Chemistry and Biochemistry at the Ruhr-Universität Bochum (RUB)
The perfect plastic composition is key to ensuring that your rubber duck maintains its radiant yellow even after hours in the bath. And you can thank state-of-the-art Schenck Process feeder technology for this composition. But this isn’t the only application for our technology. It is also used to put the right number of gherkins in a jar, to generate energy in a highly efficient and environmentally friendly way or to mix the right material for a complex bridge construction.

Schenck Process employs 3,000 members of staff at 34 locations and has been a world leader in measuring and process technology, industrial weighing, feeding, screening and automation for more than 125 years. www.schenckprocess.com
Welcome

It is my pleasure to welcome you to the Faculty of Chemistry and Biochemistry at the Ruhr-Universität Bochum (RUB). On the occasion of the Bunsen-Tagung 2015, this brochure may serve to showcase the people at our Faculty, as well as our many activities.

Located in the midst of the dynamic metropolitan area of the Ruhr, in the heart of Europe, RUB with its 20 faculties is home to ca. 500 professors, over 5 500 employees and more than 41 000 students from 130 countries. Although only 50 years old, RUB is not just one of the biggest German Universities but also unique with its broad range of subjects taught. Faculties at RUB include all Physical and Life Sciences, Humanities, a Law School and Media Sciences, Engineering, a Medical School and even Sport Sciences. The aerial photograph nicely demonstrates that this unique variety of Faculties is all assembled on one coherent campus, which is also beautifully located in the southern suburbs of Bochum. The nearby Lake Kemende (seen at the top right corner of the photo) is used not only for students relaxing at a barbecue near the lakeside, but also for sports and serious training. As just one example, four out of the eight members of the men’s coxed eight rowing boat which won the gold medal for Germany at the 2012 Olympics were students of RUB.

Officially, RUB was founded in Bochum in 1965 – by the way the first “new” University built in all in Germany after World War II – and its 50th anniversary will be celebrated in June 2015 with several spectacular events. Teaching in Chemistry started already in 1969. Originally, the Faculty started with two Chairs in Inorganic, Organic and Physical Chemistry, and one chair each in Analytical, Theoretical and Technical Chemistry. Towards the end of the 1980s, two Chairs in Biochemistry were founded and in autumn 1990, a Biochemistry course was added to the Faculty’s teaching portfolio. Accordingly, the Faculty was renamed Faculty of Chemistry and Biochemistry. In response to the societal need for a strong scientific training also of teachers-to-be, a new Professorship “Didaktik der Chemie” was established in 2004, who oversees the education of future teachers in Chemistry at RUB, using inter alia the facilities of Germany’s largest “Schülerlabor” (Physical Sciences lab for school-children of all ages). Today, 1400 students are enrolled in a total of seven Bachelor and Master programs at the Faculty, with ca. 250 first-year students starting each autumn. There are 25 full-time professors, and an additional number of 10 independent groups led by early career researchers – most of them funded independently by competitive grants like the Emmy-Noether program of the German Science Foundation DFG. The Faculty is proud of the fact that the total budget it receives from the University has been more than doubled by such competitive third-party money in each of the last couple of years. Additional funding comes from industrial collaborations, of which also our students and PhD candidates benefit through direct contacts and research placements. As just one example, an endowed “Evonik Chair of Organic Chemistry” will be established in 2016 with generous support from Evonik Industries. Our Faculty has also recognized the potential for reviving our curriculum by switching to the European Bachelor and Master system, and was among the first in Germany to make the move away from the established Diploma system in 2001. Finally, the Faculty’s Graduate School celebrates between 50 – 60 PhD graduations every year.

Among the many collaborative research projects that members of our Faculty have successfully managed over the last years - EU projects, Collaborative Research Centers (SFB) and Research Units (FOR) – the Cluster of Excellence “RESOLV – Ruhr Explores Solvation” (EXC 1069, funded since autumn 2012 in the last round of the so-called German Excellence Initiative) certainly stands out. The topic of “Solvation Science” provides a common roof to many research activities in areas as diverse as Molecular and Biomolecular Chemistry, Life Sciences, Material Sciences and Nanoscience. The growing Faculty will have an additional research building ZEMOS (Center for Molecular Spectroscopy and Simulation of Solvent-driven Processes), fully equipped with state-of-the-art laboratories, offices and dedicated rooms for various specialized applications at its disposal as of spring 2016. Individual articles on both RESOLV and ZEMOS are included in this brochure.

But, as you will be aware from own experiences, it is not numbers, buildings, or euros that matter, but the people and their ideas, their imagination, their visions that really make a difference. In this sense, I invite you to take a virtual tour through our Faculty by browsing through the pages of this brochure, and get to know the researchers of this Faculty!

Nils Metzler-Nolte
Dean of the Faculty of Chemistry and Biochemistry at the Ruhr-Universität Bochum
Content

1 Welcome
Prof. Dr. Nils Metzler-Nolte, Dean of the Faculty of Chemistry and Biochemistry at the Ruhr-Universität Bochum

3 RESOLV – Ruhr Explores Solvation Cluster of Excellence
Prof. Dr. Martina Havenith-Newen, Speaker of the Executive Board

6 Novel Research Infrastructure for Solvation Science
Prof. Dr. Martina Havenith-Newen, ZEMOS – Center of Molecular Spectroscopy and Simulation of Solvent-driven Processes

7 Electrochemistry: From Bioelectrochemistry to Electrocatalysis
Prof. Dr. Wolfgang Schuhmann, Analytical Chemistry

9 Analytical Chemistry – Biointerfaces: Understanding Biological Adhesion Processes
Prof. Dr. Axel Rosenhahn, Analytical Chemistry

11 Center for Electrochemical Sciences (CES)
Dr. Nicola Plumeré, Dr. Fabio La Mantia, Dr. Sabine Seisel, Prof. Dr. Wolfgang Schuhmann

13 Bioinorganic and Medicinal Inorganic Chemistry
Prof. Dr. Nils Metzler-Nolte and Dr. Ulf-Peter Apfel, Inorganic Chemistry I

16 Synergy between Synthesis, Computational Chemistry and Materials Development
Prof. Dr. Roland A. Fischer, Jun. Prof. Dr. Radim Beranek, Prof. Dr. Anjana Devi, PD Dr. Rochus Schmid, Inorganic Chemistry II

22 Ionotropic Glutamate Receptors: Structure, Function, Regulation and Modulation
Prof. Dr. Michael Hollmann, Biochemistry I

24 Molecular Neurobiochemistry: Towards Protection and Regeneration of Brain Neurons
Prof. Dr. Rolf Heumann, Biochemistry II

26 Electrobiochemistry: Molecular Regulation of Voltage-Gated Transmembrane Ion Currents Underlying Fast Signaling in Living Cells
Prof. Dr. Irmgard Dietzel-Meyer, Biochemistry II

28 Biomolecular Spectroscopy: NMR to Study the Structure and Function of Medically Relevant Proteins
Prof. Dr. Raphael Stoll, Biochemistry II

30 Chemistry Education: Scientific Ways of Thinking and Working
Prof. Dr. Katrin Sommer, Didactics

32 Systems Chemistry: Self-Replication and Self-Assembly
Prof. Dr. Gunter von Kiedrowski, Organic Chemistry I

34 Multidentate Halogen Bonding in Solution: Organocatalysis and Supramolecular Chemistry
Prof. Dr. Stefan M. Huber, Organic Chemistry I

36 Natural Product Research: Chemical, Enzymatic and Fermentative Synthesis of Medicinally Important Compounds
Prof. Dr. Frank Schulz, Organic Chemistry I

38 Physical Organic Chemistry: Understanding Reactions
Prof. Dr. Wolfram Sander, Organic Chemistry II

40 Metals in Catalysis and Self-Organization
Prof. Dr. Gerald Dyker, Organic Chemistry II

42 Reactions of Molecules on Hybrid Surfaces
Prof. Dr. Karin Morgenstern, Physical Chemistry I

44 Biophysical Chemistry: Protein Interactions
Prof. Dr. Christian Herrmann, Physical Chemistry I

46 Physical Chemistry: From Microsolvation to Bulk Water Dynamics
Prof. Dr. Martina Havenith, Physical Chemistry II

48 Biopolymers In Vivo – from the Test Tube into the Cell
Jun.-Prof. Dr. Simon Ebbinghaus, Physical Chemistry II

50 Ultrafast Photochemistry: In Hot Pursuit of Chemical Reactions
Prof. Dr. Patrick Nürnberg, Physical Chemistry II

52 Heterogeneous Redox Catalysis: From Fundamental Insight to Industrial Application
Prof. Dr. Martin Muhler and Dr. Wei Xia, Industrial Chemistry

55 Heterogeneous Catalysis: Relations between Structure and Performance of Catalysts
Prof. Dr. Wolfgang Grünert, Industrial Chemistry

58 Ab Initio Simulations: Chemical Reactions in the “Virtual Laboratory”
Prof. Dr. Dominik Marx, Theoretical Chemistry

61 Quantum Chemistry
Prof. Dr. Christof Hättig, Theoretical Chemistry

63 Theoretical Chemistry: Molecular Simulation
Prof. Dr. Lars Schäfer, Theoretical Chemistry

65 Large-Scale Molecular Dynamics Simulations of Complex Systems Employing Neural Network Potentials
PD Dr. Jörg Behler, Theoretical Chemistry

67 Quantum Chemistry: Wavefunction-Based Electronic Structure Theory
Prof. em. Dr. Volker Staemmler, Theoretical Chemistry

68 Physical Chemistry at High Pressures
Prof. em. Dr. rer. nat. Dr. hc(UA) Gerhard M. Schneider, Physical Chemistry II
Solvation Science @ RUB –
Who we are and what we do

A liquid environment is natural to almost all chemical reactions in nature and technology. It is known for many decades that the solvent, forming the surrounding of a reaction, has a certain influence. Therefore solvation, as one of the core topics in chemistry, has been the subject of extensive research for many years. Furthermore solvation processes recently have attracted considerable attention from physicists, engineers, and biologists. However, in most cases expensive and time consuming trial and error experiments are still necessary to find the optimum solvent for one specific reaction. Besides this, the influence of the solvent e.g. on protein functions in biological systems is poorly understood, so far.

Over 50 scientific working groups have joined their forces in RESOLV to work together on developing a bottom up approach to understand solvation. Distributed over seven institutions in the Metropolis Ruhr they intensively expand the frontiers of science. Over 80 Ph.D. students have joint the integrated Graduate School Solvation Science (GSS) and spend a three-month research stay abroad at one of over 20 international partner institutions within the RESOLV International Faculty. A main effort, named TranSOLV, is undertaken to transfer the research results to industry and to establish joint scientific-industrial projects. We have recently hired three new faculty members within the field of Solvation Science. Next year an endowed chair by Evonik Industries will be appointed.

The scientific strategy of RESOLV is vastly different from the traditional, empirical, macroscopic, and descriptive approach which is often followed. RESOLV is instead working on a unifying, bottom-up framework, being as universal and comprehensive as possible. The aim is the development of predictive Solvation Science based on a molecular rational-design perspective. Within this framework, solvent molecules are regarded to be functional themselves and employed as active species or reactive agents in solvent-mediated and solvent-controlled processes, respectively, rather than only being considered as inert and passive bystanders.

RESOLV is intimately coupling the most sophisticated state-of-the-art experimental, spectroscopic, and synthetic approaches with the most recent advances in computer simulation to tackle the important scientific challenges. Understanding solvation phenomena on this molecular level will most directly impact a wide range of applications, such as pitting corrosion of steel, biosensor development, biomass conversion for platform chemicals, microcapsules for drug release, fluid extraction/purification processes, high-tech batteries, "green" asymmetric organocatalysis, and low-energy brine electrolysis.
Tackle the Problem –
The Canon of Methods in RESOLV

The experimental techniques in physical chemistry which are available in RESOLV cover the time scales of femto-seconds (fsec-spectroscopy group of Patrick Nürnberg), sub-pico-seconds (THz spectroscopy by Martina Havenith), nano-seconds (dielectric relaxation by Hermann Weingärtner and EPR by Wolfgang Lubitz), micro-seconds (Overhauser dynamic nuclear polarization by Songi Han) to milli-seconds (FRel by Simon Ebbinghaus). Furthermore there are equilibrium measurements available by diffraction methods (Roland Winter) as well as calorimetry (Christian Herrmann) and the scanning microscopy (Karina Morgenstern).

This is complimented by state-of-the-art theory techniques: ab initio MD (Dominik Marx), MD simulations (Lars Schäfer), and QM/MM (Walter Thiel, Elsa Sanchez-Garcia, and Eckhard Spohr).

Partners in RESOLV –
Reaching higher Levels of national and international Cooperation

RESOLV achieved a new stage in the cooperation between three universities and four non-university institutions within a 30 kilometers radius from the RUB by mutually granting free access to their core facilities. Moreover, all institutions are linked by joint research projects and an overarching education platform, which includes a Graduate School Solvation Science (GSS). Within RESOLV, we have established joint Early Career Researchers Groups (ECRGs), which are simultaneous members of a Max-Planck-Institut (Düsseldorf, Mülheim) or Fraunhofer Institute as well as Ruhr-Universität Bochum, thereby granting full-right privileges to the ECRG leaders in both groups of institutions.

RESOLV successfully established an International Faculty of Solvation Science (IF) as an international network of top institutions in the US, Europe, Asia, and Israel to foster long-term mutually beneficial scientific collaborations. The IF is a strategical key element to promote the exchange of knowledge, people, and ideas between leading scientists at all levels of their scientific careers. The IF groups include more than 30 leading scientists in Solvation Science and are linked to RESOLV by joint-funded proposals, and individual exchange visits of students and postdocs, as reflected by joint publications. The IF has embedded these partnerships at the institutional level and provides flexible funds for ensuring their long lasting implantation.

Splitting the Problem –
The Research Areas of RESOLV

Research Area A – Understanding and Exploiting Solvation in Chemical Processes

The understanding of chemical reactivity is of key importance for the development and optimization of chemical processes in both the laboratory and in industry. Solvation not only changes the properties of the reactants and the products, but also affects transition states and intermediates. Solvents thus influence the thermodynamics, the kinetics, and the product selectivity in liquid phase reactions. The selection of a suitable solvent frequently determines the success or failure of a chemical reaction. One example with possibly broad implications is the synthesis of enantiomerically pure products that is mandatory for any new drug development. This poses the scientific challenge to develop highly stereoselective synthetic strategies, for which the choice of a suitable solvent system is crucial.
RESOLV addresses key questions on this topic. To achieve these ambitious goals, RESOLV draws on the state-of-the-art experimental and theoretical methods and thus contributes to the development of Solvation Science in the biomolecular realm.

Research Area C – Ion Solvation and Charge Transfer at Interfaces

Interfaces play a dominant role in molecular science. Heterogeneous catalysis is the prime example where reactions are accelerated due to the presence of surfaces including catalytically active liquid-solid interfaces. Within the last decades, surface science has triggered an impressive boost in the molecular understanding of catalytic processes at solid-gas interfaces. In stark contrast, close to nothing is yet known about how reactants de-solvate, intermediates stabilize, and products re-solvate at liquid-solid interfaces. It is unclear which of the concepts developed for reactions at gas-solid interfaces— if any — can be transferred to those at liquid-solid interfaces. Even less understood are the mechanisms of electrocatalytic reactions. The scientific challenge arises from the strong influence of the solvent on the properties of electrified interfaces, adsorbed species, and transition states. Improvements in chemical energy conversion depend to a large extent on the control of reactions at aqueous interfaces. One focus of RESOLV will be the investigation of the molecular basis of oxygen reduction reactions at liquid-solid interfaces. Achieving a detailed molecular understanding of these fundamental processes would be a vital step towards enabling major breakthroughs in key technologies, since these processes not only determine the performance of fuel cells, but also have an impact on corrosion, the efficiency of metal-air batteries, and the performance of photo-electrochemical cells.

All these strategies will serve to RESOLVE urgent questions related to Solvation Science while crossing traditional boundaries of academic subjects, disciplines, departments, and nations.

The Cluster of Excellence RESOLV (Ruhr Explores Solvation: EXC 1069) is funded by the Federal Ministry of Education and Research and by the state North Rhine-Westphalia within the framework of the German Excellence Initiative.
Novel research infrastructure for Solvation Science

Prof. Dr. Martina Havenith-Newen; ZEMOS – Center for Molecular Spectroscopy and Simulation of Solvent-driven Processes

The Ruhr-Universität Bochum (RUB) is implementing a new research infrastructure on campus for a novel research field: the investigation of solvation processes. Solvation – dissolving of a chemical substance – is one of the most basic processes in chemistry, in chemical engineering, and in biology. ZEMOS (German: “Zentrum für molekulare Spektroskopie und Simulation solvensgesteuerter Prozesse”) is an essential part of the collaborative research project RESOLV (Ruhr Explores Solvation), a Cluster of Excellence funded by the DFG. The German Science Council (German: Wissenschaftsrat (WR)) recommended funding the research building with 44 M€ in 2011. The new building with a total area of 3,891 square meters will offer space for about 100 scientists ranging from chemists, biochemists to engineers. The Foundation Stone Ceremony took place on May 26th, 2014. The construction is making good progress and is planned to be completed by spring 2016.

The research within ZEMOS is dedicated to three cross-linked topics:

A. Understanding and Exploiting Solvation in Chemical Processes
B. Connecting Solvation Dynamics with Biomolecular Function
C. Ion Solvation and Charge Transfer at Interfaces

The attractive scientific infrastructure within the ZEMOS building will host special Laser laboratories for spectroscopy, microscopy and high pressure studies as well as analytical, biophysical and chemical laboratories. In addition, in ZEMOS we will integrate three core facilities, each of which will provide a specific technology platform for the scientists. The distinct groups will have access to a major computer cluster in house. Scientific and technical staff will support the researchers. The architecture is set-up such that it serves to facilitate the collaboration between the different scientific disciplines and communication between the scientists by integration of communication zones next to the offices.

Thus, ZEMOS will become an efficient incubator platform for research dedicated to Solvation Science. It is particular attractive for young scientists to start their own research groups. Please contact the ZEMOS team (zemos@rub.de) if you are interested to apply for a research grant and are interested in more information on the opportunities in Bochum.

ZEMOS aims to be an internationally leading institution for Solvation Science at the Ruhr-Universität Bochum. The new center will bundle the expertise of more than 20 research groups of RUB, Max Planck Institutes (“Kohlenforschung”, Mülheim, and “Eisenforschung”, Düsseldorf), and the Fraunhofer Institute “UMSICHT” (Oberhausen). It will intensively and immediately collaborate with international world-class institutions in this research field, including research groups located in Cambridge, Berkeley, Yale, and at the Israeli Weizmann Institute.

www.rub.de/zemos

SPONSORED BY

Federal Ministry of Education and Research

Ministerium für Innovation, Wissenschaft und Forschung des Landes Nordrhein-Westfalen
The Schuhmann group does research based on a number of electrochemical methods and especially microelectrochemical methods. Main research topics are focusing on electrocatalysis for energy conversion, high-throughput materials characterization for solar energy conversion, bioelectrochemistry for biofuel cells, DNA assays and biosensors, as well as microelectrochemistry for the elucidation of local processes in Li-ion and Zn/air batteries.

The design of specifically adapted redox polymers was further used to wire the protein complexes photosystem 1 and photosystem 2 from algae to electrodes allowing light-induced electron-transfer reactions and the design of a semi-artificial Z-scheme analogue of photosynthesis. Recently, the concept of the design of suitable redox polymers was extended to the entrapment of hydrogenases. It could be shown that the design of a viologen-based redox polymer is able to protect hydrogenases from both high-potential deactivation as well as from damage by molecular oxygen. New concepts for the visualization of DNA hybridization were proposed.

**Scanning electrochemical microscopy (SECM)**

In SECM the convolution between information about local electrochemical reactivity and the tip-to-sample distance has to be overcome. Application of SECM for the visualization of biological activity evolved to an important field of research. The development of novel detection modes in SECM by integrating potential-pulse sequences allowed for the visualization of local catalytic activity for oxygen consumption or for local impedance measurements based on AC perturbations, the determination of the onset potential of catalysts for the oxygen evolution reactions and the visualization of the activity of catalysts for oxygen reduction. The concept of electrode positioning was extended to the implementation of a scanning-droplet cell which allows high-throughput characterization of catalyst materials or materials for solar energy conversion.

**Electrocatalysis**

Conversion of energy and sustainable energy production and distribution is of high importance. This implies on the one hand to develop new analytical tools for the evaluation of the catalytic activity of electrocatalysts but even more importantly to replace scarce noble-metal based catalysts by abundant materials. Moreover, the surface area of electrodes has to be substantially enlarged to allow for high reaction rates. These topics were addressed by designing carbon nanotube based materials, three-dimensional hierarchical carbon nanotube composites with high electrical conductivity, nitrogen-doped carbon nanotubes, noble-metals supported on nitrogen doped carbon nanotubes as well as pyrolysis of nitrogen-containing metal complexes such as porphyrins or pyrolysis of nitrogen-containing polymers. In addition to the investigation of oxygen reduction and oxygen evolution catalysts chlorine evolution was intensively studied and new mechanistic insights especially on gas-bubble departure could be provided.

**Lithium-ion batteries**

In addition to energy conversion and energy storage in chemical bonds, energy storage using batteries is of high importance. It became evident, that the available test cells did not allow to obtain reliable information using electrochemical impedance spectroscopy nor on the formation of the solid electrolyte interphase formed due to...
electrolyte decomposition. Therefore, new measuring cells for impedance spectroscopy in sealed battery cells were developed and a SECM was integrated within a glove box to allow for in-situ investigation of the formation of the solid-electrolyte interphase [12].

Selected References


Wolfgang Schuhmann obtained his diploma degree in chemistry from the University in Karlsruhe, Germany (1982) and his PhD from the Technical University of Munich (1986). After finishing his habilitation thesis at the Technical University of Munich in 1993, he was appointed professor for Analytical Chemistry at the Ruhr-Universität Bochum in 1996. In 2000 he received the Biosensors & Bioelectronics Award. In 2005 he was appointed Fellow of the Royal Society of Chemistry (FRSC). In 2008 he was awarded with the Julius-von-Haast Fellowship of the Royal Society of New Zealand and the Humboldt Foundation and in 2011 he received the Katsumi-Niki-Award of the International Society of Electrochemistry (ISE) and in 2012 he was appointed fellow of the International Society of Electrochemistry (ISE). In 2014 he received the Howard Fellowship of the University of New South Wales, Sydney. He is the member of several editorial boards (ChemPlusChem, Biosensors & Bioelectronics, Electroanalysis,) and chair of the board of ChemElectroChem. He published more than 450 publications in international peer-reviewed scientific journals.
The Rosenhahn group aims on understanding the interaction of microorganisms and cells with surfaces and its implication for biofouling and biomedical research. Surface modification in conjunction with surface characterization is used to correlate surface properties with biological response. To gain a deeper insight into the structure and dynamics of surface colonization by microorganisms, microfluidic assays, 3D tracking techniques, and X-ray imaging are developed and applied.

**Functional interfaces**

Functional interfaces with full control of their chemical composition, elasticity, hydration, morphology, hydrodynamics and charge are prepared by self-assembly. Monolayers based on thiol and gold chemistry are excellent tools to test the impact of a specific surface chemistry on adhesion\(^{(1,2)}\). Thicker polymer chemistries are prepared by dipping-robot assisted layer by layer deposition\(^{(3)}\) and reversible-deactivation radical polymerization. Key applications include the development of non-toxic anti-fouling coatings\(^{(2,4,5)}\) and surfaces for tissue engineering\(^{(6)}\).

**Surface analysis**

Before biological testing all interfaces are characterized by state of the art surface analysis. Spectral ellipsometry, contact angle goniometry, surface IR spectroscopy, SEM+EDX, fluorescence microscopy and XPS are applied to characterize the chemistry and properties at the interface.
Biological adhesion

The functional interfaces are applied to investigate adhesion of microorganisms, marine organisms and cells. To test the foul release potential of surfaces, microfluidic adhesion assays of bacteria and diatoms are applied. More complex organisms like green and brown algae, barnacles and mussels are tested in collaboration with partners from marine biology. To mechanistically understand surface colonization, holographic and stereoscopic 3D tracking techniques are developed and applied (7,9). In biomedical research our focus is on the CD44-HA interaction (6). The catch-bond mediated interaction and its relevance for hematopoiesis, leukemia and cancer is studied.

X-ray spectromicroscopy and coherent scattering

X-ray spectromicroscopy at synchrotron sources combines high spatial resolution with chemical specificity at high penetration depth (10). This renders the technique ideal to study biological systems and adhesion processes. Local chemistry and elemental distributions are correlated with spatially resolved vibrational spectroscopy (Raman and IR) to understand distribution of metals in organelles and biofoulers. In addition, X-ray scattering provides insight into the ultrastructure of organelles and microorganisms.

Selected publications


Axel Rosenhahn has been Professor for Analytical Chemistry at the Ruhr-University Bochum since 2012. He received his chemistry diploma at the University of Bonn and completed his Ph.D. in 2000 in the Physical Chemistry Department under the supervision of K. Wandelt. Moving to the Materials Sciences Division of the Lawrence Berkeley National Laboratory he worked at the Advanced Light Source as postdoc with C.S. Fadley. In 2002 he joined the Applied Physical Chemistry group of M. Grunze to do his habilitation on Biointerfaces and coherent imaging. Between 2009 and 2012 he worked at the Institute of Functional Interfaces at the Karlsruhe Institute of Technology on microbial interactions with surfaces. (More information at www.rub.de/biointerfaces)
As one winner of the HighTech.NRW competition the Center for Electrochemical Sciences (CES) of the Ruhr-Universität Bochum has been founded in October 2009 by the Ruhr-Universität Bochum and the Max-Planck-Institut für Eisenforschung Düsseldorf, with additional financial support by ThyssenKrupp Steel. CES is regarded as a Center of Excellence with the task to ensure international competitive research in all aspects of modern electrochemistry at the highest standard. The key missions of the center are the coordination of large-scale research projects of its members and establishing cooperations with external partners from industry as well as other research institutions.

Research facilities

A modern electrochemistry laboratory has been built up and equipped with various potentiostats including different electrochemical quartz micro (eQCM) balances, impedance spectroscopy, scanning electrochemical microscopy (SECM), scanning electron microscopy (eSEM), atomic force microscopy (AFM), surface plasmon resonance (SPR), raman spectroscopy (SERS) and dynamic light scattering. The electrochemical equipment, SECM as well as AFM can also be operated under inert atmospheres (H₂O/O₂ free or O₂ free in a glove box) offering a unique facility for the investigation of water or oxygen sensitive systems. To promote young researchers, young research groups have been established within CES offering them full access to all equipment.

Research activities

At CES research activities on different areas of electrochemistry such as among others Li-ion-batteries, semiconductors, photoelectrochemistry, photoelectrochemical water splitting, catalysts for oxygen reduction/oxidation, (bio)fuel cells, and biosensors are performed. Members of CES are participating in a number of joint research projects funded by BMBF, DFG, Helmholtz Society and EU.

Young research group “Molecular Nanostructures”

The group of Dr Plumeré is essentially involved in the design of electron relays to bridge redox proteins and electrodes for sensing and energy conversion. Redox enzymes have extreme activities and selectivities for various reactions and are hence attractive for technological applications. We use synthetic chemistry to build redox interfaces on electrode surface to accommodate the target biomolecules with respect to their properties and intended applications. The main projects involve biosensing, biophotovoltaics and biofuel cells. In each of these cases the redox proteins are connected to the electrodes via electron mediators. For example, in nitrate biosensing, the mediators with high affinity for an enzyme that selectively reduces nitrate are associated to a scavenger [1].

For interferences such as oxygen to allow for on-site quantification without sample preparation [2], in light to electricity conversion, the immobilization of photosynthetic proteins requires electron mediators with redox potentials adjusted to the one of the protein to achieve fast electron transfer at low overpotential [3]. The use of redox hydrogels as immobilization matrix have recently yielded photocurrents [4] and voltages [5] that raise the expectation to eventually achieve practical efficiency from biophotovoltaic devices. Redox enzymes may also play a role as substitute for noble metals in chemical fuel to electricity conversion. In this case, the main issue is the stability of the biocatalysts. We have shown that the electron mediator can be designed to protect the catalyst from various degradation processes to achieve stability over weeks unter constant turn-over conditions for H₂ oxidation in biofuel cell [5].

Dr. Nicolas Plumeré studied chemistry at the University of Strasbourg (France) and the University of the West of Scotland, Glasgow (UK). He obtained his PhD in inorganic chemistry in 2009 from the University of Tübingen (Germany). The main focus of his thesis was on synthesis and electrochemistry of redox-active nanoparticles. He was awarded a DFG fellowship for his PhD as well as a DAAD fellowship for a research visit at the San Jose State University (CA, USA). After a postdoctoral stay in the field of bioelectrochemistry for sensing applications (USDA fundings) at the laboratory of Prof. Wilbur H. Campbell (NECi, Lake Linden, MI, USA), he started as a junior group leader at the Center for Electrochemical Sciences (CES) at the Ruhr-Universität Bochum (Germany) in 2010. He is coauthor of 30 publications dealing with electrochemical biosensors, energy conversion based on biomolecules and redox-active materials. The research activities of his group at CES focus on the development of new strategies for efficient electrical connectivity between redox enzymes and electrodes.

Young research group “Semiconductor & Energy Conversion”

The group “Semiconductor & Energy Conversion” focuses its research in the field of aqueous metal-ion batteries for electrochemical energy storage of grid power. Although aqueous batteries are cheaper than their organic counterparts, the electrochemical stability of the former is limited to 1.23 V. At this aim, the dependence of the electrochemical stability of the electrolytes on the components (salt and additives) was investigated[1]. By choosing the proper salts and additives, it was possible to rise the electrochemical stability window of water up to 2.2 V. Based on this, a novel zinc-ion battery, with 1.73 V operating potential, working in near-neutral environment, and containing non-toxic and low-cost components has been developed[2]. The battery shows a significantly improved stability (more than 100 cycles), and could be a promising substitute of lead acid batteries for several applications. The group of “Semiconductor & Energy Conversion” works also on other aspects of applied and experimental electrochemistry: lithium recovery from brine and seawater[3]; recovery of heavy metals from wastewater; membranes and separators for alkaline electrolyzers[4]; electron- and ion-transfer at the solid/liquid interface[5]; amorphous semiconductor/liquid junction theory.


Fabio La Mantia has obtained his master degree in chemical engineering at the University of Palermo (Italy) in 2004, with the thesis entitled “Characterization of Thin Amorphous Semiconducting Films by EIS and Differential Admittance”. From 2005 to 2008 he has undertaken the doctoral studies at the Eidgenössische Technische Hochschule Zürich and Paul-Scherrer Institut (Switzerland), which have been focused on lithium-ion batteries, and in particular the characterization of such systems by means of differential mass spectrometry and electrochemical impedance spectroscopy. In 2008, Dr. La Mantia moved to Stanford University (California) where he was involved in research related to the development of new materials for batteries, both aqueous and organic, as well as supercapacitors based on carbon nanotubes. Since June 2010, Dr. Fabio La Mantia has been leader of the group “Semiconductor & Energy Conversion” at the Center for Electrochemical Sciences - CES at the Ruhr-Universität Bochum (Germany), which deals with several aspects of fundamental and applied electrochemistry in the field of energy conversion.
Bioinorganic and Medicinal Inorganic Chemistry

Prof. Dr. Nils Metzler-Nolte and Dr. Ulf-Peter Apfel; Chair of Inorganic Chemistry I – Bioinorganic Chemistry

Research at the Chair of Bioinorganic Chemistry revolves around the synthesis of new biologically relevant metal complexes and their bioconjugates. These compounds are investigated for their properties as drug candidates, as biosensors, tools for molecular biotechnology, and as functional mimics for metalloenzymes. Our research is very often inspired by questions of medicinal or biological relevance.

The groups at the Chair of Inorganic Chemistry I utilize the unique properties of metal complexes for the detection of biological targets, manipulation of drug interactions, and mimicking of biological systems.

Targeted Antitumor Agents

While numerous metal compounds possess strong anti-proliferative activity against many cells, their use as actual drugs is limited by their poor selectivity. Research in the Metzler-Nolte group aims to improve the selectivity of metal-based anticancer drug candidates for cellular targeting by attaching them to biological signalling molecules like peptides. The peptides are derived from sequences known for enhanced and/or cell-type specific uptake (e.g. TAT peptides or octreotate), or for intra-cellular delivery (such as nuclear or mitochondrial localization, Fig. 1).

Fig. 1: Metalloocene-peptide conjugates for intra-cellular nuclear localization of metal complexes.

The group has developed a unique combination of synthetic methods for the preparation of metal-peptide conjugates even with very sensitive metal complexes. Furthermore, the group is specialized on the investigation of the metal complexes’ spectroscopic properties, in conjunction with cell biological investigations in our own cell culture lab.

Metal-Based Antibiotics

Since the discovery of modern antibiotics such as the penicillins in the first half of the last century, bacterial infections that would have been fatal only 100 years ago can be successfully treated at relatively low cost. On the other hand, even in developed countries with excellent healthcare facilities, the fight against bacterial infections is a continuous endeavor. Resistance against many common antibiotics develops rapidly as evidenced by the upsurge of multi-resistant bacteria (MRSA) in the last two decades. Therefore, there is an urgent need for new classes of antibiotics. To match this need, metal-containing compounds hold particular promise. In the Metzler-Nolte group, we have successfully modified the activity of anti-microbial peptides (AMPs) by substitution with metal complexes. Derivatization of a short hexameric AMP by metalloenes (such as ferrocene and ruthenocene carboxlic acid derivatives) yielded not only more active derivatives in general. Moreover, depending on the nature of the metalloocene and its position within the peptide sequence, we could optimize the activity of such conjugates to otherwise resistant strains and achieve good activity even against MRSA (Fig. 2).

In collaboration with microbiologists, the mechanism of action of our new metal-containing AMPs was elucidated, and the metalloocene-peptide lead structure was thoroughly optimized by chemical modifications. In a different project, we have synthesized new metal complexes with a Re(CO)₃ fragment as promising anti-microbial agents. Again, membrane interaction was demonstrated to be crucial for the mode of action.

Tools for Molecular Biotechnology

In addition to their medicinal activity, many metal complexes also provide unique spectroscopic properties and reactivity, which can be applied to study biological problems or manipulate biological molecules such as DNA, RNA or proteins. The Metzler-Nolte group has developed Re(I) complexes as promising probes for cellular imaging (Fig. 3).
These complexes can be attached to peptides for the imaging of intracellular organelles such as mitochondria and the endoplasmic reticulum. We are also using metal conjugates with analogues of nucleic acids (so-called peptide nucleic acids or PNA) as artificial nucleases for the sequence-specific cleavage of RNA and DNA. In collaboration with researchers in Canada and at RUB, we have also used such PNA conjugates with redox-active metal complexes as sequence-specific electrochemical DNA sensors. Complementary DNA sequences could be detected with high sensitivity and excellent mismatch discrimination.

Metalloenzyme mimics: Bioinspired CO₂ activation and hydrogen generation

The research work of Dr. Apfel’s group (Emmy-Noether Fellow) is focused on the multi-electron reduction of CO₂ and protons, and developing functional model compounds for these metalloenzymes. Although easily performed in nature, the selective and reversible reduction of CO₂ to CO under mild conditions is a fundamental challenge for chemists. In a novel bioinspired approach, the group aims at the synthesis of heterobimetallic, low-valent and low-coordinate Fe/Ni-complexes which are supported by tripodal ligands that will enable a selective, direct electrochemical 2-electron reduction of CO₂ to exclusively afford CO (Fig. 4). The direct multi-electron reduction allows for lowering of the overpotential and an increase of rate constants for this important process. As a principal method to investigate the bonding properties of CO₂, the communication between the metals as well as the catalytic potential of the complexes, spectro-electrochemical methods, Mößbauer as well as EPR spectroscopy are applied.

Fig. 4: Schematic representation of bimetallic Ni-Mo/Fe complexes for selective CO₂ binding and reduction to CO.

Hydrogen is a promising candidate for energy storage and transportation. An inexpensive and robust catalyst is required that makes the transformation of water into hydrogen possible. Nature uses a powerful enzymatic system to transform protons into hydrogen – the hydrogenases. In collaboration with groups at RUB and abroad, both the Apfel and Metzler-Nolte groups are exploring ways to manipulate the enzymatic performance of [FeFe] hydrogenases by implementing artificial, tailored mimics into the natural enzymatic environment, and by devising completely new enzyme mimics.

Selected Publications

Nils Metzler-Nolte is full professor of Inorganic Chemistry at RUB since 2006. He studied chemistry at the Universities of Hamburg, Freiburg, and Munich. After a PhD in main group chemistry in 1994 and a postdoc period with Prof. M. L. H. Green in Oxford he started his independent research on Bioorganometallic Chemistry at the Max-Planck-Institut für Strahlenchemie (today: MPI for Chemical Energy Conversion) in Mülheim in 1996. He was appointed professor for Pharmaceutical and Bioinorganic Chemistry at the University of Heidelberg in 2000, and full professor of Inorganic Chemistry at the Ruhr-University Bochum in 2006. He has served as Dean of the University-wide graduate school from 2009 – 2012 and was Vice President for Early Career Researchers and International Affairs of the University. Prof. Metzler-Nolte was Speaker of the DFG-funded Research Unit “Biological Function of Organometallic Compounds” and is currently Council Member of the Society of Biological Inorganic Chemistry. He serves on the international advisory boards of several journals and is Associate Editor for Dalton Transactions. He is Chair-Elect for the Gordon Conference on Metals in Medicine in 2016.

Ulf-Peter Apfel received his Diploma (2007) and PhD (2010) from the Friedrich-Schiller-Universität Jena with W. Weigand as a fellow of the Studienstiftung des deutschen Volkes. Subsequently, he spent 2 years at the Massachusetts Institute of Technology as a Feodor-Lynen-fellow with S. J. Lippard. In 2013 he started his independent career as a group leader at the Ruhr-University Bochum, supported by the Fonds der Chemischen Industrie (Liebig fellowship). Since 2014 he is supported by the DFG with an Emmy-Noether grant by the German Science Foundation (DFG).
Synergy between synthesis, computational chemistry and materials development

Prof. Dr. Roland A. Fischer, Jun. Prof. Dr. Radim Beranek, Prof. Dr. Anjana Devi, PD Dr. Rochus Schmid

The main domain of research is on molecular chemistry with a perspective of developing new materials with different functionalities for a wide range of applications which includes homogeneous and heterogeneous catalysis, photocatalysis, micro and optoelectronics, sensing etc. The research activities at the Chair of Inorganic Chemistry II are rather diverse and segmented into four areas namely, organometallic chemistry, coordination chemistry and metal-organic frameworks (MOFs), nanomaterials in bulk, thin films and nanostructures including photoactive materials and in computational materials chemistry. The main objective is to understand how the structure, composition, reactivity of materials are related to chemical and physical functionality.

Research Group Organometallics:
Head: Prof. Dr. Roland A. Fischer and Akad. Rat Dr. Christian Gemel

The field of nanotechnology experienced an immense progress within the past two decades. Amongst various kinds of nanomaterials, especially intermetallic clusters and nanoparticles have been in the focus of research, for example to study the transitional region between molecular compounds and the solid state. However, compositional control of bimetallic clusters turns out to be challenging, especially when the two metals are of a very different nature. The “Organometallics subgroup” focuses on the investigation of transition metal main group metal (nano)clusters A\(_a\)B\(_b\), of a defined composition \((a/b)\). Their compositions and structures mimic situations known from classic intermetallic solid state compounds such as Hume-Rothery and Laves Phases. The current research is focused on this exact spot, the synthesis of ligand-protected molecular intermetallic clusters left of the Zintl-border with B representing group 12 or 13 metals (i.e. B = Zn, Cd; Al, Ga, In). Since as early as 1990, we have been working on the development of a tool-box for the reliable, wet-chemical synthesis of such compounds based on the coordination chemistry of low-coordinated organo main group species R-B towards transition metal centers \(A\) (R = CH\(_3\), bulky aryl, alkyl and in particular Cp\(^*\) = pentamethylcyclopenta-diienyl).\([1]\) Recently we moved to study the surface reactivity of such Hume Rothery inspired molecular clusters with respect to applications in nanocatalysis (e.g. selective multiple bond hydrogenation (Figure 1) and transferred our chemistry towards multiply heterometal atom doped gold clusters.\([2,3]\) This work is currently funded with the Priority Program 1708 of the German Research Foundation, “Materials Synthesis near Room Temperature”.

![Synthesis and reactivity of \([\text{Cp}^*\text{AlCu}]_6\text{H}_4\) (Cu: orange; Al: pale blue; C: grey, N: deep blue).\([2]\)](image)

**Selected Publications**


Research Group Metalorganic Frameworks:
Head: Prof. Dr. Roland A. Fischer

Metal-organic frameworks, MOFs, are a fascinating and novel class of porous materials with giant specific surface areas and pore volumes, which are formed by linking metal ion containing nodes with organic linkers to three dimensional networks. MOFs feature zeolite-like architectures, are crystalline but in contrast to zeolites are structurally responsive and uniquely tuneable with respect to the chemistry of the internal coordination space for host/guest interactions. MOFs are interesting for various applications ranging from gas storage and catalysis to sensing and microelectronics. We have been contributing to MOF materials research since 2005 in the areas of catalysis (“metals@MOFs”),\([1]\) MOF thin films for integration in devices,\([2]\) flexible MOFs and functionalized MOFs for selective gas adsorption and separation.\([3]\) Recently, it was realized that the presence of various
structural defects (vacancies, dislocations, etc.) within MOFs affects their chemical and physical properties quite drastically. The targeted implementation of specific defects by synthetic means as well as the understanding of the defect structure over various length scales has become a new and important topic. A Horizon 2020 Research Grant has been recently awarded by the European Commission to highlight the collaborative investigations on Defect Network Materials (www.defnet-etn.eu).

**Selected Publications**


**Research Group**

**Inorganic Materials Chemistry**

Head: Prof. Dr. Anjana Devi

The downscaling of device dimensions and the constraints posed on materials selection and properties for technological applications especially in the area of microelectronics and optoelectronics, motivates materials chemists to look out for new materials with enhanced functionalities. The research activities of the Inorganic Materials Chemistry group, encompasses the field of fabrication of nanostructured materials using vapor and solution based processes. This includes metalorganic chemical vapor deposition (MOCVD), atomic layer deposition (ALD) and chemical solution deposition (CSD) of various functional materials such as metals, metal oxides and metal nitrides. These processes are compatible with other device fabrication processes and especially for high throughput coatings on complex device geometries. In all these processes, the precursor plays a pivotal role. The Inorganic Materials Chemistry (IMC) research group specializes in the development of novel precursor chemistries and their evaluation for the fabrication of nanostructured functional materials. The principle concept of research is to transform molecules (precursors) to materials and investigate the influence of precursor chemistry on the material characteristics. The application of the functional materials is directed in the field of microelectronics, optoelectronics, photovoltaics, sensors, catalysis, spintronics etc. While group IV metal oxides namely, ZrO₂ and HfO₂ exhibit a wide range of functional properties which make them very promising for technological applications ranging from high dielectric constant (k) material in complementary metal oxide semiconductor (CMOS) technology to optical fibers, sensors, thermal barrier coatings waveguides etc., TiO₂ is an interesting class of material, very well investigated for several applications that include UV protection, photocatalysis, pigments, dye-sensitized solar cells etc. Rare earth (RE) oxides (e.g. Y₂O₃, Sc₂O₃, Gd₂O₃, Dy₂O₃, Er₂O₃) are very appealing for use in microelectronics, optoelectronics, magnetic devices etc. and rare earth nitrides (GdN, DyN, ErN) are being projected to be highly promising for spintronic based devices. Recently, the research focus of IMC has been directed into the field of transparent conducting oxides (TCOs) that include ZnO, In₂O₃ and Ga₂O₃ nanostructures and barrier coatings such as TiO₂, Al₂O₃ and SiO₂ for polymer surfaces. The research project on plasma enhanced ALD of barrier coatings on polymer surfaces...
is currently funded by the German Science Foundation (DFG-SFB-TR-87).

As CVD and ALD processes are in the main stream of future technology development, one of the missions of the group is to train young researchers in this field. In this context two European level training networks under the FP7 programme of the EU were installed and coordinated at RUB (www.enhance-itn.eu and www.rapid-itn.eu), especially addressing the research themes that are of direct interest to research and development.

Selected Publications


Research Group

Photoactive Materials:

Head: Jun. Prof. Dr. Radim Beranek

The research of the Beranek group is focused on development of chemistry-based approaches to solar energy conversion, particularly the synthesis and characterization of novel hybrid and composite materials for use in photochemical systems capable of harnessing solar energy to drive useful chemical transformations (for example, hydrogen production through water splitting, degradation of harmful pollutants, or selective photooxidation reactions). In the field of solar water splitting, the group has been recently developing a novel class of photoanodes for solar water splitting utilizing visible-light photoactive inorganic/organic hybrid materials coupled to metal oxide co-catalysts for water oxidation (Figure 4a) [1]. Within the EU-funded 4G-PHOTOCAT project, novel composite photocatalysts for solar detoxification of water are being developed (Figure 4b) [2].

Selected Publications


Research Group

Computational Materials Chemistry:

Head: PD Dr. Rochus Schmid

Embedded into the experimental environment of the Chair of Inorganic Chemistry II, the CMC group is both developing and applying computational methods in close collaboration with experimental partners. The research focuses on specific problems in materials science by theoretical methods in order to shed light on atomistic details. The majority of such problems consist of large systems with many atoms, which means that often multiple length and time scales have to be covered in a theoretical simulation. As a consequence it is usually impossible to solve these problems by employing the most accurate quantum mechanical methods available in a direct and “brut-force” way. Instead, clever combinations of approximate methods with different resolution need to be combined in order to succeed. Such multiscale simulation methods need to be developed and tuned for any materials science problem, since in each case different approximations can or cannot be used.
The current main research target is the simulation of metal-organic frameworks (MOFs), in close interaction with the experimental work in the Fischer group. The novel porous materials are mostly too large for periodic DFT methods. In addition, a key property is their “softness” and flexibility, which makes parameterized molecular mechanics models the method of choice for configurational sampling. However, for the coordination compound type nodes, accurate parameter sets are not available. Over the years the CMC group has developed a systematic parameterization method to close this gap. By evolutionary strategies, force field parameters are derived from first principles reference data (Figure 5a). The resulting MOF-FF represents the first consistent and accurate force field for this class of materials [1]. These force fields have been used to predict the diffusion of guest molecules through the pores [2], or the curious shrinking of the materials with increasing temperature [3]. Again, with a genetic algorithm global search strategy the Reversed Topological Approach (RTA) was developed to predict even experimentally unknown MOF structures [4]. Recently, defects within MOFs with a potential use in catalysis have been investigated by QM/MM methods.

Selected Publications


Fig. 5: (a) Derivation of force field parameters from non-periodic model systems on the example of MOF-5. (b) Computed acetate terminated [111] surface of HKUST-1.
Roland A. Fischer studied chemistry at Technische Universität München (TUM) and received his Dr. rer. nat. in 1989 under the guidance of Wolfgang A. Herrmann. After a postdoctoral collaboration with Herb D. Kaesz at the University of California, Los Angeles (UCLA), he returned to TUM in 1990, where he obtained his Habilitation in 1995. In 1996 he was appointed Associate Professor at Ruprecht-Karls Universität Heidelberg. In 1998 he moved to Ruhr-Universität Bochum where he took the Chair of Inorganic Chemistry II. He has been Vice Rector of RUB for teaching affairs (2000-2002), Dean of the Faculty of Chemistry and Biochemistry (2005-2007) and Speaker of the Ruhr University Research School (2006-2009). Currently he is member of the Editorial Board of Angewandte Chemie and member of the DFG Senate commission of Collaborative Research Centers.

Christian Gemel studied chemistry at the Institute of Inorganic Chemistry, Vienna University of Technology (Austria). He obtained his PhD in 1997 under the supervision of Prof. Karl Kirchner in the field of stoichiometric and catalytic organometallic chemistry of Ruthenium. After two postdoctoral research stays with Prof. Ken Caulton (Indiana University, Bloomington) and Prof. Richard Poerschke (MPI Mülheim), he joined the research group of Prof. Roland Fischer at Ruhr University Bochum in 2001 and was soon after appointed as Akademische Rat at the Chair of Inorganic Chemistry II.

Anjana Devi obtained B.Sc. and M.Sc. from Mangalore University followed by PhD from the Indian Institute of Science (IISc), Bangalore (India). In 1998, she moved to Germany for post doctoral research with a fellowship awarded by the Alexander von Humboldt foundation (AvH) (1998). Her post doctoral research focused on metalorganic chemical vapor deposition of group III nitrides which was carried out in the research group of Prof. Roland Fischer at the Ruhr University Bochum (Germany). In 2002 she was appointed as a Junior Professor and in 2011 as a professor at the Ruhr University Bochum and is currently heading the Inorganic Materials Chemistry Research Group in the Faculty of Chemistry and Biochemistry.

Radim Beránek studied chemistry at the Institute of Chemical Technology in Prague (Czech Republic), and obtained his PhD in inorganic chemistry from the University of Erlangen-Nürnberg (Germany), working under the supervision of Prof. Horst Kisch. In 2010 he joined the Faculty of Chemistry and Biochemistry at the Ruhr University Bochum (Germany) as a Junior Professor and head of the Photoactive Materials Group. He received the 2008 Research Award for Young European Scientists of The European Society for Quantum Solar Energy Conversion and has been a member of the Global Young Faculty of the Mercator Foundation (2011-2013). Currently he is the coordinator of the collaborative EU-FP7 project “4G-PHOTOCAT” (309636).

Dr. Rochus Schmid studied chemistry at the Technical University Munich (TUM) and received his PhD in the group of Wolfgang A. Herrmann in 1997. After a postdoctoral stay with Prof. Tom Ziegler at the University of Calgary (Canada) he returned to the TUM in 1999. In 2003 he joined the group of Prof. Roland A. Fischer at the Ruhr-University Bochum, where he finished his Habilitation in 2009 on the topic “Atomistic Models in Materials Chemistry”. He is leading the Computational Materials Chemistry research group at the Chair of Inorganic Chemistry II, and is focusing on multiscale simulation methods using first principles parameterized force fields for porous coordination polymers and other hybrid materials.
Wir sparen lieber am Konservierungsmittel. Nicht an der Wirkung.«

WHAT IS PRECIOUS TO YOU?


what is precious to you?
Ionotropic Glutamate Receptors: Structure, Function, Regulation and Modulation

Prof. Dr. Michael Hollmann | Department of Biochemistry I - Receptor Biochemistry

Structure, function, regulation, and modulation of ionotropic glutamate receptors is investigated by molecular biological, electrophysiological, proteinbiochemical and immunocytochemical methods. We analyze structural and functional properties of members of the extended protein family of ionotropic glutamate receptors as well as their many interacting proteins in heterologous expression systems such as Xenopus laevis oocytes and HEK293 cells. In our studies we include vertebrate (23 known genes) as well as invertebrate glutamate receptors such as those of Caenorhabditis elegans (15 genes) and lately also plant glutamate receptor homologs like those 20 genes found in Arabidopsis thaliana.

After cloning the first glutamate receptor in 1989 [1], discovering the calcium permeability of certain heteromeric glutamate receptor subunit combinations [2] and clarifying the correct transmembrane topology of glutamate receptor subunits [3], the group of Michael Hollmann currently focuses on the little-known delta-type glutamate receptors of mammals, the pressure-sensitivity of NMDA receptors, plant glutamate receptor homologs, the modulation of ionotropic glutamate receptor function by auxiliary proteins, and the analysis of autoantibodies to glutamate receptors in humans.

Functional analysis of delta-type glutamate receptors

Delta-type glutamate receptors form a separate subfamily of glutamate receptors that comprises two subunits, GluD1 and GluD2, that have not been shown to bind glutamate, and for which the activating agonist remains unknown. Their membership in the glutamate receptor family is purely based on sequence homology considerations, and many groups favor the theory that these receptors are not meant to work as ion channels. We managed to demonstrate via ligand binding domain transplanation between delta receptors and kainate receptors that delta receptors indeed have a functional ion channel domain [4,5]. For reasons still unknown and currently investigated, however, this channel domain does not receive activating signals from the receptor’s ligand binding site.

Plant glutamate receptor homologs as biosensors for certain amino acids

The sequencing of the Arabidopsis thaliana genome, finished by the year 2000, revealed the presence of an astonishing 20 genes that looked like mammalian glutamate receptors in terms of their primary sequence as well as their predicted transmembrane topology. However, expression of these proteins, termed GLRs (glutamate-like receptors), in heterologous systems did not reveal functional ion channels activatable by any glutamatergic agonist. By transplanting the ion pores of GLRs in mammalian glutamate receptors we could show that those Arabidopsis GLR ion channels indeed are functional domains [6]. We then proceeded to analyze full-length GLRs in the Xenopus oocyte expression system and were able to demonstrate that at least one of the twenty genes, AtGLR1.4, is a receptor activated by hydrophobic amino acids such as methionine, tryptophane, tyrosine, phenylalanine, and leucine [7]. When the AtGLR1.4 gene is knocked out, seedlings of Arabidopsis do not respond to methionine any longer.

We currently analyze additional AtGLR subunits to see if they also can also act as biosensors for certain amino acids.

Fig. 1: Glutamate does not bind to the GluD2 receptor’s own (red) ligand domain and thus does not open the ion channel. If the GluD2 ligand binding domain is replaced by the (blue) kainate receptor ligand binding domain, the GluD2 receptor’s ion pore opens and allows current.

Fig. 2: The Arabidopsis thaliana glutamate-like receptor subunit AtGLR1.4 responds to hydrophobic amino acids and threonine when expressed in oocytes. Upon knock-out of the plasmamembrane-expressed AtGLR1.4, plants become unresponsive to methionine.
Glutamate receptors are trafficked and functionally modulated by auxiliary proteins

TARPs (transmembrane AMPA receptor regulatory proteins) were discovered about 10 years ago through a coincidental observation in a mutant mouse strain. This observation revealed the protein stargazin, the first member of a family of eventually six proteins later named TARPs, to be an essential protein that facilitates the trafficking of the AMPA receptor subtype of glutamate receptors to the plasma membrane in cerebellar granule cells. Interestingly, stargazin also modulates the biophysical functions of these receptors. We investigated the family of TARPs and could show that each TAR has its own profile of functional modulation and its own set of AMPA receptor subunits and variants that it modulates[6]. We later showed that TARP transfection into cortical organotypic slices via a gene gun leads to an upregulation of transfection into cortical organotypic slices that even normal people have an astonishing high probability to carry autoantibodies against glutamate receptors of neurological disorder. Further analysis will have to show how widespread these autoantibodies are, and why they are being produced.

Selected Publications


Michael Hollmann has been a Full Professor of Biochemistry at the Ruhr University Bochum since 1999. He studied biochemistry in Tübingen and received his PhD from the University of Tübingen for a project carried out at the Max Planck Institute of Biophysical Chemistry in Göttingen, under the supervision of Wilfried Seifert (1988). He spent six years (1988-1994) as a Postdoctoral Research Associate with the late Stephen F. Heinemann at the Salk Institute for Biological Studies in La Jolla, California, USA. He returned to Germany on a Heisenberg Fellowship and set up his independent research group at the Max Planck Institute for Experimental Medicine in Göttingen, where he received his Habilitation in Biochemistry from the Medical Faculty of the University of Göttingen in 1998. For more details see www.ruhr-uni-bochum.de/bc1.
Molecular Neurobiochemistry: Towards protection and regeneration of brain neurons

Prof. Dr. Rolf Heumann (Department of Biochemistry II – Senior research group Molecular Neurobiochemistry, Faculty of Chemistry and Biochemistry)

The Heumann group investigates and exploits the intracellular signaling mechanisms of extracellular ligands to regulate survival, neurotransmitter synthesis and connectivity in brain neurons. The group established that the universal intracellular signaling protein Ras GTPase regulates fibre growth and synaptic activity in response to environmental sensory stimuli through transient activation of downstream protein phosphorylation cascades. The group investigates if neuronal cell death and axonal degeneration can be counteracted by Ras activity in neurodegenerative diseases such as Parkinson’s disease. Dopaminergic neurons derived from neural stem cells are protected from toxic treatment by Ras activation, while formation of synaptic contacts and normal functions of sodium and potassium channels involved in action potentials are preserved as shown in collaboration with the Dietzel group.

A 2nd messenger is required for the biological activity of nerve growth factor.

Extracellular ligands such as steroid hormones regulate cellular protein expression by penetrating the cell membrane to bind to cytoplasmic or nuclear receptors that then modify promoter transcription activity of the nuclear DNA. Alternatively, ligands bind to their cognate cell surface receptors thereby inducing transmembrane signaling cascades either directly across the membrane at the inner cytosolic face of the plasma membrane or after receptor mediated endocytosis. We demonstrated that a protein regulating neuronal survival and fiber outgrowth, named nerve growth factor, is taken up into the cell, yet induces its neurotrophic effects by triggering an intracellular transmembrane receptor mediated mechanism.

Actication of Ras prevents neuronal cell death induced by deprivation of neurotrophic factors.

Neurotrophic factors interact with their cognate Trk receptors to regulate the number of neurons and their fiber growth during ontogenetic development by limiting neurotrophic supply from target tissue that has to be innervated. By introduction of permanently activated Ras protein into the cytoplasm of deprived neurons we could demonstrate that Ras protein mimics the intracellular signaling mechanism of neurotrophins promoting neuronal survival and fiber outgrowth. Conversely, intracellular inhibition of Ras activity by function blocking Fab-fragments prevented neurotrophic factor induced effects. Thus, the aforementioned 2nd messenger mechanism of neurotrophic factors was identified.

Ras homolog enriched in brain (Rheb).

Rheb is a homolog of Ras GTPase that regulates cell growth, proliferation, and regeneration via mammalian target of rapamycin (mTOR). Because of the well established potential of activated Ras to promote survival, the ability of Rheb signaling to phenocopy Ras was investigated. Unexpectedly, Rheb-mTOR activation not only promoted normal cell growth but also enhanced apoptosis in response to diverse toxic stimuli via an apoptosis signalling regulated kinase mediated mechanism. Pharmacological regulation of the Rheb/mTORC1 pathway using rapamycin should take the presence of cellular stress into consideration, as this may have clinical implications.

Poinflammatory cytokines enhance regeneration of sensory axons.

Interleukin-6 is a multifunctional cytokine mediating inflammatory reactions, immune response and pain. By applying electrophysiological, morphological, biochemical and behavioral methods in mice lacking the gene coding for interleukin-6 we showed that this cytokine is essential to enhance sensory functions in regenerating axons after peripheral nerve lesion.

Neuroprotection in the synRas mouse model.

In order to investigate the in vivo function of neuronal Ras activity we have generated a transgenic mouse model expressing permanently activated Val12 Ras, selectively in neurons. Using this model named synRas mice (Figure 1) we showed that neuronal Ras activity is involved in the dynamics of dendritic spine formation of brain neurons, in the regulation of synapse number and their efficiency and in the suppression of adult neurogenesis in the hippocampus. This Ras-induced modulation of adult neurogenesis was associated with changes in short term memory processes. Furthermore, activation of Ras could prevent mechanical lesion-induced degeneration of motor neurons. Dopaminergic neurons with enhanced Ras activity were generated from synRas-derived stem cells. Phosphatidylinositol kinase was involved in the molecular mechanism of signaling for Ras-mediated protection against neurotoxin-induced neuronal degeneration. Yet, in these Ras-activated dopaminergic neurons formation of synaptic contacts and normal functions of sodium and potassium channels involved in action potentials were preserved. These results suggest that Ras activity could be a target for pharmacological stabilization of neurons in neurodegenerative diseases such as Parkinson’s disease.

Fig. 1: In the synRas mouse model expression of a Ras gene with point mutation from glycine to valine in amino acid 12 permanently enhances Ras activity in brain neurons.
Selected Publications


Fig. 2: The Heumann and Dietzel groups in December 2013.

Rolf Heumann is an expert in molecular neuroscience and biochemistry. He studied Microbiology (1975) and performed his PhD thesis at the Max-Planck-Institute for Biochemistry, Martinsried, Germany, under the guidance of Bernd Hamprecht (1978). In 1979 he switched to the Institute for Psychiatry at the Max-Planck-Institute in Martinsried. There he established and supervised a project group named “Dynamics and Stabilisation of Neural Structures”. In 1988, he finished his Habilitation. From 1991 to 2012 he was the head of the Department of Molecular Neurobiochemistry as a full professor of Biochemistry at the Ruhr-University Bochum (RUB). From 2006 to 2015 he was the director of RUBION which is a service unit of RUB offering scientific, technical and administrative service for ionbeams and radionuclides. Currently, he continues his research as a senior professor of his molecular neurobiochemistry group at the RUB.

NAP-XPS Solutions

NEAR AMBIENT PRESSURE
IN SITU SURFACE ANALYSIS SYSTEMS

SPECS Surface Nano Analysis GmbH
T +49 30 46 78 24-0
E info@specs.com
W www.specs.com

KEY FEATURES
- In Situ Analysis up to 100 mbar
- Backfilling or Reaction Cell
- PHOIBOS 150 NAP Analyser
- NAP Laboratory X-ray and UV Sources
- Windowless Synchrotron Beam Entrance Stage
The Dietzel group studies the molecular regulation of the expression of voltage-gated ion currents underlying neuronal excitability, the molecular mechanisms leading to cytokine-induced damage of immature oligodendrocytes and is involved in the development of Scanning Ion Conductance Microscopy.

Voltage-gated ion currents underlying neuronal excitability

Informations are processed in biological systems by transient stimulus-induced reversals of the potential difference across cell membranes, called action potentials. The propagation speed of these action potentials depends on the current density carried through voltage-gated Na⁺ channels in the membranes, which in turn depends on the open probability, single channel conductance and membrane density of opened Na⁺ channels. Our experiments showed, that exposure to the thyroid hormone triiodo-L-thyronin (T3) for several days increases the Na⁺ current density in hippocampal and cortical neurons from postnatal rats. Further investigations provided evidence, that this is not a direct effect, but requires the secretion of soluble factors from neuronal satellite cells and that this effect can be blocked by neutralizing antibodies against fibroblast growth factor-2 (Figure 3). Apart from providing an explanation for changes in mental speed observed during dysfunctions of the thyroid gland our results suggest that the surrounding satellite cells can modulate neuronal excitability by secreting proteins that influence the number of available Na⁺ channels in the membranes [1].

Scanning Ion Conductance Microscopy

Scanning ion conductance microscopy (SiCM) is a scanning probe technique especially suited for long-term monitoring of topographical changes of delicate surfaces of the membranes of living cells. Topographical representations are generated by mapping surfaces of equal resistance changes sensed by an electrolyte filled glass pipette approaching an insulating surface. By introducing a back-step recording mode we have refined this method to reproducibly monitor the entire soma contours of living cells with up to 50 repeated scans at a lateral resolution of 1μm steps and quantify cell volumes with errors of less than 10% [2]. Using this method we demonstrated that during saltatory migration of oligodendrocyte precursor cells frontal volume...
changes precede accelerated migration[3]. Our observations confirm the hypothesis that water fluxes through the somata are involved in generating the directed forces driving the propulsion of the cell nucleus.

Selected Publications


Irmgard D. Dietzel studied physics at the RWTH Aachen and developed her interest in synchronization of nerve cells during her Diploma thesis at the Institute of Physical Chemistry under the guidance of U. F. Franck. To investigate the role of extracellular potassium in inducing epileptiform neuronal hyperactivity she joined the department of Neurophysiology at the Max-Planck-Institute for Psychiatry in Munich, then headed by H.D. Lux in 1978. Together with U. Heinemann she discovered shrinkages of the extracellular space during epilepsy-like neuronal hyperactivity due to electrolyte and water-flux induced volume changes of glial cells[4]. Following postdoctoral work on the presynaptic regulation of transmitter release in the laboratory of J. G. Nicholls[5] (at Stanford University and the Biocenter in Basel, funded by the award of an Otto Hahn Medal of the Max-Planck Society), she returned to the group of H.D. Lux at the MPI for Psychiatry to investigate the ontogenetic development of voltage-activated ion currents. After obtaining her “Habilitation” for Physiology at the LMU Munich at 1992 she joined the Department of Molecular Neurobiochemistry at the Ruhr-University.
Biomolecular Spectroscopy: NMR to study the structure and function of medically-relevant proteins

Prof. Dr. Raphael Stoll | Faculty of Chemistry and Biochemistry, Ruhr University of Bochum, Germany

Our research focuses in the main on medically-relevant proteins, specifically those involved in the development of cancerous tumours, in order to better understand the causes of the condition and propose more effective treatment strategies. Examples include oncogenic proteins, tumour suppressors as well as proteins involved in malignant melanoma, to name but a few. Other current areas of investigation also cover the structure, function, dynamics and interaction of proteins associated with the transduction of physiological signals.

Biochemistry seeks to understand life at a molecular level by examining the relationship between the structure and function of biomolecules, such as nucleic acids and lipids. To achieve this, we use a variety of techniques, particularly biomolecular NMR spectroscopy, in order to determine the three-dimensional structures and dynamics of biomolecules as well as how they interact with each other and other molecules in solution at near-physiological conditions. Cancer cells are hallmarked by the ability to divide unrestrictedly, posing an often lethal threat to an organism. Thus, the development of selective small antagonistic ligands that are vital for growth processes in cells. The substance, short BPA, is contained in many plastic products and is suspected of being hazardous to health. To date, it had been assumed that bisphenol A produces a harmful effect by binding to hormone receptors. But recently, we have discovered that the substance also affects the so-called small GTPases (Fig. 1).[3].

**Fig. 1: Bisphenol A binds to the switch protein K-Ras, which is vital for cell growth processes and plays a role in tumourigenesis. A HADDOCK model of K-Ras/GDP in complex with bisphenol A is shown.**

Small GTPases are enzymes that occur in two states within the cell: in the active form when bound to the GTP molecule; and in the inactive form when bound to GDP, a lower-energy form of GTP. These switch proteins are crucial for transmitting signals within the cell. We could demonstrate that bisphenol A binds to two different small GTPases, K-Ras and H-Ras, thereby preventing the exchange of GDP for GTP (Fig. 2).

Various organisations have pointed out that bisphenol A may be hazardous to health: the Federal Institute for Risk Assessment (Bundesinstitut für Risikoforschung), the European Food Safety Authority, the US Food and Drug Administration (FDA), the US National Institutes of Health (NIH) and the US-American Breast Cancer Foundation. However, those organisations have not yet provided a final assessment of the substance’s hazardous potential. Nevertheless, the European Commission banned the use of bisphenol A in the manufacture of baby bottles in 2011. Academic studies indicate that the substance may increase the risk of cardiovascular diseases, breast and prostate cancer as well as neuronal diseases. The non-profit organisation German Cancer Aid (Deutsche Krebshilfe e. V.) has funded this project.

**Selectively modifying hormones through metal complexation and using them as medicinal substances**

Together with Prof. Metzler-Nolte and his co-workers from our faculty at the Ruhr University of Bochum as well as Berkeley we have used metal complexes to modify peptide hormones and could determine the three-dimensional structure of the resulting metal-peptide compounds for the first time (Fig. 3). These hormones – enkephalin and somatostatin – influence the sensation of pain and tumour growth. In this collaborative study we have analysed the peptide hormone encephalin, which is important for the sensation of pain, and octreotide [6]. The latter is a synthetic derivative of the growth hormone somatostatin, approved as a medicinal substance and already used in the treatment of certain tumours.
Fig. 3: Using NMR spectroscopy, we have determined the three-dimensional structure of the metal-peptide complexes. The metal atom, rhodium (shown in magenta), binds to the peptide’s amino acid tyrosine, more specifically to the phenol group (carbon atoms are shown in green, nitrogen atoms in blue, and oxygen atoms in red, whereas hydrogen atoms have been omitted for clarity). The second circular carbon structure that is also shown in green above the rhodium atom represents a 1,2,3,4,5-Pentamethylcyclopentadienyl group (Cp*). Through metal coordination, rhodium is bound between the two carbon rings. The gray net symbolizes the surface of the molecule.

Peptide hormones consist of amino acids and they convey bodily sensations such as pain and hunger, but they also transmit growth signals. One example of this is insulin, which is important for the control of blood sugar levels. Upon interaction with specific receptors, the G-protein-coupled receptors, peptide hormones transport messages to cells. The hormones can be specifically chemically modified so that their effect changes, for example pain tolerance is lowered, or tumour growth inhibited. Interestingly, the reaction with the metal complex was highly selective. Although the hormones consist of hundreds of atoms, the rhodium compound was always found to be coordinated by the aromatic carbon ring system of the tyrosine – the phenol moiety.

The future goal is to develop other metal-containing, peptide-like substances based on the basic studies on these basic studies as these could modulate the effect of naturally occurring peptide hormones and, for example, be used as a novel remedy for pain or cancer. The German Research Foundation (SFB 642 and Research Unit 630) and the Research Department for Interfacial Systems Chemistry at RUB supported the work.

Selected Publications


Raphael Stoll is Professor of Biomolecular Spectroscopy in the Faculty of Chemistry and Biochemistry at the Ruhr University of Bochum. He is also a founding member of the SFB 642 that has been established in 2004, and was a member of the EU-funded INTCHEM consortium. From 1990 until 1996, he studied Physiological Chemistry and Biochemistry at the Universities of Tübingen, Germany, and Oxford, UK, as a fellow of the „Studienstiftung“ and DAAD. Supported by a fellowship from the FCI, he carried out his doctoral research at the Max Planck Institute for Biochemistry in Munich and received his PhD from the Technical University of Munich in the year 2000. After a stay as a research associate at The Scripps Research Institute, CA, USA funded by first a DAAD- and then an Emmy-Noether fellowship, he initially joined the Ruhr-University of Bochum as Juniorprofessor in 2003. For further details please refer to the following web page: www.rub.de/bionmr

Finden Sie uns auf Facebook
www.facebook.com/opusmundi.de
Our research activities centre around the understanding of chemical procedures. There is a particular focus on model experiments and on didactic concepts for out-of-school learning environments that provide learners with opportunities to encounter chemical ways of working and thinking. Experiments allow learners to carry out chemical procedures and use scientific ways of thinking to gain insights into the science of Chemistry. School and university students as well as interested lay people are the target audiences of our research. Thus, our research contributes to the field of science communication across university, schools and the public.

Model experiments in the Chemistry classroom

This research area covers the potential of model experiments in the Chemistry classroom. It is based on a profound distinction between experiments and model experiments that allows classifying model experiments systematically and determining their degree of modelling.

Particular model experiments are being used to investigate in how far secondary school students identify the analogies between the original and the model experiment. The results will be used to provide recommendations for the development of model experiments that will support students in bridging the gap between model and original.

One example of such a model experiment is the determination of the sodium chloride fraction in shampoo. The influence of sodium chloride on the viscosity of shampoo can be used to determine the sodium chloride fraction in a shampoo (Fig. 1).

KEMIE — Kinder erleben mit ihren Eltern Chemie

Is it possible to make parents and their children feel that experiencing "scientific inquiry" together is just as usual and everyday as a visit to the football pitch? You can find a potential answer to this question disguised in five letters: K – E – M – I – E is the acronym for "Kinder Erleben Mit Ihren Eltern Chemie" (Kids experience chemistry with their parents). Children (Grades 3 to 6) and their parents (Fig. 2) can take part in this project. The project is a series of nine consecutive units with monthly topics; each unit takes three hours.

The core idea of the project is to make the participants acquainted with various aspects of scientific inquiry. These stretch from observation and measurements to controlling variables and testing hypotheses. Chemical methods are introduced through a curriculum following an upward spiral of complexity. This way, the chemical methods serve as a guiding structure. The examples are taken from everyday life, for example a self-heating can, creams and packing made from aluminium. The different units can also be used in school chemistry lessons.

After six years experience in the project, we can state: The common laboratory visit is a fix date in the families' leisure program. 70% of parent-child dyads attend seven or more of the nine units. It has been shown that parents rate the relevance of science in their everyday life higher after they attended the project. So far, the research focus has been on the outcomes of the project. A new research project investigates parent-child-communication during the project.

"How it is to be a researcher" ("Forscherwelt", Henkel)

“Forscherwelt” is an educational initiative set up by Henkel to introduce children up to the age of 10 to the fascinating world of science. In 2010 Henkel asked us to develop and implement a didactic concept for the out-of-school learning environment „Forscherwelt“. With Henkel as a research-focused company, it seemed only natural to put the research process and the research environment at the heart of the didactic concept for the "Forscherwelt". This core idea is reflected in the title of the concept: “How it is to be a researcher”[5].

The didactic concept includes the following aspects of scientific inquiry: Scientific methods and critical testing, analysis and interpretation of data, science and questioning (especially the ability to identify and formulate questions) and creativity. It is important to introduce the children to the scientific work place because children believe that scientists are people who work alone, but the world of work looks very different.
A strong focus on research processes and environments asks for authenticity. Authenticity can only be created when the complete didactic concept evolves from Henkel’s research topics. And this exactly what it does. The contents in the „Forscherwelt“ are the research topics of Henkel (adhesives, washing/cleaning and cosmetics) and also one more topic which is important for the whole economy: sustainability. It is really a didactic challenge to simplify and select the research topics of this global company in a way that will bring them to life for eight- to ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.

Currently, didactic concepts are being developed to engage students and the public with the research of the RESOLV Cluster of Excellence. One-day projects for ten-year-old children (see also: http://www.henkel-forscherwelt.de/berg-des-wissens/wereunteuerrichtsdowloads/).

Experts at Henkel play a special role in the didactic concept. They are key to conceptualizing the learning units as well as to implementing them. During the concept phase, the experts introduce their fields of research – from the composition of products across product control and quality management to packing and marketing. All the experts are prepared to give short talks to the children to offer them authentic insights into their topics (Fig. 3). This close collaboration between experts and educators in conceptualizing and delivering activities in an out-of-school learning environment marks a new route of creating learning environments.
Self-replication and self-assembly are two of the major principles without which life could not exist. The emergence of self-replicating systems on the early earth is generally believed to have taken place before the advent of instructed protein synthesis based on a complex translation machinery. Whether the origin of self-replication is identical to the origin of the hypothetical RNA world or whether it existed at an earlier stage of evolution is an open question that has stimulated chemists to search for chemical systems capable of making copies of themselves via autocatalytic reaction networks. Their investigation, utilization and integration into even more complex dynamic super systems defines the field of systems chemistry.

Self-Replicating Oligonucleotides

The first successful demonstration of non-enzymatic self-replication was achieved by chemical ligation of two triexonucleotides A and B yielding a self-complementary hexadeoxynucleotide template C. [1] Autocatalysis resulted from a pathway embedding the reaction sequence

\[ A + B + C \rightarrow ABC \rightarrow C_2 \rightarrow 2C \]

where ABC is a termolecular complex, and C₂ a template duplex held together by reversible base pairing. As the result of templating, the reactive ends of A and B in-side ABC are brought into close spatial proximity facilitating covalent ligation to yield the template duplex C₂. The latter needs to decompose to start a new autocatalytic cycle. Typically, the autocatalytic growth of template molecules is parabolic as a consequence of the interplay of autocatalysis and product inhibition (Fig. 1).

Parabolic growth was also observed in more complex systems in which autocatalytic and crosscatalytic ligation pathways compete for the formation of self-complementary and complementary template products. [2] Exponential growth was achieved by utilizing surface immobilization of templates as a means to prevent product inhibition. [3] More recently, the natural 3'-5' phosphodiester linkage was replaced by an isosteric 3'-5' disulfide linkage (Fig. 2), whose formation exhibits the fastest ligation chemistry so far developed for oligonucleotide systems. [3] Self-replication was also demonstrated for peptide nucleic acids [10] which have been discussed as potential RNA precursors.

Organic Replicator Systems

Small organic replicators facilitate the study of self-replication using simpler molecules and complexes suitable for computational studies at the DFT level. [5] Kinetic monitoring by ¹H NMR allows to observe both structural and dynamic changes which result in much deeper insight compared to methods such as HPLC monitoring. Autocatalytic growth of template molecules is typically observed both in the sigmoidal increase of NMR signal intensities and in a characteristic shifting of chemical shifts. The latter source of information is useful for the analysis of reaction systems which include equilibration steps occurring rapidly on the NMR time scale.

We developed the method of "kinetic NMR titration" to simulate and fit time series of both chemical shifts and NMR integrals for arbitrary reaction models. [7] This enabled a facile extraction of rate and equilibrium parameters at various temperatures and allowed to construct experimentally derived enthalpy and entropy profiles for a series of organic replicators which could be compared with theory.

Self-Assembling Trisoligonucleotides

Self-assembly is nature's key recipe to create structural complexity on the nano to micrometer scale. The ribosome is an example for a functional nanoarchitecture which may be viewed as a threedimensionally defined array of 51 modular proteins positioned by the rRNA scaffold. We developed biomimetic approaches towards the 3D-nanoscaffolding of modular functions based on trisoligonucleotides [4, 8], viz. synthetic 3-arm junctions in which either the 3'-ends or the 5'-ends of three oligonucleotides are connected by a suitable linker. Maximal instruction was employed as a design principle to generate noncovalent 3D-nanoobjects in which both, the topology and the geometry is defined. Examples include dodecahedral nanoscaffolds composed from 20 trisologs each bearing three individually defined sequences (Fig. 4). [8]
Fig. 4: (a) Computer model of a DNA dodecahedron self-assembled from a set of 20 trisoligonucleotides each containing three individual 15mer sequences connected at their 3’-ends by a C₃h-symmetric linker. The nanoobject contains 30 individual DNA duplexes and has a diameter of about 20 nm. (b) AFM of dodecahedra absorbed on mica reveal compressed objects with lateral sizes larger than their vertical counterparts.

It was demonstrated that the connectivity information in the nanoscaffold junctions can be copied by chemical means. Chemical copying schemes may be seen in conjunction with “surface-promoted replication and exponential amplification of DNA analogues” (SPREAD)\(^1\). Applications of such scaffolds include the positioning of modular functions such as multidentate thioether-based gold cluster labels (RUBi-Gold)\(^6\) which were tailored for monoconjugability and thermostability.

Selected major publications


\[7\] I. Stahl, G. von Kiedrowski, "Kinetic NMR titration": including chemical shift information in the kinetic analysis of supramolecular reaction systems such as organic replicators, J. Am. Chem. Soc. 128, 2006, 14014-14015.


Our group aims to utilize halogen bonding in catalysis and supramolecular chemistry. To this end, we synthesize polyfluorinated or cationic polyiodinated compounds and perform systematic studies on their interaction with organic substrates. These experimental studies are accompanied by quantum-chemical calculations and the determination of thermodynamic binding data.

Halogen-bonds are attractive non-covalent interactions between electrophilic halogen substituents and Lewis bases: R·X -- LB (X = Cl, Br, I / LB = Lewis base). They share many similarities with the well-known hydrogen-bonds, but rely on bromine or iodine instead of hydrogen substituents. Reasonably strong halogen-bonds are only obtained when the halogen is attached to a very electronegative group, e.g., a perfluorinated or cationic backbone. These interactions can be similar in strength to hydrogen-bonds, but in contrast to the latter, feature a high directionality: the R·X -- LB angle is always close to 180°. In the last 25 years, halogen-bonds have been established as reliable building blocks for the rational design of solid-state structures (“crystal engineering”). In contrast, there are only few examples of applications of halogen-bonds in solution.

Synthesis of multideterminate halogen-bond donors

The basis of our experimental work is the design, synthesis, and characterization of halogenated organic compounds. As common structural motif, all target molecules feature at least two Lewis-acidic halogen substituents directed towards the same point in space. As backbone structures, polyfluorinated aromatics or cationic heterocyclic moieties like imidazolium or pyridinium groups are used. They either feature a high directionality: the R·X -- LB angle is always close to 180°. In the last 25 years, halogen-bonds have been established as reliable building blocks for the rational design of solid-state structures (“crystal engineering”). In contrast, there are only few examples of applications of halogen-bonds in solution.

Applications in catalysis

While hydrogen-bonds have already been successfully used in organocatalysis, applications of halogen bonding in this field are extremely rare. Thus, our long-term goal is the development of halogen-bond based enantioselective organocatalysis. Because of the different electronic nature of the interaction compared to hydrogen-bonds, different substrate scopes and selectivities are to be expected in comparison to classical non-covalent organocatalysts. In our studies, benchmark reactions are monitored by spectroscopic methods, typically NMR. Determination of thermodynamic data and benchmarking

The binding strength of halogen-bond based adducts in solution are determined by NMR titrations or calorimetric measurements. For the latter, we employ isothermal titration calorimetry (ITC). These thermodynamic measurements form the basis for a rational optimization of our halogen-bond donors. All our experimental projects are usually also accompanied by quantum chemical calculations. Semi-empirical methods are used to quickly identify suitable catalyst candidates, while DFT calculations serve to determine the binding strength of non-covalent adducts and to model the mode of action of catalysts on the transition state of benchmark reactions.

While this first application was based on the stoichiometric use of the halogen-based Lewis acid, subsequently we have also successfully employed these kinds of activators in catalytic amounts. One such example is depicted in Scheme 2, which also features a neutral polyfluorinated halogen-bond donor (3) instead of the cationic one of Scheme 1.

Recently we could also apply this organocatalytic principle towards the activation of typical organic substrates like carbonyl groups.

Fig. 1: Activation of benzhydryl bromide 2 by halogen-bond donor 1 as a benchmark case for the acceleration of organic transformations by halogen bonding.

Fig. 2: Catalytic use of halogen-bond donor 3 in a test reaction.
Applications in supramolecular chemistry

In parallel, we also utilize halogen-bond based multipoint interactions for the design of supramolecular donor-acceptor pairs. While the initial characterization of these species is usually performed in the solid state (X-ray analysis), we ultimately strive to study and apply these interactions in solution.

Selected Publications


Stefan M. Huber has been associate professor of organic chemistry at the Ruhr University Bochum since 2014. He studied chemistry at the Friedrich-Alexander University Erlangen-Nuremberg and obtained his Ph.D. in organic chemistry with Robert Weiss in 2007. Subsequently, he worked as a postdoctoral fellow with Christopher J. Cramer at the University of Minnesota (2007) and with Laura Gagliardi at the University of Geneva (2008). After a further short postdoctoral stay with Harald Gröger in Erlangen, he started his independent career in 2009 at the Technical University of Munich. For more details, see: www.rub.de/oc1/huber (Picture: A. Heddergott).
The Schulz group pursues different projects to break up important limitations in current natural product research. Both the limited availability and derivatization of different compounds are addressed, rendering new compounds with diverse biological activities available.

**Microbial Synthesis**

Polyketides form a large family of natural products and many polyketides are applied for the treatment of diseases such as cancer or infections. However, the large and polyfunctional structures of many polyketides complicate the derivatization that is required to develop them into clinically useful compounds. Biosynthetic pathways show an enormous capability of generating molecular complexity. Genetic engineering of polyketide-producing bacteria is thus used to direct the biosynthetic derivatization of polyketides, yielding compounds with altered biological activities.

The introduction of synthetic compounds into biosynthetic pathways combines the strength of both regimes. In precursor-directed mutasynthesis, synthetic compounds are accepted by wild-type enzymes from a native producer organism and can carry artificial functional groups into the corresponding compound.

Limitations of biosynthesis are thus broken up by enzyme engineering. A logical extension of this is the partial synthesis of further derivatives. These synthetic efforts start from compounds obtained through engineered biosynthesis and as well directly from interesting natural products for projects within medicinal chemistry to identify new molecules with interesting antibacterial or anti-tumor activities.

**Artificial Functionalization of Natural Products**

Biosynthetic pathways bring about structural complexity but are inflexible in comparison to synthetic organic chemistry. In many cases, enzymes from the biosynthetic reaction cascade do not accept a synthetic building block as substrate and the intended modified biosynthesis fails. We recently introduced the enzyme-directed mutasynthesis as a concept to engineer the substrate specificity of key enzymes from polyketide biosynthesis facilitate the acceptance of malonic acid-based building blocks into a natural product. In a first study, organic synthesis, enzyme engineering and fermentation technology are combined towards the derivatization of the antibiotic erythromycin A.
In enzyme-directed mutasynthesis, engineered enzymes are utilized inside a microbial producer to accept synthetic building blocks as substrates for the targeted derivatization of a natural product, in this case the antibiotic erythromycin A.\(^3\)

**Heterologous Fermentation of Terpenes**

In many cases, natural sources do not provide enough material to investigate the promising biological activity of natural products. This is particularly true for members of the terpenoids family of natural products. We express key enzymes towards terpenes in baker’s yeast to synthesize preparative amounts of the corresponding compounds in synthetically meaningful quantities.

---

**Selected Publications**


---

Frank Schulz was appointed professor of organic chemistry at the Ruhr-University Bochum in autumn 2013. He received his diploma degree in chemistry in 2003 and the Dr. rer. nat. under supervision of Manfred T. Reetz in 2007. Subsequently, he moved to the Department of Biochemistry at the University of Cambridge into the group of Peter F. Leadlay where he investigated the mechanism of stereospecificity in polyketide synthases. In 2009 he moved to the Max-Planck Institute of Molecular Physiology in Dortmund as Liebig Fellow of the Foundation of the Chemical Industry (FCI) and was later on appointed Beilstein-Professor of Organic Chemistry at the TU Dortmund. Research in his group focuses on the derivatization of natural products using synthetic, fermentative and enzymological approaches.
Physical Organic Chemistry: Understanding Reactions

Prof. Dr. Wolfram Sander, Lehrstuhl für Organische Chemie II

Chemistry is the science of changes of matter, and thus chemical reactions are at the very heart of chemistry. The focus of the research of the Sander groups is on the exploration of reaction mechanisms, thus investigating details of reactive intermediates, their interactions and reactions. To achieve this goal, modern methods of chemical synthesis, spectroscopy, and computational chemistry are combined. The spectroscopic methods include matrix isolation spectroscopy, time resolved spectroscopy, EPR, and advanced IR spectroscopy. Unusual media for performing reactions used by the group are solvents at extremely low temperature, rare gases such as neon, parahydrogen, or amorphous water ice.

From Radicals to Molecular Magnets

Radicals are formed by homolysis of chemical bonds, and their reactivity strongly depends on substituents at the radical center. A prototype of a highly reactive radical is the phenyl radical, a typical σ-radical, while the benzyl radical or the phenoxy radical, typical π-radicals, are far less reactive. Important reactions of these radicals include reactions with solvent molecules, molecular oxygen and hydrogen, carbonmonoxide etc. An interesting finding was that the highly reactive phenyl radical is able to abstract hydrogen atoms from water to form a complex between the hydroxyl radical and benzene. The reactions of these radicals are not only important for organic synthesis but also for tropospheric chemistry, combustion, and oxidation processes in living cells.

A combination of several radical centers results in polyradicals such as the trimethylenebenzene shown in Figure 1. These polyradicals show unusual reactivity and magnetic properties and find applications as building blocks for organic magnetic materials. Molecular magnets with up to six unpaired electrons and septet electronic ground states could be synthesized and characterized.

Tunneling in Chemistry

While quantum mechanical tunneling (QMT) was recognized as a an interesting phenomenon that might influence reaction rates decades ago, it is still regarded as somehow exotic to most chemists. However, more and more evidence is found that tunneling not only influences the kinetics, but also the selectivity of chemical reactions. Low temperature spectroscopy is ideal to investigate tunneling, since the competing thermal reactions are suppressed at low temperatures. In particular, for hydrogen abstractions and hydrogenations with molecular hydrogen large tunneling contributions are observed. A number of tunneling reactions, including both hydrogen and heavy atom tunneling, were discovered and studied during the past years. The prediction weather or not QMT is involved in a chemical reaction is still challenging. The work of the Sander group helps to find generalizable and predictive rules for tunneling reactions.

Non-Covalent Chemistry and Solvation

The chemistry in condensed phase is dominated by non-covalent interactions, and therefore are of key importance for the understanding of chemical reactions. An example is the unfolding of a peptide, that is governed by the interplay between internal and external hydrogen bonds. A detailed analysis allowed the scientists to unravel the solvent effects that control the conformation of peptides.

Solvent-solute interactions are in particular difficult to understand at the molecular level, and therefore this is studied within the framework of the Cluster of Excellence RE-SOLV using the tools of physical organic chemistry. Strong solvent effects are observed for all reactions where during the course of a reaction a charge-separation takes place. Intriguing solvent effects were found for the solvation of highly reactive carbenes. Dilution of methanol in an inert medium at very low temperatures results in diffusion controlled reaction while bulk methanol is completely inert at the same temperature. This demonstrates the high non-linearity of solvent mixtures. This work resulted in the development of a new method for the stabilization of highly reactive cations: isolation in amorphous water ice.

Fig. 1: Spin density distribution in trimethylene benzene (TMB). The molecule was synthesized in an argon matrix at 3 K and investigated by IR, UV-vis, and EPR spectroscopy.

Fig. 2: Electron density difference plot before and after a tunneling reaction. The colors show how electron density is shifted during QMT.

Fig. 3: Crystal structure of a cyclic peptide that was synthesized for conformation studies.
Selected Publications


Wolfram Sander is a Professor of Organic Chemistry at the Ruhr-Universität Bochum (RUB). He obtained his Ph.D. at the University of Heidelberg in 1982 and was a postdoctoral fellow at UCLA with Prof. O. L. Chapman from 1982 to 1984. He was Associated Professor at the Technische Universität Braunschweig from 1990 to 1993 before accepting his present position in 1993. In 2007 he received the Adolf-von-Baeyer Gold Medal of the German Chemical Society (GDCh).

His main research interest in the field of Physical Organic Chemistry is the investigation of reactive intermediates, organic high spin molecules, and non-covalently bound species using a variety of experimental and computational techniques.
The Dyker group’s research is focused on preparative Organic Chemistry, with special emphasis on the application of stoichiometric as well as catalytic organometallic methods.

The target structures range from extended π-systems to steroid frameworks and functionalized molecular cavities.

Gold- and Platinum-Catalyzed Domino Processes

Alkynes are effectively activated by gold- and platinum chloride for the attack of various carbon, oxygen and nitrogen nucleophiles. [1] For an intramolecular process even ketones and aldehydes are nucleophilic enough to generate benzopyrylium intermediates, which can be readily trapped by cycloaddition reactions, f.i. for the synthesis of terpenoids and for building up a steroid framework. [2-3] The straight forward synthesis of heliophenanthrone illustrates this fascinating type of rearrangement. [4]

Functionalized Pentaarylcyclopentadienes

A palladium-catalyzed multifold arylation opens up a new entry to sterically shielded cyclopentadienes. [5]

Chiral Transition Metal Complexes

Based on pentaarylcyclopentadienes ruthenium complexes - chelated by a chiral oxazoline moiety — were developed, which exhibit a second chiral center directly at the metal. [8]

Self-Organization of Molecular Cavities

A fourfold Sonogashira coupling reaction with a chiral propargylic alcohol led to the formation of a functionalized calixarene, which formed hydrophilic channels with a helical symmetry in the crystal lattice. Thus point chirality is translated to helical chirality. [6]

Agostic and Anagostic Interactions

While agostic interactions are often involved in transition metal catalyzed CH activation processes, the rare anagostic interactions may cause significant anisotropic downfield shifts in proton NMR spectra. Due to the through space interaction of hydrogen atoms with the electron sphere of chelated palladium salts the signal of aliphatic CH groups was registered at up to 8.5 ppm, the signals of aromatic CH-groups at up to 11.1 ppm. [9]
Selected publications


Gerald Dyker studied chemistry at Dortmund University. After completing his dissertation on nitrogen and sulfur heterocycles in 1988 under the guidance of R. P. Kreher he developed ruthenium catalyzed reactions with B. M. Trost at Stanford University. As research chemist at Bayer AG, Monheim, he worked in the fields of veterinary pharmaceuticals and agricultural chemistry. He finished his habilitation at the Technical University of Braunschweig in 1994, moved to Duisburg University in 1995 as associate professor of Organic and Organometallic Chemistry. In 2000 he joined the Faculty of Chemistry and Biochemistry at the Ruhr-Universität Bochum.
The far reaching goal of the research in the group of Karina Morgenstern at the Chair for Physical Chemistry I is to modify metallic and dielectric surfaces on the nanoscale by systematically employing strain and quantum-size effects and modify the immediate chemical environment in order to promote non-adiabatic reactions on these nanostructures into a desired direction. For this aim, the different parts of the system, the support, the nanostructures, the adsorption of molecules on the support and on the nanostructures have to be characterized and understood in detail. The research is mainly performed with scanning tunneling microscopy.

Geometrical and electronic structure of nanostructures

Model systems were utilized to gain a profound understanding of ripening phenomena on metallic surfaces. Effects of both quantum-size effects and strain were recently described for the systems NaCl/Ag(111) and Cu/Ag(100).

Also the phonon structure of the surfaces is investigated locally.

Functional molecules on metal surfaces

Electronic switches are essential as basic components for storage and logical operations. We investigated isomerisation reactions of single molecules adsorbed on surfaces that have a potential as a molecular switch in future molecular electronics; mainly, but not exclusively, constitutional, configurational, and geometric isomerisation reactions.

The isomerisation is induced either by light or by electrons, from the STM tip. Some reactions are similar to those observed for the molecule in the gas phase, but some are observed or even possible only on a surface. The detailed investigation of the isomerisation yield dependence on several parameters gives insight into the underlying processes of the reaction. A miniature switch, consisting just of the reorientation of one single bond within a molecule has been recently realized.

Water

Water is all around us. It wets surfaces and many reactions in the troposphere as well as in living organisms proceed in a humid environment. In our group, the structure of water grown at different parameters on metallic and salt surfaces was investigated with respect to formation, restructuring with temperature and electron solvation. With the aid of the tunnelling electrons we also produced amorphous ice clusters from adsorbed water molecules, then crystallized the clusters, dissociated the water molecules, and finally oxidized the surface.

Combinations

The isomerisation reactions were repeated on NaCl layers, the water was attached to several azobenzene derivatives. In future, we will investigate the influence of the solvent onto the reaction on the nanostructured surface.

Selected publications

[1] Size dependence of the dispersion relation for the interface state between NaCl(100) and Ag(111), S. Heidorn, A. Sabellek, K. Morgenstern, Nano Letters, 14, 13 (2014).
[3] Local determination of the amount of integration of an atom into a crystal surface, K. Volgmann, H. Gawronski, Ch.


Karina Morgenstern has been full professor of physical chemistry at the Ruhr-Universität Bochum since 2012 after having been a full professor of solid state physics at the Leibniz University of Hannover from 2005 to 2012. She studied physics and computer science at the Friedrich-Wilhelm-Universität Bonn and the University of Tennesse in Knoxville and received her PhD from the University in Bonn in 1993 having performed her thesis work predominantly at the Forschungszentrum Jülich and partly at the Universität Aarhus in Denmark. After Postdoctoral stays at the Universities in Lausanne, Aarhus, and Berlin she finished her Habilitation in Experimental Physics at the FU Berlin in 2002, where she stayed with the aid of a Heisenberg fellowship till 2005. She received the Günther-Leibfried-Preis of Forschungszentrums Jülich in 1997 and the Hertha-Sponer-Preis of the German Physical Society in 2002.

Finden Sie uns auf Facebook
www.facebook.com/opusmundi.de
Proteins interacting with small molecules, lipid membrane systems or other protein binding partners are characterized in terms of affinity and specificity as well as binding kinetics. In addition, the role of water and of co-solvents and co-solutes in defining the thermodynamic characteristics of the above-mentioned interactions is investigated by employing biophysical techniques like microcalorimetry, fluorescence stopped flow and temperature jump.

With the aim to understand biochemical processes on the molecular level our research work is devoted to the quantitative characterization of protein complex formation. Fundamental features are addressed like the impact of the interaction of the solvent with the protein surface as well as the thermodynamics and kinetics of more complex biochemical systems like nucleotide dependent protein oligomerisation and lipid membrane attachment.

Ionic co-solutes and crowding compounds in protein stability

As we and others have shown for various examples the strength of interaction between proteins is strongly reduced by the addition of salt to the solution the extent of which depends on the number of charge based interactions on the protein surfaces. In our recent studies we could demonstrate that the nature of the salt may also have a strong impact on protein interaction and stability\[1\]. In particular, for a number of ionic liquid compounds employed as co-solutes in protein stability and enzymatic activity assays Hofmeister type rankings of anions and cations were established\[2,3\] (Fig. 1). In another study we were able to demonstrate that the crowding effect on protein folding stability for some compounds is based on enthalpy changes while other crowding compounds exert their impact on protein stability by shifting entropic contributions\[4\].

Binding induced protein folding

Regulated turning on and off of enzymatic activities and protein interactions is crucial to many biological processes, e.g. cellular signal transduction. Our project aims at the analysis of the changes of structure and dynamics of multi-protein complexes involved in signaling in order to understand the molecular mechanism of differentiation between multiple pathways. In particular, we have investigated a family of proteins harboring a short helical domain which becomes structured after homo- or heterodimer formation\[5,6\] (Fig. 2). In recent years intrinsically unfolded proteins have emerged as a new biochemical feature which may adopt to a multitude of binding partners and thereby may fulfill various functions.

Nucleotide dependent protein interactions at membranes

A large number of proteins is known to reside within a lipid membrane or to be attached to the membrane surface through hydrophobic anchors. Interferon-induced human Guanylate Binding Protein 1 represents a multidomain protein (Fig. 3). We have characterized its enzymology as well as structural changes which could be shown to be coupled to nucleotide binding and hydrolysis\[7-10\]. Most intriguingly, we observe nucleotide dependent membrane attachment which may be crucial for the antipathogenic activity of this protein.

![Fig. 1: Thermograms from differential scanning calorimetry of ribonuclease A in the presence of various ionic liquid compounds (see ref. 2).](image)

![Fig. 2: Folding of an alpha-helical domain induced by homodimer formation as indicated by CD spectroscopy at increasing protein concentrations from top to bottom at 222 nm (see ref. 5-6).](image)

![Fig. 3: X-ray structure of human Guanylate Binding Protein 1 revealing three protein domains.](image)
Selected Publications


Christian Herrmann has been Professor for Physical and Biophysical Chemistry at Ruhr University Bochum since 2003. After studying chemistry he received his doctoral degree under the supervision of W. Knoche from the University in Bielefeld in 1991 as well as his habilitation in 2001. After a postdoctoral stay with T. Barman and F. Travers from 1991-1993 at INSERM/CNRS in Montpellier he joined the department of Fred Wittinghofer at the Max Planck Institute for Molecular Physiology in Dortmund until 2003. For more details see www.rub.de/proin
The research of the Havenith group is deeply embedded within the Cluster of Excellence RESOLV. The majority of chemical reactions, including many that are central to important industrial and virtually all biological processes, take place in a liquid-state environment. The Havenith group has developed IR and THz laser technologies to address solvation on a molecular scale. The group has pioneered THz spectroscopy as a new tool to probe the collective hydration dynamics of ions and biomolecules. This has led to insights as to the role of water in biological function and transcended the traditional view of water as an inert medium, acting solely as a passive spectator. Water molecules and the coupling of the protein to the solvent are now increasingly recognized as playing an active role in their own right. Recent experimental advances in combination with theoretical progress made in the Havenith group in this newly emerging field have shown the great potential “Solvation Science” has. Additionally, time resolved Kinetic THz absorption spectroscopy (KITA) has been developed in the group. KITA allows changes in the coupled protein/hydration dynamics during biological function to be probed in real time. Unraveling the microscopic contribution of water as an “active” solvent to fundamental biomolecular processes is a vital ingredient towards achieving an understanding of molecular recognition and, thus, a step towards de novo enzyme synthesis. Within RESOLV, the Havenith group is dedicated to establishing “Solvation Science” as a research field in its own right.

Laser technology to probe solvation dynamics

The Havenith group has set up a number of state-of-the-art laser spectrometers, some of which are unique. This incorporates 3 Terahertz (THz) absorption spectrometers, including a high power (2W) p-Ge difference spectrometer, an infrared (IR)-near-field microscope in the chemical fingerprint region and a high power IR Optical Parametric Oscillator for the high resolution IR spectroscopy of clusters embedded in superfluid helium nanodroplets. Within the last years, the group has used these cutting-edge laser technologies to explore fundamental questions in chemistry such as the solvation of ions and biomolecules on a microscopic level. The research spans a wide gap between the microsolvation of single molecules and bulk solvation of large biomolecules in our laboratory.

The helium droplet – An ultracold trap for individual molecules

The Havenith group has set up a high-resolution IR laser spectrometer and combined it with a superfluid helium nanodroplet machine, allowing the successive solvation of solutes with single water molecules. A superfluid helium droplet creates an environment which facilitates the formation of \([\text{HCl}]_n(\text{H}_2\text{O})_m\) clusters under controlled conditions at 0.37 K. The droplets are formed by expansion of high-pressure helium gas through a small cooled nozzle into a vacuum; they have a temperature of 0.37 K and contain about 10,000 helium atoms that are basically frictionless. These helium droplets serve as an ultracold trap, which

![Fig. 1: Aggregation induced dissociation of HCl. Shown is the cluster formation within the superfluid helium nanodroplet upon successive pick up of single water molecules.](image)
can catch single molecules, cool them down to 0.37 K and retain them inside the cluster interior, where they bond one by one to form molecular aggregates of well-controlled sizes, or where reactions can take place at ultracold conditions (Figure 1). Furthermore, the cold environment allows one to obtain spectra with only a few quantum levels populated. The spontaneous dissociation of HCl into (H$_3$O)$^+$($\text{H}_2\text{O})_{n-1}$ and Cl$^-$ is a classic textbook example: Combining IR laser techniques with the suprafluid helium apparatus means that acid formation can now be observed on the level of a step wise aggregation process.\[1\]

Terahertz laser spectroscopy – bulk water dynamics

Prof. Havenith’s group has pioneered THz absorption spectroscopy as a new, powerful tool able to study solute/solvent interaction. Using state of the art THz spectrometers, including a unique p-Ge spectrometer (2.4-2.7 THz), an FT spectrometer (50 - 500 cm$^{-1}$), and time domain THz spectrometers (0-2 THz) allowed the detection of subtle changes in the dynamical orientation of water molecules by giving direct access to collective water network dynamics.\[2,3\]

Hydration funnel facilitates substrate binding in enzymes

Although it was initially thought that enzymatic catalysis could be attributed to direct structural interactions between enzymes and substrates, it is now becoming widely accepted that the functions of enzymes are mediated by their dynamic character and by interactions with the solvent. In particular, there is ongoing research aimed at elucidating the dynamical features of protein-water coupling on the picosecond timescale (corresponding to the THz spectral range), as many processes in water occur on this timescale. In joint THz spectroscopy and classical molecular dynamics simulation studies of model enzymes and human membrane type-1 matrix metalloprotease a steep gradient of fast-to-slow coupled protein-water motions towards the active site and substrate was observed – the so-called “hydration funnel” (see Figure 2). It has been proposed that the observed gradient may assist enzyme-substrate interactions.\[4,5\]

This heterogeneous hydration, or more specifically, a gradient of hydrogen bond dynamics towards the catalytic site of enzymes is postulated to assist molecular recognition. Up to now, the solvent has been an underestimated or even neglected element of the multilateral partnership that makes up biomolecular function.

Antifreeze proteins keep fish alive in sub-zero surroundings

An important example for this new concept of assisted molecular binding by a hydrogen dynamics funnel was given for the ice-binding site of antifreeze proteins. Antifreeze proteins are found in some vertebrates and ensure their survival in sub-zero environments, e.g. certain types of fish in the Antarctic (Figure 2). Although the antifreeze activity of several types of antifreeze proteins has been characterized, the details of the mechanism at the molecular level remained controversial. With the help of THz spectroscopy, CD spectroscopy and accompanying MD simulations, our group showed that the antifreeze activity of AFPs can be attributed to two distinct molecular mechanisms: (i) a short-range direct interaction of the protein surface with the growing ice face and (ii) a long-range interaction through protein-induced water dynamics extending up to 20 Å (5 – 7 water shells) from the surface of the AFP protein.\[6\] These important findings could change the way in which enzymes and drugs are designed in the future.

KITA – monitoring real-time hydration dynamics

In Bochum, our group has set up the first-ever experiment able to observe changes in solvation dynamics in real time during biological function, namely kinetic THz absorption spectroscopy (KITA), see Figure 3.\[7\] Dynamical processes such as protein folding are initiated by stopped-flow mixing and the subsequent changes in solution dynamics are mapped in real time using a THz time domain spectrometer. In a proof-of-principal experiment we could show that changes in water dynamics considerably precede the acquisition of a native-like structure during protein folding. We could map the changes in the low frequency spectrum during protein folding and enzyme/substrate docking.\[4,5,6,7\]

Fig. 2: Schematic representation of the hydration funnel, i.e. the retardation of the hydrogen bond dynamics of the water molecule in an enzyme-substrate complex (the enzyme is shown in grey, the substrate in green, and the retarded water molecules in red) (left-hand side) and for the insect antifreeze protein AFP III (the ice binding site with the regular spaced threonine is shown in yellow, and the retarded water molecules in red) (right-hand side).

Fig. 3: Professor Havenith calibrating the KITA laser (Copyright: RUBIN, Foto: Nielinger).
Raman microscopy

Chemical microscopy is used in our group for the label-free characterization of surfaces:

Interfaces: We were able to characterize local opto-mechanical forces generated within photosensitive azobenzene containing polymer films by a red shift of the G band of graphene. This graphene-based nanoscopic gauge opens new possibilities to characterize opto-mechanical forces generated within photosensitive polymer films. [3]

Plasma medicine: Patients with chronic, non-healing wounds often suffer severe physical and emotional stress, however, treatment with so-called “cold plasma” can improve their condition considerably. It’s treatment with so-called “cold plasma” can improve their condition considerably. It’s physical and emotional stress, however, treatment with so-called “cold plasma” can improve their condition considerably. It’s

for more details see www.rub.de/pc2

Selected Publications


Martina Havenith-Newen received her Dr. rer. nat. degree in physics from the Rheinische Friedrich-Wilhelms-University, Bonn in 1990 and her Habilitation in experimental physics in 1997. She has been Professor of Physical Chemistry at the Ruhr-University in Bochum since 1998. Prof. Havenith is a member of the North Rhine-Westphalian Academy of Sciences, Humanities and Arts and the German National Academy of Sciences Leopoldina. In her research she has developed new laser technologies to explore fundamental questions in chemistry. She has pioneered THz spectroscopy as a new tool to probe the collective hydration dynamics of biomolecules, leading to new insights into the role of water in biological function. She has published more than 170 research papers and has given more than 220 invited lectures. Prof. Havenith has received numerous prizes acknowledging her work such as the Heisenberg Grant, the Bennigsen Foerder Prize, the Human Frontier Science Award and the Innovation Prize of the RUB. Recently she has been awarded a Visiting Miller Professorship at UC Berkeley, USA in combination with the Gabor A. und Judith K. Somorjai Visiting Miller Professorship Award. She is founder and coordinator of the DFG funded Cluster of Excellence RESOLV as well as a Centre of Molecular Spectroscopy and Simulation of Solvent Controlled Processes (ZEMOS) at the Ruhr-University. She is advancing the field Solvation Science, which aims to provide a unifying framework for understanding and predicting solvent processes. For more details, see www.rub.de/pc2.

Biopolymers in vivo – from the test tube into the cell

Jun.-Prof. Dr. S. Ebbinghaus, Lehrstuhl für Physikalische Chemie II

Most biopolymers like proteins, DNA, and RNA molecules function inside the cell. The Ebbinghaus group is interested in studying biomolecular structure, function and aggregation directly in cellular environments. Therefore, special in-cell techniques are used and the results are interpreted by comparative in vitro experiments in cell-like environments and dilute solutions (Fig. 1).

Protein stability in the crowded cell

Compared to the test tube where most biochemical studies are conducted, cells are highly crowded. The macromolecular
concentration reaches 400 mg per ml of cytosol meaning that 1/3 of the available volume in the cell is occupied by macromolecules. Biomolecules behave differently under such conditions. For example, macromolecular crowding effects can stabilize proteins in the cellular environment compared to aqueous solution [1,2,3] and prevent protein aggregation [4]. Moreover, the stability varies within the cytoplasm of a single living cell [5] or between different compartments [6]. A high heterogeneity was found between different cells of a cell population [7].

The physicochemical origin of macromolecular crowding effects

A central dogma in crowding theories was that crowding effects are solely mediated by hard-core repulsions between the macromolecules and therefore steric excluded volume effects. This ideal excluded volume effect results in an entropic stabilization of the protein while the enthalpy remains unchanged. However, using artificial crowding agents like Ficoll 70 our group has recently shown that crowding effects on protein stability can be primarily mediated by enthalpic effects (Fig. 2) [1]. In the cellular environment, excluded volume effects are further compensated by unspecific interactions [8]. However, hypertonic stress can evoke significant excluded volume effects that lead to high compression forces acting on biomolecules in cells [8]. Such effects could endanger proteostasis and promote protein aggregation. Future studies will show how crowding effects act on the organism level (e.g. C. elegans) and how cells utilize the cellular milieu to actively control biomolecular function.

The group is currently funded by the Ministry of Innovation, Science and Research of the State of North Rhine-Westphalia (Rückkehrprogramm), the Cluster of Excellence RESOLV (EXC 1069) funded by the German Research Foundation (DFG), and by the International Graduate School of Neuroscience (Ruhr-University Bochum, Germany).

Selected Publications


Simon Ebbinghaus has been a Junior Professor at the Ruhr-University Bochum (Department of Physical Chemistry II) since 2011. Before that, he worked as a Feodor Lynen Research Fellow with Martin Gruebele at the University of Illinois (Urbana-Champaign) from 2008 to 2010. He received his Ph.D. (Dr. rer. nat.) from the Ruhr-University Bochum in 2007 under the supervision of Martina Havenith. For more details, see www.rub.de/pc2/ebbinghaus.
Ultrafast photochemistry: In hot pursuit of chemical reactions
Prof. Dr. Patrick Nürnberger, Workgroup “Ultrafast photochemistry”, Physical Chemistry II

The group is concerned with the development and application of a variety of advanced femtosecond spectroscopy techniques in order to identify the intermediates and products of photochemical reactions. The research aims to unravel and control the primary dynamics induced by laser light in systems relevant for synthesis, lithography, biology, and other fields of application. Special emphasis is put to the impact of the solvent environment as well as the role of excess energy with regard to photodynamical processes.

Deciphering ultrafast processes

Femtosecond spectroscopy has become a very powerful tool for the investigation of photophysical and photochemical phenomena. The characteristic time scales of fluorescence, electronic and vibrational coupling, charge and energy transfer, and many further processes can be determined with high accuracy. In the common approach, a pump pulse triggers the reaction and a probe pulse at an adjustable time delay monitors the progression of the reaction. By virtue of the short duration of the laser pulses, the dynamics are followed in real time, and also quantum-mechanical events like coherent wavepacket motion (Fig. 1) can be induced and observed [1].

Additional insight into the photochemical dynamics of a system can be achieved by multipulse approaches. In case of a reversible functionality, e.g. in a molecular photoswitch, a second pump pulse can be employed to investigate how fast the system can be driven back and forth [2].

The adequate timing of a further pulse may also give access to reactions which necessitate an excitation to a higher-lying electronic state [3] or a reexcitation after intersystem crossing to a triplet state.

When transient absorption is not sufficient to reveal complex photo-induced dynamics, coherent multidimensional electronic spectroscopy can be used to further separate the signal contributions originating from different processes. The information about the excited species is then intrinsically preserved and hence an intuitive visualization of the route from reactant to product is possible, e.g. in case that several absorbing species are initially present in solution and only some of them can perform a certain photoreaction [4].

Light-triggered reaction sequences

Many ultrafast studies investigate purely photophysical effects or the dynamics of excited species until a bond is broken, i.e. up to the first photochemical step. However, often a multifaceted reaction sequence will set in after the bond cleavage. Utilizing sensitive ultrafast transient absorption spectroscopy with vibronic excitation and mid-infrared probing [5], intermediate species and the time scales associated with their formation can be identified, and it is possible to decipher how the reaction sequence proceeds. Due to the characteristic vibrational signatures of the possible intermediates, competing reaction pathways or the issue of concerted versus sequential reaction mechanisms can be disclosed [6,7].

These kinds of experiments provide valuable information for photochemical applications: for instance, the Wolff rearrangement and subsequent processes (Fig. 2) are key reactions in UV photolithography, which are completed within a few nanoseconds in room-temperature solution [8]. A further example is the photo-induced ligand release in organometallic complexes (Fig. 3) which is of vital importance to understand the biological activity of these compounds that are relevant for therapeutic applications [9].

Control of photochemistry

Femtosecond laser pulses do not consist of monochromatic light but exhibit a broad spectrum. With pulse-shaping techniques, the temporal ordering of these spectral components and their relative phase can be adjusted in a well-defined way, so that the laser pulse can be tailored to the properties of the molecular system. Depending on the pulse shape, a desired reaction path can be enhanced whereas unfavorable ones may be suppressed. In this way, bond-forming reactions among small molecules in an adsorbate can be controlled [10]. By employing a pulse shaper for mid-infrared laser pulses [11], the impact of excess energy in certain vibrational modes on the photoreaction and the possibility to thereby manipulate its outcome is explored.

The solvent’s role in ultrafast reactions

In various experiments, the group addresses the influence of the environment on ultrafast processes in solution, especially the reaction dynamics in solvent mixtures and in the presence of cosolutes. The role of the solvent may be crucial: on the one hand, it influences the speed, yield and pathway of the reaction; on the other hand, the solvent may even take part in the reaction, e.g. by reacting with a carbene or ketene intermediate (Fig. 2). For ultrafast energy transfer or its localization in a system with excitonic character, the dynamics in the molecule might compete with rearrangement of the...
solvent shell. Current projects are directed to elucidate this interplay between competing reactions mediated by solute-solvent interactions.

Since 2012, the group is supported by the DFG within the Emmy-Noether program, and since 2014 as part of the cluster of Excellence RESOLV (EXC1069).

Fig. 3: UV excitation of a metal carbonyl compound in solution leads to the release of one CO ligand (arrow), as observable by an infrared probe pulse\(^a\).

Selected publications


\([5]\) J. Knorr, P. Rudolf, P. Nuernberger, A comparative study on chirped-pulse upconversion and direct multichannel MCT detection, Opt. Express 2013, 21, 30693


Patrick Nürnberg studied physics at the Julius-Maximilians-Universität Würzburg and at the State University of New York at Stony Brook. He received a Master of Arts degree in physics from SUNY Stony Brook in 2003, followed in 2004 by a diploma in physics and in 2007 by a doctoral degree from JMU Würzburg under the supervision of Gustav Gerber. From 2008 to 2010, he was a Leopoldina postdoctoral fellow at the Laboratoire d’Optique et Biosciences at Ecole Polytechnique in Palaiseau, France. Back in Germany, he set up a junior research group at the Institute for Physical and Theoretical Chemistry in Würzburg, supported by an Emmy-Noether grant from the Deutsche Forschungsgemeinschaft. In 2013, he finished his habilitation in physical chemistry. Since 2014, he has been a professor for physical chemistry at the Ruhr-Universität Bochum. For more details on his research, see www.rub.de/ag-nuernberger.
Heterogeneous redox catalysis: From fundamental insight to industrial application

Prof. Dr. Martin Muhler and Dr. Wei Xia, Laboratory of Industrial Chemistry, Ruhr-University Bochum, Germany.

The Laboratory of Industrial Chemistry performs fundamental research in the area of heterogeneous catalysis aiming at developing catalysts based on mechanistic insight. The scientific challenge is the elucidation of the reaction mechanisms on the atomic level and their interplay with the complex surface chemistry of heterogeneous catalysts, which usually consist of many phases and components, often present as X-ray amorphous nanoparticles or layers.

The reactions investigated by Prof. Dr. Martin Muhler belong to industrial redox chemistry. Reduction catalysis comprises methanol synthesis, Fischer-Tropsch synthesis, and the synthesis of higher alcohols. Oxidation catalysis focuses on the selective oxidation of propene and methanol, the oxidative dehydrogenation of hydrocarbons, and the selective oxidation of alcohols in the gas phase and in the liquid phase. Recently, we entered the fields of electrocatalysis and heterogeneous photocatalysis. Liquid-phase oxidation and electrocatalysis require a deeper understanding of solvation-related phenomena.

For the synthesis of catalysts a large repertoire of methods is available including chemical vapor deposition, spray drying and co-precipitation. In recent years the catalytic growth and surface modification of multiwalled carbon nanotubes (CNTs) has become a major topic due to the numerous applications of CNTs in electrocatalysis. All the necessary bulk- and surface-sensitive techniques for catalyst characterization are available with a strong focus on sorption techniques.

For improving the catalysts we first of all study steady-state kinetics. Numerous continuously operated flow set-ups with online analytics are available allowing us to screen the parameter space efficiently under full computer control using LabVIEW. The role of the various elementary steps is investigated by applying transient kinetic methods such as temperature-programmed...
med reactor operation, dosing pulses and concentration steps, and using isotopes. For these methods we strongly rely on fast online quantitative mass spectrometry. In addition, we try to gain as much spectroscopic information as possible using mainly FTIR and photoelectron spectroscopy. Recently, static and dynamic microcalorimetry have been developed into versatile tools to probe the surface properties quantitatively.

Dr. Wei Xia’s research focuses on nanstructured materials playing vital roles in energy conversion and storage. Carbon is essentially indispensible since it is the only material that is highly conductive and (electro-)chemically stable. Oxides, although often less conductive, can further improve the stability and surface reactivity of carbon. Research on these nanomaterials often covers morphology and agglomerate, porosity and surface area, phase composition and structure, surface defects and functional groups, adsorption and desorption, mass transfer, activity and selectivity, corrosion and stability, electronic and ionic conductivity.

**Fig. 2: Bifunctional electrocatalysts for the ORR and OER: NCNTs with Co-Mn spinels synthesized by catalytic growth and oxidative cutting.**

His research in electrocatalysis comprises the modification of carbon nanomaterials, the development of hybrid materials, the fundamental understanding on the surface chemistry, and the impact of materials properties on electrocatalysis. Various surface and...
bulk sensitive characterization techniques are employed including X-ray photoelectron spectroscopy, Raman spectroscopy, physi- sorption, chemisorption, temperature-programmed techniques, electron microscopy, X-ray diffraction, thermogravimetry and electrochemical methods like cyclic voltammetry, rotating disc electrode voltammetry and electrochemical impedance spectroscopy.

Selected Publications


Martin Muhler was appointed full Professor of Industrial Chemistry at the Ruhr-University Bochum in 1996. He studied chemistry at the Ludwig-Maximilians-University in Munich and received his Ph.D. in 1989 from the FU Berlin under the supervision of Prof. Dr. G. Ertl at the Fritz Haber Institute of the Max Planck Society in Berlin. He then joined the Department of Fundamental Research in Heterogeneous Catalysis at Haldor Topsøe A/S in Denmark as postdoctoral fellow for two years.

Wei Xia studied chemistry (B. Sc.) in Shanghai (China) and Halle-Wittenberg (M. Sc.) and received his Ph.D. in 2006 from the Ruhr-University Bochum. He spent one year as a Postdoctoral Research Associate at the Laboratory of Industrial Chemistry at the Ruhr-University Bochum and became the leader of the group “Carbon materials and electro-catalysis” in 2008. He received the invention prize of the Ruhr-University Bochum three times (2005, 2008 and 2010). In 2010 he received the prize of the inventors competition in Northrhine-Westphalia for a method of modifying carbon nanotubes.
The group’s research is focused on the elucidation of active site structures and promoting interactions in heterogeneous catalysts by combining reaction rate data with results of structural studies, including in-situ and operando work. Reactions investigated are often related to environmental catalysis.

Analytical expertise covers photoemission, low-energy ion scattering (LEIS) and X-ray absorption methods while other spectroscopic techniques and electrochemical studies are contributed by cooperation partners (Prof. A. Brückner, Rostock, Prof. M. Bron, Halle, Prof. M. Muhler, Bochum).

In environmental catalysis, the group has been studying selective catalytic reduction (SCR) of nitrogen oxides with different reactants for two decades, but extended onto tree-way catalysis and low-temperature CO oxidation more recently.

SCR with ammonia

The group has significantly contributed to present-day knowledge on Fe zeolite catalysts, which are being commercialized for Diesel exhaust treatment according to Euro VI standards. This includes the finding that SCR of NO and of NO/NO₂ mixtures (“standard” and “fast” SCR) proceed on different sites and via different mechanisms on Fe zeolites [1], and the rejection of a popular view according to which binary Fe-O-Fe pairs are required to catalyze standard SCR [2]. Instead, the reaction proceeds on all exposed Fe sites that remain three-valent in the feed, with a particular contribution of oligomeric oxide clusters in the zeolite voids [3, 4]. Fast SCR is catalyzed by a minority Fe site comprising an isolated Fe ion stabilized in the +2 state by two adjacent framework Al [3]. A popular mechanistic concept according to which standard SCR proceeds as a sequence of NO₂ formation from NO with subsequent fast SCR over Fe zeolites was rejected [4, 5] (Fig. 1). Recent work is focused on the identification of active sites for NO oxidation and on the utilization of the above-mentioned sequence in hybrid catalysts.

A project on standard SCR over traditional V-W/TiO₂ catalysts resulted in a new view upon the origin of the promoting effect of tungsten and revealed unexpected thermal effects on the behavior of these catalysts [6], which has been widely appreciated just in industrial groups.

Low-temperature CO oxidation

Metal-support interactions in Au/TiO₂ CO oxidation catalysts were investigated with model catalysts containing both components as guests in a siliceous host (MCM-48) [7]. The study resulted in the conclusion that epitactic relations between metal and support as observed in literature are irrelevant for CO oxidation, that the active Au⁰ sites are in clusters of <1 nm size, and that most sites are poisoned, probably by carbonate, under stationary conditions. In a study with conventional Au/TiO₂ catalysts,
it was observed that CO oxidation can proceed with high rates also sites containing cationic gold. After their complete conversion to Au\(^0\), the reaction proceeds on the perimeter between the support and positively charged Au\(^+\) clusters (cf. \([8]\)) which are most likely oligomeric structures or even atoms stabilized by oxygen vacancies in the support \([9, 10]\) (Fig. 2).

**Three-way catalysis**

Reactions of three-way catalysis have been studied with noble-metal substituted perovskites to examine claims in literature that these materials release Pd\(^0\) and resorb Pd\(^2+\) on the time scale of \(\lambda\) fluctuations in the exhaust of gasoline engines. While this claim was found unrealistic. Pd was observed to form alloy phases with perovskite components (Fe, Co), which are highly active in NO reduction and N\(_2\)O decomposition. At present, the potential of gold as a component of three-way catalysts is investigated.

**Active sites of MoS\(_2\)**

The catalytic activity of MoS\(_2\) in simple test reactions (e.g. ethene hydrogenation) was studied with materials made from different precursors and activated with different treatments in order to relate activities to the extent of coordinative unsaturation at the Mo ion assessed via oxygen chemisorption. All test reactions were found to proceed also on surfaces that were unable to adsorb oxygen \([11]\). This result is a highly debated contribution to an ongoing change of paradigms in views on active sites of sulfide catalysts, from models requesting multiple vacancies on Mo for hydrogenation to models with saturated hydrogenation sites, which had not yet been demonstrated in reality.

**Electrochemical Oxygen Reduction (ORR) on Leached Pt Alloy Nanoparticles**

The ORR activity of Pt-X alloy nanoparticles is known to be enhanced by leaching the less noble component via chemical or electrochemical treatments. The latter, superior route was described to result on core-shell nanoparticles with a multilayer Pt core covering an alloy core of original composition. Our multitechnique study on the structure of chemically leached Pt-Cu particles, with key impact of LEIS, revealed that the treatment affects the whole particles, resulting in a Pt monolayer covering a Cu-depleted alloy core. As these results challenge the model established for electrochemically leached particles in literature, detailed analyses with the given set of methods are going on.

**Selected Publications**


bei ης στιγμήν
die Zeitwic...  

... präsentieren Sie zielgerecht Ihre Produkte und Dienstleistungen!

» preiswerter  
   All-in-one-Service!

» Druckerzeugnisse von A-Z

» Lernen Sie uns kennen –  
   wir visualisieren Ihr Know-how

VMK Druckerei GmbH
Faberstrasse 17
67590 Monsheim
Tel. 0049.6243.909.110
Fax 0049.6243.909.100
info@vmk-druckerei.de
www.vmk-druckerei.de
Leitmotives of the Marx Group are, on the one hand, the development of novel quantum and quasi-classical simulation techniques for molecular many-body systems, and on the other, their application in terms of High-Performance Scientific Computing.

The general theme of our research consists in understanding structure, dynamics, and chemical reactions of complex molecular many-body systems. Our aim is to capture nature as closely as possible by theoretical means – the basic entities being nuclei and electrons. This implies that we have to use atomistic ab initio computer simulation techniques which are capable of including dynamics and quantum mechanics – of course only approximately. The notion “ab initio” or “first principles” means for us that we neither want to fit to experimental data nor do we want to adjust any parameters.

The central working horse to turn these ideas into practical numerical tools are in particular the ab initio simulation methods going back to the ground-breaking ideas of Car and Parrinello (1985).

In Bochum, major methodological developments of the Marx group have been devoted to continuing the extension and broadening of the “standard” Car-Parrinello method, for which a few highlights are given in the following.

Nonadiabatic ab initio dynamics

In 2002, a general approach to go beyond the usual Born-Oppenheimer approximation has been developed and implemented in collaboration with Nikos Doltsinis. The basic idea of this nonadiabatic ab initio dynamics technique is to use Tully’s surface hopping algorithm in combination with the so-called restricted open-shell Kohn-Sham Ansatz. This efficient approach “beyond the Born-Oppenheimer approximation” allows us to study photochemical reactions with particular focus on laser-induced processes in solutions or complex environments.

Spin-projected multideterminant ab initio dynamics

Together with Nisanth Nair and Eduard Schreiner, a multi-determinant Car-Parrinello propagation scheme, which enables the description of the dynamics of electronic states that cannot be represented using a single Kohn-Sham determinant, has been developed starting in 2007. Using this strategy, we have computed Heisenberg’s antiferromagnetic exchange coupling obtained from a spin-projected, Hubbard-corrected, two-determinant ground state. Generating the time evolution of this quantity “on the fly” provides access to magnetic-structural dynamics, which arise from the intricate coupling of molecular motion and magnetic properties. More recently, the method has been extended toward spin-density constraint DFT to deal with cases where the +U correction fails.

Ab initio/bosonic path integral MD/MC

Among the most recent developments, together with Harald Forbert and Lukasz Walewski, is a method that allows us to solvate reactive molecular complexes in superfluid helium droplets at sub-Kelvin temperatures. It combines ab initio path integrals to treat chemically complex molecular solutes with bosonic path integral Monte Carlo sampling of the helium environment to establish quantum mechanical indistinguishability - as required by the Bose-Einstein quantum statistics of liquid 4He. This approach opens the doorway to studying chemical reactivity in the absence of thermal energy, such as aggregation-induced dissociation phenomena and cryochemical reactions (Fig. 1).

Mechanochemistry and molecular nanomechanics

Another field pioneered in Bochum is the general theory and computer simulation of covalent mechnochemistry in collaboration with Jordi Ribas-Arino. In contrast...
to thermochemistry, photochemistry or electrochemistry (where temperature, light or electricity are used to trigger reactions), mechanochemistry utilises mechanical force to activate and control chemical reactions\(^{[5]}\). Advances in this field impact on areas of application such as molecular nanomechanics of single-molecule junctions, functionalized surface coatings, and mechanoenzymes (Fig. 2).

**Catalysis and spectroscopy from ab initio molecular dynamics**

Finally, successful ab initio molecular dynamics based approaches have been developed for fields where radically different methods have been used traditionally, which includes theoretical heterogeneous catalysis\(^{[6]}\) with Bernd Meyer and Johannes Frenzel as well as theoretical infrared and THz spectroscopy\(^{[7]}\) together with Gerald Mathias, Sergei Ivanov and Harald Forbert.

Much of the methodological development of Dominik Marx and his coworkers is contained in the Marx-Hutter monograph on "Ab Initio Molecular Dynamics"\(^{[8]}\).

**Solvation Science**

The ever-growing family of ab initio simulation techniques, in conjunction with high-performance computing, is ideally suited to the investigation of disordered systems at finite temperatures; molecular liquids being a prime example of this. As such, this set of methods provides the most direct insight into the structure and dynamics of solvation shells, the impact of hydrogen bonding on the properties of aqueous solutions, and, most importantly, the influence of solvation on chemical reactivity\(^{[9,10]}\) (Fig. 3).

**Beyond science**

The Marx group also provides fertile grounds for independent young investigators to mature. Nikos Doltsinis and Bernd Meyer, who both habilitated in Bochum, are professors in the meantime. Currently, Jörg Behler is the head of a Heisenberg group as a Privatdozent subsequent to his Emmy Noether and Liebig Fellowships, whereas Michael Römelt just started to establish his Otto Hahn research group. In addition, Theoretical Chemistry in Bochum traditionally attracts Humboldt Fellows and Awardees from all over the world.

Last but not least, the Marx group is very active in fostering graduate and postgraduate training by co-organizing schools for PhD students and postdocs on computer simulation techniques together with the Jülich Supercomputing Centre (JSC at Forschungszentrum Jülich) on topics such as "Computational Trends in Solvation and Transport in Liquids" (2015), "Hierarchical Methods for Dynamics in Complex Molecular Systems" (2012), "Multiscale Simulation Methods in Molecular Sciences" (2009), and "Computational Nanoscience: Do It Yourself!" (2006).
Selected Publications


Dominik Marx studied chemistry and physics at Universität Mainz and the University of California at Irvine, where he worked with Max Wolfsberg on isotope effects. In Mainz, he received his Diplom in Chemistry (1990) working with Karl Heinzinger (MPI für Chemie) on MD simulations of non-aqueous electrolyte solutions and his Ph.D. (1992) with Kurt Binder (Institut für Physik) on Quantum Monte Carlo simulations of phase transitions. Thereafter, he worked as a Postdoctoral Fellow at IBM Zurich Research Laboratory (Rüschlikon) with Michele Parrinello, as a staff scientist at MPI für Festkörperforschung, and obtained the Habilitation on in Theoretical Physics at Universität Stuttgart (1998), before he received the chaired professorship of Theoretical Chemistry at Ruhr-Universität Bochum (1999). Several Chairs in Germany and abroad, including the Coulson Chair of Theoretical Chemistry at Oxford in conjunction with a Professorial Fellowship at University College, were offered to him. Dominik Marx was fascinated from early on by the multifaceted problems that are posed by the physics and chemistry of complex molecular systems which can only be tackled using utmost realistic computer simulation approaches.

Professional Support of Scientific Activities to obtain a better Understanding of Complex Chemical Systems

Prof. Dr. Wolfgang Schuhmann / Dr. Sabine Borgmann – Research Department „Interfacial Systems Chemistry“ (RD IFSC)

The Research Department „Interfacial Systems Chemistry“ (RD IFSC) is a research network located at Ruhr-Universität Bochum (RUB) in Germany. The Research Departments (RDs) of RUB are an integrated part of the institutional “Research Campus RUB” strategy promoting excellent research with a unique interdisciplinary approach. RDs function as large, collaborative research platforms which each span over several disciplines.

The RD IFSC was founded in 2009. Research performed in RD IFSC is related to chemistry and neighboring disciplines. The goal is to obtain a better understanding of complex chemical systems.

With the Shared Laboratory Concept including state-of-the-art instrumentation and support by a Shared Lab Manager, the RD IFSC provides - together with the excellent knowledge base of the members - an international and state-of-the-art research environment.

Contact: www.rub.de/ifsc.
The research of the Quantum Chemistry group focuses on Computational Chemistry, in particular on molecular and electronic structure calculations with quantum chemical methods ranging from density functional theory to explicitly correlated coupled cluster methods. The group applies these methods to a large variety of problems ranging from heterogenous catalysis and thermochemistry to linear and nonlinear electronic spectroscopy. Beside this, the group is involved in the development of the world-wide distributed TURBOMOLE program package.

The research in the Hättig group is concerned with the application and development of various computational chemistry methods for the prediction of molecular structures, interactions, properties and spectra, with emphasis on correlated wavefunction methods for electronic spectra and excited states in molecules. Its aim is to improve the understanding and prediction of experimental results with quantum chemical calculations and the implementation of robust and efficient computational chemistry methods, which are used by many groups at academic research institutions and in industry[1].

Spectra and structure of excited states

Electronically excited states have usually a complicated electronic structure, and often the molecular geometry is different from that in the ground state and difficult to predict. Chemical calculations are an important tool for the understanding of the molecular spectra and the photochemical reactivity of molecules. Modern electronic structure methods, as e.g. density functional and coupled-cluster response methods allow to investigate excited states of relatively large molecules, to predict their spectra and to determine their equilibrium structures. The Hättig group applies for these investigations in addition to TDDFT mainly the CC2 method, for which the group has developed an efficient implementation[2] which since 2002 is distributed as part of the TURBOMOLE program package and is well-suited for applications on medium sized and large organic chromophores (up to ca. 100 atoms). Examples which have been studied with CC2 range from medium-sized molecules like amino-benzonitriles[3] to substituted porphyrins[4] and chlorophylls[5].

Explicitly correlated wavefunctions

A serious limitation for the application of high-level electronic structure methods for the prediction of thermochemical and spectroscopic properties of larger molecules is their slow convergence with the atomic orbital basis sets which is caused by cusps in the many-electron wavefunction. In cooperation with the groups of W. Klopper (KIT), D.P. Tew (Bristol) and A. Köhn (Stuttgart) the Hättig group develops explicitly correlated so-called F12 Møller-Plesset perturbation theory and coupled-cluster methods which tackle this problem by including functions that depend on the interelectronic distances in the wavefunction ansatz. This leads to a large enhancement of the basis set convergence[6] and allows to apply such methods to larger systems.

Solvation and environment effects on electronic spectra

Apart from laboratory measurements carried out in ultra high vacuum and the interstellar space molecules don’t appear as isolated species but in a chemical environment where the interaction with other molecules influences their properties and spectra[6]. The interaction between molecules is of electric nature, but because of the many possible ways how the electric interaction can become apparent, e.g. as interaction between electric dipole moments or as dispersion interaction the detailed description of intermolecular interactions in terms of molecular properties is rather complex. To predict and study the origin of inhomogenous broadening of electronic spectra in solution and at interfaces the group became recently involved in the development of a polarizable embedding scheme for the RI-CC2 approach[7].

Pair natural orbital methods

To extend the applicability of wavefunction methods for thermochemistry and spectroscopic properties to larger systems and molecular structures at interfaces current research is concerned with the development of approaches that reduce the scaling
of the computational costs with the system size. Based on recent advances for pair natural orbital (PNO) expansions it has been possible to develop CC2 and ADC(2) implementations for excitation energies\cite{9} and the explicitly correlated coupled-cluster singles-and-doubles CCSD[F12] model\cite{10} with reduced computational scalings.

Selected Publications


\[10\] G. Schmitz, C. Hättig, D.P. Tew, Explicitly correlated PNO-MP2 and PNO-CCSD and their application to the S66 set and large molecular systems.

Fig. 2: Structure of a calix-4-arene · H2O complex for which a binding energy of 10.7 kcal/mol has been calculated with PNO-CCSD[F12] on 6 Xeon E5430 CPU cores within 170 h.

Christof Hättig has been Professor for Theoretical Chemistry at Ruhr-Universität Bochum since 2006. He studied Chemistry at the University Bonn, Germany, where he received his Ph. D. degree in Theoretical Chemistry in 1995. His thesis on the development of a correlated wavefunction method for dispersion coefficients for intermolecular interactions was supervised by Prof. Bernd A. Hess. In 1996 he joined first as a postdoctoral research associated and since 1997 as Forskingsadjunkt (Assistant Research Professor) the Theoretical Chemistry group at Aarhus University, Denmark, where he worked with P. Jørgensen on coupled-cluster response methods for the calculation of nonlinear optical properties. From 1999 to 2000 he has been a researcher at the Institute of Nanotechnology (INT) of the Forschungszentrum Karlsruhe (today KIT), Germany, in the group of R. Ahlrichs. In 2000 he became head of an independent junior research group at the INT and in 2003 he completed his Habilitation in theoretical Chemistry at the University Karlsruhe (today KIT). During this time he started to work on the development of approximate coupled-cluster methods for electronic spectra and excited states in large molecules for which he received in 2004 the Hans G.A. Hellmann Prize of the Arbeitsgemeinschaft Theoretische Chemie. He is member of the TURBOMOLE GmbH and since 2009 one of scientific coordinators of the TURBOMOLE program package.
The Schäfer group is driven by the aim to understand life at the molecular level: can we describe biomolecular systems from the basic principles of chemistry and physics? Molecular dynamics (MD) computer simulations can provide a deep and causal understanding of the structural dynamics and energetics underlying biomolecular processes, and are thus one of the most powerful tools to achieve this goal.

The group is active in the development and application of simulation methods for describing the structure and dynamics of large biomolecular assemblies on long time scales. This requires efficient classical molecular dynamics (MD) type simulations, in which Newton’s equations of motion are iteratively solved in small time steps and empirical potentials (force fields) are employed for describing the interatomic interactions. In addition to using conventional fully atomistic MD simulations, the group also contributes to improving the accuracy of computationally highly efficient coarse-grained approaches, as well as to the development of hybrid multiscale methods that combine different levels of resolution. In the following, we highlight a few recent applications and methodological advancements.

Membrane Proteins

Membrane proteins are not only of great interest due to their intriguing chemical and biophysical principles, but also because of their pharmaceutical importance: about half of all current drugs target membrane proteins. We use MD simulations to probe the free energy landscapes and corresponding thermodynamic driving forces behind the molecular mechanisms of these nano-machines. Recent work focused on both secondary active transporters such as EmrE \(^1\), and ATP binding cassette transporters such as ThiT \(^2\) and the transporter associated with antigen processing (TAP) \(^1\). Whereas the former two proteins were studied in a conventional lipid bilayer surrounding, the latter was embedded in a so-called nanodisc, a special environment with several experimental advantages (Fig. 1). The simulations thus show how computational techniques can probe the interactions between the different components (proteins, lipids, solvent molecules) that govern the structure and dynamics – and hence the function – of membrane protein complexes.

Solvation Science

Water molecules can play a major role for molecular recognition processes, such as protein-protein and protein-ligand binding. We investigate how water (and other (co-)solvents) can modulate the thermodynamics of biomolecular interactions. One focus is on serine protease inhibitors, in collaboration with Christian Herrmann (Ruhr-University Bochum). Free energy simulations provide detailed atomistic insights into the molecular thermodynamics, including the origins of different enthalpic and entropic contributions to the free energy of binding, and the role of the solvent. Together with microcalorimetry experiments, they open the way toward a targeted and rational design of improved inhibitors.

Protein-Protein Interactions

Protein complexes are crucial for many cellular processes, yet often very little is known about their structural organization. Improving the predictive power of computed protein-protein interactions is a long-standing challenge. We study both soluble proteins and, often even more demanding, membrane proteins \(^3\). As a prime example for a protein super-complex, we investigate the molecular architecture of the major histocompatibility complex (MHC) class I peptide loading complex (PLC), a key player in the mammalian antiviral immune response, the rejection of organ transplants, and cancer. Enabled by high-performance parallel supercomputers and GPU computing, we use atomistic MD simulations to study the spontaneous association of the two central proteins in the PLC, tapasin and MHC-I (Fig. 2). Previously, due to the lack of structural data, the molecular mechanism of this protein complex remained elusive. Our simulations now provide for the first time a basis for an in-depth understanding of its working mechanism. In addition, in another project, the Schäfer group collaborates with Boehringer Ingelheim Pharma GmbH & Co. KG on improving the aggregation behavior of biopharmaceuticals.

Multiscale Modeling

One of the major bottlenecks of today’s atomistic MD simulations is the sampling problem: Due to the enormous computati-
ional costs, only processes at nanosecond to microsecond time scales (or faster) can be studied directly. To overcome this limitation, we develop computationally efficient hybrid multiscale approaches that combine atomistic and coarse-grained levels of resolution \[^{[6,7]}\], in addition to our ongoing efforts to improve fast coarse-grained force fields \[^{[8,9]}\]. The basic idea of hybrid modeling is to use models of different resolution in separate spatial domains, e.g., the protein and its direct surrounding are described by an atomistic force field, whereas a coarse-grained model is used for the remainder (Fig. 3). The aim is to trade off the size and complexity of the system against the efforts of a fully atomistic description. Successful implementation of such hybrid approaches enables to directly simulate large-scale self-assembly processes in atomic detail, with possible impact on related fields in which complex collective processes play a role, such as material science and nanotechnology.

Selected Publications


Lars Schäfer has been appointed Professor of Molecular Simulation at the Ruhr-University Bochum in February 2014. He studied chemistry at the TU Braunschweig and did his Ph.D. with Helmut Grubmüller at the MPI for Biophysical Chemistry in Göttingen (2007), as a Ph.D. fellow of the Boehringer Ingelheim Fonds. Subsequently, he received a Veni fellowship from the Netherlands Organisation for Scientific Research to work as a postdoc at the University of Groningen with Siewert Jan Marrink (2008-2012), and an Emmy-Noether grant from the Deutsche Forschungsgemeinschaft to work as an independent research group leader at Goethe-University Frankfurt. For more details, see www.molecular-simulation.org
The main topic of the Behler group is the development and implementation of accurate and efficient potential-energy surfaces for complex systems using artificial neural networks and electronic structure methods. These potentials are applied to study problems in materials science, heterogeneous catalysis and solvation.

Neural Network Potentials

The reliability of the results obtained in computer simulations of chemical processes strongly depends on the quality of the underlying potential-energy surface. While electronic structure methods like density-functional theory (DFT) provide an accurate description of the atomic interactions, the high computational costs prevent the investigation of many interesting problems. In recent years artificial neural networks, which are trained to first-principles data, have become a valuable tool to construct high-quality atomistic potentials (Fig. 1) [1-2]. We have been able to extend the applicability of this method to high-dimensional structures containing thousands of atoms, which now enables the simulation of large condensed systems [3-5] with an accuracy close to ab initio molecular dynamics simulations.

Materials Science

Neural network potentials (NNPs) are able to describe all types of bonding from covalent bonds via metallic bonding to dispersion interactions for equilibrium and non-equilibrium configurations with comparable accuracy making them ideal candidates for applications to materials science. Questions, which have been studied to date, include the high-pressure phase diagram of silicon [6], the graphite to diamond phase transition of carbon [7] as well as the phase change material GeTe [8].

Heterogenous Catalysis

The investigation of the structure of "real catalysts" including large-scale defects is an important prerequisite to study catalytic reaction mechanisms in detail. Employing neural networks, in the SFB 558 "Metal-Substrate Interactions in Heterogeneous Catalysis" we have been able to construct a potential for the copper-zinc-oxygen system, which is an important industrial catalyst for methanol synthesis (Fig. 2). This potential can provide total energies differing only a few meV per atom from DFT.

Water and Solvation

Water is the most abundant solvent in chemistry and of central importance for many chemical processes from biochemistry to the storage of energy in batteries. For understanding reactions in solution and at the solid-liquid interface, reactive water potentials, which are able to provide a reliable description of other species like ions and metal surfaces are required. NNPs, which we have developed in the context of the DFG cluster of excellence RESOLV – "Ruhr-Explores SOLVation" can be applied to water clusters [9] as well as to liquid water (Fig. 3) and can be used to speed up ab initio molecular dynamics simulations by several orders of magnitude.

Fig. 1: Schematic structure of a neural network potential [2]. In this example the energy \( E \) is a function of three coordinates \( G_1, G_2 \) and \( G_3 \).

Fig. 2: Model of a copper cluster supported at zinc oxide.

Fig. 3: Simulation of liquid water using a neural network potential.
Dr. Jörg Behler is the head of an independent Junior Research Group at the Lehrstuhl für Theoretische Chemie. He studied chemistry at the Universität Dortmund and obtained his PhD at the Fritz-Haber Institut der Max-Planck Gesellschaft and the Technische Universität Berlin under the supervision of Prof. Matthias Scheffler (2004). For his thesis he was awarded the Otto-Hahn medal of the MPG. After a postdoctoral stay at the Fritz-Haber Institut with Dr. Karsten Reuter he joined the group of Prof. Michele Parrinello at the ETH Zürich, USI Campus Lugano, in 2006. In 2007 he moved to the group of Prof. Dominik Marx at the Ruhr-Universität Bochum, where he established an independent Junior Research Group funded by a Liebig Fellowship of the Fonds der Chemischen Industrie (2007-2008), an Emmy Noether Group of the DFG (2008-2014) and a Heisenberg Fellowship of the DFG (2014-). In 2013 he was awarded the Hans G.A. Hellmann Prize of the Arbeitsgemeinschaft Theoretische Chemie. In 2014 he finished his Habilitation in theoretical chemistry. Homepage: http://www.theochem.rub.de/research/behler/index.html

Selected Publications


The main research interest of Volker Staemmler’s group has been and still is the development and application of advanced computational methods for the description of the electronic structure of molecules in open-shell and excited states using accurate wavefunction-based quantum chemical ab initio techniques. By an efficient treatment of electron correlation effects in such states an approximate coupled cluster program, called MC-CEPA, could be developed, which has been successfully applied to various systems with complicated electronic structures, as for instance in transition metal complexes.

For all of the following applications the own MC-CEPA program has been used.

Spectroscopic properties of small molecules

Accurate open-shell quantum chemical methods are needed for a proper description of spectroscopic properties, in particular electronic excitation energies, as well as for the calculation of potential energy surfaces for elementary chemical reactions. Our recent applications cover (a) ground and excited electronic states of small radicals, (b) molecular Rydberg states and (c) metastable molecular anions and dissociative electron attachment.

Adsorption of small molecules on oxide surfaces

The first decisive step in heterogeneous catalysis is the adsorption of the reactants (atoms, radicals, small molecules) on the solid surface of the catalyst. Using embedded cluster models combined with quantum-chemical methods we have studied the adsorption of atoms (H, Cu), small molecules (H₂, CO, NO, N₂) on oxide surface (Figure 1). The aim is to determine adsorption energies and geometries, adsorbate-induced modifications of the surface, change of the molecular properties upon adsorption, spectroscopic properties of adsorbed species.

Magnetic exchange coupling in transition metal complexes

The magnetic properties of transition metal complexes are characterized by the exchange coupling constant J, the g tensor and the zero-field splitting tensor D. Using our open-shell programs, in particular the MC-CEPA part, and including spin-orbit coupling we were able to calculate the energies of the different spin states for several transition metal complexes and to extract the parameters J, g, and D. In combination with ab initio molecular dynamics we have determined the magnetostructural dynamics of iron-sulfur cores in ferredoxin and Rieske proteins (Figure 2), by calculating the fluctuations of the antiferromagnetic coupling constant J at finite temperatures.

X-ray spectroscopy

X-ray spectroscopies of different kind are widely used experimentally to get element-specific information on the electronic structure of molecules. Such techniques are particularly important for adsorbates on solid surfaces. Our open-shell programs have been modified to calculate such spectra. Recent examples are X-ray photoelectron spectra (XPS) and NEXAFS (near edge X-ray absorption fine structure) spectra for Cl₂, N₂, and Cl₂ core levels in isolated and adsorbed molecules, Zn₂⁺ and Zn₂⁺ core levels in Zn metal and ZnO, and surface core level shifts in MgO. In many cases accompanying ab initio calculations are needed to understand and correctly interpret the experimental X-ray spectra.

Selected Publications

The main fields of research were physicochemical investigations predominantly at high pressures the accent being on phase behaviour and critical phenomena of fluid mixtures as well as supercritical fluid chromatography (SFC), investigations using thermal methods (DTA, DSC), application of pressure jump relaxation techniques, a.o.

Phase equilibria and critical phenomena of highly compressed fluid mixtures

The phase and critical behaviour of binary, ternary and more complex mixtures (lg, ll, gs etc.) between -200 °C and +400 °C and at pressures up to 4 kbar was measured, the investigations being of interest for fluid extraction and supercritical fluid chromatography (SFC) \([1,2]\). The measurements could be extended up to about 20 kbar by diamond anvil techniques \([3]\).

Supercritical Fluid Chromatography (SFC)

The use of highly compressed gases in their critical temperature range as mobile phases allows the separation of thermolabile and/or low-volatile substances and the determination of some physicochemical properties such as capacity ratios, diffusion coefficients, a.o. \([4]\).

Thermal methods (DTA, DSC) at high pressures

Selected substances (organic compounds, liquid crystals, plastic crystals) were studied by differential thermal analysis (DTA) up to 7 kbar and differential scanning calorimetry (DSC) up to 5 kbar \([5]\).

Pressure jump relaxation studies at high pressures

Experimental setups for pressure jump relaxation measurements up to 2 kbar were developed and used for investigations on the kinetics of phase separation in fluid mixtures and of chemical reactions in solution.

Selected Publications

\([1]\) G. M. Schneider, The continuity and family concepts - useful tools in Fluid Phase


Bei uns findest Du Deinen Traumberuf!

www.opusmundi.de

Besuch‘ uns auf

www.facebook.com/Opusmundi.de

Hol‘ Dir die App!

app.opusmundi.de
Wir gratulieren der RUB zum 50-jährigen Jubiläum!

Evonik. Kraft für Neues.

Sie wollen Pflanzen zum Leuchten bringen? Machen wir’s möglich!

Als ein weltweit führendes Unternehmen der Spezialchemie suchen wir kreative Naturwissenschaftler, die mit ihren innovativen Entwicklungen unsere Welt aktiv mitgestalten und bereichern. Erkennen Sie sich darin wieder? Dann entdecken Sie die zahlreichen Karrieremöglichkeiten auf evonik.de/karriere und werden Sie Teil unseres internationalen Teams.

Exploring opportunities. Growing together.