Departments. F. Neese was freshly appointed to the Institute with its foundation, W. Lubitz was already at the MPI for Bioinorganic Chemistry and R. Schlögl was given a fractional Department in his capacity as founding director with the dedication to withdraw his activities once the founding process would be stable. In this configuration we managed to begin the turnaround into the new direction. We gave the Institute a clear internal structure. This process was and is proactively supported by the whole workforce of the Institute and namely also by the workers council of the Institute. Without their support we would not have been able to come to the present situation of a productive and collaborative Institute.

We were able to attract two Max-Planck-Fellows from Ruhr University Bochum, namely M. Muhler and B. Roldan Cuenya supporting us with multiple aspects in chemical engineering and with nano science in electrochemistry. We succeeded in creating an International Max-Planck Research School (IMPRS RECHARGE). Here we decided to go for a highly focused topic, namely educating graduate students in the combined use of theory and spectroscopic experimentation. This is a difficult section within the difficult area of Physical Chemistry. We consider this ability as a fundament for the successful work of the Institute and limit us thus to a small but dedicated number of students. We use the central resources entirely to support students from the partner universities Bonn, Duisburg-Essen and Bochum whereas the students coming from MPI CEC and MPI KOFO are supported by regular funds of the sending Departments. R. Gröver effectively coordinates the IMPRS under the auspices of F. Neese.

The MPI CEC was instrumental in creating and coordinating the MAXNET energy initiative. In this inter-institute activity we coordinate research interests of colleagues in the CPT section of the MPG who are working on water electrolysis. Aspects of process design, of fundamental mechanistic relevance and of material design and synthesis are topics of the MAXNET. The coordinator A. Auer from the Neese Department has succeeded in building now a team of researchers anchoring the collaborative work within each of the participating institutes. The network addresses multiple challenges in reliably testing activity and stability of electrochemical water splitting materials and devices. This work sets the basis of comparing different approaches and measurement strategies on a rational basis that we miss much in the published literature. We aim at setting up a “MPG electrolyser" that has all materials and the process design from within MAXNET in order to explore systemic aspects of operating electrochemical water splitting under full control of all aspects relevant. MAXNET energy has two international partners namely the Universities of Cardiff and Virginia who contribute broader synthetic approaches to the MAXNET portfolio.

We installed a Max-Planck Forschungsgruppe on photochemical reduction reactions at the University Duisburg Essen. J. Strunk started with great enthusiasm looking into the unambiguous identification of the photochemical reduction of $CO_2$ with water to hydrocarbons and also solved the integration problem between the MPI CEC where she did not get lost and the UDE where she integrated with several related ongoing activities. Her successful start did not remain unobserved and thus we lost her already, as she became appointed as professor in Rostock University with a directing function in the renowned LICAT Institute for Catalysis belonging to the Leibniz association. We plan to renew the Forschungsgruppe also within the same topical area. A call for nominations is underway during the meeting of the Fachbeirat.

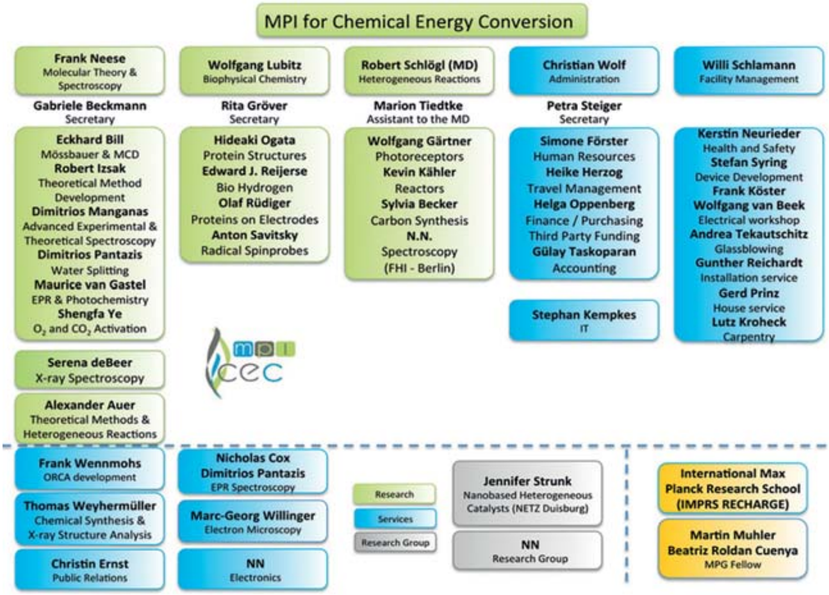

**Figure 2.** Structure of MPI CEC between 2014 and 2017.

The structure of the Institute is shown in the organizational chart of Figure 2. Considering that the Schlögl Department is only fractional and that the Lubitz department will cease to exist in 2017 due to retirement of the director, it can be seen that the Institute would run into a somewhat undercritical situation in the period to come. This was also pointed out at the last Fachbeirat and the Institute tried to come up with a solution to this problem. The solution presented was made possible in the process of consolidating and erecting the MCC namely the scientific connection to the MPI KOFO.

### The Mülheim Chemistry Campus (MCC)

When the directors of the two MPI in Mülheim come together for joint directorate meetings we all feel that it should be possible to join forces and activate scientific synergies between the two institutes working in multiple complementary fields of catalysis science. Even if such a process may take time, the reward should be worth the effort. What was missing is a point of nucleation with intense collaboration.

This point became an option with the attempt to fill the position of W. Thiel at MPI KOFO who is leaving in 2017 for retirement. The best possible successor for theory of molecular species and their reactions was F. Neese, sitting however in the "wrong" institute. It was thus decided and agreed by the MPG bodies that F. Neese should move to MPI KOFO with the following construction. The Neese group is active both in advanced molecular spectroscopy and in high-level theory with a strong brand for elucidating molecular structures as observables from spectroscopic signatures. That this is possible with chemical precision also for complex structures was put in evidence with the strong involvement in elucidating structures of biological relevance.

The Department moves now physically with its theoretical branch in the other institute. The spectroscopic branch with its complex infrastructure that is also needed as core asset by the MPI CEC, remains physically at MPI CEC but stays integral part of the Neese Department at MPI KOFO. The two institutes form a "joint workspace" to which belong the spectroscopic activities of the Neese group and the CEC facility "EPR spectroscopy" under the guidance of a W2 professor (A. Schnegg) who was selected by an MPG panel and is being appointed at present. In addition some physical office space is dedicated for coworkers of both institutes who collaborate in the area of advanced spectroscopy and theoretical analysis. This construction is defined in a contract between both institutes with the regulation that only a decision by all directors can dissolve or modify the structure. A managing team from both institutes cares for the practical operation; joint director meetings decide all major issues. We expect this construction to become operational formally at April 1st 2017 and practically in the second half of 2017.

### The modified MPI CEC

With the scientific foundation of the MCC, the MPI CEC has the option to move forward with its own appointment process. The scientific basis of the collaboration with MPI KOFO lies in molecular catalysis and functional analysis of molecular transformations. The work at MPI KOFO is product-oriented whereas the work at CEC is process-oriented if one wishes to delineate the complementarity. It is thus logical that at MPI CEC, we should strengthen our ability beyond the advanced spectroscopy group to look into molecular structures and reactions and find a candidate who is willing to translate these studies also into solid systems in order to bridge between interfacial and molecular catalysis.

It happens that the MPI CEC has already the ideal candidate for this department mission: Serena DeBeer is a worldwide known expert for the application of X-ray methods to the questions listed above. She uses both synchrotron-based methods and laboratory methods and creates innovative solutions for in operando X-ray emission spectroscopy that is in principle be applicable to solids and molecules. Her focus covers many high-energy spectroscopic methods with a focus on high-resolution experiments amenable to meaningful theoretical treatment for structure elucidation. This was also seen in exactly the same way by the perspective commission and the appointment commission of the CPT section of the MPG. The result is that Serena DeBeer is now being appointed with the negotiations being conducted as the Fachbeirat visits.

Chemistry is not done without a strong synthetic component. The Institute needs thus a Department of experimental molecular catalysis focusing on small molecule activation and on generating generic insight beyond phenomenological solutions. When focusing on the reductive activation of $CO_2$ it is hardly possible not to come across Walter Leitner who is located presently at Aachen University (RWTH). This was seen likewise by the perspective and appointment commissions who voted in favor of this solution leading to the ongoing attempt to appoint Walter Leitner as scientific Director to the MPI CEC.

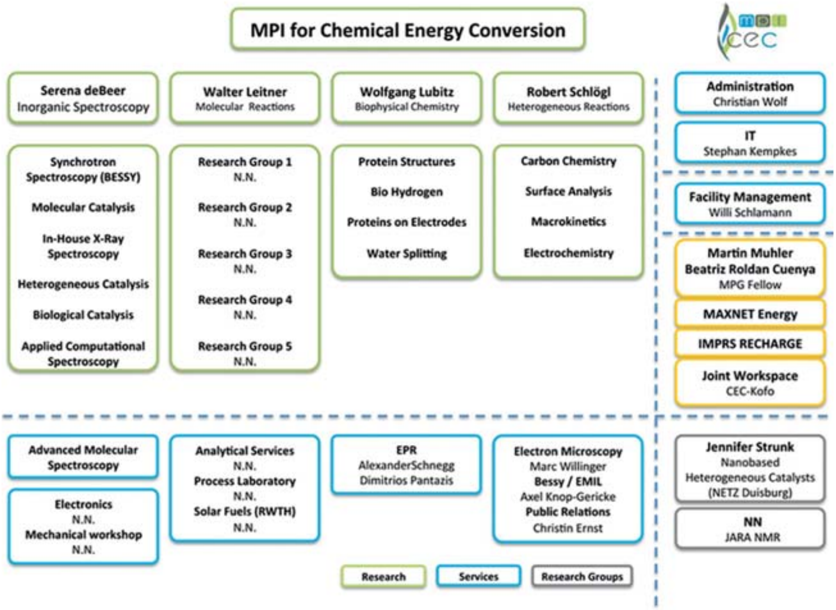

**Figure 3.** Structure of MPI CEC following the ongoing appointments.

The situation here is somewhat more involved. The MPG and in particular also the MPI CEC are interested in building a strong relation of the RWTH without creating, however, bounds limiting the decision-making of the two institutions. We have contracted collaboration on the subject of advanced NMR spectroscopy. The MPG installs a Forschungsgruppe at Aachen University (RWTH) and the University takes over the successful group leader after 5 years as full professor for NMR spectroscopy. This collaboration includes also the Forschungszentrum Jülich with its strong NMR activities. In addition, Walter Leitner is principal PI in several multi-year projects dealing with the transformation of biomass and $CO_2$ into propulsion fuels. This activity is strongly supported by a Cluster of Excellence at RWTH that should be continued. The MPI CEC is highly interested in the underlying chemistry but would not study properties of resulting molecular structures in propulsion applications where excellent expertise is located at RWTH. It is thus logical to try to combine the appointment of Walter Leitner with a suitable collaborative structure that is larger than a Forschungsgruppe and that allows Walter Leitner to remain principal PI in the projects mentioned without compromising his involvements in the MPI CEC. The research topic would be synthesis and application potential of solar fuels. It is intended to create a bi-directional collaboration with the successor of Walter Leitner at RWTH being also partly associated with the MPI CEC in order to deepen the synthetic capacity for issues of small molecule activation. The details of such a construction are currently worked out and we hope that we can create a successful development out of this appointment.

The MPI CEC will then move into the structure shown in Figure 3. It is obvious that this structure is much more stable. The aspects of molecular reactions are broadly accounted for and the institute can take the time required by the building operation to consolidate itself and move towards appointing the colleagues representing experiment and theory related to interfacial catalysis.

The execution of this plan requires a provisional location of the Leitner Department in building (B) of our institute and in office space of building (D). Additional space may be required either at MPI KOFO or in the old chemistry labs of MPI CEC to be removed for building (C). The details are being worked out at present but the appointment will not fail on these aspects. The planning has progressed to substantial detail and auxiliary measures in redistributing activities in building (D) to order space for the new Department DeBeer and for liberating space for the Leitner department will be executed during summer 2017.

### Operation of the Institute

The normal operation of the Institute continued during the restructuring activities. The multiple results obtained will be presented in the respective sections of the report. Here we show the number of scientific publications over time as indication that it was possible to maintain scientific productivity at a high quantitative and qualitative level through all the years of restructuring the Institute. To a good deal this wade made possible by the positive attitude of all coworkers in the Institute who trust in the future of the transformation and continue working also for some of them in new areas.

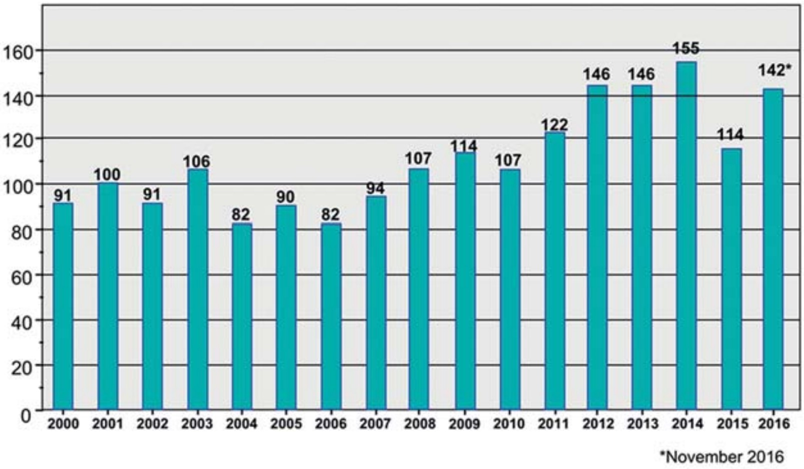

**Figure 4.** Scientific publications of the MPI for Bioinorganic Chemistry (until 2011) and the MPI CEC thereafter.

In all departments significant methodical contributions were reached notably in the Neese group. Such contributions are considered of particular relevance for the profile of the Institute in pursuing its mission of creating tools for others in the broader area of chemical energy conversion.

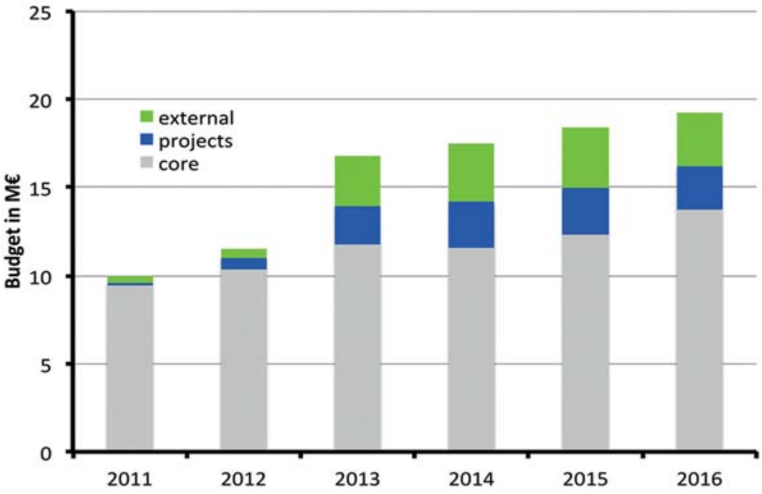

**Figure 5.** Financial evolution of the budget of MPI CEC. Core and project funding come from MPG, external funding from EU, DFG and BMBF (Federal Ministry of Science).

Creating new experimental instrumentation and infrastructure for the broader use in the departments of the institute was made possible by increased funding. Such an increase was agreed in the foundation document and we execute the plan as decided in 2011. This is reflected in the financial structure together with the outside reputation of the institute amongst funding agencies (EU, DFG, BMBF). As the institute is limited in growth by the missing buildings we cannot grow significantly in our workforce although we added new personnel to our central scientific groups at BESSY and to the fractional department of R. Schlögl. There was a substantial increase in the early years of the MPI CEC with the creation of the Neese department that will largely compensate through the new Department DeBeer when F. Neese moves to MPI KOFO. A substantial increase in additional funding over the core budget goes into the large projects and into new scientific infrastructure. We take the time evolution as sign of an active institute. We recognize, however, that this cannot continue without substantial influx of additional scientists who make use of this infrastructure.

For the future we expect thus a consolidated evolution of the budget containing less resources for projects plus a substantial reduction for the closed department of W. Lubitz. When Walter Leitner joins the institute with his (provisional) workforce we expect an over compensation of the loss. The resources for the building operation are not included in the numbers. Here we thank the Administration of the Institute, namely S. Förster (human resources) and H. Oppenberg (finance and procurement) under the guidance of Ch. Wolf for the precise work and the supporting attitude, creating an enabling rather than a hindering culture with the complex and plentiful administrative activities. The Institute is grateful to the President and the Management of the MPG for the continuous and generous support of the delicate transformation phase we are living through at present.

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# Scientific Research Reports 2014-2016

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**Dr. rer. nat.**
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**Habilitation**
Freie Universität Berlin (1982)

**Research Fellow**
University of California, San Diego (1983 – 1984)

**Assoc. Professor**
Organic Chemistry, Freie Universität Berlin
(1986 – 1989)

**Assoc. Professor**
Experimental Physics, Universität Stuttgart
(1989 – 1991)

**Full Professor**
Physical Chemistry, Max-Volmer-Institut,
Technische Universität Berlin (1991 – 2001)

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MPI CEC and Scientific Member
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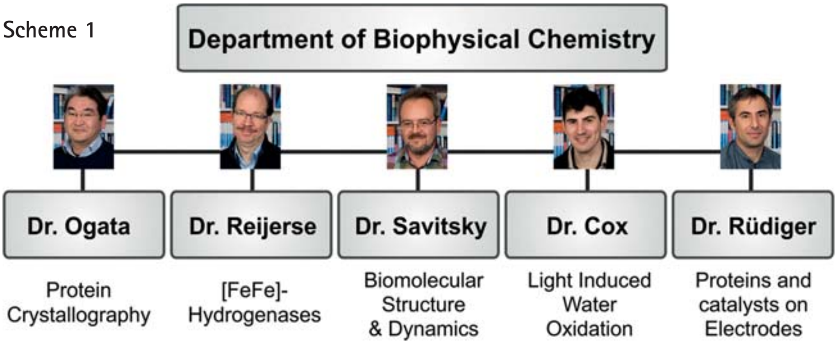
## The Department of Biophysical Chemistry

The department of Biophysical Chemistry has been established in 2000 by Prof. Wolfgang Lubitz after his appointment as a director of the Max Planck Institute for Bioinorganic Chemistry, formerly Radiation Chemistry, which in 2012 was renamed Max Planck Institute for Chemical Energy Conversion (MPI-CEC). At present there are approximately 30 scientists, postdocs, doctoral students and technicians working in the department. Five research groups, each headed by a group leader, are working on specific topics (scheme 1).

Scheme 1



"Artificial photosynthesis", the concept that is explored in the department, is illustrated in Figure 1. More specifically, we are studying native systems (enzymes) to understand the ingenious concepts of Nature with the aim to use this knowledge to design and synthesize chemical systems for efficient light energy capturing, energy conversion and storage in chemical compounds. In this broad research field we are focusing on two biological systems that contain complex transition metal catalysts in their active sites: i) the water oxidizing complex (WOC) - or oxygen evolving complex (OEC) - of oxygenic photosynthesis; and ii) hydrogenases that produce or convert molecular hydrogen. We use a variety of different physical techniques to study these systems, including X-ray crystallography, X-ray spectroscopy, Mössbauer spectroscopy, magnetic resonance (EPR/NMR), optical and vibrational spectroscopy as well as electrochemistry. Particular emphasis is placed on characterizing the magnetic properties of the metal sites and their ligand sphere, for which advanced electron paramagnetic resonance (EPR) techniques are employed. Most of the investigated systems are prepared in-house, allowing sample optimization and modification in an efficient way. The information obtained from such spectroscopies is supplemented by modern quantum chemical approaches, with the aim of understanding the catalytic function at the atomic level (cooperation with Dr. Pantazis, *Molecular Theory and Spectroscopy Department* of Prof. Neese). In this way, insight into enzymatic water splitting and hydrogen production and consumption in Nature has been obtained, providing new and important design criteria for synthetic bioinspired catalysts for energy conversion (cooperation with the Department Schlögl, *Heterogeneous Catalysis*). Our recent work has been summarized during the report period in two overview articles on water oxidation [1] and hydrogenases [2].

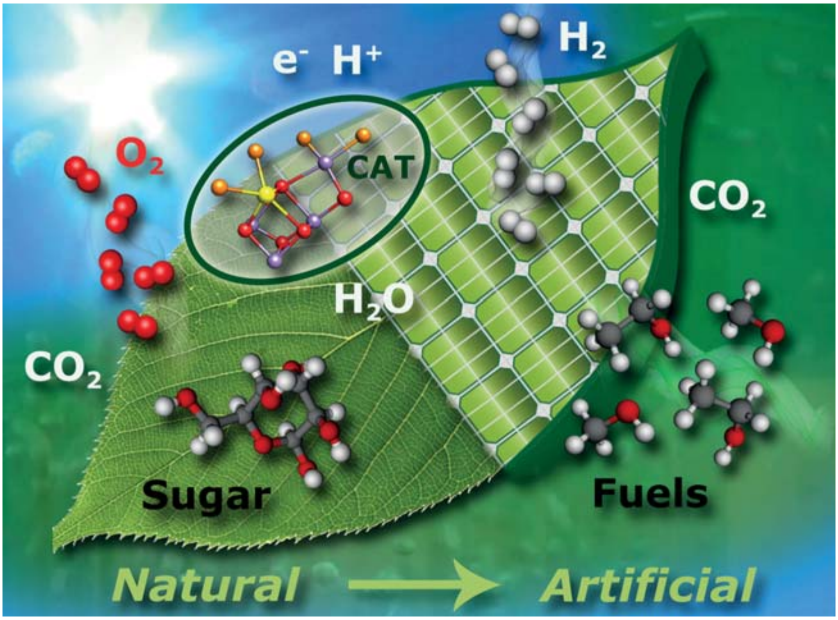
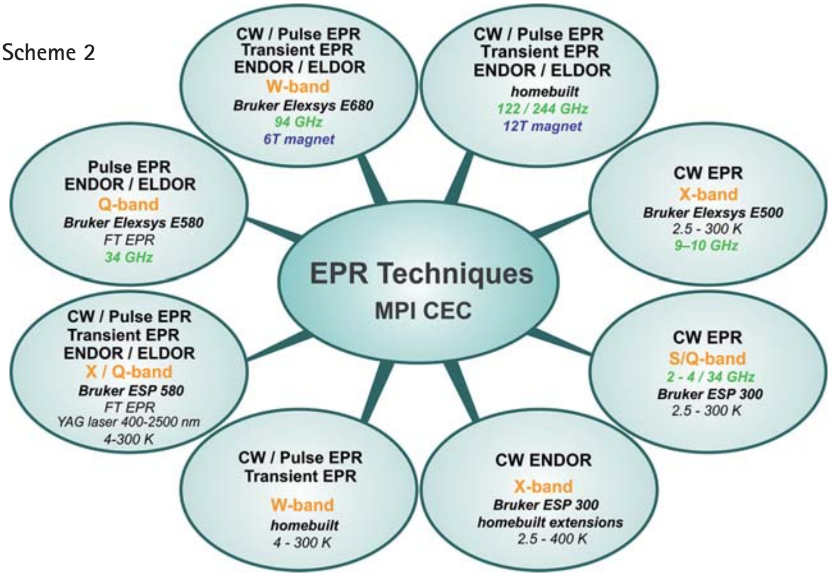


**Figure 1**. Artistic sketch of natural and artificial photosynthesis (cover: special issue *Phys. Chem. Chem. Phys.*, **16** (24) 2014; editors J. Messinger, W. Lubitz, J.-R. Shen)

## Instrumentation and Methodologies

A central mission of our department is the development of new instrumentation, methodologies and experimental techniques. In this endeavor we are closely working together with the technicians, engineers and the excellent workshops of the institute. A more detailed overview of the methods available in the MPI has been given in the last Scientific Research Report (2010- 2013). We are recognized as a center for multifrequency EPR and related spectroscopies. The 8 major instrumental EPR stations (Scheme 2) span the microwave frequency range from 2 to 244 GHz at fields between 0 and 12 T, operating in both CW and pulse mode configurations and at temperatures from 1.5 K to significantly above room temperature. To become independent of liquid helium supply we have started to replace all cryostats (for sample cooling) and high field magnets with cryogen-free systems. Accessories for additional MW channels and RF (NMR) irradiation for multiple resonance experiments are available as well as an arbitrary wave form generator (AWG) for pulse shaping and multifrequency MW pulse sequences. Furthermore we are building our own probe heads (MW resonators) adapted to specific applications. Most instruments allow in-situ laser irradiation for studying light-dependent processes. Short-lived paramagnetic species can be studied down to lifetimes of a few nanoseconds. Recently high pressure equipment has been set up that allows high field EPR experiments to be performed at up to 2.5 kbar (4 kbar peak).

Scheme 2



These developments in the MPI together with improvements in related microwave technology and data acquisition have led to a substantial increase in the sensitivity and stability of the EPR measurements (see reports by Drs. Anton Savitsky, Nicholas Cox and Edward Reijerse). This has dramatically expanded the array of chemical systems that can be characterized using EPR techniques, including large protein supercomplexes with multiple paramagnetic centers, fast relaxing spin systems such as transition metal complexes and related materials, species with higher spin states and samples with constrained dimensions, e.g. small single crystals - to name only a few. EPR experiments on single crystals are of particular importance; in the department we are therefore running a crystal growth laboratory (see report by Dr. Hideaki Ogata). Using microresonators we are now able to investigate very small single crystals with volumes of only a few nanoliters. Short-lived intermediates in reaction cycles (lifetimes of a few milliseconds) can be trapped by a recently implemented rapid freeze-quench system developed in our laboratory. This has been successfully employed for trapping several intermediates (S-states) in the light-driven water splitting clockwork of PS II using laser excitation combined with fast injection of $^{17}O$ labeled water in the catalytic cycle (Kutin/Cox et al., to be published).

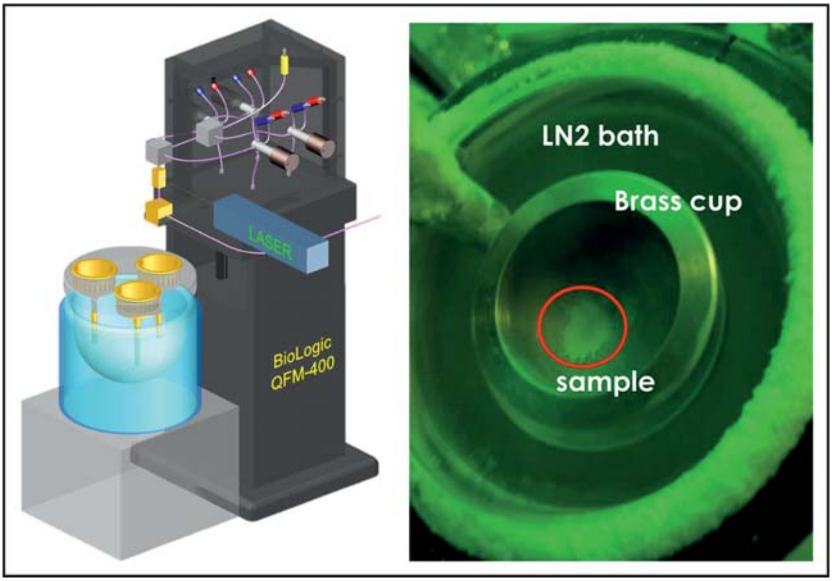


**Figure 2.** Rapid Freeze-Quench set-up based on a BioLogic QFM 400 showing the mixing chamber and the laser for sample flashing as well as the brass cups in a liquid nitrogen bath for sample freezing (left) and a single cup with a frozen sample (right). W-band EPR tubes are fixed at the bottom of the cup to which the frozen snow is then transferred mechanically.

Another important recent development is the construction of a chemical reactor engineered inside an EPR resonator, allowing the *in situ* real time detection of the active species in a reaction using a heterogeneous catalyst. This station is combined with analytic gas analysis of the reaction products [3] (see report by A. Savitsky).

Particular emphasis is placed in our EPR laboratory on methods that are able to resolve the electron-nuclear hyperfine couplings between the electron spin and the nuclear spin(s) that are delivering a map of the spin density distribution of the system – unique information that is only available by advanced EPR methods. Next to the more established techniques, electron spin echo modulation (ESEEM) and electron-nuclear double resonance (ENDOR), we have developed and used electron-electron double resonance- (ELDOR) detected NMR (EDNMR) at a range of mw frequencies together with simulation software. In this way even for magnetic nuclei with high nuclear spin like $^{61}$Ni, $^{55}$Mn, $^{17}$O and $^{14}$N the hfcs could be measured in complex metallobiomolecules with excellent sensitivity. The methodology has been described in recent articles by our group [4] (see reports by N. Cox and A. Savitsky).

During the last two years we have started to use NMR techniques to determine the structure of metalloproteins in solution. First results have been obtained and published on the ferredoxin (petF) from a green algae that acts as shuttle between the photosynthetic electron transport and other proteins, e.g. hydrogenase (producing hydrogen) [5a]. In a subsequent publication we were able to determine a much more complete NMR structure by substituting the paramagnetic iron ions in the [2Fe-2S] cluster in petF by two gallium ions, that are diamagnetic [5b] (see also report by E. Reijerse). Very recently we have also started to use paramagnetic NMR to study the active site of various genetically modified and/or labeled, artificially matured [FeFe] hydrogenases.

In recent years we have expanded our activities to obtain also vibrational data that often allow detection of all intermediates in a reaction cycle. For hydrogenase and also photosynthesis research FTIR techniques are very important. We have set up two instruments for experiments covering a wide temperature range (4K to 350K) with light access of the cryostat to follow photoinduced reactions. An ATR (attenuated total reflection) cell for surface IR experiments is also available. Spectroelectrochemistry can be performed in an optical transparent thin layer electrochemical (OTTLE) cell. A similar cell is also used for UV-VIS detection of redox processes for which we have a separate instrument. Furthermore time resolved FTIR experiments are possible in step-scan mode performed on our second FTIR instrument. Another smaller FTIR instrument is placed in a glove box for surface enhanced infrared absorption (SEIRA) spectroscopy in combination with electrochemical control (see report of Olaf Rüdiger). In the department of Frank Neese a sensitive new Raman instrument has been built that will be used for joint Resonance Raman (RR) experiments (see report of M. van Gastel). Vibrational data have also been obtained using inelastic Mössbauer scattering (nuclear resonance vibrational spectroscopy, NRVS) in cooperation with Stephen Cramer (UC Davis) on a synchrotron using respective monochromators (<1 meV resolution) at the beamline [6]. This technique allows detection of vibrations that are often not accessible by FTIR or RR, e.g. of metal-hydrides in larger proteins [6]. In the optical regime a new sensitive MCD instrument is available in the Neese Department that we are using together with Eckhard Bill with whom we are also collaborating on Mössbauer spectroscopy [7]. X ray absorption (XAS) and emission (XES) experiments have been started together with Serena DeBeer in the MPI [8].

As mentioned above the extension of our electrochemistry facility has made great progress during the last 3 years. Next to the classical techniques (cyclic voltammetry, coulometry, spectroelectrochemistry etc.) protein film electrochemistry (PFE) can now be performed routinely under controlled environmental conditions in two glove boxes equipped with gas mixers (see report by O. Rüdiger). Furthermore, we have successfully started to perform advanced EPR experiments on electrodes to follow the paramagnetic species and their conversion in the investigated processes ("electrochemical EPR"). This is particularly important for the detection of species (catalysts) on surfaces and embedded in polymer matrices [9, 10].

In close collaboration with the Department of Prof. Neese, DFT and *ab initio* calculations are being performed to relate measured spectroscopic parameters to structure and obtain reliable, unified electronic and geometrical structural models, for example of catalytic intermediates, important for the elucidation of reaction mechanisms, see [6, 11, 12].

### Collaborations within the Max Planck Institute for Chemical Energy Conversion, the Mülheim Chemistry Campus and with Neighbouring Universities

Between our *Biophysical Chemistry Department* and the *Molecular Theory and Spectroscopy Department* of Frank Neese exist very close and successful ongoing collaborations both for the water oxidation project and the hydrogenases, which is demonstrated by a large number of joint publications. Water oxidation is studied with spectroscopic techniques (Dr. N. Cox) and theoretical methods (Dr. D. Pantazis); the joint effort has led to an atomic level understanding of the structure and the structural changes of the water splitting unit, including an assignment of oxidation and spin states of the individual manganese ions in each of its metastable transition states, as well as an assignment of the sites of substrate water binding, the process of O–O bond formation and $O_2$ release [1, 11, 12]. Collaboration with Dr. M. van Gastel has led to a significant advancement in the understanding of the structure and function of the catalytic site in [NiFe] hydrogenases [13]. Together with Dr. E. Bill, new important information using Mössbauer and EPR spectroscopy has been obtained for the regulatory hydrogenase, a sensor protein [7]. The work has been complimented by XAS and XES measurements on [NiFe] model systems with Prof. S. DeBeer [8]. With Dr. T. Weyhermüller we are collaborating to synthesize model systems both for water oxidation (manganese clusters) and particularly for hydrogen production [14]. Together with the recent ultrahigh resolution crystallographic studies in our department [15] a near complete understanding of the [NiFe] hydrogenase catalytic cycle is within reach.

With the Department Schlögl *Heterogeneous Catalysis* we have started to set up EPR experiments to detect paramagnetic species in photocatalysis (see report by A. Savitsky). A close collaboration in a joint project on manganese clusters on surfaces and in solution has been established within the BMBF project "Verbundvorhaben MANGAN" (principal investigators: S. DeBeer, N. Cox, D. Pantazis, A. Knop-Gericke). With Dr. S. Becker's group functionalized carbon nanotubes for MnO electrocatalysis have been investigated with EPR. With the independent research group leader Dr. Jennifer Strunk (MPI CEC/Universität Duisburg/Essen) an EPR characterization of surface doped $TiO_2$ particles for photocatalysis has been performed.

With the neighboring *MPI für Kohlenforschung* we have an ongoing collaboration with Dr. C. Farès to obtain protein structures in solution using NMR techniques [5]. We have also initiated a project with Prof. F. Schüth/Dr. Ryan Wang on *in situ* EPR detection of the catalytically active sites in $CuO/CeO_2$ for the preferential gas phase oxidation of CO to $CO_2$ [3]. This novel technique is highly interesting also for other similar catalytic reactions, e.g. the water-gas shift reaction that is currently under study. Within the Cluster of Excellence (RU Bochum) we are also collaborating with the theory group of Prof. W. Thiel on protein dynamics including the solvent shell (QM/MM) (Decaneto et al., submitted).

Since 2012 Prof. W. Lubitz is PI in the *Cluster of Excellence "RESOLV"* at the Ruhr University Bochum and several members of the department (Anton Savitsky, Olaf Rüdiger, Edward Reijerse, Nicholas Cox and formerly Markus Knipp) have a close collaboration on solute-solvent interactions with members of RESOLV. This encompasses cooperations with Prof. M. Havenith (on THz spectroscopy on dynamic proteins in water), Prof. W. Schuhmann/Dr. N. Plumeré (on electrochemistry using engineered redox hydrogel matrices), Prof. M. Rögner/Dr. M. Nowaczyk (role of water in oxygenic photosynthesis), Prof. T. Happe/Dr. M. Winkler (on the effect of the solvent/matrix on hydrogenase activity), Prof. W. Sander (on highly reactive intermediates such as carbenes and nitrenes), Prof. S. Huber (on halogen-bonds in organic synthesis and homogeneous organocatalysis), and Prof. R. Winter from the University Dortmund (on temperature and pressure effects on a dynamical protein in solution). These collaborations have led to a significant number of joint publications.

## Hydrogenases

Hydrogenases are Nature's catalysts for the oxidation of molecular hydrogen or the reverse reaction, the production of $H_2$ from protons. A basic understanding of the structure, function and dynamics of this class of enzymes is of key importance for a future biologically based hydrogen production technology and for the design and synthesis of bioinspired *model systems* for hydrogen conversion or production catalysis. In our department both the [NiFe] and the [FeFe] hydrogenases are studied along with appropriate model systems in a combined effort of different groups and by applying a broad range of physical techniques.

*[NiFe] Hydrogenase:* During the report period the structures of all intermediates in the activation path and catalytic cycle of [NiFe] hydrogenases were finally resolved. The result is shown in Figure 3.

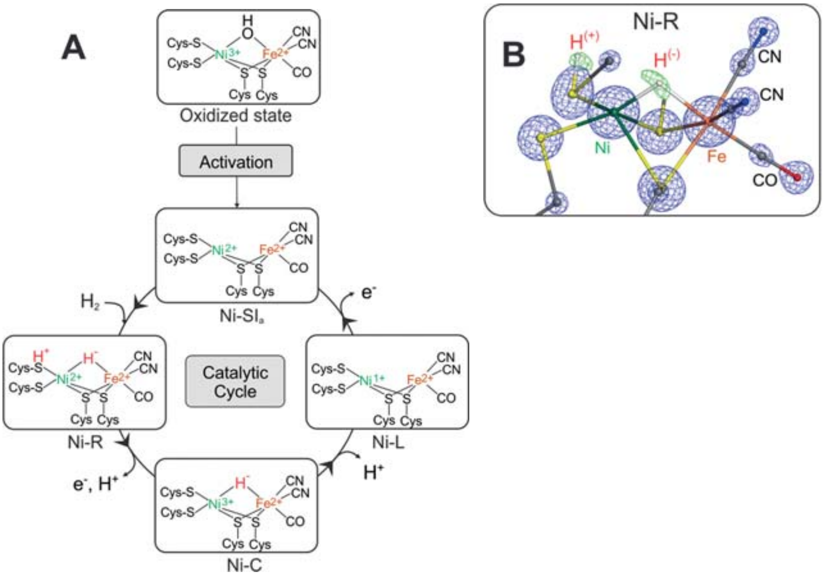


**Figure 3: (A):** Reaction cycle for standard [NiFe] hydrogenases including the activation from the oxidized state(s), Ni-A/Ni-B; and the enzymatic cycle including 4 states. $H_2$ oxidation to $2H^+$ and 2 $e^-$ is presented; a reverse reaction is also possible. Ni (redox active) is taking up $H_2$, whereas Fe remains low spin Fe(II). The hydride is found in the Ni-Fe bridge that is occupied by $OH^-$ in the oxidized state. The proton is accepted by a Cys sulfur acting as a base. **(B):** Electron density plot of the Ni-Fe active site in the Ni-R1 form of the enzyme showing the hydride in the bridge between Ni and Fe and the extra hydrogen at a cysteine sulfur, for details see [15].

The active species is Ni-$SI_a$, a diamagnetic complex, Ni(II)Fe(II), with an open bridge between nickel and iron - prepared structurally *and* electronically to take up $H_2$. Ni-SIa has been characterized using FTIR and Mössbauer spectroscopy [7]. This species attaches dihydrogen to yield Ni-R. We have obtained an ultrahigh resolution X-Ray crystallographic structure (0.89 Å resolution) [15] of Ni-R in single crystals of the [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F, in which the product of heterolytic splitting of $H_2$ ($H^+$ and $H^-$) could directly be identified; the hydride is sitting in the bridge between Ni and Fe (closer to Ni) and the proton is attached to the sulfur of one of the terminal cysteines next to the putative proton transfer canal. Furthermore, over 90% of the other hydrogens at ligating cysteines and surrounding amino acids near the active center could be detected including some water molecules (see report by H. Ogata).

In this structure the CO and $CN^-$ ligands could be distinguished for the first time and the proton transfer channel mapped out. Furthermore, the hydrogen bond network is available in unprecedented precision since the crucial hydrogens could directly be seen in many cases (see report by H. Ogata). The loss of an electron and a proton leads to Ni-C that only carries the hydride bridge, as shown in our earlier EPR work (Brecht et al., *J. Am. Chem. Soc.* 2003) and corroborated by DFT calculations on a large model of the active site together with the Neese group (Krämer et al., *ChemBioChem*, 2013). Ni-C is converted back to Ni-$SI_a$ by loss of a proton and an electron, most probably in two steps (via a Ni-L like state). The sequence of these PCET reactions is not yet fully elucidated; it may involve several intermediates, (Ni-L and Ni-R states). The reductive activation of the oxidized state (Ni-B/Ni-A) to Ni-$SI_a$ is done by loss of water (protonation of the $OH^-$ bridge, see Figure 3). The spectroscopic signatures of the two oxidized states present in standard [NiFe] hydrogenases could also be explained by EPR and FTIR experiments together with QC models [13].

*[FeFe] Hydrogenase:* As discussed above the catalytic $H_2$ splitting and $H_2$ formation in [NiFe] hydrogenases is performed by the nickel ion aided by a terminal cysteine sulfur acting as a base. In the [FeFe] hydrogenases an iron ion is employed in concert with a special azadithiolate ligand bridging the two irons, in which the nitrogen is functioning as a base (see Figure 4). The existence of the nitrogen, first shown by pulse EPR and ENDOR in our group (Silakov et al., *Phys. Chem. Chem. Phys.*, 2009), was finally proven by the insertion of several biomimetic complexes into the apo-protein of bacterial and algal [FeFe] hydrogenases. This seminal work has been done together with M. Fontecave (Paris), V. Artero (Grenoble) and T. Happe (Bochum) and was published in 2013 (Berggren et al., *Nature*; Esselborn et al. *Nature Chem. Biol.*). These first experiments on the artificial maturation of [FeFe] hydrogenases had far-reaching consequences for hydrogenase research, since the observed spontaneous cluster assembly could be used for obtaining larger amounts of hydrogenases, for isotopic labeling and changing metals and/or substituents or ligands, and to this end obtaining improved properties and function of the hydrogenase hybrids. Furthermore, the results could offer pathways to probe the theory of geobiochemical evolution of the hydrogenases and other related enzymes (see report by E. Reijerse).

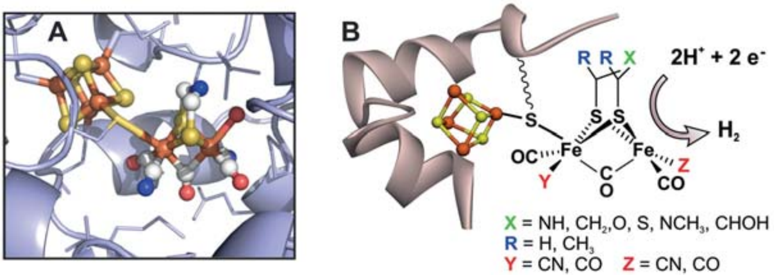


**Figure 4.** (A) The H-cluster of the active site of [FeFe] hydrogenases in its protein surrounding, showing the two subclusters [4Fe-4S]$_H$ (left) and [2Fe]$_H$ (right); (B): picture showing a selection of non-native active site mimics of the [2Fe]$_H$-subcluster that could be introduced into the apo-protein (carrying only the [4Fe-4S]$_H$-subcluster) via artificial maturation of the hydrogenase from *Chlamydomonas reinhardtii*; for details see [16].

In Figure 4 a series of compounds with changed ligand sphere is shown that could be incorporated into the apo-protein. It is interesting that all complexes showed much lower activity than the native enzyme both for $H_2$ oxidation and production; only the compound with one instead of two $CN^-$ ligands attained 50% activity of the natural system [16]. In Figure 5 an example is shown demonstrating how specific labeling can lead to new information. Here a hydrogenase with the native cofactor is investigated for which either the [4Fe-4S]$_H$-cluster or the [2Fe]$_H$-cluster is $^{57}$Fe labeled. This allows the separate detection and assignment of data from Mössbauer and $^{57}$Fe EPR/ENDOR spectroscopy for these subsites for different states in the catalytic states [17]; for more data see report by E. Reijerse.

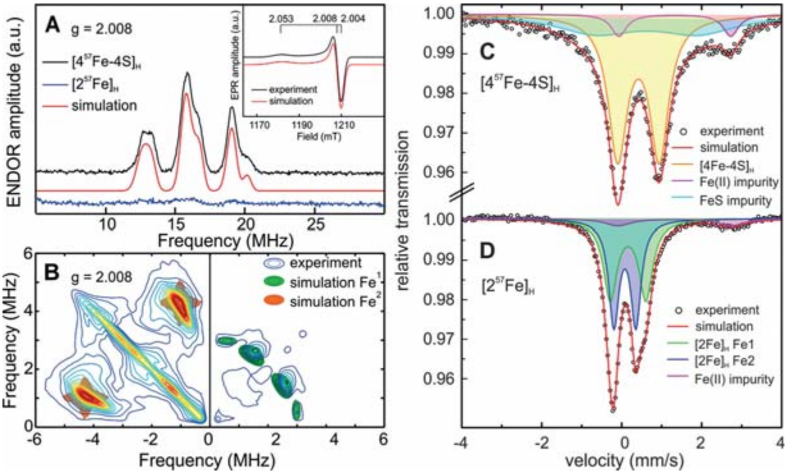


**Figure 5.** $^{57}$Fe ENDOR, HYSCORE and Mössbauer spectra of the CO-inhibited H-cluster in the [FeFe] hydrogenase of *Chlamydomonas reinhardtii.* **A**: EPR (inset) and $^{57}$Fe ENDOR spectra of the H-cluster in which either the [4Fe-4S]$_H$ or the [2Fe]$_H$ subcluster was labeled (large couplings of the 4Fe-cluster). **B**: $^{57}$Fe HYSCORE spectrum of labeled [2Fe]$_H$-subcluster (small couplings of the 2Fe-cluster, assignment). **C:** $^{57}$Fe Mössbauer spectra of the H-cluster in which only the [4Fe-4S]$_H$-subcluster was $^{57}$Fe-labeled. **D**: $^{57}$Fe Mössbauer spectra of the H-cluster in which only the [2Fe]$_H$-subcluster was $^{57}$Fe-labeled.
The Mössbauer simulations with different iron species are shown in shaded colors; for details see [17].

The specific $^{57}$Fe labeling of the $[2Fe]_H$-subcluster also allowed the preparation (and stabilization) of the key intermediate that is carrying the hydride end-on at the distal Fe. For the detection vibrational spectroscopy (NRVS) at the synchrotron SPring8 (Hyogo, Japan) was used in collaboration with the group of S. Cramer (UC Davis), employing H/D exchange and a special cofactor that blocks proton transfer and stabilizes the transient intermediate, see Fig. 6 (Reijerse et al., submitted).

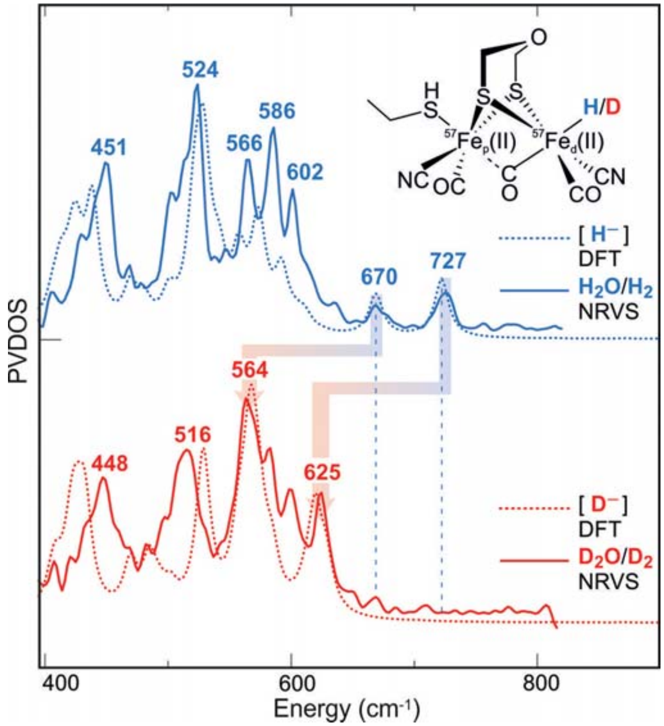


**Figure 6.** NRVS (nuclear resonance vibrational spectroscopy) directly detecting the iron-hydride bending vibrational modes (range 400-800 cm$^{-1}$) for an [FeFe] hydrogenase from *C. reinhardtti,* artificially matured with a $[2^{57}Fe]_H$ cofactor carrying an oxodithiolate bridge (odt). Solid lines: sample in $H_2O/H_2$ (blue), sample in $D_2O/D_2$ (red). Dotted line: DFT calculated spectra. Top right: model of the $[2^{57}Fe]_H$ subcluster of the active site carrying a hydride/deuteride at the distal $Fe_d$ position. Note that the O in the bridgehead of the odt is less basic than the native N in this position (adt) and is thus a poor proton relay. This stabilizes the (transient) hydride-carrying state.

Furthermore, the availability of modified (hybrid) [FeFe] hydrogenases opened the possibility to detect and assign the proton nuclei of the active site using paramagnetic NMR, a collaborative research project with C. Farès (KOFO, Mülheim) and C. Luchinat (Florence) (Rumpel et al., in preparation).

*Electrochemistry of Hydrogenases:* The oxygen sensitivity of the [NiFe] hydrogenases is a major drawback for practical applications in (bio)fuel cells or water electrolysis. Fortunately, several oxygen tolerant [NiFe] hydrogenases are known,

e. g, from Knallgas bacteria. How these are dealing with the attack of $O_2$ has been a topic of intense research in the past 5 years, see [2] for details. Together with the group of W. Schuhmann (RUB) we could show that a special designed smart matrix (a viologen-based polymer/hydrogel) is able to protect an embedded $O_2$-sensitive [NiFe] hydrogenase against oxygen attack and high potential deactivation [9]. This approach therefore eliminates two of the major problems that prevented the use of hydrogenases in biotechnological devices (see report of O. Rüdiger). Recently we could show that such a protection can also be achieved with the much more $O_2$-sensitive [FeFe] hydrogenases [10a]. We currently work on active hydrogenase model systems in cooperation with Wendy Shaw (PNNL, USA). In Figure 7 cyclic voltammograms are shown for $H_2$ reduction on Pt compared with [NiFe] hydrogenase and a model complex both covalently attached in the same way to the electrode. This demonstrates the excellent performance of both the native and model system - depending on experimental conditions [10b].

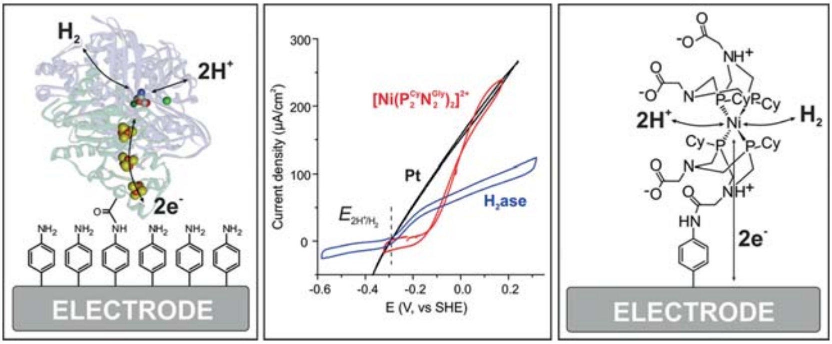


**Figure 7.** Cyclic voltammetry measurements of a Pt disc electrode (black trace), a *D. vulgaris* MF [NiFe] hydrogenase modified electrode (blue trace), and a $[Ni(P^{Cy}_2N^{Gly}_2)_2]^{2+}$ complex (red trace) modified electrode, comparing the onset potentials for each catalyst under exactly the same experimental conditions (pH 5.0, 25°C, 1 bar $H_2$). The vertical dashed line represents the equilibrium potential for the $2H^+/H_2$ couple. The structures of the hydrogenase (left) and the catalyst (right) immobilized on the pyrolytic graphite electrode (PGE) are shown; for details see [10b].

*Hydrogenase Model Systems:* In recent years we have started to synthesize new structural and functional model systems for [NiFe] and [FeFe] hydrogenases and characterized them (for an overview see section 6 in ref. [2]). Interesting first results were the demonstration of a reversible protonation of sulfur in a NiFe-model, the design of a complex with Ni(low spin) Fe(high spin) and Fe as active site, and also a mono-iron compound with $(P^R_2N^R_2)$- and Cp*- ligands for $H_2$ production, for which an Fe-hydride species could be clearly detected and characterized [14]. We have also performed a large number of spectroscopic experiments on hydrogenase model systems of other groups, see [18] for an example.

**Wateroxidase**

In photosystem II of oxygenic photosynthesis a protein-bound oxygen-bridged $Mn_4Ca$ cluster performs the process of light-induced water oxidation in a complex catalytic cycle, thereby releasing molecular oxygen, protons and electrons. The protons are used to form a gradient across the membrane driving ATP production, whereas the electrons are used to form NADPH; with both molecules (ATP, NADPH) subsequently used in the dark reactions (Calvin cycle) to reduce $CO_2$ to carbohydrates. During water splitting the cluster passes through five intermediate states $S_0$ to $S_4$, where the subscript denoted the number of transiently stored oxidizing equivalents. For many decades, the lack of structural data, the absence of spectroscopic methods with high resolution and sensitivity, and the complexity of the water splitting reaction led to rather slow progress in this highly important research field. With the advent of atomic level X-ray structures in Japan (Shen et al.; Nature, 2011 and 2015), concomitant progress in X-ray spectroscopy and time-resolved X-ray diffraction in USA, and with the development of novel sensitive magnetic resonance techniques here in Mülheim, this field has witnessed an explosion of research activity in recent years. Together with theoretical calculations performed in the Department of Frank Neese an understanding of the process of light-induced water oxidation in Nature is now in sight (see also reports by N. Cox and D. Pantazis).

In our department we have used mainly magnetic resonance techniques to study the trapped S-states of the water splitting cycle. Using advanced multifrequency pulse EPR, ENDOR and EDNMR techniques we were able to detect and characterize the flash-generated, freeze-trapped paramagnetic states $S_0$, $S_2$ and $S_3$ ($S_1$ is diamagnetic and $S_4$ is a transient state). By a careful analysis – backed up by QC calculations – we determined the site oxidation and spin states of all Mn ions and their spin coupling for all intermediates of the catalytic cycle [11].

The binding of the first substrate water and its incorporation into the Mn-cluster had already been measured by us using magnetically labeled water ($H_2{}^{17}O$) and detection by high field $^{17}O$ EDNMR (Rapatskiy et al., JACS, 2012). In more recent work the second water binding event was proposed to take place in the $S_2 \rightarrow S_3$ state transition; $S_3$ is the last metastable intermediate of the complex prior to O-O bond formation [12]. In the $S_3$ state, the two substrate oxygens are ideally located, bound between two Mn sites, allowing highly efficient O-O bond formation in the final $S_4$ state (Figure 8). This supports an oxo-oxyl coupling model originally proposed by Per Siegbahn (Stockholm).

Figure 8 summarizes the collected knowledge about the water oxidation cycle in oxygenic photosynthesis based on our joint spectroscopic and theoretical results in Mülheim.

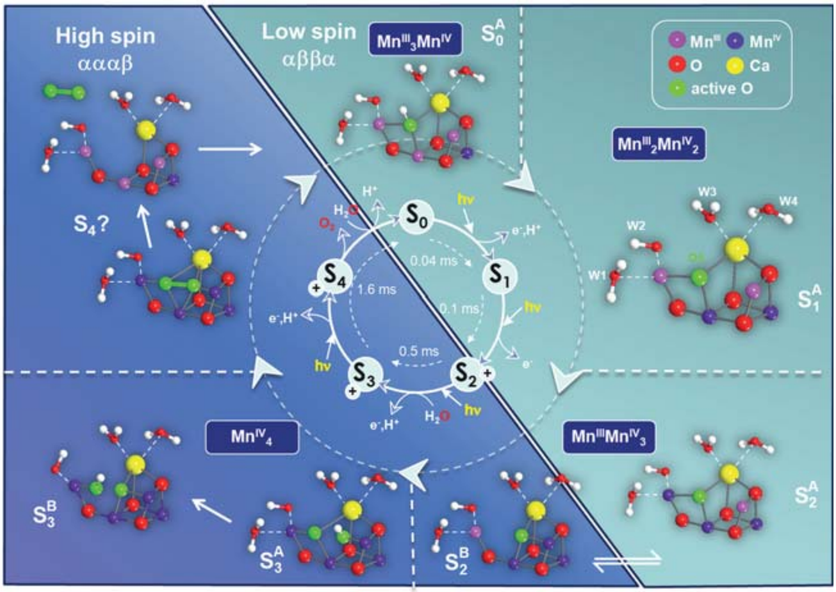


**Figure 8.** The water splitting clockwork of PS II in oxygenic photosynthesis showing the flash-induced S-state cycle ($S_0$ – $S_4$) with the release of electrons and protons, the water binding events and the time constants for each step. Furthermore the oxidation states of the 4 Mn ions are given. The outer circle shows the $Mn_4O_xCa$ cluster passing through the S-state cycle; atoms are color labeled. Note that the "active" oxygen atoms are in green, the others are in red. In the $S_2$-state two isomeric forms are possible (A and B) indicating a switch from a low spin state to a high spin state of the cluster (indicated by the light blue and the dark blue shaded background) [11b].

An interesting aspect is that in the $S_2$ state two structural isomers have been found that allow a low-barrier transition from a low-spin $S_2^A$ ($S_{tot}$ = 1/2) to a high-spin $S_2^B$ ($S_{tot}$ = 5/2) configuration (Pantazis et al. *Angew. Chem.* 2012). The two species are in full agreement with known EPR data. The high-spin state, which is a consequence of a closed cubane configuration with the dangling Mn(III) having a vacant coordination site, enables formation of the $S_3$ ($S_{tot}$ = 3) high-spin state (with four Mn(IV) ions), concomitant binding of the second water molecule, proton release and entering of the $OH^-$ into the "reaction zone". This is now located in perfect juxtaposition to the oxygen (O5) of the first substrate water bound to the complex. We believe that this sequence of events favors O-O bond formation and release of triplet dioxygen in the $S_4$ state [1, 11, 12].

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**Dr. Nicholas Cox**

The Cox Arbeitsgruppe studies enzymes using both magneto-optical spectroscopy and magnetic resonance techniques. These methods can be used to monitor oxidation states, transient/intermediate states, substrate binding and conversion as well as product formation and release, providing important complementary information to static spectroscopic and diffraction methods.[1] A key motivation of our research is to understand how biological systems use earth abundant metals including manganese to perform the difficult oxidative/reductive chemistry of small molecules such as water and oxygen. We are developing new methods for these systems that are in principle transferable to metal oxide materials, which should in the future allow molecular level characterization of heterogeneous catalysis interfaced with electrodes.

**Biological Catalysis (with AG Knipp, Gärtner and Pantazis).**
Over the last two years we have studied a series of biological systems that catalyze a diverse number of biological reactions including:

a) Heterodinuclear Mn/Fe cofactors which represent models for $O_2$ activation (Griese/Cox et al. PNAS 2013) i.e. O-O bond cleavage, an important industrial reaction with applications in fuels cells.[2,3]
b) Nitrophorins and heme domain proteins, which catalyze the dismutation of nitrite ($NO_2$) to NO and nitrate ($NO_3$) via oxygen atom transfer (OAT)[4] or act as novel signaling proteins,[5] respectively.
c) Matrix metalloproteinases, an important class of proteases that degrade and remodel the extracellular matrix i.e. collagens (Decaneto et al. *submitted*).
d) Nature's water splitting cofactor, a tetramanganese-calcium cluster bridged by five oxygens.[6] In recent years my group with AG Pantazis have used the high field EPR spectroscopies to study the mechanism of O-O bond formation

by elucidating the sequence of substrate (water) binding events which take place during the catalytic cycle (**Fig. 1A**).[7,8] Midway through its catalytic cycle ($S_2$), we have been able to show that labelled water is taken up as a fully deprotonated oxygen bridge at a specific site termed O5 (**Fig. 1B,D**).[7]

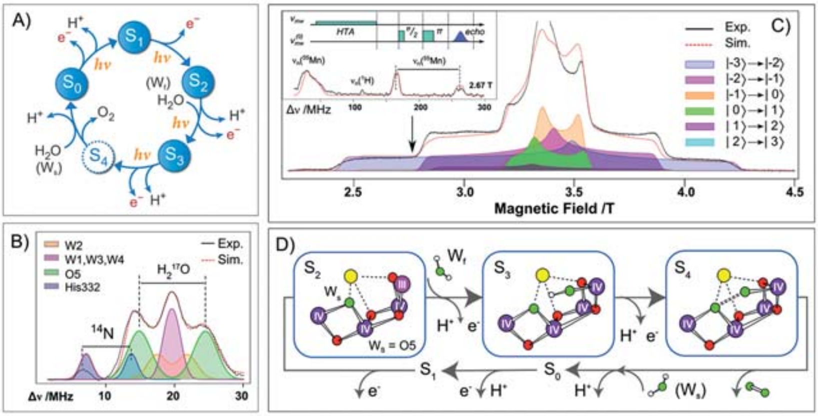

**Fig. 1** **(A)** The reaction cycle of nature's water splitting catalyst.[9-11] **(B)** $^{17}O$ EDNMR spectra (94 GHz) of the OEC exchanged in $H_2{}^{17}O$ and poised in the $S_2$ state, modified from Pérez-Navarro/Cox et al. PNAS 2013 **(C)** New high-field (W-band) EPR data of the catalyst prior to O-O bond formation.[12] **(D)** Possible water insertion pathway taking the catalyst from the resting states ($S_0$-$S_2$) to the active state ($S_3$); suggested mechanism for O-O bond formation involving O5 and the newly inserted water (OH) molecule.[6,10]

A recent highlight of this work has been our study of the structure of the cofactor immediately prior to the O-O bond formation step (**Fig. 1C**).[12] These data, which examine the oxidation state and coordination number of the four manganese ions, indicate that formation of this state requires the binding of a new molecule near the O5. It is these two waters/oxygens which then join to form the O-O bond[6,10-13] (**Fig. 1D**). Resolution of the mechanism of O-O bond formation is an ongoing project in the Cox/Pantazis groups, including time-resolved measurements and stop-flow/freeze quench techniques coupled to the new spectroscopic approaches described above (Kutin et al. *in preparation*). Importantly, this work provides new design principles for biomimetic water splitting catalyst technologies based on cheap, abundant 1st row transition metal materials.[6] Such catalysts typically represent heterogeneous materials which, owing to fast relaxation properties, cannot readily be characterized using conventional EPR techniques. As described below, however, the new high-field approaches used for the tetra-manganese-calcium cluster are robust against fast relaxation, allowing such systems to be studied.

**The development and application of new magnetic resonance for the characterization of transition metal materials (with AG Savitsky and Rüdiger).** The work described above was only made possible due to our continuing development of high-field pulse EPR methods such as ELectron-electron DOuble Resonance (ELDOR) detected NMR (ED-NMR).[1] These new techniques overcome limitations in terms of broad band detection and sensitivity inherent of conventional EPR techniques. **Fig. 2** shows the ED-NMR 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. Surprising double-nuclear transitions (those involving two nuclei) were also observed, allowing nuclear-nuclear coupling interactions to be assessed via nutation experiments.

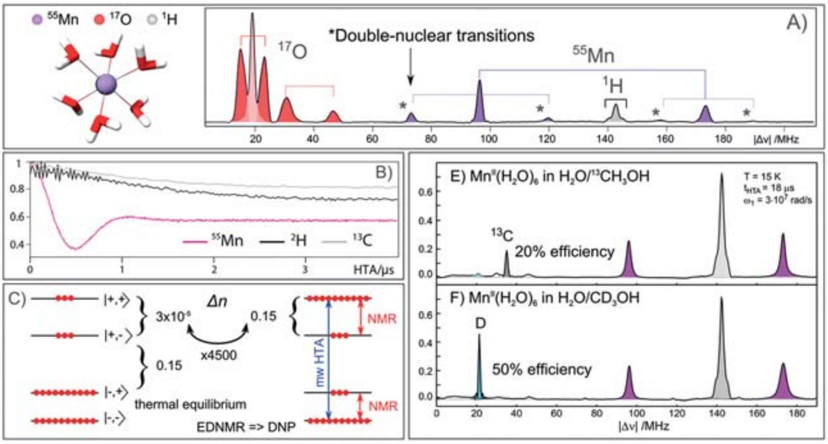

**Fig. 2** **(A)** Structure of a solvated $Mn^{II}$ ion in aqueous solution and W-band ELDOR-detected NMR of $Mn^{II}(H_2{}^{17}O)_6$ at 20 K. Transitions from all three magnetic nuclei of the complex ($^{17}O$, $^{55}Mn$, $^{1}H$) are marked by red, magenta and gray colour, respectively. Both single and double quantum transition of the three magnetic nuclei of the complex are observed. Transitions involving a change in projection of two nuclei (*) are also observed. **(B)** Nutation data showing the amplitude of the ELDOR-detected NMR signal as a function of the HTA pulse (pump) length. **(C)** Expected NMR signal enhancement via the pumping of spin forbidden transition. **(E)** and **(F)** Detection of distant (2nd/3rd coordination shell) solvation molecules using ELDOR-detected NMR. Appropriately optimized, the $^{13}C$ and $^{2}H$ signals observed for non-coordinating $CH_3OH$ are 20 and 50% of the primary spin-echo intensity, respectively.

The very high sensitivity of this method can be further demonstrated by the addition of labeled, non-coordinating solvent molecules such as methanol (**Fig. 2E, F**). These distant nuclei still couple sufficiently to the electronic spin such that their transitions can be efficiently pumped i.e. visualized. Even deuterium ions and more distant $^{13}C$ atoms of methanol can sense these transitions, thus allowing the 2nd/3rd coordination shell of the paramagnetic ion to be characterized (Savitsky, Cox et al., *submitted*). This opens the door to using simple paramagnetic molecules, introduced as a structural probe (contrast agent), to characterize solvation, reactivity and catalysis of a very large number of systems of interest, analogous to more established spin labeling techniques. In addition these methods are compatible with tandem EPR/electrochemistry cell currently under development (see AG Savitsky/ Rüdiger). As proof of principle, a purpose built electrochemical setup has already been developed in which a hydrogenase enzyme was embedded in a conductive polymer and measured by EPR during cyclic voltammetry (Rüdiger et al., *submitted*).

The methods described above represent polarization transfer techniques. The efficient transfer of the electronic polarization to nearby nuclei also forms the basis of new methods aimed at improving NMR sensitivity, termed dynamic nuclear polarization (DNP). As shown in **Fig. 2C**, such signal enhancements can be 3 orders of magnitude and they are coupled with enhanced selectivity – only nuclei in the vicinity of the electronic spin are observed. The experiments described in **Fig. 2** are thus DNP-like experiments, where detection of the state of interest is achieved via a microwave (MW) pulse sequence as opposed to a RF pulse sequence. Thus the method described above complements the traditional formulation of the DNP experiment and provides an important quantitative means to assess polarization transfer mechanisms amongst competing contrast agents.

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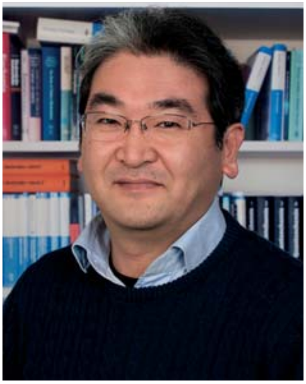

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**Dr. Hideaki Ogata**

## Protein Crystallography

Protein crystallography is a powerful 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, nitrophorin 4 and nitrophorin 7, and membrane type-1 matrix metalloproteinase) have been determined at high resolution, which gives detailed insight into the function of these enzymes.

### 1. Hydrogenases

Hydrogenases catalyze the reversible oxidation of dihydrogen.[1] The active site of [NiFe] hydrogenase 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 is found between the metals. Indeed, we performed the single crystal EPR and ENDOR spectroscopy on the oxidized (Ni-A) state of *Desulfovibrio vulgaris* [NiFe] hydrogenase in $H_2O$ and $D_2O$ buffer.[2] The spectra analysis combined with the DFT calculations revealed the presence of a hydroxyl ligand at the bridging position in the inactive Ni-A state (Collaboration with group of Dr. M. van Gastel).

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). In 2015, we reported the subatomic resolution crystal structure of the fully reduced (Ni-R) state of [NiFe] hydrogenase at 0.89 Å resolution.[3] The ultra-high resolution structure analysis revealed the presence of the hydride bridge at the [NiFe] active site in the catalytic active Ni-R state (see Prof. Lubitz report). A protonated thiolate sulfur ligand (Cys546) of the Ni is postulated based on the electron density. Furthermore, the detailed analysis allowed identification of the electron density of the hydrogen atoms including the amino acid residues and also the water molecules. The hydrogen bond networks showed that the possible proton transfer pathways which are important process of the hydrogen catalysis in the enzyme (Figure 1).

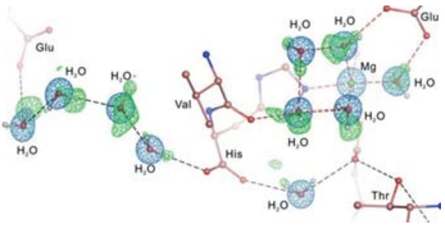

**Figure 1.** A possible proton transfer pathway via hydrogen bond network. The electron density maps of the water molecules are shown in blue (2Fo-Fc map) and green (Fo-Fc map), respectively. The green mesh represents the electron density of the hydrogen atom.

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). We identified the Ni-H$^{-}$-Fe wag mode (Figure 2) that is fully supported by the DFT calculations (Collaboration with groups of Prof. F. Neese and Dr. M. van Gastel).[4,5] The DFT calculation showed that the spin state of the Ni$^{2+}$ ion in the Ni-R state is the low spin which is in good agreement with the crystallographic study.[3,4]

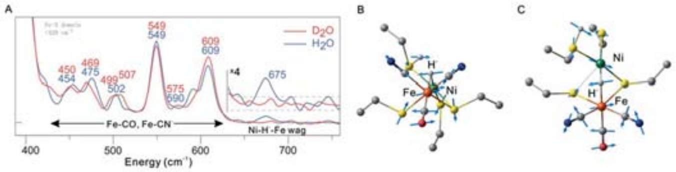

**Figure 2.** (A) NRVS spectra of $^{57}$Fe-labeled [NiFe] hydrogenase. The peak at 675 cm$^{-1}$ shows the Ni-H$^{-}$-Fe wag mode. (B) The DFT calculated model (low-spin Ni$^{2+}$) and the normal mode analysis of the wag mode. The arrows represent the vibrational mode. (C) The side view of (B).

### 2. Nitrophorin 7

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 nitric oxide (NO) from the insect saliva to the blood vessels of a host species where it acts as a vasodilator and blood-coagulation inhibitor. Four nitrophorins, designated NP1-4, were isolated from the insect saliva. Another nitrophorin, NP7, was recently established from a cDNA library and then recombinantly expressed. The NO transport is accomplished through the binding of NO to a heme iron and the subsequent release inside the host tissue. The protein experiences a significant pH change when subjected from the acidic pH of the saliva (between 5 and 6) to those of the blood plasma (~7.4) which decreases the affinity for NO. In NP7, the heme *b* cofactor is located inside an 8-standed β-barrel which is an unusual case for a heme protein (figure 3A). The heme iron is coordinated by a His residue where the 6th coordination site is open for the binding of various ligands including the native ligands NO and histamine.[6] The protein fold has been classified as a lipocalin type of fold, which is very common among the proteome and is typically found in proteins that bind lipophilic molecules.

NP7 is a particularly interesting case among the NPs because it is the only type that attaches to cell membranes. This interaction is accomplished by a positively charged surface opposite to the heme mouth (figure 3B). For the detailed understanding of the NP7-membrane interaction structural information is key. Therefore, on the basis of this information, a novel crystallization screen, which takes the strong charge dipolar nature of NP7 into account, was successfully applied. The analysis of the X-ray crystal structures of NP7 at low and high pH and with different heme ligands show the existence of a large resemblance in the overall fold, which is also similar to the spatial arrangement found in other NPs.[7] In particular, the large structural resemblance observed in the heme pocket for liganded and unliganded forms of NP7 support the functional role as a reservoir for NO storage (figure 3C). A peculiar feature of NP7, nevertheless, is the extensive clustering of Lys side-chains at the protein surface opposite the heme pocket, which is implicated in the charge-stabilized head-to-tail interaction observed in the crystal lattice (figure 3B). Furthermore, it provides a basis to realize the ability of NP7 to bind to negatively charged membranes. These features, together with the presence of tunnels and cavities in the interior of the lipocalin fold, suggest that NP7 could have specific pathways for direct exchange of NO with the membrane.

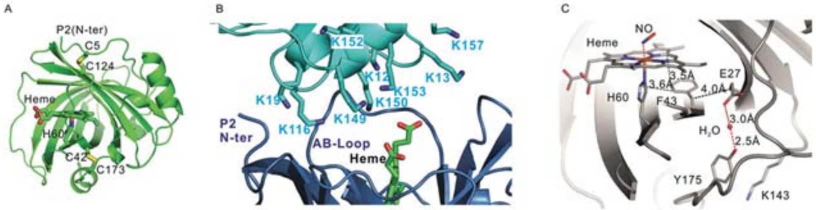

**Figure 3.** (A) The overall structure of Nitrophorin 7. (B) The interaction of the Lysin-rich region and the gate loop (AB-Loop) via crystallographic packing. (C) Structural detail of the heme and the surrounding amino acid residues in NP7 (NO bound form).

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## [FeFe] Hydrogenases

In the search for effective and affordable (electro) catalysts for hydrogen production from protons and electrons, nature's solution to this challenge forms a continuous source of inspiration. Hydrogenases occur in many micro-organisms (from bacteria to eukaryotes) where they play a role in hydrogen metabolism. These enzymes use abundant metals (Ni and Fe) in their active sites and catalyze the reversible oxidation of molecular hydrogen at ambient pressure and temperature with high turnover rates. [FeFe] hydrogenases are particularly active in $H_2$ production (up to 10.000 turnovers/second). They accommodate an active site (the "H-cluster") containing a unique binuclear iron cluster connected to a "standard" [4Fe-4S] via a bridging cysteine from the protein pocket. The iron atoms in the binuclear subcluster are coordinated by 2 CN and 3 CO ligands as well as a bridging „azadithiolate" (ADT) ligand (see figure 1). The distal iron (with respect to the [4Fe-4S] cluster) has an open coordination site where the substrate ($H_2$) and inhibitors ($O_2$ and CO) can bind.

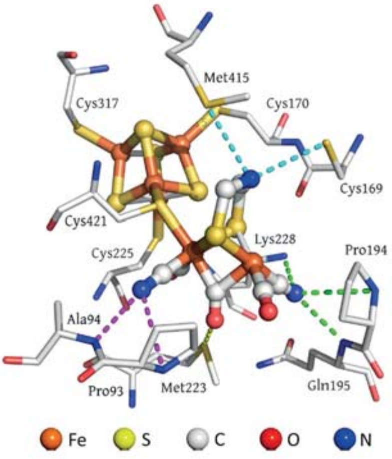

**Figure 1.** H-cluster in *C. reinhardtii* HydA1 with its protein surrounding (Coordinates are based on PDB-3C8Y, *C. Pasteurianum*). Interactions of the proximal CN ligand with the protein backbone are shown in pink and of the distal CN in green. Interactions of the bridging nitrogen with the protein surrounding are depicted in cyan. The interaction of the bridging CO with Met223 is shown in yellow.

In the last decade, our group has made significant contributions to the understanding of the electronic structure of the H-cluster as well as the catalytic mechanism of [FeFe] hydrogneses (Lubitz et al. Chem. Rev.2014,114, 408). In addition to the well-known redox states $H_{ox}$ and $H_{red}$ in which the [4Fe-4S] cluster is oxidized and the binuclear subcluster has configuration Fe(I)Fe(II) and Fe(I)Fe(I) respectively, we could identify a doubly reduced state $H_{sred}$ in HydA1, the [FeFe] hydrogenase of *Chlamydomonas reinhardtii*, for which the [4Fe-4S] is also reduced (Adamska et al. Angew. Chem., Int. Ed.2012, 51, 11458). It is believed that this doubly reduced state must be part of the catalytic cycle. Very recently, we could show that the CO inhibited state $H_{ox}$-CO characterized by a Fe(I)Fe(II) configuration can also be reduced. But, in contrast to $H_{red}$, the reduction equivalent in this transition goes to the [4Fe-4S] cluster [1]. This would support the idea that the [4Fe-4S] sub-cluster is not just a spectator moiety but is actively involved in the redox cycling of the H-cluster as a whole.

Further insight into the role of the structural elements of the H-cluster was obtained by exploiting the artificial maturation technique that we developed in collaboration with the groups of Marc Fontecave (Paris), Vincent Artero (Grenoble) and Thomas Happe (Bochum). This method allows to insert mimics of the binuclear subcluster into the apo-enzyme that has been expressed in *E-coli.*(Berggren et al. *Nature* **499**, 66-+ (2013**)**, Esselborn et al. *Nat.chem. biol.* **9**, 607-609 (2013)). Obviously, modifications of the bi-nuclear site are limited by the size of the protein pocket of the active site. Nevertheless, we were able to synthesize more than 10 variants of the bi-nuclear part of which 8 could be inserted into the enzyme [2]. As could be expected, most of these variants (see figure 2) did not show hydrogenase activity but, interestingly, the ADT variant with only one CN ligand, showed 50% of the native activity.

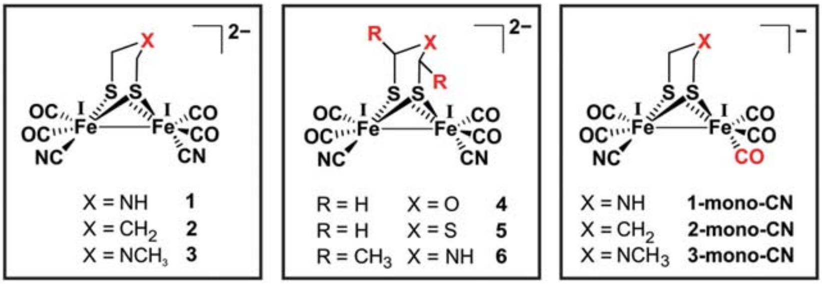

**Figure 2.** Variants of the binuclear subsite that can be inserted into the apo-protein of HydA1 containing only the [4Fe-4S] cluster.

From this, we concluded that the CN ligands are not essential for the catalytic mechanism but, instead, serve to stabilize the binuclear part inside the protein pocket through H-bonds. The second largest residual activity was shown by the variant with the methylated ADT amine. This indicates that the bridging amino group, which is strategically positioned with respect to the open coordination site, is essential for the catalytic mechanism as proton shuttle.

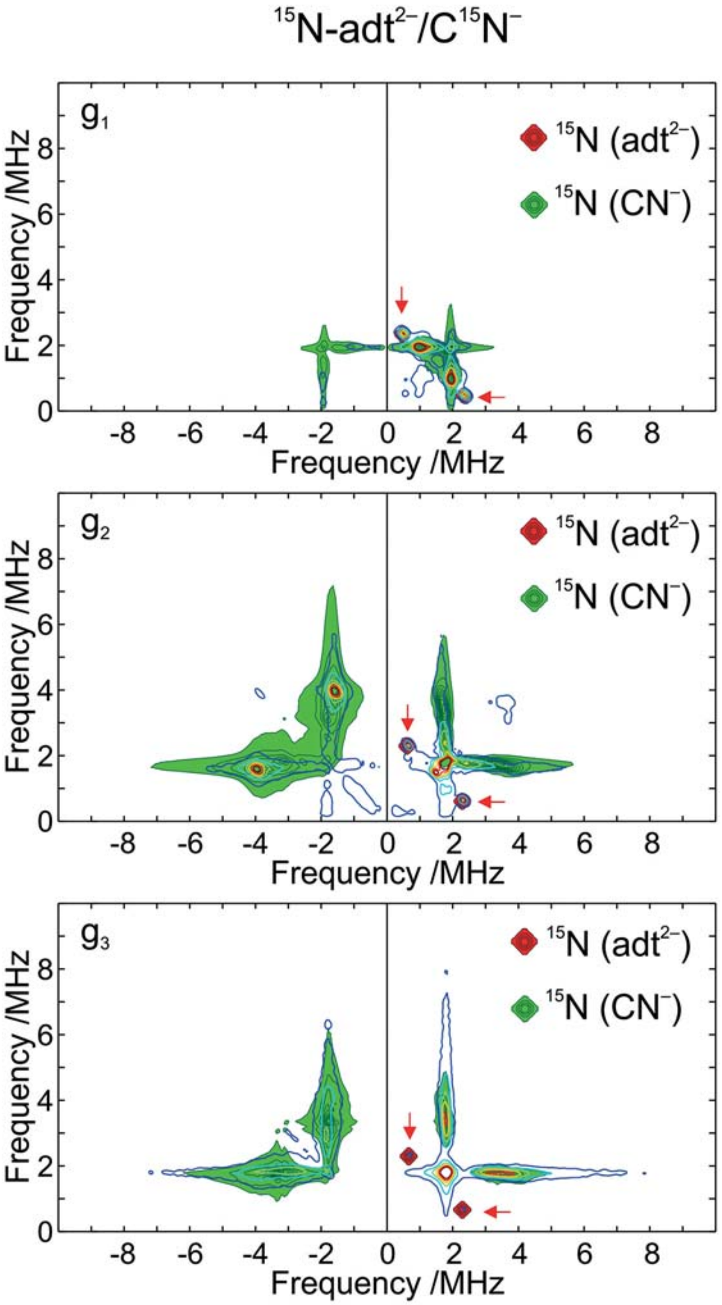

**Figure 3.** HYSCORE spectra of $^{15}$N labeled HydA1-adt recorded at the canonical field positions magnetic field positions corresponding to g1, g2, g3. The signals of the bridging amine and the CN are nicely separated.

The artificial maturation techniques also facilitated the isotope labelling of the CN ligands as well as the bridging ADT ligand in the H-cluster. In collaboration with the groups of Fontecave and Artero we prepared [FeFe]hydrogenase variants where the CN ligand and/or the ADT ligand were labeled with $^{15}N$. This allowed us to disentangle the overlapping $^{14}N$ HYSCORE spectra of the native H-cluster in the $H_{ox}$ state (Figure 3).

Our improved analysis of the nitrogen couplings in the H-cluster will ultimately facilitate the study of the native maturation pathway of the H-cluster in the cell [3]: Using isotope labeled maturases and substrates the groups of Britt and Swartz could show that the Fe atoms in the binuclear sub-site as well as its CN and CO ligands are originating from the maturase enzyme HydG a Radical SAM protein that metabolizes tyrosine as substrate. The origin of the ADT ligand, however remains as yet a mystery. A good candidate would be the maturase HydE, which is a radical SAM protein very similar to HydG, for which, however, no substrate or product is known. Our accurate values for the $^{15}N$ hyperfine couplings will be of key importance in the screening of $^{15}N$ labeled potential substrates.

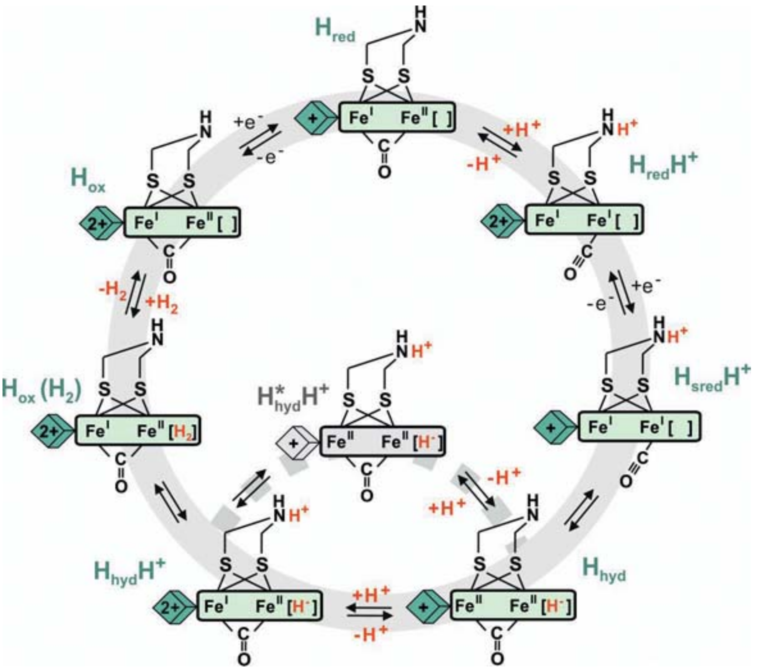

**Figure 4.** Working model of the catalytic cycle of [FeFe] hydrogenases. The $H_{red}$, $H_{sred}H^+$, and $H_{hyd}H^+$ states were identified for the first time in our group.

The same artificial maturation technique was used in collaboration with the group of Thomas Rauchfuss (Urbana, USA) to insert a $^{57}$Fe labeled bi-nuclear sub-cluster into the enzyme. Using selective $^{57}$Fe labeling (either 2Fe or [4Fe-4S] subcluster) we could determine the $^{57}$Fe couplings in the H-cluster more accurately using ENDOR and Mössbauer spectroscopy. In collaboration with the group of Steven Cramer (Stanford) also the first Nuclear Resonance Vibrational (NRVS) spectra were recorded on a selectively $^{57}$Fe labeled H-cluster [4]. In a very recent study the same NRVS technique was further used to identify for the first time a terminal iron hydride as catalytic intermediate in the active cycle of [FeFe] hydrogenases (under review). To this end our group prepared very highly concentrated samples of [FeFe] hydrogenase which was maturated with a $^{57}$Fe enriched 2Fe subcluster lacking the amine Brønsted base function and thus trapping the hydride intermediate. In systematic pH dependent spectroelectrochemical study on active [FeFe] hydrogenase we were able to stabilize and identify another intermediate in the catalytic cycle (Sommer et al. 2017 JACS 10.1021/jacs.6b12636). Summarizing, in the last decade our group was able to identify three of the five currently known intermediates in the catalytic cycle (see figure 4).

In a high resolution NMR study of the interaction between HydA1 (the [FeFe] hydrogenase from the green algae *Chlamydomonas reinhardtii* ) and its native redox partner PetF the contact surface between these partners was mapped out (see figure 5). On the basis of these data targeted mutants of PetF could be designed that improve the *in vivo* hydrogen production *of C. reinhardtii*. [5]

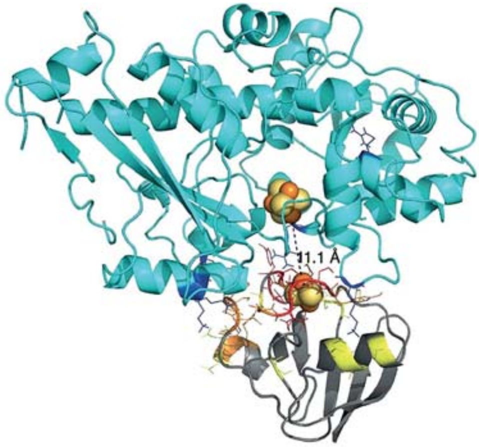

**Figure 5.** HADDOCK model of the PetF/HydA1 complex structure. The coordinates for the apo HydA1 structure (on top) were taken from PDB-3LX4 while the coordinates of the ferredoxin PetF from *C. reinhardtii* (bottom part) were submitted under PDB-2MH7.

## External Collaborations

In another collaboration with the group of Thomas Rauchfuss (Urbana, USA) we characterized a novel synthetic model for the active site of [NiFe] hydrogenases using EPR, ENDOR and Mössbauer Spectroscopy [6]. This model complex represents the first mimic of the so-called Ni-L state that shows the actual redox configuration Ni(I)Fe(II) found in the native system.

Our group was also involved in a collaboration with the group of Franc Meyer (Göttingen) that synthesized a unique ferromagnetically coupled (S=1) peroxodicopper complex. High field EPR at 244 GHz allowed us to estimate the Zerofield interaction (2.15 $cm^{-1}$) of the Copper dimer unit [7].

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## Proteins and Catalysts on Electrodes

Our group's research is focused on the electrochemical study of hydrogen cycling catalysts, more specifically hydrogenases and bio-inspired molecular catalysts. Hydrogenases are the most efficient noble-metal-free catalysts for $H_2$ production or oxidation. These enzymes use earth abundant metals in the active site (as Ni or Fe) and work at almost no overpotential under mild conditions.[1] Chemists have been studying these enzymes to understand their unique properties and learn how to design bio-inspired catalysts avoiding the use of noble metals. The goal is to have efficient catalysts for implementation in energy conversion devices. These devices could be employed to efficiently store energy from discontinuous renewable sources in chemical bonds as a fuel and recover that energy when required.

**Protein film electrochemistry** has been proven as a highly useful technique to study immobilized hydrogenases to gain fundamental information about the enzyme kinetics and their sensitivity towards inhibitors such as $O_2$ and CO.[2] Much less is known about homogeneous **bio-inspired catalysts.** In recent years, there has been significant improvement in the development of bio-inspired synthetic catalysts based on earth abundant metals like Fe, Ni or Co. These catalysts have so far been studied using methods very different from the ones used with enzymes. We have shown that we can immobilize some of these catalysts on electrodes and characterize them under conditions mimicking those of a device e.g. a fuel cell or a $H_2$ producing electrode. We can now also compare the activity of the bio-inspired catalysts for $H_2$ oxidation with the enzyme.[3,4]

When designing an immobilization strategy for a catalyst on an electrode, it is possible to improve the electron transfer and the stability of the catalytic currents. But for delicate catalysts, sensible to oxidative inactivation, directly interfacing the catalyst with the electrode leads to a rapid loss of electrocatalytic current if the catalyst is exposed to a harsh environment, as is found in an operating fuel cell. In the last years we have specifically designed **redox polymers** to protect sensitive hydrogenases from oxidative inactivation and demonstrated the protection mechanism.[5-7]

Immobilization of catalysts on electrode surfaces allows precise redox control of the immobilized molecules and measurements of catalytic currents. On the other hand, electrochemistry alone does not provide information about the electronic structure of our catalysts. Therefore, in the last years we started developing several **in situ** spectroelectrochemical cells (**EPR, FTIR**) to detect the species participating in catalysis.

### Redox Polymers as Protecting Matrix

In collaboration with the groups of Prof. W. Schuhmann and Dr. N. Plumeré from the Ruhr Universität in Bochum, we designed polymers modified with redox moieties selected specifically to accept electrons from the hydrogenase. The viologen group was chosen as electron relay based on three criteria: i) Its potential is slightly more positive than that of the $H^+$ reduction potential, so it has enough driving force to accept electrons from the enzyme; ii) It is more negative than the enzyme inactivation potential, avoiding the inactivating oxidation of the enzyme by positive potentials from the electrode; iii) Viologen is capable of reducing $O_2$ and thus should protect the enzyme from oxidative damage. We demonstrated the feasibility of this concept using the $O_2$ sensitive [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F (*Dv*MF).[5] We proposed a protection mechanism based on the reduction of $O_2$ on the surface of the electrode by reaction with the reduced viologen groups (Figure 1). This prevents the penetration of $O_2$ in the polymer film, so the enzyme maintains its activity. Thus, electrons from the catalytic $H_2$ oxidation by the enzyme are used for the catalytic $O_2$ reduction by the viologen.[5]

Other authors proposed alternative explanations for the increased $O_2$ tolerance, based on physical limitation of the $O_2$ diffusion through the polymer, as it was proposed for graphite porous electrodes (Xu, L. *et al. RSC Adv.* 2015) or on a reactivation of the $O_2$ inactivated enzyme by reduced viologen (Morozov, S. V. *et al. Electrochem. Commun.* 2006). To demonstrate our mechanism we adopted two different strategies. We initiated a collaboration with Christophe Léger, to build a theoretical model which could simulate the reactivity of our polymer films to gain a deeper understanding of the mechanism. In this way we obtained the time dependency of the concentration profiles in the polymer/enzyme film. The model gave us the limiting conditions required for the catalytic current to reach an apparent steady state in the presence of $O_2$, which has important implications for the applicability of these polymer films in practical devices ensuring long-term protection of the catalyst in the presence of $O_2$.[6] Confirmation for our model came for an enzyme, which is irreversibly inactivated by $O_2$, e.g. [FeFe] hydrogenase. We showed that using a viologen modified polymer, this very $O_2$ sensitive hydrogenase could continuously oxidize $H_2$ in the presence of $O_2$ in the gas feed (Figure 1). This enabled us to build for the first time a fuel cell using a [FeFe] hydrogenase.[7]

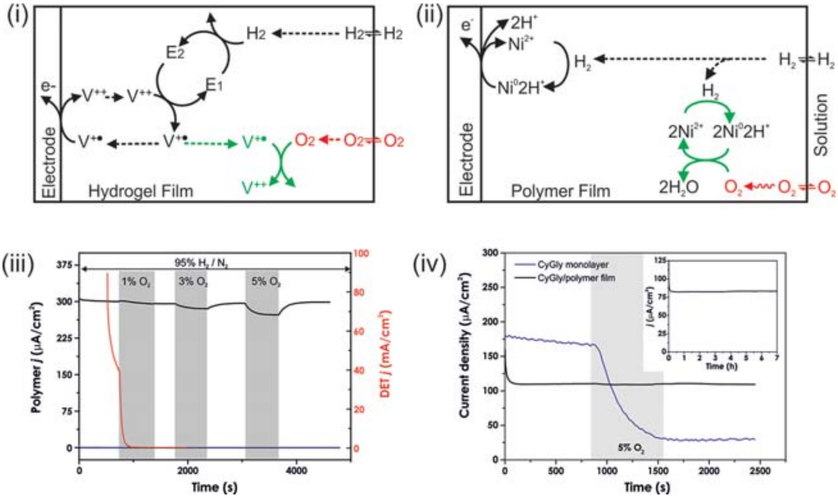

**Figure 1. (i)** Proposed model for the $O_2$ protection mechanism of hydrogenases in redox hydrogel films. $O_2$ is reduced in a thin layer close to the hydrogel–solution interface preventing $O_2$-induced deactivation of the hydrogenase in the inner layers of the film. **(ii)** Proposed $O_2$ protection mechanism for the polymer/synthetic catalyst film. On the surface of the porlymer, $H_2$ reduced catalyst molecules consume $O_2$, preventing its penetration into the inner layers of the polymer where the Ni complex is electrocatalytically oxidizing $H_2$. **(iii)** Chronoamperometry (CA) for evaluation of oxygen tolerance. Black trace: glassy carbon electrode (GCE) drop-coated with *Chlamydomonas reinhardtii* [FeFe] hydrogenase/polymer, blue trace: GCE drop-coated with the polymer only, red trace: pyrolytic graphite electrode with the same enzyme in direct electron transfer regime. **(iv)** CA for evaluation of the $O_2$ inactivation of $[Ni(P^{Cy}{}_2N^{Gly}{}_2)_2]^{2+}$ complexes immobilized on a monolayer, blue trace, and on a polymer film, black trace. The inset shows a CA experiment measured continuously using a 90 % $H_2$ / 5 % $O_2$ gas feed during seven hours.

## Bio-inspired Catalysts

The DuBois group at Pacific Northwest National Laboratory designed a family of Ni bio-inspired catalysts that use a pending amine base analogous to that found in [FeFe] hydrogenases (DuBois, D. *Inorg. Chem.* 2014). This pending amine group plays a key role in catalysis to facilitate proton transfer to and from the active site (Figure 2) resulting in excellent catalytic properties. The group of Wendy Shaw improved the catalytic performance of these Ni complexes by including enzyme-inspired amino acid residues at the outer coordination sphere of the catalyst to create a $H^+$ transport pathway, which also increases the water solubility of the complex, improves its catalytic rates, and reduces its overpotential. We used the carboxylic groups of the incorporated amino acid residues as anchoring groups to covalently attach the catalyst to the electrode[3] using a method we developed earlier for hydrogenases (Adamska, A. *et al. Angew. Chem., Int. Ed.* 2012). The immobilized catalyst displays very similar activity as the catalyst measured in solution, with a slight increase of the turnover frequency at the same overpotential. We compared the performance of these immobilized catalysts with the [NiFe] hydrogenase from *Dv*MF, measured under exactly the same experimental conditions (Figure 7, W. Lubitz report).[3] While at higher pH values the enzyme shows higher activity, at low pH and in the presence of CO, a known inhibitor of the hydrogenase, the synthetic catalyst is much more active. We used the same strategy to immobilize a water insoluble catalyst and we could confirm that it performs reversible catalysis in aqueous solutions (Figure 2). Furthermore, when this class of materials were immobilized on carbon nanotubes we could measure high catalytic currents and enhanced stability.[4] This makes these catalysts ideal candidates for fuel cells using inexpensive low purity $H_2$. We also reported a decrease in the catalytic current during catalysis, something that was not observed with the catalyst in solution. Using surface enhanced infrared absorption spectroscopy (SEIRA), we demonstrated that the amide bond between catalyst and enzyme is stable during the whole measurement, which confirms that the catalyst is still attached to the electrode[3], and the lack of stability is an inherent property of the catalyst. We are currently conducting experiments in collaboration with the group of Prof. Schlögl to further characterize the nature of the catalyst inactivation, and to examine the molecular nature of the catalytically active species, using *in situ* measurements combining electrochemistry with XAS measured under turnover conditions.

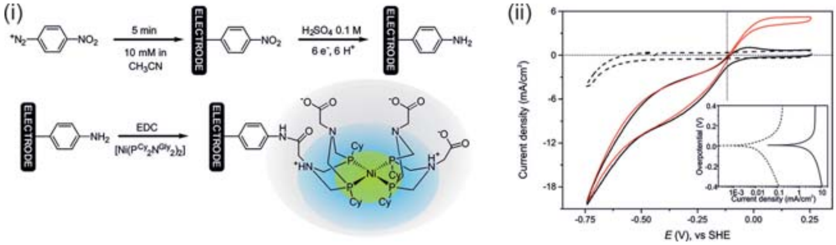

**Figure 2.** **(i)** Idealized schematic representation of the covalent immobilization of the $[Ni(P^{Cy}{}_2N^{Gly}{}_2)_2]^{2+}$ catalyst on a carbon electrode. The colors represent the first and second coordination sphere of the catalyst (green and blue respectively) and the outer coordination sphere where the amino acid residues are placed, in this case a glycine (grey).
**(ii)** Cyclic voltammograms (CV) of pyrolytic graphite electrode (PGE) coated with multi-walled carbon nanotubes (MWCNT) where no catalyst was attached (black dashed line) and an PGE electrode coated with MWCNTs to which $[Ni(P^{Cy}{}_2N^{Gly}{}_2)_2]^{2+}$ catalyst was covalently attached under 1 bar $N_2$ (black solid line) and under 1 bar $H_2$ (red solid line). The vertical dotted line indicates the $H_2/2H^+$ thermodynamic potential and the horizontal dotted line indicates the zero current. The inserted graph shows a Tafel plot comparing a flat HOPGe electrode (dotted trace) with the MWCNT electrode (solid trace).

Continuing this approach, we are currently working on the protection of these bio-inspired catalysts using polymer matrices. For these catalysts we took advantage of the ability of the catalyst to reduce $O_2$ to $H_2O$ (Yang, Y.Y. *et al. Dalton Trans.* 2009) to protect the catalyst. We have seen that in order to maintain $O_2$ reduction activity, it is important that the catalyst does not perform electrocatalysis, since only the $H_2$ reduced Ni(0) complex is capable of reducing $O_2$. This is only possible if the catalyst is not in direct contact with the electrode surface. To this end we used a non-conductive polymer to support the catalyst and obtain a layered polymer containing two discrete phases: (i) a phase close to the electrode surface where the catalyst can directly exchange electrons with the carbon electrode. This layer is responsible for the $H_2$ oxidation catalysis. (ii) a solvent exposed phase, where the catalyst cannot exchange electrons with the electrode, but can be reduced by $H_2$ and thus constitutes the protection layer (Figure 1). This type of electrode shows enhanced stability for the $H_2$ oxidation currents, but more importantly it avoids $O_2$ damage during catalysis (Figure 1).

## EPR Spectroelectrochemistry

In collaboration with the groups of N. Cox and A. Savitsky, we have designed an EPR spectroelectrochemical cell to study catalysts immobilized on electrode surfaces. The system can be applied to the study of enzymes in redox hydrogels or heterogeneous materials immobilized on the electrode surface. The Nocera CoPi catalyst (Kanaan *et al. Science,* 2008) has been used as a model system, since this self-healing inexpensive material has been proposed as a good candidate for larger scale water oxidation catalysis.

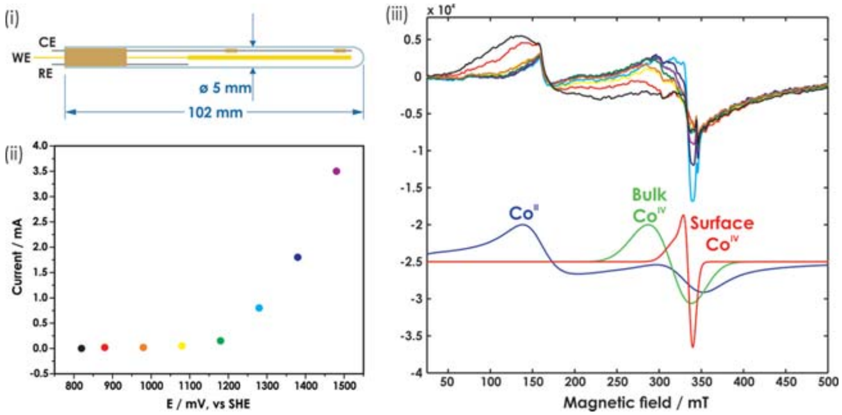

**Figure 3.** (i) Schematic representation of spectroelectrochemical cell for X-band EPR. A Pt wire is used as counter electrode (CE), Ag wire coated with a AgCl layer is used as quasi-reference electrode (RE) and a gold plate acts as working electrode (WE). The catalyst is deposited on top of this gold plate. (ii) Currents vs potential plots showing at which potential each EPR spectrum was measured. (iii) Top, CW X-band EPR spectra measured at different applied potentials (same color scheme used for current vs potential plot). Bottom, spin Hamiltonian simulations of the three Co species identified during catalysis: blue – precursor $Co^{II}$ state; green - bulk $Co^{IV}$ state, red – surface $Co^{IV}$ state, the catalytically active species.

Additionally, ex-situ EPR measurements have already been reported providing benchmark data (McAlpin *et al. J. Am. Chem. Soc.* 2010). Our measurements confirm that the film becomes oxidized from Co(II) to Co(IV), but more interestingly, at the potentials where catalytic $H_2O$ oxidation starts, a new Co(IV) signal appears, disappearing at higher potentials, probably due to the formation of EPR silent species ($Co^{V}=O/Co^{IV}-O^{\bullet}$). The EPR spectrum of this new signal is similar to that of molecular $Co^{IV}$ corrole models (Harmer *et al. J. Phys. Chem. B,* 2002). Using pulse EPR and theory we are analyzing the nature of this signal and its possible implications in the water oxidation catalytic mechanism.

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## Structure, Dynamics and Reactivity of Catalytic Reactions Studied by EPR

During the past two decades, EPR spectroscopy has become an increasingly valuable technique for the investigation of biological and chemical systems because of significantly improved detection sensitivity and spectral as well as time resolution.

(1) The research of our group is focused on methodological and instrumental developments and improvements of new EPR techniques.
(2) The application of these new EPR techniques is geared to a number of topics including:
(2.1) natural energy converting nanostructures;
(2.2) heterogeneous and homogeneous catalysis;
(2.3) structure, dynamics and solvation of molecular systems.

### 1 Methodological and instrumental development of advanced multifrequency multiresonance EPR spectroscopy

Advanced EPR methodologies allow for a detailed characterisation of the electronic structure and the microenvironment of paramagnetic systems. We are currently developing high-field ELDOR-detected NMR (EDNMR) and dipolar high-field EPR methods. In the last two years extensive efforts were undertaken (in cooperation with AG Cox, MPI CEC) to establish the EDNMR method as an alternative for classical ENDOR (electron-nuclear double resonance) [1-3]. EDNMR is well-suited for investigations of materials with fast magnetic relaxation, such as transition metal ions with future applications for heterogeneous metal oxide catalysis. 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 for the determination of structural constrains within (bio)macromolecules. The development of the methodology for spin labels based on $Gd^{3+}$ and $Mn^{2+}$ is in the focus of our research [4; 5] (in cooperation with AG Jeschke, ETH Zürich and AG Godt, Uni Bielefeld).

The new EPR methods require increased stability, sensitivity, resolution and bandwidth. To this end we are developing microwave bridges and EPR probeheads including modification of commercial spectrometers and/or home-built EPR equipment. For instance, a Q-band accessory for a commercial X-band pulsed EPR spectrometer (Bruker Elexsys II 580) was developed, which delivers 10 W microwave power. It is dedicated to Q-band EDNMR experiments in conjunction with an AWG (Arbitrary Waveform Generator). The construction of a new generation W-band microwave bridge, which would allow for CW and pulse AWG-based EPR experiments with 2 W microwave power, is in progress.

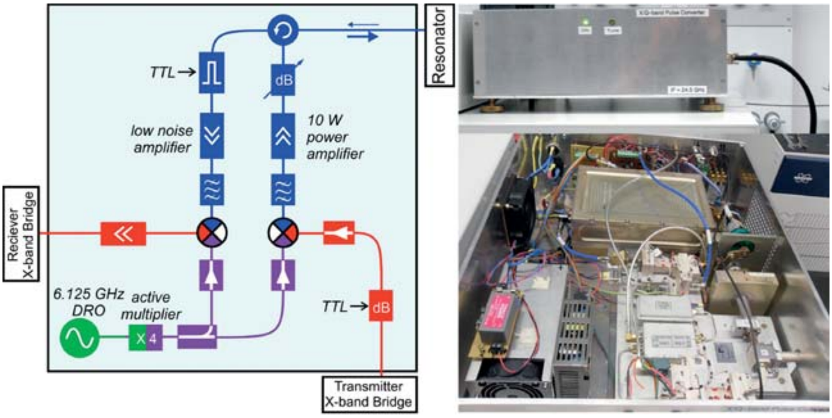

**Figure 1.** Block diagram and photographs of X-band (9.5 GHz) to Q-band (34 GHz) pulsed microwave converter. The key features are: 10 W output microwave power; 4 dB detection noise figure.

## 2 Applications

### 2.1 Investigations of natural energy converting nanostructures

The main goal of the project is to elucidate the complex physical interactions between nanoscale protein particles and liquid solvents or amorphous matrices, together with an investigation of the molecular regulation mechanisms of electron and proton transfer processes. Energy-transducing photosynthetic systems, such as bacterial reaction centers (bRC) and photosystems I and II (PS I, PS II), represent very important models for such studies. Physical and photochemical processes in these complexes - light absorption, energy migration, electron and proton transfer, generation of a transmembrane electric potential difference, and synthesis of high-energy compounds - occur over a wide time-scale, ranging from tens of femtoseconds to tens of seconds. An important practical goal of the project is the elucidation of the cryoprotective and stabilizing effects of disaccharides on electron and proton transfer processes in photosynthetic complexes at various levels of humidity, temperature and pressure. The analytical methods are femtosecond and nanosecond laser spectroscopy, fluorometry, calorimetry, potentiometry, cw and time-resolved EPR spectroscopy at high magnetic fields and external pressure, pulse absorption spectrometry, as well as methods of statistical physics and molecular dynamics. In the last years significant progress was achieved concerning (i) the structural and dynamical characterization of disaccharide matrices [6; 7]; (ii) the influence of matrix properties on bRC [8] and (iii) on PS I [9; 10].

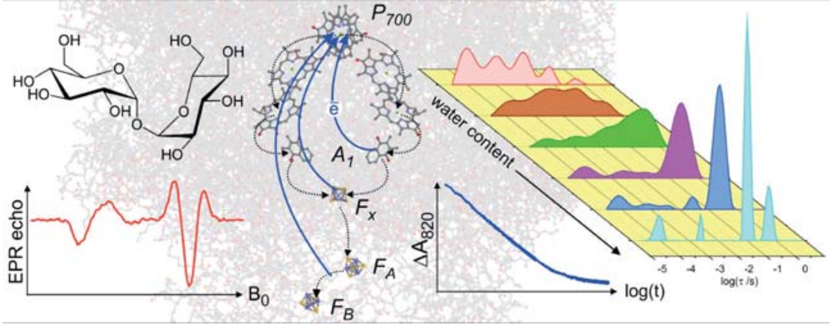

**Figure 2.** High-field EPR and optical investigations of trehalose matrix effects on charge-recombination kinetics in Photosystem I of oxygenic photosynthesis at different dehydration levels. For details see [9].

## 2.2 Heterogeneous and homogeneous catalytic systems

The active site of the water-splitting complex in PS II and other metallo-enzymes inspired the design of many inorganic catalytic materials performing small molecule reactions. Potentially, paramagnetic intermediates in these materials can be studied using advanced EPR techniques. They provide key information on the oxidation states as well as the electronic structure of the various sites in the material and their interaction with the substrate. Since heterogeneous catalytic materials are less well defined than the active sites in metallo-proteins it is important to study the material directly "in-operando" under different (catalytic) conditions, i.e., temperature, pressure, light illumination etc., in order to extract as much information as possible and to identify the species that are actually active in the catalytic processes. For many "in-operando" experiments it is necessary to trap the species of interest in the catalytic processes since advanced EPR studies are typically performed at cryogenic temperatures. The established cooperation projects (e.g., (i) CuO-Ce$O_2$ catalyst for gas oxidation catalysis, AG Schüth, MPI-KoFo; (ii) surface doped Ti$O_2$ catalyst for photocatalysis, AG Strunk, MPI-CEC, AG Tüysüz MPI-KoFo; (iii) functionalized carbon nanotubes for MnO electrocatalysis; AG Becker, MPI-CEC) have made clear that specific EPR techniques and instrumentation are needed for the investigation of heterogeneous catalytic materials and processes.

In the most developed project we aimed at understanding the redox properties of the $CuO$-$CeO_2$ catalyst for preferential CO oxidation (PROX). *In situ* EPR spectroscopy, combined with on-line gas analysis, X-ray photoelectron spectroscopy, X-ray diffraction, temporal analysis of products (TAP) reactor studies, and mass spectrometry, were utilized to study the redox behavior of $CuO$-$CeO_2$ catalysts under PROX conditions (preferential oxidation of carbon monoxide in hydrogen). From these measurements a *synergetic mechanism*, involving the redox pair $Ce^{4+}/Ce^{3+}$ during oxidation of $Cu^0/Cu^+$ species to $Cu^{2+}$, and a *direct mechanism* that bypasses the redox pair $Ce^{4+}/Ce^{3+}$ could be distinguished [11].

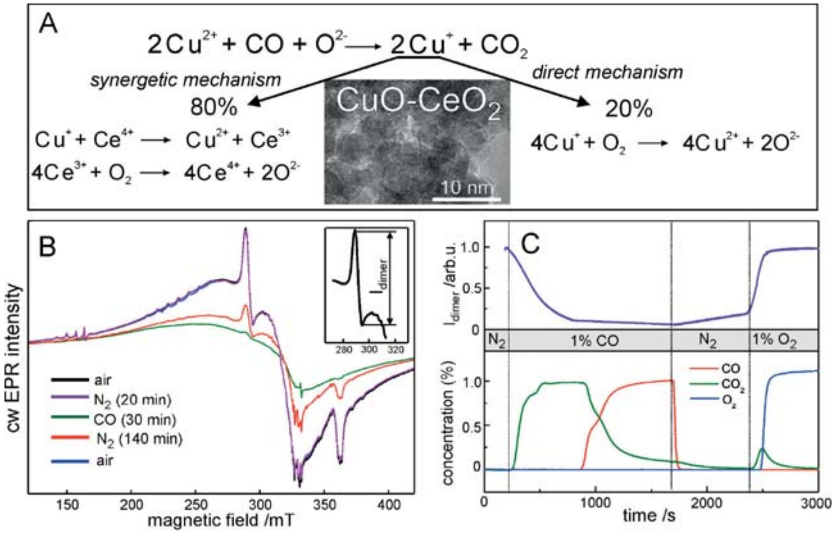

**Figure 3 (A)** Reaction scheme demonstrating the elucidation of synergetic and direct CO oxidation mechanisms on the $CuO$-$CeO_2$ catalyst. **(B)** X-band cw EPR spectra of 20 wt% $CuO$-$CeO_2$ recorded at 453 K during treatment with air/$N_2$/CO/$N_2$/air. The durations of the particular gas treatments are indicated. The insert shows the dimer EPR signal used for kinetic measurements. **(C)** Upper trace: Time dependence of the $Cu^{2+}$ dimer EPR signal intensity at 289 mT during the $N_2$/CO/$N_2$/air cycle at 453 K. Lower traces: Corresponding CO, $CO_2$ and $O_2$ concentration simultaneously recorded by the gas analysis system. For more details see [11].

We are also working on the development of EPR nitroxide spin-probe methods to obtain information about the efficiency of halogen-bond donors and their modulation by solute-solvent interactions [12]. This information is particularly important for improving the *multidentate* halogen-bond donors' design for organic synthesis and homogeneous organo-catalysis, e.g., for the activation of electrophiles (cooperation with AG S. Huber, University of Bochum, within the Cluster of Excellence RESOLV).

### 2.3 Structure, dynamics and solvation

We are applying well established nitroxide spin-probe and site-directed-spin-labeling (SDSL) methods to probe the structure and dynamics of macromolecular complexes of biological relevance. Spin-probe methods are being applied to investigate (i) changes in the microenvironment of nitroxide radicals around the glass transition temperature [13]; (ii) hydrogen bonding of nitroxide spin labels in membrane proteins [14]; and (iii) structural organization of heterogeneous disaccharide matrices [6; 7]. In October 2015, the PhD thesis titled "Multifrequency and multiresonance EPR techniques applied to nitroxide radicals and nitroxide-labeled systems" was successfully defended by Dr. A. Nalepa, a member of the group. She is also involved in a German-Israeli DIP cooperation project with Prof. I. Willner, Hebrew Univ. Jerusalem, on EPR investigations of conformational changes of DNA nanomachines.

We are studying the influence of the solvation on structure and reactivity of triplet ground state carbenes (cooperation with AG W. Sander, University of Bochum, within the Cluster of Excellence RESOLV). Carbenes possess two nonbonding electrons that 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 and the control of carbene spin multiplicity [15]. Additionally, high-field EPR was applied for the investigation of high-spin nitrenes with large spin-orbit contribution to the zero-field splitting [16; 17].

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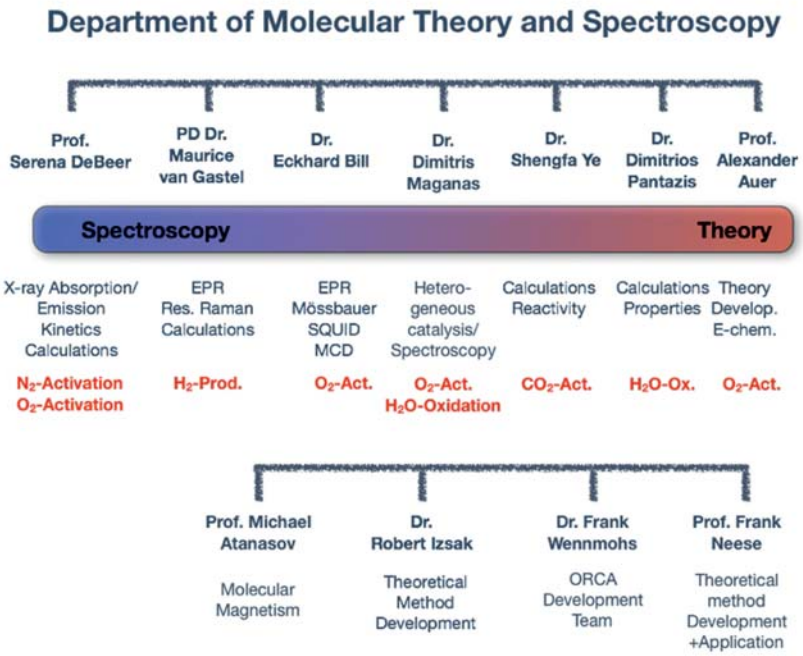
## Department of Molecular Theory and Spectroscopy

### Structure of the department

The department of molecular theory and spectroscopy headed by Prof. Neese was initiated in 2011 and has now been firmly established at the MPI-CEC. The department currently consists of 8 group leaders, 2 project leaders, around 4-6 Ph.D. and Masters students, around 30 postdoctoral researchers as well as around 10 technicians and staff members together with a variable number of guests on internships or scientific exchange visits. The core of our activities can be seen from the chart that summarizes the scientific activities of the group and project leaders in the department.

The group is engaged in a very wide variety of activities ranging from chemical synthesis (collaboration with service group Weyhermüller), advanced experimental spectroscopy (DeBeer, Bill, van Gastel, Manganas), computational chemistry (De Beer, Pantazis, Ye, Auer, Atanasov, Manganas) to theoretical method development (Izsak, Auer, Manganas, Neese). All activities are tightly integrated and there is a vivid exchange between all group and project leaders as witnessed by a weekly group leader meeting and a variety of regular joint seminars (reactivity seminar, magnetism seminar, developer's meeting). Likewise, the members of the department are engaged in a large number of in-house collaborations with the departments of Prof. Schlögl and Prof. Lubitz as well as outside collaborations and third party funded programs on the national and European level as described below.



Prof. Neese is involved in all of the department's activities and personally supervises the Ph.D. students and postdocs who focus on theoretical method development and that are not part of Prof. Auer's and Dr. Izsak's groups. Dr. Wennmohs and the ORCA development orchestrate the technical aspects of the ORCA development efforts and make invaluable contributions in ensuring that the code features state of the art performance is highly users friendly and is as bug-free as possible. The development of ORCA during the evaluation period is described in section "MPI CEC in Scientific Dialogue" of this report.

The department has declared the goal to contribute to the understanding of a number of fundamental chemical reactions that are central to energy research:

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

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.

The individual group and project leaders each focus on one or several of these reactions with the goal to establish the fundamental mechanisms and, importantly, obtain insight into the parallels and differences of homogeneous, heterogeneous and biological systems.

Furthermore, the department is fully committed to further the advancement of fundamental science and technology. It contributes to these areas through its activities in theoretical method development and in the field of molecular magnetism that has been a stronghold of our activities over the past several decades and has enjoyed significant success over the evaluation period.

## Publications and Scientific Highlights

Over the evaluation period (spring 2014 to October 2016), the department has published well over 200 peer-reviewed papers in international journals including a Science paper on the structure and mechanism of the oxygen evolving complex (jointly with Prof. Lubitz), four Nature papers on molecular magnetism, six Angewandte Chemie, nineteen Journal of the American Chemical Society, nine Chemical Science papers as well as over twenty papers in method development oriented journals (Journal of Chemical Physics, Journal of Chemical Theory and Computation). See "List of Publications"in this report.

As scientific highlights, the following studies are mentioned:

1) The *Science* paper[1] describing our studies on the S3 state of the oxygen evolving complex, jointly done between the group of Dr. Pantazis with the department of Prof. Lubitz, clarified many of the open questions about the structure and mechanism of the photosynthetic oxygen evolving complex. Furthermore, a careful theoretical study published in *Chemical Science* has laid rest to the decades-old question of the correct oxidation state assignment of the OEC and demonstrated that only the 'high-oxidation' state scheme is consistent with experiment.[2] The unique combination of theory and spectroscopy that has characterized our studies has been internationally recognized to make important contributions to the very fundamental understanding of how nature oxidizes water. It is probably

fair to say that a detailed consensus picture is about to emerge in the photosystem community that features important contributions from the MPI-CEC.[3, 4] These studies are being now extended into the realm of surfaces and solids.

2) The group of Dr. Manganas together with the department of Prof. Schlögl, we have demonstrated that the theoretical spectroscopy oriented approach to study catalytic intermediates is equally applicable to the field of heterogeneous catalysis.[5] The system of choice consisted of industrially highly relevant vanadium oxide catalysts for which studies established the predominance of trimeric structures under maximally active conditions. Importantly, these studies can be performed using in-situ spectroscopy and under turnover conditions. We believe that this approach holds great promise. A conceptual paper summarizing our ideas was published in *Faraday Transactions*.[5]

3) The group of Prof. DeBeer has made important advances in the understanding of the active site of nitrogenase. Using a combination of advance X-ray spectroscopic techniques and quantum chemistry, it was demonstrated that the molybdenum center in the FeMoCo active site is in the oxidation state Mo(III), contrary to the conventional wisdom. The results lead to a reconsideration of the mechanisms of nitrogenase that is currently pursued. The results were published in *Chemical Science*.[6] Furthermore, pioneering studies on the geometric and electronic structure of vanadium containing nitrogenases were published.[7]

4) The studies of Profs. Atanasov and Neese, in collaboration with the group of Profs. Long in Berkeley and van Slageren in Stuttgart lead to discovery of mononuclear single molecule magnets with high blocking temperatures. These complexes are based on iron and cobalt. Our studies, published in *Nature*[8] and *Inorganic Chemistry*[9], lead to a detailed understanding of the mechanisms leading to magnetic blocking. Importantly, the ab initio ligand field theory, developed in 2012 allows us to connect high-level electronic structure calculations to chemical concepts.[10, 11] It also became apparent, that the classical theories of spin relaxation are insufficient and need to be extended to a proper quantum dynamics treatment. We are currently pursuing the molecular theory of spin relaxation together with our collaborator Prof. Marzlin.

5) The studies of Dr. Bill and Manganas on super-oxidized iron complexes (oxidation states Fe(V) and Fe(VI)), led to the discovery of the 'inverse' Haber-Bosch reaction in which the N-N bond of $N_2$ is formed from the reaction of a mononuclear Fe(V) nitride complexes with itself. These results have been published in *Angewandte Chemie*.[12]

6) An important JACS paper by the group of Prof. DeBeer demonstrates that current methods to predict EXAFS spectra from first-principles are insufficiently

accurate to draw any sound conclusions about the accuracy of assumed or predicted structures.[13] This was particularly important in the framework of the oxygen-evolving complex since theoretical EXAFS calculations have been repeatedly instrumentalized to argue in favor of computed structures.

7) The Nature Communications paper of Dr. van Gastel in collaboration with the department of Prof. Lubitz led to the identification of a hydride bridge in Nickel-Iron hydrogenases through a combination of nuclear resonant vibrational spectroscopy and quantum chemistry.[14]

8) Our theoretical method development efforts have progressed well. In particular, a linear scaling DLPNO-CCSD(T) method was developed that, for the first time, allows coupled cluster level calculations on systems with more than 1000 atoms and over 20000 basis functions.[15] These achievements were made possible by the careful analysis of truncation schemes that led to the development of a theory of 'Sparse Maps' and a 'Linked Index Rule'.[16] These concepts were implemented into a computer library and serve to develop linear scaling electronic structure theories more efficiently. These developments were described in an important conceptual paper that exemplifies the use of the SparseMap technology through the development of the highly efficient DLPNO-MP2 method. Further developments concern a linear scaling multireference perturbation theory (DLPNO-NEVPT2)[17], the DLPNO-CCSD density[18], first steps towards DLPNO based excited state methods[19] as well as the first local multireference coupled cluster theory LPNO-Mk-MRCC.[20] DLPNO methods have been carefully tested[21-25] are currently start to be embraced by the computational chemistry community and it is foreseeable that they will be used in large scale in the future. These methods are under intense development in our group.

Prof. Neese has changed his activities from being an associate editor of *Physical ChemistryChemicalPhysics* (until December 2014) to serving as an associate editor of the ACS journal *Inorganic Chemistry* (starting January 2015), where he is dominantly handling the physical and theoretical inorganic chemistry related submissions. Several group members serve on the advisory boards of international journals including, among others, the *Journal of Chemical Theory and Computation*, the *Journal of Biological Inorganic Chemistry* and *Faraday Transactions*.

### Talks

During the evaluation period, department members have been highly active as participants of international conferences around the world, invited speakers and plenary speakers. Altogether around 150 lectures were given including plenary (DeBeer) and keynote (Neese) lectures at ICBIC 17 (Beijing) and a number of named lectureships at US universities listed below.

## Instrumentation

Over the evaluation period department member have been actively involved in building and improving the available scientific instrumentation.

BESSY, in house spectrometer, Mößbauer spectrometer

During the 2014-2016 time frame, the DeBeer group has been actively leading the design and construction of the PINK beam line at the BESSY synchrotron in Berlin. The beam line will provide an intense source of X-rays in the 2-10 keV range enabling dispersive two-color X-ray emission (both resonant and non-resonant) for applications in chemical catalysis.

Funded by the ERC, the DeBeer group, in collaboration with the group of B. Kangießer (TU Berlin) has built an in-house X-ray emission spectrometer, which enables dispersive XES in the 3-9 keV range. The instrument is presently in a commissioning phase and the first research applications are planned for December 2016.

A two-dimensional Mössbauer and X-ray emission spectroscopy (Mb-XES) instrument is presently under construction at the MPI CEC. The instrument will use the intrinsically high resolution of the Mössbauer transition in order to select for a specific iron site within a mixture of species. Following the nuclear excitation in a Mössbauer experiment, decay occurs, via internal conversion resulting in the production of fluorescent photons, which give rise to an X-ray emission spectrum (XES). XES is intrinsically a bulk probe. However, by using the neV resolution of the Mössbauer excitation, unprecedented selectivity can be achieved – allowing for the sensitivity of Mössbauer to spin state and oxidation state to be coupled to the intrinsic sensitivity of valence XES to ligand ionization energies.

Computer components

In the period 2014 - 2016 the following computer components were purchased by the Neese group:

1. An HPC Compute Cluster with 30 Compute Nodes for calculations with high storage requirements and 53 Compute Nodes for medium storage requirements. The cluster contains a total of 182 CPUs and 1428 cores.

2. A server for calculations with very high storage requirements. It contains 4 CPUs and 64 cores and 3 TB RAM.

3. Two GPU servers with two NVIDIA and AMD GPUs each.

### Resonance Raman

The in-house Resonance Raman spectrometer, previously equipped with a $N_{2(l)}$ quartz finger dewar for performing experiments at cryogenic temperatures, has been improved by (1) installing a Cryostream cooling system and (2) using a parabolic mirror. The former eliminates the presence of gaseous $N_2$ bubbles in the optical path and eliminates two quartz transitions. Both lead to a reduction of noise and background by a factor of three, which is a direct result of a better image quality projected onto the CCD camera. The second improvement allows for a collection aperture of almost 180 degrees, eliminates spherical and chromatic aberration of the first collection optic and also allows a better adaptation to the numerical aperature of the monochromator system, resulting in an illumination of the CCD camera of about 90%. The spectrometer has also been equipped with an array of 7 new solid state lasers which allow quick startup-times of only several minutes. As such, the Raman spectrometer is now ideally with 7 fixed wavelengths and one tunable laser system for excitation profiles and optimized collimation optics. On the sample holder side, a room-temperature cell has been developed for *in-situ* spectro-electrochemical Raman experiments.

### Cryostats

**Closed-Cycle Magnet Cryostats in the Mössbauer and MCD Labs – Investments for the Future**

Powerful Mössbauer and MCD spectrometers require strong magnetic fields, for which until 2016 we used 7T and 10 T cryo-magnets cooled by liquid helium. Both instruments had been in regular and intense use since1995 and 1999, respectively, but sporadic failures due to wearing off at electrical and vacuum connectors, sealings and control electronics suggested major refurbishments or replacements in near future.

In this situation a foreseeable upcoming shortage of helium due to its extraction from natural gas, and even more the drastic variations in availability on the international markets and the increase in prices seen in recent years prompted us in 2016 to replace the cryo-magnets by cryogen-free closed cycle models. This was possible and reasonable because of a strong drop of prices in recent years, in conjunction with amazing new technical developments that in particular allow us to reach base temperatures well below 4.2 K without efforts. For both MCD and Mössbauer spectroscopies, such low temperatures ae essential for future research, but had not been available with closed-cycle system five years ago, and had been very costly and needed elaborate handling with liquid helium.

With the new cryogen-free magnet systems for 7T and 11 T fields we acquired two state-of-the-art instruments that

- significantly reduce the cost for consumables (liquid helium)
- make us independent of helium suppliers and fluctuations on the markets

- provide excellent experimental conditions, are stable, easy to operate at variable temperatures, and can work permanently at base temperatures of 1.7 K without cryogen-filling issues etc.

### External Funding

The members of the department have been highly active in securing third party funds. Currently, a total of 28 third party projects are either funded by various institutions and or for which proposals have been submitted. An average of 1.15 M€/year has been raised over the evaluation period with a tendency to increase over the next years. The funding includes large award grants (Leibniz award to Prof. Neese and ERC consolidator grant to Prof. DeBeer), European projects (NoNoMeCat - Non-Noble Metal Catalysis, COST actions - ECOSTBio, EUSpec), international collaborations funded by the DAAD (German-Czech Republic), the German Israeli foundation, or the French ANR/DFG binational program. Furthermore, the department is involved in various priority program (SPP 1601, "New frontiers in sensitivity for EPR spectroscopy: from biological cells to nano materials", SPP 1807 "Control of London Dispersion Interactions", SPP 1927 "Iron-Sulfur for Life"), The cluster of excellcence RESOLV at the university of Bochum, the large-scale BMBF project "Mangan" as well as the Max-Planck internal MAXNET Energy initiative. Two SFB initiatives involving department members are at the planning stage at the universities of Aachen, Duisburg-Essen together with two German-wide 'Forschergruppe' with the universities of Bielefeld and Bochum respectively.

These activities one hand secure that the structure of the department can be maintained despite steeply rising expenses for personnel and on the other hand, more importantly, help to establish the MPI-CEC as an important collaborator and a place of scientific excellence in the German and European research landscape.

### Teaching

The department members are committed to educating the next generation of scientists. To this end, department members are highly involved in teaching activities. Prof. DeBeer and Dr. van Gastel teach regular courses at the university of Bochum and Duisburg-Essen respectively.

The department has been instrumental in establishing the international Max Planck research school (IMPRS) Recharge in collaboration with the MPI Kofo and the universities of Bochum, Bonn and Duisburg/Essen. The IMPRS is described in detail in section "MPI CEC in Scientific Dialogue" of this report.

The summer school 'Molecular Methods in Energy Research' (MMER) is now firmly established and has continuously attracted more than 100 students from all over the world. In the past, the school has been dominantly taught by members of the department. This school is now part of the IMPRS Recharge and will involve all MPI-CEC members. In 2016, the school, for the first time, integrated concepts of homogeneous and heterogeneous catalysis.

Prof. Neese is an established staff member of the highly established European Summer School of Quantum Chemistry (ESQC, Sicily), which is held biannually for about 60 selected students. In 2016 a second theory oriented school was be established by Prof. Neese and Prof. Gauss (Mainz) with the title 'Wavefunction based ab initio quantum chemistry'. It will be the successor of the popular Sous-trup quantum chemistry school, which has ceased existence after its last edition in 2014. The school was highly successful and received excellent evaluations from the 65 students who took part in it.

Furthermore, during the evaluation period, Prof. Neese has taught at a number of additional schools including the winter school of molecular modeling (Stockholm), the FEBS advanced course on 'Metals in Biology' (Louvain-la-Neuve), the Summer School of the European Federation of EPR Spectroscopists (Berlin), the Summer School "Advanced Metal-Organic Chemistry and Catalysis" AMOCC 2014 (Deurne, The Netherlands) and the 3rd and 4th Penn State Bioinorganic Workshop, (Penn State, USA).

Finally, a number of lectures has been given by the members of the department that focus on various advanced spectroscopies and theoretical concepts. These internal lectures happen at irregular intervals upon request of group members or following the arrival of new group members.

### Awards and honours

Prof. DeBeer was awarded the highly prestigious 'early career award' of the international society of bioinorganic chemistry during the award ceremony at ICBIC 17 in Beijing. In addition she received the prestigious 'Inorganic Lectureship Award' with a ceremony and dedicated award symposium at the American Chemical Society meeting in Philadelphia 2016.

In the evaluation period, Prof. Neese was listed among the top 1% most highly cited scientists worldwide by Thomson-Reuters in 2015. Furthermore, he was invited to a number of honorable lectureships including the centennial lecture at the MPI Kofo, the 'Davidson lecture' at the university of Denton/Texas, the 'Moscowitz' memorial lecture at the university of Minnesota and the 'Coulson lecture' at the university of Athens, Georgia, the "The Roger E. Miller Lecturer" at the university of Waterloo, Canada. In addition he has served on the advisory board of the cluster of excellence 'UniCat', as the chair of the Hellmann award committee of the German Theoretical Chemistry Society, on the selection committee for the Liebig medal of the German Chemical Society, on the scientific advisory board of the Czech academy of Sciences in Prague and was elected to the advisory board of *Faraday Discussions*. Finally, Prof. Neese was elected as expert referee ('Fachgutachter') of the German Science Foundation for the field of Theoretical Chemistry 2016-2019.

### Guests and Visits

The department of molecular theory and spectroscopy has always welcomed guests, visitors and collaborators. In the evaluation period, we enjoyed hosting a number of prominent researchers.

Together with Prof. Marzlin, St Francis Xavier University, Antigonish, Nova Scotia, Canada, we pursue a new theory of spin relaxation that made excellent progress during two visits in spring and winter of 2015.

Our DAAD funded project with our Partners Prof. Pittner and Dr. Demel from Prague has already led to a remarkable publication on local multireference coupled cluster theory and will be continued in the future. A total of six visits took place.

Many of the department's collaborators stayed for visits at the institute including Celestino DeAngeli (Ferrara, Italy, NEVPT2 developments), Carol Duboc (Grenoble, France, EPR spectroscopy and manganese chemistry), Eric Glendening (Madson, USA, interfacing ORCA to NBO), Ed Valeev (Blacksburg, USA, explicitly correlated electronic structure theory), Ali Alavi (MPI Stuttgart, Full-CI quantum Monte-Carlo), Paul Bagus (Denton, USA, Core level spectroscopy calculations) and Gunnar Wernecke (Marburg, magnetic properties of linear transition metal complexes).

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## Project "Molecular Magnetism"

### I. Motivation

Molecular magnetism is a multidisciplinary field that combines synthesis of molecules with desired magnetic properties and theoretical analysis aiming at mechanistic understanding of the relation of these properties with the electronic structure. Spectacular advances in the development and implementation in the program ORCA of spin-dependent relativistic correlated electronic structure methods for large systems by Prof. Dr. Frank Neese and his developer team supplied the infrastructure and serves as a firm theoretical basis for this project. The combination of experiment and theory on a one-to-one basis allows to *both interpret and to predict* (rationally design) magnetic properties of target magnetic materials. Molecular magnetism has a big impact on closely related disciplines such as molecular electronics and chemical reactivity (homogeneous and heterogeneous catalysis). The latter has been inspired by the action of transition metal spin centers at the active sites in enzymes such as the spitting of water on a four nuclear mixed-valence manganese complex (Photosystem II) and oxygen and hydrogen atom transfer in heme and non-heme high-valence iron enzymes leading to molecules for energy storage. All this motivated the creation in 2013 of a group on molecular magnetism at the institute. Basic tools in the work on this project have been: i) computational protocols allowing to extract magnetic and spin-Hamiltonian (SH) parameters from ab intio correlated wavefunctions [1a], and ii) an ab initio based ligand field theory (AILFT) that allows to relate the magnetic parameters with the nature of the metal-ligand bonds and the complex geometries [1b].

## II. Molecular Magnetism

Open d- or f-shell transition metals or lanthanides and actinides in complexes give rise to an unique response to an external magnetic field governed by the preferred alignments of their magnetic moments. This property is termed magnetic anisotropy. In axial symmetry this anisotropy is described by one parameter $D$ which quantifies the zero-field splitting of the 2S+1 sublevels $M$ ($-S \leq M \leq S$ ) of the spin $S$ ($E=DM^2$) of the non-relativistic ground state. Magnetic anisotropy arises from coupling between orbital and spin angular momenta. Below a given temperature (called the blocking temperature, $T_B$) the resulting total angular momentum and its magnetization induced by an external magnetic field may persists after switching off the field. The specific life-time of this magnetic state, the relaxation time, depends on the magnitude of the orbital angular momentum and its coupling to its dissipative surrounding (thermal bath). Orbital momenta are maximal in atoms and ions with orbitally degenerate ground states, such as $Fe^{I}$ $^4F(d^7)$ or $Fe^{II}$ $^2D(d^6)$. However, because of their spherical symmetry, such orbital moments are isotropic. Anisotropic magnetic moments are intrinsic for molecules possessing axial (four of threefold) symmetries, which in addition, are in orbitally degenerate or nearly-denerate ground states. Spin-orbit coupling introduces atomic like orbital moments which couple with the spin and this leads to an entirely anisotropic magnetization (Ising anisotropy). This magnetization is maximal along the axis of quantization (the easy axis, $D<0$) and (in weak magnetic fields) very small in directions perpendicular to it.

During the period 2014-2016 our work focused mainly on the following three topics:

### III.1 Electronic structure and magnetism of 3d-complexes with linear $ML_2$ cores.

$Fe^{II}(d^6)$ and $Fe^{I}(d^7)$ complexes with linear $FeC_2$ cores (C= the mono anionic $[C(SiMe_3)_3]^-$ ligand) are in $^5E$ and $^4E$ orbitally degenerate ground states (Fig. 1) that give rise to $M_J=M_S+M_L$ spin-orbit coupled ground state magnetic sublevels $M_J=\pm4$ and $\pm7/2$, respectively. In a fruitful collaboration with the group J.R. Long (Berkely, USA) slow relaxation of the magnetization in an applied magnetic field of six complexes of $Fe^{II}(d^6)$ were reported and rationalized in terms of first principles complete active space self-consistent field (CASSCF) calculation in which dynamical electronic correlation was taken into account. [2a-b] More specifically, it was shown, that rigid and bulky ligand scaffolds of the reported complexes suppress vibronic coupling, which tends to quench the orbital moment, thus maximizing the orbital contributions to the S=2 spin. Expanding on the analysis of this series electrochemical reduction of $[Fe^{II}C_2]$ has led to an analogous $[Fe^{I}C_2]^{1-}$ complex. [2c] Large $d_{z2}$-4s mixing and non-Aufbau orbital occupation lead to $^4E$ ground state (Fig.1). Alternating current magnetic susceptibility measurements reveal slow magnetic relaxation below 29K in zero applied direct current field.

The S=3/2 complex was shown to exhibit an effective reversal barrier of $U_{eff}$=226(4) $cm^{-1}$ and magnetic blocking below 4.5 K. Within the same theoretical framework, metal-ligand interactions of a series of linear M(I) ($M^{I}$=$Cr^{I}$,$Fe^{I}$,$Co^{I}$) complexes with a nitrogen donor ligands have been characterized [2d].

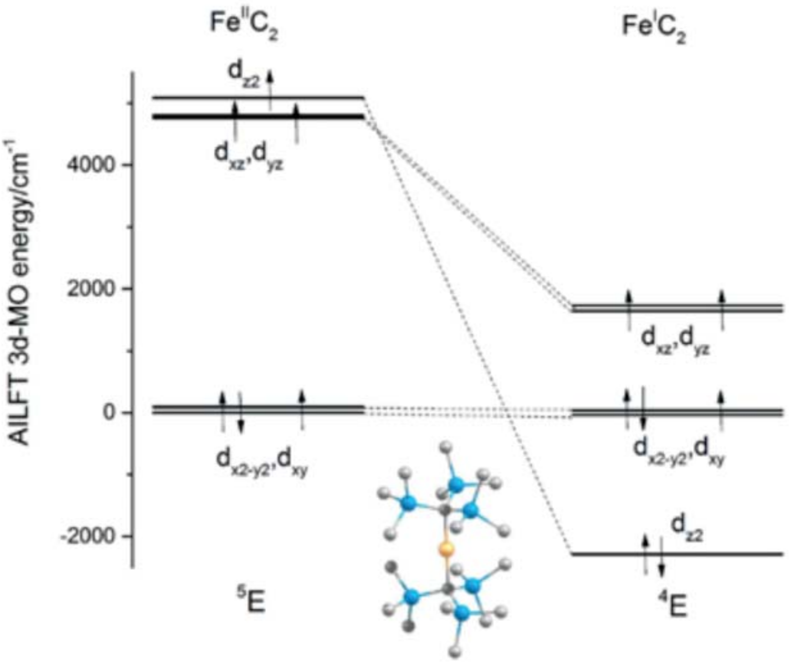

**Figure 1.** Ground state electronic configurations and ground states of $Fe^{II}$ and $Fe^{I}$ complexes with linear $FeC_2$ cores and the mono-anionic ligand $[C(SiMe_3)_3]^-$; orbital energies result from the AILFT effective Hamiltonian with ligand field parameters from a least squares fit to CASSCF/NEVPT2 many-electron matrix elements; structures of the two-coordinate Fe(II) and Fe(I) complexes are schematically shown; orange, cyan and grey spheres represent Fe, Si and C atoms, respectively; H-atoms have been omitted for the sake of clarity.

## III.2 Magneto-Structural Correlations in Pseudo-tetrahedral $Co^{II}$ Complexes [3c].

Cobalt(II) tetra-thiolate $[Co(SPh)_4]^{2-}$ was reported as a first example of a mononuclear SMM that shows a slow relaxation of the magnetization in the absence of an external magnetic field. [3a] Substitution of the donor ligand atom by oxygen or selenium dramatically changes the ZFS and the relaxation time. The series of complexes $(PPh_4)_2[Co(XPh)_4]$ (X=O, S, Se) [3b] have been studied using multireference ab initio methods with the goal of exploring the effect of the tetragonal elongation $T_d \rightarrow D_{2d}$, described the angle $2\theta<109.47^{\circ}$, and the torsion angle $\psi$ describing the change of symmetry from $D_{2d}$ ($\psi=0^{\circ}$, all-vertical configuration) toward various degrees of $S_4$ distortions ($\psi=90^{\circ}$,, ultimately all-horizontal configuration), the latter being imposed by the second coordination sphere by the C atoms directly connected to X Fig. 2). Magnetostructural correlations are then deduced that take into account the nature of metal-ligand covalent bonding, ligand spin-orbit coupling and the geometric distortions just described. The absolute value of the zero-field splitting D increases when the ligand field strength decreases across the series from oxygen to telurium. The zero-field splitting (ZFS) of the ground state of the hypo-thetical $[Co(TePh)_4]^{2-}$ complex has been computed to be about twice as large as for the well-known $(PPh_4)_2[Co(SPh)_4]$ compound. It is shown that magneto-structural correlations in $[Co(OPh)_4]^{2-}$ type complexes differ from $[Co(S/SePh)_4]^{2-}$ due to the π-anisotropy of the ligand donor atoms (S, Se). In the case of almost isotropic OPh ligand only variations in the first coordination sphere affect magnetic properties, but in the case of S/SePh ligand variations in the first and second coordination sphere become equally important for the magnetic properties.

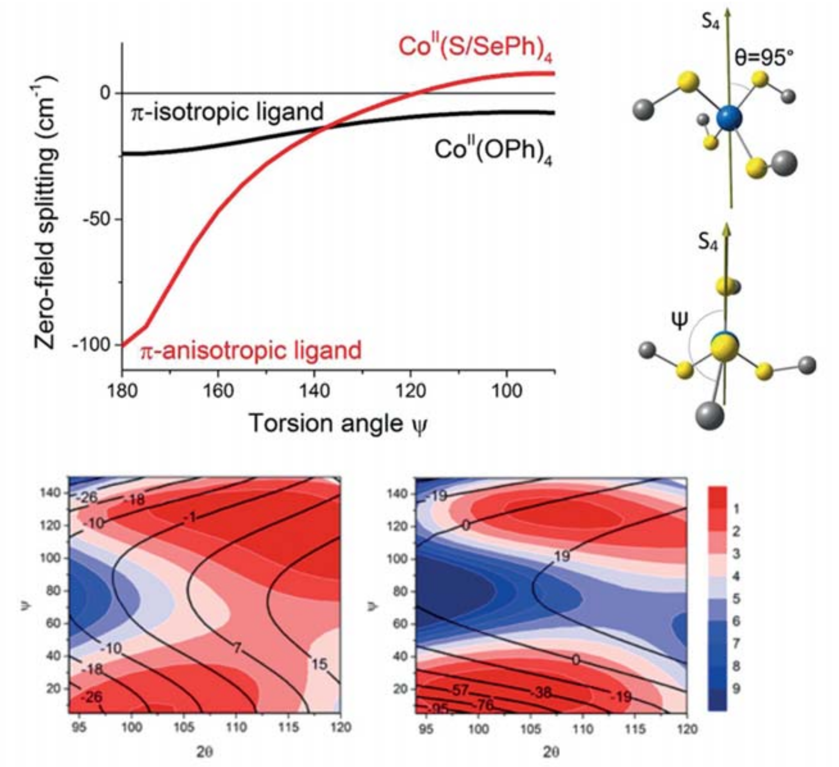

**Figure 2.** The first and the second coordination sphere of Co ion along with the two angles θ and ψ defining the lowering of symmetry from $T_d$ to $D_{2d}$ and $S_4$(top, right); interplay between Co-X π-antibonding and ψ and their effect on D (top left) and two-dimensional relaxed surface scan (shown in colors according to color code on the right in kcal/mol) and the corresponding values of the zero-filed splitting (black contour lines in $cm^{-1}$) of the $[Co(OMe)_4]^{2-}$ (left) and $[Co(SeMe)_4]^{-2}$ (right) complexes (adopted from Ref. 3c ).

Along the same lines we have analyzed the electronic structure of a new magnetically bi stable mononuclear tetragonally elongated tetrahedral cobalt(II) complex $(HNEt_3)_2[Co^{II}(L^{2-})_2]$ with nitrogen donors (Fig. 3) [3d]. The two very acute axial NCoN chelate angles along with the strong ligand field induce a large $t_2$ splitting and leads to a lowest $^4B_2$ excited states which is only 500 $cm^{-1}$ above the ground state and thus comparable with spin-orbit coupling parameter $\zeta$. The large mixing of these states via spin-orbit coupling leads to easy axis anisotropy and an unusually large D parameter (-115 $cm^{-1}$). It explains the observed magnetic bi stability manifesting in an open hysteresis loop (coercitivity) in the magnetization at a sweep rate dB/dt=3.0T/min.[3d]

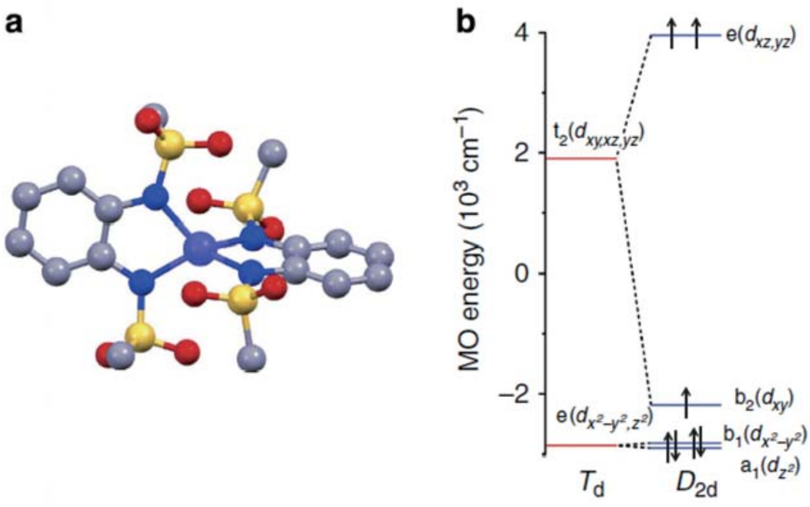

**Figure 3.** Molecular and electronic structure of the complex $[Co^{II}(L^{2-})_2]$: a)Crystallographic structure, Cobalt, Oxygen, Sulfur, Nitrogen and Carbon are shown in blue, red, yellow, violet and grey, respectively, Hydrogen atoms are omitted for clarity. b) Molecular obital diagram from CASSCF/NEVPT2 AILFT analysis of CAS(7,5) wave functions; horizontal lines depict orbital energies while arrows pointing up or down stand for single electron spins; the given configuration pertains to the $^4B_1$ ground state which mixes with the lowest excited $^4B_2$ state via the $L_zS_z$ part of the spin-orbit coupling operator (adopted from Ref. 3d).

From these studies design principles toward novel SMM with improved magnetic anisotropies emerge as follows: magnetic bi stability in tetrahedral Co(II) complexes is enforced by:

i) Soft ligands inducing week ligand fields along with a tetragonally elongated complex ($D_{2d}$) geometry.
ii) Chelate ligands with strong donor ligands (such as N) imposing very acute NCoN trans chelate angles that afford large $D_{2d}$ $^4B_2$<$^4E$ splitting of the $^4T_2$ excited state and, via SOC mixing of $^4B_2$ with the ground state $^4B_1$ highly anisotropic magnetic moments.

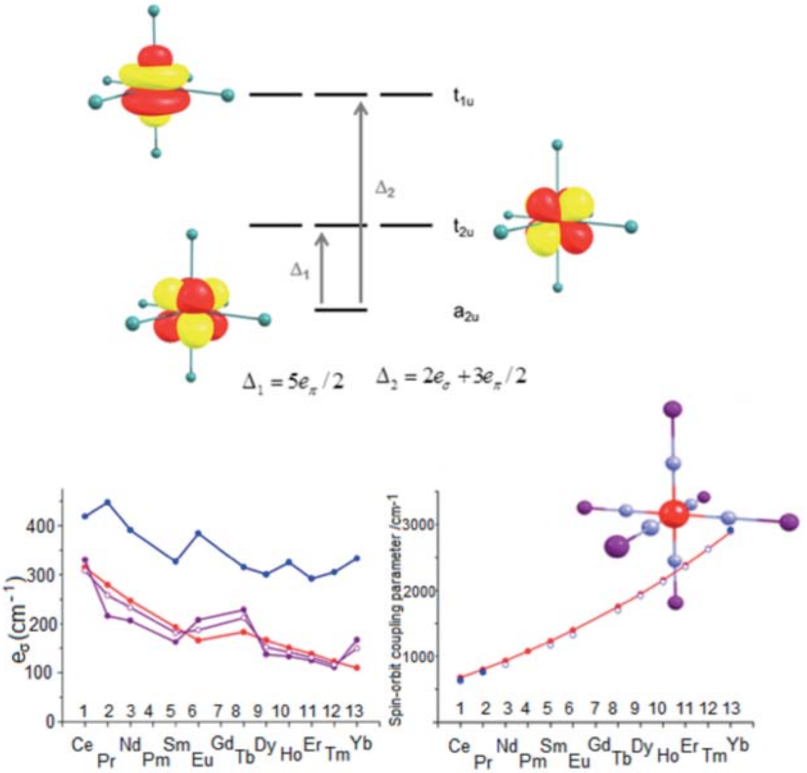

**Figure 4.** Splitting of f-orbitals in octahedral ligand field (top); Experimental (blue) and calculated (CASSCF:red, NEVPT2: purple) $\sigma$-antibonding parameters for $LnCl_6$(bottom left); $\pi$-antibonding (not shown) displays a similar trend; ab initio spin-orbit coupling parameter $\zeta$ for lanthanide ions: available experimental data from free ions (blue filled circles) and for the $Cs_2NaLn^{III}Cl_6$ series (blue open circles), bottom right; the electron occupation of the f-shell is shown above the abscissa.

### III. Complexes of lanthanides [4].

Periodic trends on structural and spectroscopic properties of complexes of lanthanides have been examined through complete active space self-consistent field (CASSCF) followed by second order N-electron valence perturbation theory (NEVPT2) calculations including both scalar relativistic and spin-orbit coupling effects [Fig. 4]. Energies and wave functions from electronic structure calculations are further analyzed in terms of *ab initio* Ligand Field theory (AILFT), which allows one to rigorously extract angular overlap model (AOM) ligand field, Racah and spin orbit coupling parameters directly from high-level *ab initio* calculations. We investigated the elpasolite $Cs_2NaLn^{III}Cl_6$ ($Ln^{III}$=Ce-Nd, Sm-Eu, Tb-Yb) crystals because these compounds have been synthesized for most $Ln^{III}$ ions. $Cs_2NaLn^{III}Cl_6$ elpasolites have been also thoroughly characterized with respect to their spectroscopic properties, providing an exceptionally vast and systematic experimental database allowing one to analyze the periodic trends across the lanthanide series.

Particular attention has been devoted to the apparent discrepancy in metal-ligand covalency trends between theory and spectroscopy described in the literature. Consistent with earlier studies, natural population analysis indicates an increase in covalency along the series, while a decrease in both the nephelauxetic (Racah) and relativistic nephelauxetic (Spin-orbit coupling) reduction with increasing atomic number is calculated. These apparently conflicting results are discussed on the basis of AILFT parameters. The AILFT derived parameters faithfully reproduce the underlying multireference electronic structure calculations. The remaining discrepancies with respect to experimentally derived data are mostly due to underestimation of the ligand field splittings, while the dynamic correlation and nephelauxetic effects appears to be adequately covered by CASSCF/NEVPT2.

Achievements of our work on this project (3d elements) have been documented in recent review, Ref. [5a] as well in joint publications with other groups reflecting internal and external collaborations within the field (Refs [5b-g]).

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## Theoretical Methods and Heterogeneous Reactions

Work in our group covers a broad range from development of novel approximations and algorithms to applications of electronic structure methods to problems in catalysis and materials science. In method development, the focus lies on novel approaches to represent the wavefunction. This can be explored to reduce the steep scaling of electron correlation methods with the number of electrons.

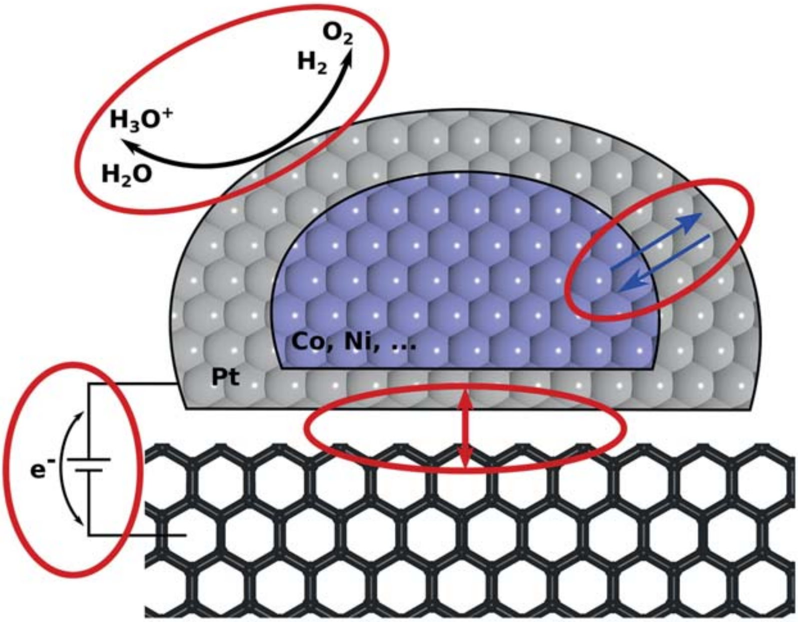
Applications are aimed at a fundamental understanding of electrocatalysis on the basis of cluster calculations with implicit inclusion of solvent and explicit inclusion of the electrochemical potential. Research in materials science originates from a very fruitful cooperation with the TU Chemnitz, where our group is involved in a DFG Forschergruppe on Twin Polymerization for the synthesis of nanocomposites and a joined SPP project on heavy main group elements as dispersion energy donors with the group of M. Mehring.

### Tensor Decomposition Techniques for Full Configuration Interaction (FCI)

Our group has been active in the development of approximations based on tensor decomposition. In previous projects, the canonical product (CP) tensor format has been explored to reduce the computational requirements for perturbation theory and the coupled cluster hierarchy of methods [1]. Novel work focuses on applying similar techniques for the numerical solution of the electronic n-particle Schrödinger equation [2]. For this purpose, a CP representation of the n-electron wavefunction has been adapted that has been developed in the field of applied mathematics. From this, a tensor representation of the Fock space follows, that is characterized by tensor representations of the Hamiltonian and the wavefunction parameters. It can be shown that storing the Hamiltonian and its Eigenvectors scales only as $N^5$ (N beeing the number of orbitals) in comparison to the exponential scaling for conventional FCI. However, solution of the FCI problem still exhibits a steep scaling with the number of orbitals due to demanding tensor representation reductions. As a consequence, finding better solutions for this step is now the primary goal for the ongoing cooperation with scientists from applied mathematics (M. Espig, RWTH Aachen) [3].

### Density Functional Theory algorithms with explicit inclusion of the electrochemical potential

In recent years, the group has build up expertise in atomistic calculations of nanoparticles in electrocatalysis. This includes studies on Pt and Pt alloy nanoparticles as well as intermediates of the oxygen reduction reaction on Pt surfaces [4]. We have extended these studies to the development of an open SCF procedure for DFT methods in which, in contrast to conventional SCF procedures, the number of electrons is not constant, but the (electro-) chemical potential of the system is fixed. This allows to explicitly include the potential present in electrocatalysis in the calculation. This approach is currently being explored in benchmarks and applications [5]. With this expertise the group also contributes to the MAXNET Energy compound by computations on the spectroscopy of noble metal catalysts and reaction paths for the oxygen evolution and reduction on carbon based catalysts [6].

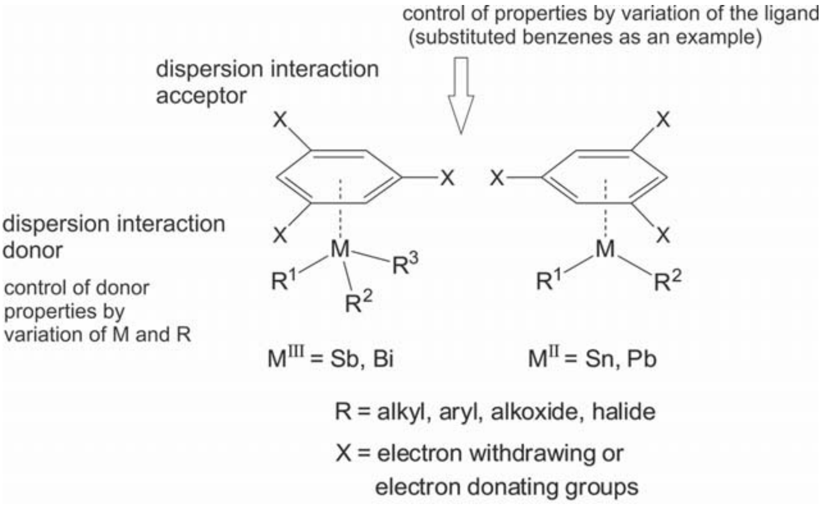


Electronic structure simulations in electrolysis - essential aspects of our work are particle-support adhesion, the electrochemical potential in DFT simulations and the oxygen evolution and reduction reactions. Taken from [5].

### Heavy Main Group Elements as Dispersion Energy Donors

In this project, which is funded within the SPP 1807 ("Control of London dispersion interactions in molecular chemistry"), experimental work is combined with quantum chemical studies in order to assess heavy main group elements as dispersion energy donors. While in recent years, the concept of dispersion interaction in molecular and supramolecular chemistry has been extensively described as an important element of structure formation in organic compounds, heavy main group element atoms exhibit all features that make them potent dispersion energy donors. An appealing feature of these systems is that often weak dispersion interactions compete or interplay with donor-acceptor-interaction, such that a broad variety of interaction motifs are accessible which have not been investigated in detail.

While first steps in rationalizing the major influences in dispersion interactions in coordination compounds of heavy main group elements have been taken, this study aims at a detailed and systematic understanding of the interplay of different interaction mechanisms in this interesting class of compounds.



Schematic overview of the systematic approach to build a molecular library, in which the molecular interactions can be tuned and investigated by means of experiment and theory.

### Twin Polymerization – A Novel Synthesis Route to Organic / Inorganic Hybrid Materials

"Twin Polymerization" is a novel technique in polymer chemistry developed in the group of S. Spange at the TU Chemnitz. Starting from a monomer, which combines two polymerizable units in one molecule, polymerization results in an organic/inorganic hybrid material in which the domains of the different components are in the nanometer size regime. This unique feature has made the synthesis of several novel nanocomposites, like hybrid polymers of organic resins and silica structures, possible. The project has been funded by the DFG in the framework of a Forschergruppe (FOR 1497 „Organisch-Anorganische Nanokomposite durch Zwillingspolymerisation") since 2011 and has been granted an extension after successful evaluation by the DFG in 2014.

In the second period, our group participates in the joined research activities with mechanistic studies of the thermal twin polymerization. During the fist funding period, the focus of our research has been the proton catalyzed twin polymerization, for which the basic mechanism is by now - due to intensive experimental and theoretical studies - fairly well understood. While it was discovered that the reaction can also be initialized at elevated temperatures, the mechanism is still under debate [7-11]. Systematic simulations of possible mechansims and intermediates are carried out to rationalize the basic reaction mechanism and possible influences on the kinetics and possible product distributions.

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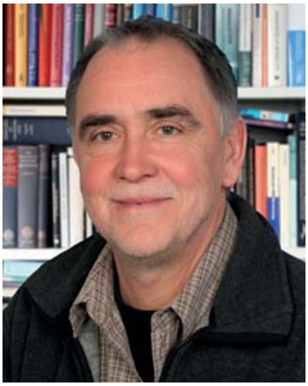

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# Inorganic Spectroscopy of Molecular Transition Metal Complexes

Spectroscopic studies of molecular transition-metal based catalysts can provide fundamental insight into many energy-relevant chemical reactions. Since the molecular structures of the active sites often can be readily determined, this provides a unique basis for gathering detailed information about valence electron distribution and electronic state energies, i.e. the decisive electronic parameters that control reactivity of the metal-ion sites. Inorganic spectroscopy can provide such information from high-resolution measurements of the electronic ground state properties, as well as from probing excited states by using optical spectroscopy. We applied this complementary approach for experimental studies on a number of molecular transition metal complexes with interesting catalytic, electronic or magnetic properties. The applied experimental spectroscopy techniques were $^{57}$Fe-Mössbauer spectroscopy, multi-frequency cw-EPR spectroscopy, magnetic susceptibility measurements and vis/NIR MCD (magnetic circular dichroism) spectroscopy. Much of the work was performed in collaboration with external groups working in synthetic inorganic chemistry, as well as with local colleagues from theory, contributing ultimate quantum-chemistry based interpretation. Some results are highlighted in the following.

**Oxygen and Nitrogen Activation and High-Valent Iron Oxo Complexes.**
The activation of oxygen by molecular compounds for selective functionalization of C-H bonds and other oxidative reactions is still an interesting process illuminating fundamental steps of redox-dependent catalysis. Its electronic conditions can be systematically explored in great detail due to the large number of available synthetic compounds with a variety of iron ligands that control energetics and distribution of the valence orbitals involved in the formation and decay of the reactive iron-oxygen intermediates and final products. The advances in quantum chemistry in this department in the quantum-chemical calculation of reaction

pathways, calibrated by spectroscopic properties of the key intermediates, allowed us new insights in such systems. In particular electronic absorption and MCD data proved to be most relevant in this program. The following studies have been performed in close collaboration and interaction with my colleagues Dr. Shengfa Ye and Dr. Mikhail Atanasov and their groups on the theoretical interpretation of the spectroscopic data.

i.) Low-temperature absorption spectra and temperature and field-dependent MCD spectra as well as high-resolution MCD VTVH intensity data (variable-temperature-variable-field) have been recorded for two types of oxo iron(IV) complexes supported by a tripodal amine ligand (**1**) and a new tetragonal carbene macrocycle ligand (**2**). The compounds are from the labs of Prof. Lawrence Que, Minneapolis and Prof. Franc Meyer, Göttingen, respectively[1-3]. Comprehensive data sets and their interpretation in terms of spin Hamiltonian and ab-initio calculations demonstrate and elucidate the different electronic configurations prevailing for the two ferryl species, which both have triplet ground states, but different reactivity.

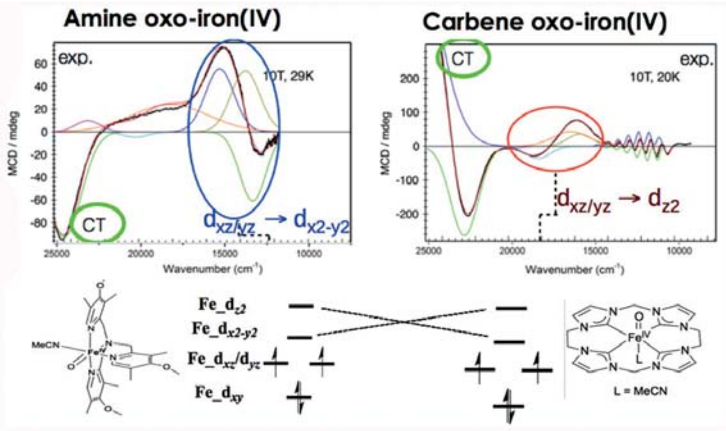
Amine oxo-iron(IV)
Carbene oxo-iron(IV)

**Figure 1**. Top: Experimental MCD spectra of complexes (**1**), left and (**2**), right, recorded at 29 and 20 K with 10 T applied. Note the different up-down vs. down-up shape of the key bands around 14 000 and 18 000 cm$^{-1}$. Bottom: Schematic views of the molecular and electronic structures of the compounds.

The key features are different d-d transitions showing up best in the MCD spectra recorded at 2–80 K with very strong 10 T applied field. The compounds are distinguished by characteristic pseudo-A bands around 14 000 and 18 000 cm$^{-1}$ (Fig. 1), which both are a superposition of overlapping C-type transitions of opposite signs. The shapes with different up-down vs. down-up pattern are typical for the electronic structures of the compounds. The distinct differences could be readily explained by transitions of the type $d_{xz/yz} \rightarrow d_{x2-y2}$ for the amine complex (**1**) and $d_{xz/yz} \rightarrow d_{z2}$ for the carbene complex (**2**). In particular the results for (**2**) support and quantitate the 'tuning effect' of the supporting ligand for the orbital energies as it was intended by using this ligand. The effect is based on the notably strong in-plane σ-interaction of the carbene groups. The spectral analyses are now taken by the Ye group as basis for the detailed theoretical reactivity studies of the systems.

ii.) The spectral assignments for the mononuclear complex (**1**) helped us to understanding also the more complicated MCD spectra of a di-nuclear Fe(IV) complex (**3**) from the Que group which has a $Fe^{IV}(O)(\mu\text{-}O)Fe^{IV}(OH)$ core that is supported by the same tripodal amine ligand as the monomer. Based on MCD/ABS intensity ratios, calculated excitation energies, polarizations, and MCD signs, the key transitions of complex (**3**) have been assigned as ligand-field- or oxo/hydroxo-to-metal charge transfer transitions. A comparison of the results reveals that, despite the difference in nuclearity, the distinct ferryl sites in (**1**) and (**3**) actually have very similar electronic structures that lead to similar reactivities for C–H bond oxidation and O-atom transfer[1].

III.) Another interesting complex relevant for oxygen activation, was a bioinspired peroxo-di-copper compound (**4**) from the F. Meyer group with stable Cu(II)-O-O-Cu(II) core[4]. Due to the presence of a designed 90°core-twist imposed by the supporting ligand, compound (**4**) represents the first example with sizable ferromagnetic exchange coupling of the Cu(II) ions, mediated by a peroxo group ($J=+72\ cm^{-1}$). Similar electronic conditions have been suggested previously for the initial stages of oxygen binding by so-called type III dicopper sites in nature. Interestingly, multi-field susceptibility measurements and HF-EPR studies in collaboration with Ed. Reijerse (Biophysical department) revealed substantial zero-field splitting of the triplet ground state for the model compound. This can be expected for such a simple spin pair only when substantial anti-symmetric exchange prevails. The unusual magnetic properties[4] and their electronic origin are stimulating theoretical investigations.

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## X-ray Spectroscopy

Research in the DeBeer group focuses on the development and application of X-ray spectroscopic methods to understand challenging questions in biological and chemical catalysis. We are interested in the development of both static and time-dependent probes of transition metal electronic structure, and in particular the development of two-dimensional X-ray spectroscopic probes, which enable enhanced selectivity. Challenging questions in energy research motivate our research. Herein, the progress in my research group during the 2014-2016 time-frame is briefly summarized.

### Spectroscopy Developments

Previous work in my group has focused on developing the chemical information content of valence to core X-ray emission spectroscopy (VtC XES) [1]. This is an element selective method, which allows for the identity, ionization energy and protonation state of ligands bound to an absorbing atoms of interest to be selectively identified. Notable examples utilizing VtC XES, include the identification of a central carbon atom in the FeMoco active site of nitrogenase and the identification of oxo bridges in the $Mn_4CaO_5$ complex of photosystem II. VtC XES may also be used as a probe of small molecule bond activation (e.g. the cleavage or formation of an O-O or N-N bond) [1]. To this end, we are developing dispersive VtC XES, as a time-resolved probe of transition metal catalysis. Presently funded by an ERC Consolidator Grant (N2RED, PI: DeBeer), we have constructed an in-house dispersive XES setup, which utilizes a laboratory X-ray source (Excillum, Metal Jet, with $3.5 \times 10^{11}$ X-ray/sec/mm$^2$) in combination with a cylindrical Highly

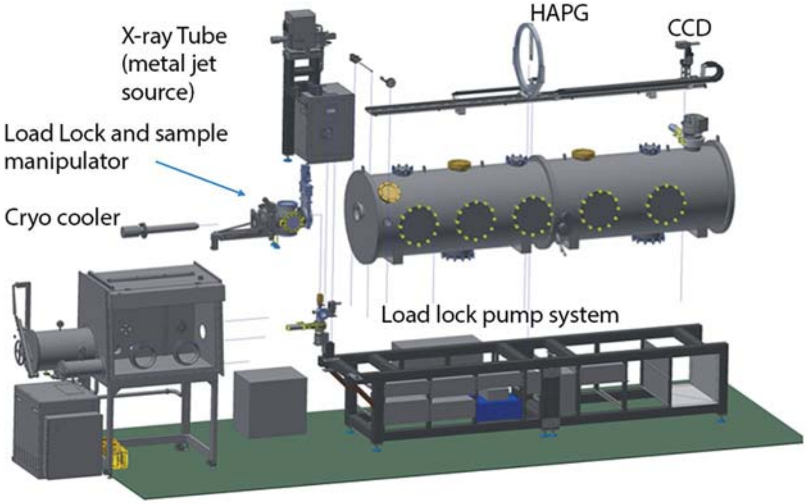

**Figure 1.** In-house dispersive XES setup. The X-ray source, HAPG optic and CCD are enclosed within a 3 meter vacuum chamber. Temperature control of the sample is achieved with a Helium displex cryocooler, enclosed within a custom anaerobic glove box for $O_2$- and $H_2O$ free manipulations.

Annealed Pyrolytic Graphite (HAPG) crystal and a CCD detector to obtain XES in the 2-10 keV range (Figure 1). The instrument is operating to planned specifications and is currently in a commissioning phase. In addition, we are presently designing and building up the PINK beam line at the Energy Materials In-situ Laboratory in Berlin, which will provide an intense source for simultaneous "two-color" XES measurements of heterometallic catalysts.

### Development of "Ligand-Selective" X-ray Absorption Spectroscopy

To further enhance the selectivity of valence XES, we are developing resonant valence XES [2]. This is a two-dimensional measurement where one resonantly excites a metal 1s core electron into the partially occupied and unoccupied states localized on the photoabsorber (i.e. the equivalent of an X-ray absorption edge scan), while simultaneously monitoring the highest energy emission processes (i.e. VtC XES). In doing so, one is able to construct a two-dimensional plane, with the incident energy on the x-axis and the emission on the y-axis (Figure 2). The horizontal cuts through this plane, then represent the XAS data at a given emission energy and effectively correspond to "ligand selective XAS". While the vertical cuts represent the XES data at a given incident energy or valence RXES. The first demonstration experiments were published in JACS in 2014 and selected as a "spotlight article" [2]. We believe this approach should be of particular utility for detecting the XAS of different types of metal-ligand interactions within complex media. We are presently working together with D. Maganas and F. Neese in order to develop the theoretical approaches needed to interpret RXES spectra. Preliminary VtC RXES data have now been obtained on dilute protein systems and on iron-based heterogeneous catalysts.

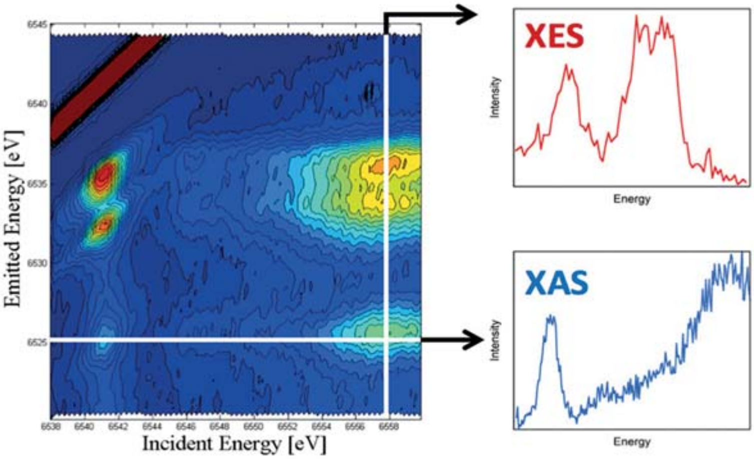

**Figure 2.** Valence RXES data on a Mn model. The x-axis corresponds to XAS and the y-axis to XES. The vertical cut corresponds to resonant emission at the Mn K- pre-edge. The horizontal cut corresponds to XAS data at the N 2s emission line of a Mn-nitrido complex, thus corresponding to "ligand-selective" XAS.

### Development of 2p3d resonant inelastic X-ray scattering as a probe of d-to-d transitions

In addition to the ligand selective XAS, described above, we are developing the information content of 2p3d resonant inelastic X-ray scattering. In this 2D X-ray measurement, one first excites a $2p^63d^n$ ground state to $2p^53d^{n+1}$ intermediate state and then monitors the emission to $2p^63d^{n'}$ final state. The difference between the initial and final states is the equivalent of a formally dipole forbidden d-to-d transition, however, it is arrived at via two dipole allowed transitions. Due to spin orbit coupling in the intermediate state, formally spin forbidden transitions can also be observed. Recently, we have applied this approach to molecular vanadium [3] and iron complexes. The application of 2p3d RIXS to more complex iron sulfur clusters is in progress.

### Kβ Mainline XES as a probe of Metal-Ligand Covalency

The Kβ mainline region of an XES spectrum derives from a metal 3p to 1s transition, which due to 3p-3d exchange splits into Kβ' and $K\beta_{1,3}$ features. As such, these spectra have been utilized as fingerprints for metal oxidation state and spin state. Recently, we have shown that the experimental spectra are further modulated by contributions from metal-ligand covalency [4]. Ligand field expressions have been derived that describe the Kβ mainline behavior for any $d^n$ count. Further a RAS-CI approach has been demonstrated that allows for the direct calculation of Kβ mainline spectra. Importantly, these studies show that caution must be utilized in using Kβ XES as an isolated measure of $d^n$ configuration or metal spin state. Nonetheless, the ability to interpret these spectra within a rigorous theoretical framework, further the quantitative information that can be obtained from Kβ mainline spectra.

### Applications

**N2ase.** – The conversion of dinitrogen to ammonia is a challenging, energetically intensive process, which biologically is enabled by the nitrogenase family of enzymes. In the Mo-dependent enzymes, the catalytic active site is comprised of an unusual $MoFe_7S_9C$ cluster, the so-called FeMo cofactor (FeMoco). FeMoco has been, and continues to be, a longstanding enigma in bioinorganic chemistry. Many details of the geometric and electronic structure of even the resting form of the enzyme have been, until very recently, unknown. Efforts in my research group, have provided important experimental evidence to define to the atomic composition, oxidation state distribution and total charge on the cluster [5-7]. Specifically, VtC XES studies in our research group provided among the first evidence for the central carbon in this unusual biological cofactor. More recently, using high-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) at the Mo K-edge, we have shown that the resting form of this enzyme contains an unprecedented spin-coupled Mo(III) site, which is stabilized through interactions with the neighboring Fe atoms [5,6]. Parallel spectroscopic studies on a synthetic $MoFe_3S_4$ cluster, provided further support for this electronic structure assignment. With the Mo oxidation state assigned, we then turned to the question of the total charge on the cluster. Of the three possible total charge states that could be consistent with the S=3/2 ground state, we were able to show through a combination of Mössbauer spectroscopy, Fe K-edge HERFD XAS, S K-edge XAS and computations, that only a Mo(III)3Fe(II)4Fe(III) oxidation state distribution, which corresponds to a $[MoFe_7S_9C]^{1-}$ cluster is consistent with all available experimental data. These findings mark significant progress in our understanding of FeMoco, as knowledge of the resting state electronic structure is a prerequisite for future mechanistic studies.

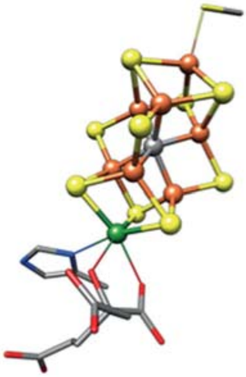

**Figure 3.** Proposed structure of the FeVco cofactor in the V-dependent Nitrogenase. Vanadium (green), iron (orange), sulfur (yellow), and the recently identified carbon (gray).

In addition to our studies on the Mo-dependent nitrogenases, we have also made significant progress on understanding the V-dependent nitrogenases [8]. While it is generally assumed that the V-dependent enzymes contain a FeVco active site analogous to FeMoco (Figure 3), in fact no crystal structure of a V nitrogenase is available. There is, however, great interest in understanding the differences between the Mo- and V-dependent enzymes, as the later is also able to effect C-C bond formation. We have been interested in understanding the role the heterometal may play in modulating the active site electronic structure and enabling these differences in reactivity. Using VtC XES, we have established that a carbon is also present in FeVco [8]. In addition, we have utilized a combination of Fe Ka and Kb HERFD to perform a detailed comparative description of the FeMoco and FeVco active sites. These studies show that FeVco contains a greater complement of reduced Fe and longer heterometal-iron bond lengths than FeMoco.

**Photosystem II** – Unraveling the complex process of photosynthetic water oxidation that is enabled by the $Mn_4CaO_5$ oxygen-evolving complex (OEC) of photosystem II requires the application of new spectroscopic tools, as well as an understanding of the limitations of existing methods. In this context, we have 1) developed Ca XAS and XES as probe of the local Ca environment [9] and 2) demonstrated intrinsic limitations in the ability to predict an EXAFS spectrum given a known structure [10]. The later is particularly important in the context of the structural understanding of the OEC, as EXAFS data have often been used to support a specific topological arrangement of atoms. In many cases, the same EXAFS data have been used by different research groups to argue for entirely different structures. We have demonstrated that these differences result from limitations in the ability to accurately predict amplitudes using the present state-of-the-art multiple-scattering-based approaches for EXAFS analysis. These findings have important implications not only for the OEC, but also for EXAFS studies of all complex clusters.

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## Theoretical Method Development

The group was established in late 2014 for the development of various methods of molecular theory with special emphasis on fast approximate methods, excited states and eventually spectroscopic applications. The first postdoctoral coworker arrived in early 2015, while two other coworkers, a guest and a PhD student has joined the group since less than a year.

Large scale molecular applications of any kind benefit enormously from efficient approximations of accurate wave function methods which are otherwise mostly out of reach for chemistry. Such approximations are especially desirable for excited state systems for which the range of methods available for large systems is even more limited. The methods developed are available in the ORCA program package for users in and outside the institute. Excited state methods can be applied fruitfully in collaboration with other groups in the institute, e.g., for the calculation of ionization potentials and electron attachment energies or for a wide range of spectroscopic applications also planned in the near future.

### The Chain of Spheres Approximation

The Chain of Spheres (COS) approximation is an efficient tool for accelerating Hartree-Fock and Density Functional Theory calculations. For the Fock exchange (X), the COSX approximation amounts to replacing the exact exchange with

$$K_{\mu\nu} \approx \sum_{\kappa\lambda} P_{\kappa\lambda}\,\mu(\mathbf{x}_g)\kappa(\mathbf{x}_g)w_g \int \frac{\nu(\mathbf{x})\lambda(\mathbf{x})}{|\mathbf{x}-\mathbf{x}_g|}d\mathbf{x},$$

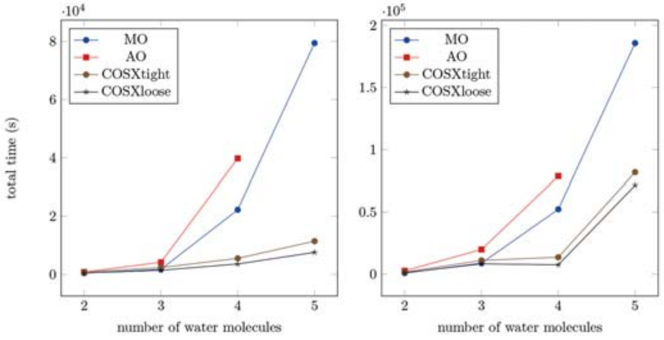
which is essentially a numerical integration carried out on a molecular grid. Since 2011, the original method has been improved[1,2] and adopted for a variety of correlated wave function methods and more recently for the calculation of molecular Hessians. Molecular Hessians are important tools in the optimization of potential energy surfaces and exploring chemical reactions. Since they are also related to molecular vibrations, their application also ranges from chemical thermodynamics to vibrational spectroscopy. It should also be mentioned that a recent study of available methods for the computation of the Fock exchange reveals COSX to be a very good compromise between reliability, accuracy and efficiency among the methods studied.[3]

### Equation of Motion Coupled Cluster Theory

For correlation calculations, Coupled Cluster (CC) theory is considered nowadays to be the gold standard of quantum chemistry for electronic ground states. It has also been extended to the simultaneous calculation of several excited states in the framework of equation of motion (EOM) coupled cluster theory, using a linear excitation operator *($\hat{R}$)* on the coupled cluster ground state, which is normally truncated at the singles and doubles level. Since the CC Hamiltonian *($\hat{H}$)* is non-symmetric, the calculation of left hand states *($\hat{L}$)* is also necessary if various properties are also needed. Using such a parametrization, the excitation energy for the *k*th state ($\omega_l$) can be computed from the equations:

$$\langle 0 | \hat{L}_k^\dagger \bar{\hat{H}} \hat{R}_l | 0 \rangle = \delta_{kl} E_l, \qquad \langle 0 | \hat{L}_k^\dagger \hat{R}_l | 0 \rangle = \delta_{kl}.$$

The solution of the left hand side problem is relatively simple once the right hand sides are available. The latter are normally found using the Davidson algorithm, designed for finding a few roots of the eigenproblem of a large matrix. The current research of Dr. A. K. Dutta in our group is focused on the development of an efficient EOM based method for excited states. The standard canonical EOM method was made available recently in ORCA for closed shell systems. Combined with the COSX approximation,[4] EOM calculations can be accelerated to a previously unseen extent, see Figure 1.



EOMEA EOMEE

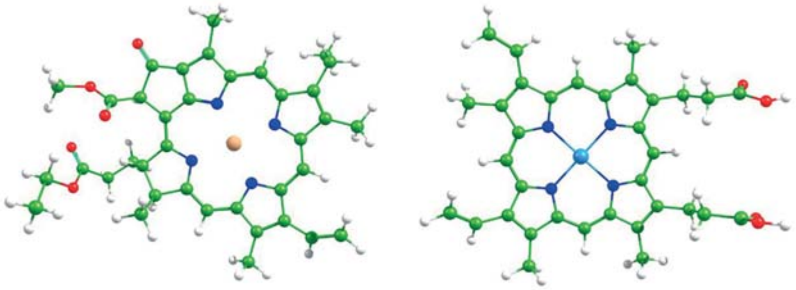
**Figure 1.** Total timings for EOMEE and EOMEA calculations for molecular orbital (MO), atomic orbital (AO) and COSX implementations using tight and loose grid settings.

We were able to calculate the first two excited states of the trans retinal molecule (539 basis functions) in less then two days on eight cores only, which is the first such EOM calculation reported in the literature for such a large system.

The excitation operators in EOM are "electron conserving", since all the electrons removed from occupied orbitals are placed at virtual ones. Ionization operators can be obtained by removing an occupied or a virtual label form an excitation operator. The resulting equations are special cases of the general EOM equations for ionization potentials (IP) and electron attachments (EA), which can be easily implemented. The advantages of the COSX approximation are even more significant in the EA case than for regular EOM; calculations up to a hundred atoms can now be carried out using our code. The accurate calculation of IP and EA values can be a valuable contribution to redox potential calculations, such as those involved in Photosystem II studied in the group of Dr. D. Pantazis which we plan to investigate.

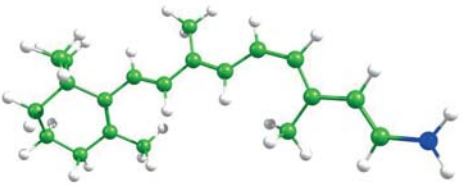
In order to speed up EOM calculations to an even larger extent, we currently use a strategy which employs the domain based pair natural orbital (DLPNO) framework of Prof. F. Neese for the ground state coupled cluster calculation in combination with the similarity transformed equation of motion (STEOM) method of Prof. Marcel Nooijen for the excited state part.[5] The DLPNOs are back transformed for the purposes for the excited state calculation, while the excitation manifold is truncated to the singles space, while the effect of the doubles is still taken care of using a similarity transformation. The latter is parametrized in terms of IP and EA eigenstates, which also benefit from the COSX approximation. This way, we have been able to calculate excitation energies for molecules of 80-90 atoms (e.g., Chlorophyll A, more than a 1000 basis functions), thus providing an alternative for time dependent density functional theory for systems which are out of reach for traditional EOM calculations, see Figure 2.

In order to calculate properties like UV-Vis transition moments, one needs to evaluate the EOM left vectors in an efficient way, which is the subject of an ongoing study. The calculation of core level excitations is another field which we currently investigate especially since such calculations may contribute to the evaluation of X-Ray spectroscopy experiments in the group of Prof. S. DeBeer. Finally, various improvements on the STEOM scheme are also possible, among others a scheme for the automatic selection of active spaces, and a DLPNO variant of the IP/EA equations, which take a significant amount of time in STEOM calculations.



Chlorophyll a

Zn protoporphyrine



11-cis-retinal protonated Schiff base

**Figure 2.** Examples of molecular systems for which the back transformed DLPNO EOM and STEOM schemes can be applied to.

### Methods for Molecular Spectroscopy

In the previous section, some spectroscopically oriented developments have already been described, mostly based on the work of Dr. A. K. Dutta. The open shell variants of the STEOM/EOM equations are currently also being implemented by Dr. L. Huntington, using an automatic code generation scheme. Code generation in conjunction with the DLPNO framework is a promising field of research for the development of novel methods of spectroscopic and other interests. The work of Dr. A. Sen is focused on the formulation of a spin adapted open shell ionization potential scheme (ROCI-IP), which may be applied to transition metal chemistry and XPS spectroscopy, especially in a manner similar to ROCIS calculations in the group of Dr. D. Manganas. Since the late summer, Dr. B. de Souza has joined our group as a Humboldt research fellow to develop robust theoretical methods for the calculation of the relevant transition rates in photochemical processes. In collaboration with the group of Prof. A. Auer, we also wish to explore efficient ways to calculate NMR parameters within the DLPNO framework. I have also submitted a DFG grant proposal with a similar NMR related theme. Finally, M. De Santis has joined our group as a PhD student very recently. His project involves the evaluation of EPR parameters using DLPNO-CC.

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## Advanced Experimental and Theoretical Spectroscopy

Over the last 3 years the Advanced Experimental and Theoretical Spectroscopy group led by Dimitrios Manganas has shown activity in developing and applying theoretical spectroscopic protocols in the fields of X-Ray Spectroscopy and magnetism.

### Theoretical X-ray spectroscopy

*Metal L-edge spectroscopy*

We have recently shown that the DFT Restricted Open-Shell Configuration Interaction with Singles (ROCIS) method can successfully treat the metal L-edge problem on classes of molecular systems from transition metal compounds up to polymetallic clusters with several 100s of atoms.[1] In this respect we have explored this methodology to treat the metal L-edge problem on various close and open shell compounds and polymetallic clusters.[2-4]

*Resonance X-ray Emission*

Entering the field of resonant inelastic scattering X-ray spectroscopy (RIXS), we have shown that for small molecules the problem can be treated on the framework of wavefunction based multireference configuration interaction (MRCI) methods.[5] Inspired by this performance we have extended the applicability of the DFT/ROCIS method to treat various valence to core resonant X-ray emission (VtC-RXES) spectra. We show that in a case study of a Mn(V) complex the DFT/ROCIS protocol is able to interpret both the X-ray Absorption (XAS) as well as the non-resonant X-ray emission (XES) and VtC-RXES experimental trends that could not be reproduced by any computational protocol based on particle/hole theories (Figure 1).

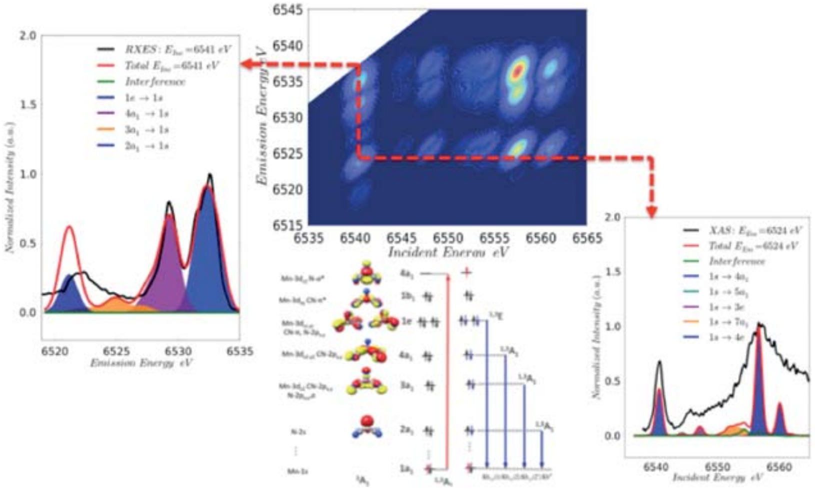

Figure 1. A DFT/ROCIS VtC-RXES protocol.

*Core PNO-ROCIS for spectacular performances and applications*

In this work we combined the efficient implementation of the ROCIS method with the pair of natural orbitals (PNOs) machinery in order to expand the applicability of the method to systems with 100s of atoms and 1000s of states at affordable computational cost. We show that this approach provides direct access to the metal L-edge spectra of biological and surface metal centers.[6]

*Energy shifts in X-ray spectroscopy*

Prediction of relative energies in the X-ray region contain quite high but systematic errors. These error can be taken into account by introducing the concept of an element specific (or element dependent) shift. In an attempt to provide a unified description oft he problem we have employed the DFT/ROCIS method on a large number of transition metal complexes in a variety of coordination environments, oxidation and spin states and across all the edges. Subsequently the highly accurate second order *n*-Electron Valence State Perturbation Theory (NEVPT2) *ab initio* method is employed for the respective atoms series in order to extract the reference values. We show that all shifts can be described by a linear equation that is valid across all edges while the chemical information is retained.[7]

## Theoretical spectroscopic protocols for catalysis

*A unified view of homogeneous and heterogeneous catalysts*

Identifying catalytically active structures or intermediates in homogeneous and heterogeneous catalysis is a formidable challenge. In this concept we employed a combination of spectroscopic methods to study two closely related systems from the heterogeneous (the silica-supported vanadium oxide VOx/SBA-15) and homogeneous (the complex K[VO($O_2$)Hheida]) domains. The results of the study demonstrate that: a) a combination of several spectroscopic techniques is of paramount importance in identifying signature structural motifs and b) quantum chemistry is an extremely powerful guide in cross connecting theory and experiment as well as the homogeneous and heterogeneous catalysis fields. It is emphasized that the calculation of spectroscopic observables provides an excellent way for the critical experimental validation of the theoretical results (Figure 2).[8]

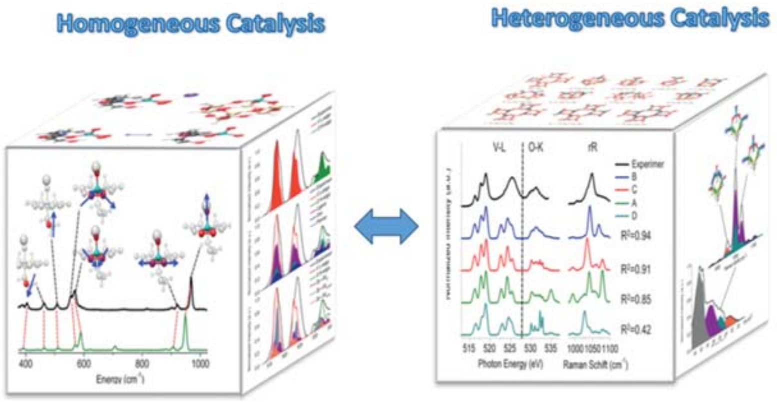

**Figure 2.** A unified view of homogeneous and heterogeneous catalysts through the eyes of theoretical spectroscopy

*Developing the information content of MoVOx catalysts*

Absorption as well as, multiwavelength resonance Raman spectroscopies are widely used to investigate the electronic structure of transition metal centers in coordination compounds and extended solid systems. In combination with computational methodologies that have predictive accuracy, they define powerful protocols to study the spectroscopic response of catalytic materials. In this work, we study the absorption and resonance Raman spectra of the M1 $MoVO_x$ catalyst. It is shown that due to the local nature of the involved electronic transitions, band assignment protocols developed for molecular systems can be directly applied to describe the calculated spectral features of the cluster models as well.[9]

### Accurate energetics for surfaces

Coupled cluster theory with single, double and perturbative triple excitations (CCSD(T)) is widely considered to be the 'gold standard' of *ab initio* quantum chemistry. Using the domain-based pair natural orbital local correlation concept (DLPNO-CCSD(T)), allows for *ab initio* calculations providing reference adsorption energetics at solid surfaces with an accuracy approaching 1 kcal/mol. (Figure 3).[10]

### Collaboration with other groups with in CEC

The group has in addition shown activity in the joint projects of Molecular Magnetism[11-14] and X-Ray spectroscopy.[15-17]

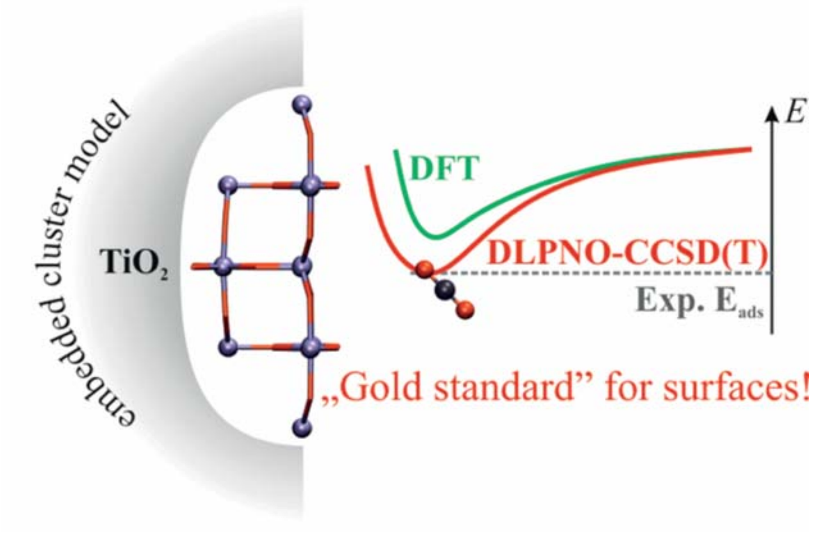

**Figure 3.** Adsorption energies of $H_2O$, $NH_3$, $CH_4$, $CH_3OH$ and $CO_2$ at the $TiO_2$ surface are obtained with chemical accuracy (~1 kcal/mol)

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Research in the Pantazis group has contributed significantly to understanding the structural and electronic determinants of biological water oxidation. Nature's unique catalyst for this challenging chemical transformation is the oxygen-evolving complex (OEC) of Photosystem II (PSII), a $Mn_4CaO_5$ cluster that undergoes a series of four metal-centered oxidations until it extracts four electrons from two molecules of water and releases dioxygen (Figure 1). Our approach is based on the quantum chemical prediction of spectroscopic observables and aims at the construction of chemical and mechanistic models that are externally consistent in terms of reproduction of all available experimental data, and simultaneously internally consistent in terms of chemical progression through the various catalytic states. This approach has been instrumental in uncovering fundamental principles of biological water oxidation[1] and is extended to synthetic molecular and heterogeneous catalytic systems.

### Metal oxidation states in biological water oxidation

In addition to the decades-old uncertainties regarding the precise structure of the inorganic core of the oxygen-evolving complex, a question of central importance concerns the absolute oxidation states of the constituent manganese ions in each step of the catalytic cycle. Two competing oxidation state schemes have developed historically, the "low-valent" scheme, which assumes that the lowest oxidation state attainable (i.e. the $S_0$ state of the catalytic cycle in Figure 1) corresponds to Mn(II,III,III,III) or equivalent, and the "high-valent" scheme, which instead requires the most reduced state to be Mn(III,III,III,IV). The two paradigms have drastically diverging implications for the interpretation of experimental data and for the most crucial step in natural water oxidation, the O–O bond formation. Owing to the complexity of the biological water oxidizing system several experimental observations can in principle be interpreted in a way that fits either oxidation state paradigm. However, no explicit comparison between the two schemes had been made on the basis of computationally optimized models for the catalytic states against experimental observables. In the last few years we took on the challenge of developing the most extensive set of models for both the low-valent and the high-valent scheme, for all catalytic intermediates in various protonation states and ligand configurations. Relative energies are of limited value for such a study; evaluation of the different models must rely instead on their electronic, magnetic and spectroscopic properties, as predicted by theoretical chemistry, and on their ability to accommodate and rationalize experimental observations. This work employed the widest possible range of criteria, including spin states, EPR, ENDOR and EDNMR data, structural parameters in relation to crystallography (XRD and XFEL-XRD) and EXAFS, and X-ray absorption spectroscopy. The results, which have been widely highlighted in the field, established beyond any doubt that only the "high-valent" paradigm provides a fully consistent representation of the OEC.[2] The derived models of the inorganic core of the OEC for all stable states are shown in Figure 1.

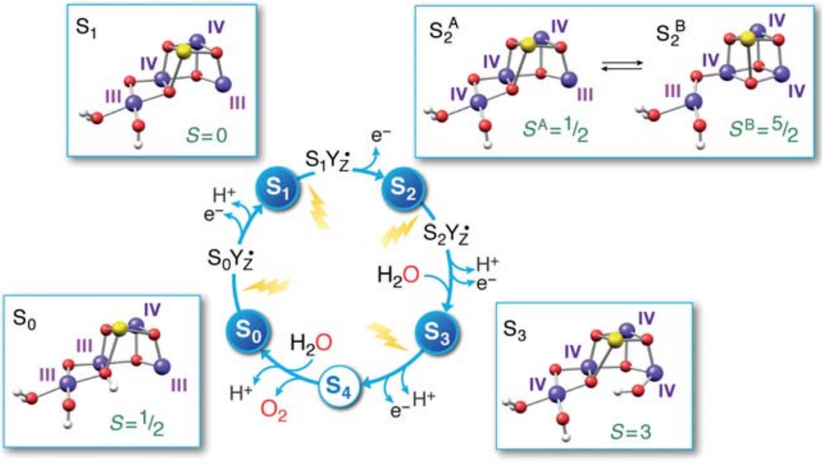

**Figure 1**. The catalytic cycle of the OEC with spectroscopically consistent models of the inorganic core, individual Mn oxidation state assignments and total spin states.

In addition to this comprehensive comparison of the two oxidation state paradigms, we achieved an interpretation of new EPR data (in collaboration with Nicholas Cox) on the $S_3$ state of the OEC, the final metastable state of the catalyst that prepares it for O–O bond formation. Our calculations established a correspondence between a precise topology of the inorganic core and the spectroscopic data and managed to provide a structural interpretation demonstrating that the OEC in the $S_3$ state contains four octahedrally coordinated Mn(IV) ions.[3] Having thus completely specified the electronic evolution and geometric structure of the catalyst up to the final catalytic step, this work forms the basis for all current and future experimental and theoretical investigations on the mechanism of water oxidation.

### Catalytic intermediates and mechanistic principles

Insight into stable catalytic states is essential but not sufficient to decipher finer details of the reaction mechanism. For this reason we extended our efforts towards establishing the identity of intermediates formed transiently as the catalyst progresses from one catalytic state to the next. In some cases experimental data exist on potential intermediates, but no such data had received a structural interpretation. A principal target was to understand the transition between the $S_2$ and $S_3$ states of the catalytic cycle that involves oxidation of the cluster, deprotonation and water binding, preparing the OEC for the final catalytic step. We characterized the first intermediate of this transition, formed when the redox-active tyrosine that is part of the electron transfer chain of photosystem II is oxidized by the reaction center chlorophylls (the $S_2Y_Z^\bullet$ state). We probed the spectroscopic properties of the tyrosyl radical in detail, both intrinsically and with respect to changes in its hydration environment (Figure 2). This study led us to propose a role of calcium in terms of ordering the hydrogen-bonding environment of the redox-active tyrosine and thus indirectly regulating the redox potential of the residue and its interaction with the manganese cluster.[4]

This was followed by a detailed analysis of all intermediates in the $S_2$–$S_3$ transition.[5] The scheme shown in Figure 2 summarizes some of the new insights gained by this study: it was confirmed that the structural bistability observed in the $S_2$ state is functionally critical for catalytic progression, since only one of the two structural forms (the closed-cubane) can progress to the $S_3$ state. We identified an unprecedented five-coordinate Mn(IV) species with an approximate trigonal bipyramidal coordination geometry and demonstrated, using *ab initio* multireference methods, that it explains a series of puzzling observations regarding an EPR-silent but near-infrared (NIR) active component of the $S_3$ state.[5] Along with the important achievement of precisely elucidating how the substrate analogue methanol interacts with the OEC[6] the characterization of this intermediate allowed the identification of a novel water binding mode and of the unique channel used for substrate delivery to the otherwise well-isolated water oxidation active site. These studies have provided unprecedented insight into mechanistic principles of biological water oxidation, among others revealing the crucial role of the Jahn–Teller effect, and excluding substrate binding along the "running" catalytic cycle.

### Studies of synthetic systems

Part of our research program but also of our collaborations with internal and external experimental groups involves the study of synthetic systems, both as structural or spectroscopic models of the natural catalyst and as functional analogs. A major component of our established research program is the analysis of magnetic and redox properties of exchange-coupled transition metal clusters. As contributors to the BmBF MANGAN project, during the last two years we have been studying the effect of redox-inert metals on the properties of small manganese clusters. Moreover, we have been developing computational models of heterogeneous manganese-based oxides, which will be used in calibration studies focusing on structure–spectroscopy correlations (for example using XAS and XES data), and subsequently in studies that will address fundamental mechanistic aspects of their activity as oxygen evolving catalysts.

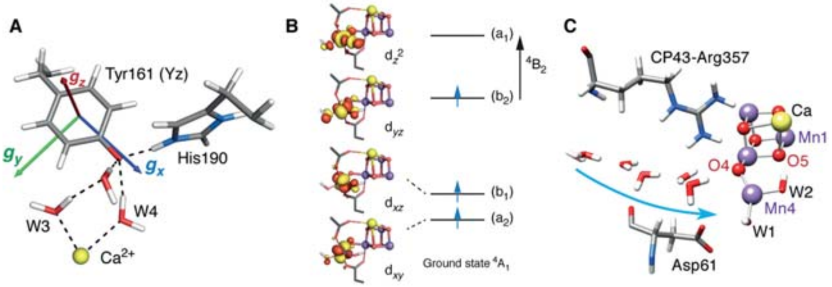

**Figure 2**. A: The tyrosyl radical and its hydration environment. B: Electronic structure of the five-coordinate NIR-active $S_3$-state intermediate. C: Water delivery channel.

## Accurate energetics of redox processes

In the last few years our group has been developing a research program targeted at exploring and developing the applicability of first-principles wave function based correlated methods to the prediction of highly accurate energetics for redox processes (in collaboration with Robert Izsák and Frank Neese). The aim is to identify and eliminate specific sources of error in the prediction of properties such as reduction potentials and acidity constants, by using modern theoretical approaches that include the local pair natural orbital (LPNO) approach and the equation of motion (EOM) coupled cluster theory. Part of this effort is conducted within the framework of the cluster of excellence RESOLV, and so far involves a series of benchmark studies on multi-electron and one-electron transformations, ionization energies and aqueous reduction potentials, and spin-state energetics of carbenes and transition metal complexes, with extensions towards treatment of explicit solvation at the same *ab initio* level, and studies on solvent-controlled reactivity.

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## Theory and spectroscopy related to $H_2$ catalysis

Nature has developed a variety of enzymes called hydrogenase that efficiently catalyze the reduction of protons to molecular hydrogen.[1] Over millions of years, these enzymes have been optimized to work close to the thermodynamic potential, and as such, hydrogenases also catalyze the reverse reaction, $H_2$ oxidation. Among the natural hydrogenase enzymes, [FeFe]-hydrogenase displays the fastest rates for production of $H_2$ at turnover frequencies (TOF) up to $1 \times 10^4\ s^{-1}$.[2] A key feature of the [FeFe]-hydrogenase active site is the presence of a pendant amine group near an open coordination site of Fe (Figure 1), and it is believed that this pendant amine facilitates proton transfer between Fe and the surrounding protein matrix.

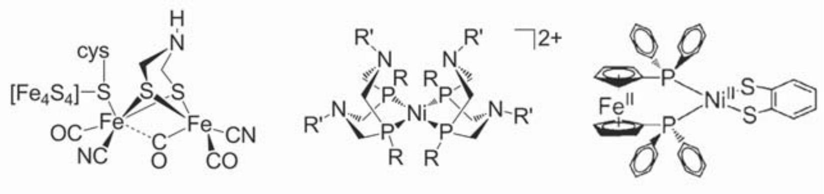


**Figure 1.** Structure of [FeFe]-hydrogenase active site (left), a $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ catalyst (middle)[3] and the "Jones" catalyst[4] (right).

In our group, we are especially interested in unraveling reaction mechanisms for proton reduction or $H_2$ oxidation of catalytically active molecules. By a combination of synthesis, spectroscopy and quantum chemistry in collaboration with Dr. E. Wiedner et al. at PNNL, we have analyzed the intermediates in the catalytic reaction of the biomimetic $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ catalyst. A schematic overview of the reaction intermediates is shown in Figure 2; for more detailed information, as well as for EPR, ENDOR and HYSCORE spectra, the reader is referred to reference [5]. Most importantly, the catalyst in its eH state (Figure 2, left) binds a hydride to nickel and a proton to a spatially nearby base, so that $H_2$ can be formed.

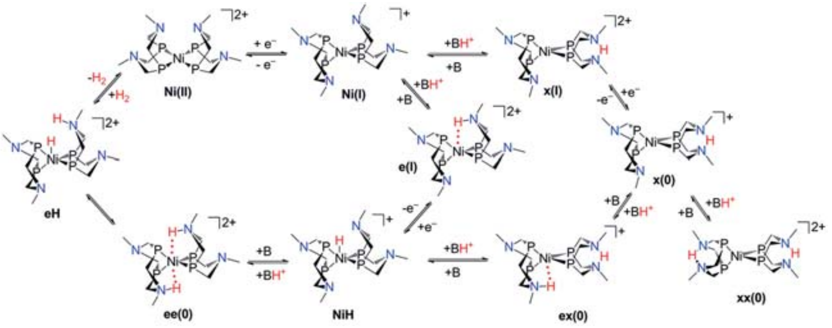
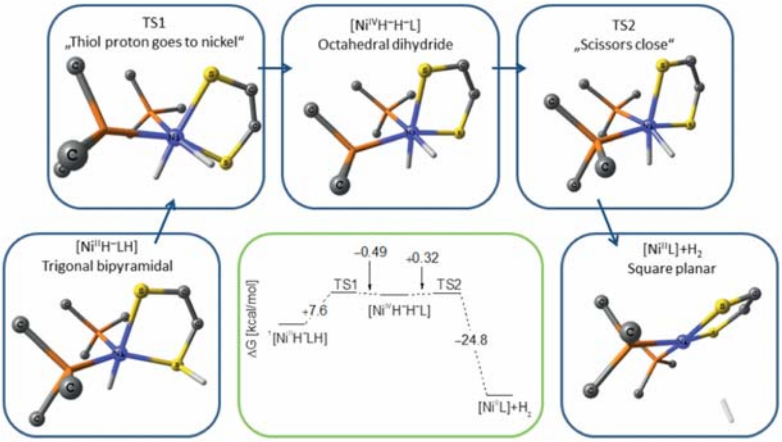


**Figure 2.** Proposed catalytic cycle for electrocatalytic $H_2$ production (clockwise) and oxidation (counterclockwise) by $[Ni(P^R{}_2N^R{}_2)_2]^{2+}$.[5] The R and R  groups have been omitted for clarity.

As such, a particular focus has been to investigate the ligand fields at the redox active metals in critical reaction intermediates and how these ligand fields poise the catalyst to perform efficiently. For example, for the "Jones" catalyst, we found that the critical intermediate for $H_2$ formation has an octahedral ligand field at nickel and contains one equatorial and one axial hydride bound to the nickel ion (Figure 3). Interestingly, in this catalyst, the $H_2$ formation proceeds by proton transfer to nickel, which must be able to accept an equatorial hydride in addition to an axial one.[6] In the Jones complex this is accomplished by the ability of nickel to adapt a trigonal bipyramidal coordination. The subsequent driving force for the forward reaction is the formation of the H-H bond.


TS1 „Thiol proton goes to nickel"

$[Ni^{IV}H^-H^-L]$ Octahedral dihydride

TS2 „Scissors close"

$[Ni^{II}H^-LH]$ Trigonal bipyramidal

$[Ni^{II}L]+H_2$ Square planar

**Figure 3.** Pictorial representation of the critical steps including transition states (TS) for the mechanism of formation of $H_2$ from protons as catalyzed by the Jones complex.[6] Phenyl groups and the ferrocene nits have been omitted for clarity.

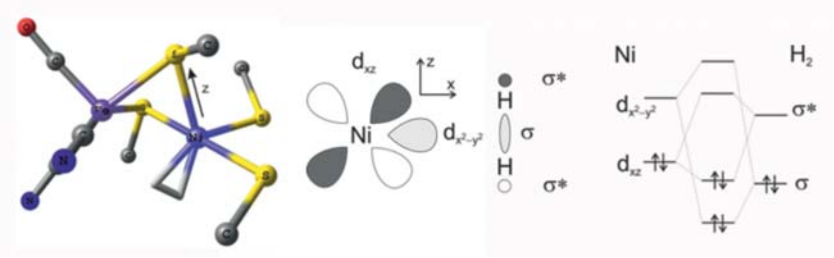


**Figure 4.** Critical intermediate for $H_2$ oxidation in [NiFe] hydrogenases and Kubas mechanism.[6,7]

For $H_2$ oxidation in [NiFe] hydrogenase, we found that equatorial and bidentate ($h^2$) binding of $H_2$ to a formal Ni(III) intermediate is a prerequisite. The relevant orbitals are the unoccupied $d_x2_{-y}2$ orbital and the doubly-occupied $d_{xz}$ orbital and $H_2$ acts as a s-donor into the former orbital and as a p acceptor into its s* orbital from the latter 3d orbital. The s donation from the s($H_2$) orbital and p back-donation into the s*($H_2$) orbital both weaken the H-H bond to an extent that bond cleavage is barrierless. The general mechanism is already known in literature as the Kubas mechanism,[7] which thus is applicable to [NiFe] hydrogenases as well.

### Raman spectroscopy of a $CO_2$ reducing catalyst

With the gained understanding of proton reduction and $H_2$ oxidation at the molecular electronic structure level, we recently set out to explore the reductive chemistry of a $CO_2$ reducing catalyst based on rhenium. $CO_2$ is kinetically inert and its chemical transformation is thermodynamically challenging and usually involves multi-electron redox processes, coupled with proton transfers via complicated reaction pathways. The *fac*-[Re(X)(bpy-R )$(CO)_3$] system (X = anionic ligand or neutral ligand with a counter anion; bpy-R  = R -substituted 2,2 -bipyridine), first reported by Lehn et al. in the 1980s,[8] is one of the most robust and efficient $CO_2$ reduction catalysts known to date and affords CO under both photochemical and electrochemical conditions. Regrettably, the Mn analogue, turned out to have poor stability owing to its light sensitivity.

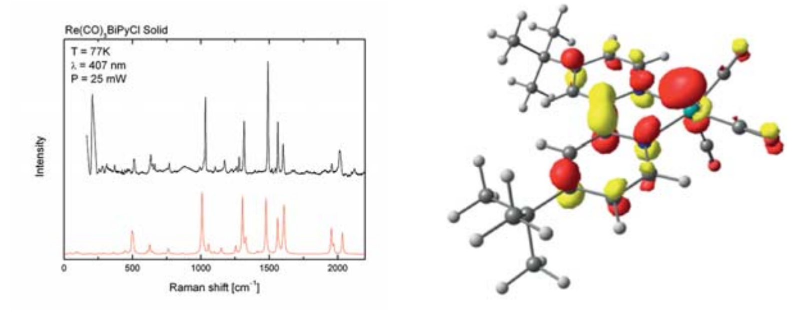


**Figure 5.** (left) Raman spectrum (black) and calculation (red) of the $ReBiPy(CO)_3Cl$ catalyst for $CO_2$ reduction; (right) singly occupied natural orbital of the one-electron reduced complex $ReBiPy(CO)_3$.

For the Rhenium compound, investigation by the combination of theory and Raman spectroscopy is an ideal tool. With the aid of theory, all bands in the Raman spectrum have been assigned to particular vibrations of the molecule.[9] Overall, our study demonstrates that Raman spectroscopy in combination with quantum-chemical calculations allows obtaining local information about geometric and electronic structure in catalysts with non-innocent ligands irrespective of the presence or absence of unpaired electrons. The investigations point out a closed-shell singlet state for the doubly reduced complex giving rise to a *formal* $\{Re^{I}(bpy\text{-}R)^{2-}\}$ moiety, but the *actual* charge distribution is more comparable with a $\{Re^{0}(bpy\text{-}R^{\cdot})^{-}\}$ species, where the first reduction effectively takes place at bpy-R and second reduction occurs at the metal center. As such, both the metal and the ligand cooperate in the reductive two-electron chemistry related to $CO_2$ activation.

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**Dr. Thomas Weyhermüller**

## Bringing together Experimental Spectroscopy and Quantum Theory

Chemical activation of inert small molecules like carbon dioxide, methane, nitrogen and others is a key problem in energy research. In the future, energy from renewable sources will be used on a big scale to transform these abundant materials to chemicals for industry and agriculture. Metal catalysts are needed to make such transformations energetically and chemically efficient and selective. We strongly believe that a deep understanding of mechanistic functionality and electronic structure of catalytic systems vastly supports the process of developing better catalysts. It is our approach to combine spectroscopic methods (EPR, MCD, Mössbauer, Resonance Raman, X-Ray methods, etc.) with quantum theory to shine light on the chemical and electronic structure of catalytically active centers. The combination of experiment with theory allows to interpret even very complicated spectroscopic data and to extract the desired chemical information.

Research in my group focuses on the synthesis of metal complexes for spectroscopic investigations. Directed variation of structural and electronic parameters in a series of compounds allows to systematically studying their spectroscopic response. Our samples are typically analyzed by standard methods (elemental analysis, IR, UV/vis, NMR, XRD) before they are further investigated as mentioned above. Such compounds with known molecular structure provide a reliable basis to collect high quality spectroscopic data. In the following, two examples of recent projects are given.

### Elucidating the electronic structure of a $CO_2$-reducing catalyst

There are a number of homogenous catalysts known which can reduce carbon dioxide from industrial processes back to valuable chemicals like carbon monoxide, formic acid or formaldehyde. Direct hydrogenation with heterogeneous catalysts can even produce methanol from $CO_2$. One of the most promising methods to reduce $CO_2$ to useful chemical building blocks is the electrochemical reduction employing an electrocatalyst. Unfortunately, the first reduction step forming the anion radical $CO_2^{\bullet -}$ is at very negative potential and is associated with a huge over potential. Proton coupled reduction is much more favorable in this respect as shown in equation 1.[1]

$$\text{eqn. 1}\qquad \begin{array}{lll} CO_2 + e^- & CO_2^{\bullet -} & E^{\circ\prime} = -1.90\ V \\ CO_2 + 2H^+\ 2e^- \rightarrow & CO + H_2O & E^{\circ\prime} = -0.53\ V \\ CO_2 + 2H^+\ 2e^- \rightarrow & HCO_2H & E^{\circ\prime} = -0.61\ V \\ CO_2 + 4H^+\ 4e^- \rightarrow & HCHO + H_2O & E^{\circ\prime} = -0.48\ V \end{array}$$

Iron porphyrins have been investigated as potential electrocatalysts for quite some time now. In their super-reduced $[(TPP)Fe]^{2-}$ form – formally a "Fe(0)" state – they are known to act as potent electrocatalysts for $CO_2$ reduction (Fig. 1). The groups of Costentin and Saveant recently added internal proton donor functionalities making the catalyst even more effective.[2] There is, however, a lot of controversy on the exact nature of the electronic ground states of $[(TPP)Fe]^{1-}$ and $[(TPP)Fe]^{2-}$, since the reductions can be either metal or ligand centered. We have therefore started a project to elucidate the electronic structure of these species since we feel that it is crucial to understand the catalytic mechanism to design new and more efficient catalysts.

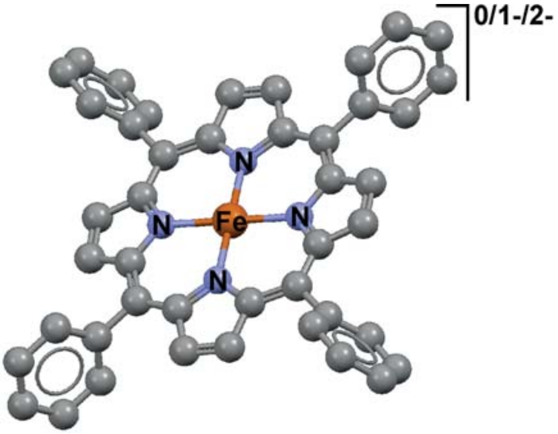

**Figure 1.** Structure representation of a simple $CO_2$ reducing electrocatalyst $[(TPP)Fe]^0$ (TTP=Tetraphenylporphyrine) which can be reduced to a monoanionic and a dianionic, catalytically active form.

Preparation of $[(TPP)Fe]^{0/1-/2-}$ species was done by stepwise reduction of $[(TPP)Fe^{III}Cl]$ (**1**) using the published procedure by Scheidt et al.[3] Isolated complexes $[(TPP)Fe(THF)_2]^0$ (**2**) ($S = 2$), $[(TPP)Fe]^0$ (**3**) ($S = 1$), and sodium salts of $[(TPP)Fe]^{1-}$ (**4**) ($S = ½$) and $[(TPP)Fe]^{2-}$ (**5**) ($S = 0$) were investigated using EPR, resonance Raman, Mössbauer and XAS spectroscopies. Structural parameters of all complexes and their spectroscopic properties were thoroughly calculated using DFT methods. Experimental results clearly evidence that the iron centers in **3**, **4** and **5** are of the same, namely intermediate spin Fe(II) character (S=1), which is nicely demonstrated by XAS spectra shown in Figure 2. DFT studies of a hypothetical low spin $d^7$ Fe(I) state for **4** and a low spin $d^8$ Fe(0) state for **5** show that the energy separations between low spin states and intermediate spin states are 188.5 and 47.9 kcal/mol higher in energy for low spin states, far beyond the error range of a DFT calculation. We found that spectroscopic results of the redox series $[(TPP)Fe]^{0/1-/2-}$ only fit with quantum chemical models if the reduction processes are ligand centered, not metal centered. Reduction equivalents are stored in the $\pi^*$-orbital of the porphyrin ligand to form radical states which are antiferromagnetically coupled to the central intermediate spin iron(II) centers. The porphyrin ligand functions as an electron relay and donates the two electrons necessary to reduce $CO_2$ to CO.

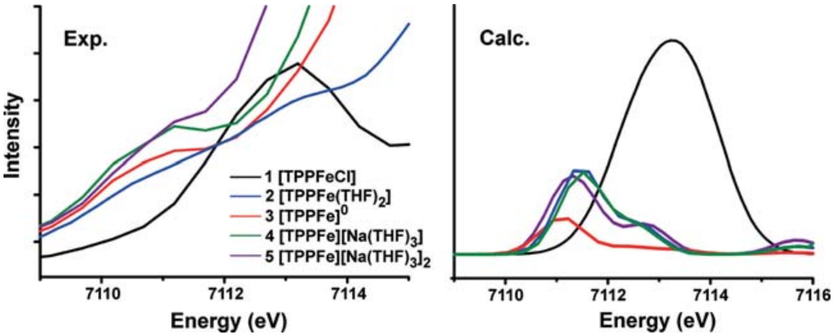

**Figure 2.** Experimental (left) and calculated (right) pre- and near-edge region of XAS-spectra of [TPPFe]-complexes **1–5** showing that the Fe oxidation state does not change in complexes **1–4** which can be attributed to i.s. Fe(II).

### What is the oxidation state of molybdenum in the FeMoco-factor of nitrogenase?

Nitrogenase is a bacterial enzyme which catalyzes the conversion of nitrogen from air to ammonia, an essential source for the biosynthesis of nitrogen containing compounds like peptides or nucleobases. The activation of nitrogen is very challenging since it is probably the most inert small molecule one could think of. A lot has been learned about the chemistry and structure of nitrogenase but the actual exact electronic structure and the catalytic mechanism are still a myth.

One of the two metal containing co-factors in nitrogenase, namely FeMoco, has been identified to be the active site of the enzyme where nitrogen binds and ammonia is released. It is basically composed of seven iron-, a molybdenum-center, nine sulfides, and a light atom, probably interstitial carbide ion. A long debate is going on what the oxidation states of the metal centers are and what the role of molybdenum is. So far, most authors favored Mo(IV) as the oxidation level for the resting state but no final conclusion could be made.

We felt challenged to contribute to the solution of this problem and started a project in which we prepared a number of molybdenum model complexes resembling structural features of the natural co-factor. Model complexes and the natural enzyme were investigated using a combined experimental and theoretical approach. High-energy resolution fluorescence detected XAS spectroscopy (HERFD-XAS) was used to analyze complexes and enzyme. This method is superior to normal XAS spectroscopy due to better energy resolution. A detailed computational study in which all meaningful combinations of oxidation states were calculated was performed and results were compared with experimental data.

Our analysis shows that the molybdenum atom in FeMoco of Mo-dependent nitrogenase is best described as a Mo(III) coupled to the iron atoms in the cofactor (Figure 3). This is in sharp contrast to the previous description of the molybdenum as a closed-shell Mo(IV).

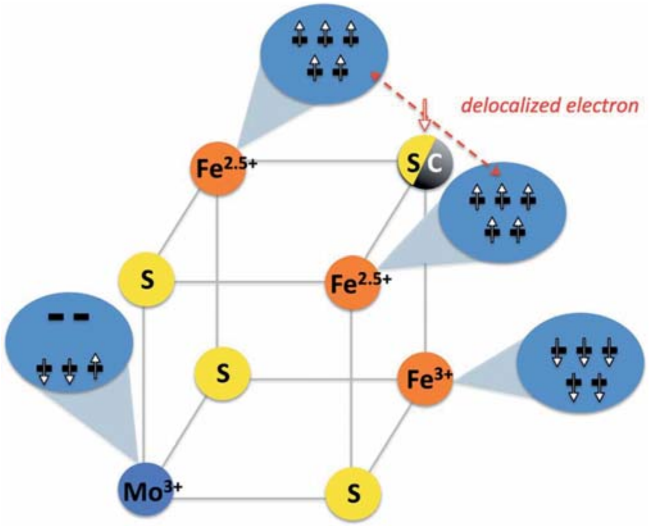

**Figure 3.** Provisional spin coupling diagram for $[MoFe_3S_3C]^{1+}$ and $[MoFe_3S_4]^{3+}$ cubanes based on broken-symmetry DFT calculations. Top iron atoms couple ferromagnetically and form a mixed-valence delocalized pair which is antiferromagnetically coupled to a high-spin Fe(III). The Mo(III) ion, here shown in a provisional non-Hund doublet state, couples to the irons to give a ground state spin of S=3/2 for the cubane.

Crucial to this oxidation state assignment was to utilize HERFD-XAS as well as a direct comparison of the MoFe protein with synthetic $[MoFe_3S_4]^{3+}$ model compounds. The electronic structure of the FeMo cofactor, however, is still not fully understood. Understanding the spin coupling between not only the irons but also molybdenum and irons will be an important topic of future studies. Similarly, understanding the effect of the interstitial carbon atom on the electronic structure remains an open question.

## 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.

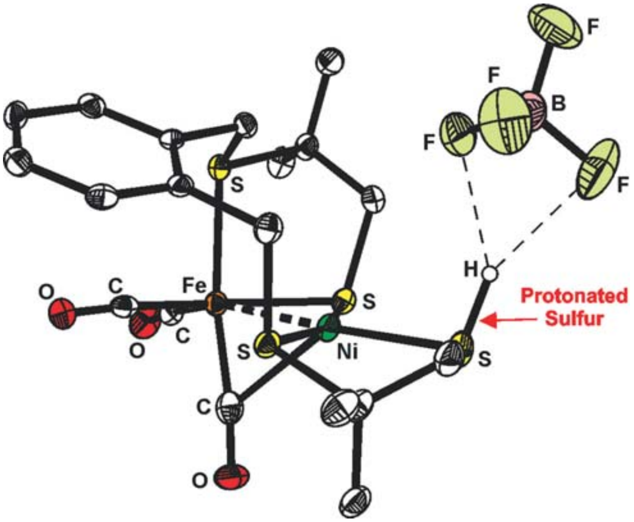

**Figure 4.** X-ray structure of a heterobinuclear iron-nickel hydrogenase model complex. The structure clearly shows that a coordinating thiolate has been protonated.

Figure 4 shows a crystal structure from a recent publication in which we studied protonation properties of hydrogenase model complexes.[5] Structures of both, unprotonated and protonated species could be determined and the protonation site could be clearly located.

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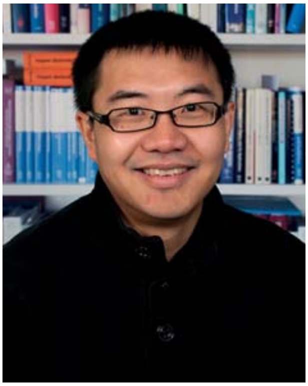

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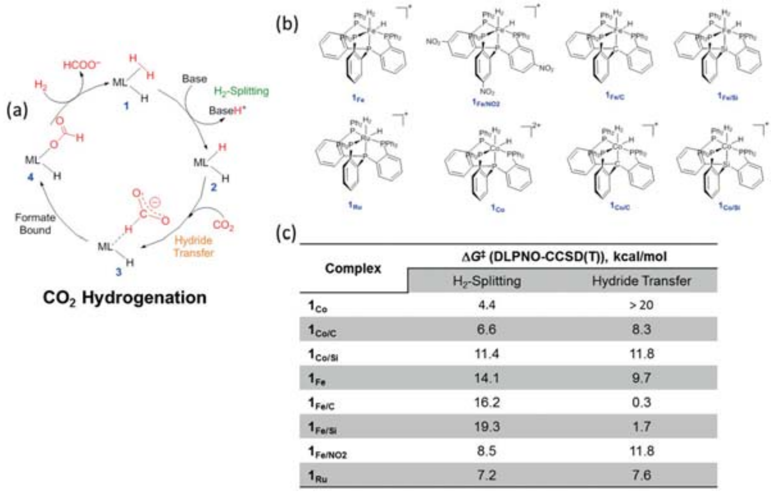
# $CO_2$ Activation

Conversion of carbon dioxide into liquid fuels and useful chemicals has been the focus of energy research in recent decades. However, the transformation is challenging due to the high thermodynamic stability and kinetic inertness of $CO_2$;[1] efficient catalysts are thus highly desired. To date, noble metals such as Ru, Rh and Ir have been extensively employed in this field, whereas only a handful of base-metal catalysts have been developed. Our main goal of this project is to understand $CO_2$ reduction mechanism and provide new ideas for designing more efficient 3d transition metal catalysts. We presently focus on the C1 chemistry of $CO_2$ functionalization, namely, $CO_2$ hydrogenation to formate and $CO_2$ reduction to CO.

## $CO_2$ hydrogenation to formate

$CO_2$ hydrogenation to formate or formic acid involves two key reaction steps, viz. base-promoted $H_2$-splitting (**1** → **2**) and hydride transfer (**2** → **3**) to $CO_2$ (Figure 1a), either of which can be the rate-determining step (RDS) of the overall catalytic cycle. We carried out a comparative mechanistic study on the reactivity of $\mathbf{1}_{Fe}$, $\mathbf{1}_{Co}$ and $\mathbf{1}_{Ru}$ (Figure 1b), and proposed that the hydride donation ability or the hydricity of the dihydride species (**2**) can dictate the nature of the RDS and even modulate the RDS barriers.[2] Recently, following this notion, a series of potential catalysts with differential hydricity have been designed. We computationally evaluated their catalytic activity, and the results nicely verified our catalyst-design strategy. Specifically, enhancing the electron-donating power of high-hydricity catalyst lowers the barrier for the hydride-transfer RDS step ($\mathbf{1}_{Co}$ vs. $\mathbf{1}_{Co/C}$ and $\mathbf{1}_{Co/Si}$) (Table 1c). Conversely, the same modification leads to even greater barrier for the $H_2$-splitting RDS for low-hydricty catalyst ($\mathbf{1}_{Fe}$ vs. $\mathbf{1}_{Fe/C}$ and $\mathbf{1}_{Fe/Si}$).[3]



| Complex | ΔG‡ (DLPNO-CCSD(T)), kcal/mol | |
|---|---|---|
| | $H_2$-Splitting | Hydride Transfer |
| $1_{Co}$ | 4.4 | > 20 |
| $1_{Co/C}$ | 6.6 | 8.3 |
| $1_{Co/Si}$ | 11.4 | 11.8 |
| $1_{Fe}$ | 14.1 | 9.7 |
| $1_{Fe/C}$ | 16.2 | 0.3 |
| $1_{Fe/Si}$ | 19.3 | 1.7 |
| $1_{FeNO2}$ | 8.5 | 11.8 |
| $1_{Ru}$ | 7.2 | 7.6 |

**Figure 1**. Catalytic $CO_2$ hydrogenation to formate.

### $CO_2$ reduction to CO

Reduction of $CO_2$ to CO by low-valent metals typically entails $CO_2$ coordination and subsequent C–O bond cleavage. Our earlier work demonstrates that $CO_2$ binding to $[Ni(cyclam)]^+$ only cause a partial electron transfer from $Ni^+$ to $CO_2$, and the second electron transfer has to be achieved via an outer-sphere mechanism (Figure 2a).[4] This reflects the inability of a single metal center to accommodate two readily accessible reducing equivalents, especially for 3d transition metals, which ultimately decreases the catalytic activity. Our recent study on $CO_2$ reductive disproportionation (Figure 2b) suggests that the reaction follows a similar mechanism as that found for $[Ni(cyclam)]^+$, in which Co(I) serves as the electron donor, and then the resulting oxidized metal center act as a Lewis acid to facilitate the second electron transfer from another Co(I) fragment to $CO_2$. Alternatively, non-innocent ligands may function as more flexible and accessible electron reservoirs, because redox processes occurring on conjugated macrocyclic rings are likely to suffer from less reorganization energies than metal-centered redox events.[5] Thus we turned our attention to $CO_2$ reduction mediated by a formal Fe(0)-porphyrin complex (Figure 2c). Our preliminary work shows that the catalytically active Fe(0) species is best formulated as a Fe(II) chelated by a porphyrin tetra-anionic diradical ligand. More importantly, during the reaction the physical oxidation state of the iron center remains unchanged.

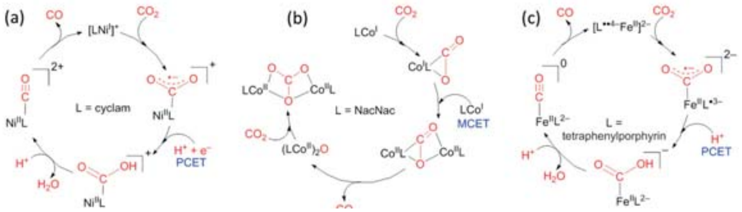


**Figure 2**. Catalytic $CO_2$ reduction to CO.

# $O_2$ Activation

In biology, nature utilizes a range of heme and nonheme iron enzymes to functionalize substrate C-H bond coupled with $O_2$ activation. The C–H cleaving agent has been experimentally identified as high-valent oxo-iron(IV) intermediates. To date, over fifty ferryl model complexes has been reported, and the majority of them possess a triplet ground state with an electron configuration of $(d_{xy})^2(\pi^*\text{-}d_{xz/yz})^2(\sigma^*\text{-}d_{x^2-y^2})^0(\sigma^*\text{-}d_{z^2})^0$. In collaboration with Profs. Larry Que (University of Minnesota) and Franc Meyer (University of Göttingen), Dr. Bill's and my group undertook a detailed study on the electronic structures of S = 1 oxo-iron(IV) species using magnetic circular dichroism (MCD) spectroscopy. Based on the independent determination of MCD signs and wavefunction based ab initio calculations, we could unequivocally assign the key ligand field features for $[(\text{SR-TPA})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$ (SR-TPA = tris(3,5-dimethyl-4-methoxypyridyl-2-methy) amine)[6] and $[(\text{L}^{\text{NHC}})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$ ($\text{L}^{\text{NHC}}$ = 3,9,14,20-tetraaza-1,6,12,17- tetraazonia-penta-cyclohexacosane-1(23),4,6(26),10,12(25),15,17(24),21-octaene) (Figure 3).[7] Specifically, the excitations ($d_{xy} \rightarrow d_{xz/yz}$ and $d_{xz/yz} \rightarrow d_{z^2}$ ) within the $(\text{FeO})^{2+}$ core of both complexes have similar transition energies, whereas the excitation energy for $d_{xz/yz} \rightarrow d_{x^2-y^2}$ is significantly lower for $[(\text{SR-TPA})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$ (12 000 $\text{cm}^{-1}$) than that observed for $[(\text{L}^{\text{NHC}})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$ (24 300 $\text{cm}^{-1}$). Therefore, in contrast to the classical electron configuration found for the majority of ferryl complexes such as $[(\text{SR-TPA})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$, $[(\text{L}^{\text{NHC}})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$ features a distinct electron configuration of $(d_{xy})^2(\pi^*\ d_{xz/yz})^2(\ ^*\text{-}d_{z^2})^0(\sigma^*\text{-}d_{x^2-y^2})^0$ with the $d_{x^2-y^2}$ orbital lying higher in energy than $d_{z^2}$. This subtle difference in the electronic structures of $[(\text{L}^{\text{NHC}})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$, in fact, results in a decisive consequence to its reactivity. Classical ferryl model compounds typically follow a mechanistic scenario of two-state reactivity for C-H bond activation. They usually have a low-lying quintet state (~3 kcal/mol) with an electron configuration of $(d_{xy})^1(\pi^*\text{-}d_{xz/yz})^2(\sigma^*\text{-}d_{x^2-y^2})^1(\sigma^*\text{-}d_{z^2})^0$, and the quintet $\sigma$-pathway involves a much lower barrier than that for the triplet $\pi$-channel, the system hence first undergoes a spin-crossover to the quintet state and the subsequent C-H bond cleavage process takes place on the quintet surface. In contrast, a significantly greater quintet-triplet energy separation (18.2 kcal/mol) is found for $[(\text{L}^{\text{NHC}})\text{Fe}^{\text{IV}}(\text{O})(\text{MeCN})]^{2+}$, due to a different electron configuration ($(d_{xy})^1(\pi^*\text{-}d_{xz/yz})^2(\sigma^*\text{-}d_{z^2})^1(\sigma^*\text{-}d_{x^2-y^2})^0$) for the lowest-energy quintet state. Thus, the entire reaction is likely to exclusively occur on the triplet surface, viz. single-state reactivity (Figure 3d). Our calculated barrier for the rate-determining step of H-atom transfer (14.4 kcal/mol) matches the experimental kinetic data ($\Delta G^{\ddagger}$ (20° C) = 15.2 kcal/mol) very well, lending further credence to our proposed electronic structure.

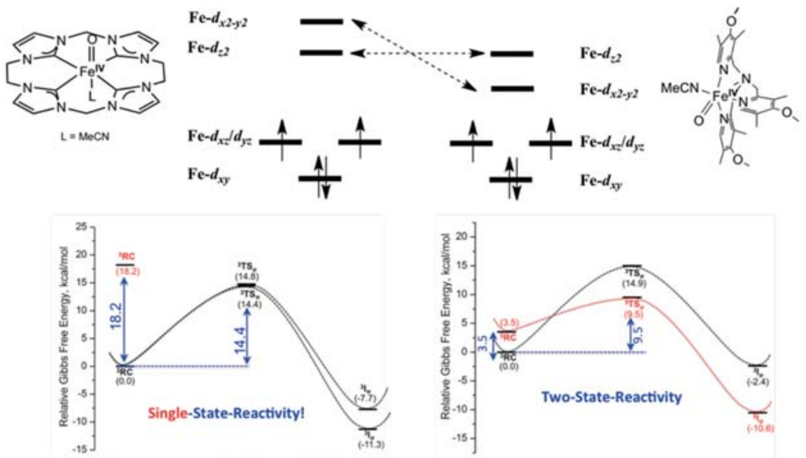


**Figure 3.** Comparison of classical and non-classical triplet Fe$^{IV}$(O) model complexes.

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# Department of Heterogeneous Reactions

The Department is a fractional activity at MPI CEC. This follows from the function of RS as Founding Director with the clear mission to move out of the Institute once the foundation process is stable. The purpose of the activity is to prepare the infrastructure and to introduce concepts of interfacial catalysis until the regular Department working in this area can be installed. The fractional activity is thus connected back to the FHI part of the Department and concentrates on generic aspects of interfacial catalysis relevant for energy applications.

## General Concept of Work

We consider interfacial catalysis as a system[1] of elementary reactions with the catalyst consisting of a matrix on which several types of sites exist. The matrix supports deliberately deposited or segregated nanostructures that form interfaces to the matrix. The result is a spatially heterogeneous interface to the reactants. In addition, the sites behave under performance conditions dynamical. This means that their structure is not stable in time but fluctuates around an average structure. The driving force for the fluctuation is a kinetically hindered phase transition triggered by the chemical potential of the mixture of reactants and products. The process of formation of this system is called activation and involves reactant components that react with the matrix and/or the deposited pre-catalyst. This general concept was found to be applicable to chemo-catalysts as well as to electro-catalysts.

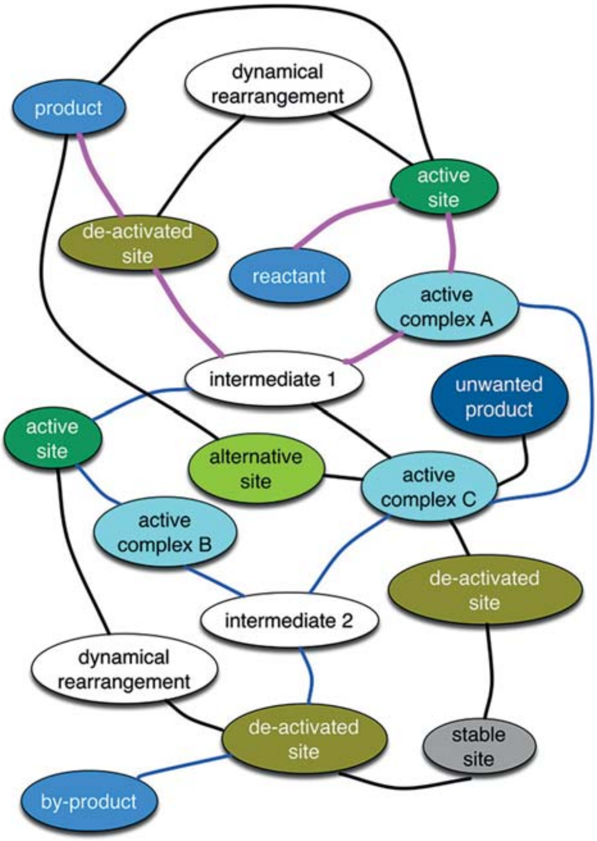

**Figure 1.** Catalytic systems are entangled net-works of elementary reactions. Relevant is structural dynamics as universal concept to ascertain a global cyclic operation.

The complete catalysis system is composed of two reaction networks: one deals with the chemical and structural dynamics of the active sites going through cycles of activation by dynamical restructuring, formation of complex with reactants, reaction between reactants leading to deactivation of the active site and dynamical restructuring leading to desorption of products. The other reaction network describes the transformation of the reactants. The operation of a catalytic process is determined by the convolution of the reaction pathways to product(s) (red), their byproduct(s) (blue), and unwanted side product(s) as shown in Figure 1.

If one wishes to optimize the selectivity or activity of such a system one seeks control over the chemical and structural details of the active sites in space and time. We usually have conceptual ideas about the reaction network of the reactants ("mechanism") but we lack insight into the material aspects of the active sites and into their structural dynamics. From a now broadly rolled out theory on catalytic processes using the Broensted-Evans-Polany (BEP) relation and deriving scaling relations for reactions, we understand that a catalyst with a single type of sites cannot be optimized for a process shown in Figure 1. The reason is shown in Figure 2. As a rigid relation exists between the chemical bonding of all intermediates to a given site, it is the undesired consequence that, if we change the interaction energy of one elementary step in the desired reaction, we automatically adjust all other interactions energies simultaneously. The Department seeks to find generic ways how to describe this systemic situation and find methods of breaking the undesired situation shown in Figure 2.

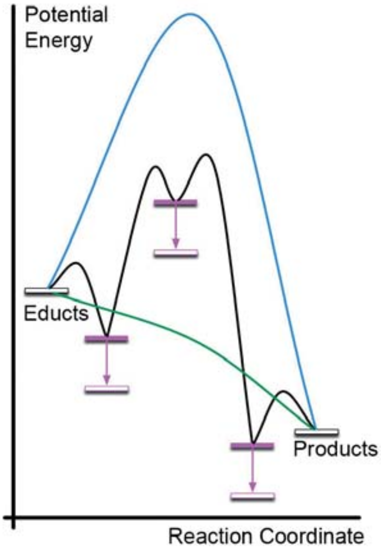

**Figure 2.** Simplified profile of an uncatalyzed reaction (blue), a catalyzed reaction with a single intermediate (black) and the spontaneous reaction as the best possible pathway. The red arrows indicate the consequence of modifying the properties of the catalytic sites for the highest energy barrier.

### Organization of the Department

The descriptive part requires functional analysis of a working system in the essential multi-scale regimes. To this end the Department has developed a suite of competencies and technologies over the past 20 years[3]. Figure 3 shows the organization of the work in the Department. The scientific projects are collaborations between members of the competence teams. In the context of the work at MPI CEC and in accordance with the general theme of the Neese Department we focused in the past years on electrochemical water splitting[4], on $CO_2$ hydrogenation to methanol and on ammonia synthesis[5].

In addition, the Department was active in creating collaborative projects allowing for outreach into the scientific community and to knowledge transfer into technological applications. The project MANGAN aims at a rational identification of the potential of manganese compounds in water splitting. Here we augment the experimental work by the development of a test protocol to generate a database of performance indicators that can be compared with known confidence between all partners. The MAXNET Energy aims at focusing the potential of interested other MPI in developing, testing and understanding the function of a broad array of electrode materials[6] for water splitting. After building the community we now focus on building a MAXNET cell with a set of materials all stemming from the consortium in order to rigorously understand their systemic interplay based upon full control of their individual genesis and performance.

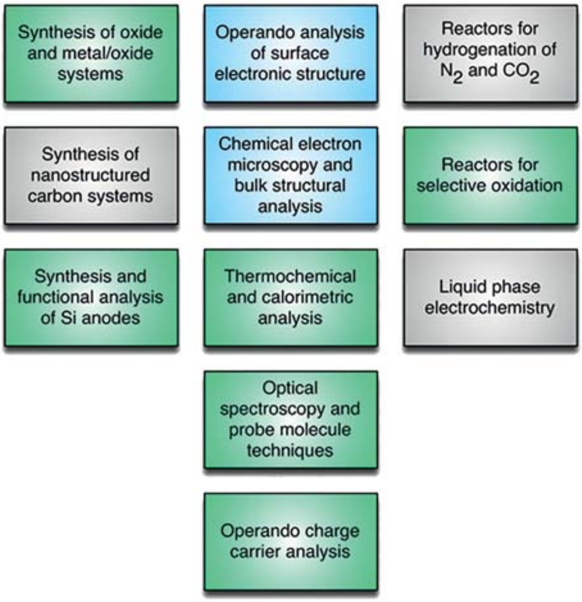

**Figure 3.** Structure of the Department. Activities are in MPI CEC (grey) in transition from FHI to MPI CEC (blue) and at FHI Berlin (green).

The project CARBON2CHEM (C2C) is a large national activity trying to create a network of catalytic systems with the aim to convert $CO_2$ from the Duisburg steel mill of thyssenkrupp with green hydrogen into useful chemicals with several outlets into materials, intermediates and transportation fuels. The Department is involved in this demanding project in several roles ranging from overall design, to the critical analysis of the raw gas streams with innovative technologies, to developing operation protocols for the methanol synthesis plants and to support partners with high-end functional analysis.

The innovative design part of the work in our Department seeks to decouple the interaction of reactants and intermediates with the active site. In order to overcome the universality of bonding interaction of the relevant non-hydrogen small molecules and fragments with solid interfaces we follow two avenues.

One is to modify the geometry of interaction for different molecular entities by confining the space of interaction. This is a very demanding challenge, as we need not to overlook the multi-scale nature of catalysis on one side and the requirement of chemical dynamics of the catalytic material on the other side. These conditions limit the choice of options and make us understand concepts realized in enzymes with their flexible cavities for locating active sites. We intend to work in this area using single atom catalysts with modified local environments. In oxides we found such a case with Mo/$SiO_2$ that is only active in frustrated local geometry[7]. The absolute prerequisite for such studies is detailed knowledge of the molecular electronic structure. Here we collaborate with the Theory Department[8] using VxOy and IrxOy as systems of joint interest. We further collaborate with Cardiff University (MAXNET) where we started a study into the possibility of single gold atom catalysis that is often advocated but for which only limited evidence exists. In the process of studying the synergy of Cu with Ag in oxygen activation[9] we discovered the possibility to dissolve individual atoms (of Cu) in a metal matrix (Ag) and found unexpectedly a unique novel electronic structure of such a system that we exploit presently as model catalyst. In conjunction to this we study with Cardiff the potential of individual atoms[10] on carbon supports. We also expand the synthetic possibilities by depositing individual transition metal atoms[11] (Mn, V) on carbon and test them in selective oxidation reactions.

The other option is to create a dual-site situation: on a matrix the restructured surface of which presenting one active site, we deposit or segregate another chemical compound in 2-dimensional form. Between the two phases we need a semiconducting interface[12] and laterally we need a patchy morphology creating a long perimeter line where we would localize the active sites. This concept of self-supported segregated systems was found in several cases of performance selective oxidation catalysts[13]. It is studied prominently in the FHI branch in the context of BASCAT ( a collaborative long-term project with BASF and the cluster of Excellence at TU Berlin). In the context of MPI CEC we study the systems Cu-ZnO[2, 14], the systems Fe-MxOy and the system carbon–functional group[11, 15] oxides.

### Selected Results

In the following we illustrate the mode of operation of the Department by collecting results relevant for the ongoing discussions in the chemical energy science community. Within the examples we present only part of the evidence for the sake of conciseness. More details can be found in the literature and in the reports of the working groups.

### Working structure of $IrO_2$ during oxygen evolution

Electrolytic oxygen evolution in acid media is energy-efficient and forms the basis of PEM electrolysis being capable of using volatile electricity. This variant of electrolysis is thus of importance for chemical energy conversion and has reached technological maturity. The only really working catalyst for oxygen evolution (OER) as yet is $IrO_2$, a very scarce material even when only small amounts are required. This is seen as a bottleneck for the technology and multiple attempts are made to replace the material; massive stability problems impede progress so far. Substantial efforts are ongoing[4a] in the literature in order to understand its function as prerequisite for a rational replacement strategy. We chose an in-situ approach making use of the developments at BESSY for in-situ photoelectron spectroscopy (see below) and applying in-situ RAMAN spectroscopy connected to theoretical support from the Neese group[16] (M. van Gastel) and our own capacity (T. Jones). The experiments were conducted in the Knop-Gericke group, key investigators were V. Pfeifer and M. Hävecker. V. Velez developed the flow-through cell with in-situ XPS observation capacity.

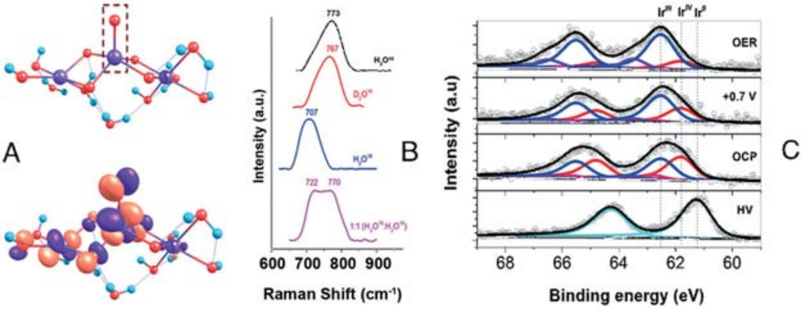

**Figure 4.** In situ experimentation on IrO2 during OER. (A) Molecular model of the oxyl local structure of an active site. (B) Response of the oxyl feature in (A) to isotope labeling reveling its mono-oxo nature. (C) series of Ir 4f spectra of an Ir/C electrode made from 5 nm Ir structures in flowing 0.05 m H2SO4 at various potentials indicated.

We discovered with our presently uni-que in-situ photoemission experiment[17] that the active state of $IrO_2$ under steady-state OER condition[18] is an oxy-hydroxide with an average oxidation state of close to 3. We found unambiguous evidence[19] for the presence of oxyl species forming spontaneously during synthesis of the oxide by precipitation from a chloride precursor leading to redox disproportionation. The final confirmation for the low oxidation state of Ir comes from a steady-state in-situ observation presented in Figure 4 C. The unusual fact that a lower oxidation state creates a higher binding energy in photoemission was clearly explained in the reference experiment[20]. Together with the isotope exchange experiments shown (Ch. Ranjan) and the theoretical modeling of the position of the stretching vibration of Ir-O species (M. van Gastel) we confirm the existence of the oxyl species that was also evidenced by its amazing oxidizing capacity leading to full conversion of CO to $CO_2$ at ambient temperature[19]. The model shown in Figure 4 is a closer description of the active OER state than the previously used rutile $IrO_2$ structure. It is remarkable that this compound forms spontaneously oxyl not only at the surface but also as bulk defect. The tendency to auto-reduce is in line with general trends of chemistry in the periodic table and can be explained by the unusual electronic structure of $IrO_2$ with almost no HOMO-LUMO splitting in the tetravalent state causing also the record-low binding energy of Ir-O of about 100 kJ/mol. The formation of a trivalent state significantly increases the HOMO-LUMO splitting. Ongoing work uses grazing incidence in-situ X-ray diffraction and all methods of chemical electron microscopy to elucidate the mesoscopic structure of this clearly non-dense oxy-hydroxide. The aim is to provide a safe basis for mechanistic discussions and to find a lead structure for working OER catalysts.

### Carbon as electrode in OER

Elemental carbon in sp2 configuration is a semi-metal. Along the basal planes of graphene layers we observe high electronic conductivity. At the edge sites or at point defects the termination of the sp2 structure creates a covalent bond to heteroatoms. If this is hydrogen the edge is chemically sealed. If it is oxygen or nitrogen we can use it for chemical reactions such as water dissociation and oxygen oxidation. This is illustrated with fundamental experiments shown in Figure 5 A and B. The che-mical anisotropy is expected but unusual. S. Buller coordinates the work performed in the project. Her team collaborates with Y. Yi and the electrochemistry experts, with the Ruhr University Bochum (RUB) for the plasma modification and with Forschungszentrum Jülich (R. Eichel) for NMR analysis.

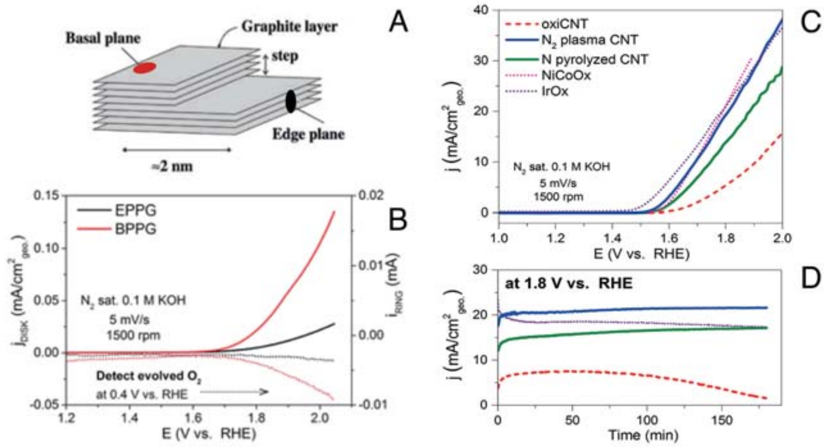

**Figure 5.** Carbon in OER. (A) chemical anisotropy of graphite, (B) seen in OER performance detected as RRDE experiment. (C) oxidized and post oxidation nitride MWCNT in OER against IrO2 and NiCoOx as metal oxide benchmarks. (D) same.

Here we realize in molecular dimensions the concept of a metallic matrix (red dot in Figure 5 A) with a semiconducting overlayer (black dot in Figure 5 A). The stability of the sp2 bond in carbon creates a high kinetic barrier at room temperature for its combustion, which would be the thermodynamically much preferred reaction over the desired water oxide oxidation. Care is taken in all experiments to determine the loss of current to carbon oxidation, which can be limited to few% Faradaic efficiency. The successful synthesis of such very cheap, metal-free and abundant electrode material requires careful optimization of reactivity towards water and stability against oxidation through the intermediate $\{O\text{-}O\}^{n-}$ species. We use a dual strategy; one avenue starting from *de novo* synthesis of carbon by hydrothermal condensation[21] of biomass (glucose as model) whereas the other starts from pre-fabricated carbon nanotubes[11, 22] (MWCNT) as matrix. Our work focuses mainly on an effective modification of the semiconducting edge sites. We found that a combined chemical etching for producing a stable interface followed by nitrogen functionalization with either N-oligomers or by various plasma treatments is a productive way to achieve performance data quite comparable with technically used oxide electrodes as demonstrated in Figure 5. Comparing Figures 5 B and C allows realizing the improvement in performance of two orders of magnitude coming from our targeted chemical functionalization. We have now a platform for further optimization of the reactive structure by using concepts from organic chemistry about carbon-nitrogen bonding and about stabilization of free radical structures[23] on carbon. A branch of this work allows us targeted fixation of single metal atoms on a conducting non-metal support. We can predetermine local environments such as curved carbon sheets or etched cavities in which we deposit individual atoms by ALD on controlled functional groups. A practical outlet of this work could be a material concept of using green carbon sources to produce catalytically sacrificial OER electrodes (such as used in aluminum production) without adding to the $CO_2$ emission footprint.

### Ammonia Synthesis over Iron-based Nanostructures

This project is performed in collaboration with the DeBeer group and with M. Behrens from the University Duisburg-Essen. K. Kähler is the responsible coordinator.  H. Fang at FHI synthesizes the nano sheets. The purpose of this only seemingly old-fashioned project is to unravel the true material disposition of the working ammonia catalyst as a basis to apply the general concept of the Department. We know since long that iron is the core component for ammonia synthesis but that some still unknown modification is essential for the function. It is argued that this modification is purely geometric and concerns maximization of monoatomic steps. There is, however the unusual property of ammonia iron to be resistant against the thermodynamically expected[24] nitride formation. In addition it is very hard to obtain sustained catalytic activity from any pure iron nanostructure as very rapid restructuring into bulk alpha iron occurs, being fully inactive. This is much at variance with the long lifetime of technical catalyst of about 2500 days. The archaic synthesis procedure is adverse to study and to controlled modification of the iron material. We thus develop two avenues of green synthesis of potent iron catalysts and study their structure under in-situ conditions. Here we profit much from the expertise of the DeBeer group in iron and nitrogen spectroscopy. The synthesis control allows further unraveling the complex mode of operation of the additive packages added to the technical catalyst and discriminating their roles as structural or electronic promoters.

We concentrate on the task to generate meaningful kinetic data suitable for modeling and thus being free form oxygen poisoning. The activation period of these catalysts is absolutely critical and needs special optimization for each system tested. In addition we achieved the possibility to isolate the used catalysts and subject them to microscopic study being a difficult task with pyrophoric nanostructures.

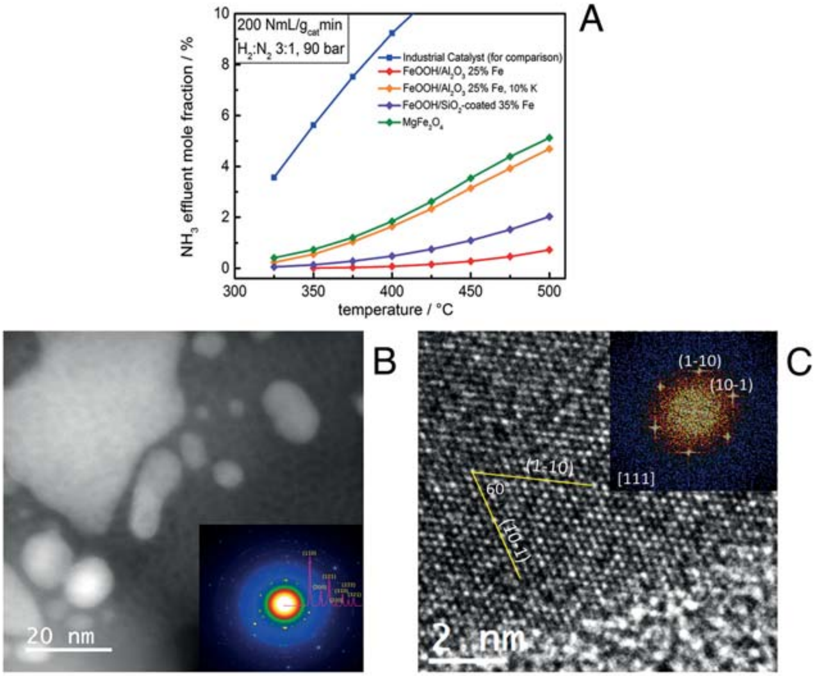

**Figure 6.** Nano iron in ammonia synthesis. (A) Performance of several nanostructures in comparison with a technical optimized system. 1g catalyst is used in each experiment. (B,C) ABF STEM and HR-TEM of iron nano sheets that were supported on silica by a co-generation procedure. The metallic iron phase is clearly identified together with its orientation exposing the (111) facet. Note the atomic resolution of metallic iron after transfer from the reactor.

The first task was to find synthesis pathways that would result in catalysts of a comparable activity than an industrial benchmark catalyst. There is a large multitude of catalysts described in the literature but very few of them that do not arise from a melting process, reach activity and stability compatible with the technical system. Such performance is essential to be sure to study the steady state structural details of the working system and not a transformation being related to activation or deactivation of the catalyst that requires easily several hundred h time on stream. In Figure 6 we show performance data and selected structural details of one of the systems. The comparison is highly conservative as we use the same amount of catalyst for the experiments and not the same amount of iron or the same amount of iron surface area. These quantities are hard to determine prompting us for now to stay with this conservative approach. We started from iron metal nano-sheets that are inactive in unsupported form as they immediately restructure into iron cubes. Upon supporting them on alumina or silica we obtain stable performance.  Alternatively, we use the LDH approach for generating an iron-MgO system from re-structuring of homogeneous precursors rather than from impregnation iron onto MgO.

In both cases we obtain iron metal with a large interface to the support structure. The activation for ammonia synthesis must create enormous dynamical movements of the iron as the well-developed homogeneous interface is complete re-structured in the working state. Figure 6 reveals the patchy nature of metallic iron on the supporting oxide. The high-resolution image shows that a thin sheet is bound to the support. The complex phase contrast occurs either due to interference with the support and/or designates that we see overgrown support. The shape of the activity-time curves are indicative of the latter as they show a progressing activation with temperature possibly caused by the reductive atmosphere liberating iron sites with increasing dynamics of the oxide over layer. Preliminary results from probe molecule spectroscopy with CO point in this direction. We see significant catalytic activity although the iron is neither massive nor consists of many step structures.

One sees from the performance data in Figure 6 that promotion by K, as $K_2CO_3$, is a potent means to activate the system. The loading is not yet optimized as the support is also reacting with the promoter, which will require measures to first suppress this reaction with still studied effects on the iron-support interaction. In this respect the ex-LDH approach is more convenient, as we obtain high performance without additional promotion. The microstructure is, however, much more involved and makes thus the derivation of causal structure-function relations more difficult. What can be said clearly is that "iron metal" can be quite different in ammonia synthesis. It is obvious that not the bulk material itself but rather a real structure derived from the bulk metal is responsible for the catalytic function.

### Deactivation of Cu/ZnO in $CO_2$ Reduction

The chemical reduction of $CO_2$ is a key reaction in chemical energy conversion. The technical synthesis of methanol with interfacial Cu/ZnO systems is a well-developed process operating originally with a mixture of CO and $CO_2$. As we know that $CO_2$ is the precursor to the methanol molecule[25] it is logical to extend the reaction to pure $CO_2$ in hydrogen. In contrast to reports in the literature this is quite possible by using the technical promoted Cu/ZnO system.

Studying the deactivation processes is of practical relevance. Here, however, we use the long-term observation of performance coupled to in-depth analysis, to disentangle the role of the ZnO component. The synergy between the two compounds namely metallic Cu and oxidic Zn is a puzzle since decades and still creates debates between friends of a surface alloy and those of a metal-oxide interface as explanation. We consider the resolution of this issue as landmark in understanding industrial catalysis.

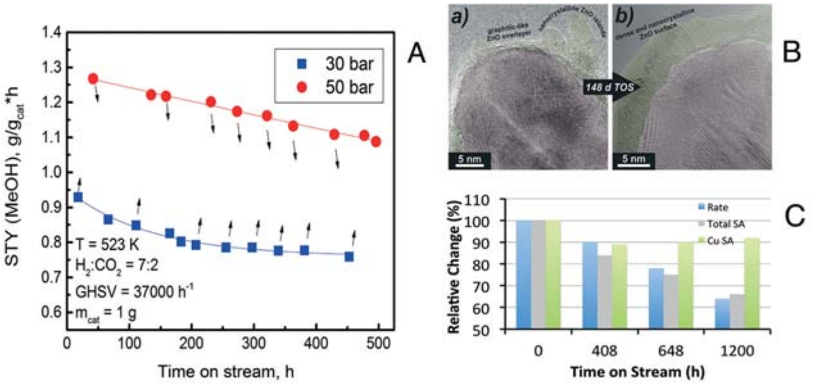

**Figure 7.** Cu/ZnO (Al doped) in MeOH synthesis. (A) performance during frequent change of total pressure (arrows indicate direction). (B) HR-TEM images of a catalyst sample of the same material than used for (A) kept in a dedicated TEM microreactor at 30 bar for up to 148 days being inspected by the IL technique. (C) Summary of quantitative changes of synthesis rate at 60 bar, of the BET surface area and of the Cu surface area measured by low-T hydrogen chemisorption. [2]

The work is coordinated at CEC by K. Kähler and M. Bukhtiyarova who perform the demanding kinetic experiments. At FHI T. Lunkenbein works on dynamical electron microscopy, the group of A. Trunschke is working on probe molecule spectroscopy and in the group of S. Cap we study the semiconducting properties of the working catalyst. We know that ZnO overgrows Cu in the finale phase of the initial activation of the pre-catalyst. A modified Cu is necessary for fixing the overlayer that is limited in thickness to max 4 monolayers forming a hexagonal metastable phase with large amounts of defects enhancing the conductivity of the adlayer. In-situ probe molecule spectroscopy with CO together with the microscopy data and the quantification data of Cu and ZnO surface by specific adsorption with $H_2$ and $N_2O$[2] presented in Figure 7 (B) and (C) confirm that the ZnO is defective and that it is patchy giving rise to free Cu in contact with the overgrowth. Long-term deactivation reveals that the ZnO overgrowth is the critical part of the structure as it gradually becomes stable wurzite and grows into a static thick hull over the copper terminating its activity.

Here we asked the question how a repeated change in working conditions affects the stability and productivity of the catalyst. Such an operation could be part of a scheme of adaptive chemical energy conversion[5c] where more hydrogen is produced with excess green electricity and less hydrogen is used from a storage facility when green electricity is needed for other applications. The result in Figure 7 (A) shows that the repeated change in pressure does not harm the catalyst. The deactivation behavior is, however, different for high and low-pressure regimes. If we compare the observed behavior with the long term observation on the same catalyst[2] illustrated in Figure 7 (C) we conclude that sintering of Cu is a rapid phenomenon occurring also at low hydrogen pressure whereas the high-performance conditions seem to continuously destroy the ZnO in its defective form leading to stoichiometric and thick overgrowth illustrated in Figure 7 (B).

The collection of results indicated here prompt us to believe that the working state of the Cu/ZnO system is indeed a metal/oxide interface at least under performance conditions. Even if an alloy would be formed under low conversion conditions the substantial water partial pressure during $CO_2$ hydrogenation would rapidly destroy such an alloy and restore the metal-oxide interface.[26]

Next steps are the investigation of the chemical origin of the ZnO restructuring that we see presently in the water load[14], working as hydrothermal synthesis agent on the defective oxide. We further study the exact nature of Cu under water: we know from model experiments performed in the CP Department of the FHI by H.J. Freund that pure Cu metal does not wet with ZnO; consequently the copper seen in Figure 7 (B) cannot be pure Cu. We suspect that sub-surface oxygen is modifying the electronic structure. We characterized such species several times[27] in contexts of using Cu in selective oxidation.

### Methodical Developments

The Department sees a role in implementing research infrastructure into the MPI CEC that is suitable of coping with the dynamical nature of working catalysts. Setting up such an infrastructure as asset for the institute was part of foundation plan and led to the creation of several competence groups. Currently are under construction the groups for operando spectroscopy at BESSY and for operando microscopy pursuing chemical electron microscopy in the gas phase.

We also see it as important asset that the institute conducts high-level theory that we can use to extract structural information from spectroscopic evidence that we detected ex situ or in operando. Here we established a stable working relation with the Neese Department where we study oxides of vanadium and Ir in oxidation reactions. D. Manganas has spent a great effort on this subject resulting in several[8, 28] joint publications.

### Synchrotron spectroscopy

At BESSY, the Berlin synchrotron, we significantly contribute to shape the profile of the institution in the direction of chemical applications of synchrotron radiation in the low and tender energy range (0.1-8.0 keV). We join here forces with the DeBeer group establishing a dedicated operando XES instrument, leading us to concentrate on XAS and on photoemission as the key techniques. We abstain of using synchrotron scattering techniques for our purposes partly because so much beam time is already spent on these techniques by others and partly as bulk transformations of catalysts occur so slowly that they can also be followed with laboratory sources what we do extensively at FHI. A. Knop-Gericke coordinates the work with his team. M. Hävecker, R. Blume, E. Stotz, K. Skorupska and D. Teschner are mentioned by name. We further greatly profit from the extensive contributions of the workshops of the FHI led by P. Bischof and G. Heyne.

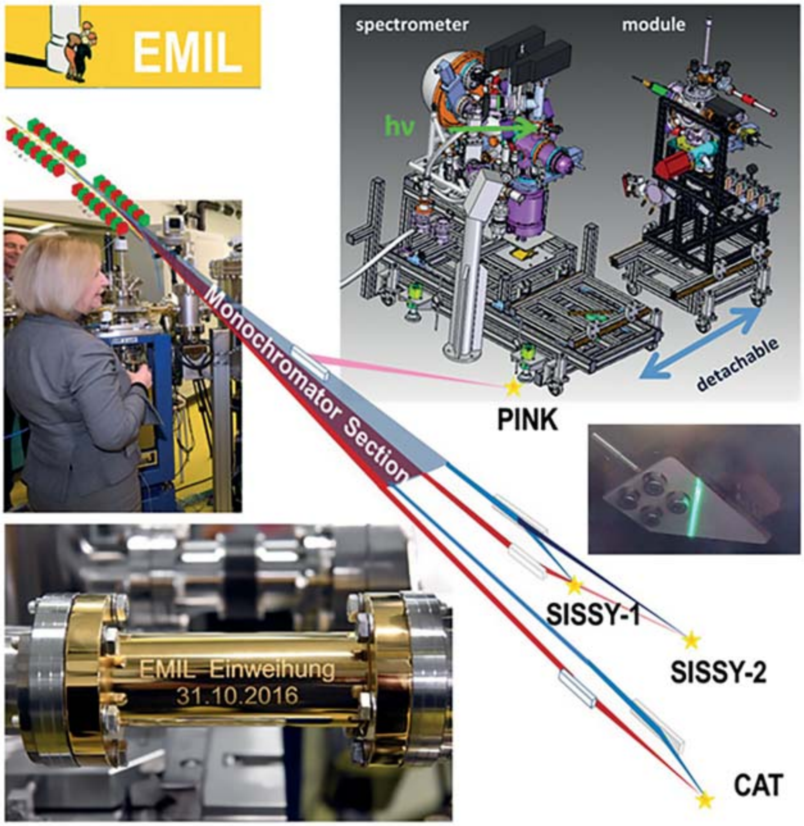

**Figure 8.** EMIL@BESSY. "PINK" and "CAT" are the MPI CEC instruments. The green line is "first synchrotron light" at EMIL (15.12.2016).

Besides our workhorse beamline ISSIS, we managed to create two larger infrastructure projects at BESSY over the past years. In the project EMIL that we operate jointly with the HZB from Helmholtz association we exploit photoemission at tender energies. The instrument CAT@EMIL is capable to operate catalysis reactor modules for gas phase and for electrochemical liquid phase processes in an energy range where we can exploit the variable kinetic energy as non-destructive depth profiling method to locate e.g. the Helmholtz layer above an electrode in electrolyte and can determine its composition under working conditions. Further we will be able to experimentally deduce information on orbital hybridization of a chemical bond from its cross section modulation with excitation energy, should the stability of the system allow for extended measurements. The EMIL project is a worldwide unique installation as it uses two undulators in the same straight section of a synchrotron to generate two X-ray beams at an angle allowing focusing both beams at the same spot. This gives us the capability for continuous scanning the energy over a record wide range. Two undulators and two types of monochromators are necessary to reach a constant performance in illumination and in energy resolution.

We were critically involved in design, setting up and constructing the technical infrastructure. In addition, we developed the endstation in a two-stage process in collaboration with SPECS. This instrument is working already. Finally we developed the concept of modular sample environments and created the flow-cell design and the high-pressure gas phase reaction cell. Both of these techniques rely on our insight and ability to work with defect-free graphene as window material. A longstanding activity stemming from several EU projects jointly with the university of Cambridge[29] is the scientific base for the technological development. We obtained several first results[30] and are in the process of making the techniques safe enough for a more routine use. The hardware of the EMIL experiments is still under construction and was officially inaugurated with the German Minister of Science in October 2016. This system of beamlines also supports the PINK experiment of the DeBeer group that is presently under construction. First synchrotron light was obtained at Dec. 15, 2016.

Our second large project is the creation of an extended version of our overbooked ISSIS beamline. By using an undulator belonging previously to the FHI and by activating a non-used bending magnet port, we construct in collaboration with HZB the BELCAT laboratory for operando catalysis science. The CEC supports this with 4 permanent scientist positions, with the infrastructure for doing chemical experiments safely at a synchrotron and with 2 of the 3 necessary experiment end stations. In addition we transfer the know-how and construction details of our modules to the user environment group of HZB to make this technology available to the general users of BESSY and to all users of BELCHEM. This is a major service to the international community that is heavily interested in access to this infrastructure. The status is, that we signed the contractual work and that the design of the necessary hardware has begun. We profit here from re-using the development parts that were necessary for creating the CAT@EMIL endstation.

### Operando microscopy

The MPI CEC in the context of its building extensions will obtain a center for chemical electron microscopy[3] specializing on operando microscopy. In preparation of this mission we develop several microscopy techniques putting us in a position to routinely perform operando microscopy. This development is largely done at FHI and involves a series of development contracts with the microscope vendor FEI in order to make our techniques available in a professional form. This collaboration puts us in the position to modify the hardware of microscopes, which is today impossible without deep support form the manufacturer. We expect to be able to buy a dedicated chemical electron microscope with several techniques for operando experiments in about 2020, just in time to be deployed to our new microscopy building. We are currently already putting aside financial resources to be able to have the first of these commercial instruments at a significant discount due to our contributions.

Here we wish to report about a first activity to prepare suitable specimen for such operando observation. Interfacial catalysis is a multi-scale phenomenon as seen in the introduction to this chapter. Consequently we need to be able to image working catalysts at several length scales. We have developed a first version of a chemical scanning electron microscope[29] based upon an ESEM instrument that lets us see the progress of catalyst transformations at the meso-scale. For Cu as selective oxidation catalyst we discovered an intermediate phase[9] between CuO and $Cu_2O$ being intimately connected with the activity. Surface operando spectroscopy revealed that the active phase should be a defective form of $Cu_2O$ without delivering information about the long-range order. There are speculations about a $Cu_3O_4$ phase that could be our candidate for an active phase. It might also be, however, that just some locally defective phase of $Cu_2O$ forms the active phase being in transition to the stable CuO phase.

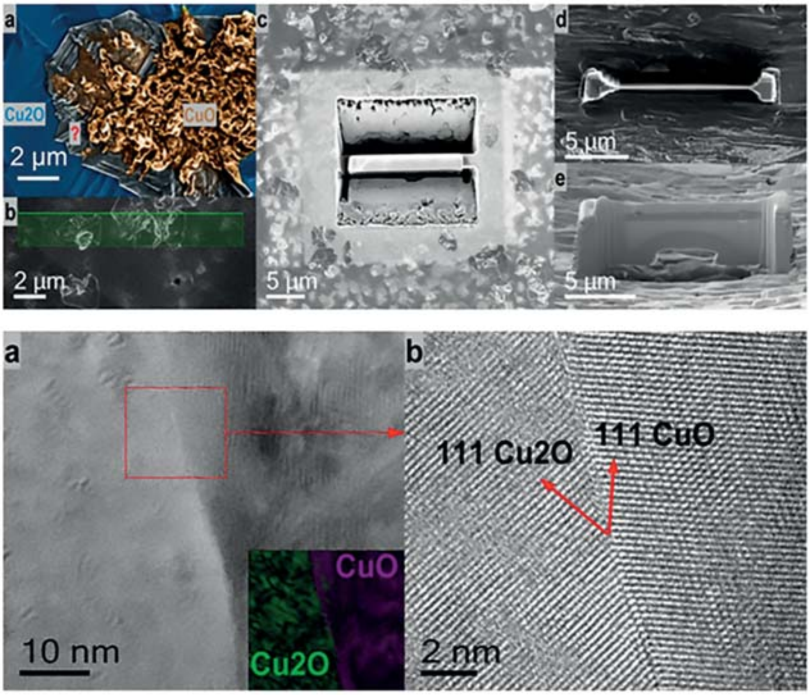

**Figure 9.** Chemical electron microscopy. Top: (a) transient phase between Cu2O and CuO synthesized during methanol oxidation in ESEM. (b) transfer and fixation of ROI by Pt overlayer (c) preparation of lamella by FIB. (d,e) top and side view of specimen before transfer to TEM. Bottom (a) Interface between Cu2O and unknown phase. From EELS and EDX it is CuO. Note the multiple defect contrasts in the Cu2O phase. (b) HR-TEM of the epitactic interface between defective Cu2O and well-ordered CuO. The interface is atomically sharp.

Such a proposition being in line with our general concept outlined at the beginning of this contribution requires inspection of the interface and the underlying bulk structure by microscopy as diffraction did not bring about more hints than distorted reflections of copper oxide.

Figure 9 reveals how we used target preparation of a reactive interface by an adapted FIB technique. Observation with HR-TEM clearly showed an atomically clean interface between CuO and $Cu_2O$ with no indications of an extra phase. The multiple indications of local defects in the $Cu_2O$ phase cannot be analyzed in detail as yet, as separation of preparation-induced defects from pre-existing defects is still ambiguous. We will be able to anneal such specimen under gas flow in the TEM and then verify the likely defective $Cu_2O$ phase as catalytically active material.

### Laboratory photoemission

Operando surface analysis can effectively only be performed at synchrotrons where the beam damage issue can be minimized by suitable fast scanning techniques. In many cases it would be most useful to know the steady state composition of dynamical catalyst such as “copper” under different situations of chemical potential without actually performing a reaction. Such data are not accessible at present outside of synchrotron experiments. We are now setting up laboratory instrumentation to deliver such information. We use the expertise from designing endstations at BESSY to build a modified version of that fitted with laboratory excitation sources for X-rays and UV-photons. This instrument under supervision of M. Greiner will be operational in 2017 and will be used first to study Cu in various chemical environments. Its high-performance capabilities make the instrument further ideal for trace analysis. This capacity will be applied in connection with the Carbon2Chem project where we look for particulate contaminants from the tail gas of the steel mill and we will study surface properties of particulate emissions from micro-plastics and from automotive vehicle traffic. We will further study strategies to measure frozen liquid samples of molecular catalysts supplied by MPI CEC and by MPI KOFO. All these activities are expected to support and enhance the productivity of the BESSY activities. In addition, they will broaden our knowledge on transient and metastable materials be they thin films or particulate matter.

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# Carbon Synthesis and Applications

## 1.1 Introduction

The aim of our research is the knowledge-based development of advanced electrode materials consisting of a structured carbon backbone with specific functional groups that have the ability to anchor the catalytically active metal component and stabilize even small metal clusters. The work is focused on electrode materials for OER in water electrolysis. Furthermore, we develop concepts of functional carbon materials for battery applications and gas phase catalysis (e. g. ODH).

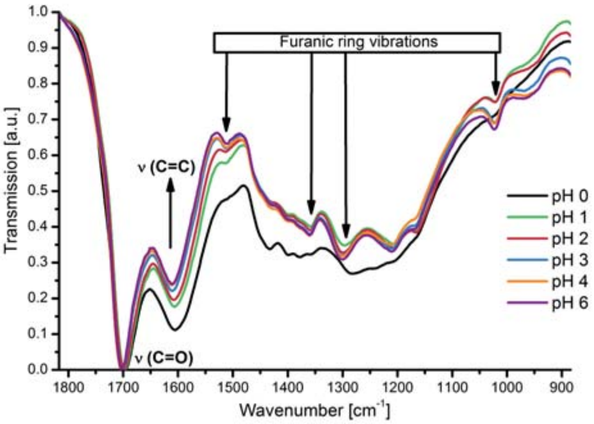

**Figure 1.** pH-dependent structural changes of HTC by FT-IR.

## 1.2 Functionalized Carbon Materials – Synthesis and Characterization

The carbon synthesis strategy of the group is based on the use of molecular precursors and controllable condensation reactions in liquid phase. The model precursor of this bottom-up approach is glucose. By hydrothermal treatment the glucose converts into carbonaceous materials highly functionalized by oxygen functional groups. The distribution of the oxygen functional groups, as well as the morphology of the carbonaceous product, is controlled by process parameters, in particular the pH.[1] For lower initial synthesis pH, i. e. pH 0, extended carbonaceous structures were confirmed by Raman spectroscopy, whereas for $pH > 3$ furanic structural entities from the 5-hydroxymethyl furfural intermediate remained the dominant structural motive of the carbon (Figure 1). The high number of functional groups leads to intrinsic binding properties that allow the preparation of functional disc electrodes by pressing and thermal annealing to 900° C. Hence, the general used concept of drop coated glassy carbon discs for electrochemical testing can be replaced by carbon based disc electrodes of controllable structure and functionalization. In the absence of Nafion, material-only properties can be studied for further fundamental understanding of electrochemical processes. The macroscopic dimension of the bulk electrode allows quantitative analytical investigations after electrochemical testing.

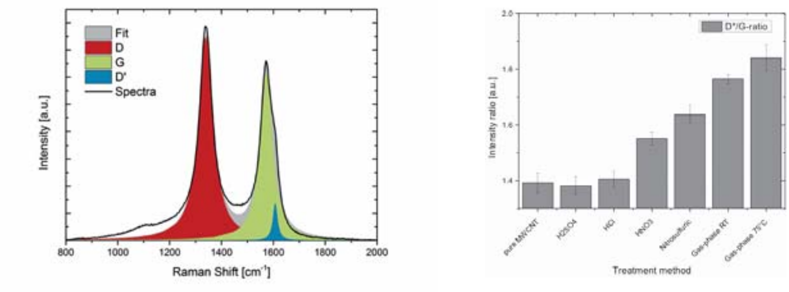

**Figure 2.** MWCNT Raman spectra fitted by theory based process (left). D*/G-ratio for different functionalization techniques. D* corresponds to sum of peak areas of D- and D -Bands (right).

For further variation of the functionalization i. a. nitrogen containing precursors are applied. The addition of urotropine to the glucose solution, yielded HTC materials with up to 19 wt% of nitrogen within the carbonaceous structure. The enhancement of the electron transfer processes could be approved by cyclic voltammetry measurements in $K_4[Fe(CN)_6]$ electrolyte. Post-functionalization techniques such as plasma treatment, electrochemical oxidation and (hydro) thermal treatments in active gases/solvents complete the methodical variety for the introduction of desired surface termination for the stabilization of catalysts.[2] In order to distinguish differently functionalized carbon materials by Raman spectroscopy, a fitting procedure was developed based on MWCNTs.[3] The theory derived fit resulted in accurate ratios of the ideal graphitic lattice vibrations (G-Band) and lattice vibrations induces by defects/functional groups (D- and D'-Band). Supported by further characterization techniques such as microscopy, XPS and thermal analysis the type and quantity of functionalization of graphitic carbon materials can be derived (Figure 2).

Profound characterization of the different functional groups was performed by thermal analysis. The implementation of a stepwise temperature program, divergent from the classical linear heating, allows the thermal separation due to different thermal stabilities of the functional groups. The assignment of the functional groups was confirmed by the detection of volatile $CO_2$ and CO gases, by chemical derivatization reactions as well by the reaction of specific groups with $H_2$ under the formation of water. This method enables a semi-quantitative analysis of oxygen functional groups in carbon structures as shown in Figure 3.

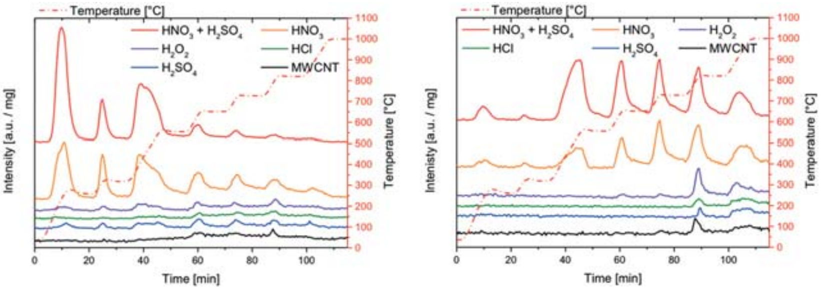

**Figure 3.** Thermal separation of decomposing functional groups in MWCNT by a stepwise temperature program. The influence of pre-treatment on the formation of specific functional groups can be observed.

### 1.3 Metal deposition

We further studied options of anchoring metals on structured carbon materials. We assume that for oxygen activation in the process of water splitting small cluster rather than single atoms are relevant for the active site.[4] A close contact of catalytic active species to electric conductive carbon support is essential for high activity and stability of the materials. Therefore we applied special methods to achieve different complexities of the deposited central atom. Single atoms, atom ensembles, cluster or solids correspond to a gradual increase of the complexity of the system. Techniques like atomic layer deposition (ALD), wet impregnation, application of ionic liquids and adsorption of colloids (Figure 4) were applied.

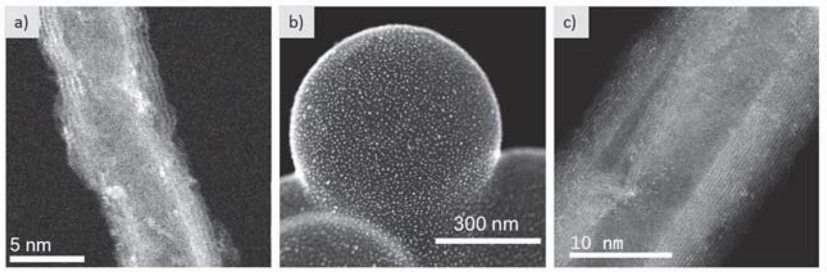

**Figure 4.** Manganese deposited on MWCNTs with (a) wet impregnation (b) colloidal Au on spherical HTC particles and (c) vanadium oxide on MWCNT by ALD technique.

We focused on deposition of manganese oxides to draw back on the expertise and methodical assembly developed for photosystem II (Department Lubitz, MPI CEC). We synthesized different pre-treated multi-walled carbon nano-tubes and studied the influence of functional groups and defects on the surface on the stability of the impregnated manganese oxides. In comparison to ALD deposition, it turned out that for wet impregnation rather defects in the structure have a stabilizing effect than the functional groups itself.[5]

The aforementioned thermal analysis enables the identification of reactive functional groups that are relevant for the ALD procedure. A precise process controlling is therefore possible, that ensures a self-limiting monolayer growth.

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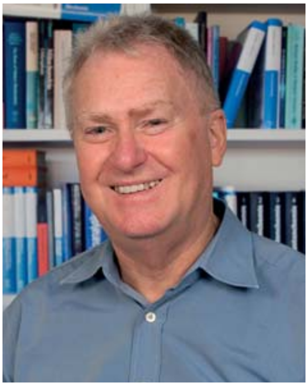

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## Introduction

Targets of our research are biological photoreceptors. For this, we have defined three mainlines: (i) searching for novel photoreceptors with so far unknown properties (genome mining approach), (ii) functional and structural characterization of novel light-activated proteins, and (iii) application of novel photoreceptors in microscopy and optogenetics. As a side-activity, DNA-repair enzymes from extremophiles are characterized (Ph.D. thesis Julian Simon); this part of our research on light as an energy source is a collaborative project with LIMLA, CONICET group in Tucuman, Argentina.

Two classes of photosensory pigments are in our focus: proteins that employ FMN (flavin mononucleotide) and those carrying bilins (open-chain tetrapyrroles) as chromophores. FMN-binding photoreceptors are classically blue light (BL) sensitive, whereas canonical bilin-binding proteins, e.g., the plant photoreceptor family of phytochromes, are red light activated. During the last four years, a subgroup of bilin-binding photoreceptors, coined cyanobacteriochromes (CBCRs), has gained remarkable scientific attention due to the wide range of spectral sensitivity of these chromoproteins (extending from near-UV into the far red range). We are investigating structural and functional properties and potential applications of these photoreceptors in collaboration with Prof. Kai-Hong Zhao (State Key Laboratory in Microbiology, Agricultural University, Wuhan, China). Still the immediate light-driven reactions of photoreceptors are enigmatic. To gain better understanding of this essential reactivity, we have teamed up with Prof. Igor Schapiro, Hebrew University Jerusalem.

## Bilin-based photoreceptors

(i) The sensing domain of canonical phytochromes is composed of three protein domains, PAS, GAF, PHY that bind the bilin chromophore. Non-photosynthetic bacteria and fungi employ biliverdin (BV) as chromophore. Three representative proteins of these BV-phytochromes have been characterized for the entire photochemistry in the sub-us to ms time domain (Ph.D. thesis Alexander Gutt).

(ii) Cyanobacteriochromes (CBCRs) are found so far only in cyanobacteria. They comprise a novel class of bilin-binding photoreceptors. In contrast to canonical phytochromes these proteins exhibit a repetitive arrangement of GAF domains. Here, already the isolated CBCR GAF domains show the capability for chromophore binding and for photochromic photochemistry akin classical phytochromes, yet, with a much wider spectral range. 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. We have selected GAF3 domain of Slr1393 from *Synechocystis* PCC6803 for detailed structural and functional characterization. Ultrafast (collaboration J. Wachtveitl, Frankfurt, Fig, 1, left) and us-ms spectroscopy identified the entire range of absorption changes [1,2]. Attempts to crystallize both, dark- and photoproduct form, were also successful, providing by comparison between both structures, deep insight into chromophore-mediated protein conformational changes as indications for the light-induced signal transduction (unpublished, Fig. 1, right).

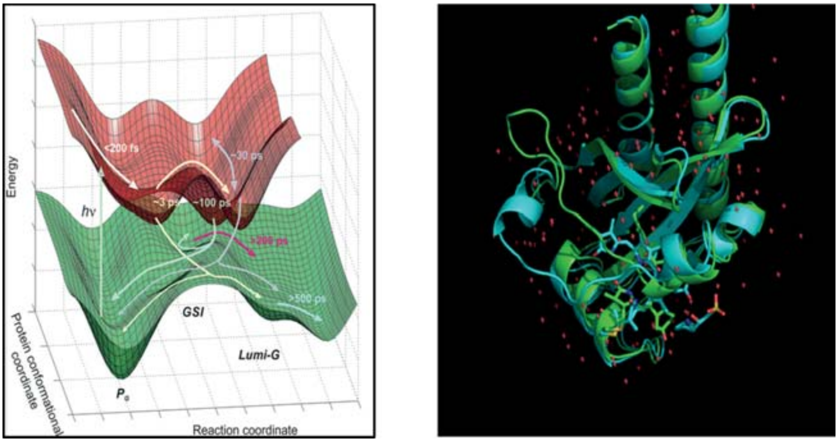

**Figure 1.** Conformational and structural analysis of GAF3 domain of Slr1393 from *Synechocystis* PCC6803. Left, cartoon presentation of ultrafast reactions of Slr1393g3 for the light-induced re-conversion of the parental state from its green-absorbing photoproduct [1]. Right, overlay of (green) parental and (teal) photoproduct structures documenting conformational changes between both states (WG, unpublished).

### Blue light sensing photoreceptors

Research on BL sensing receptors is performed since many years in close collaboration with the Physics Dept. of Univ. of Parma, Italy, and is based on photoreceptor sequence identification from database-mining. We hereby are aiming for new photoreceptor genes yielded sequence signatures indicative for photoreceptor genes thus allowing precise identification of novel photoreceptor genes in complete genomes [3]. Comparative database surveys brought to light a coincidence between plants and plant-pathogenic bacteria such that both often show the same ensemble of photoreceptors (Fig. 2). This finding suggests that plant-pathogenic bacteria identify environments that are positive for growing plants and thereby provide potential targets for infection.

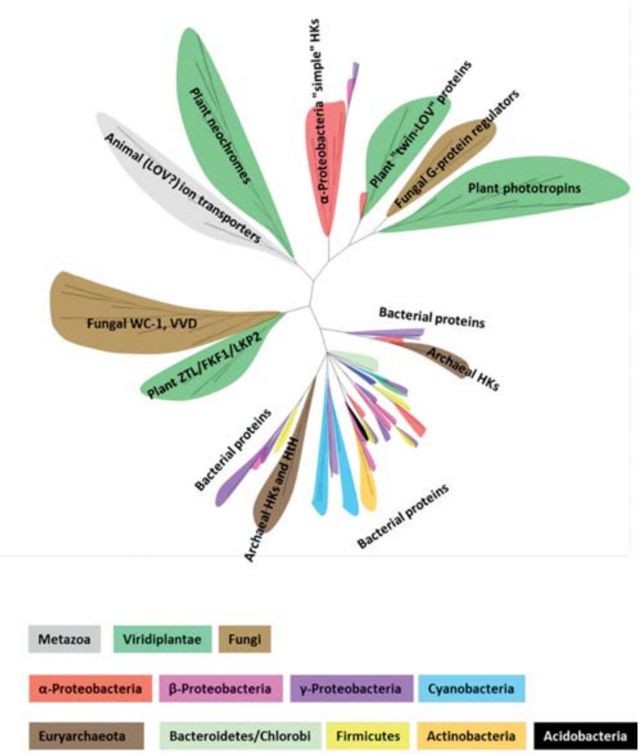

**Figure 2.** Left, rootless phylogenetic tree of blue light-sensing (LOV-domain containing) photoreceptors based on 3'600 sequences. Sequence number was 'simplified' yielding 180 representatives with bootstrap values >80% probability [4].

The role of light as a regulating factor for bacterial infectivity comes only slowly into the scientific focus. Investigations on *Pseudomonas syringae* pv. *tomato* demonstrate the paramount role of light for the infectivity of this plant pathogen [4–6].

## Applications

Signaling in many photoreceptor classes is accomplished through a light-regulated enzyme function located in a separate protein domain fused to the photosensory part. Wide-spread examples are light-regulated enzymatic activity of adenylyl cyclases, histidine kinases or cyclic-di-GMP phosphodiesterases. This finding has enabled optogenetics studies in living cells, even by combining sensing and signaling domains that do not exist (or so far have not been found) in nature.

We could recently show cAMP formation by a blue light-sensing adenylyl cyclase in an irradiation-dependent manner. cAMP is a very important "second messenger" also in higher organisms that among other functions regulates open/close state of membrane channels. Expression of this protein in neuronal cells caused channel opening upon irradiation, resulting in an 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, upon certain life conditions, enzymatic cAMP secretion 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 in a *Dictyostelium* AC-deletion mutant led to cell aggregation and fruiting body formation (collaboration P. Schaap, Univ. Dundee, G. Nagel, Univ. Würzburg) [8].

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In the catalytic technology group heterogeneously catalyzed reactions are investigated. Catalysis is of major importance for an energy-effective and sustainable conversion of reactants as it lowers the activation barrier of a chemical reaction by changing its reaction mechanism. In heterogeneous catalysis, usually, the catalyst is a solid, whereas the reactants exist in the surrounding fluid phase. Deeper understanding of catalytic processes can help to improve the efficiency of reactions and, therefore, help to save resources and lower the overall energy demand.

In the catalytic technology group heterogeneously catalyzed reactions are focused, which are of interest in the scope of energy conversion and storage. Nowadays, solar, wind, and hydro energy are often regarded as sustainable energy sources and can help to solve the shortage of hydro carbon-based energy sources in an environmentally friendly way. Electro-catalytic hydrogen production is investigated in the institute and is often discussed as key technology to store the fluctuatingly appearing renewable energies. Numerous techniques to store the hydrogen have been suggested including the generation of ammonia and methanol, which are investigated in the catalytic technology group. Both substances offer the advantage of high hydrogen contents and are easy to store as they are condensable [1].

### Analysis of exhaust gases from steel mill plants

Besides the electro-catalytic generated $H_2$ as potential feed, the capability of industrial exhaust gases as potential feed gases for ammonia and methanol synthesis is determined in the catalytic technology group. An extensive analysis of real exhaust gases from steel mill plants is performed for all kind of trace components including metals, sulfur-, nitrogen-, and chlorine-containing compounds, polycyclic aromatic hydrocarbons, and BTEX-aromatics, as well as for gaseous components. Exhaust gas analysis for blast furnace gas, coke oven gas, and converter gas was already performed. As the composition of the exhaust gases depends on the production conditions as well as the raw materials and is time dependent, a detailed analysis over longer time period is mandatory. That is why the catalytic technology group constructed a mobile high-end gas analysis laboratory housed in a container to analyze the steel mill gases directly on-site. The container is equipped with a new generation PTR-SRI-QiTOF-MS for high performance analysis and reactors for catalytic testing in methanol synthesis.

**Methanol synthesis**

Nowadays methanol is produced from feed gas mixtures containing CO, $CO_2$, and $H_2$ in a conventional, continuously performed process using a $Cu/ZnO/Al_2O_3$ catalyst. A future sustainable and environmental friendly production route from exhaust gases renders a deeper understanding of the $CO_2$ hydrogenation and an expansion of the known parameter space of a Cu-based catalyst important. The usage of $CO_2$-rich feed gases, possibly without any CO at all, and dynamic operation conditions pose typical challenges for such a process and are investigated in the catalytic technology group. The influence of parameters such as pressure, temperature and space velocity is investigated with respect to the reaction performance to help to establish a fundament for the usage of exhaust gases of e.g. steel mill plants.

It is found that an industrial $Cu/ZnO/Al_2O_3$ can operate in a stable way without CO in the feed gas. The reactor applied houses sufficient catalyst to determine the productivity by volumetric analysis of condensate and high-precision GC-MS product analysis (higher oxygenates). Water contents in the product stream seem not to destroy the catalyst. A stable productivity up to 0.96 $g_{CH3OH} \cdot g_{cat}^{-1} \cdot h^{-1}$ is achieved at 250 °C and 30 bar using a GHSV of 46000 $h^{-1}$. Additionally, it is possible to operate the catalyst under intermittent production conditions simulated by dynamic pressure changes from 30 to 50 bar. No restraining influence on the performance at 30 bar was observed by the temporal changes to 50 bar.

Furthermore, the influence of impurities of the exhaust gases on the catalyst activity and stability is investigated. Systematic reactivity and stability studies in methanol synthesis have been started. Feed gases consist of $CO_2$, hydrogen, and additionally trace components, which are usually found in the exhaust gases, like benzene as a representative of BTEX-aromatics. Figure 1 (A) shows the reaction rate of methanol production over a time period of 230 h in a long-term stability test at 15 bar. The reaction rate stays in the same order of magnitude compared to benzene-free feed gas, which is represented in the first data point. Drops in the reaction rate after 50 and 165 h are caused by a decrease in the instrument pressure due to sample taking. A further purification step of the steel mill gases from BTEX aromatics does not seem to be necessary as the impurities do not affect the catalyst's stability and activity.

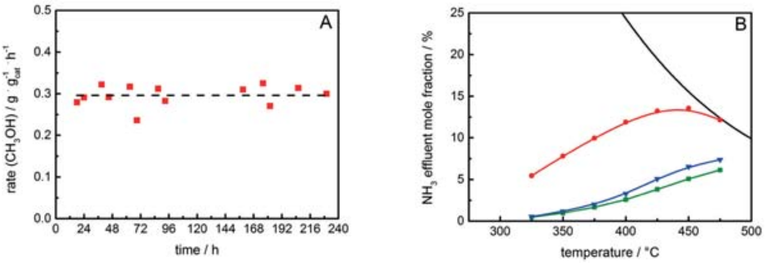

**Figure 1 (A)** Methanol synthesis measurement at 250 °C and 15 bar in $H_2/CO_2/$(500 ppm $C_6H_6$ in $N_2$) feed gas with ratio of 60:20:7 and a GHSV of 5200 $h^{-1}$. First data point is recorded in $C_6H_6$-free feed gas. **(B)** Ammonia synthesis measurement at 325 – 500 °C and 90 bar in 75% $H_2/N_2$ with a total gas flow rate of 100 ml · $min^{-1}$ · $g_{cat}^{-1}$ over an industrially used Fe-based catalyst (red), an unpromoted $MgFe_2O_4$ model catalyst (green), and a $MgFe_2O_4$ model catalyst promoted with 2 wt-% of K (blue). Maximum $NH_3$ concentrations in thermodynamic equilibrium are additionally shown (black).

### Ammonia synthesis

Ammonia synthesis represents an additional way to store hydrogen produced with renewable energy sources. It is well known that ammonia synthesis is a structure sensitive reaction [2]. Nevertheless, there is still a large pressure and material gap between activity data at industrial relevant conditions and surface science approaches. That is why it was planned to investigate a systematic series of catalysts with different surface structures and to correlate their activity to their structure. Figure 1 (B) shows the effluent mole fraction of ammonia in steady state during ammonia synthesis at 90 bar over an industrially used Fe-based catalyst in comparison to $MgFe_2O_4$ model catalysts synthesized from a layered double hydroxide precursor prepared by the group of M. Behrens in the University of Duisburg-Essen. All catalysts show high stability in ammonia synthesis. It is possible to achieve already more than 30 % of the productivity of an industrially established multiple promoted Fe catalyst (8.7 µmol·$g_{cat}^{-1}$·$s^{-1}$) with an unpromoted model catalyst (2.7 µmol·$g_{cat}^{-1}$·$s^{-1}$) at 425 °C and 90 bar. The productivity of the model catalyst can even be increased to more than 40 % by impregnation with 2 wt-% of potassium (3.6 µmol·$g_{cat}^{-1}$·$s^{-1}$). Therefore, the $MgFe_2O_4$ system is a promising starting point for further catalyst development. In the next steps variations of the catalyst's composition and addition of promoter components are planned to further modify the catalyst's structure and investigate the influence on the activity.

This is currently underway also in collaboration with Serena DeBeer (department Frank Neese) performing XAS and XES analysis on the iron. To allow for this, a special reactor was constructed allowing the disassembly of the catalyst inside a glove box without contact to the ambient for ex-situ characterization methods. This may help to elucidate whether surface, subsurface, or bulk nitride species are generated during the reaction, as the active phase of the Fe-based catalyst under industrially used conditions is still unclear [3]. The very low conversion in ammonia synthesis at mbar pressure precludes direct in-situ analysis and the extreme air-sensitivity of the activated catalysts represents a major hurdle in getting insight into the chemistry of the active form of ammonia iron.

FeOOH-based nanosheet catalysts prepared in the inorganic chemistry department at the FHI in Berlin, with varying Fe loading, support materials, and potassium promoter concentration are additionally investigated. For the Fe-nanosheet-based catalysts $Al_2O_3$ as a catalyst support is mandatory to achieve a stable productivity in contrast to unsupported or MgO supported catalysts. Additionally, it is possible to achieve active catalysts by encapsulation of the nanosheets by $SiO_2$.

The key point in the alternative catalyst preparation routes is the circumvention of the high-temperature melting process of the iron oxide precursor by low-temperature self-organization of layered iron-oxihydroxide precursor supported on a mineral carrier. Such a "green" synthesis allows studying the interplay of morphology and promoter chemistry in the formation of the active iron species.

### Oxidative dehydrogenation of ethyl benzene

For the investigations of the oxidative dehydrogenation (ODH) of ethyl benzene forming styrene, a kinetic flow set-up was constructed in the catalytic technology group. ODH is an energy saving candidate for the synthesis of styrene. Additionally, ODH is employed for the characterization of carbon materials, which are produced in the "carbon synthesis and application" group in the institute. Carbon materials are active in the ODH reaction and are, therefore, interesting and cost-effective materials [4]. (Di)carbonyl surface functional groups that can be modified by additional dopants such as nitrogen are assigned to be the active sites [5]. An extensive characterization and correlation to activity data can shed light into this assignment. If the structure-activity relation is identified, the ODH of ethyl benzene can outstandingly supplement the existing characterization methods and can be incorporated perfectly in the master plan of the institute.

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## Nanobased Heterogeneous Catalysts

### Introduction

Apart from electrochemical reactions for energy storage and the synthesis of liquid fuels employing heterogeneous catalysts, a third process option is photocatalysis: Using charge carrier generation in semiconductors and the subsequent separate transfer of electrons and holes onto adsorbed reactants, even highly endergonic reactions such as the splitting of (pure) water and the reduction of carbon dioxide can be realized. Such processes essentially copy natural photosynthesis, but use purely inorganic photocatalysts to form small molecules of high energy density such as methane or hydrogen. While the concept sounds simple, photocatalysts for energy conversion reactions that achieve yields sufficient for industrial application have not yet been developed, in spite of more than thirty years of research [1]. A possible reason for the slow advancement might be that fundamental understanding of the relevant processes has rarely been achieved, likely due to the complexity of all necessary requirements: Appropriate photophysical (band gap, band edge positions, charge carrier lifetime), electrochemical (charge migration, interfacial transfer) and catalytic properties (adsorption and charge transfer sites) all need to come together and interact favorably in the photocatalyst. The understanding of existing active materials and the design of superior ones thus crucially depends on the characterization of the structural and electronic properties on the nanoscale [2].

The independent research group "Nanobased heterogeneous catalysts" (NanoCat) has been established in October 2014. Scientifically, it is our main aim to further develop the fundamental understanding of photocatalytic processes for energy conversion reactions, in particular the reduction of carbon dioxide, but also oxygen evolution in water splitting. Photoactive materials must be cheap, abundant, and ideally also environmentally benign, so research focus is put on semiconducting oxides. For the synthesis of model catalysts and the design of more active photocatalysts, the nanostructure of materials is manipulated purposefully, and particles in the nanosize regime are applied. From an organizational point of view, the NanoCat group aims to set up close cooperation of the research activities on energy conversion at the CEC and on nanomaterials within the Center for Nanointegration Duisburg-Essen (CENIDE) at the University Duisburg-Essen. For this purpose, the NanoCat group has set up a new laboratory for catalyst synthesis/characterization, surface modification, and photocatalytic testing in the *NETZ*, a new research facility with modern infrastructure for nanomaterial characterization at the Duisburg campus.

The scientific approach of the NanoCat group lies in the clarification of fundamental processes of photocatalytic reactions under controlled conditions of highest purity. We operate a high-purity gas phase photoreactor constructed entirely from stainless-steel equipment for high-vacuum systems and top- or side-illuminated quartz three-phase reactors. Highly sensitive trace gas analysis by newest generation gas chromatography and quadrupole mass spectrometry allows most reliable comparative and mechanistic studies of photocatalytic $CO_2$ reduction [3,4] and water splitting.

### New insights into the mechanism of photocatalytic $CO_2$ reduction

Under reaction conditions of highest purity in batch mode the main products of photocatalytic $CO_2$ reduction on $TiO_2$ P25 are identified to be $CH_4$ and CO (Figure 1A). No $CH_3OH$ is formed. Our results clearly rule out CO as reaction intermediate on the way to $CH_4$ or any other potential product, since reference measurements with CO instead of $CO_2$ in the gas phase showed no CO conversion on $TiO_2$.

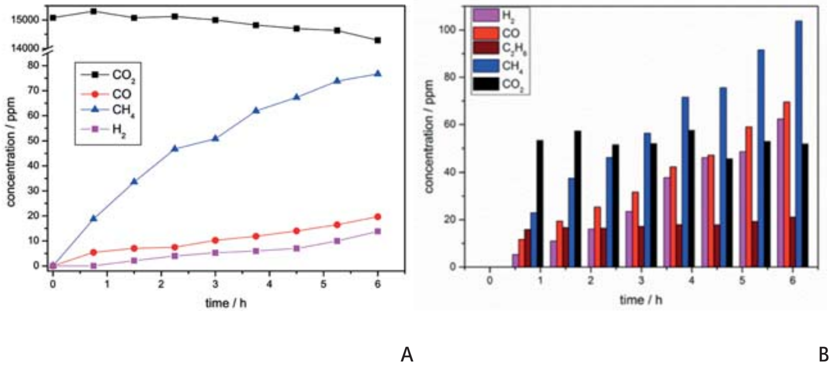
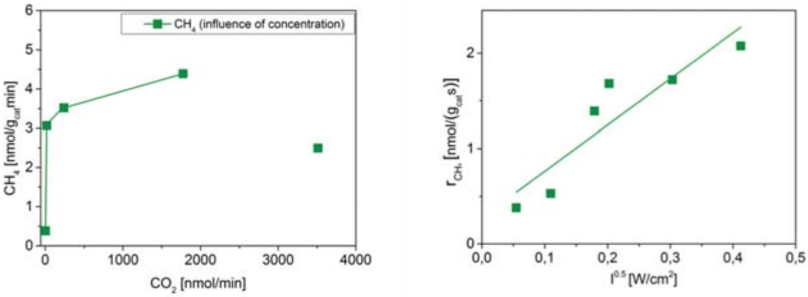


**Figure 1. A)** Product formation in photocatalytic $CO_2$ reduction on $TiO_2$ P25, 6000 ppm $H_2O$, 1.5% $CO_2$, balance He, 200 W Hg/Xe lamp; **B)** Photocatalytic reaction of acetaldehyde on $TiO_2$ P25.

Carbonates are not likely as intermediates, either, because improvement of carbonate formation on $TiO_2$ decreased $CH_4$ yields. Other potential $C_1$ intermediates (e.g. methanol, formic acid) showed no tendency for $CH_4$ formation under the tested conditions [4]. We support instead a mechanism involving an intermediate formation of a C-C bond and $C_2$ intermediates such as acetaldehyde [5]. Reacting acetaldehyde and acetic acid on $TiO_2$ led to product distributions rather similar to those obtained from $CO_2$ under standard reaction conditions, strongly supporting a $C_2$ mechanism.

Corresponding experiments in continuous flow mode subsequent to photocatalytic cleaning revealed a proportional dependence of $CH_4$ formation on $CO_2$ concentration and ceasing $CH_4$ formation when switching off the lamp. Accelerated $CH_4$ formation upon increasing $CO_2$ concentration was only observed up to a certain maximum (Figure 2A), tentatively assigned to a limited availability of photogenerated charge carriers at the $TiO_2$ surface or a lack of suitable catalytically active sites. Light intensity variation studies showed that $CH_4$ formation rate increases with the square root of the light intensity, most likely due to an increasing charge carrier recombination rate at higher light intensities (Figure 2B). Even traces of $O_2$ in the reactor completely hindered $CH_4$ formation, so the lack of concomitant oxygen evolution observed in previous measurements on $TiO_2$ is likely beneficial for the overall process. The studies are a first step towards performing true steady-state kinetic studies on photocatalytic $CO_2$ reduction.



A B

**Figure 2. A)** Effect of reactant concentration on the photocatalytic formation of $CH_4$, **B)** Effect of light intensity on the photocatalytic formation of $CH_4$.

### Fundamental studies on manganese oxide-based materials in photocatalysis

Manganese oxides are already a major research focus at the MPI-CEC. We complement the existing research initiatives by unraveling the fundamental photophysical and (electro)chemical properties of a variety of stable bulk manganese oxides ($MnO$, $Mn_3O_4$, $Mn_2O_3$, $MnO_2$) as a function of oxide stoichiometry and nanosize. Due to the wide range of reported physicochemical parameters (e.g. band gap, band positions) [6] we created our own reference database using bulk oxides in highest available purity.

It is the aim to evaluate whether a certain (modified) Mn oxide can be used as light absorber, as water splitting catalyst, or to take over both functionalities. First results indicated favorable properties of MnO and $Mn_3O_4$: While oxygen evolution activity in presence of a sacrificial agent was observed for commercial MnO (Figure 3A), $Mn_3O_4$ displayed band edge positions not too far away from the thermodynamic optimum for photocatalytic water splitting. Potential benefit of bringing particle sizes of those oxides down to nanosize by laser fragmentation is currently under investigation in cooperation with Prof. Dr. S. Barcikowski from CENIDE. Additionally, isolated Mn cations and small agglomerates of Mn oxides (8 nm) were prepared by different synthetic routes on mesoporous silica (Figure 3B), to study in detail their photophysical properties, and to test them as potential (single-site) photocatalysts.

Since Raman microscopy (Figure 3A) could only partially identify the supported oxide phase as $Mn_2O_3$ and MnO, more reliable means for manganese oxide phase identification of amorphous or nanocrystalline samples are needed. Temperature programmed reactions in a gas phase plug flow reactor were studied with bulk manganese oxides over a wide range of temperature programmed reduction and oxidation cycles (Figure 3B). Reaction parameters and the detection process via mass spectrometer were optimized for phase identification (Figure 3B).

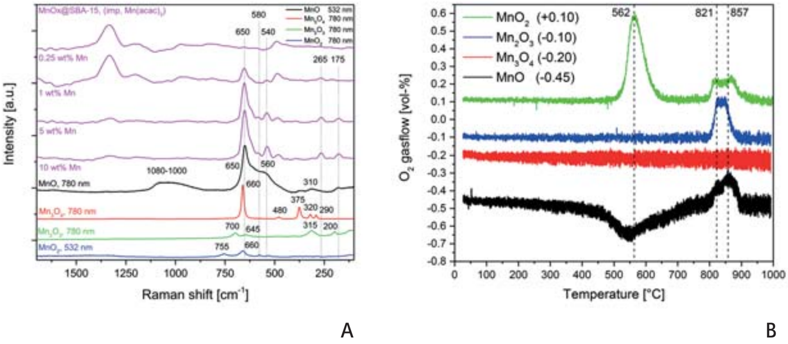


**Figure 3. A)** Raman spectra of manganese oxide nanoparticles on mesoporous silica with different amounts of Mn and reference spectra from bulk oxides. **B)** Temperature programmed oxidation of reference bulk oxides.

### Photoelectrochemical analyses

In addition to photocatalytic gas-phase and liquid-phase experiments we aim to establish reliable and reproducible photoelectrochemical measurements. An improved homemade photoelectrochemical cell (PEC) was built which is fast equilibrating, prevents formation of air bubbles and allows the use of a double junction electrode. Comparative photocurrent measurements with $BiVO_4$ proved unrestricted usability of the homemade cell. A general validation of the setup was carried out by conducting a range of cyclic voltammetry (CV), electrochemical impedance (EIS) and photocurrent measurements with suitable standards.

Currently, different ways of reproducibly preparing suitable photoelectrodes are assessed.

### Photocatalytic alcohol oxidation on commercial Au/$TiO_2$ catalysts

In cooperation with the Cluster of Excellence RESOLV (EXC 1069) at the Ruhr-University Bochum, the mechanism of photocatalytic alcohol oxidation on commercial Au/$TiO_2$ and pure $TiO_2$ was studied using *in situ* ATR-IR spectroscopy. It was found that the alcohol is oxidized by the holes on $TiO_2$ directly. The main role of the gold nanoparticles lies in their function as cocatalyst to accelerate the electron transfer to oxygen [7]. In-depth mechanistic studies using electron paramagnetic resonance are in progress in cooperation with the group of Dr. A. Savitsky. Further structural investigations using Raman microscopy in the line-scanning mode and UHV-IR spectroscopy revealed the formation of a reduced $TiO_{2-x}$ phase near the gold nanoparticles that eventually leads to rutile formation in the material [8].

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## Activities of the Electron Microscopy Group

Besides routine characterizations of samples in terms of structure, morphology, and elemental composition, which is provided as a service for all members of the institute, the EM group has concentrated on the full exploitation of the analytical power of the microscopes and on the development of methods for the investigation of active catalysts. The recognition of the dynamic nature of an active catalyst is the driving force for the joint development and exploitation of *in situ* electron microscopy techniques together with the electron microscopy group at the Fritz Haber Institute in Berlin. We have understood that electron microscopy has to go beyond the conventional investigation of samples in vacuum in order to contribute to a mechanistic understanding of working catalysts. The aim is therefore to directly observe how active centres are formed or transformed under reaction in response to the chemical potential of the surrounding gas phase [1,2].

Our approach can be summarized by the term "Chemical Electron Microscopy". It stands for analytical electron microscopy with a strong focus on the chemical state of the investigated materials by spectroscopic analysis and especially, under consideration of catalytically relevant dynamic processes.

### Chemical information from seeing where the atoms are

With regards to the analytic power of the recently acquired double corrected JEOL ARM, we have demonstrated that direct imaging of the oxygen sub lattice of a molybdenum-vanadium mixed oxide reveals the distortion of the different metal-oxygen octahedra constituting the structure. Using this information, we were able to draw conclusions about the distribution of oxidation states of molybdenum and vanadium cations at different metal sites [3]. It is therefore possible to obtain chemical information directly from the recorded atomic arrangement and the position of the atoms.

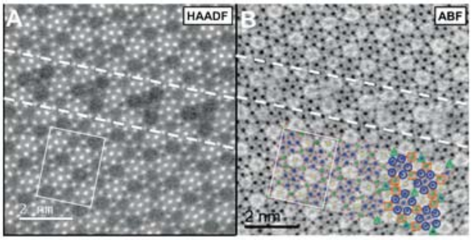
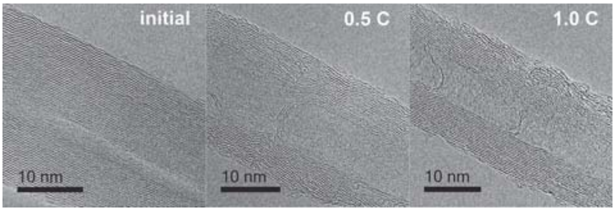


**Figure 1.** High-angle annular dark field (HAADF) and annular bright field (ABF) images provide local information about the distribution of Mo and V in the atomic columns. Direct imaging of the oxygen sub-lattice allows drawing conclusions about the d-band occupancy at different sites.

## Local chemical information from electron energy-loss spectroscopy

In the microscope, structural information is obtained at high-resolution and combined with simultaneously obtained spectroscopic information. On the basis of well-prepared samples and reproducible experimental conditions, we are able to explain properties that are observed during catalytic testing. One example is the electrochemical degradation of multi-walled carbon nanotubes (MWCNTs) under conditions of oxygen evolution in acidic media [4]. The loss of structural order due to the accumulation of defects can be followed by high-resolution imaging in the TEM. Defects give rise to a change in the electronic structure, which we trace by electron energy-loss spectroscopy as small variations in the fine structure of the carbon K ionization edge.



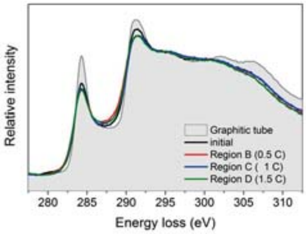


**Figure 2.** HRTEM images showing the electrochemically induced degradation of MWCNTs. Accumulation of defects and loss of order is reproduced in the fine structure of the carbon K edge that is recorded by EELS.

The combination of high-resolution imaging and electron energy-loss spectroscopy (EELS) provides key insights about the degradation mechanism. It was used to confirm the formation of a self-limiting, highly stable surface oxide, which kinetically hinders further corrosion of the multi walled carbon nanotubes.[4]

### In-situ observations in the TEM

Since the beginning of 2015, we are using a commercial sample holder for *in situ* experiments inside the column of a TEM. In combination with a home-built gas-feeding and analysis unit, we are now able to operate the holder under defined gas flow at pressures of up to 1 bar and temperatures of up to 900 °C.

The nickel-carbon system was chosen as a first test system for the new set-up. We were especially interested in the pressure dependence of processes that lead to CNF/CNT growth and the effect of the electron beam on the observed dynamics. Metallic Ni particles were produced *in situ* by oxidative decomposition of a precursor and subsequent reduction of the obtained NiO to Ni (see Fig. 3).

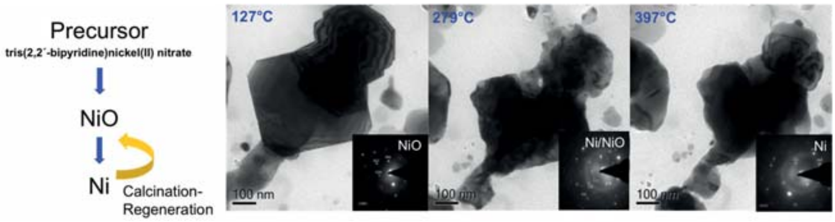


**Figure 3.** *In situ* preparation of the catalyst by thermal decomposition of the precursor and subsequent reduction can be monitored in real-time using imaging, diffraction and spectroscopic techniques.

After reduction, the atmosphere was switched to a 1:1 mixture of $C_2H_4$:$H_2$. Images were recorded *in situ* during temperature ramping from room temperature to 300 °C at a pressure of 200 mbar (Figure 4) and a total flow of 0.1 ml/min.

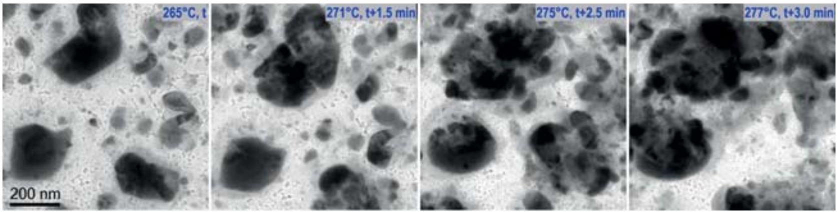


**Figure 4.** Sequence if images recorded during the heating of Ni particles in an atmosphere of $C_2H_2$:$H_2$ (1:1), showing the disintegration of Ni particles and the simultaneous formation of carbon structures.

*In situ* TEM observations impressively demonstrate the breaking-up of metallic Ni particles during exposure to the reaction feed. The process, known as "metal dusting", leads to the disintegration of bulk Ni to fine nanoparticles due to the vivid formation carbon. These nanoparticles subsequently catalyse the growth of carbon nanofibers and tubes (Figure 5).

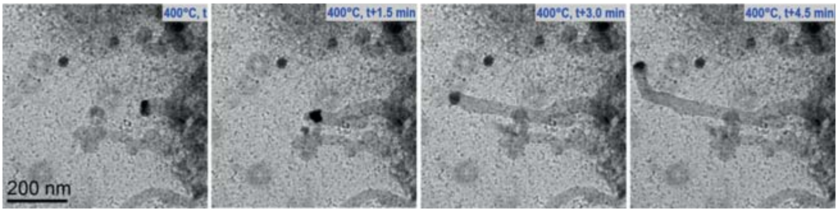


**Figure 5.** *In situ* observation Ni catalysed CNT and CNF growth at 200 mbar in a $C_2H_4$:$H_2$ (1:1) mixture.

Using the combination of *in situ* SEM and TEM, we have recently started to investigate the redox dynamics of active metal catalysts. One example is copper under hydrogen oxidation (see Figure 6). Oscillatory redox transformation between Cu and $Cu_2O$ is observed (see Figure 6), while at the same time, the formation of water is detected.

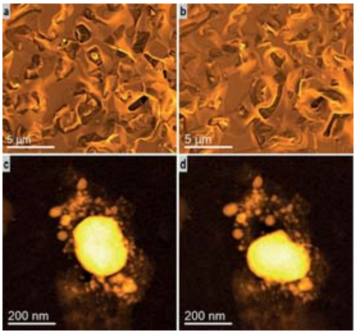


**Figure 6.** (a) and (b) show *in situ* SEM images of a copper surface in a $H_2$/$O_2$ (20:1) atmosphere at 0.2 mbar and 650 °C. Image (b) was recorded 8 minutes after image (a). *In-situ* STEM images are shown in (c) and (d).
They demonstrate the dynamic behaviour of the system under redox conditions (image (d) was recorded 3 s after image (c)).

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## ORCA – A Powerful Tool for Quantum Chemistry

A major activity in the department is the development of the ORCA quantum chemistry project (https://orcaforum.cec.mpg.de).[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. These developments, led 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.

In the two years since the Fachbeirat in 2014, significant progress has been made in the ORCA program, which keeps gaining popularity in the scientific community. For example, the Wire's article describing ORCA's basic functionality has been cited more than 1000 times between its appearance in the January 2012 and October 2016.[1] In Figure 1, one can observe that ORCA has been continuously increasing in popularity. While the market-leading program is still the Gaussian package, ORCA was already the third most used program in 2014 and the second most used program by 2016. Given the much higher speed of innovation relative to the commercial packages and the stronger and secure development base at the MPI CEC, we expect ORCA to receive an even higher market share in the future. In fact, the development team is committed to turn ORCA into the leading quantum chemistry tool worldwide.

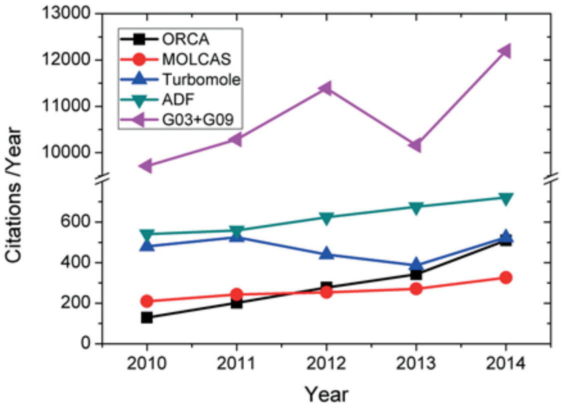

**Figure 1.** Citation statistics of ORCA in relation to other quantum chemistry program packages.

Due to the growing interest in ORCA, the development group has decided to organize a yearly user meeting, which first took place in October of 2015 and was continued in 2016.

In version 4.0, to be released prior to the Fachbeirat meeting in March 2017, significant overall performance and parallelization efficiency gains have been realized. For example, careful re-design of the integral digestion algorithms have led to a speedup of a factor of two in the Hartree-Fock and hybrid SCF procedures. The implementation of efficient algorithms for graphics cards has begun. With these improvements ORCA rivals the most efficient dedicated programs in this respect while maintaining a much broader functionality than most of its competitors. Below specific areas of activity since spring 2014 will be highlighted.

We have previously developed the domain-based local coupled cluster method with single-, double- and triple excitations (DLPNO-CCSD(T)).[2] This method recovers 99.9% of the canonical CCSD(T) correlation energy, but is many orders of magnitude faster. It hence promises to be a major tool for computational quantum chemistry. During the evaluation period, we have followed three major routes: a) perform extended validation tests on closed-shell DLPNO-CCSD(T),[3] b) Demonstrate its utility through large-scale chemical applications[4] and c) continue its development by making the code more efficient and extending the applicability to new areas such as molecular properties,[5] open-shells, excited states,[6] explicitly correlated methods and multireference methods.[7]

In the process of optimizing the performance of the code, we have developed a new and systematic 'SparseMap' infrastructure for reduced scaling electronic structure theory that has applications far beyond the DLPNO-coupled cluster framework.[7a] The important conceptual SparseMap publication outlines a fundamental 'Linked Index Rule' for linear scaling algorithms and the definition of multiplicative vs additive sparsity. In this work, we also have arrived at a new rigorous and non-empirical way for domain construction and organization of local function spaces that is based on differential overlap integrals.[7a] On the basis of the SparseMap infrastructure fully linear scaling DLPNO-MP2 and

DLPNO-CCSD(T) methods have been developed which allow calculations on systems with more than 1000 atoms and 20000 basis functions. In many cases, the preceding Hartree-Fock calculation becomes the computational bottleneck.

In terms of new functionality, the closed-shell DLPNO-CCSD density has been successfully implemented in terms of the well-known Lambda-approach, which allows for calculations of first-order properties.[5] Furthermore, a new restricted open-shell DLPNO-CCSD method was developed that has the attractive feature of only requiring a single (instead of three) integral transformation and smoothly reduces to the closed-shell method if the reference is a closed-shell determinant.[8] Perhaps more spectacularly, the PNO based multireference coupled cluster method based on the Mukherjee Ansatz was developed together with our collaborators in Prague.[7b] Important progress towards a PNO based equation-of-motion coupled cluster method for excited and ionized states has been made.[6] A large scale implementation is expected to be finished in 2017. Finally, we have developed a linear scaling multireference perturbation theory (DLPNO-NEVPT2), which, for the first time, allows for multireference perturbation calculations on hundreds of atoms and thousands of basis functions.[9] The linear scaling code has an early crossover with the already highly efficient canonical NEVPT2 code and is expected to be of major utility in the field of molecular magnetism.

A second project that was pursued intensely was the generation of an automated code generation infrastructure that will allow for the automatic generation of efficient native ORCA code from nothing else but a wavefunction Ansatz. This infrastructure will allow us to reduce development times from years down to days, if not hours. The tool chain presently generates code, which is within a factor of two of hand-optimized code in terms of its efficiency for standard cases such as CISD or CCSD. Multireference wavefunctions are also supported. The first application was the large-scale implementation of a fully internally contracted multireference configuration method.[10]

A third area, where significant progress was made in the development was the slightly parameterized restricted open-shell configuration interaction singles method (ROCIS/DFT), which has been shown to be an efficient method for the calculation of core-level excitation spectra.[11] In particular it performs well for metal L-edge excitations, where particle-hole theories such as time-dependent density functional theory or the Bethe-Salpeter approach fail qualitatively. We have recently extended this methodology towards the computation of valence excited states, ground state magnetic properties and two-dimensional X-ray (RIXS) as well as resonant X-ray emission spectra.[12] Furthermore, we have published a number of applications of this method to problems in solid-state and surface as well as molecular science. It is expected to be a major workhorse for spectral calculations in the next evaluation period. We have recently succeeded to implement the PNO concept into ROCIS, which leads to spectacular speedups that render calculations on hundreds of states of big systems with hundreds of atoms nearly trivial.

Last but not least, we have developed an new approach to approximately solving the full CI problem for large active space with dozens of orbitals and dozens of electrons.[13] The new method is called 'Iterative configuration expansion' (ICE-CI) and can be thought of as an extension of Malrieu's pioneering CIPSI approach. We have demonstrated that the method is accurate and efficient and we are currently exploring new multireference dynamic correlation theories based on ICE-CI.

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4. a) D. G. Liakos, F. Neese, *Journal of Chemical Theory and Computation* **2015**, *11*, 2137-2143; b) M. Sparta, C. Riplinger, F. Neese, *Journal of Chemical Theory and Computation* **2014**, *10*, 1099-1108; c) M. Sparta, F. Neese, *Chemical Society Reviews* **2014**, *43*, 5032-5041.
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6. A. K. Dutta, F. Neese, R. Izsak, *Journal of Chemical Physics* **2016**, *144*.
7. a) P. Pinski, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2015**, *143*, 034108-034108; b) O. Demel, J. Pittner, F. Neese, *J. Chem. Theory Comput.* **2015**, *11*, 3104-3114.
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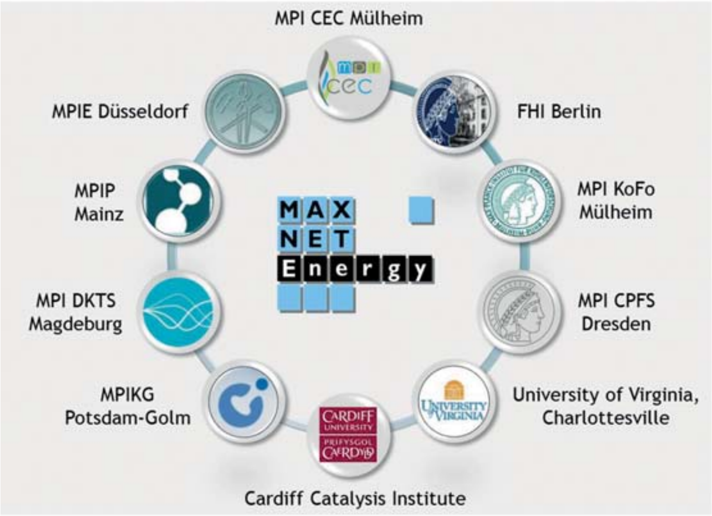
9. Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *Journal of Chemical Physics* **2016**, *144*.
10. K. Sivalingam, M. Krupicka, A. A. Auer, F. Neese, *Journal of Chemical Physics* **2016**, *145*.
11. a) D. Maganas, M. Roemelt, T. Weyhermüller, R. Blume, M. Hävecker, A. Knop-Gericke, S. DeBeer, R. Schlögl, F. Neese, *Phys. Chem. Chem. Phys.* **2014**, *16*, 264-276; b) D. Maganas, S. DeBeer, F. Neese, *Inorg. Chem.* **2014**, *53*, 6374-6385; c) M. Roemelt, F. Neese, *J. Phys. Chem. A* **2013**, *117*, 3069-3083; d) M. Roemelt, D. Maganas, S. DeBeer, F. Neese, *J. Chem. Phys.* **2013**, *138*, 204101-204122.
12. D. Maganas, A. Kubas, F. Neese, *J. Chem. Phys.* **2016**, *in preparation.*
13. A. K. Dutta, F. Neese, R. Izsak, *J. Chem. Phys.* **2016**, *144*.

## The MAXNET Energy Research Compound

The diversity and nature of the challenges described above has been an attractive playground for many groups in the scientific community in general and within the Max Planck Society specifically. Besides the departments of internationally acknowledged capacities with a focus on electrochemistry like Martin Stratmann, the current president of the Max Planck Society, many activities focus on the electrocatalytic activation of small molecules:

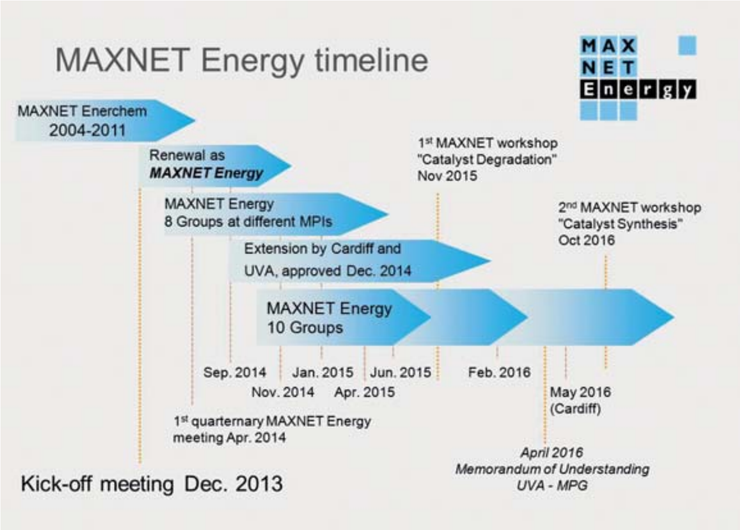
Institutes with background in chemical engineering have become interested in electrolyser systems, institutes that focus on catalytic processes have developed activities in electrocatalysis, groups with expertise in material science work on novel catalyst or membrane materials and groups working in the field of theoretical chemistry have been interested in exploring elementary processes on electrified interfaces.

This is why the Max Planck Society has made a commitment to support the many efforts on catalysis in energy conversion in a large research compound focused in synergy between the institutes. The MAXNET Energy initiative funds eight Max Planck Institutes all over Germany to employ motivated young scientists that work on energy conversion related topics with the function to form a network of focused cooperation.



Participants of the MAXNET Energy consortium: Max Planck Institute for Chemical Energy Conversion (MPI CEC), Fritz Haber Institute (FHI), Max Planck Institute for Kohlenforschung (MPI KoFo), Max Planck Institute for Chemical Physics of Solids (MPI CPFS), University of Virginia, Cardiff Catalysis Institute (CCI), Max Planck Institute for Colloids and Interfaces (MPIKG), Max Planck Institute for the Dynamics of Technical Systems (MPI DKTS), Max Planck Institute for Polymer Research (MPIP) and Max-Planck-Institut für Eisenforschung (MPIE).

The MAXNET Energy originated from the ENERCHEM initiative of the Max Planck Society that was founded in 2004 and has successfully brought together scientists within the MPG from different fields of chemistry, physics and engineering until 2011. Afterwards the decision was to renew the very successful energy conversion initiative as MAXNET Energy, the kickoff meeting was held in December 2013. Since then quarterly meetings have been held at the newly entitled Max Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr and the Harnack Haus in Berlin. The first focused workshop on catalyst stability was held in November 2015, the second on material and catalyst synthesis in October 2016. With the inclusion of two external members in 2014, the MAXNET Energy consortium reached its full size and potential. As external members, the Cardiff Catalysis Institute (UK) and the University of Virginia (USA) contribute essential expertise and complete the spectrum of materials science, system analysis and engineering solutions.

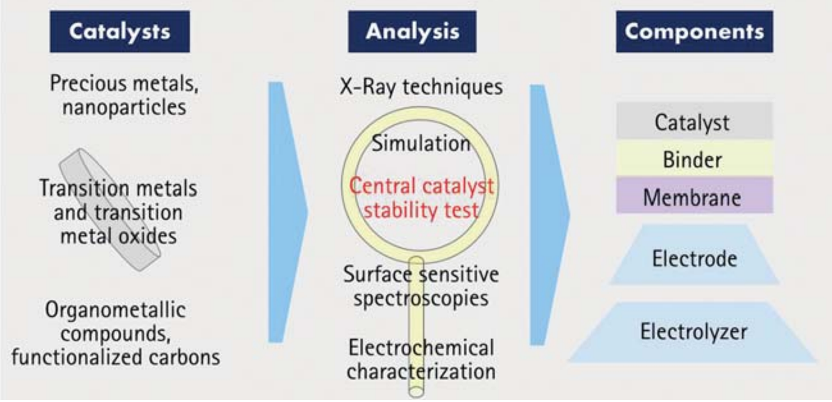


Overall, the MAXNET Energy consortium includes 10 participating groups, over 35 scientists and a budget of 1 Mio euros/year. The span of the projects within MAXNET Energy ranges from atomistic insight of catalytic reactions to details of engineering solutions for technical systems, from quantum simulation to synchrotron measurements and from synthetic chemistry to materials science.

As the central subject of research, the MAXNET consortium has decided to choose the most prominent but also most complex problem – besides the hydrogen evolution (HER) and oxygen reduction reaction (ORR), the anodic **oxygen evolution reaction (OER)** will be in the focus of the activities of groups in the MAXNET Energy initiative.

In science, finding a balance between complete freedom in action and rigorous focus of research to solve a given problem has always been the subject of debate. Two extreme opinions would be: If science is understood as breeding ground for novel ideas that might eventually initiate a technology push process, the unfolding projects must not be steered or directed. If solving problems that originate from a market pull is the aim, development must require focused, directed problem solving strategies in order to find the best solution. Within MAXNET Energy, a balance is aimed at, which - due to its focus on fundamental research - lies on innovation in materials and in-depth understanding by analysis. Certainly, Max Planck's famous quotation that "insight must precede application" also stands as the guiding principle in this work.

However, in order to focus and optimally connect the different activities, MAXNET Energy is designed in a unique way, including two dedicated modes of cooperation that go beyond bilateral interaction or common-aim research compounds. These can be characterized as "shared" and "joined" mode of cooperation, in combination aimed at facilitating focused development and maximal freedom in research at the same time:



The **shared mode** includes cooperation by sharing expertise, samples and materials or resources. This way, the knowledge and facilities within MAXNET Energy are used in an optimal way and communication and cooperation are facilitated. This is supported by a lively exchange of personnel at the working level, such that postdocs and PhDs working in one group can acquire expertise of other groups with the network.

In the **joined mode**, participants define and use common reference systems, standards and standard protocols for materials, systems and measurements. As a consequence, each working group uses predefined common experimental parameters in order to guarantee the same experimental conditions and thus comparability and transferability of the results between all groups. A central point is the catalyst stability testing unit, which offers its service to all participants and is supposed to guide catalyst development towards systems that are not only active, but also stable.

This way, added value for each participant is generated not only by the availability of state-of-the-art catalysts and materials, advanced analysis methods or novel upscaling approaches, but also by allowing each group to gain an insight into the special problems that arise at different levels of complexity in synthesis, analysis and engineering. For instance, materials scientists benefit from interaction with engineers building electrolyser cells, chemists working on novel catalysts benefit from profound experience in electrochemical analysis and theoreticians benefit from experimentalists insight.

As both interaction schemes are combined at the different levels of cooperation, the wide variety of materials developed in the consortium can be compared on common ground, unified test protocols ensure that globally comparable results are obtained in the analytics and clear specifications allow for target driven development, once a novel system has been explored.

*MAXNET Energy is coordinated at the MPI CEC, scientific coordinator is Alexander A. Auer. In January 2016, the overview given above appeared under the title "MAXNET Energy - focussing research in chemical energy conversion on the electrocatalytic oxygen evolution" to the De Gruyter journal "Green - a systemic approach to energy".*

# MANGAN – electrochemical water splitting

Electrochemical water splitting for hydrogen production is widely seen as a key technology in a sustainable energy scenario [1, 2]. The overarching aim of the BMBF-funded cluster project MANGAN is to evaluate the technical boundary conditions under which manganese-based compounds might be able to replace noble metal-based state-of-the-art catalysts for electrochemical water splitting. A diverse range of manganese-based compounds and composites are to be tested for the potential to serve as electrocatalysts in water electrolysis. Instead of developing a device or electrolyzer of superior characteristics to existing solutions, the project tries to establish a fundamental understanding of the underlying structure-function relationships.

**Figure 1.** logo of the cluster project

### Project partners and their expertise

Project partners in MANGAN comprise 25 research groups in 15 sub-projects. Partners come from the Fritz Haber Institute of the Max Planck Society, the Helmholtz Center Berlin, the Max Planck Institute for Chemical Energy Conversion and the Max Planck Institute for Iron Research, the technical universities of Aachen, Berlin, and Darmstadt, as well as the universities of Bochum, Duisburg-Essen, Erlangen-Nürnberg, Freiburg, Gießen, and Mainz, and BASF as partner from industry. Partners cover various approaches to synthesis of manganese-based compounds from oxides to composites to biomimetic complexes. To cover the full systemic complexity of water splitting, MANGAN includes work on new electrode materials as well as on analytic capacities ranging from fundamental electrochemistry to high-end spectroscopic techniques and theoretical modeling. A sub-project which is located at the MPI-CEC deals with the coordination of the project to ensure synergetic effects between the partners and provide basic functionalities of the project such as coordination of exchange of samples, standardized electrochemical testing and a common database to compile and analyze results. At the MPI-CEC, the research groups of Saskia Buller (Carbon and Applications), Serena De Beer (x-ray spectroscopy), Nicholas Cox (model water splitting), and Dimitrios Pantazis (water splitting) are involved in MANGAN.

### Electrochemical Standard Measurements

Functional evaluation of manganese-based electrocatalysts within MANGAN is focusing on the oxygen evolution reaction (OER, [3]). OER is generally considered the part reaction in water splitting with the most sluggish reaction kinetics. Hence, electrocatalysts for OER generally suffer from high overpotentials and a real breakthrough in this line of research is still missing. A major drawback in the search for suitable catalysts for OER is the lack of a standardized electrochemical testing protocol which allows for systematic evaluation of catalyst performance and enables comparison of different material classes. In order to tackle this problem, a standardized electrochemical protocol based on a rotating disk electrode (RDE) methodology drawing from existing attempts of standardization [4] was defined in close collaboration of all project partners during a workshop on electrochemical measurements. RDE measurements yield a series of defined key performance indicators (KPI) to ensure a common measure for the catalytic performance of novel manganese-based compounds. Another aspect which is given high consideration is catalyst stability.

Thirteen project sites are equipped with identical electrochemical equipment in order to achieve highly comparable results and use standard materials as benchmarks and means of quality control. Standardized testing is facilitated by the coordination project which also serves as focal point for electrochemistry within MANGAN.

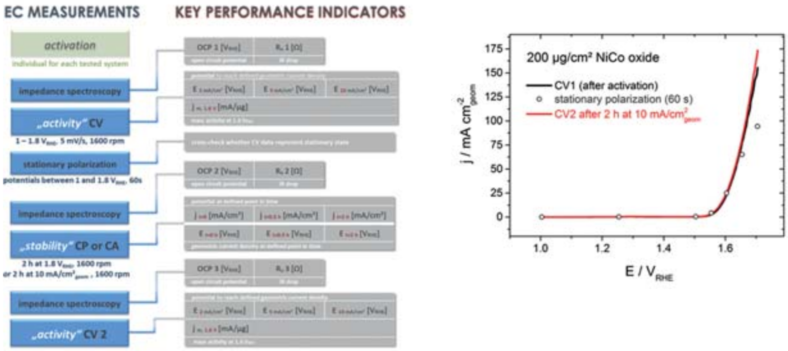


**Figure 2, left:** sequence of electrochemical standard measurements and KPI. **Right:** cyclic voltammograms (1 M KOH, 25°C, 5 mV/s, 1600 rpm) and stationary polarization measurement (60 s at respective potentials) of a standard material (commercial nickel cobalt oxide) before and after constant-current chronopotentiometric stability test (2 h at 10 $mA/cm^2_{geometric}$)

## In-depth analysis

Naturally, electrochemical standard measurements are only the starting point of analysis and are not considered complete characterization of a catalyst. However, RDE measurements help to identify promising candidates for highly active and stable electrocatalysts. Such catalysts are exchanged within the partners to take full benefit from the mutually complementing analytic capacities. As the systems under study have a highly dynamic nature, analysis is done pre- and post-electrochemistry as well as in-situ measurements.

### Database

The main output of the project is a common database set up by the coordination project at MPI-CEC (https://mangan.cec.mpg.de) that contains information on all samples generated within MANGAN. General information on each sample such as way of synthesis and elemental and structural composition are complemented by key performance indicators from electrochemical standard measurements and additional analysis. As all measurements, good and bad, are included in the database, the database will eventually allow to elucidate structure-function relationships of manganese-based catalysts for electrochemical water splitting.

### Project activities

Since the start of the sub-projects in May 2015, MANGAN coordination organizes semi-annual project meetings and regular workshops on electrochemistry, synthesis and advanced structural analysis. Regular visits of the coordinator to the project sites ensures quality control of electrochemical measurements. A two-day conference during which all project partners presented their findings to a wider audience was held in Harnackhaus in Berlin on 13 and 14 October 2016.

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3. Katsounaros, I., Cherevko, S., Zeradjanin, A. R. , Mayrhofer, K. J. J., Oxygen Electrochemistry as a Cornerstone for Sustainable Energy Conversion, *Angew. Chem. Int. Ed.*, 53, 102-121 (2014).
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**Publications and Presentations**

This list includes only the papers, oral and poster presentations of the coordination project.

Ioannis Spanos, Alexander Auer, Sebastian Neugebauer, Xiaohui Deng, Haru Tuysuz, Robert Schlögl, *Standardized benchmarking of water splitting catalysts in a combined electrochemical flow cell/ICP-OES setup*, **ACS Catalysis**, submitted.

Sebastian Neugebauer, Praveen Narangoda, Ioannis Spanos, Saskia Buller, Sebastien Cap, Robert Schlögl, *Standardized Electrochemical Measurements of Catalysts for the Oxygen Evolution Reaction*, Oral Presentation during the **4th German-Russian Seminar on Catalysis**, 5-7 September 2016, Kloster Banz, Germany.

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Sebastien Cap, Robert Schlögl, *MANGAN - Standardized Electrochemical Measurements for the Oxygen Evolution Reaction*, Oral Presentation during the **4th Ertl Symposium on Chemical Processes on Solid Surfaces**, 11-13 October 2016 in Berlin, Germany.

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Sebastien Cap, Robert Schlögl, *Standardized Measurements for Oxygen Evolution Reaction- Rotating Disk Electrode Measurements and Beyond*, Poster Presentation during the **18th Topical Meeting of the International Society of Electrochemistry**, 8-11 March 2016 in Gwangju, South Korea.

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Sebastien Cap, Robert Schlögl, *Standardized Rotating Disk Electrode Measurements of Electrocatalysts for Oxygen Evolution Reaction*, Poster Presentation during the **49th Jahrestreffen Deutscher Katalytiker**, 16-18 March 2016, Weimar, Germany.

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Sebastien Cap, Robert Schlögl, Electrochemical Standard Measurements of catalysts for the oxygen evolution reaction, Poster Presentation during the **Manfred Eigen Talks of the German Bunsen Society for Physical Chemistry**, 6-8 April 2016 in Mülheim an der Ruhr, Germany.

## The Institute in Public

The Research Communications team is responsible for press and public relations, for all graphic design tasks as well as photographs and the documentation of the institute's activities.

The team strives to serve as an interface between the institute and the public, and to create awareness for the important role of basic research in the field of chemical energy conversion. It promotes the perception of the research among the community, press, government, corporate partners, prospective students, alumni and internal stakeholders. Therefore, the team informs journalists with press releases, provides background knowledge and also invites them to visit the institute.

Moreover, the organization of various scientific and also public oriented events is a major part of the team's work:

The biggest of which being the yearly **Summer School**, which used to be hold in cooperation with the department of Molecular Theory and Spectroscopy. For the first time in 2016, the Summer School program was largely extended and combined themes from the Molecular Theory and Spectroscopy as well as the Heterogeneous Reactions group.

Another event, which was only just initiated in 2015, is the two-day conference for ORCA users, who had the chance to exchange thoughts and talk to the software developers in person.

Other considerable events the Research Communications team plans and coordinates are the Frontiers Award lecture series and the **Ernst Haage Award** ceremony, which was preceded in 2015 for the first time by a two-day symposium on chemical energy conversion. In 2016, the institute celebrated the 10th anniversary of the prize, and accompanied the ceremony again by an impressive symposium which took place at Schloss Broich. By hosting the conference in a well-known place in Mülheim an der Ruhr, the CEC aims to increase the international awareness of Mülheim as an extraordinary location for science.

Besides these recurring scientific events, the CEC hosted an open house, and also frequently opens its doors for school classes and other visitor groups. Together with two Mülheim institutions – the Hochschule Ruhr West and the Haus Ruhrnatur – the institute provided a group of school students with the opportunity to participate in a three-day vacation program including scientific experiments and tours of the laboratories. This program was initiated in 2014, and established as an annual project.

Additionally, the communication team organizes a **Girls' Day** every year, which aims to interest girls in scientific and technical professions.

The CEC also took part in the big science event **"WissensNacht Ruhr"**, and displayed excerpts of its research to public. Participation was initiated and coordinated by the Research Communications department, and successfully implemented by a group of CEC apprentices.

The Research Communications team, furthermore, regularly updates and improves the website and facebook page, and frequently generates content to be provided there, as well as taking care of all posters and printed media of the institute.

Another important aspect is the execution of internal communication activities, to provide transparency and keep all employees informed about the institute's proceedings. This is mainly done through the intranet, emailing, and a screen in the foyer.

The communicative goals in the upcoming years are to foster attractiveness for Mülheim as a scientific location, to strengthen cooperation with the city of Mülheim, and our neighboring institute with regards to the newly established joint campus. And to find new formats to bring together scientists and citizens to make our research more visible and tangible for the public. Furthermore, a relaunch of the institute's intranet is in planning, to further improve internal communication efforts.

## Teaching Activities

### 2014

Auer A. A.: Electron correlation, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2014-08-30 to 2014-09-04.

Bill, E.: Spin Hamiltonian Formalism and Magnetism, In-house Training Course MPI-CEC, Mülheim/Ruhr, Germany, 8 h, 2014.

Bill, E.: Mössbauer Spectroscopy, COST Action: CM1105 Training School 'Chemistry of Metals in Biological Systems' at Université Catholique De Louvain, Louvain-La-Neuve, Belgium, 2014.

Bill, E.: Mössbauer Spectroscopy, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2014-08-30 to 2014-09-04.

Bill, E.: Methods in Molecular Energy Research: Theory and Spectroscopy, IRTG 1422 (Metal Sites in Biomolecules: Structures, Regulation and Mechanisms) and SFB 1073 (Atomic Scale Control of Energy Conversion), Göttingen, Germany, 2014.

Braslavsky, S.E.: Biological Photoreceptors; Molecular Basis, Universidad de Santa Fé, Argentina, 30 h, 2014.

Gärtner, W.: Photobiology (lectures, excersise and practical training), Heinrich-Heine-Universität, Düsseldorf, WS 2013/2014

Gärtner, W.: Photobiology, Huazhong Agricultural University, Wuhan, China, 18 h per week, 2014.

Lubitz, W.: Probing Structure and Function of Hydrogenases and Hydrogenase Model Systems by Spectroscopic Techniques, Department of Chemistry, Texas A&M University, College Station, USA, 2014.

Lubitz, W.: Light-induced Water Splitting and Hydrogenase Production in Nature, Department of Chemistry, University of Alabama, Tuscaloosa, USA, 2014.

Neese, F.: COST Action: CM1105 COST Combined Practical and Lecture Workshop, (with tutorial), Training School "Chemistry of Metals in Biological Systems", Louvain-la-Neuve, Belgium, 2014.

Neese, F.: MPI CEC Summer School 2014 Methods in Molecular Energy Research: Theory and Spectroscopy. Lectures on ligand field theory, quantum chemistry, vibrational spectroscopy, effective Hamiltonians (with tutorial). Gelsenkirchen, Germany. 2014.

Neese, F.: Summer School "Advanced Metal-Organic Chemistry and Catalysis". Lectures on quantum chemical methods in catalysis (with tutorial), AMOCC 2014, Deurne, The Netherlands, 2014.

Neese, F.: 3rd Penn State Bioinorganic Workshop. Lectures on ligand field theory, quantum chemistry, vibrational spectrosocpy, theoretical spectroscopy (with tutorial), Penn State Uninverstity, USA, 2014.

Neese, F.: SeSE Winter School in Multiscale Modeling at the Royal Institute of Technology. Lectures on correlated ab initio methods (with tutorial), Stockholm, Sweden, 2014.

Pantazis D. A.: Computational prediction of EPR properties, and Computational approaches to magnetically coupled systems, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2014-08-30 to 2014-09-04.

Van Gastel, M.: Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2014-08-30 to 2014-09-04.

Van Gastel, M.: Allgemeine Chemie für Physiker, University Duisburg-Essen, Germany (WS 2014/2015)

Van Gastel, M.: Magnetische Eigenschaften der Materie, University Duisburg-Essen, Germany (WS 2014/2015)

Van Gastel, M.: Moderne Methoden der Biophysikalischen Chemie, University Duisburg-Essen, Germany (SS 2014)

Van Gastel, M.: Kinetik, University Duisburg-Essen, Germany (SS 2014)

### 2015

Auer A. A.: Band structure for chemists, IMPRS RECHARGE, 2015-11.

Bill, E.: Methods in Molecular Energy Research: Theory and Spectroscopy, IMPRS RECHARGE, Mülheim/Ruhr, Germany, 2015.

Gärtner, W.: Photobiology, Huazhong Agricultural University, Wuhan, China, 18 h per week, 2015.

Braslavsky, S.E.: Optoandina; Quito, Ecuador, 2015.

Braslavsky, S.E.: Photochemistry, Universidad de Buenos Aires, Argentina., 4 h, 2015.

Lubitz, W.: Water Oxidation and Proton Reduction - Chemistry of Molecular Model Systems (in Nature), Ringvorlesung, Fritz Haber Institut, Berlin, Germany, 2015

Lubitz, W.: Nature's Blueprints for an Artificial Photosynthesis, Lecture, Korean Academy of Science and Technology, Sogang University, Seoul Korea, 2015.

Lubitz, W.: Lecture Series "Methods in Biophysical Chemistry – EPR Spectroscopy", at the MPI for Chemical Energy Conversion in Cooperation with the Düsseldorfer Heinrich Heine Universität, Mülheim an der Ruhr, Germany, 2015.

Lubitz, W.: Applications of EPR Techniques: Detection of Radicals and Transition Metal Complexes in Biology and Chemistry; The Water Oxidizing Complex of Photosystem II; Metalloenzymes in Hydrogen Conversion, EFEPR Summer School, Bildungszentrum Elstal, Germany, 2015.

Neese, F.: Summer School of the European Federation of EPR Spectroscopists, Nature of the Spin Hamiltonian and Hyperfine Interactions (with tutorial), Berlin, Germany, 2015.

Neese, F.: MPI CEC Summer School 2015 Methods in Molecular Energy Research: Theory and Spectroscopy. Lectures on ligand field theory, quantum chemistry, vibrational spectroscopy, effective Hamiltonians (with tutorial), Gelsenkirchen, Germany, 2015.

Neese, F.: 1st ORCA User Meeting – Methods, applications and development. Lectures on ligand field theory, quantum chemistry, vibrational spectroscopy, effective Hamiltonians (with tutorial), Gelsenkirchen, Germany, 2015.

Neese, F.: European Summer School in Quantum Chemistry 2015 (ESQC 2015). Lectures on Algorithm Design, quantum chemical approximations and local correlation theory (with tutorial), Torre Normanna, Sicily, Italy, 2015.

Pantazis D. A.: Computational prediction of EPR properties, and computational approaches to magnetically coupled systems, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2015-09-18 to 2015-09-04.

Van Gastel, M.: EPR Spectroscopy, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2015-08-30 to 2015-09-04.

Van Gastel, M.: Allgemeine Chemie für Physiker, University Duisburg-Essen, Germany (WS 2015/2016)

Van Gastel, M.: Moderne Methoden der Biophysikalischen Chemie, University Duisburg-Essen, Germany (SS 2015)

Van Gastel, M.: Kinetik, University Duisburg-Essen, Germany (SS 2015)

## 2016

Auer A. A.: IMPRS RECHARGE, Introduction to Quantum Chemistry. 2016-01.

Auer A. A.: Lecture at TU Chemnitz - "Spektroskopie und Struktur". 2016-05/06.

Bill, E.: EPR - and Mössbauer Spectroscopy, Winter School 'EPR and Mössbauer Spectroscopy', COST Action CM1305 (ECOSTBio), at MPI-CEC Mülheim/Ruhr, Germany, 2016.

Braslavsky, S.E.: Biological Photoreceptors; Molecular Basis, Universidad de Mar del Plata, Argentina, 30 h, 2016.

Braslavsky, S.E.: "How to organize an International Meeting", Graduate School IMPRS-RECHARGE, MPI CEC, Mülheim/Ruhr, Germany, 2016.

Lubitz, W.: Lecture Series "Methods in Biophysical Chemistry – EPR Spectroscopy" at the MPI for Chemical Energy Conversion in Cooperation with the Düsseldorfer Heinrich-Heine-Universität, Mülheim an der Ruhr, Germany, 2016.

Neese, F.: 4th Penn State Bioinorganic Workshop. Lectures on ligand field theory, quantum chemistry, vibrational spectrosocpy, theoretical spectroscopy (with tutorial), Penn State, USA, 2016.

Neese, F.: 2nd ORCA User Meeting – Methods, applications and development, MPI for Chemical Energy Conversion, Mülheim/Ruhr, Germany, 2016.

Neese, F.: MPI CEC Summer School 2016 Physical Methods in Molecular and Heterogeneous Catalysis. Lectures on ligand field theory, quantum chemistry, vibrational spectroscopy, effective Hamiltonians (with tutorial), Gelsenkirchen, Germany, 2016.

Neese, F.: MWM 2016 Summer School Modern Wavefunction Methods in Electronic Structure Theory. Lectures on Algorithm Design, Large Molecules SCF and MP2 and Coupled Cluster Methods, Gelsenkirchen, Germany, 2016.

Ogata H., Photon and Molecules II, Graduate school of Nara Institute of Science and Technology, Nara Japan, 2016.

Pantazis D. A.: Computational prediction of EPR properties, and Computational approaches to magnetically coupled systems, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2016-10-02 to 2016-10-08.

Van Gastel, M.: EPR Spectroscopy, Summerschool MPI CEC, Wissenschaftspark Gelsenkirchen, Germany, 2016-10-02 to 2016-10-08.

Van Gastel, M.: Allgemeine Chemie für Physiker, University Duisburg-Essen, Germany (WS2016/2017)

Van Gastel, M.: Moderne Methoden der Biophysikalischen Chemie, University Duisburg-Essen, Germany (SS 2016)

Van Gastel, M.: Kinetik, University Duisburg-Essen, Germany (SS 2016)

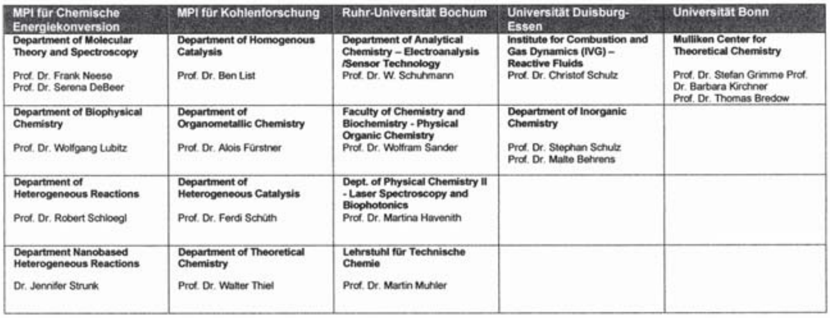
# IMPRS-RECHARGE
# International Max Planck Research School on Reactive Structure Analysis for Chemical Reactions

The International Max Planck Research School on Reactive Structure Analysis for Chemical Reactions (IMPRS-RECHARGE) was established in 2015. It is a co-operative effort of the following partners:

- Max-Planck-Institut für Chemische Energiekonversion (MPI CEC)
- Max-Planck-Institut für Kohlenforschung (MPI KOFO)
- Ruhr-Universität Bochum (RUB)
- University of Bonn (MCTC)
- University of Duisburg-Essen (UDE)

The spokesperson of the school is Prof. Frank Neese (MPI CEC).

### Institutes and Professors involved in IMPRS-RECHARGE



| MPI für Chemische Energiekonversion | MPI für Kohlenforschung | Ruhr-Universität Bochum | Universität Duisburg-Essen | Universität Bonn |
|---|---|---|---|---|
| **Department of Molecular Theory and Spectroscopy**<br>Prof. Dr. Frank Neese<br>Prof. Dr. Serena DeBeer | **Department of Homogenous Catalysis**<br>Prof. Dr. Ben List | **Department of Analytical Chemistry – Electroanalysis /Sensor Technology**<br>Prof. Dr. W. Schuhmann | **Institute for Combustion and Gas Dynamics (IVG) – Reactive Fluids**<br>Prof. Dr. Christof Schulz | **Mulliken Center for Theoretical Chemistry**<br>Prof. Dr. Stefan Grimme Prof. Dr. Barbara Kirchner<br>Prof. Dr. Thomas Bredow |
| **Department of Biophysical Chemistry**<br>Prof. Dr. Wolfgang Lubitz | **Department of Organometallic Chemistry**<br>Prof. Dr. Alois Fürstner | **Faculty of Chemistry and Biochemistry - Physical Organic Chemistry**<br>Prof. Dr. Wolfram Sander | **Department of Inorganic Chemistry**<br>Prof. Dr. Stephan Schulz<br>Prof. Dr. Malte Behrens | |
| **Department of Heterogeneous Reactions**<br>Prof. Dr. Robert Schloegl | **Department of Heterogeneous Catalysis**<br>Prof. Dr. Ferdi Schüth | **Dept. of Physical Chemistry II - Laser Spectroscopy and Biophotonics**<br>Prof. Dr. Martina Havenith | | |
| **Department Nanobased Heterogeneous Reactions**<br>Dr. Jennifer Strunk | **Department of Theoretical Chemistry**<br>Prof. Dr. Walter Thiel | **Lehrstuhl für Technische Chemie**<br>Prof. Dr. Martin Muhler | | |

### Mission of the IMPRS-RECHARGE

The guiding ideas behind the establishment of the IMPRS-RECHARGE are twofold: a) the necessity to unite cultures of the fields of homogeneous- and heterogeneous catalysis and b) to educate students in the theory and application of advanced physical and theoretical methods. Both goals serve the aim to provide the education background that allows the students to tackle complex problems in the analysis of catalytic reaction mechanisms. The ultimate goal is a detailed atomistic understanding of these processes in solution or at (electrode) surfaces, which would ultimately allow for rational design approaches towards catalysis to be established. This ambitious goal clearly requires a dedicated interdisciplinary effort. The necessary expertise to this endeavor is provided by the very strong partnership between the partners that are committed to the IMPRS-RECHARGE.

### Education, Doctoral Program, Curriculum, Teaching

The doctoral program combines the excellent research conditions of the partners with an intensive interdisciplinary teaching program. The IMPRS-RECHARGE will cover the following research topics:

- Heterogeneous Catalysis
- Homogeneous Catalysis
- Biological Catalysis
- Magnetic and Optical Spectroscopy
- Physical Organic Chemistry
- Electrochemistry
- Laser Spectroscopy and Biophotonics
- Inorganic Chemistry
- Theoretical Chemistry
- Computational Chemistry

The IMPRS-RECHARGE curriculum consists of mandatory as well as voluntary offers. With this offers the scientific background of the students will be deepened, their soft skills will be enhanced and their integration in the scientific community will be supported.

The requirements to receive the final IMPRS-RECHARGE certificate are:

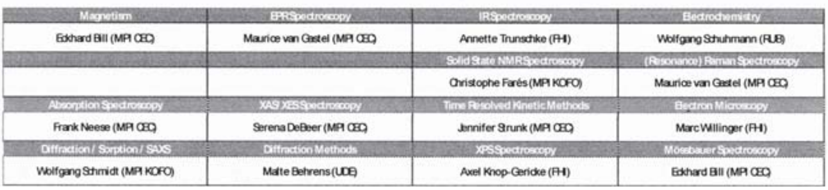
- Attendance of Basic Courses
- Attendance of Advanced Courses
- Participation in Summer Schools
- Organization of the International Symposia Series
- Participation in Discussion Meetings
- Attendance of Additional Skills Courses
- Organization of Thesis Advisory Committee
- Final Oral Presentation

The official commencement of IMPRS-RECHARGE took place on August 30, 2015 and was followed by the first teaching activity, the **Summer School on "Methods in Molecular Energy Research: Theory and Spectroscopy"** (Aug 30 – Sept 4, 2015, Wissenschaftspark, Gelsenkirchen).

During the winter term 2015/16 the **Lecture Series on "Introduction to Recharge. Theory and Experiment"**, a basic course, was held:

| Ligand Field Theory | Spin Hamiltonians | Introduction to Solids | Nanoparticles |
|---|---|---|---|
| Mihail Atanasov (MPI CEC) | Eckhard Bill (MPI CEC) | Malte Behrens (UDE) | Hartmut Wiggers (UDE) |
| Electron and Proton Transfer | Introductory Band Structure | Metal Organic Reaction Mechanisms | Organic Reaction Mechanisms |
| Chinmoy Ranjan (MPI CEC) | Alexander Auer (MPI CEC) | Stephan Schulz (UDE) | Wolfram Sander (RUB) |
| Quantum Chemistry I | Photocatalysis | Heterogenous Catalysis | Reaction Engineering and Kinetics |
| Alexander Auer (MPI CEC) | Jennifer Strunk (MPI CEC) | Martin Muhler (RUB) | Martin Muhler (RUB) |
| Basic Molecular Dynamics Simulations and Calculation of Spectroscopic Properties (Quantum Chemistry II) | | | |
| Barbara Kirchner (MCTC) | Barbara Kirchner (MCTC) | Barbara Kirchner (MCTC) | Barbara Kirchner (MCTC) |
| Day of Catalysis (MPI für Kohlenforschung) | | | |
| Homogeous Catalysis (B. List) | Heterogenous Catalysis (G. Prieto) | Organometallic Chemistry (A. Fürstner) | Theoretical Chemistry (W. Thiel) |

During the summer term 2016 the **Lecture Series on "Physical Methods in Homogeneous and Heterogeneous Catalysis"**, a basic course in physical methods, was held:



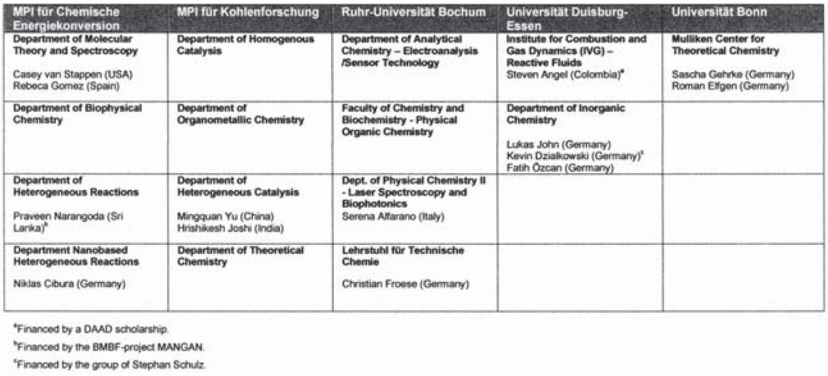
| Magnetism | EPR Spectroscopy | IR Spectroscopy | Electrochemistry |
|---|---|---|---|
| Eckhard Bill (MPI CEC) | Maurice van Gastel (MPI CEC) | Annette Trunschke (FHI) | Wolfgang Schuhmann (RUB) |
|  |  | **Solid State NMR Spectroscopy** | **(Resonance) Raman Spectroscopy** |
|  |  | Christophe Farès (MPI KOFO) | Maurice van Gastel (MPI CEC) |
| **Absorption Spectroscopy** | **XAS XES Spectroscopy** | **Time Resolved Kinetic Methods** | **Electron Microscopy** |
| Frank Neese (MPI CEC) | Serena DeBeer (MPI CEC) | Jennifer Strunk (MPI CEC) | Marc Willinger (FHI) |
| **Diffraction / Sorption / SAXS** | **Diffraction Methods** | **XPS Spectroscopy** | **Mössbauer Spectroscopy** |
| Wolfgang Schmidt (MPI KOFO) | Malte Behrens (UDE) | Axel Knop-Gericke (FHI) | Eckhard Bill (MPI CEC) |

The physical methods lecture series was followed by the **Summer School on "Physical Methods in Molecular and Heterogeneous Catalysis" (**September 18-25, 2016 Wissenschaftspark, Gelsenkirchen).

A committee of IMPRS-RECHARGE students commenced the organization of the International Symposia Series on June 20, 2016. The first International Conference on **"Catalysis for Energy Conversion: Theory meets Experiment"** is scheduled for September 17-21, 2017 at the NanoEnergieTechnikZentrum (NETZ) at University of Duisburg-Essen (Campus Duisburg). The initial phase of the organizational work of the students was inaugurated with the talk "A Scientific Conference: Purpose, Subject, Organization, and Financing" by Professor Silvia Braslavsky (MPI CEC) and accompanied by a series of meetings, in which experienced scientists (Professor Wolfgang Gärtner, Dr. Maurice van Gastel, MPI CEC) advised the students.

**Admission of Doctoral Candidates / countries of origin / gender relationship**

IMPRS-RECHARGE accepts applications throughout the year, there are no deadlines. The applicants shall submit a letter of motivation, CV, transcript and degree certificate of Bachelor degree, transcript and degree certificate of Master degree, and two reference letters. Promising applicants will be interviewed via phone or video conference.



| MPI für Chemische Energiekonversion | MPI für Kohlenforschung | Ruhr-Universität Bochum | Universität Duisburg-Essen | Universität Bonn |
|---|---|---|---|---|
| **Department of Molecular Theory and Spectroscopy**<br>Casey van Stappen (USA)<br>Rebeca Gomez (Spain) | **Department of Homogenous Catalysis** | **Department of Analytical Chemistry – Electroanalysis /Sensor Technology** | **Institute for Combustion and Gas Dynamics (IVG) – Reactive Fluids**<br>Steven Angel (Colombia)[a] | **Mulliken Center for Theoretical Chemistry**<br>Sascha Gehrke (Germany)<br>Roman Elfgen (Germany) |
| **Department of Biophysical Chemistry** | **Department of Organometallic Chemistry** | **Faculty of Chemistry and Biochemistry - Physical Organic Chemistry** | **Department of Inorganic Chemistry**<br>Lukas John (Germany)<br>Kevin Dzialkowski (Germany)[c]<br>Fatih Özcan (Germany) |  |
| **Department of Heterogeneous Reactions**<br>Praveen Narangoda (Sri Lanka)[b] | **Department of Heterogeneous Catalysis**<br>Mingquan Yu (China)<br>Hrishikesh Joshi (India) | **Dept. of Physical Chemistry II - Laser Spectroscopy and Biophotonics**<br>Serena Alfarano (Italy) |  |  |
| **Department Nanobased Heterogeneous Reactions**<br>Niklas Cibura (Germany) | **Department of Theoretical Chemistry** | **Lehrstuhl für Technische Chemie**<br>Christian Froese (Germany) |  |  |

[a] Financed by a DAAD scholarship.

[b] Financed by the BMBF-project MANGAN.

[c] Financed by the group of Stephan Schulz.

Top candidates will be invited to take part in a selection colloquium at the Max-Planck-Institut für Chemische Energiekonversion or at one of the partner institutions. IMPRS-RECHARGE will have an overall size of about 20 students. So far IMPRS-RECHARGE has accepted 14 doctoral students (see chart above).

### Publications

1. Gehrke, S., Hollóczki O.: A molecular mechanical model for N-heterocyclic carbenes. *Phys. Chem. Chem. Phys.* 18, 22070 – 22080 (2016).

2. Elfgen, R., Hollóczki O., Ray, P., Groh, M.F., Ruck, M., Kirchner, B. Theoretical investigation of Te4Br2 molecule in ionic liquids. Z. Anorg. Allg. Chem, 643, 41-52 (2017).

### Talks

N. Cibura: $MnO_x$ in photocatalysis: structural characterization and photoelectrochemistry. (Center for Nanointegration Duisburg-Essen (CENIDE), Duisburg, Germany 2015-12-07)

R. Elfgen: Inorganic materials in ionic liquids from theoretical considerations. (Symposium "Material Synthesis in Ionic liquids and Interfacial Processes", Goslar, Germany, from 2016-04-13 to 2016-04-15)

### Posters

N. Cibura, S. Ristig, J. Strunk: Fundamental studies of manganese oxides in photocatalysis. (Jahrestreffen Deutscher Katalytiker 2016, Weimar, Germany, from 2016-03-16 to 2016-03-18)

N. Cibura, S. Ristig, J. Strunk: Fundamental studies of manganese oxides in photocatalysis. (Manfred-Eigen-Nachwuchswissenschaftlergespräch: "Physical Chemistry of Solar Fuels Catalysis" 2016, Mülheim an der Ruhr, Germany, from 2016-04-06 to 2016-04-08)

N. Cibura, S. Ristig, J. Strunk: $MnO_x$-based material development for photocatalytic application. (The materials chain: from discovery to production, Bochum, Germany, from May 30 – June 1, 2016)

C. M. Van Stappen, E. Bill, S. DeBeer, F. Neese: Towards uncovering the heterometal role of N2ase reactivity: an MCD investigation of vanadium. (Penn State University, State College, USA, from 201606-02 to 2016-06-10)

R. Elfgen, P. Ray, B. Kirchner: Ionic Liquids and Template-Effects. (International Conference on Ionic Liquids - Priority Program 1708 "Material Synthesis near Room Temperature", Potsdam, Germany, from 2016-09-28 to 2016-09-30)

S. Angel, H. Wiggers, C. Schulz: Spray-flame synthesis of LaCoO3 perovskite using low-cost precursors. (CENIDE-Jahrfeier, Kreuzeskirche Essen, Germany, 2016-11-22).

### Scholarships

Steven Angel had been awarded with a DAAD scholarship on 2015-03-02.

### Special Equipment Provided to the Doctoral Researchers

A DFT/ORCA Computer Cluster had been delivered and implemented in 2016. Calculations will start at the beginning of 2017.

# Scientific Output and Statistics

## List of Publications

### 2014

Adamska-Venkatesh, A., Krawietz, D., Siebel, J., Weber, K., Happe, T., Reijerse, E., Lubitz, W., New Redox States Observed in [FeFe] Hydrogenases Reveal Redox Coupling Within the H-Cluster, *J. Am. Chem. Soc.*, 136, 11339-11346 (2014).

Albarracin, V. H., Simon, J., Pathak, G. P., Valle, L., Douki, T., Cadet, J., Borsarelli, C. D., Farias, M. E., Gärtner, W., First characterisation of a CPD-class I photolyase from a UV-resistant extremophile isolated from High-Altitude Andean Lakes, *Photochem. Photobiol. Sci.*, 13, 739-750 (2014).

Ali, M. E., Nair, N. N., Retegan, M., Neese, F., Staemmler, V., Marx, D., The iron-sulfur core in Rieske proteins is not symmetric, *J. Biol. Inorg. Chem.*, 19, 1287-1293 (2014).

Altun, A., Breidung, J., Neese, F., Thiel, W., Correlated Ab Initio and Density Functional Studies on $H_2$ Activation by $FeO^+$, *J. Chem. Theory Comput.*, 10, 3807-3820 (2014).

Anders, K., Gutt, A., Gärtner, W., Essen, L. O., Phototransformation of the Red Light Sensor Cyanobacterial Phytochrome 2 from Synechocystis Species Depends on Its Tongue Motifs, *J. Biol. Chem.*, 289, 25590-25600 (2014).

Arnet, N. A., Dugan, T., Mercado, B., Brennessel, W., Bill, E., Holland, P. L., Synthesis and characterization of an iron sulfide hydride complex as a model for a nitrogenase intermediate, *Abstr. Pap. Am. Chem. Soc.*, 248, 1 (2014).

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*, 7, 179-194 (2014).

Asami, K., Takashina, A., Kobayashi, M., Iwatsuki, S., Yajima, T., Kochem, A., van Gastel, M., Tani, F., Kohzuma, T., Thomas, F., Shimazaki, Y., Characterization of one-electron oxidized copper(II)-salophen-type complexes; effects of electronic and geometrical structures on reactivities, *Dalton Trans.*, 43, 2283-2293 (2014).

Björnsson, R., Lima, F. A., Spatzal, T., Weyhermüller, T., Glatzel, P., Bill, E., Einsle, O., Neese, F., DeBeer, S., Identification of a spin-coupled Mo(III) in the nitrogenase iron-molybdenum cofactor, *Chem. Sci.*, 5, 3096-3103 (2014).

Blusch, L. K., Mitevski, O., Martin-Diaconescu, V., Propper, K., DeBeer, S., Dechert, S., Meyer, F., Selective Synthesis and Redox Sequence of a Heterobimetallic Nickel/Copper Complex of the Noninnocent Siamese-Twin Porphyrin, *Inorg. Chem.*, 53, 7876-7885 (2014).

Böhm, K. H., Banert, K., Auer, A. A., Identifying Stereoisomers by ab-initio Calculation of Secondary Isotope Shifts on NMR Chemical Shieldings, *Molecules*, 19, 5301-5312 (2014).

Bravo-Rodriguez, K., Ismail-Ali, A. F., Klopries, S., Kushnir, S., Ismail, S., Fansa, E. K., Wittinghofer, A., Schulz, F., Sanchez-Garcia, E., Predicted Incorporation of Non-native Substrates by a Polyketide Synthase Yields Bioactive Natural Product Derivatives, *ChemBioChem*, 15, 1991-1997 (2014).

Burton, K. M. E., Belli, R., Huang, C., Pantazis, D. A., Rosenberg, L., Ru-mediated hydrophosphination of alkenes and alkynes, *Abstr. Pap. Am. Chem. Soc.*, 248, 1 (2014).

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Carrero, C. A., Schlögl, R., Wachs, I. E., Schomaecker, R., Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts, *ACS Catal.*, 4, 3357-3380 (2014).

Chan, S. C., England, J., Wieghardt, K., Wong, C. Y., Trapping of the putative 1,2-dinitrosoarene intermediate of benzofuroxan tautomerization by coordination at ruthenium and exploration of its redox non-innocence, *Chem. Sci.*, 5, 3883-3887 (2014).

Chandrasekaran, P., Greene, A. F., Lillich, K., Capone, S., Mague, J. T., DeBeer, S., Donahue, J. P., A Structural and Spectroscopic Investigation of Octahedral Platinum Bis(dithiolene)phosphine Complexes: Platinum Dithiolene Internal Redox Chemistry Induced by Phosphine Association, *Inorg. Chem.*, 53, 9192-9205 (2014).

Chaudhuri, S., Bera, S., Biswas, M. K., Roy, A. S., Weyhermüller, T., Ghosh, P., Oxidovanadium(IV), oxidomolybdenum(VI) and cobalt(III) complexes of o-phenylenediamine derivatives: oxidative dehydrogenation and photoluminescence, *Inorg. Chem. Front.*, 1, 331-341 (2014).

Chen, Z. H., Raffelberg, S., Losi, A., Schaap, P., Gärtner, W., A cyanobacterial light activated adenylyl cyclase partially restores development of a *Dictyostelium discoideum*, adenylyl cyclase a null mutant, *J. Biotechnol.*, 191, 246-249 (2014).

Codesido, N. O., Weyhermüller, T., Olabe, J. A., Slep, L. D., Nitrosyl-Centered Redox and Acid-Base Interconversions in $[Ru(Me_3[9]aneN_3)(bpy)(NO)]^{3,2,1+}$. The p$K_a$ of HNO for its Nitroxyl Derivative in Aqueous Solution, *Inorg. Chem.*, 53, 981-997 (2014).

Cormanich, R. A., Durie, A., Bjornsson, R., Rittner, R., O'Hagan, D., Buhl, M., Density Functional Study of Interactions between Fluorinated Cyclohexanes and Arenes, *Helv. Chim. Acta*, 97, 797-807 (2014).

Cox, N., Retegan, M., Neese, F., Pantazis, D. A., Boussac, A., Lubitz, W., Electronic structure of the oxygenevolving complex in photosystem II prior to O-O bond formation, *Scienc*e, 345, 804-808 (2014).

Cramer S. P., Wang H., Dapper C., Newton W. E., Ogata H., Lubitz W., Kuchenreuther J. M., Swartz J.R., LeBrun N., Yoda Y., Nuclear Resonance Vibrational Spectroscopy (NRVS) of Iron-Based Enzymes for Hydrogen Metabolism, Nitrogen Fixation, Small Molecule Sensing, DNA Repair, Photosynthesis, and Iron Storage. *SPring-8 Information*, 19, 18-21 (2014).

Darmon, J. M., Yu, R. P., Semproni, S. P., Turner, Z. R., Stieber, S. C. E., DeBeer, S., Chirik, P. J., Electronic Structure Determination of Pyridine N-Heterocyclic Carbene Iron Dinitrogen Complexes and Neutral Ligand Derivatives, *Organometallics*, 33, 5423-5433 (2014).

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Falkenhagen, J. P., Braun, B., Bill, E., Sattler, D., Limberg, C., A Cubic Fe4Mo4 Oxo Framework and Its Reversible Four-Electron Redox Chemistry, *Inorg. Chem.*, 53, 7294-7308 (2014).

Ferre, N., Huix-Rotllant, M., Filatov, M., Gozem, S., Schapiro, I., Olivucci, M., Chen, S. F., Navizet, I., Lindh, R., Liu, Y. J., Approximate density functional theory for complex photoreactions in biological systems, *Abstr. Pap. Am. Chem. Soc.*, 247, 2 (2014).

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Geng, C. Y., Ye, S. F., Neese, F., Does a higher metal oxidation state necessarily imply higher reactivity toward H-atom transfer? A computational study of C-H bond oxidation by high-valent iron-oxo and -nitrido complexes, *Dalton Trans.*, 43, 6079-6086 (2014).

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Hsieh, C. H., Ding, S. D., Erdem, Ö. F., Crouthers, D. J., Liu, T. B., McCrory, C. C. L., Lubitz, W., Popescu, C. V., Reibenspies, J. H., Hall, M. B., Darensbourg, M. Y., Redox active iron nitrosyl units in proton reduction electrocatalysis, *Nature Commun.*, 5, 3684 DOI: 3610.1038/ncomms4684 (2014).

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Kathawate, L., Joshi, P. V., Dash, T. K., Pal, S., Nikalje, M., Weyhermüller, T., Puranik, V. G., Konkimalla, V. B., Salunke-Gawali, S., Reaction between lawsone and aminophenol derivatives: Synthesis, characterization, molecular structures and antiproliferative activity, *J. Mol. Struct.*, 1075, 397-405 (2014).

Kempe, P., Löschner, T., Auer, A. A., Seifert, A., Cox, G., Spange, S., Thermally Induced Twin Polymerization of 4H-1,3,2-Benzodioxasilines, *Chem. Eur. J.*, 20, 8040-8053 (2014).

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**135 Publications in 2014**

## List of Publications

### 2015

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**149 Publications in 2015**

## List of Publications

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Wang, C. C., Chang, H. C., Lai, Y. C., Fang, H. Y., Li, C. C., Hsu, H. K., Li, Z. Y., Lin, T. S., Kuo, T. S., Neese, F., Ye, S. F., Chiang, Y. W., Tsai, M. L., Liaw, W. F., Lee, W. Z., A Structurally Characterized Nonheme Cobalt-Hydroperoxo Complex Derived from Its Superoxo Intermediate via Hydrogen Atom Abstraction, *J. Am. Chem. Soc.*, 138, 14186-14189 (2016).

Wang, F., Büchel, R., Savitsky, A., Zalibera, M., Widmann, D., Pratsinis, S. E., Lubitz, W., Schüth, F., *In Situ* EPR Study of the Redox Properties of CuO-$CeO_2$ Catalysts for Preferential CO Oxidation (PROX), *ACS Catal.*, 6, 3520-3530 (2016).

Wang, G. H., Cao, Z. W., Gu, D., Pfänder, N., Swertz, A. C., Spliethoff, B., Bongard, H. J., Weidenthaler, C., Schmidt, W., Rinaldi, R., Schüth, F., Nitrogen-Doped Ordered Mesoporous Carbon Supported Bimetallic PtCo Nanoparticles for Upgrading of Biophenolics, *Angew. Chem. Int. Ed.*, 55, 8850-8855 (2016).

Wang, M., Weyhermüller, T., Bill, E., Ye, S. F., Wieghardt, K., Structural and Spectroscopic Characterization of Rhenium Complexes Containing Neutral, Monoanionic, and Dianionic Ligands of 2,2 ‘-Bipyridines and 2,2 ‘:6,2 ’’-Terpyridines: An Experimental and Density Functional Theory (DFT)-Computational Study, *Inorg. Chem.*, 55, 5019-5036 (2016).

Weide, P., Schulz, K., Kaluza, S., Rohe, M., Beranek, R., Muhler, M., Controlling the Photocorrosion of Zinc Sulfide Nanoparticles in Water by Doping with Chloride and Cobalt Ions, *Langmuir*, 32, 12641-12649 (2016).

Werncke, C. G., Suturina, E., Bunting, P. C., Vendier, L., Long, J. R., Atanasov, M., Neese, F., Sabo-Etienne, S., Bontemps, S., Homoleptic Two-Coordinate Silylamido Complexes of Chromium(I), Manganese(I), and Cobalt(I), *Chem. Eur. J.*, 22, 1668-1674 (2016).

Willinger, E., Yi, Y. M., Tarasov, A., Blume, R., Massué, C., Girgsdies, F., Querner, C., Schwab, E., Schlögl, R., Willinger, M. G., Atomic-Scale Insight on the Increased Stability of Tungsten-Modified Platinum/Carbon Fuel Cell Catalysts, *ChemCat Chem*, 8, 1575-1582 (2016).

Ye, S. F., Bill, E., Neese, F., Electronic Structures of the $[Fe(N_2)(SiP^{iPr}_3)]^{+1/0/-1}$ Electron Transfer Series: A Counterintuitive Correlation between Isomer Shifts and Oxidation States, *Inorg. Chem.*, 55, 3468-3474 (2016).

Ye, S. F., Kupper, C., Meyer, S., Andris, E., Navratil, R., Krahe, O., Mondal, B., Atanasov, M., Bill, E., Roithova, J., Meyer, F., Neese, F., Magnetic Circular Dichroism Evidence for an Unusual Electronic Structure of a Tetracarbene-Oxoiron(IV) Complex, *J. Am. Chem. Soc.*, 138, 14312-14325 (2016).

Yuan, C., Li, H. Z., Tang, K., Gärtner, W., Scheer, H., Zhou, M., Zhao, K. H., Near infrared fluorescent biliproteins generated from bacteriophytochrome AphB of Nostoc sp PCC 7120, *Photochem. Photobiol. Sci.*, 15, 546-553 (2016).

**145 Publications in 2016**

## Invited and Plenary Lectures at Conferences

### 2014

Adamska-Venkatesh, A.; Simmons, T.; Siebel, J.; Artero, V.; Reijerse, E.; Lubitz, W.: Pulsed EPR Studies of an [FeFe] Hydrogenase with a Non-native Cofactor (22th Benelux EPR Society Meeting, Maastricht, The Netherlands, 2014)

Bill, E.: Iron Complexes at the Limits of Classical Valence State Assignments (SFB Meeting, Joint Workshop, Göttingen, Germany, 2014)

Bill, E.: Spectroscopy of Iron in Enzymes, Molecules and Solids (Excellence Cluster 'General Meeting of UniCat', Berlin, Germany, 2014)

Braslavsky, Silvia E.: XXVth IUPAC Symposium on Photochemistry, Bordeaux, France (2014)

Conzuelo, F.; Stapf, S.; Markovic, N.; Zhao, F.; Hartmann, V.; Alsheikh Oughli, A.; Rüdiger, O.; Rögner, M.; Lubitz, W.; Plumeré, N.; Schuhmann, W.: Redox-hydrogel Embedded Hydrogenase and Photosystem I: Study of Properties and Applications (572nd Wilhelm und Else Heraeus Seminar on "Exploring Solvation Science" organized by RESOLV, Bochum, Germany, 2014)

Cox, N.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation (Gordon Research Conference: Photosynthesis - From Evolution of Fundamental Mechanisms to Radical Re-Engineering, West Dover, VT, USA, 2014)

Cox, N.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation (EPR Symposium of the Rocky Mountain Conference on Magnetic Resonance, Copper Mountain, Colorado, USA, 2014)

Cox, N.: The Structure of Nature's Water Splitting Catalysis Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (ASU, Tempe, USA, 2014)

Cox, N.: The Structure of Nature's Water Splitting Catalysis Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (Caltech, USA, 2014)

Cox, N.: The Structure of Nature's Water Splitting catalysis Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (UC Berkeley, USA, 2014)

Cox, N.: The Structure of Nature's Water Splitting Catalysis Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (UC Davis, USA, 2014)

Cox, N.: EPR Methods for the Study of Photosynthetic Systems (DIP Meeting on "Biomaterials and Bioinspired Assemblies for Nanoengineered Optobioelectronic Systems", Berlin, Germany, 2014)

Cox, N.; Pérez-Navarro, M.; Lohmiller, T.; Rapatskiy, L.; Neese, F.; Boussac, A.; Lubitz, W.; Pantazis, D. A.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (12th Nordic Congress on Photosynthesis, NPC12, 2014)

Cox, N.: Pérez-Navarro, M.; Lohmiller, T.; Rapatskiy, L.; Neese, F.; Boussac, A.; Lubitz, W.; Pantazis, D. A.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation: Water Binding and Water Splitting in Photosynthesis (ELI-ALPS Workshop and COST Training School Szeged, Hungary, 2014)

Cox, N.; Retegan, M.; Neese, F.; Boussac, A.; Pantazis, D. A.; Lubitz, W.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation (IES-APES Nara, Japan, 2014)

Cox, N.; Retegan, M.; Neese, F.; Boussac, A.; Pantazis, D. A.; Lubitz, W.: The Structure of Nature's Water Splitting Catalyst Immediately Prior to O-O Bond Formation (ESF EuroSolarFules Network Meeting, Passau, Germany, 2014)

DeBeer, S.: X-ray Spectroscopic Insights into Biological Catalysis, (Brookhaven National Laboratory, NY, USA, 2014-04)

DeBeer, S.: Insights into Biological Dinitrogen Reduction - New Tools for Understanding Small Molecule Activation, (Catalytic Routines for Small Molecule Activation Meeting, Venice, Italy, 2014-05)

DeBeer, S.: Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES..., (3rd Penn State Bioinorganic Workshop, State College PA, 2014-06)

DeBeer, S.: Insights into Biological Dinitrogen Reduction, (Frontiers in Metallobiochemistry III, State College, PA, 2014-06)

DeBeer, S.: X-ray Spectroscopy as a Probe of Catalysis, (U. K. Catalysis Network Meeting, Bristol, United Kingdom, 2014-06)

DeBeer, S.: New Tools for Understanding Metalloprotein Active Sites, (Physics Departmental Colloquium, TU Berlin, Berlin, Germany, 2014-07)

DeBeer, S.: Insights into Biological Dinitrogen Reduction - New Tools for Understanding Small Molecule Activation, (12th European Conference on Bioinorganic Chemistry, Zürich, Switzerland, 2014-08)

DeBeer, S.: Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES..., (Methods in Molecular Energy Research Summer School, Gelsenkirchen, Germany, 2014-08)

DeBeer, S.: Making and breaking bonds: X-ray absorption and emission studies of small molecule activation in biology, (TU Dortmund, Physics Department Colloquium, 2014-10)

DeBeer, S.: Metal Sites in Biomolecules, (International Research Training Group (IRTG), RWTH Aachen, Aachen, Germany, 2014-12)

Gärtner, W.: Kinetic and Spectroscopic Characterization of Isolated GAF Domains from Cyanobacteriochromes, (Gordon Conference: Photosensory Receptors & Signal Transduction, Barga, Italien, 2014-04)

Gärtner, W.: DFG-Start-up Meeting Schwerpunkt Optogenetics, (DFG-Start-up Meeting Schwerpunkt Optogenetics, Bad Homburg, Germany, 2014-06)

Gärtner, W.: Biological Photoreceptors as Tools in Superresolution Microscopy and Optogenetics Applications, (Bi-Annual Meeting Am. Soc. Photobiology (ASP), San Diego, 2014-06)

Gärtner, W.: Regulation of chromophore photochemistry by amino acids in the protein binding site in bilin-binding GAF domains, (ICPP (Intl. Congress on Porphyrins and Phthalocyanins), Istanbul, Türkei, 2014-06)

Gärtner, W.: The Dual Function of Microbial Photoreceptors – Regulation of Microbial Lifestyle and Toolbox for Biotechnological Applications, (International Congress on Photobiology, Cordoba, Argentinien, 2014-09)

Gärtner, W.: The Dual Function of Microbial Photoreceptors – Regulation of Microbial Lifestyle and Toolbox for Biotechnological Applications, (Tucuman, Argentinien, 2014-09)

Lubitz, W.: The Water Splitting Machine of Photosynthesis: An Enzyme that Changed the World (The 49th Winterseminar, Biophysical Chemistry, Molecular Biology and Cybernetics of Cell Functions. Klosters, Switzerland 2014)

Lubitz, W.: Artificial Hydrogenases for Hydrogen Production (Gordon Research Conference on Renewable Energy: Solar Fuels. Ventura, USA, 2014)

Lubitz, W.: Learning from Nature: Design of Catalysts for Water Splitting and Hydrogen Production/Conversion (Künstliche Fotosynthese, acatech, München, Germany, 2014)

Lubitz, W.: Water Splitting in Photosynthesis ("From the end to a new era in photosynthesis", The David Lopatie Conference Center, Weizmann Institute of Science, Rehovot, Israel, 2014)

Lubitz, W.: Light-Induced Water Oxidation in Photosynthesis Studied by Magnetic Resonance Techniques (Institut für Physikalische und Theoretische Chemie der Goethe-Universität Frankfurt und GDCh-Ortsverband Frankfurt, Frankfurt, Germany, 2014)

Lubitz, W.: The Enzymes Wateroxidase and Hydrogenase - Learning from Nature's Ingenious Concepts Symposium "Sustainable Hydrogen and Fuels – Stauts and Perspectives", Leibniz-Institut für Katalyse e.V. der Universität Rostock, Rostock, Germany, 2014)

Lubitz, W.: EPR - A Key Technique to Understand Metal Biocatalysis (International Conference on Magnetic Resonance: Fundamental Research and Pioneering Applications (MR-70), Kazan, Russia, 2014)

Lubitz, W.: Wateroxidase and Hydrogenase: Lessons from Nature (Theo Murphy International Scientific Meeting "Do we need a global project in artificial photosynthesis (solar fuels and chemicals)?" The Royal Society, Chichely Hall, Home of the Kavli Royal Society International Centre, Buckinghamshire, UK, 2014)

Lubitz, W.: Nature's Water Splitting Machine Probed by Advanced EPR Techniques (IXth EF-EPR Conference, Marseille, France, 2014)

Lubitz, W.: Wie Pflanzen Wasser spalten (128. Versammlung der Gesellschaft Deutscher Naturforscher und Ärzte e.V. (GDNÄ), Mainz, Germany, 2014)

Lubitz, W.: Light-induced Water Splitting: Learning from Nature (Turkish - German Conference on Energy Technologies, Middle East Technical University (METU), Ankara, Turkey, 2014)

Lubitz, W.: The Spin as Functional Probe in Biological, Energy Conversion and Storage (43rd Southeastern Magnetic Resonance Conference, University of Alabama, Tuscaloosa, Alabama USA, 2014)

Lubitz, W.: Molecular Catalysis for Water Splitting and Hydrogen Production/Conversion (Workshop "Künstliche Fotosynthese – Technikzukünfte", acatech, Berlin, Germany, 2014)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Conversion in Nature: Basis for Artificial Photosynthesis (Joint Conference of Asia-Pacific EPR/ESR Society (APES) Symposium 2014, International EPR(ESR) Society (IES) Symposium, and the 53rd The Society of Electron Spin Science and Technology (SEST) Annual Meeting, Nara, Japan, 2014)

Lubitz, W.: The Spin as Functional Probe in Metal Biocatalysis International Conference on Artificial Photosynthesis ICARP2014 (Awaji Yumebutai International Conference Center in Awaji City, Awaji Island, Japan, 2014)

Lubitz, W.: Spectroscopic Studies of Metalloenzymes with Complex Metal Centers (7th Asian Biological Inorganic Chemistry Conference (AsBIC-7), Gold Coast, Queensland, Australia, 2014)

Nalepa, A. I.; Malferrari, M.; M., O. R.; Möbius, K.; Venturoli, G.; I., W.; Lubitz, W.; Savitsky, A.: Advanced EPR Techniques Applied to Nitroxide Spin Probes and Nitroxide Spin-labelled Systems (Integrating Spectroscopic and Theoretical Methods to Analyse Molecular Machines, Schloss Ringberg, Kreuth, Germany, 2014)

Nalepa, A. I.; Malferrari, M.; Möbius, K.; Venturoli, G.; Lubitz, W.; Savitsky, A.: Application of W-band ELDOR-detected NMR to Microenvironment Characterisation and Local Water Sensing in Nitroxide-labeled Systems (The 7th International Conference on Nitroxide Radicals (SPIN-2014), Zelenogradsk, Russia, 2014)

Neese, F.: Theoretical Approaches to the Magnetic Properties of Systems with Strong Spin-Orbit Coupling (International Symposium "Integrating spectroscopic and theoretical methods to analyse molecular machines", Kreuth, Germany, 2014)

Neese, F.: Accurate ab initio quantum chemistry for large molecules. New developments and future opportunities (ETH Zurich, Laboratory of Organic Chemistry, Montagskolloquium series, Zurich, Swithzerland, 2014)

Neese, F.: Accurate ab initio quantum chemistry for large molecules. New developments and future opportunities (Julius-Maximilians Universität Würzburg, Würzburg, Germany, 2014)

Neese, F.: Progress towards large scale wavefunction based ab initio calculation of EPR parameters. DLPNO-CCSD (Universität Göttingen, SPP1601 Annual Meeting, Schwerte, Germany, 2014)

Neese, F.: Spins, Molecular Magnetism and Quantum Chemistry (Rheinische Friedrich-Wilhelms-Universität Bonn, Collaborative Research Center 813, International Symposium of the CRC/SFB 813 "Chemistry at Spin Centers 2014", Bad Honnef, Germany, 2014)

Neese, F.: First principles approaches to X-ray absorption spectrosocopy. Theory and applications (Université Catholique de Louvain, EUSpec COST Action MP1306: Modern Tools for Spectroscopy on Advanced Materials, Louvain-la-Neuve, Belgium, 2014)

Neese, F.: Recent development in pair natural orbital based local coupled cluster methods (Université de Namur ASBL, 16th European Seminar on Computational Methods in Quantum Chemistry (ESCMQC 2014), Houffalize, Belgium, 2014)

Neese, F.: Ligand Field Theory (Université Catholique de Louvain, Combined Practical and Lecture Workshop 'Chemistry of Metals in Biological Systems', Louvain-la-Neuve, Belgium, 2014)

Neese, F.: Theoretical Spectroscopy of Open Shell Transition Metals in Enzymes and Model Complexes (University of Zurich, Department of Chemistry, 12th European Biological Inorganic Chemistry Conference (EuroBIC 12), Zurich, Switzerland, 2014)

Neese, F.: The Chemistry of Clean Energy: Lessons from Nature (Max-Planck-Institut für Kohlenforschung, Ceremony and Scientific Symposium on the occasion of the 100 birthday, Mülheim an der Ruhr, Germany, 2014)

Neese, F.: Theoretical Approaches to the Magnetic Properties of Systems with Strong Spin-Orbit Coupling (Max-Planck-Institut für Chemische Energiekonversion, International Symposium "Catalytic Systems for Chemical Energy Conversion", Mülheim an der Ruhr, Germany, 2014)

Neese, F.: Fundamentals of Quantum Chemistry Applied to Catalysis Research (University of Amsterdam, Research School of Molecular Chemistry, Netherlands Institute for Catalysis Research, "Advanced Metal-Organic Chemistry and Catalysis" AMOCC 2014 Summer School, Deurne, The Netherlands, 2014)

Neese, F.: Molecular Magnetism and Quantum Chemistry (The University of Wisconsin-Madison, Department of Chemistry, Madison, Wisconsin, USA, 2014)

Neese, F.: Insights into Biological Energy Conversion in Photosystem II from a Combination of Quantum Chemistry and Spectroscopy (, Moscowitz Memorial Lectureship, The University of Minnesota, Department of Chemistry, Minneapolis, Minnesota, USA, 2014)

Neese, F.: Pushing the boundaries of wavefunction based ab initio approaches (Harvard-Smithsonian Center for Astrophysics, Pfizer Lecture Hall at the Harvard Dept. of Chemistry and Chemical Biology (CCB), Cambridge, Massachusetts, USA, 2014)

Neese, F.: New Insights into Biological Energy Conversion in Photosystem II. Through a Combination of Quantum Chemistry and Spectroscopy (PC-Kolloquium, The University of Basel, Switzerland, 2014)

Neese, F.: Combined spectroscopic and quantum chemical studies on single molecule magnets (University of St. Andrews, School of Chemistry, CMR Seminar, St. Andrews, Scotland, UK, 2014)

Neese, F.: Molecular magnetism and quantum chemistry (The University of Manchester, School of Chemistry, EPR Symposium, Manchester, UK, 2014)

Neese, F.: Neue Einblicke in Struktur und Mechanismus des ‘Oxygen-Evolving-Complex’ in Photosystem II durch eine Kombination von Spektroskopie und Quantenchemie (Universität Marburg, Fachbereich Chemie, 2014)

Pantazis, D. A.: Multiscale modelling of the photosynthetic water oxidizing catalyst (Chemistry Department, University of Grenoble, France, 2014)

Pantazis, D. A.: Manganese oxidation states in the natural oxygen evolving complex (Umeå Renewable Energy Meeting, Chemical Biological Centre, Umeå, Sweden, 2014)

Pantazis, D. A.: Biological water oxidation by Photosystem II (LeadNet meeting – Renewable Energy and Energiewende, Mainz, Germany, 2014)

Pantazis, D. A.: Manganese oxidation states in natural water oxidation (Dalton Conference, Warwick, UK, 2014)

Pantazis, D. A.: The many roles of calcium in natural water oxidation (Interface between experimental and theoretical approaches to energy-related enzyme catalysis, London, 2014)

Pantazis, D. A.: The diverse functions of calcium in natural water oxidation (12th European Biological Inorganic Chemistry Conference, Zürich, Switzerland, 2014)

Rodríguez-Maciá, P.; Dutta, A.; Lubitz, W.; Shaw, W. J.; Rüdiger, O.: Covalent Attachment of Nickel-Based Catalyst into HOPGe Electrode: Comparison with Hydrogenases (5th junges Chemiesymposium Ruhr, Ruhr-Universität, Bochum, Germany, 2014)

Rüdiger, O.: Study of hydrogenases using electrochemistry (DIP Meeting on "Biomaterials and Bioinspired Assemblies for Nanoengineered Optobioelectronic Systems", Berlin, 2014)

Rüdiger, O.; Alsheikh Oughli, A.; Plumeré, N.; Williams, R.; Vivekanathan, J.; Pöller, S.; Schuhmann, W.; Lubitz, W.: Efficient Electron Harvesting from Hydrogenases (Turkish-German Conference on Energy Technologies, Middle East Technical University (METU), Ankara, October 2014)

Schlögl, R.: Chemical energy conversion - More than just "storage" (Leopoldina Symposium "Energiespeicher - Der fehlende Baustein der Energiewende?", Halle, Germany, 2014)

Schlögl, R.: Energiespeicher – Ein Zustandsbericht (E-world energy & water 2014, 18. Fachkongress Zukunftsenergien der EnergieAgentur.NRW, Essen, Germany, 2014)

Schlögl, R.: Synthetic fuels: On the way towards sustainable fuels (35. Internationales Wiener Motorensymposium, Wien, Austria, 2014)

Schlögl, R.: Kohlenstoff: Viel mehr als ein Material zum Verfeuern (Carl Friedrich Gauß-Kolloquium, Braunschweig, Germany, 2014)

Schlögl, R.: Catalysis and Energy Supply – Future Challenges (Centennial Shell Catalysis Conference 2014 (CSCC 2014), Shell Technology Centre, Amsterdam, The Netherlands, 2014)

Schlögl, R.: Solar Fuels: Key to Integration of Renewable Energies? (Workshop "Materials Challenges in Devices for Fuel Solar Production and Employment", Trieste, Italy, 2014)

Schlögl, R.: Energiewende 2.0 (Berliner Physikalisches Kolloquium, Berlin, Germany, 2014)

Schlögl, R.: Chemical Energy (Joint EPS-SIF International School on Energy 2014, Varenna, Italy, 2014)

Schlögl, R.: How Gas and Renewable Energies Create a new Business Model, International Gas Union Research Conference 2014, Copenhagen, Denmark, 2014)

Schlögl, R.: Chemische Energiekonversion: Nicht so einfach wie gedacht! (ProcessNet Jahrestagung, Aachen, Germany, 2014)

Schlögl, R.: Energiewende aus der Sicht eines Chemikers (POF Evaluierung für Energie Universität Köln, Köln, Germany, 2014)

Schlögl, R.: Energiewende 2.0 (Lionsclub Mülheim/Ruhr, Mülheim an der Ruhr, Germany, 2014)

Schlögl, R.: Energiewende aus der Sicht eines Chemikers: Energy transformation from a chemist's viewpoint (GDCh Kolloquium, Darmstadt, Germany, 2014)

Schlögl, R.: Dynamics of Catalysts (2014 MRS Fall Meeting & Exhibit – Material Research Society, Boston, MA, USA, 2014)

Siebel, J. F.; Adamska-Venkatesh, A.; Weber, K.; Rumpel, S.; Reijerse, E.; Lubitz, W.: Synergy between chemistry and biology: Synthesis and characterization of hybrid [FeFe]-hydrogenases (12th European Biological Inorganic Chemistry Conference, Zürich, Switzerland, 2014)

## Invited and Plenary Lectures at Conferences

### 2015

Adamska-Venkatesh, A.; Siebel, J. F.; Simmons, T.; Gilbert-Wilson, R.; Souvik, R.; Artero, V.; Fontecave, M.; Rauchfuss, T. B.; Reijerse, E.; Lubitz, W.: Understanding the Active Site of [FeFe] Hydrogenases (57th Annual Rocky Mountain Conference on Magnetic Resonance, Snowbird, USA, 2015)

Adamska-Venkatesh, A.; Siebel, J. F.; Simmons, T.; Weber, K.; Souvik; Rumpel, S.; Artero, V.; Fontecave, M.; Reijerse, E.; Lubitz, W.: Lessons from Nature: Modified Active Sites in [FeFe] Hydrogenases (1st International Solar Fuels Conference, Uppsala, Sweden, 2015)

Braslavsky, Silvia E.: Universities of Tucumán, of Santiago del Estero, of Córdoba, of Buenos Aires (2015)

Cibura, N.: $MnO_x$ in photocatalysis: structural characterization and photolectrochemistry. (Center for Nanointegration Duisburg-Essen (CENIDE), Duisburg, Germany 2015-12-07)

Cox, N.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation as Determined by Multifrequency Pulse EPR (ANZMAG 2015, Bay of Islands, New Zealand, 2015)

Cox, N.: Two-State Reactivity in Nature's Water Splitting Catalyst: Interplay between Structural Flexibility and Spin Crossing (Annual French society for photosynthesis meeting, Paris, 2015)

Cox, N.: The Water Oxidizing Complex in Photosystem II: Water Binding and Water Splitting in Photosynthesis (Paris-Sud University, Orsay, 2015)

Cox, N.: The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation as Determined by W-band (EPR 23rd Benelux-EPR Society Meeting, Ghent, Belgium, 2015)

DeBeer, S.: X-ray Emission Spectroscopy as a Probe of Spin State, Covalency and Coordination Sphere - "New" spins on "Old" Spectroscopy, (Explicit Control Over Spin States in Technology and Biochemistry (ECOST-Bio) Meeting, Marseille, France, 2015-01)

DeBeer, S.: Resonant and Non-resonant X-ray Emission Spectroscopic Studies of Biological Catalysis, (European Synchrotron Radiation Facility User's Meeting, Grenoble France, 2015-02)

DeBeer, S.: Spectroscopic Insights into Biological Nitrogen Reduction, (Inorganic Reaction Mechanisms Gordon Conference, Galveston, TX, USA, 2015-03)

DeBeer, S.: Frontier Leaders Lectureship, (Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Portugal, 2015-05)

DeBeer, S.: X-ray Emission Spectroscopy as a Probe of Catalysis" and "Modeling X-ray Emission Spectroscopy With Density Functional Theory, (CHESS XES Workshop, Cornell University, Ithaca, NY, USA, France, 2015-06)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (13th International Symposium on Applied Bioinorganic Chemistry (ISABC13), Galway, Ireland, 2015-06)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (International Conference on Biological Inorganic Chemistry (ICBIC), Beijing, China 2015-07)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (INDABA8, Kruger National Park, South Africa, 2015-08)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction, (The 16th International Conference on X-ray Absorption Fine Structure (XAFS-16), Karlsruhe Institute of Technology, Karlsruhe, Germany, 2015-08)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (Chemistry & Biology of Iron-Sulfur Clusters, Autrans, France, 2015-09)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (Max Lab User's Meeting, Lund, Sweden, 2015-09)

DeBeer, S.: Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES..., (Methods in Molecular Energy Research Summer School, Gelsenkirchen, Germany, 2015-09)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction in molybdenum and vanadium nitrogenases, (International Conference on Nitrogen Fixation, Pacific Grove, CA, USA, 2015-10)

Decaneto, E.: Cobalt (II) Substitution of the Zinc(II) Ions of Membrane-type 1 Matrix Metalloproteinase (RESOLV Workshop, RUB Conference Center, Bochum, Germany, 2015)

Gärtner, W.: Biological Photoreceptors – Properties and Applications. (New Delhi, Mumbai, Indien 2015-02/03)

Gärtner, W.: Biological Photoreceptors – Basics and Modern Applications, (North-Eastern Univ. Illinois and Univ. Chicago, USA (Chicago) 2015-03)

Gärtner, W.: Biological Photoreceptors – Basics and Modern Applications, (Symposium 'Synmicro, Univ. Marburg, Germany, 2015-04)

Gärtner, W.: Biological Photoreceptors – Basics and Modern Applications, (GDCh-Vortrag, Univ. Leipzig, Germany, 2015-06)

Gärtner, W.: CBCR GAF domains - light induced structural changes, cAMP formation … and fluorescence-based applications, (Teilnahme an DFG Rundgespräch 'Spektroskopie an Photorezeptoren', Frauenchiemsee, Germany, 2015-10)

Gärtner, W.: GAF3 domain of cyanobacteriochrome Slr1393 from Synechocystis PCC6803 – a useful tool for structure analysis, enzyme function regulation, and FRET experiments, (ICTPPO (Intl. Congress on Photoreceptors in Photosynthetic Organisms), Isreal, 2015-10)

Gärtner, W.: Bacterial Photoreceptors – Basics and Modern Applications, (Austauschprogramm DAAD-CONICET, Rosario, Tucuman, Santiago del Estero, Argentina, 2015-11/12)

He, C.: Toward Development of Innovative Peptide Therapeutics (Sun Yat-sen University, Guangzhou, China, 2015)

He, C.: Toward Development of Innovative Peptide Therapeutics (South China University of Technology, Guangzhou, China, 2015)

Holzwarth, A. R., Savitsky, A., Pawlak, K., Reus, M., Lubitz, W.: Converting Light-harvesting Antenna Complex LHCII into a Charge Sparation Unit (International Conference on Tetrapyrrole Photoreceptors of Photosynthetic Organisms (ICTPPO), Upper Galilee, Israel, 2015)

Lohmiller, T.: EPR-Spectrosopic Investigations of Structure, Solvation and Reactivity of Carbenes (RESOLV Cross-linking Topic 3 “Control of Reactivity by Solvents”, Discussion Meeting, Bochum, Germany, 2015)

Lohmiller, T.: Reversible Spin-State Interconversion and Triplet-State Structure of Bis(p-methoxyphenyl)carbene (RESOLV Workshop Research Area A, Bochum, Germany, 2015)

Lubitz, W.: Water Oxidation and Proton Reduction - Chemistry of Molecular Model Systems (in Nature) (Lecture series, Fritz Haber Institut, Berlin, Germany, 2015)

Lubitz, W.: Lichtinduzierte Wasserspaltung in der Photosynthese (XLAB Science Festival 2015, Göttingen, Germany, 2015)

Lubitz, W.: Mechanismus der lichtinduzierten Wasserspaltung: Lernen von der Natur (6. Energiekolloquium der Chemiegesellschaften „Solar Fuels“, DECHEMA-Haus Frankfurt, Germany, 2015)

Lubitz, W.: I. Electron and Nuclear Spin Probes in Solvation Science, II. Water’s Unique Function as Solvent and Substrate in Oxygenic Photosynthesis, III. Hydrogenases in Water and Redox Gels (RESOLV Workshop, Velen, Germany, 2015)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Production in Nature: Basis for the Design of Bioinspired Molecular Catalysts and Devices (1st International Solar Fuels conference (ISF-1), Uppsala, Sweden, 2015)

Lubitz, W.: Light-induced Water Splitting and Hydrogen Production – Learning from Nature’s Ingenious Concepts (14th Cardiff Chemistry Conference, Cardiff, UK, 2015)

Lubitz, W.: Light-induced Charge Separation and Water Oxidation in Photosystem II (International Concerence of the Russian Photobiological Society “Primary Electron Transfer in Photosynthetic Reaction Centers”, Pskov, Russian Federation, 2015)

Lubitz, W.: The Catalytic Cycle of Biological Water Oxidation Probed by Electron and Nucelar Spin Resonance Techniques (International Conference Spin Physics, Spin Chemistry and Spin Technology, St. Petersburg, Russian Federation, 2015)

Lubitz, W.: Lichtinduzierte Wasserspaltung und Wasserstofferzeugung in der Natur: Basis für das Design bioinspirierter molekularer Katalysatoren (GDCh-Vortrag, Jena, Germany, 2015)

Lubitz, W.: Wateroxidase and Hydrogenase – Key Enzymes in Biological Energy Conversion (ICBIC17, Peking, China, 2015)

Lubitz, W.: Water Oxidation and Hydrogen Conversion in Nature (IRTG 1422 Abschlusssymposium, Georg-August-University Göttingen, Göttingen, Germany)

Lubitz, W.: The Light-Driven Water Splitting Machine of Photosynthesis: An Enzyme that Changed the World (Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Lisboa, Portugal, 2015)

Lubitz, W.: Photosystem II and Water Oxidation (The 2nd DIP Meeting on "Biomaterials and Bioinspired Assemblies for Nanoengineered Optobioelectronic Systems, Jersualem, Israel, 2015)

Lubitz, W.: Interdisziplinäre Forschungsansätze zur Energiekonversion: Biophysikalische Chemie und Mikrobiologie (Symposium „Thema Lebenswissenschaften im Wandel" on the occasion of the 70th birthday of Bärbel Friedrich, Leopoldina/Halle, Germany, 2015)

Lubitz, W.: Mechanism of Water Oxidation and Hydrogen Conversion in Nature – Inspiration for the Design of Molecular Catalysts (Inter-Academy Seoul Science Forum, Seoul, Korea, 2015)

Lubitz, W.: Biologcial Water Splitting – the Substrate/Solvent Interface (RESOLV Workshop Area B, RUB Conference Center, Bochum, Germany, 2015)

Lubitz, W.: Mechanism of Light-induced Water Splitting – Learning from Nature's Ingenious Concept (Pacifichem 2015, Hawaii Convention Center, Honolulu, USA, 2015)

Nalepa, A.: Spin Labeling and Distance Measurements Using Pulsed EPR (The 2nd DIP Meeting on 'Biomaterials and Bioinspired Assemblies for Nanoengineered Optobioelectronic Systems, Jersualem, Israel, 2015)

Neese, F.: The chemistry of clean energy - Lessons from nature (The Inter-Academy Symposium of the Israel Academy of Sciences and Humanities and the German National Academy of Sciences, Leopoldina – Chemistry "The Central Science" on the occasion of the 50th anniversary of the establishment of diplomatic relations between Israel and Germany, Jerusalem, Israel, 2015)

Neese, F.: Insight into weak intermolecular interactions from small to large systems using accurate wavefunction based ab initio and valence bond methods (1st SPP 1807 "Control of London dispersion interactions in molecular chemistry" Workshop, Göttingen, Germany, 2015)

Neese, F.: Understanding Single Molecule Magnets through a Combination of Experiment and Quantum Chemistry (Indaba 8 "SERENDIPITY vs PREDICTION", Skukuza Camp, Kruger National Park, South Africa, 2015)

Neese, F.: Electronic structure contributions to reactivity in oxo-iron(IV) model compounds (17th International Conference on Biological Inorganic Chemistry (ICBIC17), Beijing, China, 2015)

Neese, F.: Grundlegende Einblicke in die Speicherung von chemischer Energie in der Photosynthese (Nordrhein-Westfälische Akademie der Wissenschaften und der Künste, Düsseldorf, Germany, 2015)

Neese, F.: In praise of CIPSI (European Workshop on Theoretical approaches of Molecular Magnetism: Jujols VIII, Bages, France, 2015)

Neese, F.: New insights into the key reaction of photosynthesis: structure and mechanism of the water-oxidizing manganese cluster in photosystem II (Westfälische Wilhelms-Universität Münster, GDCh/CMTC-Kolloquium, Münster, Germany, 2015)

Neese, F.: Progress in the design of accurate, efficient and robust linear scaling wavefunction methods for routine computational chemistry applications (International CECAM-Workshop "Perspectives of many-particle methods: total energy, spectroscopy and time-dependent dynamics", Bremen, Germany, 2015)

Neese, F.: Theoretical Approaches to mononuclear single molecule magnets (48th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry, Southampton, United Kingdom, 2015)

Neese, F.: Insights into photosynthetic water oxidation from a combination of spectroscopy and quantum chemistry (11th Ernest R. Davidson Lecture, University of North Texas, Denton, USA, 2015),

Neese, F.: Accurate wavefunction based ab initio quantum chemistry for hundreds of atoms (University of North Texas, Denton, USA, 2015)

Neese, F.: Combined experimental and theoretical studies in molecular magnetism (Ruhr-Universität Bochum, RESOLV Symposium EPR Spectroscopy, Bochum, Germany, 2015)

Neese, F.: Accurate ab initio quantum chemistry for large molecules. New developments and future opportunities (55th Sanibel Symposium, St. Simons Island, USA, 2015)

Neese, F.: Neue Einblicke in die Schlüsselreaktion der Photosynthese: Struktur und Mechanismus des wasseroxidierenden Manganclusters im Photosystem II (Rheinische Friedrich-Wilhelms-Universität Bonn, GDCh-Lecture, Bonn, Germany, 2015)

Neese, F.: Development of efficient ab initio methods for the accurate prediction of hyperfine and quadrupole interaction parameters in large molecules (Universität Göttingen, Evaluation Colloquium SPP 1601, Göttingen, Germany, 2015)

Neese, F.: Insights into heterogeneous catalysts from theoretical spectroscopy (3rd International Symposium on Chemistry for Energy Conversion and Storage (ChemEner2015), Berlin, Germany, 2015)

Ogata, H.: Structure and Function of the $O_2$-sensitive [NiFe] Hydrogenase (Seminar series in molecular, celluar, and environmental microbiology, MPI für terrestrische Mikrobiologie, Marburg, Germany, 2015)

Ogata, H.: Catalytic Reaction Mechanism of the O2-sensitive [NiFe] Hydrogenase (1st International Symposium on High Quality Protein Crystallization Technology, University of Tokyo, Tokyo, Japan, 2015)

Ogata, H.: Super High Resolution Structure Analysis Using PHENIX (Space Science of High Quality Protein Crystallization Technology, University of Tokyo, Tokyo, Japan, 2015)

Ogata, H.: Subatomic Resolution Structure Analysis of [NiFe] Hydrogenase (The 7th joint BER II and BESSY II User Meeting, Berlin, Germany, 2015)

Oughli, A. A.: A Redox-hydrogel Protects Hydrogenases Against Oxygen and High Potential Damage (ISF-1 Young, Satellite Meeting of the 1st International Solar Fuels Conference, University of Uppsala, Sweden, 2015)

Pantazis, D. A.: Spectroscopically constrained modelling of metalloenzymes (ECOSTBio (COST Action CM1305) meeting, Marseille, France, 2015)

Rüdiger, O.: Combining Electrochemistry and EPR to Study Enzymes in Redox Hydrogels (RESOLV Workshop, RUB Conference Center, Bochum, Germany, 2015)

Rüdiger O.; Alsheikh Oughli, A.; Stapf, S.; Conzuelo, F.; Winkler, M.; Happe, T.; Schuhmann, W.; Lubitz, W.; Plumeré, N.: Stabilization of Oxygen Sensitive Hydrogenases Towards Oxidative Damage by Redox Hydrogels (ACS Fall Meeting, Boston, MA, USA, 2015)

Rüdiger, O.; Rodriguez-Maciá, P.; Dutta, A.; Lubitz, W.; Shaw, W.: Direct Comparison of the Performance of a Bio-inspired Synthetic Ni-Catalyst and a [NiFe]-Hydrogenase Covalently Attached to Electrodes (ACS Fall Meeting, Boston, MA, USA, 2015)

Rüdiger, O.: Exploiting Hydrogenases and Bio-inspired Catalysts (Brandeis University, MA, USA, 2015)

Rüdiger, O.: Exploiting Hydrogenases and Bio-inspired Catalysts (Ohio State University, OH, USA, 2015)

Rüdiger, O.: Exploiting Hydrogenases and Bio-inspired Catalysts (Texas Christian University, TX, USA, 2015)

Rüdiger, O.: Exploiting Hydrogenases and Bio-inspired Catalysts (Texas A&M University, TX, USA, 2015)

Rüdiger O.; Alsheikh Oughli, A.; Stapf, S.; Conzuelo, F.; Winkler, M.; Happe, T.; Schuhmann, W.; Lubitz, W.; Plumeré, N.: Protection of Hydrogenases from Oxidative Damage Using Redox Hydrogels (XXXVI Reunión del grupo de electroquímica de la RSEQ, Vigo, Spain, 2015)

Rüdiger, O.; Lubitz, W.: Spectroelectrochemical Study of Hydrogenases (23rd International Symposium on Bioelectrochemistry and Bioenergetics of the Bioelectrochemical Society, Malmo, Sweden, 2015)

Schlögl, R.: Sustainable energy systems: Remarks on critical bottlenecks (3rd International Symposium on Chemistry and Energy Conversion and Storage, Berlin, Germany, 2015)

Schlögl, R.: Energiesysteme der Zukunft (Neujahrsempfang, Nationale Akademie der Wissenschaften Leopoldina, Halle, Germany, 2015)

Schlögl, R.: Strategische Forschungsagenda 2015 – Energie und Raumfahrt: passt das? (GdCh Kolloquium Universität Münster, Münster, Germany, 2015)

Schlögl, R.: Energy Transformation: Heterogeneous Catalysis from a Fundamental Perspective (150 Jahre BASF, Ludwigshafen, Germany, 2015)

Schlögl, R.: Grenzflachen und Grenzgange: Surface Science and the Energy Transformation (79. Jahrestagung der DPG und DPG-Frühjahrstagung 2015 der Sektion Kondensierte Materie (SKM), Berin, Germany, 2015)

Schlögl, R.: Energiewende 2.0 (Seminar Max-Planck-Institut für Plasmaphysik, TU München, Munich, Germany, 2015)

Schlögl, R.: Fraunhofer UMSICHT: Mit Energie in die Zukunft (25 Jahre Fraunhofer, Fraunhofer UMSICHT, Oberhausen, Germany, 2015)

Schlögl, R.: Carbon!! Chemistry for (Organic) and Inorganic Chemists (GDCh-Vortrag, Universität Ulm, Ulm, Germany, 2015)

Schlögl, R.: Benchmarking Electro-catalysts in Relation to Chemo-catalysts (DOE-BES Catalysis PI Meeting, Benchmarking for Catalysis, Annapolis MD, USA, 2015)

Schlögl, R.: Energy Challenge and Catalysis: How they interconnect (University of Malaya, Kuala Lumpur, Malaysia, 2015)

Schlögl, R.: The Role of Catalysis in the Energy Challenge (Summerschool at SLAC, Workshop Stanford University, Menlo Park, CA, USA, 2015)

Schlögl, R.: $CO_2$ Reduction: Power to X (L) (6. Sitzung der „Expertengruppe Power-to-Gas“ des Netzwerks Brennstoffzelle und Wasserstoff NRW, Fraunhofer UMSICHT, Oberhausen, Germany, 2015)

Schlögl, R.: Technische Möglichkeiten und Grenzen der Energiewende aus wissenschaftlicher Sicht (Baden-Badener Unternehmer Gespräche e. V., Baden-Baden, Germany,2015)

Schlögl, R.: Chemical Energy Conversion (Siemens Council, New York NY, USA, 2015)

Schlögl, R.: Energiewende - Chancen und Herausforderungen für Unternehmen (Wirtschaftsimpuls Ruhr „Energie mit Zukunft!“, Folkwang Museum, Essen, Germany, 2015)

Schlögl, R.: Chemical Energy Conversion (German-Israeli Cooperation Workshop on Microbial Biotechnology and Renewable Energy, Greifswald, Germany, 2015)

Schlögl, R.: $CO_2$ utilization from large-scale industrial point sources (The 15th IERE General Meeting & German Forum: International Energy Systems in Transition-Perspectives from Science and Industry, Berlin, Germany, 2015)

Schlögl, R.: Chemie für die Energiewende (Tag der Chemie, Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany, 2015)

Schlögl, R.: Catalysis for Energy (Kick-off Meeting, International Center for Advanced Studies of Energy Conversion, Göttingen, Germany, 2015)

Schlögl, R.: Energiewende 2.0 – Eine Gemeinschaftsaufgabe (SIEMENS AG, Erlangen, Germany, 2015)

Schlögl, R.: In-situ electron spectroscopy for energy applications (2nd Annual Workshop on Ambient Pressure X-ray Photoelectron, Berkeley, CA, USA, 2015)

Van Gastel, M.: EPR Spectroscopy (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, 2015)

Zalibera, M.; Wang, F.; Büchel, R.; Savitsky, A.; Widmann, D.; Pratsinis, S.E.; Lubitz, W.; Schüth, F.: In situ EPR Study on Redox Properties of $CuO–CeO_2$; the Catalyst for Preferential CO Oxidation (XXVI International EPR Seminar, Graz, Austria, 2015

## Invited and Plenary Lectures at Conferences

### 2016

Bill, E.: 'Spectroscopy of Iron Complexes for Chemical Energy Conversion (2nd Mediterranean Conference on the Applications of the Mössbauer Effect, Cavtat, Croatia, 2016)

Birrell, J. A.; Rodriguez-Maciá, P.; Pawlak, K.; Reijerse, E. J.; Rüdiger, O; Lubitz, W.: Artificial Maturation of a Highly Active [FeFe] Hydrogenase (DIP Meeting, Bochum, Germany, 6th – 9th October 2016)

Braslavsky, Silvia E.: Universidad de Málaga, Spain (2016)

DeBeer, S.: Making and Breaking Bonds: X-ray spectroscopic studies of Biological Catalysis, (The 5th International Conference on MEXT Project of Integrated Research on Chemical Synthesis - Chemical Science for Future Societies, University of Nagoya, Nagoya, Japan, 2016-01)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction, (11th SOLEIL User's Meeting, Paris, France, 2016-01)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction, (GDCh Seminar, University of Greifswald, Greifswald, Germany, 2016-01)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction, (GDCh Seminar, Technical University Braunschweig, Braunschweig, Germany, 2016-04)

DeBeer, S.: X-ray spectroscopic studies of nitrogenase and hydrogenase active sites, (Girona Seminar, Girona, Spain, 2016-04)

DeBeer, S.: X-ray spectroscopic studies of nitrogenase and hydrogenase active sites, (115th General Assembly of the German Bunsen Society for Physical Chemistry, Rostock, Germany, 2016-05)

DeBeer, S.: X-ray spectroscopic studies of biological dinitrogen reduction, (Chemistry Department Seminar, University of Washington, Seattle, Washington, USA, 2016-05)

DeBeer, S.: A brief review of inorganic chemistry - a spectroscopic perspective, (Penn State Bioinorganic Workshop, State College, PA, USA, 2016-06)

DeBeer, S.: Advanced X-ray Spectroscopy, (Penn State Bioinorganic Workshop, State College, PA, USA, 2016-06)

DeBeer, S.: Recent insights into the Active Sites of Molybdenum and Vanadium Nitrogenases from Advanced X-ray Spectroscopy, (Metallocofactors, Gordon Research Conference, Easton, MA, USA, 2016-06)

DeBeer, S.: Making and Breaking Bonds: New Insights into Catalytic Processes Using Advanced X-ray Spectroscopic Approaches, (Hard X-ray Spectroscopies and Imaging Workshop CHESS Cornell University, Ithaca, NY, USA, 2016-06)

DeBeer, S.: X-ray spectroscopic studies of nitrogenase and hydrogenase active sites, (27th International Conference of Organometallic Chemistry, 2016-07)

DeBeer, S.: X-ray spectroscopic studies of nitrogenase, (252nd American Chemical Society National Meeting, IC Award Symposium Philadelphia, PA, USA, 2016-08)

DeBeer, S.: Advanced X-ray Spectroscopic Studies of Iron-Sulfur Clusters, (252nd American Chemical Society National Meeting, IC Award Symposium Philadelphia, PA, USA, 2016-08)

DeBeer, S.: Making and Breaking Bonds: New Insights into Catalytic Processes Using Advanced X-ray Spectroscopic Approaches, (International Conference on Dynamic Pathways in Multidimensional Landscapes Berlin, Germany, 2016-09)

DeBeer, S.: Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES…, (Physical Methods in Molecular and Heterogeneous Catalysis Summer School, Gelsenkirchen, Germany, 2016-09)

DeBeer, S.: Bridging the gap between homogeneous and heterogeneous catalysis: From molecules to surfaces and beyond…, (Physical Methods in Molecular and Heterogeneous Catalysis Summer School, Gelsenkirchen, Germany, 2016-09)

Gärtner, W.: Biophysical Chemistry, Molecular Biology and Cybernetics of Cell Functions. ('Skiseminar', Klosters, Schweiz, 2016-01)

Gärtner, W.: Structure, Photoconversion Kinetics, and Optogenetics Applications of Cyanobacteriochromes. (Gordon Conference: Photosensory Receptors & Signal Transduction, Galvaston, USA, 2016-01)

Kutin, Yu.; Srinivas, V.; Fritz, M.; Kositzki, R.; Shafaat, H. S.; Birrell, J.; Bill, E.; Haumann, M.; Lubitz, W.; Högbom, M.; Griese, J.J.; Cox N.: Divergent Assembly Mechanisms of the Mn/Fe Cofactors in R2lox and R2c Proteins (79th Harden Conference: "Oxygen Evolution and Reduction — Common Principles", Innsbruck, Austria, 16-20 April 2016).

Kutin, Yu.; Srinivas, V.; Fritz, M.; Kositzki, R.; Shafaat, H. S.; Birrell, J.; Bill, E.; Haumann, M.; Lubitz, W.; Högbom, M.; Griese, J.J.; Cox N.: EPR Study of Assembly Mechanisms of the Mn/Fe Cofactors in R2lox and R2c Proteins (Regional Interdisciplinary Conference – Humboldt Kolleg «Energy conversion: from nature to technology», Novosibirsk, Russia, 28 August - 2 September 2016).

Kutin, Yu.; Srinivas, V.; Fritz, M.; Kositzki, R.; Shafaat, H. S.; Birrell, J.; Bill, E.; Haumann, M.; Lubitz, W.; Högbom, M.; Griese, J.J.; Cox N.: EPR Study of Assembly Mechanisms of the Mn/Fe Cofactors in R2lox and R2c Proteins (38th FGMR Discussion Meeting, Düsseldorf, Germany, 12-15 September 2016).

Lubitz, W.: Lichtinduzierte Wasserspaltung in der Natur: Auf dem Weg zur künstlichen Photosynthese (GDCh-Kolloquium, GDCh-Ortsvorstand Darmstadt, Technische Universität Darmstadt, Germany, 2016)

Lubitz, W.: The Spin as Structural and Functional Probe in Photosynthetic Charge Separation and Water Splitting Catalysis (Mitteldeutsches Resonanztreffen MDR–37, Leipzig, Germany, 2016)

Lubitz, W.: Mechanism of Light-Induced Water Oxidation and Oxygen Release in Photosynthesis (115th Bunsentagung in Rostock, Germany, 2016)

Lubitz, W.: Lichtinduzierte Wasserspaltung in der Natur: Auf dem Weg zur künstlichen Photosynthese (GDCh Campus Event der JungChemikerForen Dresden und Freiberg, TU Dresden, Germany, 2016)

Lubitz, W.: Water Binding to the Oxygen Evolving Complex in Photosystem II (Gordon Research Conference on Metallocofactors, Stonehill College, Easton MA, United States, (2016)

Lubitz, W.: Mechanism of Photosynthetic Water Oxidation Investigated by Advanced Magnetic Resonance Techniques (Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, USA, 2016)

Lubitz, W.: Water Splitting in Photosynthesis (21-st International Conference on Photochemical Conversion and Storage of Solar Energy, Sankt Petersburg, Russia 2016)

Lubitz, W.: ELDOR-detected NMR as a Versatile Method to Study Metalloenzymes (The XXVIIth International Conference on Magnetic Resonance in Biological Systems. Frontier of Magnetic Resonance in Biological Systems. Kyoto International Conference Center, Kyoto, Japan, 2016)

Lubitz, W.: The Light-driven Water Splitting Machine of Photosynthesis: An Enzyme that Changed the World (Interdisciplinary Conference – Humboldt Kolleg «Energy conversion: from nature to technology» Novosibirsk Scientific Center, Academgorodok, Russia, 2016)

Lubitz, W.: The Spin as Probe for Structure and Function in Metal Biocatalysis (Xth International Workshop on EPR in Biology and Medicine, Jagiellonian University, Krakow, Poland, 2016)

Lubitz, W.: Insights into the Mechanisms of Hydrogenase and Wateroxidase - Inspiration for the Design of Molecular Catalysts (5th International Symposium on Solar Fuels and Solar Cells, Dalian, China, 2016)

Lubitz, W.: EPR Spectroscopy for Probing the Solvation Dynamics and Reactions under HP Conditions; Solvation Dynamics (Solvation under Extreme Conditions, RESOLV Workshop, Ruhr-Universität, Bochum, Germany, 2016)

Lubitz, W.: Advanced Pulse EPR Studies of the Water Oxidation Cycle in Photosynthesis (Horizons of Magnetic Resonance" and "Modern Development of Magnetic Resonance 2016", The Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, the Academy of Sciences of the Republic of Tatarstan and the Kazan Federal University, and the anniversary Zavoisky Award 2016 ceremony supported by the Government of the Republic of Tatarstan, Kazan, Russia 2016)

Lubitz, W.: Mechanisms of the Water Oxidation and Proton Reduction Reactions in Nature (Kolloquium der Physik und Chemie an der TU Ilmenau, Germany, 2016)

Neese, F.: Systematically approaching the full CI limit with an iterative configuration expansion algorithm (Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, 2016)

Neese, F.: Coupled Cluster Theory for systems with hundreds of atoms (The Roger E. Miller Lecturer at 2016 Symposium on Chemical Physics (SCP 2016), University of Waterloo, Waterloo, Canada, 2016)

Neese, F.: Interplay of high-level spectroscopy and quantum chemistry: A powerful tool to unravel enzymatic reaction mechanisms (24th Solvay Conference on Chemistry "Catalysis in Chemistry and Biology", Brussels, Belgium, 2016)

Neese, F.: Linear scaling Single- and multi reference wavefunction based approaches for large molecules (Conference „Theory and Applications of Computational Chemistry“ (TACC 2016), Seattle, USA, 2016)

Neese, F.: Coupled Cluster Theory for Hundreds of Atoms (Oregon State University, College of Science, Corvallis, USA, 2016)

Neese, F.: How is Metal Covalency Reflected in Ligand Field Parameters? (252nd ACS National Meeting & Exposition, Inorganic Chemistry Lectureship Award Symposium in Honor of Serena DeBeer, Philadelphia, USA, 2016)

Neese, F.: Ab initio Ligand Field Theory for d- and f-elements. A powerful link between theory and experiment (42nd International Conference on Coordination Chemistry (ICCC 2016), Brest, France, 2016)

Neese, F.: Efficiently, accurately and reliably approaching the full CI limit for larger active spaces (8th Molecular Quantum Mechanics Conference (MQM 2016), Uppsala, Sweden, 2016)

Neese, F.: Structure and Spectroscopy of Reactive Intermediates in Metalloenzymes and Model Systems (Metallocofactors Gordon Research Conference "Inorganic Components of Nature that Drive Metabolism", Easton, USA, 2016)

Neese, F.: Correlation of geometric structure, electronic structure, spectroscopy and reactivity in high valent iron centers (4th Penn State Bioinorganic Workshop, State College, USA, 2016)

Neese, F.: New developments in domain based pair natural orbital correlation methods (Low-scaling and Unconventional Electronic Structure Techniques Conference (LUEST) 2016, Telluride, USA, 2016)

Neese, F.: Chemie, Quantenmechanik und moderne Computer: Möglichkeiten, Herausforderungen und Perspektiven (179. ZENIT-Unternehmertreff zum Thema „Computergestützte Forschung – was ist in der Zukunft zu erwarten“, Mülheim an der Ruhr, Germany, 2016)

Neese, F.: Die Chemie sauberer Energie: Inspirationen aus der Natur (Festvortrag anlässlich des Festkolloquiums zur Verleihung der Dr. Barbara Mez-Starck-Preise, Ulm, Germany, 2016)

Neese, F.: Ab initio Ligand Field Theory and Molecular Magnetism (SFB-Seminar Universität Hamburg, Hamburg, Germany, 2016)

Neese, F.: Spin States and Molecular Magnetism (COST Action CM1305 Explicit Control Over Spin-states in Technology and Biochemistry (ECOSTBio 2016), Prague, Czech Republic, 2016)

Neese, F.: Insights into photosynthetic water oxidation from a combination of spectroscopy and quantum chemistry (Manfred-Eigen-Nachwuchswissenschaftler-Gespräche 2016 der Deutsche Bunsen-Gesellschaft für Physikalische Chemie am Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany, 2016)

Neese, F.: Iron-sulfur cluster electronic structural evolution and its contribution to diverse functionality (Review Meeting Priority Program 1927 "Iron-Sulfur for Life", Potsdam, Germany, 2016)

Neese, F.: Reactivity trends in C-H bond activating high-valent iron centers (RWTH Vortrag im Rahmen des Seminars in Technischer Chemie mit Schwerpunkt Molekulare Katalyse, Aachen, Germany, 2016)

Neese, F.: Insights into photosynthetic water oxidation from a combination of spectroscopy and quantum chemistry (ENSCP - Chimie ParisTech, Chimie Théorique et Modélisation, Paris, France, 2016)

Neese, F.: Ab initio Ligand Field Theory for d- and f-elements. A powerful link between theory and experiment (Farewell-Symposium Claude Daul et al, Fribourg, Switzerland, 2016)

Neese, F.: Accurate wavefunction based calculations for large molecules (University of Illinois Urbana-Champaign, Lecture series Theoretical and Computational Biophysics Group at Beckman Institute, Urbana, USA, 2016)

Neese, F.: Give us insight and numbers - The Case of Molecular Magnetism (29th Annual Charles A. Coulson Lecture, Universiy of Georgia, Athens, USA, 2016)

Neese, F.: Coupled cluster theory for hundreds of atoms (University of Georgia, Athens, USA, 2016)

Neugebauer, S.; Narangoda, P.; Spanos,I.; Buller, S.; Cap, S.; Schlögl, R.: Standardized Electrochemical Measurements of Catalysts for the Oxygen Evolution Reaction (4th German-Russian Seminar on Catalysis, Kloster Banz, Germany, 2016)

Neugebauer, S.; Spanos, I.; Yi, Y.; Cap, S.; Schlögl, S.: MANGAN - Standardized Electrochemical Measurements for the Oxygen Evolution Reaction (4th Ertl Symposium on Chemical Processes on Solid Surfaces, Berlin, Germany, 2016)

Ogata H.: Catalytic reaction mechanism of [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F. (Seminar at Nara Institute of Science and Technology, Nara Japan, 2016)

Ogata H.: Catalytic reaction mechanism of [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F. (Seminar at University of Hyogo, Hyogo Japan, 2016)

Ogata H.: Reaction mechanism of the $O_2$ sensitive [NiFe] hydrogenase (Seminar at University of Hyogo, Hyogo Japan, 2016)

Ogata H.: Catalytic reaction mechanism of [NiFe] hydrogenase (Gordon Research Conference, Enzymes, Coenzymes & Metabolic Pathways, Waterville Valley USA, 2016)

Ogata H.: Catalytic reaction mechanism of hydrogenase (Seminar at Hokkaido University, Sapporo Japan, 2016)

Oughli, A. A., P. Rodriguez-Maciá, A. Ruff, N. Priyadarshani, N. Plumeré, W. Shaw, W. Schuhmann, W. Lubitz , O. Rüdiger: Stabilization of an Oxygen Sensitive Bio-inspired Ni Catalyst in a Polymer. A Self-Defense Case (DIP Meeting, Bochum, Germany, 6th – 9th October 2016)

Pantazis, D. A.: Polymorphism and catalytic control in photosynthetic water oxidation (University of Marseille, France, 2016)

Pantazis, D. A.: Polymorphism and catalytic control in biological water oxidation (Girona Seminar - Predictive Catalysis: Transition-Metal Reactivity by Design, Girona, Spain, 2016)

Pantazis, D. A.: Connecting spectroscopy to structure in biological photosynthesis (Structural and Functional Annotation of Bioinorganic Systems: Perspectives and Challenges from Theory and Experiments (CECAM Workshop), Pisa, Italy, 2016)

Pantazis, D. A.: Interaction of methanol with the oxygen-evolving complex: structural models, species dependence, and mechanistic implications (International Congress on Photosynthesis Research, Maastricht, Netherlands, 2016)

Pantazis, D. A.: The mechanism of biological water oxidation: insights from spectroscopy-oriented quantum chemistry (ECOSTBio (COST Action CM1305) meeting, Krakow, Poland, 2016)

Pantazis, D. A.: Spectroscopy-oriented quantum chemistry applied to biological water oxidation (Interface processes in photochemical water splitting: Theory meets experiment (CECAM Workshop), Lausanne, Switzerland, 2016)

Pantazis, D. A.: Applications of spectroscopy-oriented quantum chemistry to bio-inorganic catalysis (Athens International Catalysis Symposium, Athens, Greece, 2016)

Schlögl, R.: Catalysis for Sustainable Energy (Annual Cardiff Catalysis Institute Conference, Cardiff University, UK, 2016)

Schlögl, R.: The role of fossil carbon in energy transformations (Jahrestagung am GFZ Potsdam, Potsdam, Germany, 2016)

Schlögl, R.: Elemente und Akteure der Systemtransformation(?) (E-world energy & water, Essen, Germany, 2016)

Schlögl, R.: Power to Liquids: A challenge for catalysis science ("Perspectives on Power-to-Liquids & Power-to-Chemicals" Workshop, Fraunhofer ISE, Freiburg, Germany, 2016)

Schlögl, R.: Surface chemistry of OER electrodes (18th Topical Meeting of the International Society of Electrochemistry, Gwanju, South Korea, 2016)

Schlögl, R.: Towards a sustainable energy system - The German model(?) (80. Jahrestagung der Deutschen Physikalischen Gesellschaft, Regensburg, Germany, 2016)

Schlögl, R.: Concepts of Oxidation under Reaction Activities (Moscow State University, Moscow, Russia, 2016)

Schlögl, R.: Towards a sustainable energy system - The German model (?) (Manfred-Eigen-Nachwuchswissenschaftlergespräche 2016 der Deutschen Bunsen-Gesellschaft "Physical Chemistry of Solar Fuels Catalysis", Mülheim/Ruhr, Germany, 2016)

Schlögl, R.: Energy systems of the Future: Why Chemistry? (Pusat Penyelidikan NANOCAT / Nanotechnology & Catalysis Research Centre, University Malaya, Kuala Lumpur, Malaysia, 2016)

Schlögl, R.: Carbon to energy: a facile link (Australian Institute for Nanoscale Science and Technology (AINST) Launch - University of Sydney, Australia, 2016)

Schlögl, R.: Designer fuels from $CO_2$ – Neue Kraftstoffe aus $CO_2$ (37. Internationales Wiener Motorensymposium, Wien, Austria, 2016)

Schlögl, R.: Fundamentals and Challenges of CCU/CCS (Industrial Carbon Capture, Utilization and Storage (iCCUS) –Workshop, acatech, Berlin, Germany, 2016)

Schlögl, R.: Carbon2Chem - Das Projekt (Auftaktveranstaltung, Duisburg, Germany, 2016)

Schlögl, R.: Energiewende und Mobilität (OBRIST Engineering, Workshop, Listenau, Germany, 2016)

Schlögl, R.: Energiewende und Chemie (Strategieklausur Wacker Chemie, Munich, Germany, 2016)

Schlögl, R.: Chemical Energy Storage - Part of a Systemic Solution ("Materials for Energy and Sustainability-V" 5th course "EPS-SIF International School on Energy" 3rd course 2016, Erice, Italy, 2016)

Schlögl, R.: Chemical Energy Conversion (Inauguration of VILLUM Center for the Science of Sustainable Fuels and Chemicals, Humblebæk, Denmark, 2016)

Schlögl, R.: Ir Oxide - a Prototypical Case for an OER Catalyst (International Conference on Advances in Semiconductors and Catalysts for Photoelectrochemical Fuel Production (SolarFuel16), Berlin, Germany, 2016)

Schlögl, R.: Energy. Global. Digital (ProcessNet-Jahrestagung und 32. DECHEMA-Jahrestagung der Biotechnologen, Aachen, Germany, 2016)

Schlögl, R.: Electrocatalysis (Summer School "Physical Methods in Molecular and Heterogeneous Catalysis", Gelsenkirchen, Germany, 2016)

Schlögl, R.: Inorganic Materials for Sustainable Energy (Wöhler-Vereinigung für Anorganische Chemie der Gesellschaft Deutscher Chemiker e.V, 18. Vortragstagung der Anorganischen Chemie, Berlin, Germany, 2016)

Sidabras, J. W., Suter, D., Reijerse, E.J., Savitsky, A., Lubitz, W.: Micro-resonators for Electron Paramagnetic Resonance Spectroscopy of Size Limited Samples at 9.5 GHz (38th FGMR Discussion Meeting 2016, Düsseldorf, Germany, 12.-15. Sept. 2016)

Sidabras, J. W., Suter, D., Reijerse, E.J., Savitsky, A., Lubitz, W.: Resonator Developments for Studying Protein Single Crystals of Limited Dimensions (Xth International Workshop on EPR in Biology and Medicine, Krakow, Poland, 2.-6. Oct. 2016)

Sommer, C., Rumpel, S., Reijerse, E., Lubitz W.: Magnetic Resonance and Infrared Spectroscopy of a [FeFe]-hydrogenase with Modified Active sites (Annual Meeting bio-N3MR, Düsseldorf, Germany 2016)

Rumpel, S.: NMR spectroscopy as a novel tool in hydrogenase research (38th FGMR Discussion Meeting 2016, Düsseldorf, Germany, 12.-15. Sept. 2016)

Yi, Y.: Carbon Materials for Oxygen Elecrocatalysis (4th Ertl Symposium on Chemical Processes on Solid Surfaces, Berlin, Germany, 2016)

## Awards, Honours and Memberships of the CEC Staff

### 2014

Dr. Nicholas Cox was awarded the "Young Investigator Award (John Weil)" of the International EPR/ESR Society on the Joint Conference of Asia-Pacific EPR/ESR Society (APES) Symposium 2014, International EPR(ESR) Society (IES) Symposium, and the 53rd The Society of Electron Spin Science and Technology (SEST) Annual Meeting, Nara, Japan, 2014.

Prof. Dr. Serena DeBeer was appointed Honorary Professorship at Ruhr University Bochum, 2014.

Prof. Wolfgang Lubitz was awarded with The Doctor Honoris Causa of Aix-Marseille University during the Soirée Scientifique at Aix-Marseille University, Marseille, France on November 18, 2014.

Prof. Frank Neese was awarded with the "Kohlenforschung Centennial Lectureship", Max-Planck-Institut für Kohlenforschung, Mülheim, Germany, 2014.

Prof. Frank Neese became Member of the Liebig-Denkmünze Award committee (GDCh - German Chemical Society), 2014.

Dr. Katharina Weber and Tobias Stamm were awarded with the Ernst Haage-Preis 2014 (award ceremony on 2014-12-08).

### 2015

Prof. Wolfgang Lubitz took over the Vice-President position of the Lindau Nobel Laureate Meetings (2015-01-01).

The Royal Society of Chemistry appointed Professor Frank Neese a member of the newly founded Advisory Board, Faraday Discussions for 2 years. (2015-12).

Prof. Frank Neese was awarded with the 11th Ernest R. Davidson Lectureship, University of North Texas, Denton, USA, 2015.

Prof. Frank Neese: "Thomson Reuters Highly Cited Researcher", listed among the worldwide top 1 % cited researchers, 2015.

Dr. Julia Schuhmann and Christian Klicken were awarded with the Ernst Haage-Preis 2015 (award ceremony on 2015-12-04).

Prof. Dr. Robert Schlögl was appointed as Honorary Professor in the Ruhr-University Bochum (2015-12).

Prof. Schlögl has been elected as head of the steering committee of the Kopernikus projects. (2015-10).

Prof. Robert Schlögl has been elected as external member of the Council of the University Bayreuth (2015-10).

## 2016

Dr. Agnieszka Adamska-Venkatesh was awarded with a prize for the best doctoral thesis at the Mathematisch-Naturwissenschaftlichen Fakultät, Heinrich-Heine-Universität Düsseldorf in 2015. The awardee had been honored during the graduation ceremony (2016-02-12)

Dr. Agnieszka Adamska-Venkatesh was awarded with the Otto Hahn Medal of the Max Planck Society. The award ceremony took place during the yearly General Assembly of the Max Planck Society in Saarbrücken (2016-06).

Prof. Dr. Silvia E. Braslavsky was designated with a Dr. Honoris Causa of the University of Buenos Aires (UBA) (2016-08-23).

Dr. Nicholas Cox was awarded with the International Society of Photosynthesis Research Robin Hill award 2016. The award ceremony have been held during the 17th International Congress of Photosynthesis Research in Maastricht, The Netherlands, on August 12, 2016.

Prof. Serena DeBeer wins 2016 Inorganic Chemistry Lectureship Award

Prof. Dr. Wolfgang Lubitz serves as a Member Editorial Board of the RSC journal "Energy & Environmental Sciences" from 2016-07-01 for three years.

Prof. Frank Neese: "The Roger E. Miller Lecturer" on the occasion of the The 32nd Symposium on Chemical Physics at the University of Waterloo (SCP 2016), Waterloo, Canada, 2016.

Prof. Frank Neese: "Conseils Solvay" Lecturer on the occasion of the 24th Solvay Conference on Chemistry – Catalysis in Chemistry and Biology, Brussels, Belgium, 2016.

Prof. Frank Neese: Ceremonial Lecturer on the occasion of the awards ceremony of the Dr. Barbara Mez-Starck-Stiftung, Ulm, Germany, 2016.

Prof. Frank Neese: 29th Annual Charles A. Coulson Lectureship, University of Georgia, Athens, USA, 2016.

Prof. Frank Neese serves as a Member of the Review Board "Physical and Theoretical Chemistry" in General Theoretical Chemistry of the Deutsche Forschungsgemeinschaft (German Research Foundation, DFG), 2016.

Prof. Frank Neese serves as a Member of the Editorial Board of *Struct. Bond.*

Dr. Cyrica Massué and Christian Sichelschmidt were awarded with the Ernst Haage-Preis 2016 (award ceremony on 2016-11-24).

Phillip Reck was awarded with the IHK Certificate "Die Besten" (2016-09-16)

Prof. Dr. Robert Schlögl, MPI CEC Director, received the Innovation-Award of North Rhine-Westphalia for his contributions in the energy revolution (2016-02-29).

## Theses

### 2014

Benedikt, U.: Low-Rank Tensor Approximation in post Hartree-Fock Methods. Fakultät für Naturwissenschaften, TU Chemnitz, 2014.

Lohmiller, T.: Electronic Structure and Substrate Binding of the Water-oxidizing Manganese Cluster in Photosystem II as Studied by Pulse EPR and ENDOR Spectroscopy. Fakultät II - Mathematik und Naturwissenschaften der Technischen Universität Berlin, Berlin, 2014.

Krewald, V.: Insight into Photosynthetic Water Oxidation through Theoretical Spectroscopy. Mathematisch-Naturwissenschaftliche Fakultat, Universität Bonn, 2014.

Paul, S.: Non-photochemical quenching mechanisms in plants - light induced reorganization of the thylakoid membrane. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich Heine-Universität, Düsseldorf, 2014.

Pollock, Ch.: Development of K X-ray Emission Spectroscopy as a Probe of Chemical and Biological Catalysis. Ruhr-Universität Bochum, 2014.

Weber, K.: Synthesis and Characterization of Model Complexes for the Active Sites of Hydrogenases. Fakultät II - Mathematik und Naturwissenschaften der Technischen Universität Berlin, Berlin, 2014.

### 2015

Adamska-Venkatesh, A.: Spectrocopic Investigations of [FeFe] Hydrogenases and Related Model Systems. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2015.

Böhm, K.-H.: Anwendung von Tensorapproximationen auf die Full Configuration Interaction Methode. Fakultät für Naturwissenschaften, TU Chemnitz, 2015.

Nalepa, A.: Multifrequency and Multiresonance EPR Techniques Applied to Nitroxide Radicals and Nitroxide-labeled Systems. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2015.

Schneider, W. B.: Quantenchemie in elektrochemischen Prozessen - Untersuchungen zu Stabilität, Reaktivität und Ladungsübertragung bei der platinkatalysierten Sauerstoffreduktion. Fakultät für Naturwissenschaften, TU Chemnitz, 2015.

Siebel, J. F.: Spectroscopic and Functional Investigations of the [FeFe]-hydrogenase from Chlamydomonas reinhardtii and Its Natural Electron Donor. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2015.

Wrede, K.: Heterologous Expression and Artificial Maturation of the [FeFe]-Hydrogenase from Desulfovibrio desulfuricans - Characterisation and Comparison with the Native Enzyme. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2015.

## 2016

Decaneto, E.: Structural and Spectroscopic Characterization of the Catalytic Domain of Human Membrane Type 1 Matrix Metalloproteinase: Catalytic Mechnism, Stability and Inhibition. Fakultät Chemie und Biochemie der Ruhr-Universität Bochum, Bochum, 2016.

Gutt, A.: Photochemische und strukturelle Untersuchungen neuartiger Bilinbindender Photorezeptoren. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2016.

Krahe, O.: Experimental and theoretical studies of mononuclear high-valent nitrido-iron and oxo-iron complexes. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2016.

Massué, C.: Iridium oxohydroxide electrocatalysts for the oxygen evolution reaction. Technische Universität, Berlin, 2016.

Simon, J.: Spektroskopische Charakterisierung von Blaulicht-induzierbaren Photorezeptoren - Perzeption und Nutzbarmachung von blauem Licht und UV-Strahlung. Mathematisch-Naturwissenschaftliche Fakultät der Heinrich-Heine-Universität, Düsseldorf, 2016.

## Master/Diploma

Barillone, J.: A Synthetic, Spectroscopic and Theoretical Investigation of the Electronic Structure of a Series of Co-oxo Cubane Clusters for Water Oxidation. Ruhr University Bochum, 2015.

Gomez Castillo, R.: Ruhr University Bochum, 2016.

## Conferences and Workshops organized by the Institute

### 2014

Award Lectures Series "Frontiers in Biological Chemistry 2013", Mülheim an der Ruhr, Awardee: Prof. Dr. Gabriele Centi, University of Messina, Italy, (from 2014-01-08 to 2014-01-10)

Girls Day 2014 (2014-03-27)

International Symposium on "Catalytic Systems for Chemical Energy Conversion" on the occasion of the 65th birthday of Professor Wolfgang Lubitz, Mülheim (Ruhr), Germany (from 2014-07-23 to 2014-07-25)

Summerschool "Methods in Molecular Energy Research: Theory and Spectroscopy", Wissenschaftspark Gelsenkirchen (from 2014-08-31 to 2014-09-06)

Turkish - German Conference on Energy Technologies, Middle East Technical University (METU), Ankara, Turkey organized jointly by Dr. Özlen Ferruh Erdem (MPI CEC) and Prof. Hayrettin Yücel (METU) (from 2014-10-13 to 2014-10-15)

International Congress on Photobiology (ICP), National University of Córdoba, Córdoba, Argentina. The former MPI CEC research group leader Prof. Silvia Braslavsky chaired the conference (from 2014-09-08- to 2014-09-14)

Deutsch-Israelische Projektkooperation (DIP) Meeting on "Biomaterials and Bioinspired Assemblies for Nanoengineered Optobioelectronic Systems", Harnack-Haus, Berlin, Germany (from 2014-12-14 to 2014-12-16)

1st ORCA users Meeting, MPI CEC, Mülheim an der Ruhr, organized by Prof. Auer (from 2014-09-07 to 2014-09-08)

International Symposium on "Integrating spectroscopic and theoretical methods to analyse molecular machines", Schloss Ringberg, Kreuth, Germany (from 2014-12-10 to 2014-12-13)

## 2015

Lectures Series „ Frontiers in Chemical Energy Science Award 2015 ", Mülheim an der Ruhr, Awardee: Prof. Dr. Eberhard Umbach, Karlsruhe, Germany, (from 2015-03-03 to 2015-03-05)

Girls Day 2015 (2015-04-23)

Summerschool "Methods in Molecular Energy Research: Theory and Spectroscopy", Wissenschaftspark Gelsenkirchen (from 2015-08-30 to 2015-09-04)

Meeting Board of Trustees (2015-11-06)

1st Ernst Haage Symposium, MPI CEC, Mülheim an der Ruhr, Germany (2015-12-02 to 2015-12-04)

1st workshop of MAXNET Energy on Catalyst Degradation, organized by Prof. Auer (2015-11)

## 2016

The Minerva Center for Bio-Hybrid Complex Systems 2nd German-Israeli Meeting, MPI CEC, Mülheim an der Ruhr, Germany (from 2016-02-15 to 2016-02-16)

Theory in Electrochemistry Meeting, organized by Prof. Auer, MPIE Düsseldorf (2016-04-22)

Girls Day 2016 (2016-04-28)

Manfred-Eigen-Nachwuchswissenschaftlergespräche der Deutschen Bunsengesellschaft, Topic: "Physical Chemistry of Solar Fuels Catalysis"; at MPI CEC/ Mülheim an der Ruhr, organized by J. Strunk (MPI CEC) and J.P. Hofmann (TU Eindhoven); Patron: Prof. Dr. R. Schlögl, April 6 to 8, 2016.

EPR Spectroscopy on Catalytic (Bio)chemical Systems, MPI CEC, Mülheim an der Ruhr, Germany (from 2016-06-06 to 2016-06-07)

2nd ORCA users Meeting, organized by Prof. Auer, MPI CEC, Mülheim an der Ruhr (from 2016-08-06 to 2016-08-07)

Summerschool "Physical Methods in Molecular and Heterogeneous Catalysis", Wissenschaftspark Gelsenkirchen, MPI CEC and FHI (from 2016-09-18 to 2016-09-25)

Summerschool "Molecular Wavefunction Methods", Wissenschaftspark Gelsenkirchen (from 2016-10-02 to 2016-10-08)

Deutsch-Israelische Projektkooperation (DIP) Meeting on "Biomaterials and Bio-inspired Assemblies for Nanoengineered Optobioelectronic Systems", Bochum, Germany (from 2016-10-06 to 2016-10-09)

2nd workshop of MAXNET Energy on Material and Catalyst Synthesis, organized by Prof. Auer (2016-10)

Symposium on the occasion of the 85th Birthday of Professor emeritus Dr. Kurt Schaffner, director at the Institute from 1975 to 1999 (2016-10-07)

EPR Minisymposium, Mülheim an der Ruhr, Germany (from 2016-10-28)

2nd Ernst Haage Symposium, Schloss Broich, Mülheim an der Ruhr, Germany (2016-11-23 to 2016-11-25)

Meeting Board of Trustees (2016-11-11)

Lectures Series "Frontiers in Chemical Energy Science Award 2016", Mülheim an der Ruhr, Awardee: Prof. Dr. William Tolman, University of Minnesota, Twin-Cities (USA), (from 2016-11-09 to 2016-11-11)

International Symposium on "Connecting EPR, ssNMR and DNP for the study of complex biomolecules", Schloss Ringberg, Kreuth, Germany (from 2016-12-14 to 2016-12-17)

## Guest Scientists

Alavi, Ali, Prof. Dr.
Max Planck Institute for Solid State Research, Stuttgart, Full-CI quantum Monte-Carlo (2015-01)

Bagus, Paul, Prof. Dr.
University of North Texas, Denton, USA, Core level spectroscopy calculations (2015-09)

Caserta, Giorgio, Dr.
Collège de France, Paris

Chambers, Geoffrey, Prof. Dr.
University of Illinois, Urbana, USA (2014-03)

Codolà, Zoel, Dr.
University of Girona, Spain, Preisträger "Prince of Asturien Prize", (from 2015-01-05 to 2015-02-28)

DeAngeli, Celestino, Dr.
University of Ferrara, Italy, NEVPT2 developments (2014-01)

Decaneto, Elena, M. Sc.
Italy, RESOLV (from 2013-02-01 to 2016-04-30)

Demel, Ondrej, Dr.
J. Heyrovsky Institute of Physical Chemistry, Prague, Czech, DAAD funded project (2014-10, 2015-11, 2016-05/11/12)

Duboc, Carole, Prof. Dr.
University Joseph Fourier, Grenoble, France, EPR spectroscopy and manganese chemistry (2014-02)

Espig, Mike, Prof. Dr.
RWTH Aachen, Germany, research visit (from 2014-05-07 to 2014-06-25)

Farrell, Megan, Dr.
University of Tennessee, USA, DAAD RISE Program (Research Intership in Science and Engineering) (from 2014-06-11 to 2014-08-12)

Glendening, Eric, Prof. Dr.
Indiana State University, Terre Haute, USA, interfacing ORCA to NBO (2014-03)

Gorriti, Marta, Dr.
Tucuman, Argentina, DAAD-CONICET Exchange Program, research visit (from 2015-08 to 2016-02)

Grishin, Yuri, Prof. Dr.
Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, (from 2014-07-19 to 2014-10-10, 2015-02-25 to 2015-05-05, 2015-09-17 to 2015-11-17, 2016-01-05 to 2016-03-13, 2016-04-15 to 2016-06-24)

Gromov, Oleg, Dr.
Moscow State University, Moskau, Russia, DAAD Stipendiat, (from 2016-10-15 to 2016-12-09)

Gu, Qingqing, M. Sc.
Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China (from 2016-10-18)

Hayes, Ellen, Dr.
University of Washington, USA (from 2015-05-26 to 2015-06-09)

He, Chunmao, Prof. Dr.
South China University of Technology, Guangzhou, China, Stipendiat im Gästeprogramm (from 2015-09-01 to 2016-08-31)

Heyno, Eiri, Dr.
RESOLV, Ruhr University Bochum, Germany (since 2016-04-01)

Hu, Ping-Ping, M. Sc.
Wuhan, China, CSC (Chinese Scholar Council), Sandwich-Ph.D. Program, research visit (from 2015-05 to 2015-07)

Hülsey, Max, Dr.
Universität Heidelberg, Germany, research visit (from 2016-04-04 to 2016-04-30)

Kateriya, Suneel, Prof. Dr.
New Delhi, India, Max-Planck-Travel Award, research visit (6 month in 2013-2016)

Kitschke, Philipp, Dr.
TU Chemnitz, Germany, research visit within FOR 1407 (from 2014-03-30 to 2014-04-04)

Kraiselburd, Ivana, Dr.
Rosario, Argentina, DAAD-CONICET Exchange Program, research visit (6 month in 2014)

Kulik, Leonid, Prof. Dr.
Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia, AvH Institutspartnerschaft (from 2015-02-05 to 2015-02-23, 2015-08-27 to 2015-10-10, 2016-09-06 to 2016-10-21)

Lukina, Ekaterina A.
Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia (from 2015-09-05 to 2015-09-12, 2015-12-01 to 2015-12-22, 2016-09-06 to 2016-10-21)

Marzlin, Karl-Peter, Prof. Dr.
St Francis Xavier University Antigonish, Nova Scotia, Canada, new theory of spin relaxation (2015-03, 2015-12, 2016-08)

Möbius, Klaus, Prof. Dr.
Freie Universität, Berlin, Germany (div. 2014, 2015, 2016)

Morton, Jennifer , Dr.
Australian National University, Canberra, Australia (from 2016-07-26 to 2016-08-07)

Pittner, Jiří, Dr.
J. Heyrovsky Institute of Physical Chemistry, Prague, Czech, DAAD funded project (2014-10)

Sabenya, Gerard, M. Sc.
Universitat de Girona, Short-Term Scientific Mission, payed by COST Action CM1305 (ECOSTBio), (from 2015-03-15 to 2015-04-30)

Saric, Iva, Dr.
University of Rijeka, Faculty of Civil Engineering and Center for Micro and Nano Sciences and Technologies, Kroatien, AvH Institutspartnerschaft, (from 2015-04-20 to 2015-04-30)

Takeda, Kota, Dr.
Tokyo University of Agriculture and Technology, Tokyo, Japan, (since 2016-05-01)

Tang, Kun, M. Sc.
Wuhan, China, CSC (Chinese Scholar Council), Sandwich-Ph.D. Program, research visit (from 2013-10 to 2015-06)

Uvarov, Mikhail, Dr.
Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, Russia, Novosibirsk, Russia, (from 2015-12-01 to 2015-12-22)

Valeev, Edward F., Prof. Dr.
Virginia Tech, Blacksburg, VA, USA, explicitly correlated electronic structure theory (2014-11, 2015-04)

Weiner, Lev, Prof. Dr.
Weizman Institute of Sciences, Rehovot, Israel, (from 2015-03-25 to 2015-05-10)

Wernecke, Gunnar, Dr.
Universität Marburg, Germany, magnetic properties of linear transition metal complexes (2015-11)

## Impressum

| | |
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