

1. GÖCH-Symposium 2007 "Physikalische Chemie in Österreich"

19.-20. Oktober 2007

Universität Wien, Fakultät für Chemie
Universitätszentrum Boltzmannngasse

Großer Hörsaal

Boltzmannngasse 1, A-1090 Wien

Abstracts

Organisation

Wolfgang Kautek - GÖCH-Arbeitsgruppe "Physikalische Chemie"

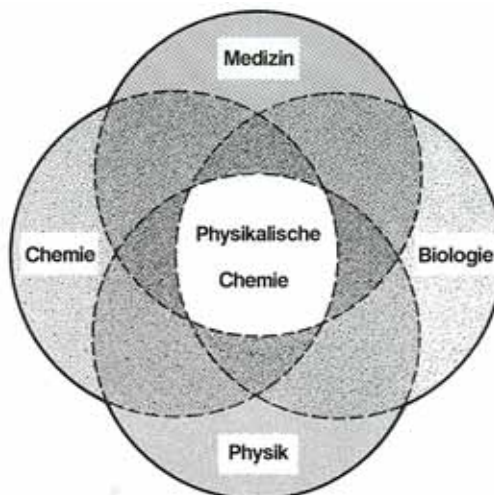
Organisationskomitee

Claudia Weber, Gabriela Ebner,
Magdalena Forster, Christoph Huber, Daniela Raab,
Günter Trettenhahn, Astrid Warter, Christian Zafiu

Vorwort

Die **Physikalische Chemie** ist eben durch die Verleihung des Nobelpreises für Chemie 2007 den Physikochemiker Gerhard Ertl für seine Studien an chemischen Prozessen an Festkörperoberflächen ins **weltweite Rampenlicht** gerückt worden.

Das zeigt, dass wir gut daran tun, alle Kräfte in **Physikalischen Chemie in Österreich zu bündeln**, um in dieser Grunddisziplin der Chemie im Brennpunkt der Naturwissenschaften - der Chemie, Physik, Biologie und Medizin - exzellente Beiträge zu leisten (siehe Schema).



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In diesem Sinne veranstaltet der **neu gegründete GÖCH-Arbeitskreis "Physikalische Chemie"** das **1. GÖCH-Symposium "Physikalische Chemie in Österreich"** an der Universität Wien. Dies tun wir im Bewusstsein, dass die 1897 gegründete Gesellschaft Österreichischer Chemiker (GÖCH) mit ihren mehr als 1900 Mitgliedern Österreichs größte chemische Gesellschaft ist (office@goech.at).

Die Motivation dieser Veranstaltung ist einerseits, dass sich die österreichischen Physikochemiker besser gegenseitig wahrnehmen, aber auch in familiärer Atmosphäre jedes Mal vor Ort ein Gastgeber-Labor kennen lernen können. Auf diese Weise beginnen wir einen Standort-Turnus der **GÖCH-Symposienreihe "Physikalische Chemie in Österreich"** in den österreichischen Universitätsstandorten Graz, Leoben, Linz, Innsbruck, Wien etc.

Ich danke dem Organisationskomitee, Frau Claudia Weber, Frau Gabriela Ebner, Mag. Magdalena Forster, Mag. Markus Gerd Fröhlich, Mag. Christoph Huber, Mag. Daniela Raab, Herrn Michael Schrems, Dr. Günter Trettenhahn und Mag. Christian Zafiu, für den unbezahlbaren Einsatz in der Vorbereitung und Durchführung des 1. GÖCH-Symposiums "Physikalische Chemie in Österreich".

Wien, 2007-10-15

Wolfgang Kautek
(Leiter der
GÖCH-Arbeitsgruppe "Physikalische Chemie"
Institut für Physikalische Chemie,
Universität Wien)



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1. GÖCH-Symposium 2007 "Physikalische Chemie in Österreich"

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Universität Wien, Fakultät für Chemie
Universitätszentrum Boltzmannngasse
Großer Hörsaal, Boltzmannngasse 1, A-1090 Wien

Organisation

Wolfgang Kautek - GÖCH-Arbeitsgruppe Physikalische Chemie

Organisationskomitee

Claudia Weber, Gabriela Ebner, Magdalena Forster,
Christoph Huber, Daniela Raab, Günter Trettenhahn, Christian Zafiu

Freitag, 2007-10-19

13:00 - 14:00

Registrierung

14:00 - 14:30	Begrüßung (1) GÖCH-Arbeitsgruppe Physikalische Chemie (2) Dekan der Fakultät für Chemie der Universität Wien (3) Deutsche Bunsen-Gesellschaft für Physikalische Chemie	Wolfgang KAUTEK Franz DICKERT Helmut BAUMGÄRTEL
14:30 - 14:50	Kurzpräsentationen der Institute (1) Johannes Kepler Universität Linz Physikalische Chemie	Serdar SARICIFCI
14:50 - 15:10	Universität Innsbruck Institut für Physikalische Chemie	Erminald BERTEL
15:10 - 17:30	Postersitzung "Physikalische Chemie in Österreich"	Getränke, Kaffee und Kuchen
17:30 - 17:50	Kurzpräsentationen der Institute (2) Karl-Franzens Uni Graz Institut für Chemie	Christoph KRATKY
17:50 - 18:10	Technische Erzherzog Johann Universität Institut für Physikalische und Theoretische Chemie	Georg GESCHEIDT-DEMNER
18:10 - 18:30	Technische Erzherzog Johann Universität Institut für Physikalische und Theoretische Chemie	Günter GRAMPP
anschließend	Gemeinsamer Heuriger	

Samstag, 2007-10-20

09:00 - 09:10	Begrüßung	
	Kurzpräsentationen der Institute (3)	
09:10 - 09:30	Montanuniversität Leoben Institut für Physikalische Chemie	Werner SITTE
09:30 - 09:50	Technische Universität Wien Institut für Materialchemie	Günther RUPPRECHTER
09:50 - 11:30	Postersitzung "Physikalische Chemie in Österreich"	Getränke, Kaffee und Kuchen
	Kurzpräsentationen der Institute (4)	
11:30 - 11:50	Technische Universität Wien Institut für Chemische Technologien und Analytik	Jürgen FLEIG
11:50 - 12:10	Universität Wien Institut für Physikalische Chemie	Wolfgang KAUTEK
12:10 - 12:30	Diskussion & Ausblick	
13:00 - 14:00	Möglichkeit des Besuchs des Instituts für Physikalische Chemie Universität Wien	

Kurzpräsentationen der Institute

All Organic “Plastic” Optoelectronic Devices

o.Univ.Prof.Dr.Mag. Niyazi Serdar Sariciftci
*Physikalische Chemie and
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Abstract

Our Institute’s activities on organic semiconductor based photovoltaic diodes (“plastic solar cells”), organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs) are reviewed. The photophysics of such photovoltaic devices is based on the photoinduced charge transfer from donor type semiconducting conjugated polymers onto acceptor type conjugated polymers or acceptor molecules such as Buckminsterfullerene, C₆₀. Similar to the first steps in natural photosynthesis, this photoinduced electron transfer leads to a number of potentially interesting applications which include sensitization of the photoconductivity and photovoltaic phenomena as well as photoresponsive organic field effect transistors (photOFETs). Examples of photovoltaic architectures are discussed with their potential in terrestrial solar energy conversion. Furthermore, organic polymeric/inorganic nanoparticle based “hybrid” solar cells will be introduced and their potential discussed. OLEDs based on energy transfer systems as well as the field of OFET devices are also reviewed with a forecast on future work in our research field.

1) "Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene"

N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science* Vol. 258, 1474 (1992).

2) "Semiconducting Polymer - Buckminsterfullerene Heterojunctions: Diodes, Photodiodes and Photovoltaic Cells", N. S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. J. Heeger and F. Wudl, *Appl. Phys. Lett.* Vol. 62 (6), 585 (1993).

3) "Plastic Solar Cells"

Christoph J. Brabec, N. Serdar Sariciftci, Jan Kees Hummelen, *Advanced Functional Materials*, Vol. 11 No: 1, pp.15-26 (2001) (this paper was selected by ISI as the top 12. cited paper in the last ten years of material science).

4) "Bio-Organic Semiconductor Field Effect Transistors based on DNA Gate Dielectric"

Th. B. Singh, N. S. Sariciftci, J. Grote, F. Hopkins, *Journal of Applied Physics*, Vol 100, 24514 (2006).

5) "Organic Photovoltaics Concepts and Realization", edited by C. Brabec, V. Dyakonov, J. Parisi and N.S. Sariciftci (eds.), Springer-Verlag, Germany, 2003.

6) "Organic Photovoltaics", edited by S.-S. Sun and N.S. Sariciftci, Taylor & Francis, Florida, USA, 2005.

6) "[Progress in Plastic Electronics Devices](#)", B. Singh, N.S. Sariciftci
Annual Review of Materials Research Vol. 36 (2006), 199-230

Institut für Physikalische Chemie der Universität Innsbruck

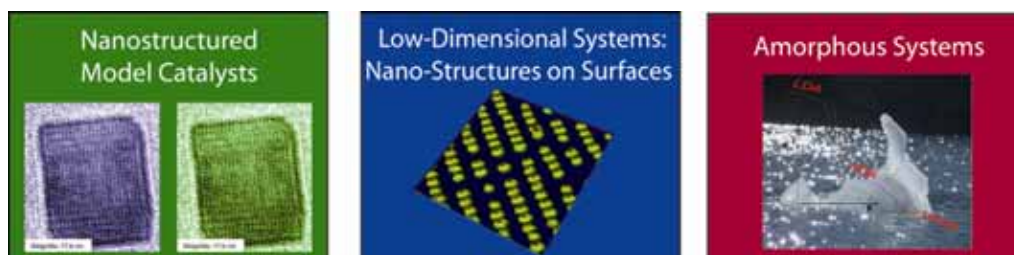
Innrain 52a, A-6020 Innsbruck; <http://www.uibk.ac.at/physchem/>
Vorstand: Univ.-Prof. Dr. Erminald Bertel, Tel.: (0512) 507 5050,
email: erminald.bertel@uibk.ac.at

Am Institut für Physikalische Chemie der Universität Innsbruck werden drei Themenbereiche bearbeitet: Nanostrukturierte Modell-Katalysatoren, Niederdimensionale Systeme auf Oberflächen und Amorphe Materialien.

Katalytische Eigenschaften nanostrukturierter Teilchen und Oberflächen werden in Zusammenarbeit mit dem Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin untersucht und optimiert. Modellkatalysatoren werden durch Modifikation von Einkristall-Oberflächen, in Form von sogenannten invertierten Modellkatalysatoren (Oxid auf Metall) und als Dünnschicht-Katalysatoren hergestellt und mit Transmissions-Elektronen-Mikroskopie charakterisiert. Im Zuge dieser Untersuchungen wird auch das kontrollierte Wachstum von Oxid-Nanoteilchen studiert. Katalytische Prozesse werden mit Massen-Spektrometrie, Gas-Chromatographie und Röntgenphotoelektronen-Spektroskopie (XPS) unter Verwendung von Labor- und Synchrotron-Lichtquellen verfolgt. Mit Hochdruck-Zellen und Molekularstrahl-Methoden sind anwendungsnahe Druckbereiche zugänglich (B. Klötzer, S. Penner).

In einer zweiten Arbeitsgruppe wird die elektronische Struktur und das Phasendiagramm niederdimensionaler, d.h. zwei-, ein- und null-dimensionaler Systeme auf Metalloberflächen mittels winkelauflösender UV-Photoelektronenspektroskopie, Raster-Tunnel-Mikroskopie und Beugung niederenergetischer Elektronen analysiert. Unterschiedliche Mechanismen der Selbststrukturierung werden untersucht und zur Herstellung periodischer Ketten- und Cluster-Anordnungen verwendet. In niederdimensionalen Systemen spielt Elektronen-Korrelation eine wesentliche Rolle und führt zum Auftreten von symmetriegebrochenen Phasen mit Ladungs-, Spin- oder Orbital-Ordnung. Auch Mott-isolierende und supraleitende Phasen treten auf, weshalb das Phasendiagramm solcher stark korrelierter Systeme sowohl aus der Sicht der Grundlagenforschung als auch in Hinblick auf technische Anwendungen von größtem Interesse ist (E. Bertel, N. Memmel, A. Menzel).

Eine dritte Arbeitsgruppe befasst sich mit „Phasenübergängen“ in amorphen Materialien, insbesondere in Wasser und Eis. Die Charakterisierung amorpher Zustände ist ein offenes Forschungsgebiet. Die Umwandlung zwischen unterschiedlichen amorphen Zuständen weist starke Parallelen zu klassischen Phasenübergängen nach Ehrenfest auf, weswegen auch in diesem Fall von „Phasenübergängen“ gesprochen wird. Analog dem Polymorphismus kristalliner Substanzen weisen amorphe Systeme einen Polyamorphismus auf. Neben der Entdeckung und Charakterisierung neuer Phasen bzw. Zustände ist vor allem die Kinetik der Phasenbildung, die Relaxationsdynamik auf molekularer Ebene und die Natur der Umwandlung zwischen verschiedenen amorphen Zuständen Gegenstand der Forschung in dieser Arbeitsgruppe. Bevorzugte Analysemethoden sind Röntgen- und Neutronenbeugung, Schwingungsspektroskopie, differentielle Kalorimetrie und Hochdruck-Dilatometrie (T. Lörting).



Structural Biology of Enzymes, Allergens and S-Layer Proteins

Christoph Kratky, Karl Gruber, Walter Keller, Monika Oberer & Ulrike Wagner

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Karl Franzens Universität
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The Structural Biology laboratory is located at the Institute of Chemistry / Physical Chemistry at the University of Graz. The laboratory – which by now consists of 4 research groups with a total of about 20 scientists – has been actively involved in crystallographic structure determination of biomolecules for many years. Research interests have focussed on the B₁₂ cofactor, both in its free and enzyme-bound state, enzymes relevant for biocatalysis, enzymes relevant for lipid biosynthesis, allergens and S-layer proteins. Members of the laboratory have participated and / or are participating in a variety of nationally and internationally funded research networks as well as national stand-alone projects. State-of-the-art instrumentation is available thanks to recent infrastructure funding, including graphic workstations, rotating anode X-ray generators equipped with multilayer optics and MAR-imaging plate goniometers for protein crystallography. The equipment and know-how of the laboratory also includes comprehensive facilities for the expression, purification and biochemical analysis of recombinant proteins, as well as instruments for the biophysical characterisation of enzymes (spectrometers, biocalorimeters, stopped-flow instruments). Expertise exists for complementary experimental and theoretical techniques, such as low-angle scattering, X-ray absorption spectroscopy, neutron diffraction, molecular modelling and structural bioinformatics. The laboratory has been upgraded by the purchase of high-throughput crystallization equipment. Very recently, the laboratory was relocated into the newly built Center for Molecular Biosciences.

Insights into the Reactivity of Paramagnetic Systems

Georg Gescheidt

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Graz University of Technology
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The reactivity of paramagnetic systems is at the focus of the research performed in our group. This presentation will highlight some recent projects comprising time-resolved EPR studies of radical reactions, CIDNP investigations of photoinduced processes, antioxidants, and enantioselective homogeneous catalysis.

References

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- (2) Dietliker, K.; Broillet, S.; Hellrung, B.; Rzedek, P.; Rist, G.; Wirz, J.; Neshchadin, D.; Gescheidt, G. *Helv. Chim. Acta* **2006**, *89*, 2211-2225.
- (3) Hristova, D.; Gatlik, I.; Rist, G.; Dietliker, K.; Wolf, J.-P.; Birbaum, J.-L.; Savitsky, A.; Moebius, K.; Gescheidt, G. *Macromolecules* **2005**, *38*, 7714-7720.

Research Group:

Spectroscopy and Chemical Kinetics

O.Univ.Prof.Dr.Günter Grampp

Ao.Univ.Prof.Dr.Stephan Landgraf

The main research activities are on the field of various charge transfer reactions in solution, on photoinduced electron transfer reactions, on the dynamics of biradicals, on spin exchange reactions, on the kinetics of redox reactions and on magnetic field effects in chemistry, etc.

Kinetic data obtained are compared with recent theories of diffusion and electron transfer theories (Marcus Theory).

Various spectroscopic and kinetic techniques are used to investigate these and related reactions:

1.) ESR-Spectroscopy:

- Kinetics of Electron-Self Exchange Reactions of organic redox couples and the application of Marcus-Theory [1].
- Intramolecular charge transfer reactions within organic donor-acceptor systems.
- High pressure ESR-spectroscopy for chemical kinetics.
- Dynamics of biradicals and spin exchange reactions in solution [2].
- Correlation times and electron transfer reactions of radicals in ionic liquids [3].

2.) Photochemistry

- Modulated fluorescence spectroscopy, single-photon counting and laser spectroscopy are used for the kinetics of photoinduced electron transfer reactions. Application of modern diffusion theories (integral encounter theory etc.) to chemical kinetics [4,5].
- Deviations from linear Stern-Volmer plots caused by diffusion, etc. [6].
- Triplet quenching reactions.
- Energetics of exciplex formation.

3.) Magnetic Field Effects in Chemistry

- Application of M.A.R.Y. (MAGnetic Field Effect on Reaction YIELD)-spectroscopy to the kinetics of electron transfer and photoionization reactions [7].

4.) Electrochemistry

- Photomodulated voltammetry for the determination of redox properties of short living organic radicals [8].
- Rotating disc electrode measurements on diffusion coefficients.

[1] "ESR and ENDOR Investigations of the Degenerate Electron Exchange Reactions of Various Viologens in Solution. Solvent Dynamical Effects", G. Grampp, B.Y. Mladenova, D.R. Kattinig, S. Landgraf, *Appl. Magn. Reson.* **30**, 145-164(2006).

[2] "Effect of Solvent Nature on Spin Exchange in Rigid Nitroxide Biradicals", A.I. Kokorin, V.A. Tran, K. Rasmussen, G. Grampp, *Appl.Magn.Res.* **30**, 35-42(2006).

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- [6] “On the Coherent Description of Diffusion-Influenced Fluorescence Quenching Experiments“, A. Rosspeintner, D. R. Kattinig, G. Angulo, S. Landgraf, G. Grampp, A. Cuetos, *Chem. Eur. J.* 13, 6278-6286 (2007).
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- [8] “Solvent influence on the electrochemical reduction of photochemically generated *cis*-azobenzene”, G. Grampp, C. Muresanu, S. Landgraf, *J. Electroanal. Chem.* 582, 171-178 (2005).

Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben

Franz-Josef-Straße 18, A-8700 Leoben;

Leiter: Univ.-Prof. Dr. Werner Sitte

Die **Forschungsaktivitäten** des Lehrstuhls für Physikalische Chemie konzentrieren sich auf das interdisziplinäre Gebiet „Solid State Ionics“. Die Aktivitäten betreffen vor allem den Masse- und Ladungstransport von ionisch und gemischt ionisch-elektronisch leitenden Festkörpern sowohl durch den Bulk als auch über/entlang Grenzflächen (Korngrenzen, Elektroden, Oberflächen) unter Einbeziehung der Defektchemie. Dabei spielen Sauerstoffaustauschprozesse zwischen Gasphase und Oxidkeramik eine wichtige Rolle. Weitere Aktivitäten betreffen die defektchemische Modellierung komplexer Oxide, die analytische und numerische Modellierung von Diffusionsprozessen in polykristallinen Materialien sowie die thermodynamische Berechnung und Modellierung von Multikomponentensystemen. Die Forschung beinhaltet sowohl grundlegende Fragestellungen als auch Aspekte der Anwendung. So werden im Detail die Kinetik der Sauerstoffeinbaureaktion in Kathodenmaterialien sowie die Transporteigenschaften von Festelektrolyten von Hochtemperatur-brennstoffzellen (SOFCs) untersucht. Weiters stehen die elektrischen Eigenschaften von Grenzflächen-kontrollierten elektrokeramischen Bauelementen als Funktion des Herstellungsprozesses im Mittelpunkt des Interesses.

Die chemische und elektrochemische Charakterisierung von ionisch und gemischt ionisch-elektronisch leitenden Materialien basiert auf folgender **Infrastruktur**:

- Messstände zur Messung der elektronischen und ionischen Leitfähigkeit mittels Gleich- und Wechselstrommethoden (Impedanzspektroskopie) als Funktion des Sauerstoffpartialdruckes (Sauerstoffnichtstöchiometrie) und der Temperatur
- Thermische Analyse (TG/DTA/DSC/DIL)
- Messstände für chemische und elektrische Relaxationsexperimente zur Bestimmung der Sauerstoffaustauschkinetik von Oxiden
- Rasterelektronenmikroskopie mit EDX, (Hochtemperatur)-Röntgendiffraktometrie
- Einrichtungen für die mechanische Probenbearbeitung (Schwingmühle, Schleif- und Poliereinrichtungen, Diamantsägen, Pressen etc.)
- Zugang zu analytischen Methoden im Rahmen des Departments (Röntgenfluoreszenzanalyse, ICP-MS, Atomabsorption).

Am Lehrstuhl für Physikalische Chemie sind derzeit fünf wissenschaftliche Mitarbeiter und vier Doktoranden tätig.

Institute of Materials Chemistry, Vienna University of Technology

The scientific mission of the institute is the investigation of structure-property relationships of modern nanoscale materials. The institute was founded in 2001 by combining the former institutes of physical and theoretical chemistry and parts of the former institute of inorganic chemistry to achieve synergies in the area of materials chemistry. The research groups of the institute are currently headed by two full professors (Rupprechter, Schubert) and four assistant professors (Dozenten) (Blaha, Diwald, Grothe, Kickelbick). Two professors retired in September 2007: Erich Knözinger (physical chemistry) and Karl-Heinz Schwarz (theoretical chemistry). The current research activities of the physical chemistry section are as follows:

Oliver Diwald: Nanostructured metal oxide surfaces and interfaces play a key role in materials research and technology such as in heterogeneous catalysis, sensors or solar energy conversion. Aim of the group is to investigate the chemical and physical activity of specific local surface structures present on metal oxide nanoparticles as model systems. Diverse preparative techniques such as chemical vapour deposition or hydrothermal processing are applied for the production of morphologically well-defined solids such as MgO cubes or titanate wires and tubes. UV/Vis diffuse reflectance, photoluminescence, electron paramagnetic resonance and IR spectroscopy are applied for their characterization in conjunction with X-ray diffraction and microscopy studies, and quantum-chemical calculations (cooperation with A. Shluger et al., University College London). In addition the group is interested to elucidate the mechanism of self-organization during the formation process of shaped metal oxide nanoparticles and to tailor their optoelectronic and chemical surface properties *via* the choice of synthesis parameters and additional surface functionalization steps. The assembly of such nanoparticles in a controlled way into a larger mesoscopically structured network represents a next step of the research activities.

Hinrich Grothe: The focal point of the investigations in the group is on particles in the micrometer and sub-micrometer range. These are carbon, ice and metal oxide particles, many of which have relevance as atmospheric aerosols and are studied in laboratory models. Particular attention is paid to nucleation mechanisms, phase compositions, phase transitions and morphologies of these particles. The group is also interested in the interaction between the particles and the gas phase, the particle's reactivity and functionalization. Currently, the oxidation, nitration and halogenation of carbon particles are investigated. Cooperation with a German researcher group exists targeted to the latter issue. A recent research proposal deals with the interaction of water with different halogen oxides. These hydrate complexes are important intermediates in the sea salt activation – a process where halogen oxides are released from sea salt surfaces by the reaction with nitrogen oxides. These transient species will be stabilized and analyzed by matrix isolation infrared spectroscopy, a sophisticated low-temperature technique.

Günther Rupprechter: The group focuses on molecular-level studies of structure-property relationships and mechanisms in heterogeneous catalysis. Comparison of results obtained from oxide supported noble metal nanoparticles and from single crystal surfaces allows determining functionalities and specific properties that require nanoscale structures. Spectroscopic measurements during catalytic reactions are performed both under ultrahigh vacuum (UHV) and ambient pressure, to reveal the effect of gas pressure that is often neglected in model studies. In-situ vibrational spectroscopy (polarization-modulation IR reflection absorption spectroscopy) is mostly applied and complemented by high-pressure photoelectron spectroscopy (XPS) and other methods within collaborations. The group performs studies in parallel on UHV-grown model catalysts and industrial-grade catalysts which allows to reveal the specifics of technological materials. Systems studied include CO oxidation and hydrogenation, hydrocarbon hydrogenation, methanol decomposition and partial oxidation, etc. The group has also developed new instrumentation such as an extended UHV surface and interface analysis system (sample preparation and transfer under UHV), coupled to a high pressure reactor fitted for in situ IR spectroscopy and to a load-lock system for analysis of technical materials.

ELEKTROCHEMIE AN DER TU WIEN

Jürgen Fleig

Institut für Chemische Technologien und Analytik

Technische Universität Wien

Im Rahmen der Reorganisation der Fakultät für Technische Chemie fusionierten 2001 das ehemalige Institut für Technische Elektrochemie mit drei weiteren Instituten (Analytik, Chemische Technologie Anorganischer Stoffe, Strukturchemie) zum neuen Institut für Chemische Technologien und Analytik. Die Aktivitäten der seither im „Bereich Elektrochemie“ dieses Instituts angesiedelten elektrochemisch orientierten Gruppen reichen von Korrosion/Korrosionsschutz/galvanische Schichten über Festkörperelektrochemie bis zu Brennstoffzellen und elektrokeramischen Bauelementen. Sowohl sehr grundlegende Fragestellungen z.B. zu den physikalisch-chemischen Mechanismen von Elektroden-polarisation als auch anwendungsnahe, in Industriekooperationen durchgeführte Untersuchungen z.B. zur elektrochemischen Oberflächenbehandlung stehen auf der Agenda.

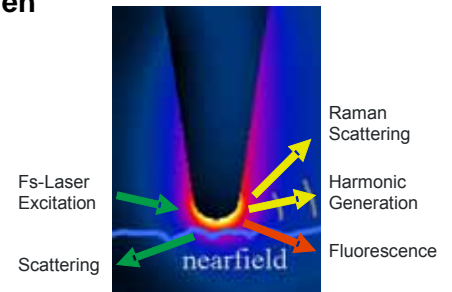
In diesem Kurzvortrag sollen exemplarisch einige Forschungsaktivitäten aus dem Feld der Festkörperelektrochemie vorgestellt werden. Dieses sich sehr dynamisch entwickelnde, international auch „Solid State Ionics“ genannte Teilgebiet der Elektrochemie zeigt gleichzeitig, dass moderne Elektrochemie weit über die klassischen Themen wässriger Elektrolyte hinausreicht und durch feste oder flüssige nichtwässrige Ionenleiter (Ionenkristalle, Polymere, organische Elektrolyte, etc. z.B. für Li-Ionenbatterien oder Brennstoffzellen) stark mitgeprägt ist. Forschung im Feld „Solid State Ionics“ ist häufig inspiriert durch die Anwendung von Oxiden in Brennstoffzellen, Sensoren oder elektrokeramischen Bauelementen (Kondensatoren, Piezoelektrische Aktuatoren, etc.). Einige der sich dabei ergebenden grundlegenden physikalisch-chemischen Fragestellungen werden an der TU Wien mit neuen Methoden und Ansätzen angegangen. Insbesondere werden Mikroelektroden und Mikrokontaktimpedanzspektroskopie eingesetzt, um beispielsweise den Mechanismus der Sauerstoffreduktion an Festelektrolyten und die Leitungsmechanismen in elektrokeramischen Materialien (z.B. Perowskiten) zu untersuchen. Die verwendeten Mikroelektroden sind mit Hilfe von gepulster Laserdeposition oder Sputtern, Lithographie und Ionenstrahlätzen erzeugt und kommen bei Messtemperaturen bis 1000 °C unter verschiedenen Atmosphären zum Einsatz.

Universität Wien, Institut für Physikalische Chemie

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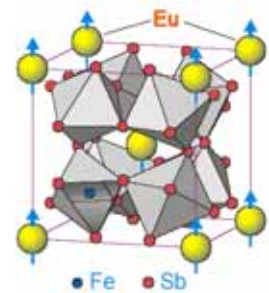
● **Physikalische Chemie und Nanotechnologien der Grenzflächen** Univ.-Prof. Dr.-Ing. Wolfgang KAUTEK

Multiphoton 3D-Microscopy,
In-situ-fs-Microscopy in aperture-free
Scanning Nearfield Optical Microscope (a-SNOM),
In-situ-fs-Laser-Nanostructuring by a-SNOM,
fs-Laser Excitation of Self-Organization of
biological, organic and inorganic solid surfaces in the nanoscale,
Femto-Electrochemistry of hot electrons (picosecond current pulses)
fs-Laser-Nanostructuring
Bioelectrochemistry: Proteins, self-organization
Laser-Cleaning of works of art and documents (paper, parchment, textiles etc.)
fs-Laser-Medicine: ophthalmology, dermatology etc.



● **Funktionelle Materialien**

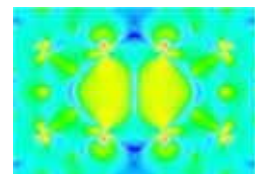
Univ.-Prof. Dr. Peter Franz ROGL
Novel Functions in Thermoelectric Materials
Refractory Superhard Materials & Corrosion Resistant High
Temperature Structural Materials
Titanium-Aluminium Base Alloys for Automotive Parts
Magneto-electric behavior of cerium, europium and ytterbium
compounds
Giant Magnetostrictive Materials based on Rare Earth



● **Komputative Physikalische Chemie und Polymerchemie**

A.o. Univ.-Prof. Dr. Peter HERZIG
A.o. Univ.-Prof. Dr. Irene SCHNÖLL-BITAI
A.o. Univ.-Prof. Dr. Gerhard ZIFFERER
A.o. Univ.-Prof. Dr. Raimund PODLOUCKY

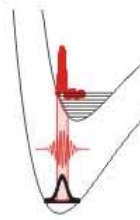
Atomistic Modelling of Systems and Processes



● **Chemische Physik**

A.o. Univ.-Prof. Dr. Harald KAUFFMANN

Optical Phase Control in Complex Molecules:
Electronic Spectroscopy in Two Dimensions
Sub-100 fs molekulare Wechselwirkungen
in 2 Dimensionen



● **Molekulare Bioenergetik**

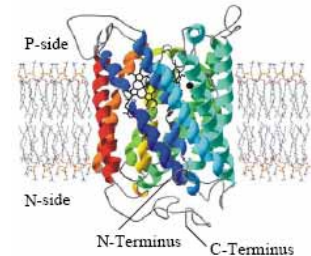
A.o. Univ.-Prof. Dr. Georg SCHMETTERER

A.o. Univ.-Prof. Dr Hans-Walter TROMBALLA

A.o. Univ.-Prof. Dr. Günter PESCHEK

Cyanobacteria (blue-green algae)

Respiratory electron transport and energy conversion (ATP synthesis), photosynthesis and respiration, enzymes responsible for the scavenging (detoxification) of reactive oxygen species (ROS).



● **Hochtemperatur-Thermodynamik
metallischer Systeme
eLearning**

A.o. Univ.-Prof. Dr. Josef TOMISKA

Knudsenzellen-Massenspektrometrie,

Didaktische Konzepte zur Neustrukturierung der Lehrinhalte
eLearning an der Fakultät für Chemie



● **Neue Materialien**

A.o. Univ.-Prof. Dr. Kurt HIEBL

A.o. Univ.-Prof. Dr. Julius C. SCHUSTER

Postersitzung
"Physikalische Chemie in
Österreich"

Organic solar cell research at the Linz Institute for Organic Solar Cells (LIOS)

R. Koeppe and N.S. Sariciftci
Linz Institute for Organic Solar Cells (LIOS)
Johannes Kepler University Linz
Altenbergerstr. 69
A-4040 Linz

The Linz Institute for Organic Solar Cells has been at the forefront of organic solar cell research since its founding by Prof. N.S. Sariciftci in 1997. The focus of research lies in the device physics, application of new materials and material systems as well as on fabrication routes and technological implementations of advanced solar cell concepts.

Efficient organic solar cells are based on the concept of a heterojunction, where two organic semiconductor materials with different electron affinities are brought in contact with each other. At this interface, photogenerated excitations are decaying via a photoinduced charge transfer mechanism to charges separated on the different materials. Extraction of these charges from a thin film (in the order of 100nm) gives rise to a highly efficient photocurrent generation in optimized devices. The most efficient organic solar cells are employing a so-called bulk heterojunction, where the two semiconductor materials are codeposited and relax into a nanoscale network during the film formation. Solar power conversion efficiencies of over 5% are reached in highly optimized devices.

There are two distinctly different ways to deposit thin films of organic semiconductor materials in controlled way: by processing from solution or condensation from the vapour phase in an evaporation procedure. In both cases, materials can be deposited simultaneously, leading to the desired intimate mixing in a bulk heterojunction. Both processes require certain compatibilities of the materials used.

The large range of organic semiconductors available for use in organic solar cells is enlarged by soluble inorganic nanomaterials that can be blended in matrices of organic semiconductors to yield organic-inorganic hybrid solar cells that utilize the advantages of both organic and inorganic semiconductors. Novel device concepts such as organic tandem solar cells, multicomponent solar cells or organic solar cells with external absorbers might further increase the performance of these devices to yield a cheap and versatile power source in the near future.

Recent literature:

"Conjugated Polymer Based Organic Solar Cells", S. Guenes, H. Neugebauer, N.S. Sariciftci, *Chemical Reviews* 107 (2007), 1324

"Morphology of polymer/fullerene bulk heterojunction solar cells", H. Hoppe, N.S. Sariciftci, *Journal of Materials Chemistry* 16 (2006), 45-6

"Photoinduced charge and energy transfer involving fullerene derivatives", R. Koeppe, N. S. Sariciftci, *Photochemical & Photobiological Sciences* 5 (2006), 1122

"Conjugated polymer photovoltaic devices and materials", A. Mozer, N.S. Sariciftci, *Comptes Rendus Chimie* 9 (2006), 568-577

"Flexible conjugated polymer-based plastic solar cells: From basics to applications", G. Dennler, N.S. Sariciftci, *Proceedings of the IEEE*, Vol 93, No 8 (2005)1429

"Low Bandgap Polymers for Photon Harvesting in Bulk Heterojunction Solar Cells", C. Winder, N.S. Sariciftci, *Journal of Materials Chemistry* Vol 14 (2004), 1077-1086

Photophysics of Conjugated Polymer/Fullerene Blends

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Abstract

The operation of organic photovoltaic devices such as solar cells is based on photophysical processes. After the photoexcitation of conjugated polymers, different processes can happen:

- formation of a singlet excitations
- relaxation via radiative (photoluminescence) or non-radiative pathways
- intersystem crossing (formation of triplet states)
- charge separation

Efficient charge separation is a basic requirement for organic photovoltaic devices. It can be achieved by mixing conjugated polymers with acceptor materials such as fullerenes. To probe photoinduced charge transfer, various techniques are used:

- transient photocurrent spectroscopy: photo-induced charge extraction by linear increasing voltage (photo-CELIV) and time of flight (TOF)
- absorption spectroscopy: photomodulated photoinduced absorption (PIA), transient PIA, light-induced electron spin resonance (LESR), Fourier transformed infrared absorption (FTIR)
- emission spectroscopy: photoluminescence (PL), photoluminescence excitation profile (PLE), transient PL and transient PLE profile

Literature

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A. Mozer and N.S. Sariciftci, Chapter 10 of the "Handbook of Conjugated Polymers Processing and Applications", edited by T.A. Skotheim and J.R. Reynolds, Third Edition, CRC Press, 2007
- [2] "[Stability Studies and Degradation Analysis of Plastic Solar Cell Materials by FTIR Spectroscopy](#)" H. Neugebauer, C. J. Brabec, J. C. Hummelen, R. A. J. Janssen and N. S. Sariciftci
Synth. Metals 102 (1999) 1002-1003
- [3] "[Photoinduced Charge Carriers in Conjugated Polymer-Fullerene Composites Studied with Light-Induced Electron Spin Resonance \(LESR\)](#)" V. Dyakonov, G. Zorinants, M. Scharber, C. J. Brabec, R. A. J. Janssen, J. C. Hummelen and N. S. Sariciftci
Phys. Rev. B 59/12 (1999) 8019-8025
- [4] "[Charge carrier mobility in regioregular poly\(3-hexylthiophene\) probed by transient conductivity techniques: A comparative study](#)" A. Mozer, N.S. Sariciftci, A. Pivrikas, R. Oesterbacka, G. Juska, L. Brassat, H. Baessler Physical Review B 71 (2005), 035214
- [5] "[Photoluminescence studies on the supramolecular interactions between a pyrrolidino fullerene and zinc-phtalocyanine used in organic solar cells](#)" R. Koeppel, P.A. Troshin, A. Fuchsbauer, R. N. Lyubovskaya, N.S. Sariciftci Full. Nanotub. Carb. Nanostruct. 14, 2-3 (2006), 441-446

Arbeitsgruppe Dr. Bernhard Klötzer/Dr. Simon Penner
Institut für Physikalische Chemie, Universität Innsbruck

Zentrales Thema der Arbeitsgruppe B.Klötzer/S.Penner ist die Herstellung, Charakterisierung und Untersuchung der katalytischen Eigenschaften nanostrukturierter Modell-Katalysatorpartikel- und Oberflächen. Das Hauptaugenmerk liegt dabei auf der Korrelation zwischen HV- und UHV-Charakterisierung und der Charakterisierung in anwendungsnahen Druckbereichen unter realen katalytischen Bedingungen. Zusammengefasst wird dies gemeinhin unter den Schlagwörtern „materials gap“ und „pressure gap“. In den letzten Jahren wurden verstärkt verschiedenartige Metall-Oxid Modell-Katalysatorsysteme untersucht, die Rückschlüsse sowohl auf die Wechselwirkung von Metall und Oxid als auch auf den Mechanismus katalysierter Reaktionen zulassen. Die untersuchten Systeme reichen von mit Oxid modifizierten Einkristall-Oberflächen und Metall-Folien (sogenannte „inverse“ Modellkatalysatoren) über Dünnschichtsysteme bis zu real-katalytisch relevanteren imprägnierten Modellsystemen. Konkret wurde die Metall-Oxid Wechselwirkung an verschiedenen SMSI („Strong Metal-Support Interaction“) Systemen studiert (Pt-CeO₂, Pt-SiO₂, Pt-Al₂O₃, Rh-CeO₂, Rh-V₂O₃, Pd-ZnO, Pd-V, Rh-Ce, Pd-Al₂O₃).

Die Schwerpunkte der Forschung liegen derzeit auf der Untersuchung struktureller und katalytischer Aspekte bimetallischer Katalysatorpartikel. Diese umfassen bimetallische oberflächennahe Legierungen bzw. dreidimensionale Legierungsphasen auf Einkristalloberflächen und polykristallinen Metallfolien. Die Katalysatoren werden mittels einer Kombination aus Oberflächenanalysemethoden (z. B. Röntgenphotoelektronenspektroskopie (XPS), Augerelektronenspektroskopie (AES), Nieder-Energie Ionenstreuung (LEIS), Temperatur-programmierter Desorption (TPD), Beugung langsamer Elektronen (LEED)), Molekülstrahlmethoden, Adsorptionstechniken (z. B. CO-Adsorption) und Katalyse unter Hochdruckbedingungen (z. B. CO Hydrogenierung, Methanol Dehydrogenierung und Dampfreformierung, Wasser-Gas Shift Reaktion) charakterisiert. Ein weiterer Teilbereich der Studien an den „inversen“ Modellkatalysatoren ist der Spektroskopie unter realen katalytischen Bedingungen gewidmet und umfasst hierbei vor allem in-situ XPS Untersuchungen mittels Synchrotronstrahlung am Bessy II im Rahmen einer Forschungs Kooperation mit dem Institut für Anorganische Chemie des Fritz-Haber Instituts der Max-Planck-Gesellschaft in Berlin. Die zu den „inversen“ bimetallischen Modellkatalysatoren komplementären Systeme umfassen bimetallische Dünnschicht- und die korrespondierenden imprägnierten Modellsysteme. Dies betrifft vor allem die reduktiv-induzierte Legierungsbildung an Oxid-getragerten Edelmetall-Katalysatorpartikeln wie Pt und Rh (z. B. Pt-CeO₂, Pt-SiO₂, Pt-Al₂O₃, Rh-CeO₂, Rh-V₂O₃, Pd-Al₂O₃), wird derzeit jedoch auf als aktive Katalysatoren für die Methanol Dampfreformierung bekannte Systeme wie Pd-ZnO, Pd-Ga₂O₃ und Pd-In₂O₃ erweitert. Zentrales Anliegen ist in diesem Zusammenhang die Aufklärung einer Struktur-Wirkungsbeziehung der für die Dampfreformierung aktiven Legierungsphasen Pd-X (X=Zn, Ga, In). Als geeignete Methoden der Charakterisierung kommen hier vor allem (hochaufgelöste) Transmissionselektronenmikroskopie (zum Teil im Rahmen einer Forschungs Kooperation mit dem Institut für Anorganische Chemie des Fritz-Haber Instituts), volumetrische Techniken wie temperatur-programmierte Reduktion, Oxidation oder Reaktion bzw. Elektrische Impedanzspektroskopie zum Einsatz und werden durch geeignete katalytische Untersuchungen ausgewählter Reaktionen ergänzt. Ein Teil dieser Untersuchungen betrifft auch reine Oxide (katalytische Eigenschaften, bulk/Oberflächenreduzierbarkeit bzw. neue Nanostrukturen wie z. B. Nanotubes, Nanowires und Nanospheres).



Arbeitskreis Thomas Loerting: „Amorphe Systeme“

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Mitarbeiter: Dipl.-Phys. Katrin Winkel
Dipl.-Chem. Michael S. Elsaesser
Dipl.-Min. Marion Bauer
Markus Seidl

Projekte: „HDA und VHDA in Relation zueinander“ (FWF)
„Charakterisierung von Kohlensäure“ (FWF)
„Mechanische Eigenschaften von Eis“ (FFG, Fa. AST)

Tieftemperatur-Analyseverfahren (ca. 10 K – 300 K):
Differenzielle Kalorimetrie (DSC bzw. DTA)
FT-IR Spektroskopie
Raman Spektroskopie
Hochdruck-Dilatometrie und Densitometrie (bis 20 kbar)
Röntgenpulverbeugung (XRD)
Isotopen-Substitutions Neutronenbeugung (am ISIS, England)
Phasenmodulierte Ellipsometrie

3 Themengebiete:

„Die Anomalien des Wassers“

mit Prof. John L. Finney, Dr. Daniel T. Bowron und Dr. Alan K. Soper (ISIS, UK)
mit Dr. Nicolas Giovambattista (Princeton)
mit Dr. Stefan Klotz (Univ. Pierre&Marie Curie, Paris)

Die Anomalien des Wassers sind im unterkühlten Zustand und im Druckbereich bis zu 2 kbar extrem ausgeprägt. Wir untersuchen daher nicht-kristallines Wasser bei tiefen Temperaturen unter Berücksichtigung der Druckachse. Zwei amorphe Zustände (LDA und HDA), die sich um 20% in der Dichte unterscheiden sind bereits seit 20 Jahren bekannt. Wir haben einen dritten amorphen Zustand (VHDA), der nochmals um 10% dichter ist, entdeckt und charakterisiert. Weiters konnten wir zeigen, dass im amorphen Zustand oberhalb von ~136 K ein flüssigkeitsartiges (!) Relaxationsverhalten einsetzt, ehe es zur Kristallisation kommt.

J. L. Finney, D. T. Bowron, A. K. Soper, T. Loerting, Erwin Mayer, Andreas Hallbrucker, **Phys. Rev. Lett.** 89 (2002) 205503.
T. Loerting, N. Giovambattista, **J. Phys. Cond. Matt.** 18 (2006) R919-R977.
I. Kohl, L. Bachmann, E. Mayer, A. Hallbrucker, T. Loerting, **Nature** 435 (2005) 440.

„Kohlensäure – Stabilisierung kurzlebiger, metastabiler Intermediate“

mit Prof. Sarah L. Price (University College London)

Kohlensäure konnte bis 1992 nicht in freier Form isoliert werden, weil sie für zu kurzlebig gehalten wurde. Mittels einer Kryotechnik ist es in Innsbruck erstmals gelungen, H_2CO_3 in freier Form zu isolieren und spektroskopisch zu charakterisieren. Es ist in weiterer Folge gelungen, einen zweiten Polymorph zu isolieren ($\alpha\text{-H}_2\text{CO}_3$ und $\beta\text{-H}_2\text{CO}_3$). Kürzlich konnten wir zwei (!) amorphe Vorläufer dieser beiden Polymorphe mittels Röntgenbeugung und Spektroskopie charakterisieren sowie die Kinetik der Kristallisation verfolgen. Unser nächstes Ziel ist es, aus den Röntgenbeugungsdaten die Kristallstrukturen zu lösen.

W. Hage, K. R. Liedl, A. Hallbrucker, E. Mayer, **Science** 279 (1998) 1332.
T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, K. R. Liedl, **Angew. Chem. Int. Ed.** 39 (2000) 891-894.
K. Winkel, W. Hage, T. Loerting, S. L. Price, E. Mayer, **J. Am. Chem. Soc.** (2007) to be published.

„Oberflächenschmelzen auf Eis: Implikationen für die Chemie der Atmosphäre“

mit Prof. Mario J. Molina (Massachusetts Institute of Technology, Univ. California San Diego)

Bei Temperaturen knapp unterhalb des Schmelzpunktes ist bei vielen verschiedenen Materialien Oberflächenschmelzen zu beobachten. Dies wurde bei Eis schon vor mehr als 100 Jahren durch Faraday beobachtet. Unsere Arbeiten zeigen erstmals, dass induziert durch Spurengase ein Oberflächenschmelzen auch beim *Abkühlen* (!) auftreten kann. Die „Chemie“ in dieser dünnen flüssigkeitsartigen Oberflächenschicht auf polaren stratosphärischen Wolken bei -80°C läuft so schnell ab, dass dadurch das Auftreten des polaren Ozonlochs erklärlich wird.

T. Loerting, A. F. Voegelé, C. S. Tautermann, K. Liedl, L. T. Molina, M. J. Molina, **J. Geophys. Res. (Atmospheres)** 111 (2006) D14307.
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Self-Assembly in Confinement – Structure, Stability and Transfer Kinetics

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^bnow at Department of Physics, University of Fribourg, Fribourg, Switzerland.

^cnow at CRMD, University of [Orléans](http://www.univ-orleans.fr), Orléans, France.

^dPermanent Address: Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia.

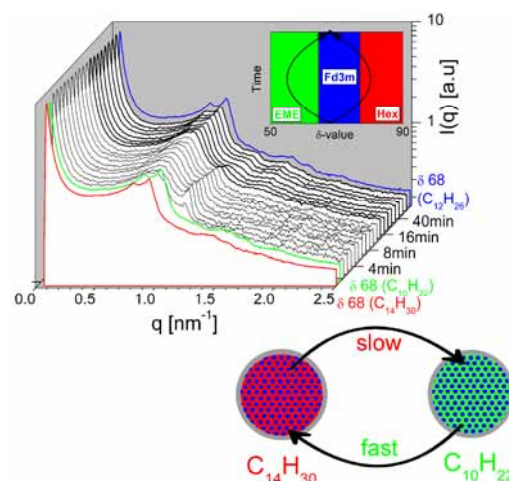
otto.glatter@uni-graz.at

In this contribution we present our latest results on hierarchically organized fluid particles, i.e., sub-micron sized droplets kinetically stabilized as an aqueous emulsion having a self-assembled nanostructured interior [1-7]. These systems were investigated by small angle X-ray scattering (SAXS), cryogenic transmission electron microscopy (Cryo-TEM) [7], and dynamic light scattering (DLS). The nanostructures in the kinetically stabilized particles are thermodynamic equilibrium structures. Recently we reported on the effect of varying temperature [1], solubilizing tetradecane [2] and changing oil type or monoglyceride purity [3,4] on the reversible structural transitions of the nanoscale interior domains of kinetically stabilized monolinolein (MLO)-based particles. We found that it is possible even at room temperature to emulsify W/O microemulsion systems by the addition of tetradecane (TC) to the MLO-water system [2]. The addition of TC induces a transition of the internal particle nanostructure from continuous Pn3m (cubosomes) to H₂ (hexosomes) and W/O microemulsions (EMEs) at a given temperature. We will also present TC-loaded particles with confined structure of Fd3m (discontinuous micellar cubic phase) [5]. Namely, we found that the addition of TC induces a transition of the internal particle nanostructure from Pn3m to H₂, and via Fd3m to EMEs at a given temperature.

Such nano-structured emulsions are stable over months, if not years, depending on their composition. Most interestingly, these systems allow us to study transfer of lipidic phases or of other molecules inserted to the interior of the droplets. After mixing two solutions with different loadings, one can measure the kinetics of transfer and equilibration if the internal structure depends on the solubilized materials [6].

So such hierarchically organized systems offer a unique possibility to study transfer between sub-micron sized confinements embedded in a continuous outer phase. In addition, these particles are potential candidates for carrier systems for functional molecules. These molecules can be lipophilic, amphiphilic or hydrophilic. Possible applications range from food systems, via pharmaceutical and cosmetic applications to plant protection systems.

- [1] L. de Campo, et al., *Langmuir* 20 (2004), 5254.
- [2] A. Yaghmur, et al., *Langmuir* 21 (2005), 569.
- [3] S. Guillot, et al., *Colloid. Surface. A* 78 (2006), 291.
- [4] A. Yaghmur, et al., *Langmuir* 22 (2006), 9919.
- [5] A. Yaghmur, et al., *Langmuir* 22 (2006), 517.
- [6] Ch. Moitzi, et al., *Adv. Materials* 19 (2007), 1352.
- [7] L. Sagalowicz, et al., *Journal of Microscopy* 110 (2006), 221..



Arbeitsgruppe „Interface Science“ am Institut für Chemie der Universität Graz

Volker Ribitsch

Der Schwerpunkt der Tätigkeit der Arbeitsgruppe sind Prozesse an der fest-flüssig Grenzfläche. Dies umfasst die Herstellung nano-strukturierter Schichten auf polymeren Substraten, die Einbettung von Nano-Partikeln in diese Oberflächen-Schichten, die Entwicklung selektiver opto-chemischer Sensorelemente und die Charakterisierung und Modellierung von Micro-, Ultra- und Nano-Filtrationsmembranen.

Polymer Interfaces – Schwerpunkt Funktionsmaterialien aus nachwachsende Rohstoffen

(Im Rahmen des European Polysaccharide Networks of Excellence EPNOE und in Kooperation mit der Universität Maribor (Slo), Jena (BRD) und Hull (GB))

Entwicklung von Grenzflächen-Prozessen zur Erzeugung funktioneller Polymer – Nanopartikel Oberflächenkomposite mit außergewöhnlichen Oberflächen-Eigenschaften (mechanische, chemische, thermische Eigenschaften, selektive Wechselwirkungen, strukturierte Funktionalitäten). Die Oberflächen-Funktionalisierung wird sowohl durch adsorptive Wechselwirkung als auch durch kovalente Bindung einer Dispersion von Nanopartikeln in löslichen Polymeren auf den Substraten erreicht. Die funktionellen Beschichtungen sind für chemisch unterschiedliche polymere Substrate wie Fasern aus Regeneratzellulose und auch synthetische Polymere anwendbar.

Herstellung und Schichtbildung photokatalytisch aktiver oder halbleitender Nanopartikel

(in Kooperation mit Joanneum Research und der TU Graz, ICTOS)

Diese Systeme haben einen weiten Einsatzbereich, von organischer Elektronik über katalytisch wirksame Oberflächen bis zu Gassensoren. Ihre Herstellung erfolgt teilweise bottom up durch Reduktionsprozesse oder top down durch high-shear Dispergierung. Die Stabilisierung zur Verarbeitung in der flüssigen Phase ist ein wesentliches Problem, das durch die Auswahl entsprechender Tensidsysteme gelöst wird.

Opto-chemische Sensor Systeme

(in Kooperation mit Joanneum Research und der TU Graz, ICTOS)

Die Entwicklung der opto-chemischen Sensorik ermöglicht die Messung von O₂, CO₂ und pH in Prozesswässern und der Biotechnologie. Der Einsatz in der biologischen Forschung und in der Diagnose erfordert miniaturisierte und selektive Systeme, bei denen Effekte wie FRET (Fluoreszenz Resonanz Energie Transfer) zum Einsatz kommen. Die Entwicklungen im Bereich organischer Leuchtdioden und Photodetektoren öffnen zudem weitere Möglichkeiten für den Einsatz in kostengünstigen BioChips, für die simultane Detektion von mehreren Parametern in der Biotechnologie und Sicherheitstechnik.

Membrane Technology (in Kooperation mit der Universität Barcelona und Moskau)

Die Membran-Aktivitäten umfassen die Charakterisierung von Mikro-, Ultra- und Nano-Filtrationsmembranen, die Untersuchung des fouling-Mechanismus und der Konzentrations-Polarisation bei der Nanofiltration und in nanofluidischen Systemen. Weiters wird an der Entwicklung eines mathematischen Modells zur Beschreibung des fouling-Prozesses in Ultra- and Nano-Filtrationssystemen und an neuen Methoden zur Membrancharakterisierung (druckgetriebene Verfahren, Chronopotentiometrie) gearbeitet.

Long Range Thermal Charge Transfer in Purely Organic Mixed-Valence Compounds

D. Kattnig, B. Mladenova and G. Grampp

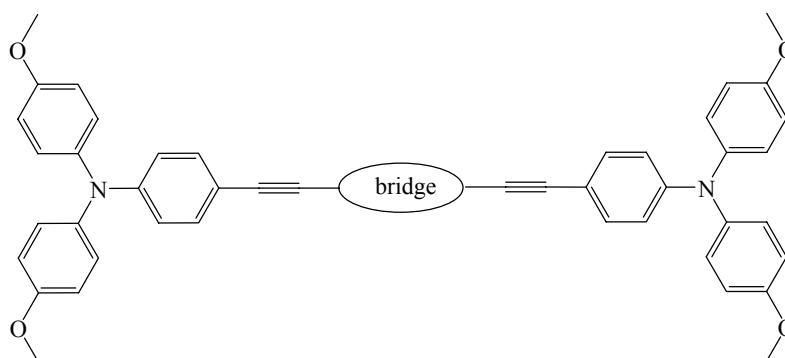
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Keywords: EPR, Intervalence Charge Transfer, Temperature Dependence, Solvent Friction Effects

Abstract

We have investigated the radical cations of a series of bistriarylamine derivatives, which have been classified as purely organic mixed valence compounds belonging to the Robin/Day class II (localized redox centres). The compounds follow the general structural principle shown below, with the π -conjugated bridges comprising ethynyl, phenylen, anthracene and [2,2]paracyclophane moieties. In particular, the distance between the amine groups amounts up to 28.7 Å corresponding to 25 unsaturated C-C bonds.



The species are known to show rather strong intervalence charge-transfer (IV-CT) bands in the NIR, which have previously been used to extract the electron coupling matrix elements, V , and the reorganization energies, λ , in the framework of Marcus-Hush theory [1-3]. As opposed to the optical charge transfer, the ultrafast thermal electron transfer has not yet been investigated. Thus, we have studied the latter process by temperature dependent EPR spectroscopy in methylene chloride, acetonitrile and *o*-dichlorobenzene as solvents. Although only three unresolved hyperfine components are apparent from the EPR spectra in the slow exchange region, simulations assuming merely two exchanging nitrogens yield only scarce agreements with experimental data. In fact, it was necessary to investigate the hyperfine structure due to the surrounding protons in more detail. On the basis of model compounds that comprise only a single triarylamine centre we could extract several hyperfine components by ENDOR spectroscopy, which aided the simulation of the exchange spectra. A simulation program based on the density matrix formalism similar to Heinzer's approach [4] has been devised to extract the kinetic information by simultaneously fitting all spectra of a temperature series. Experimental activation energies are compared to those extracted from the IV-CT transitions and *ab initio* simulations. Effects of the structural peculiarities of the bridge on the electron exchange rate are discussed. Solvent friction effects on the electron transfer have to be taken into account to model the experimental findings.

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- [3] A. Heckmann, S. Amthor and C. Lambert, *Chem. Comm.* **28** (2006) 2959.
- [4] J. Heinzer, *J. Magn. Reson.*, **13** (1974) 124.

Electron Self-Exchange Kinetics Determined by MARY Spectroscopy: Theory and Experiment

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The electron self-exchange between a neutral molecule and its charged radical, which is part of a spin-correlated radical ion pair, gives rise to line width effects in the fluorescence-detected MARY (magnetic field effect on reaction yield) spectrum similar to those observed in EPR spectroscopy. An increasing self-exchange rate (i.e., a higher concentration of the neutral molecule) leads to broadening and subsequent narrowing of the spectrum. Along with a series of MARY spectra recorded for several systems (the fluorophores pyrene, pyrene-*d*₁₀ and N-methylcarbazole in combination with 1,2- and 1,4-dicyanobenzene) in various solvents, a theoretical model is developed that describes the spin evolution and the diffusive recombination of the radical pair under the influence of the external magnetic field and electron self-exchange, thereby allowing the simulation of MARY spectra of the systems investigated experimentally. The spin evolution of the radicals in the pair is calculated separately using spin correlation tensors, thereby allowing rigorous quantum mechanical calculations for real spin systems. It is shown that the combination of these simulations with high resolution, low noise experimental spectra makes the MARY technique a novel, quantitative method for the determination of self-exchange rate constants. In comparison to a simple analytical formula which estimates the self-exchange rate constant from the slope of the linear part of a line width vs. concentration plot, the simulation method yields more reliable and accurate results. The correctness of the results obtained by the MARY method is proved by a comparison with corresponding data from the well-established EPR line broadening technique. With its less stringent restrictions on radical lifetime and stability, the MARY technique provides an alternative to the classical EPR method, in particular for systems involving short-lived and unstable radicals [1].

Recent EPR electron self-exchange measurements between the electrochemically generated radical anion of 1,2- and 1,4-dicyanobenzene and their corresponding neutral molecules in all solvents used in MARY spectroscopy show a good agreement of the determined rate constants [2] of both methods. Additionally calculations have been improved so that individual instead of averaged coupling constants can now be used in MARY simulations.

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HIGH PRESSURE CHEMISTRY: ELECTRON TRANSFER MEASURED BY ELECTRON SPIN RESONANCE SPECTROSCOPY

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At our labs we have constructed a high-pressure system for use in electron spin resonance (ESR) spectroscopy. The apparatus allows the application of pressures of up to 80 MPa to solutions and with several key solvent properties (viscosity, dielectric constant, relaxation times, refractive index) being pressure dependent, reaction kinetics may be probed via pressure variations.

Especially, solvent dynamic effects are of interest since they provide information about the role of the solvent during the electron transfer reaction [1]. Such effects have been observed in many self-exchange systems, whose kinetics are often studied by ESR line broadening experiments [2]. The obtained results are treated within the framework of the Marcus Theory, yielding valuable information on the energetics of the reaction, such as the activation parameters, and on the influence of the solvent [3].

In the case of pressure variations, the self-exchange rate constant is described by the volume of activation:

$$\Delta^\ddagger V = -RT \left(\frac{\partial \ln k_{ex}}{\partial P} \right)_T$$

When using self-exchange reactions involving an uncharged species, the volume of activation is determined by two separate contributions. One is owing to the reorganization of solvent molecules during the reaction, in analogy to the reorganization energy of Marcus (λ_o), while the other involves the dynamic effects:

$$\Delta^\ddagger V = \Delta^\ddagger V_o + \Delta^\ddagger V_{SD}$$

The two may be calculated separately using known data on the pressure dependencies of the relevant solvent properties, together with information on the self-exchange couple.

Experimental volumes of activation have been obtained for a number of combinations of solvents and exchange systems and subsequently been compared with the predicted ones. Additionally, we have been able to reinvestigate the solvent dynamic effect and make a comparison with results obtained using more traditional methods.

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Advances in LD/LED Modulation Fluorometry: Exploring the UV-Range with Subnanosecond Resolution

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Recent developments in semiconductor light source technology open a new field of photochemical investigations: excitation of molecules with UV light. Due to the effect that semiconductor light sources, such as laser diodes (LDs) and ultrabright light emitting diodes (LEDs), can be pulsed and modulated [1-3], time-resolved measurements down to less than 100 ps can be performed in an exceptionally simple way. Modulation technique is most accurate whereas single photon counting method offers more information on non-monoexponential decays. Both methods, available in a modular set-up, complement one another in a perfect manner.

In 1999 the first UV-LED became commercially available with a centre wavelength of 370 nm, 18 nm FWHM, 0.2 mW output power and 50 MHz transition frequency. Today LEDs and one LD (375 nm) are available covering the whole range between 250 and 400 nm. Very recent developments of UVTOP LEDs from 250 to 340 nm with very high transition frequencies of more than 400 MHz increase the number of possible applications dramatically. But there is still a lot of work to be done to remove long-wavelength background radiation and to find proper filter combinations. Recently it turned out that all these investigations are more and more important in UV-based fluorescence applications in biochemistry, medicine and analytical chemistry.

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Rehm-Weller and Stern-Volmer experiments in the light of remote electron transfer

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Photoinduced electron transfer (PET) in solution has been for a long time now an intensive research field. Even though, there are still basic questions to be revealed by classical experiments which remained unexplained and in contradiction with the widespread picture of the subject. Rehm-Weller (RW) and Stern-Volmer (SV) plots are well known, often used in photoinduced electron transfer studies and are usually described using classical, i.e. Markovian kinetics assuming contact reactions. In the case of Stern-Volmer plots [1] of diffusion assisted reactions this assumption is immediately to be lifted when going to high quencher concentrations and/or high solvent viscosities. The observation of an obvious non-linearity with quencher concentration is due to static quenching - per definition impossible within a contact reaction model - and the increasing importance of the transient effect (time-dependence of quenching rate constant).

A closer look at most of the Rehm-Weller plots, on the other hand, also reveals that the reactions get more and more remote the higher the exergonicity of the fluorophore-quencher pair under investigation [3]. This long known fact is actually much more appreciated and immediately seen when changing the usually chosen $\log k_q$ vs. ΔG anamorphosis to a linear one.

We obtained a Rehm-Weller plot in acetonitrile using one single fluorophore. The 20 different quenchers used allow for spanning a rather big change in reaction free energy for the PET (-1.5 to 0.2 eV). One of these fluorophore-quencher pairs was chosen as model system for obtaining Stern-Volmer plots at 8 different solvent viscosities (dmsu-glycerol mixtures) using a total of 150 data points. These two complementary experimental evidences (RW and SV plots) are analyzed and compared using the most comprehensive differential encounter theory [4], accounting not only for remote electron transfer, but also for hydrodynamic effects and solvent structure. The results show a basic inconsistency in the model because the reaction has to be considered adiabatic in acetonitrile while diabatic in the solvent mixtures [5].

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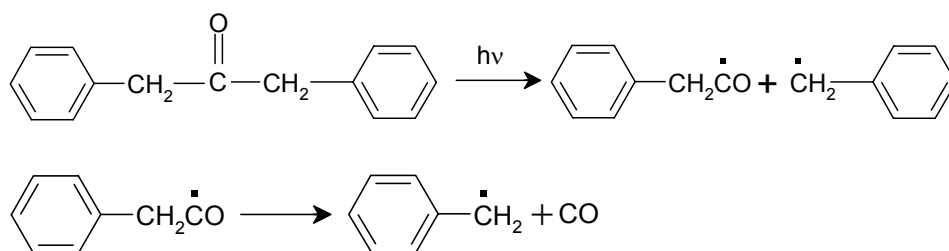
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Photomodulated voltammetry investigations on the benzyl radical

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Benzyl radicals were generated photochemically directly in the electrochemical cell, using diphenylacetone as the radical source. The ketone undergoes bond cleavage by irradiation with UV light and yields phenylacetyl and benzyl radicals [¹, ²]:



Photomodulated voltammetry (PMV), a method which combines the photochemical generation of the radicals with their electrochemical detection, allows the observation of radicals with a lifetime (τ) in the range of ms [³]. For phenylacetyl radicals $\tau < 10^{-5}$ s at $t > -50^\circ\text{C}$ [⁴], that is why the only observable radical is the benzyl radical, at room temperature. The half – wave potentials and the plateau currents of benzyl radical reduction and corresponding oxidation were determined in acetonitrile and propylene carbonate. While the half wave potentials and transfer coefficients were independent of chopper frequency and phase setting, the plateau current was markedly influenced by these parameters. The lifetime of the radical was obtained from the dependence of the phase shift of the current relatively to the excitation signal (ϕ) on the angular frequency (ω), according to:

$$\tan \phi = \omega \tau$$

The influence of precursor concentration, light intensity and nature of the solvent on the radical lifetime was investigated. As expected, the amplitude of the signal showed a decreasing dependence on the modulation frequency, for each of the investigated parameter mentioned above. Our investigations should be understood as a contribution to the topic of photomodulation voltammetry, proving that it represents an alternative and complex method, for the determination of the lifetime of transient radicals involved in photochemical reactions.

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INVESTIGATION OF Pd/Al₂O₃ FOR CO OXIDATION: CORRELATION OF PALLADIUM OXIDATION STATE AND ACTIVITY

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The activity of various PdO_x phases for CO oxidation and, in particular, the nature of the active phase (metallic Pd vs. PdO_x) has been controversially discussed in the literature recently ([1] and references therein). The aim of this study is to investigate the oxidation of CO over technical Pd-Al₂O₃ catalysts, with the palladium phase in different oxidation states. Palladium catalysts were synthesized by standard incipient wetness impregnation of alumina with Pd(NO₃)₂, followed by calcination at 500°C in air. Different Pd oxidation states were obtained by various types of catalyst pre-oxidation or were resulting from different reaction conditions. In order to correlate the oxidation state with the catalytic activity the catalysts were characterized by IR spectroscopy (using CO as probe molecule), HRTEM and XRD. Additionally, in-situ IR measurements were performed.

“Mild” oxidation conditions up to 400°C did not change the properties of the catalyst, whereas stronger oxidation (450°C, 1 bar oxygen) reduced the CO adsorption capacity and a new adsorption band corresponding to CO adsorbed on Pd^{δ+} was observed by IR. This suggests the formation of Pd₅O₄ but catalytic tests showed that a pre-oxidized catalyst exhibited only slightly lower catalytic activity for CO oxidation, due to a rapid reduction to metallic Pd under reaction conditions. Total oxidation to PdO was only obtained by pre-oxidation at temperatures around 800-1000°C. PdO turned out to be quite inactive at reaction temperatures below 200°C. In-situ IR spectroscopy is currently performed to further examine the phases present and their specific activity.

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XPS, PM-IRAS AND AFM STUDIES ON MONO- AND BIMETALLIC MODEL CATALYSTS

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Palladium is a well-known catalyst for CO oxidation and widely used in catalytic car converters. The role of Pd surface oxide phases in catalytic reactions has recently raised much attention. In the present contribution the reactivity of Pd oxides towards CO oxidation was studied with Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS) and X-ray Photoelectron Spectroscopy (XPS), from UHV to mbar pressures and at various temperatures. Pd thin films and Pd nanoparticles were grown on an NiAl(110) support, subsequently oxidized, and exposed to CO in a batch reactor. The formation of various “suboxides” was observed, which seem to exhibit reduced reactivity as compared to chemisorbed oxygen on metallic Pd [1,2].

In addition, recent results obtained on bimetallic model catalysts will be presented. AuAg nanoparticles were grown on a rutile TiO₂(110) single crystal by sequential deposition of the metals via physical vapor deposition. Atomic force microscopy (AFM) was used to follow the particle growth, whereas XPS was applied to investigate particle composition [3].

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IR spectroscopic characterization of Pd/Al₂O₃ catalysts

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Supported Pd catalysts are used for a variety of technologically important processes, in particular for hydrogenation reactions. Although studies on model catalysts have clearly shown the different activity of various sites on Pd nanoparticles, for technical catalysts the activity of corners, edges, steps, terraces, etc. needs to be investigated in more detail. Making use of CO as probe molecule vibrational FTIR spectroscopy is a versatile tool to determine the structural, morphological and electronic properties of supported metal nanoparticles before and after a reaction.

In this contribution we discuss correlations between the information obtained by IR spectroscopic characterization and the catalytic properties of the catalysts for selective hydrogenation of 1,3-butadiene.

Vibrational spectroscopy of CO adsorbed on metal nanoparticles allows examination of the available adsorption sites by providing information on the relative concentration of CO adsorbed at on-top, bridged and hollow positions.

Upon CO adsorption additional bands appeared in the region between 1200 and 1800 cm⁻¹, which were assigned to carbonate and bicarbonate species. The exact mechanism of their formation is still not clear although different routes were suggested in literature, such as CO disproportionation on Pd or CO reaction with OH groups from the supporting oxide. The first pathway seems unlikely, because these bands were also formed upon CO adsorption on Al₂O₃ (in the absence of Pd), which may support to the second pathway. The origin of these bands was further investigated by studying the adsorption of different CO isotopes by means of IR spectroscopy.

Untersuchung von Bromoxiden mittels Matrixisolationsspektroskopie und ab initio Rechnungen

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Halogenoxide spielen eine bedeutende Rolle beim stratosphärischen und troposphärischen Ozonabbau. Der Einfluss, den die Bromoxide trotz ihres relativ geringen Vorkommens auf den Ozonhaushalt der Atmosphäre haben, wurde erst in den letzten Jahren erkannt. Im Gegensatz zu den Chloroxiden sind die Bromoxide bisher noch relativ schlecht untersucht. Nur die einfachsten Vertreter dieser Verbindungsklasse, nämlich BrO, BrO₂ und Br₂O, sind sowohl mit theoretischen als auch spektroskopischen Methoden untersucht. Die höheren Bromoxide wurden überwiegend nur berechnet, und experimentelle Daten fehlen fast vollständig. Vor allem die Dimere des Bromoxids, (BrO)₂, wurden zwar als Assoziationsprodukte des BrO postuliert, jedoch sind sie experimentell unbekannt. Ebenso fehlen für verschiedene höhere Oxide jede gesicherten Hinweise auf ihre Existenz.

Zur Untersuchung der Bromoxide bietet sich die Technik der Matrixisolation in inerten Gasen an, um die Moleküle an Weiterreaktion und Zerfall zu hindern und sie ausreichend akkumulieren zu können. Die Darstellung höherer Bromoxide erfordert dabei jedoch den Einsatz radikalerer Bedingungen. Daher wurde für die hier vorgestellte Arbeit eine Mischung von Brom und Sauerstoff in Argon mit Hilfe einer Mikrowellenentladung zur Reaktion gebracht und das entstehende Speziesgemisch bei 6.5 K auf einem Probenträger kontinuierlich ausgefroren.

Zur Charakterisierung der erhaltenen Bromoxide wurde die Infrarotspektroskopie eingesetzt, da mit dieser alle Moleküle mit Ausnahme der Edukte erfasst und die Molekülgeometrien aus den Spektren einfach berechnet werden können. Des Weiteren ermöglichte ein hoher Gehalt der deponierten Matrix an unreaktiertem atomarem Sauerstoff eine Weiterreaktion der bereits gebildeten Bromoxide sowie unreaktierter Brommoleküle und -atome im Verlauf von thermischen Zyklen. Es zeigte sich, dass auf diese Weise verschiedene Bromoxide erhalten werden konnten, die bisher experimentell nicht zugänglich waren. Dazu gehören zwei Moleküle der Zusammensetzung Br₂O₂ sowie das höhere Bromoxid Br₂O₃. Die Zuordnungen der Infrarotbanden werden durch die natürlich vorkommenden Bromisotope ⁷⁹Br und ⁸¹Br sowie durch Experimente mit ¹⁸O₂ gestützt [1]. Darüber hinaus wurden Bandenlagen, Absorptionsintensitäten und geometrische Parameter der Bromoxide mit Dichtefunktionalrechnungen (B3LYP, cc-pVTZ) ermittelt [2]. Die Übereinstimmung der berechneten und gemessenen Daten ist sehr gut.

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Untersuchungen zur Oberflächenchemie von Kohlenstoffpartikeln

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Kohlenstoffpartikel gelangen zu immer größerer Bedeutung in der Atmosphärenchemie. Gründe dafür sind z.B. ihr Beitrag zum urbanen Feinstaub, ihre toxische Wirkung oder ihr Einfluß auf die globale Strahlungsbilanz. Partikuläre Emissionen wie Ruß oder sekundär gebildetes Aerosol wie HULIS (humic like substances) stellen zurzeit einen Schwerpunkt der atmosphärenchemischen Untersuchungen dar. Aus der Sicht der Physikalischen Chemie bieten sich oberflächenchemische Untersuchungen dieser Kohlenstoffpartikel [1,2,3,4] an, um die Bedeutung der Partikel für die atmosphärische Gasphasenchemie besser einschätzen zu können.

Zur Oberflächenuntersuchung dieser realen Systeme eignen sich besonders die Diffuse-Reflexions-Infrarot-Fourier-Transformations-Spektroskopie (DRIFTS), die Temperatur-Programmierte-Oberflächen-Reaktions-MassenSpektroskopie (TPSR-MS), die Temperatur-Programmierte-Desorptions-MassenSpektroskopie (TPD-MS) und die Elektronen-Spin-Resonanz (ESR) Spektroskopie. Alle vier Methoden wurden von uns für die Charakterisierung von Huminstoff und Rußproben eingesetzt. DRIFTS liefert anhand von charakteristischen Schwingungsbanden detaillierte Informationen über die Entstehung und Transformation von funktionellen Oberflächengruppen. TPD-MS gibt Aufschluss über die Stabilität dieser Gruppen und TPSR-MS verfolgt das Reaktionsverhalten mit atmosphärenchemisch relevanten Gasen. Radikale an der Oberfläche können mittels ESR untersucht werden. Die Kombination dieser spektroskopischen Techniken ermöglichte ein umfassendes Verständnis von heterogenen Reaktionen mit Kohlenstoffoberflächen auf molekularem Niveau. Untersucht wurden a) die heterogene Reaktion mit Stickoxiden und b) die Einwirkung von reaktiven Halogenverbindungen. Die Stabilität und die Reaktivität der neu gebildeten funktionellen Gruppen wurden festgestellt. Einzelne heterogene Reaktionsmechanismen konnten aufgeklärt werden.

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Morphologien von Partikeln in der Polaren Stratosphäre

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Die Morphologien von Aerosolpartikeln haben einen wichtigen Einfluss auf deren Extinktionsspektrum. Die Kenntnis dieser Spektren ist essentiell für die Identifizierung und Strukturaufklärung der Partikel. Dies gilt in besonderem Maße für Polar Stratosphärische Wolkenpartikel, die mit satellitengestützten optischen Methoden untersucht werden. In den hier vorgestellten Laborexperimenten wurden Proben präpariert, deren Phasenzusammensetzung aus Vergleichsexperimenten bereits bekannt war [1-4]. Diese Kryoproben wurden mittels einer Kryo-Transferkammer in ein environmental scanning electron microscope (ESEM) eingebracht und wurden in Temperaturabhängigkeit beobachtet. Der Vorteil dieser Technik besteht darin, dass bei Drücken bis 5 mbar gearbeitet werden kann und so eine Dehydratation der Probe vermieden wird. Für die Hydratphasen Salpetersäuretrihydrat, Salpetersäuredihydrat und deren Mischungen wurden die Morphologien bestimmt [5] und unter Zuhilfenahme der entsprechenden optischen Konstanten wurden die passenden Extinktionsspektren berechnet [6].

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Magnetostriction in Pulsed High Magnetic Fields

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Magnetostriction is a magnetic property of solid states that causes a change of dimensions or shape when subjected to a magnetic field. The effect was first identified in 1842 by James Joule when observing a sample of nickel and is applied technically today in sensor and actuator technology, e. g. generation of ultrasound, changing the form of aeroplane wings etc. The magnetostrictive phenomena can be classified in two types: On the one hand there is spontaneous magnetostriction which causes a volume change of magnetic materials without applying a magnetic field, on the other hand there is the forced (or linear) magnetostriction, which means a length change applying a magnetic field. The forced magnetostriction is technically used in sensors or actuators. The origin of magnetostriction is either a single ion effect (crystal field striction) or due to two ion effects (exchange striction) or even a band structure effect as in 3d-metals.

Measurements in high magnetic fields are required in order to distinguish crystal field and exchange striction. In principle magnetostriction measurements can be performed by microscopic methods (X-ray diffraction, neutron diffraction) and by macroscopic methods (strain gauges, capacitive dilatometers, extensometers, interferometry). The main advantages of capacitive dilatometers are the high sensitivity (up to 10^{-9}) and that the set-up is insensitive to magnetic fields. Therefore they can be used in high magnetic fields. We developed a capacitive dilatometer for this purpose. The dilatometer realizes a parallel plate capacitor design with longitudinal geometry [1,2].

The main goal is to analyse new materials, especially compounds containing rare earth elements, in pulsed high magnetic fields. The capacitive dilatometer will be used in the pulsed magnetic field at the AUSTROMAG at the TU Vienna, where magnetic field strengths up to 40 T with a pulse duration between 400 – 1000 ms can be generated [3].

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Spectroscopic properties of adjoined TiO₂ nanocrystals

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To include particle attachment and porosity in the discussion of the electronic properties of nanostructured oxide materials is indispensable for deeper insights into electronic conduction across grain boundaries and thus essential to electronics, sensor technology and photovoltaics. We investigated the condensation of isolated TiO₂-nanocrystals which results from the application of a simple hydration-dehydration cycle. After contact with water and subsequent dehydration and adsorbate removal under high vacuum conditions the powder of originally isolated nanocrystals [1] is transformed into a monolithic solid which consists of a particle network with a mesoporous structure. These monoliths show significant changes in the optical absorption properties as investigated by UV-diffuse reflectance spectroscopy. Vacuum annealing to $T > 870$ K induces oxygen vacancy formation on isolated TiO₂-nanocrystals. The electrons left behind form paramagnetic states which can be tracked by electron paramagnetic resonance (EPR) spectroscopy. On aggregated TiO₂-nanocrystals EPR measurements indicated that oxygen vacancy formation occurs at significantly lower temperatures than $T = 870$ K. In addition, polarizable conduction band electrons [2] are only observed in the network which consists of adjoined TiO₂-nanocrystals [3]. Changes in the spectroscopic properties resulting from the solvent-mediated particle aggregation process will be discussed in the light of associated structural data.

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Chemical Control of Photoexcited States in Titanate Nanostructures

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Layered TiO₂-based nanostructures have attracted much attention due to a broad spectrum of potential photochemical and electrochemical applications including photocatalysis, solar cell technology and gas sensing devices. The photochemical activity of these materials depends on the branching ratio between essentially three pathways photoexcited states can undergo: they can either recombine under photoluminescence emission or generation of heat, or become persistently trapped [1] or undergo interfacial charge transfer at the particle surface. Some of these competitive processes can be tracked by means of electron paramagnetic resonance and photoluminescence spectroscopy.

We synthesized titanate nanowires and -tubes by TiO₂ anatase powder treatment in aqueous alkaline solutions. The resulting structures are composed of layered sheets which consist of edge-sharing [TiO₆] octahedra [2]. A specific photoluminescence process which originates from the deactivation of exciton states trapped in [TiO₆] units was observed. It was found that exchange of intercalated ions provides means to adjust the branching ratio between radiative exciton deactivation, on one hand, and charge separation, on the other. Thus, chemical control over the photoelectronic properties of layered oxide structures has become feasible and the role of various ions in between the layered sheets will be discussed [3].

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LIGHT-INDUCED CHARGE SEPARATION IN TiO₂ NANOCRYSTALS

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Understanding of charge trapping effects on oxide surfaces is fundamentally important for a variety of technological applications ranging from photocatalysis to solid state electronics [1]. The aim of the present study is to investigate the role of nanostructured TiO₂ surfaces in the consumption and deactivation of photogenerated charge carriers. For this purpose, UV induced charge separation processes were investigated by a combined spectroscopic approach: delocalised electrons in the conduction band give rise to a free carrier absorption in the IR (Drude absorption) [2], whereas trapped and localised holes (O⁻) and electrons (Ti³⁺) are measured by Electron Paramagnetic Resonance (EPR) spectroscopy [3].

In the absence of electron and hole scavengers, at $p < 10^{-5}$ mbar, the majority of these charge carriers recombine within a few nanoseconds. Nevertheless, at $T \leq 140$ K charge carrier trapping processes can be observed on a time scale of minutes when irradiances in the $\text{mW}\cdot\text{cm}^{-2}$ range are used. It was found that most of the photoexcited electrons remain in the conduction band, whereas the holes get trapped and localised at the surface of the particles [3]. The presence of oxygen as an electron scavenger enhances the efficiency of charge separation during UV exposure by a factor of 10 and leads to the photoadsorption of O₂ which was used to determine the number of trapped charges per particle. These results are considered as benchmark for studies on other nanocrystalline oxide systems and will be compared to structurally more defined subjects, such as TiO₂-based nanotubes.

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Oxide islands on MgO nanocubes

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Limitations for light-emitting devices, the application of which range from full colour displays to optical communication systems, arise from the lack of materials that efficiently emit photons of required energy. Usually semiconductors where discrete electronic transitions can be reached by spatial confinement of the bulk are discussed as components for such devices. The respective situation is different for nanometer-sized alkaline earth oxides which are prototypical ionic insulators. Surface excitons with molecular-like properties can exclusively be generated at low coordinated surface sites¹ and give rise to photoluminescence emission in the range between 200 and 600 nm.

High thermal stability, a sharp size distribution and a well-defined particle morphology² make MgO nanocubes a well-suited model system for investigating the surface electronic structure of oxide particles. Unlike MgO nanocubes CaO, SrO and BaO nanoparticles agglomerate in the course of vacuum annealing and produce large grains of ill-defined morphology³. In this contribution, we present a new approach for the production of thermally stable CaO, SrO and BaO thin films supported on MgO nanocubes. UV-Diffuse Reflectance and photoluminescence measurements reveal novel optical properties compared to those of the pure oxide components. These properties will be discussed in terms of low coordinated surface elements that act as excitation and emission sites. Furthermore, chemical surface reactivity changes induced by the second metal oxide component are evidenced by the IR spectroscopic characterization of H₂ activation processes.

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² Stankic et al. *Angew. Chem. Int. Ed.* 2005, 44, 4917

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New aspects of the energetics of ordered Ti₂C and Ti₂N

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Experimentally, two ordered phases of tetragonal symmetry, namely metastable δ' -Ti₂N and stable ε -Ti₂N, are found for titanium nitrides of composition Ti₂N, whereas for titanium carbides TiC_x with x near 0.5 two ordered phases with cubic and trigonal symmetry, respectively, can be traced. By experiment, either cubic $Fd\bar{3}m$ -Ti₂C is found to be a metastable phase which transforms at lower temperatures to trigonal $R\bar{3}m$ -Ti₂C, or it is detected to be stable for C contents of $0.52 \leq x \leq 0.55$ and metastable for higher C concentrations of $0.56 \leq x \leq 0.58$. FP-LMTO calculations confirm the latter and previous FLAPW investigations the former findings.

In order to clear these discrepancies for the carbide phases and also to find a quantitative explanation for the different stabilities of the ordered defect structures of titanium carbide and titanium nitride, new first-principles FLAPW band structure calculations based on the generalized gradient approximation (GGA) for the exchange-correlation potential and using the FLAIR code with force optimization were undertaken for $Fd\bar{3}m$ - and $R\bar{3}m$ -Ti₂C, for δ' - and ε -Ti₂N, and, for comparison, also for the fictitious phases δ' -Ti₂C, ε -Ti₂C, $Fd\bar{3}m$ -Ti₂N and $R\bar{3}m$ -Ti₂N.

For the carbides, these calculations result in cubic $Fd\bar{3}m$ -Ti₂C being the most stable phase and more stable than trigonal $R\bar{3}m$ -Ti₂C by 5.0 kJ/mol at 0 K if the Ti atoms are allowed to relax.

For the nitrides and in agreement with experiment, tetragonal ε -Ti₂N is found to be the most stable phase. However, the energy difference to relaxed, tetragonally distorted δ' -Ti₂N is with 3.3 kJ/mol quite small. Experimentally, δ' -Ti₂N is found to be the metastable precursor phase for ε -Ti₂N whose direct formation from substoichiometric TiN_x is kinetically hindered. Contrarily to $Fd\bar{3}m$ -Ti₂C, $Fd\bar{3}m$ -Ti₂N is not a stable phase because of its much smaller relaxation energy.

The different relative stabilities of the carbide and nitride phases can be explained by differences in the densities of states and - especially for the $Fd\bar{3}m$ - and δ' -phases - by more or less important effects of the Ti atom relaxation on the respective chemical bonds which can be detected in the calculated electron-density contour plots.

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POINT-DEFECT ENERGETICS AND PHONONS IN THE La-H SYSTEM

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First principles calculations have been performed for the La-H system at various H concentrations in order to find energetically favourable H-vacancy arrangements. Also phonon calculations for investigating the vibrational stability of these vacancy structures have been carried out. We present the results of this work available so far which should lead to a complete phase diagram for the La-H system.

Schmetterer

Measuring magnetostriction with neutrons

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Neutron diffraction has been used in order to measure magnetostriction and thermal expansion in an unusual way. The cold neutron triple axis spectrometers IN12 and IN14 at the ILL, Grenoble, France, were used to determine the change of lattice constants with temperature and applied magnetic field by measuring the angular shift of selected Bragg reflections. The instrumental resolution of this method is hardly comparable with x-ray diffraction or dilatometric methods. Nevertheless, using neutrons allows overcoming certain experimental difficulties when using more conventional methods: Capacitance dilatometry is sensitive to parasitic forces occurring when applying a magnetic field on highly anisotropic samples. Since the penetration depth of x-ray is very small, slight movements of the sample change the scattering geometry and introduce an error, which is difficult to estimate. Here we discuss two distinct cases for which neutrons helped to explain the apparent discrepancy in previously measured experimental magnetostriction and thermal expansion data (Fig.1 and 2).

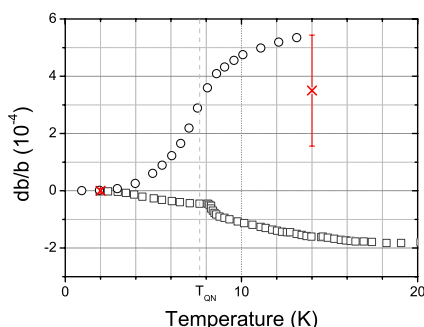


Fig. 1. Thermal expansion of Jahn Teller system PrCu_2 . Squares represent the data measured by Takeuchi et al. [1] Circles represent the data obtained by Andres et al. [2]. Crosses represent the neutron diffraction data obtained at IN14.

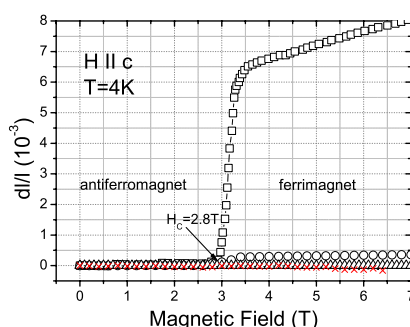


Fig. 2. Forced magnetostriction of ferrimagnetic Tm single crystal. Circles represent the data measured by Zochowski et al. [3]. Squares represent the data obtained by Barcza. Triangles represent the lowest signal obtained by Lindbaum with capacitance method. Crosses represent the neutron diffraction data obtained at IN12.

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Neutron Spectroscopy versus *ab initio* Calculation of the Dynamical Response of NdFe₄Sb₁₂

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Ternary skutterudites RM₄X₁₂ with R=rare earth, M= Fe, Co, Rh, Ru and X=P, As, Sb attracted much interest because of a variety of possible ground states and because of their large thermoelectric potential. In order to optimize open cage compounds for thermoelectric applications the thermal conductivity has to be minimized without changing the thermoelectric performance. This can be achieved by increasing the scattering of the heat carrying phonons via localized excitations. Einstein lattice modes of heavy atoms introduced in the cages of the open lattice are expected to provide such local excitations [1]. In addition, crystal field excitations might be used, provided that the crystal field phonon interaction is strong. In order to pursue these ideas the inelastic response of NdFe₄Sb₁₂ was measured by inelastic neutron scattering on powder (fig. 1) and is compared to *ab initio* lattice dynamical calculations.

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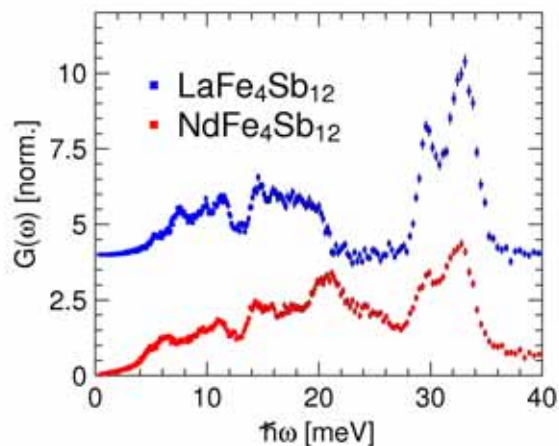


Fig. 1. Generalized phonon density of states obtained from IN6 spectra measured at room temperature. The data of NdFe₄Sb₁₂ are compared to the nonmagnetic reference LaFe₄Sb₁₂ [3]. [1] R. P. Hermann et al. Phys. Rev. Lett. 90 (2003) 135505
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THE RESPONSE OF PLANT CELLS TO HIGH TEMPERATURE STRESS: CHANGES OF MEMBRANE FLUIDITY AND PRODUCTION OF HYDROGEN PEROXIDE TRIGGER THE SYNTHESIS OF SMALL HEAT SHOCK PROTEINS (SHSPS)

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In virtually all living organisms, high temperature stress induces the synthesis of a defined set of proteins, designated as heat shock proteins (HSPs). In plants, a group of HSPs in the range of 14 to 35 kDa, small HSPs (sHSPs), function as molecular chaperones in helping to stabilize substrate proteins under unfavorable conditions. Although sHSP upregulation as the final response to sublethal high temperatures is well documented, the mechanism of temperature sensing as the prerequisite to acquire thermotolerance is still unclear. In the following cascade of events leading to sHSP upregulation hydrogen peroxide may be a key component, as has been found in many cases. In the present investigation, experimental evidence is provided that the fluid state of the cell membrane may function as a temperature sensor and that elevated production of hydrogen peroxide is necessary for induction of sHSPs synthesis in *Nicotiana tabacum* cells.

Membrane fluidity has been measured by fluorescence polarisation of 1,6-diphenyl-1,3,5-hexatriene embedded in isolated cell membranes. sHSPs have been detected after labelling the cells with ³⁵S-amino acids, separation of the proteins by SDS-PAGE and autoradiography. H₂O₂ was extracted with trichloroacetic acid (TCA). After purification of the neutral TCA extract by ion exchange, H₂O₂ was measured by a fluorimetric assay using the oxidation of scopoletin by H₂O₂ in the presence of peroxidase.

Membrane fluidity increased continuously when the ambient temperature was gradually elevated from 24 °C to 46 °C. Additions of benzyl alcohol (BA) to the membrane preparations also shifted the fluidity to higher values. Therefore, incorporation of BA into membranes could mimic elevated temperatures.

In parallel experiments with intact cells the synthesis of small sHSPs responded in the same way to the addition of BA: the threshold temperature, required for sHSPs synthesis, was markedly decreased. The results indicate that an increase in membrane fluidity could be responsible for high temperature sensing and the subsequent induction of sHSPs in tobacco cells.

Massive production of sHSPs occurred between 32 °C and 38 °C. In this temperature range a very fast and marked elevation of intracellular H₂O₂ levels was found in the first few minutes after temperature change. Iodonium diphenyl (IDP), an inhibitor of NADPH-dependent oxidases, which are a possible source of H₂O₂ production, counteracted both, the heat stress induced H₂O₂ burst and the synthesis of sHSPs. Thus a NADPH-oxidase is most likely to be activated at high temperature stress resulting in enhanced H₂O₂ production, which in turn is required as signalling component for the induction of sHSPs synthesis.

Komputative Physikalische Chemie und Polymerchemie

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Modellrechnungen eignen sich hervorragend als Bindeglied zwischen Experiment und Theorie, liefern ein besseres Verständnis von Vorgängen auf molekularer Ebene und liefern vielfach Details, die sich experimentellen Methoden entziehen. Quantenmechanische Berechnungen enthalten die wenigsten Voraussetzungen, werden aber mit steigender Zahl der Atome sehr zeitaufwändig. Auf größere Systeme ist die atomistische Molekulardynamik mit geeigneten Kraftfeldern anwendbar und wenn sich Längen- und Zeiteinheiten über mehrere Dekaden erstrecken bedient man sich mesoskopischer Verfahren.

Die Gruppen von P. Herzig und R. Podloucky wenden die Dichtefunktionaltheorie zur Ermittlung von Materialeigenschaften an. P. Herzig untersucht in Zusammenarbeit mit experimentellen Gruppen z.B. Übergangsmetallhydride, die interessante physikalische Eigenschaften aufweisen (konzentrationsabhängige Metall-Isolator-Übergänge, "switchable mirrors") und deren Zusammenhang mit elektronischen und optischen Eigenschaften sowie generell intermetallische Verbindungen und Legierungen in Bezug auf ihre strukturellen, elektronischen und thermodynamischen Eigenschaften. R. Podloucky beschäftigt sich mit der ab initio Berechnung von Materialeigenschaften von 3 dimensional Phasen wie z.B. intermetallische Verbindungen, Hartstoffen, Oxyden, Siliziden, Ausscheidungen in Legierungen (Phasen- und Strukturstabilitäten, magnetische Ordnung, Schwingungseigenschaften, Härte und Spalteigenschaften, optische Eigenschaften) und 2 dimensional Phasen wie Vielschichtsysteme (Hartstoffschichten für nanocoating) und Oberflächen (Rekonstruktion, Adsorption, Phasenstabilitäten, magnetische Eigenschaften etc.).

Die Gruppen von I. Schnöll-Bitai und G. Zifferer betreiben experimentelle und numerische Untersuchungen an oligomeren und polymeren Systemen. G. Zifferer simuliert diverse Polymersysteme (u.A. sternförmig verknüpfte Ketten) mittels Monte Carlo Methoden, Exact Enumeration Techniques und Dissipative Particle Dynamics (Mesoscale Techniken) sowie Polymerisationsprozesse mit selbst entwickelter Software und betreibt atomistische Simulation von z.B. Oligomer/Oberflächenwechselwirkungen und von Wirt/Gast/Lösemittel Systemen. Das Interesse von I. Schnöll-Bitai konzentriert sich auf polymerisationskinetische Probleme (pseudostationary polymerization, quenched instationary polymerization) und die Analyse von Polymeren mittels verschiedener Methoden. U.a. wurden zur Bestimmung unverfälschter Molmassenverteilungen mehrere Verfahren zur Bestimmung des Ausmaßes der Bandenverbreiterung bei der Gelpermeationschromatografie entwickelt.

Simulation des zentralen Schritts der Z-RAFT-Stern-Polymerisation

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Ein relativ neuer Zugang zu gut definierten Sternpolymeren wird durch die sogenannte RAFT (reversible addition fragmentation chain transfer) Methode erschlossen, die auf dem Prinzip der lebenden radikalischen Polymerisation beruht.¹ Wachsende Polymerradikale R stehen im Gleichgewicht mit trägen polymeren RAFT Spezies, z.B. Thiocarbonylthio-Verbindungen $[S=C(Z)SR]$ wobei Z die stabilisierende Gruppe darstellt. Dies führt zur gleichen Wachstumswahrscheinlichkeit für alle Ketten und somit zu einer guten Kontrolle der Molmasse sowie zu einer engen Molmassenverteilung. Multifunktionelle Polymere können durch Kopplung mehrerer RAFT Einheiten erzeugt werden: im Falle der Z-RAFT-Stern-Polymerisation sind die stabilisierenden Gruppen im Sternzentrum gekoppelt und die Arme wachsen (abgelöst vom Zentrum) in Form linearer Ketten. Der Stabilisierungsmechanismus erfordert daher eine Reaktion des radikalischen Endes einer wachsenden Polymerkette mit einer Gruppe im Zentrum des Sterns, wobei die beiden reagierenden Zentren von den umgebenden Monomereinheiten abgeschirmt werden.

Eine geeignete Beschreibung dieser sterischen Effekte ist eine Herausforderung an sich und eine Analyse von Abschirmeffekten beliebiger Monomerpositionen von allgemeinem Interesse. Fragestellungen dieser Art können hervorragend mit Hilfe von Computersimulationen bewerkstelligt werden: Ausgehend von Ensembles von Gitterpolymeren, die mittels eines Monte Carlo-Prozesses erzeugt werden, sind Abschirmeffekte² durch exakte Abzählung der entsprechenden Kontakte innerhalb selbstüberschneidungsfreier Paarkonfigurationen zugänglich.³ Die Abschirmung ist abhängig von der Position der interagierenden Segmente, von der Länge der Ketten (Arme), von der Kettensteifigkeit und der Ausdehnung des eigentlichen Sternzentrums⁴ und natürlich auch von der Funktionalität (Zahl der Arme) des Sterns.⁵

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Physical Chemistry and Nanotechnology of Interfaces

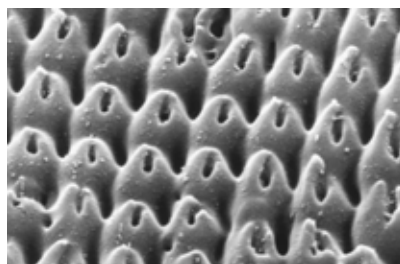
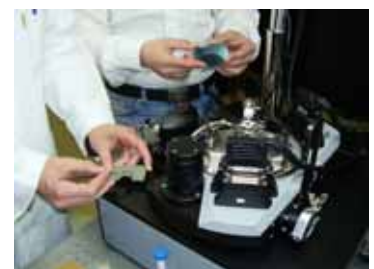
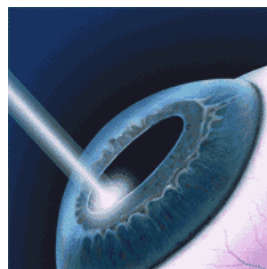
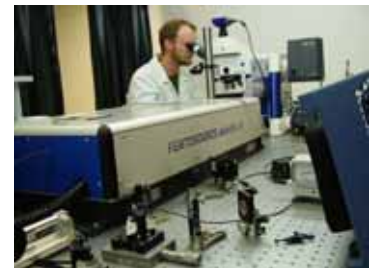
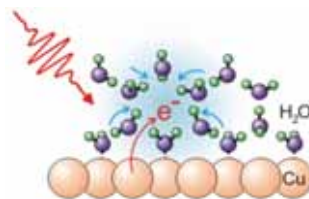
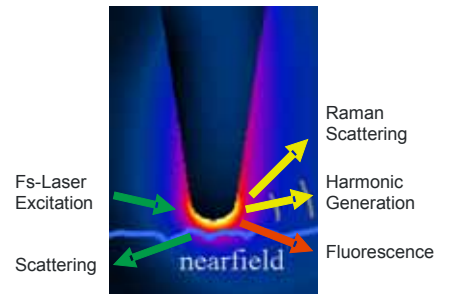
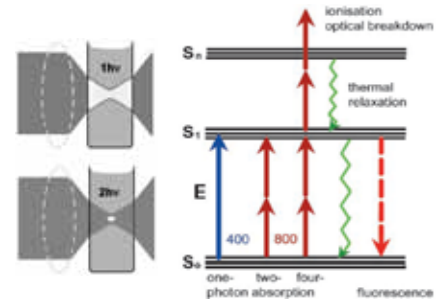
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Festkörperoberflächen im Nanoskalenbereich
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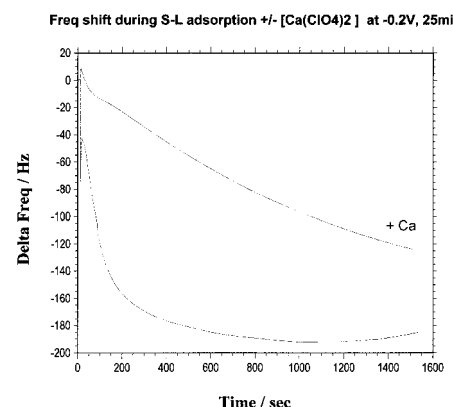
SELF-ASSEMBLY DYNAMICS OF SURFACE LAYER PROTEINS ON GOLD ELECTRODES

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Two-dimensional crystalline bacterial cell protein surface layers (S-layers) on solid substrates are of fundamental and technological interest in biotechnology [1], biomineralization [2], bio sensorics [3], and bottom-up nanostructuring technologies [4]. First electrochemical in-situ quartz microbalance and ex-situ SPM and XPS measurements showed that self-assembly dynamics and surface bonding of the protein molecules dependent strongly on the structure of the electrochemical double layer [5,6]. It could be shown that electropositive metal salts (e.g. aurates) can lead to the autocatalytic formation of metal nanodots on the protein surface [7].



In-situ-QMB: Borate Buffer pH9
+ SbpA Recrystallization

In this context, the role of calcium ions as lateral bridging agent and as competitor for protein-metal bonds has been studied by dynamic quartz-microbalance and scanning force microscopy investigations. At negative potentials, the double layer exchange of sub-monolayers of cations and anions is monitored, whereas at positive potentials, hydroxide monolayer adsorption/desorption processes can be observed.

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Electrochemical and spectroscopic characterization of a novel complex for alkane oxidation

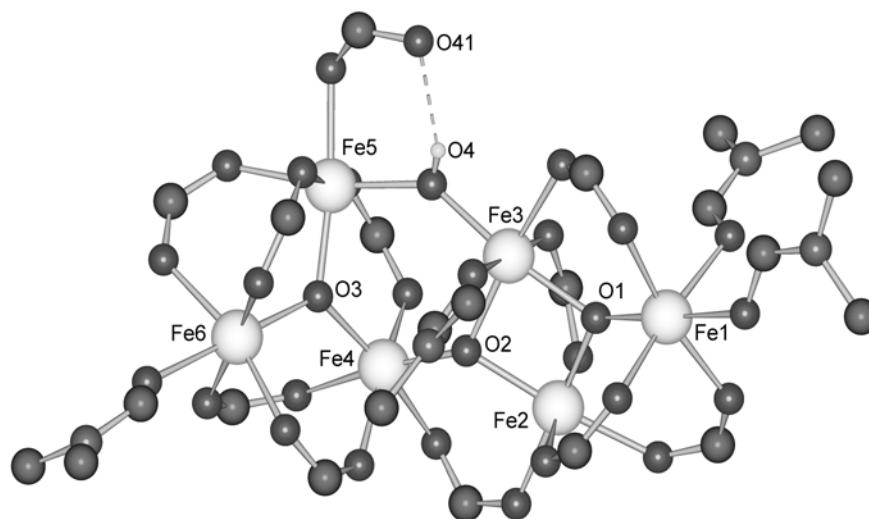
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The novel hexanuclear Fe III complex $[\text{Fe}_6\text{O}_3(\text{OH})(p\text{-NO}_2\text{C}_6\text{H}_4\text{COO})_{11}(\text{DMF})_4]$ I forms after addition of H_2O_2 a peroxo complex II, which shows remarkable activity in the oxidation of cyclohexane [1].



Molecular Structure of $[\text{Fe}_6\text{O}_3(\text{OH})(p\text{-NO}_2\text{C}_6\text{H}_4\text{COO})_{11}(\text{DMF})_4]$ (SCHAKAL Plot).
p-Nitro-phenyl rings and hydrogen atoms (except that attached to O4) are omitted for clarity

The redox behaviour of the complexes has been investigated by cyclic voltammetry in a solution of acetonitrile-DMF (10:1) using $[\text{NBu}_4][\text{BF}_4]$ as supporting electrolyte. Platinum and glassy carbon electrode materials exhibited remarkably varying behaviour. The cyclic voltammetric results were assigned to a reaction mechanism by usage of the simulation program Digisim[©].

The kinetics of the formation of the active species II was elucidated by UV-vis spectroscopy. The formation was assigned to a first order kinetics. Its activation energy was determined by an Arrhenius plot.

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Electrochemical characterisation of nickel cobalt electrolytes-for pulse reverse plating

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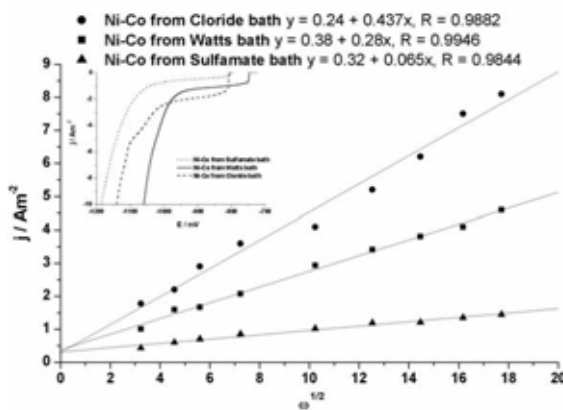
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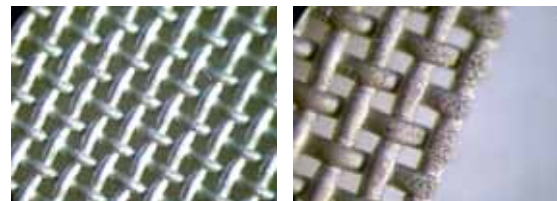
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Nickel-based alloys such as Ni-Co are used in a wide variety of applications for aerospace, energy generation, corrosion protection, but also magnetic materials and as electro-catalysts in hydrometallurgy, and are considered as hard chromium replacement. Their electrodeposition [1] and pulse reverse plating [2] from aqueous media has been demonstrated recently [3,4]. Fundamental electrochemical properties of electrolyte systems are the prerequisite for the development of a successful pulse deposition process. Three different electrolyte systems for the galvanic deposition of nickel cobalt alloys (chloride, Watts and sulfamate type) were investigated in order to unravel underlying deposition mechanisms and rate determining factors. The electrochemical experiments were supported by X-ray fluorescence analyses of the alloy composition in dependence of the current density and the type of bath. A special focus was the investigation of the passive (oxide) layer formation by the anodic pulses.



Deposition potential and Levich plots of Ni-Co alloy deposited from chloride-,Watts- and sulfamate bath



Ni-Co deposit on a steel grid with a pulsed reversal current show that the grid keeps its structure after the plating, while DC deposition leads to an extremely inhomogeneous deposit.

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Laser Cleaning and Multi-Method Diagnostics of Textile Pieces of Art at Sucevita Monastery

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Pulsed lasers are becoming new tools in arts conservation [1, 2]. The treatment of biopolymeric material, such as varnishes on paintings, biogenetic surfaces such as paper, cellulose, collagen, parchment [3-6], and of textiles such as silk [6-8] has been approached only in recent years whereas stone and façade cleaning has reached a mature commercial level [2]. Treatment of biogenetic fibrous materials at a wavelength of 1064 nm often causes yellowing and polymeric crosslinking [5, 6]. UV laser irradiation, on the other hand, leads to bond breaking and polymer scission and a decrease of the degree of polymerization [5].

The present cleaning and multi-method diagnostic study of original ancient textiles was performed during the Culture 2000 Project (CLT 2005/A1/CHLAB/RO-488, Saving sacred relics of European medieval cultural heritage; <http://inoe.inoe.ro/Moldavia>) from July 16-29, 2006, at the Sucevita Monastery, Province of Bukovina, Suceava County, Romania. Laser Cleaning was performed with a Q-switched Nd:YAG laser (6 ns, up to 9 J cm⁻².) Maximum contrast between contaminant and substrate was exploited in employing green laser light at 532 nm where the substrate exhibited minimum interaction guaranteeing minimum deterioration [3-5]. Laser-Induced Breakdown spectroscopy (LIBS) was complemented by colorimetry, multi-spectral imaging, and optical micro-copy. The objects chosen for this study were a maniple (minecute, 18th, from Parohia Beresti, St. Nicolae, Suceava; figure), and a stole (epitrachion, Sucevita Monastery). The stole exhibited metal-wrapped silk fibres and textile bordures. LIBS unveiled the chemical composition of the metal threads and the contaminants. A cleaning strategy can be developed on the basis of these findings.



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