

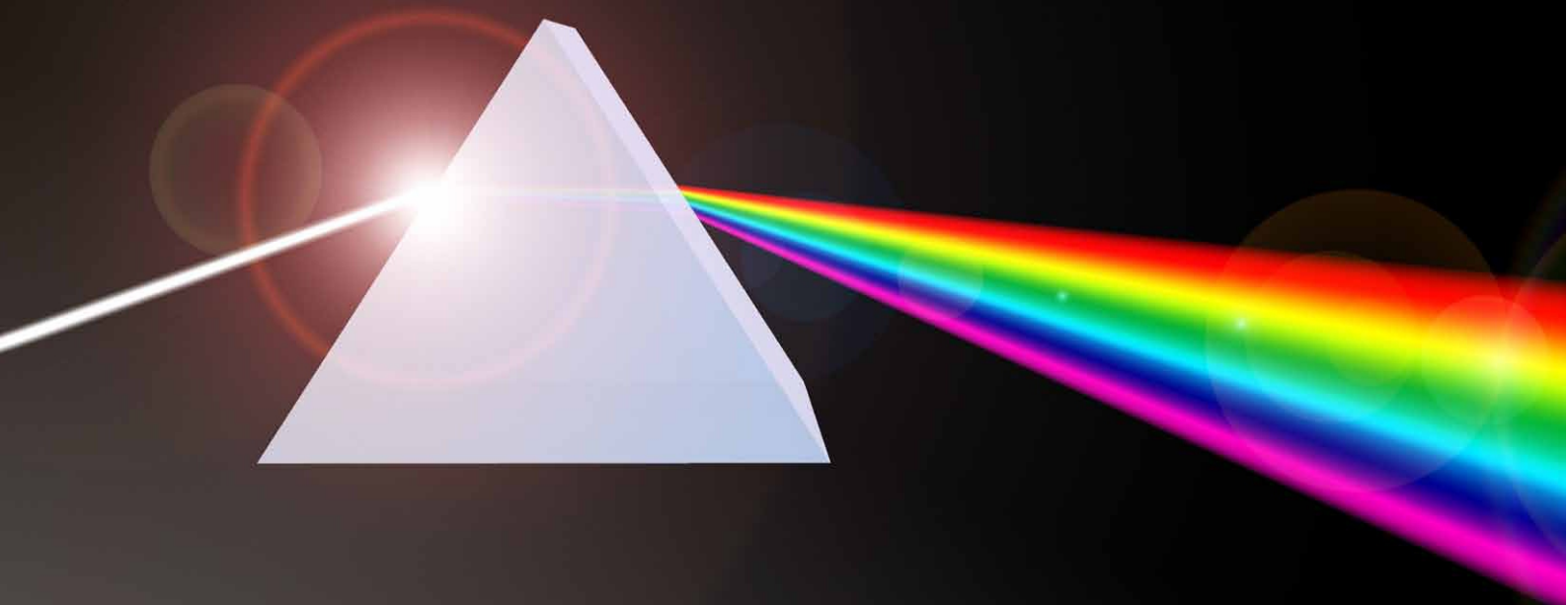
AKADEMIE DER
WISSENSCHAFTEN
IN HAMBURG

Spectroscopy – Detective in Science

Conference for young academics
and PhD students in Natural Sciences

Book of Abstracts

June 15 - 17 2011



Universität
Rostock



Traditio et Innovatio



Spectroscopy – Detective in Science

2011

Rostock, June 15 – 17

Responsible:

Department Life, Light and Matter

Universität Rostock

18051 Rostock, Germany

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Conference Program

Wednesday June 15, 2011

Chairperson: Prof. Dr. Udo Kragl

12:00	Registration with soft trinks	
13:00	Welcome Note	Prof. Dr. Udo Kragl , Dean of Faculty Interdisciplinary Research University of Rostock, GER
13:15		
13:15	Spectroscopic Viewing: A Way to Watch Catalysis at Work	Prof. Dr. Angelika Brückner , Leibniz Institute for Catalysis at the Rostock University of Rostock, GER
14:00		
14:05	Elucidating Structure-Reactivity Relationships for V-Containing Oxynitrides VMON (M = Mo, Al or Zr) in the Ammoxidation of 3-Picoline	Christiane Janke , Leibniz Institute for Catalysis at the Rostock University of Rostock, GER
14:20		
14:25	Coupled ATR-IR / UV-vis in situ-spectroscopy supported by ex situ Raman spectroscopy and X-Ray structure analysis: Elucidation of the mechanism of an organic preparation process and further optimisation of the reaction	Leif Knöpke , Leibniz Institute for Catalysis at the Rostock University of Rostock; GER
14:45		
14:50	Operando DRIFTS/UV-vis/MS studies of oxidative carbonylation of methanol over CuY-Zeolites	Jana Engeldinger , Leibniz Institute for Catalysis at the Rostock University of Rostock; GER
15:10		
16:00	Guided Tour	

Thursday June 16, 2011

Chairperson: Prof. Dr. Meiwes-Broer

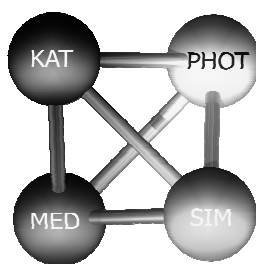
Chairperson: Prof. Dr. Udo Kragl

08:00	Single Molecule Studies of Surface and Soft Matter Interaction of Functionalized Perylene Diimides	Stefan Krause , Chemnitz University of Technology, Optical Spectroscopy and Molecular Physics; GER
08:30		
08:40	Investigation of medically relevant substances using Photoionization-Time of Flight Mass Spectrometry	Juliane Kleeblatt , Joint Mass-Spectrometry centre of the University of Rostock and the Helmholtz Zentrum München; GER
09:00		
09:00	Coffee Break	
09:30		
09:30	NMR, Peptides and the catalytic cycle, an approach	Dr. Hergen Breitzke , Institut of Chemistry, Technische Universität Darmstadt; GER
10:00		
10:10	Human Hemoglobin detection by using AgO thin films as Surface Enhanced Raman scattering (SERS) substrates	Dhanya Murali , Department of Physics, Indian Institute of Technology Madras; IN
10:25		
10:30	Features of exciton migration in cyanine dye J- aggregates	Iryna Fylymonova , Institute for Scintillation Materials, Kharkov; UA
10:45		
10:50	Ultrafast Spectroscopy Investigation of Au-FexOy Hetero-nanostructures	Kseniya Korobchevskaya , Istituto Italiano di Tecnologia, Genova; IT
11:10		
11:15	Study the atomization of the generated hydride species in a dielectric barrier discharge atomizer	Wameath Abdul-Majeed , Department of Chemical and Biological Engineering, University of Sheffield; UK
11:30		
11:35	Lunch Break with Postersession	
13:00		

13:00	Neutron and x-ray reflectometry for characterisation of polymer coated surfaces	Prof. Dr. Regine von Klitzing, Department of Chemistry, Technische Universität Berlin; GER
14:00		
14:10	Free electron lasers – the brightest x-ray sources	Prof. Dr. Wilfried Wurth, DESY Campus, University of Hamburg; GER
14:55		
14:55	to be announced	N.N. DESY Campus, University of Hamburg; GER
15:10		
15:15	Automated Analysis in Life Science Research	Prof. Dr. Kerstin Thurow, Center of Life Science Automation, University of Rostock; GER
16:00		
16:00	High Throughput Determination of Amino Acids using Mass Spectrometry	Heidi Fleischer, Institute of Automation, University of Rostock; GER
16:15		
18:45	Come Together Dinner at the Harbor Cruise with a special talk	
21:00	Spectra. Sun and light in the religions of the Ancient Near East.	Prof. Dr. Martin Rösel, Theological Faculty, University of Rostock; GER
Friday June 17, 2011		
	Chairperson: Prof. Angelika Brückner	Chairperson: Dr. Dirk Hollmann/ Prof. Dr. Lochbrunner
08:00	Modern Raman-spectroscopic methods for investigations of complex bioorganic samples	Prof. Dr. Janina Kneipp, Department of Chemistry of the Humboldt-University Berlin and BAM; GER
08:45		
08:45	Development and characterisation of new planar SERS sensors for detection of catalytic activity and other applications for investigations of complex bioorganic samples	Virginia Joseph, Department of Chemistry of the Humboldt-University Berlin and BAM; GER
09:00		
09:00	Coffee Break	
09:30		
09:30	Proteomic fingerprinting: an example for information-based medicine	Dr. Tim Conrad, Dept. of Mathematics, Freie Universität Berlin; GER
10:00		
10:00	Capturing Proteolytic Activity in Mass Spectrometry Measurements	Stephan Aiche, Dept. of Mathematics, Freie Universität Berlin; GER
10:15		
10:25	FT-IR Spectroscopy of Membrane Proteins	Dr. Ionela Radu, Department of Physics, Freie Universität Berlin; GER
10:55		
11:10	Soft photo ionization mass spectrometry for the analysis of biomass flash pyrolysis gases within the Karlsruhe bioliq® - Biomass to Liquid - Project	Alois Fendt, Joint Mass-Spectrometry centre of the University of Rostock and the Helmholtz Zentrum München; GER
11:25		
11:35	New 9,10-Anthraquinone derivatives in terms of Molecular Recognition	Anna Wcislo, Faculty of Chemistry, University of Gdańsk; PL
11:50		
12:10	Lunch Break with Postersession	
13:30		
13:30	Spectroscopy at the extremes with x-ray lasers: from structural sciences to fusion physics	Dr. Jakob Andreasson, Dr. Nic Timmeanu, Uppsala University; Swedish University of Agricultural; SE
14:15		
14:15	Spectroscopy at the extremes with x-ray lasers: from structural sciences to fusion physics	Bianca Iwan, Uppsala University; Swedish University of Agricultural; SE
14:30		
14:40	Pyrolysis-field ionization mass spectrometry and xray absorption near edge structure spectroscopy of complex biomaterials	Prof. Dr. Peter Leinweber, Faculty of Agricultural and Environmental Sciences, University of Rostock; GER
15:25		
15:30	(Py-FIMS), X-ray absorption near-edge fine structure spectroscopy (XANES) and theoretical modeling	Ashour Ahmed, Interdisciplinary Faculty, University of Rostock; GER
15:45		
	Farewell Speech	Prof. Dr. Udo Kragl Dean of Faculty Interdisciplinary Research University of Rostock, GER
15:50		
16:00	departure	

Department Life, Light and Matter

Established within the Faculty of Interdisciplinary Research at the University of Rostock, the Department Science and Technology of Life, Light & Matter is meeting the challenges of a highly complex scientific future. For this purpose, we are examining and devising atomic and molecular processes and combining laser optics with life sciences. Based on fundamental research we develop new concepts for future technologies.



Scope

The conference will take place from 15–17 June 2011 and will focus on current developments in spectroscopic methods within science and research. The academic outline is not only limited to the natural sciences, with a further impulse being provided by the humanities. In contrast to common practice, tandem lectures by top class scientists and PhD students have been planned on mutual topics. Practical workshops and poster presentations will also form a main part of the conference programme. The mixture of experts and young scientists is a unique feature of this conference.

Words
of
Welcome

Welcome to Rostock!

The organizing committee likes to welcome you at Rostock! We wish you a pleasant and interesting stay at the ***Spectroscopy – Detective in Science*** Conference.

Around twelve months ago we started to arrange an interesting program. This Academy conference from “Forum Junge Wissenschaft” is mainly supported by the Academy of Sciences and Humanities in Hamburg.

Now we are very glad to welcome all of you here at the Hanseatic City of Rostock. We hope, you will face interesting scientific discussions, enjoy the oral presentations, poster sessions, social program and make new friends at the Baltic Sea.

In case you have any questions, please do not hesitate and contact us directly.

Best regards,



Dr. Dirk Hollmann, Sebastian Reimann, Anne Walter, Kristian Kirsch, Stefanie Wenda, Stephan Reiß, Maxi Höntsch, Christian Roth, Tim Wegner, Fiete Haack, Davit Zohrabyan, Juliane Kleeblatt, Evgeni Shoifet, Slawomir Skruszewicz, Ashour Ahmed, Susanne Beyer

Professor Dr. Heimo Reinitzer

President of Academy of Sciences and Humanities in
Hamburg



The **Akademie der Wissenschaften in Hamburg** (Academy of Sciences and Humanities in Hamburg) was founded in 2004. Members of the Academy are scholars of all academic disciplines from Northern Germany. One of its goals is to intensify interdisciplinary research and collaboration between universities and scientific institutions. The Academy promotes research on issues important for our future society as well as on fundamental scientific problems. Stimulating the dialogue between scholars and the public is of utmost importance to the Academy.

With the programme “Forum Junge Wissenschaft” the Academy supports conferences organised by young academics. Each year groups of junior scientists are invited to submit proposals on interdisciplinary topics. The conference “Spectroscopy – Detective in Science” in Rostock is a good example for this concept combining natural sciences with the humanities.

We thank the organisers for the inspiring programme and wish all participants a successful meeting.

A handwritten signature in black ink that reads "Heimo Reinitzer". The script is cursive and elegant.

Prof. Dr. Heimo Reinitzer, *president*

Akademie der Wissenschaften in Hamburg

www.awhamburg.de

Professor Dr. Udo Kragl

Dean of Faculty Interdisciplinary Research University of
Rostock



Dear Participants of the Spectroscopy – Detective in
Science Conference,

as your host and dean of Faculty Interdisciplinary Research, I am pleased to welcome you to our beautiful city. I hope that you will have an enjoyable and productive stay here.

Founded in 1419, your conference venue is the oldest University in the Baltic region and one of the oldest in Europe.

In 2007 the University of Rostock gathered its research capacities into three profile lines: *Life, Light and Matter*, *Maritime Systems* and *Aging, Science and Humanities*. In 2010 a fourth was added: *Knowledge – Culture - Transformation*.

Each profile line commands its own department. Together the four departments form the Interdisciplinary Faculty – a novelty in history of German universities.

From fundamental research, *Life, Light and Matter* develop new concepts for future technologies based on atomic and molecular processes in connection with laser optics and life sciences.

The stage at which you are in your careers is one of orientation – finding for example an interesting area to work on or a great city to live in. You find what you are looking for by talking to your colleagues and looking around at other institutions. By meeting fellow scientists you will develop your interests and get into a position to plan your future. All this is surrounded by the Baltic Sea and the sand beaches in Warnemünde, only a few kilometers away.

I wish you many interesting and useful conversations while getting acquainted with each other.

Prof. Dr. Udo Kragl

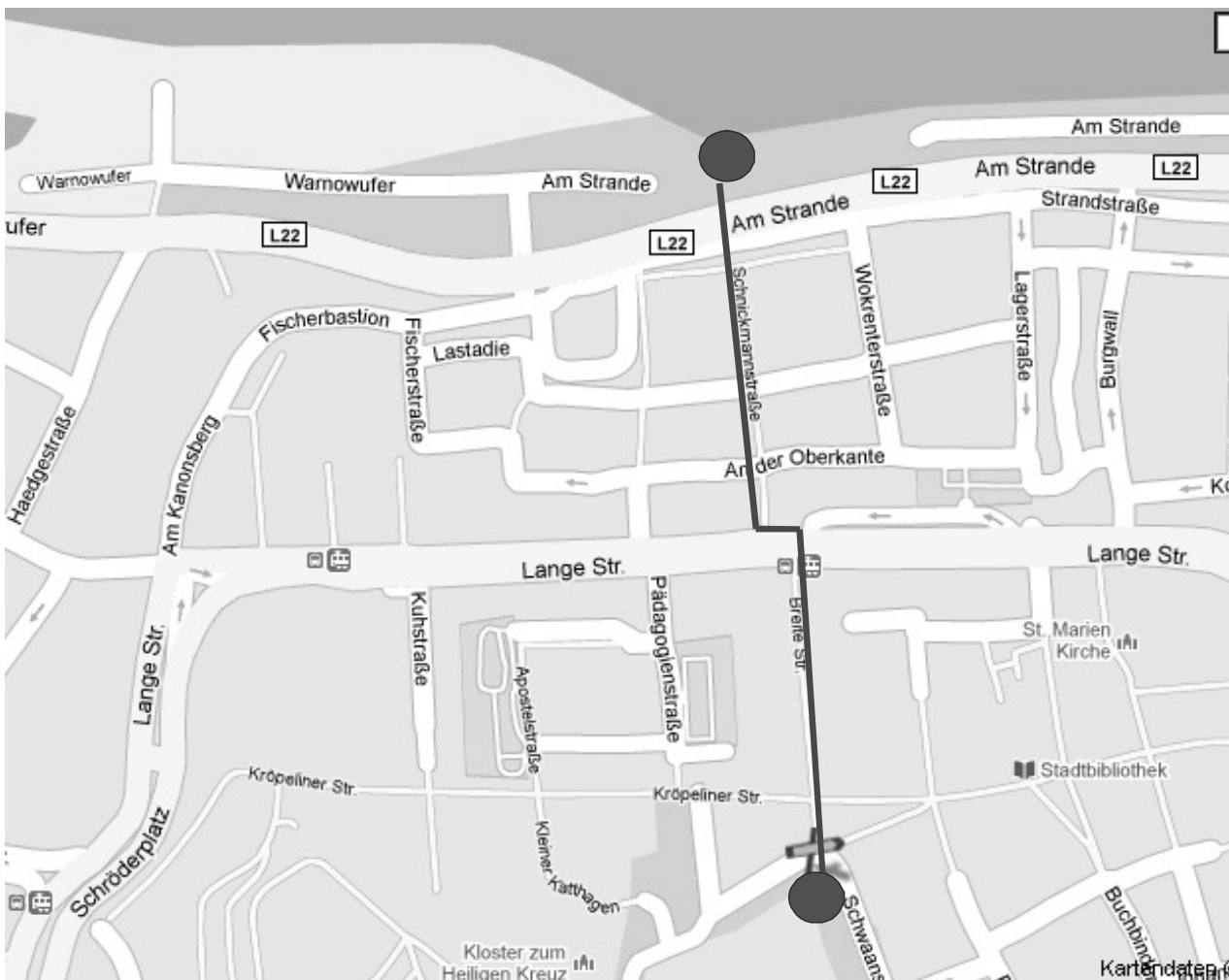
Guided Tours
and
Harbor Cruise

Come Together Dinner at the Harbour Cruise

Thursday, June 16th

We will meet at 18:45 h at Rostock harbor where the ship will depart (please check the map for further information). During the boat trip you will get some information about places of interest and a special talk from the theologian Prof. Martin Rösel with the topic:

“Sun and light in the religions of the Ancient Near East.”



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Guided Tours throughout four laboratories of the University of Rostock

Wednesday, June 15th

During the registration you will be assigned to one group and get a flyer with a map and additional information.

1. Guided Tour at the Physical Chemistry:

Lecture, discussion, demonstration of instruments regarding

- infrared spectroscopy
- Terahertz spectroscopy
- In-situ infrared Spectroscopy

2. Guided Tour at the Mass-Spectrometry Centre

Guided tour of some laboratories of the „Joint Mass-Spectrometry centre of the University of Rostock and the Helmholtz Zentrum München“: Applications of single photon ionisation (SPI) and resonance enhanced multi photon ionisation (REMPI) mass spectrometry for environmental research and combustion/pyrolysis chemistry are exemplified. Basic instrumental topics such as UV and VUV light sources generated by laser and excimer processes as well as different types of mass spectrometers (Time of flight, quadrupol) are explained directly at the instrument. The second part focuses on the instrumentation of REMPI mass spectrometry for fast real-time analysis. After a brief introduction and a demo, some advantages and problems are discussed.

3. Guided Tour at the Leibniz-Institute of Atmospheric Physics e.V. at University of Rostock (IAP)

- short introduction about the Leibniz-Institute of Atmospheric Physics e.V. at University of Rostock (IAP)
- you get some information and demonstration of instruments about the focus of the Department "Radar Soundings and Sounding Rockets" and the Department "Optical Soundings".

Optical Sounding is the groundbased optical sounding of the middle and upper atmosphere (stratosphere, mesosphere, lower thermosphere) und the scientific interpretation of the processes in these atmospheric regions, but also tropospheric processes are investigated

The focus of the department "Radar Soundings and Sounding Rockets" lies on continuous observations of dynamical and thermal parameters of the troposphere and lower stratosphere as well as the mesosphere and lower thermosphere.

4. Guided Tour at the Leibniz Institute for Catalysis at the University of Rostock (LIKAT)

The Leibniz Institute for Catalysis is the largest publicly funded research institute in Europe performing application-oriented research in the field of catalysis. We are your partner for research and development of homogeneous and heterogeneous catalysts as well as for catalytic processes.

Highly effective catalyst design based on a rational approach beyond trial and error requires authentic knowledge on relations between the structural features of catalysts and their role in catalytic reactions on a molecular basis. Such direct insight can only be obtained by analyzing the catalysts while they are working, that means under condition as close as possible to those applied in the true catalytic process.

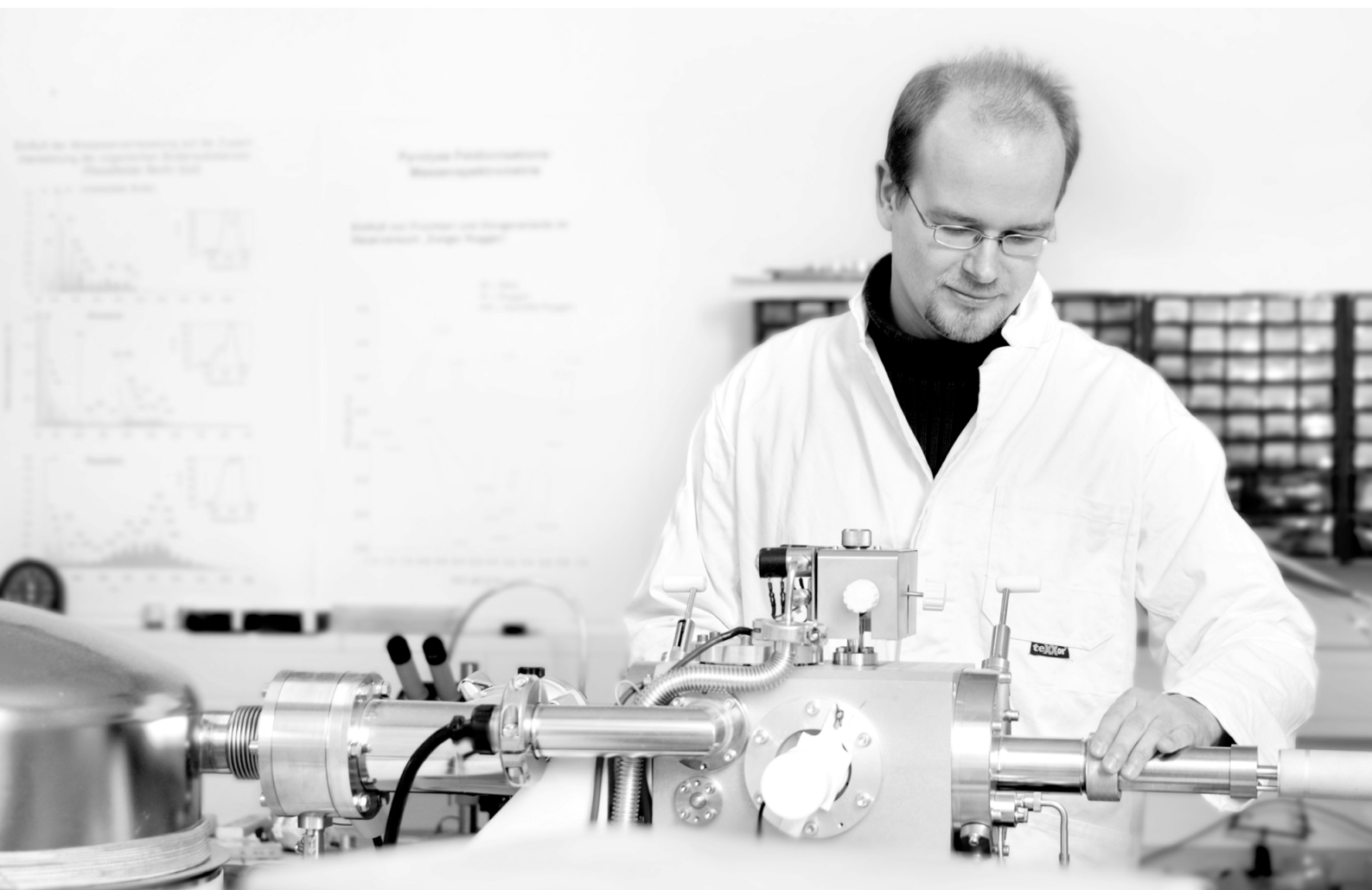
Introduced main focuses are:

Catalytic in situ studies: Coupling of different spectroscopy methods (e.g., IR/UVVIS/Raman or EPR/Raman/UV-Vis) to the clarification of structural relations and from reaction mechanisms

Solid state and surfaces analytics in real heterogeneous catalysts:

In addition the following methods are available

- Powder X-ray Diffraction (XRD)
- Transmission electron microscopy (TEM)
- X-ray Photoelectron Spectroscopy (XPS)



Abstracts of the talks

Spectroscopic viewing – A way to watch catalysts at work

Angelika Brückner

Leibniz-Institut für Katalyse e. V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock

More than 80 % of all chemical processes involve at least one catalytic step which comprises adsorption of reactants, breaking and making of chemical bonds followed by desorption of products. Rational catalyst design beyond empirical trial-and-error approaches is the ultimate goal of scientists engaged in the field of catalysis. This requires detailed knowledge on processes proceeding during catalyst synthesis as well as on the role of distinct catalyst building blocks in the different steps of catalytic reactions. This can be obtained best when catalysts are monitored during their synthesis and in their working state by a dedicated combination of spectroscopic in situ methods, each of which contributes a particular facet of information to the global view of the system under study. While vibrational in situ techniques such as FTIR and Raman spectroscopy are excellent tools for monitoring the formation of organic intermediates and vibrations of molecular moieties of catalysts, these techniques usually fail in detecting changes of structure and valence state of transition metal ions (TMI), which are part of the active sites in many catalysts. For this purpose, spectroscopies able to visualize transitions of electrons and/or electron spins are needed, such as Electron Paramagnetic Resonance (EPR), UV-vis and X-ray absorption spectroscopy (XAS).

The application potential of in situ spectroscopy for catalyst synthesis and operation will be illustrated by two examples, in which benefits arising from a combination of different methods are particularly highlighted:

1) Iron sites heterogeneous and homogeneous catalysis:

Among the variety of Fe species coexisting in Fe-ZSM-5 zeolites, those responsible for generating highly active α -oxygen from N_2O are identified by in situ EPR and UV-vis spectroscopy. These “magic” O species, which are even able to oxidize benzene to phenol at room temperature, have been identified as O^\bullet anion radicals. They are formed by decomposition of N_2O on high-spin Fe^{2+} single sites, converting them back to high-spin Fe^{3+} .

In homogeneous photocatalytic water splitting, the formation and decomposition of active iron carbonyl species is enlightened by reaction monitoring using in situ EPR, Raman and FTIR spectroscopy. Electron transfer from a photosensitizer to $\text{Fe}_3(\text{CO})_{12}$ creates different EPR-visible low-spin $[\text{Fe}_x(\text{CO})_y]^\bullet$ radical anions while the active species is diamagnetic and only seen by Raman and FTIR spectroscopy.

2) Monitoring synthesis of oxide catalysts from precursors in solution to final solids:

The first 5-in-one spectroscopy, namely simultaneous FTIR-ATR/Raman/UV-vis/WAXS/SAXS spectroscopy was used to follow particle size, particle shape, and phase formation of polyoxomolybdate precursors in a coprecipitation synthesis. To view the drying process, a droplet of the resulting slurry was levitated in an ultrasonic trap and analyzed by combined wide and small angle X-ray scattering (WAXS and SAXS) and Raman spectroscopy, which turned out that this setup is suitable to model spray-drying processes frequently used in industry. Finally, the benefits of simultaneous Raman/XRD studies for tailoring the calcination procedure of dried polyoxomolybdate precursors will be illustrated.

Elucidating Structure-Reactivity Relationships for V-Containing Oxynitrides VMON (M = Mo, Al or Zr) in the Ammoxidation of 3-Picoline

C. Janke, M. Schneider, U. Bentrup, J. Radnik, A. Martin, A. Brückner

Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Introduction

Heteroaromatic nitriles are important intermediates for the production of pharmaceuticals and agrochemicals. Thus, 3-cyanopyridine (3-CP), being the precursor for nicotinic acid, is an essential feed additive in animal nutrition. So far, the industrial benchmark catalyst for the ammoxidation of 3-picoline (3-PIC) is a KVSbTiSiO mixed oxide which reaches high conversion & selectivity of 90-98 %, however, space-time-yields (STY) did not exceed $150 \text{ g l}^{-1} \text{ h}^{-1}$ [1]. With a new class of VMON (M = Al or Zr) oxynitrides we have recently achieved the highest STY ever measured in ammoxidation of 3-PIC to 3-CP [2], yet the 3-CP selectivity remained below that of the benchmark system. It was the aim of this work to improve the $S_{3\text{-CP}}$ values. This goal has been reached with a new VMoON system. For identifying structure-reactivity relationships in VMON catalysts, we followed a comprehensive approach comprising catalytic tests and spectroscopic investigations including in situ EPR and UV-vis spectroscopy as well as a number of conventional ex situ techniques such as XPS, XRD and Raman spectroscopy.

Results and Conclusions

Each of the best catalysts within the three oxynitride series shows higher STY values than the benchmark catalyst however, except for VMoON, with lower selectivity (Fig. 1). This is particularly pronounced for VZrON, which contains a high degree of V_xO_y clusters with a mean surface V valence close to +5 and N completely enriched in the bulk, as evidenced by EPR, UV-vis & XPS. The VAION

catalyst which contains a higher percentage of single VO_x sites in a more reduced valence state between +3 and +4 is less active but more selective.

However, the best performance is shown by the VMoON catalyst, which provides virtually the same 3-CP selectivity as the benchmark catalyst but a higher STY at lower reaction temperature. Interestingly, the corresponding oxide VMoO is less active and selective than the nitrided catalyst VMoON, pointing to an outstanding role of the N sites in VMoON catalysts.

Highly effective VMON oxynitride ammoxidation catalysts must expose on their surface moderately reduced VO_x in the vicinity to N surface sites. Their lattice structure must be flexible enough to enable, besides an O-based Mars-van Krevelen redox cycle, an effective N incorporation/release cycle during reaction. This is best fulfilled in VMoON-1.5 by an active phase the composition of which varies between $V_{1.2}Mo_{0.8}O_5N_2$ and $V_6Mo_4O_{25}$, depending on the number of N atoms that might be incorporated as highly mobile, azide-like N species.

References

- [1] L. v. Hippel, A. Neher, D. Amtz (Degussa-Hüls AG), EP 0726092 B1, 1999.
- [2] C. Janke, J. Radnik, U. Bentrup, A. Martin, A. Brückner, ChemCatChem 2009, 1, 485.

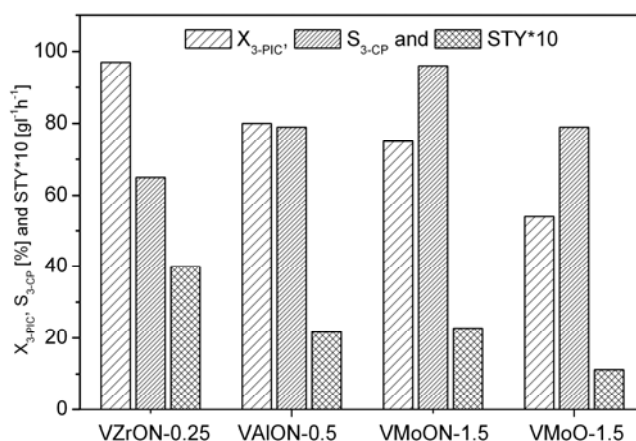


Fig. 1: Catalytic performance of VMON(N)-x.x at 360 °C; x.x = V/M-ratio.

Coupled ATR-IR / UV-vis *in situ*-spectroscopy supported by *ex situ* Raman spectroscopy and X-Ray structure analysis: Elucidation of the mechanism of an organic preparation process and further optimisation of the reaction

L. R. Knöpke, S. Reimann, U. Bentrup, A. Spannenberg, P. Langer, A. Brückner

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Albert-Einstein-Str. 29a, D-18059 Rostock, Germany*

Introduction

For elucidating reaction mechanism and kinetics a real-time monitoring of the reactions is preferably needed to overcome the disadvantages of conventional off-line analytics concerning sampling, possible consecutive reactions and time consuming analysis. Nowadays, the availability of fiber optical probes offers new possibilities for studying preparation processes under working conditions. In particular, the combination of different techniques enables a comprehensive insight into the relevant reaction system. Using this equipment an acid-moderated intermolecular Aldol-reaction between a ketenacetale and a bissilylenolether was studied.

Methods and Discussion

The product selectivity of depends on the type of applied Lewis-acid: The Mukaiyama-type reaction moderated by TiCl_4 yields to an aromatic product while the TMSOTf moderated route results a mixture of aliphatic and heterocyclic products. Coupled ATR-IR/UV-vis spectroscopy shows the formation of different transition species at room temperature at beginning of reaction. If TiCl_4 is applied, a bis-chelate complex is formed with the ketenacetale while using TMSOTf only one site of the molecule is affected. Thus, UV-vis spectroscopy shows the existence of the bis-chelate complex due to delocalisation of electrons and ATR-IR spectroscopy gives information which site of the molecule is affected. The presence of different Ti-Cl vibrations in the bis-chelate complex could be observed by Raman spectroscopy. Furthermore the molecular structure of this complex could be determined which confirms the conclusions drawn from the spectroscopic results. Measurements under reaction conditions proved this approach but have additionally shown that temperature and time significantly influence on the reaction. During the TMSOTf-route a new transition state below -10°C is formed which is important for the elucidation of the mechanism. After adding bissilylenolether to the ketenacetale-acid-mixture at -60°C the product evolution could be monitored by ATR-IR spectroscopy. Further investigations showed that TiCl_4 could be substituted by AlCl_3 which increase the yield. Contrary the application of solid acids like TiO_2 or Al_2O_3 showed only poor yields. Finally the ketenacetale could be substituted by salicylideneaniline in the TiCl_4 -route which provides the opportunity to produce cyclic amines in the same way.

Conclusion

Coupling of *in situ* spectroscopic techniques is a powerful tool for mechanistic investigations as well as for reaction monitoring. The identification and characterisation of *in situ* formed species gives a deeper insight into the reaction mechanism. Due to the knowledge of the mechanism the application of other substrates and acids could be carried out successfully.

Operando DRIFTS/UV-vis/MS studies of oxidative carbonylation of methanol over CuY-Zeolites

J. Engeldinger, M. Richter, U. Bentrup

Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Rostock, Deutschland

Objective

For elucidating the mechanism of oxidative carbonylation of methanol (MeOH) to dimethyl carbonate (DMC) over CuY zeolites, adequate knowledge concerning the adsorption process, products formation and their changes during time on stream is required in addition to the changes in the oxidation state and coordination environment of the catalytically active Cu- sites. Thus, a new operando setup consisting of a coupled DRIFTS/UV-vis/MS has been developed and successfully applied.

Experimental

For the operando-spectroscopic studies, a commercial DRIFTS reaction cell (Harrick) was modified using the quartz observation window in the dome to implement a custom-built high temperature reflection probe (Avantes) without disturbing the optical path of the IR beam. For analyzing the products, the gas outlet of the reaction cell was connected to an OmniStar quadrupole mass-spectrometer (Pfeiffer Vacuum).

Results

The formation of adsorbed methoxy species (1463 cm^{-1}), carbonates and formates ($1596/1370\text{ cm}^{-1}$) as well as carbonyl containing species (1711 cm^{-1}) have been detected by DRIFTS during the reaction of MeOH/CO/O₂ on CuY catalyst, containing 13 wt% Cu. The UV-vis spectra, simultaneously measured with DRIFT spectra, show changes of bands at 250 nm (CT O_{Zeolite}-Cu²⁺ and $3d^{10}$ - $4s^1$ -transition Cu⁺) and 800 nm (d-d-transition Cu²⁺), which indicate changes in the coordination sphere of the Cu ions caused by the formation of adsorbates. In addition, a strong decrease of the band around 500 nm (CT O_{Extralattice}-Cu²⁺ and IVCT: Cu²⁺-O²⁻-Cu⁺) at the beginning of the reaction suggests the participation of CuO_x agglomerates in the oxidation process.

The mass spectrometric analysis demonstrates that in the beginning of the reaction only CO₂ and H₂O were formed, while after 15 min time, the formation of methyl formate (MF), dimethoxy methane (DMM) and few amounts of DMC was observed.

Conclusion

MeOH is dissociatively adsorbed as methoxy species and oxidized on Cu²⁺ sites, due to the participation of lattice oxygen from CuO_x agglomerates, to formate-like species (Mars-van-Krevelen mechanism).

The formate species react further with MeOH to MF (seen in the gas phase). The formation of DMM occurs via intermediated formaldehyde with MeOH.

Another possible reaction pathway starts from CO₂, formed by reaction of CO+O₂. Methoxides react with CO₂ to monomethyl carbonate (MMC), which further react with MeOH to DMC.

Summarised it can be stated that the application of combined spectroscopic methods is suitable to study the complex processes at the catalyst under reaction conditions.

Single Molecule Studies of Surface and Soft Matter Interaction of Functionalized Perylene Diimides

Krause S.,¹ Kowerko D.,¹ Börner R.,² Hübner C. G.,² von Borczyskowski C.¹

(1) Center for Nanostructured Materials and Analysis, Chemnitz University of Technology

D-09107 Chemnitz, Germany

(2) Institute of Physics, University of Lübeck, D-23538 Lübeck, Germany

The fluorescence signal of a single molecule provides a variety of information such as intensity, lifetime, polarization and emission wavelength which allows for close insight into dynamical processes within the nanoscopic environment. Due to the high sensitivity of a single emitter to environmental fluctuations single molecule spectroscopy (SMS) has become a standard method in material sciences and biophysics. Especially tailor made organic molecules allow for various attachment routes via functional chemical substituents, sensitivity to specific reagents or steric interaction with the surrounding molecular environment.

One of the most suited dye molecules for functionalization and application as a probe molecule is the perylene diimide-type system (PDI). This class of fluorophores features high quantum efficiency and photo stability. Pyridyl functionalized PDI has been frequently used as a building block for light harvesting systems and J-aggregates [1].

Here we present a method to determine single molecule orientation, fluorescence lifetime and emission wavelength of PBI selectively bonded via pyridyl groups to silicon dioxide surfaces or embedded within a polymer matrix [2]. Using microscope objectives with high numerical aperture allows for the splitting of the fluorescence signal of a single emitter into three parts and thus the direct determination of the three dimensional orientation of the transition dipole and the related molecular axis [3]. Besides the determination of the orientation, we can also follow time-dependent reorientation processes. In terms of polymer dynamics shifts in the emission wavelength of a single molecule known as spectral diffusion processes turned out to be an ideal tool to investigate nanoscopic fluctuations which would vanish within ensemble experiments.

[1] F. Würthner, 2004. Chem. Commun., 1564-1579

[2] D. Kowerko, J. Schuster, C. von Borczyskowski, 2009. Molecular Physics, 107, 1911- 1921

[3] J. Hohlbein, C. G. Hübner, 2008. Journal of Chemical Physics, 129, 094703

Investigation of medically relevant substances using Photoionization-Time of Flight Mass Spectrometry

Kleeblatt, J., Sklorz, M., Schubert, J., Zimmermann, R.

Joint Mass Spectrometry Centre

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Photoionization-time of flight mass spectrometry (PI-TOFMS) represents an efficient method for analyzing organic trace components in real time. Due to the fact that photoionization is a soft ionization technique - which is characterized by less or even no fragmentation - even complex mixtures can be analyzed directly. After their formation the ions are separated in a Reflectron-TOF according to their mass-to-charge ratio and subsequently detected by a multichannel plate detector (MCP). Photoionization can be classified into single and multi photon processes. Single photon ionization (SPI) is based on the absorption of only one VUV (vacuum ultraviolet)-photon ($\lambda < 180$ nm). The molecule is ionized, if the photon energy is higher than the ionization potential of this substance. Generally these VUV-Photons are produced using a laser or a VUV-lamp, however, in this work we utilized the synchrotron radiation from the "Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung" (BESSY). For resonance enhanced multi photon ionization (REMPI) the absorption of more than one photon is necessary, in analytical practice mostly the one-color two-photon process is used. The energy of the first photon is lower than the ionization potential of the substance and in resonance with an excited state. Depending on the lifetime of this excited state and the light intensity, a second photon can be absorbed and the ionization potential is exceeded. The substance-specific excited state provides the very high selectivity of REMPI. In this work various medically relevant substances were investigated for determination of the most suitable method. With the knowledge of the appropriate wavelength tests to measure these substances in breath gas in real time are enabled.

NMR, Peptides and the catalytic cycle, an approach

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Solid state NMR is one of the best suited tools for structure elucidation of non crystalline solids by means of utilizing multidimensional spectroscopic techniques. While one dimensional NMR techniques provide mainly information about chemical compositions on the basis of their spectral "fingerprints", multidimensional techniques offer access to the structures and confirmations of molecules and solids.

The basic principles of one and two dimensional NMR will be exemplified by the elucidation of the binding scenario of immobilized Wilkinson's catalyst in mesoporous silica^[1] and by the revealing of the position of the substrate in Nickel superoxide dismutase^[2,3].

The latter is of particular interest in life science, since reactive oxygen species (ROS) are a major factor in the development of several types of cancer, inflammation, and related diseases. These ROS are not only cytotoxic but also involved in cell signaling. The protection from ROS is of vital importance for biological organisms. For aerobic organisms, superoxide dismutases (SODs) play the major role in protecting cells from ROS, which are generated by the reduction of molecular oxygen by reactive metabolites of the respiratory chain. Because of their biological and medical importance, SODs are a subject of intense research, which yielded more than 2000 publications in the first six months of 2010. While this research has led to detailed knowledge about their biological function and enzyme kinetics, the precise mode of action of these enzymes is still not known and two different mechanisms were proposed. A major reason for this lack of knowledge is the high catalytic rate constants of superoxide degradation ($O_2^{\cdot -}$) by SODs. SODs destroy the superoxide anion radical by converting it into hydrogen peroxide and oxygen with a rate near the diffusion limit ($k_{cat} > 2 \times 10^9 \text{ s}^{-1}$). Thus all transients involved in their action are too short lived to be amenable for a spectroscopic characterization. For this reason model systems of SODs were developed. Herein we show that the investigation of a model system of the nickel superoxide dismutase (NiSOD) by means of liquid state and solid state NMR is able to shed light into the mode of action of this enzyme and makes it possible to decide between the proposed mechanisms. In particular we are able to reveal not only the mode of binding of the substrate to the enzyme also the presence of functional water molecules in the active site of the enzyme.

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Human Hemoglobin detection by using AgO thin films as Surface Enhanced Raman scattering (SERS) substrates

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Abstract

Raman spectroscopy and Surface enhanced Raman scattering (SERS) are well established techniques in the detection of trace quantities of organic and bio-molecules. Presently, silver and gold are the widely used SERS substrates. Silver being highly reactive, it is difficult to prepare and preserve pure silver substrates/thin films. In the present work we report that (i) silver oxide thin films are efficient SERS substrates and (ii) the detection of Human hemoglobin (hHb). Silver oxide thin films are Photo-activated to produce silver nanoclusters, which are responsible for significant enhancement of Raman signal; photo-activation depends upon the incident laser power density.

The silver oxide (AgO) thin films of thickness ~ 300 nm are prepared on glass substrates at room temperature by pulsed laser deposition (PLD) technique at an oxygen chamber pressure of 30 Pa. Screened blood is collected from the hospital and hHb is separated. Optical absorption spectra (Jasco V 570 spectrophotometer) confirmed the hHb with its characteristic bands observed at 542 nm and 577 nm. Three different dilutions of 2.2×10^{-4} M, 5.8×10^{-4} M and 1.3×10^{-3} M hHb are used for the SERS detection using AgO thin films. 633 nm He-Ne laser (Jobin Yvon Model HR800UV) is used for collecting Raman spectra. Photo-induced silver nanoclusters are observed for laser intensity greater than 0.6 MW/cm^2 . Hemoglobin of 2.2×10^{-4} M is detected on AgO thin films with 633 nm excitation. For laser intensities higher than the threshold value (0.6 MW/cm^2), it is observed the hHb structure itself changes along with the photo-activation of AgO into silver nanoclusters. So for the detection of biological molecules the laser intensities should be small. With the detection of $\sim 10^{-4}$ M hemoglobin we proved that AgO thin films can be applied as SERS substrates for the detection biological molecules.

FEATURES OF EXCITON MIGRATION IN CYANINE DYE

J-AGGREGATES

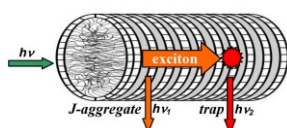
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J-aggregates (Jelley aggregates) are luminescent nanoscale supramolecular assemblies formed by well-ordered chains (linear or closed) of dye molecules, typically polymethines (cyanines, merocyanines or squaraines) and porphyrines. Their spectral properties are usually explained within Frenkel's exciton model. Due to excitonic nature of electronic excitations, J-aggregates reveal a number of unique spectral properties, one of which is an exciton migration over hundreds of monomers. Indeed, it was shown that J-aggregates are the most promising artificial systems to mimic light-harvesting complexes (LHC), which provide extremely fast and efficient energy transport of the absorbed sun light to the photochemical reaction center of plants and photosynthetic bacteria.



Using luminescent exciton traps, an efficiency of the exciton migration in cylindrical J-aggregates of an amphi-PIC dye in solutions has been investigated. Using cyanine

dye DiD as an exciton trap it has been found that 50% of amphi-PIC J-aggregates luminescence accessible for trapping is quenched at the ratio amphi-PIC/DiD = 120:1. Due to the micelle-like structure of amphi-PIC J-aggregates and large DiD hydrophobicity, the total solubilization of the trap molecules by the J-aggregates has been considered. It has been revealed that only a small part of excitons (about 30%) reach the trap even at significant trap dye concentration. Surfactant CPB is found to interact with amphi-PIC J-aggregates forming shell around J-aggregates. The amphi-PIC J-aggregates structure in this case appears to be more perfect that results in about 3 times increase in the value of the exciton delocalization length. The improvement of J-aggregates structure leads to the 30% enhancement of the exciton migration efficiency, i.e. 50% amphi-PIC J-aggregates luminescence accessible for trapping is quenched at the ratio amphi-PIC/DiD = 160:1

Ultrafast Spectroscopy Investigation of Au-Fe_xO_y Hetero-nanostructures

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We present a comparative study regarding time-resolved optical properties of Au nanocrystals, Fe_xO_y nanocrystals, and the dumb-bell hetero-dimers composed of the two. Although the single Au and Fe_xO_y particles had been investigated quite extensively, to the best of our knowledge, this is the first transient-absorption study on Fe_xO_y/Au hetero-dimers. These nanostructures attracted a considerable attention recently, because they exhibit both magnetic and plasmonic properties and have been proposed for applications in biology [1] and catalysis [2]. In particular, it has been shown that the catalytic properties of iron-oxide are enhanced by proximity of gold [3]. It has been suggested that the energy or the charge-transfer between gold and iron oxide may be involved. However, so far no conclusive explanation has been found.

In order to improve the understanding of these systems, we performed the static and time-resolved spectroscopic measurements. Static spectra of dimers showed a red shifted plasmon peak from 525nm (single gold particle) to 540 nm, which could be caused by either dielectric shift [4] or electron deficiency, due to the proposed charge transfer between the Au and Fe_xO_y [5]. Since it can be expected that such a charge transfer between particles would have an impact on the observed dynamics on the femto-second time scale, we performed the pump-probe experiments (pump central wavelength 400nm, probe 800nm) with 70fs time resolution on: Au particles (8 nm diameter), Fe_xO_y particles (12 nm) and Au/Fe_xO_y dimers. Interestingly, both dynamics of dimers and Fe_xO_y single particles were very similar, with time decay constants around 0.1ps, 5ps and 60ps. The assumption that gold plasmon red shift is caused by the electron transfer would require a transfer of 10% of the Au free electrons to Fe_xO_y. Since this fact would most likely make the time decay constants of Fe_xO_y and dimers different, we can rule out the electron transfer mechanism and suggest that the origin of the red shift is the most likely related to variation of dielectric environment.

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Study the atomization of the generated hydride species in a dielectric barrier discharge atomizer

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In the current work, a simulation study for a miniaturized dielectric barrier discharge (DBD) atomizer was conducted by using CFD. The aim was to investigate the atomization process of the hydride species in a DBD atomizer, which is intended to be used for detection of heavy metals in water samples. A simplified DBD atomizer was designed and fabricated by using microscope glass slides aligned together by a perspex chip holder. The simulation of the DBD atomizer was performed by integrating five models in Comsol 3.5a software; including momentum, heat transfer, AC power, and two models for mass transfer. The defragmentation of the hydride molecule in the atomizer was prescribed as a result of collision between the hydride molecule and the hydrogen excited particles, which are generated due to electrons reaction in the atomizer. The simulation results have shown a higher electron number density is formed in the gas channel section which is located at the end of the electrodes overlapping section. The abundance of the electrons in that position have consequently result in forming higher concentration of the hydrogen radicals and the hydrogen excited particles, and finally lead to generate the analyte free atoms. This result have indicated the above mentioned location might be an optimum position for spectrometric data acquisition along the DBD gas channel. This finding has been verified experimentally by applying the chemical vapour generation process to generate the mercury volatile species, followed by atomizing the species in the fabricated DBD atomizer. The mercury emission signals at a wavelength (253.65 nm) have been collected from several positions in order to compare the data. Two positions were selected along the DBD gas channel, whereas the third position was assigned at the end of the gas channel. The experimental results have shown 12% increase in the signal intensity upon changing from the first position (in the centre of the gas channel) to the second position (located 10 mm after passing the electrodes overlapping area), whereas the signal intensity increased *seven* orders of magnitude upon using the third position with an axial viewing. This agreement between the simulation and the experimental result would be advantageous for enhancing the design of the DBD chip.

Key words:

hydride generation process, dielectric barrier discharge Atomizers, Emission spectroscopy

Neutron and x-ray reflectometry for characterisation of polymer coated surfaces

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The talk will focus on methods, which are used for characterization of solid surfaces coated with polymers, mainly on x-ray and neutron reflectometry. Results will be shown according to 2 types of polymer films: polyelectrolyte multilayers which are built up by alternating deposition of polyanions and polycations from aqueous solutions [1, 2] and films formed by deposition of hydrogel microparticles [3]. FRAP measurements show that the mobility of the polyelectrolyte chain within the polyelectrolyte multilayers can be easily changed by e.g. the degree of polymer charge, ionic strength and type salt [4]. The water content was studied by neutron reflectometry. The temperature effects are minor due to strong interdigitation between adjacent polyelectrolyte layers [5]. Therefore another strategy is to separate thermosensitive compartments from stabilizing ones.

During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering. These polymer particles show thermoresponsive behaviour and can therefore be classified as “smart” materials. By copolymerisation with organic acids such as acrylic acid (AAc) the temperature of the volume phase transition as well as the swelling ratio can be influenced. Moreover charged copolymers are sensitive to changes in pH and ionic strength. Depending on the way of preparation one can achieve particles with rather low polydispersity which makes them more interesting for applications like surface coatings and sensor design. Our work focuses on the fabrication of stimuli responsive films and on the effect of geometrical confinement on the phase volume transition of these microgel particles [3, 6]. The effect of cross-linker and co-monomers on the swelling behaviour and on the elasticity is presented [7].

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Free electron lasers – the brightest x-ray sources

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New light sources based on linear accelerators such as the free-electron laser FLASH at DESY in Hamburg in the extreme ultraviolet, the Linac Coherent Light Source LCLS in Stanford as the world's first x-ray laser and the European XFEL currently under construction in Hamburg provide ultrashort, extremely powerful short wavelength pulses with unprecedented coherence properties.

These new sources open up new possibilities in spectroscopy and microscopy with exciting applications in physics, chemistry, materials science and life science. The talk will give an introduction into the physics of these light sources and their properties and will review recent highlight experiments with these sources.

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Automated Analysis in Life Science Research

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In the recent years, high throughput screening applications have been established in diversified fields of industry, science and research, especially in drug discovery [1]. Numerous systems based on optical methods such as absorption or fluorescence spectroscopy have been developed that enable the analysis of high numbers of compounds within short time frames. These highly parallel systems are used in biological screening applications. Although they provide rapid analytical measurement results the information content regarding the structural and elemental composition of samples is limited.

Mass spectrometric processes provide structural and elemental information and can thus be used in life sciences (proteome research, clinical diagnostics, metabolomics, pharmacokinetics), environmental and food sciences (investigations into environmental pollution, food production), elemental and polymer analytics (isotopes and elemental analytics, petrochemical analytics, synthetic and biopolymer analytics) and other areas (forensics and drug abuse testing, space and defence research). Demand for mass spectrometry equipment has been rising since mass spectrometry is more powerful, robust, versatile and intuitive in operation; apart from that, throughput rates have increased and testing capacities have grown [2, 3]. Entering these areas in the automation market will require suitable systems combining sample preparation and analytics, including flexible data analysis, to be developed. Automation systems of this description are still a novelty, and only individual cases have been documented. Analysing the data collected has proven to be a major bottleneck in every automated system. Data of interest such as concentration and conversion is not directly accessible in substance measurement technology, and needs to be extracted as secondary data from the raw data collected. Data evaluation depends on the application used, and the task at hand consists of developing versatile data evaluation modules that can be reconfigured for new requirements.

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High Throughput Analysis of Amino Acids Using Mass Spectrometry

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Amino acids are essential compounds in life. As their biological effects depend on their chiral composition a rapid enantiomeric excess determination of the enantiomers is of great importance. Commonly, the enantiomeric composition of amino acids is determined using conventional analytical methods such as HPLC, GC, or CE. Due to their relative long analysis times, high-throughput requirements often cannot be fulfilled. A method based on parallel kinetic resolution and ESI-MS with pseudoenantiomeric mass tagged auxiliaries has been developed that enables a fast determination of enantiomeric excess of amino acids in approximately two minutes per sample. The fully automated process includes sample pretreatment using liquid handlers and software-based data processing.

The enantiomeric excess determination using parallel kinetic resolution and ESI-MS provides a methodology, which allows the rapid determination of D- and L-AA's in the scope of high-throughput screenings. The use of short stop times such as 0.5 min and the high-throughput mode of the auto sampler with overlapped injection enable total analysis times of about 2.08 minutes for one sample. This includes a sample pre and post procession, each requires approximately 4 min per 96-well MTP, a derivatization time of one hour, an analysis time of 132 minutes and the time for data evaluation and visualization of 8 seconds. Therefore, this method is much faster compared to classical analytical procedures and does not require expensive chiral columns or a high amount of solvents. The method is fully automated including sample preparation using liquid handler and suitable data processing for post-run data manipulation, subsequent data evaluation and visualization using commercial and additionally implemented software. The method developed can be expanded to the determination of other biological important chiral compounds.

Modern Raman-spectroscopic methods for investigations of complex bioorganic samples

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Raman scattering information is a powerful tool for the characterization of biological molecules, but also for complex, microstructured biosamples due to its fingerprint-like nature. However, typical Raman cross-sections are very small, $\sim 10^{-30}$ cm² per molecule. As was shown in the past several years, the favorable properties of noble metal nanostructures can be employed to generate surface-enhanced Raman scattering (SERS) signals in very complex biological samples such as cells, and result in an improved sensitivity and spatial resolution.

In this talk, normal Raman scattering and SERS will be discussed in the context of applications in complex bioenvironments. In particular, exploitation of the multifunctional and multiplexing capabilities of SERS nanoprobe for bioanalytical use will be demonstrated. Our recent results have provided evidence that approaches using multivariate statistics can be applied for discrimination of SERS labels and probes, beyond the visual inspection of individual spectra that has been practiced so far (1). The data indicate that fast, multivariate evaluation of whole sets of multiple probes is feasible, and that it can also be applied for multiplex microspectroscopy.

The increased lateral resolution is very useful for imaging, and in many cases adds to the selectivity of the Raman micro-/spectroscopic experiment. We utilize Raman scattering and SERS for the analysis of cellular samples of plant and animal origin which are several tens to hundreds of microns in size. There, nanoparticles of gold and silver are used as plasmonic nanostructures to generate the enhanced local optical fields in which SERS takes place. In experiments with live cells, metal nanoparticles are transferred into the cell, and depending on their size and surface properties, can be directed to different cellular compartments. In order to find out about the interaction of the nanoparticles with the cellular ultrastructure, their morphology and possible agglomeration behaviour are studied, and viability of the cells is assessed using standard biological assays such as the XTT assay.

The second type of complex sample are pollen grains, the physiological containers that produce the male gametes of seed plants. They consist of a few vegetative cells and one generative cell, surrounded by a biopolymer shell. Their chemical composition has been a subject of research of plant physiologists, biochemists, and lately even materials scientists for various reasons. We have used normal and surface-enhanced Raman scattering to characterize and identify pollen from different plant species, also with the goal of developing fast allergy warning systems (2). Data from SERS experiments suggest that information about very localized chemical composition can help our understanding of pollen biochemistry as well as of dynamic processes occurring in the plant tissue (3).

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Development and characterisation of new planar SERS sensors for detection of catalytic activity and other applications

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Planar, nanostructured SERS substrates have become a basic tool for applications of SERS to analytical problems (1), as such a substrate permits reproducibility of SERS signals from an analyte. Here, we report on the construction of dedicated, planar SERS sensors based on immobilization of nanoparticles on glass substrates via polymers. In particular, the electromagnetic contribution to the SERS enhancement of individual gold nanospheres that are used as basic building blocks for the nanostructured surface was determined experimentally (2). So far, experimental proof of the theoretical predictions (3) of such enhancement factors was still missing. Immobilization and functionalization of the nanoparticles is a crucial step in the construction of the sensor. For the characterization of the properties of the nanoparticles in solution and on the substrate, direct (electron microscopy, scanning force microscopy) and indirect methods (UV/Vis absorption) have been used. Furthermore the stability and reproducibility of the substrate and the influence of different parameters (e.g. concentration, functional group, properties of the nanoparticles in solution) during the assembly were examined. A major hallmark of our novel sensors is the possibility to combine nanostructures of different materials.

Using novel planar composite sensors, we show how SERS can be used for the determination of catalytic activity. The fast determination of catalytic activity is important in the development of new catalysts. For hydrogenation reactions the conversion of 4-nitrophenol to 4-aminophenol by sodium borohydride is used as model reaction. Usually, the reaction is monitored by UV/Vis spectroscopy which is very time consuming. In contrast, the application of SERS is very fast and molecule-specific.

The use of an internal standard allows a relative quantification and the determination of reaction rates.

So far, this sensor was used with different catalysts such as platinum nanoparticles, copper acetylacetonat and Raney-nickel. Future applications include studies in the area of biocatalysis.

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Proteomic fingerprinting: an example for information-based medicine.

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Abstract

Mass spectrometry (MS) based techniques have emerged as a standard for large-scale protein analysis. The ongoing progress in terms of more sensitive machines and improved algorithms led to a constant expansion of its fields of application. Recently, MS was introduced into clinical proteomics with the prospect of early disease detection using proteomic pattern matching. MS based characterization and identification of peptides in blood appears to be one of the arising key technologies for biomarker discovery, understanding of biological mechanisms, and consequently, it might offer new approaches in drug development.

In this talk we will introduce the MS technology and present our algorithmic pipeline for the reliable (pre-)processing and analysis of the (very large) datasets created during MS experiments.

Further, we will show current and (possible) future applications in clinical diagnostics and information-based medicine.

Capturing Proteolytic Activity in Mass Spectrometry Measurements

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Abstract

Proteases are key players in a majority of biological processes. They are not only associated with food catabolism but play also an important role in the regulation of complex cascades like blood coagulation, cell cycle progression, and apoptosis. Despite their importance they also play a problematic role in proteomic measurements, since the *ex vivo* activity of proteases can destroy peptide profiles or lead to incorrect conclusions based on peptide profile differences which are based on degradation and not on a biological phenomena.

We therefore present an approach to identify proteolytic reactions in mass spectrometry measurements. The identified reactants are organized in a network and connected by the assumed reactions. The constructed network is used to generate a mathematical model which characterizes the activity of proteolytic reactions. The constructed mathematical model combined with time series measurements is used to estimate the reaction parameters.

We present first results of this approach on simulated data that show a good recovery of the original reaction system as well as the reaction parameters.

FT-IR Spectroscopy of Membrane Proteins

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One crucial task of spectroscopy in bioscience is to identify the structure of proteins on an atomic level. To perform their biological function, proteins may change between several related conformations. All intra- and intermolecular alterations sensitively modulate the infrared spectrum of proteins because the vibrational modes are basically determined by the structure. Fourier transform infrared spectroscopy (FT-IR) offers distinct advantages concerning restrictions pertinent to biomolecules. In particular, it is possible to monitor the temporal evolution of the reaction mechanism of complex machineries as membrane proteins, where other techniques encounter significant experimental difficulties. During the past three decades, two FT-IR techniques showed growing impact on time-dependent investigations: the rapid-scan and the step-scan technique. Both techniques could be used in conjunction, yet, step-scan technique achieves higher time resolution from microseconds to nanoseconds. Here, we provide a basic introduction to illustrate the principles of FT-IR spectroscopy together with some experimental realizations. Examples from applications to several membrane proteins are reviewed that underline the impact of time-resolved FT-IR spectroscopy on the understanding of protein reactions on the level of single bonds.

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Soft photo ionization mass spectrometry for the analysis of biomass flash pyrolysis gases within the Karlsruhe bioliq® - Biomass to Liquid - Project

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Soft photo ionization mass spectrometry is applied as detection method for organic compounds in pyrolysis gases from biomass, as a contribution to the optimization of the bioliq® process, developed at the Karlsruhe Institute of Technology (KIT). Thereby, evolving gases from flash-pyrolyzed biomass are condensed and immingled with the remaining coke, providing biosyncrude that is used for synthesis gas generation and the subsequent FT reaction. Hence, the pyrolysis gas composition influences the further steps in the process. Time-of-flight mass spectrometry (TOFMS) with two soft (i.e. fragmentation free) photo ionization techniques was for the first time applied for on-line monitoring of the signature organic compounds in highly complex pyrolysis gases at a technical pyrolysis pilot plant at the KIT. Resonance enhanced multi-photon ionization (REMPI) – TOFMS using UV laser pulses was employed for selective and sensitive detection of aromatic species. Furthermore, single photon ionization (SPI) using VUV light supplied by an innovative electron-beam pumped excimer light source (EBEL) was used to comprehensively ionize (nearly) all organic molecules. The soft (i.e. fragmentation free) ionization capability of photo-ionization techniques allows the direct and on-line monitoring of the pyrolysis gases, masking out small matrix molecules like nitrogen or carbon dioxide. The transfer of the pyrolysis gases to both mobile mass spectrometers was carried out via a heated sampling train and heating hoses containing a capillary. For the miscellaneous biomass feeds used, distinguishable mass spectra with specific patterns could be obtained, mainly exhibiting typical pyrolytic decomposition products of (Hemi-)Cellulose and lignin (phenol derivatives), and nitrogen containing compounds in some cases. Certain biomasses are differentiated by their ratios of specific groups of phenolic decomposition products. Anymore, Principal Component and Cluster Analysis describe the varied pyrolysis gas composition for temperature variations and particularly for different biomass species.

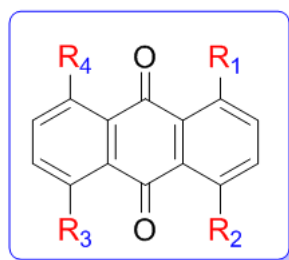
NEW 9,10-ANTHRAQUINONE DERIVATIVES IN TERMS OF MOLECULAR RECOGNITION

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Anthraquinones due to their chromophoric system were extensively used for many years to produce dyes and pigments [1,2]. Nowadays they found new field of application – medicine, pharmacy or industry. The 9,10-anthraquinone moiety is a base of many drugs, like anthracycline antibiotics used in anticancer therapy [3]. Moreover they can play important role as a sensing unit in terms of molecular recognition, because they act like good chromophores and electrophores.

The spectroscopic properties of anthraquinones are well documented. The position of the substituent affects not only spectroscopic properties of the compound by charge transfer interaction with the ring system, but also changes its acid-base and complexometric properties [4]. The knowledge about the influence of the structure of the anthraquinone derivatives and their closest environment allows us to design new sensors or drugs.



R_1, R_2, R_3, R_4 = side groups like $-NR_3$, $-OH$, $-Cl$

Scheme 1. The structures of investigated compounds.

The influence of different substituents on spectroscopic, acid-base and complexometric properties of anthraquinones derivatives were determined. By applying the potentiometric titration technique and hybrid pH-metric/UV titration methods, acid dissociation constants (pK_a) values for the series of 9,10-anthraquinone derivatives (Scheme 1) were determined. The presented results show the nature of changes in the observed equilibrium and their values that vary depending on the substituents and their position in the aryl ring of anthraquinone moiety.

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Spectroscopy at the extremes with x-ray lasers: from structural sciences to fusion physics

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X-ray free electron lasers are the latest generation of large facility radiation sources, providing unprecedented capabilities for studying matter under extreme conditions and dynamics on the femtosecond timescale. Intense coherent X-ray pulses can be exploited to create and probe extreme states of matter, and also hold the promise for structural determination of biological systems. The FLASH free-electron laser in Hamburg made its mark in the past years in the soft X-ray regime. The LCLS Linac Coherent Light Source in Stanford has recently started user experiments in the hard X-ray domain.

Any sample investigated with an extremely intense and short X-ray pulse will be ionized and destroyed extensively. Non-thermal heating and formation of plasma and warm dense matter have been investigated and ion acceleration has been observed, which could lead to obtaining nuclear fusion with X-ray lasers. Understanding and controlling the ultrafast radiation damage provides a new way to overcome the limitations in structural studies of protein acromolecules. The principle "diffract-and-destroy" has been proven experimentally and ultrafast coherent diffractive imaging of particles is now an established research frontier.

We present theoretical models for damage dynamics, based on Molecular Dynamics simulations and plasma software with non-Local Thermodynamics Equilibrium with hydrodynamics expansion. We also present flight-time spectroscopy experiments performed at FLASH and LCLS, which investigate ultrafast dynamics and plasma formation in various samples: aligned molecules, molecular clusters, bulk solids, protein macromolecules, protein nanocrystals, viruses and living cells.

Pyrolysis-field ionization mass spectrometry and x-ray absorption near edge structure spectroscopy of complex biomaterials

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The characterization of complex organic biomaterials like sedimentary or soil organic matter, humic substances, composts, manures etc. at the molecular level is a great challenge for the application of proper spectroscopic methods. As the analytical question often is to find and explain differences among samples according to different origin or treatment/management, non-targeted methods that look at the bulk organic matter are particularly useful. Pyrolysis-(soft) field ionization mass spectrometry (Py-FIMS) is such a versatile analytical method; it has been successfully applied in agricultural and environmental sciences [1]. The presentation will explain the principle of the method and demonstrate the analytical power with a few examples (plant rhizodeposition day-/night-cycles, wine quality, soil organic matter stability). However, one disadvantage is the thermal decomposition of sample upon analysis that inevitably produces pyrolysis products which must not necessarily genuine components of the original sample. This becomes particularly complicated in case of soil organic matter because wildfires and resulting pyrolytic organic matter transformation are natural processes and have affected many soils. Thus, a multi-methodological approach, involving a less destructive complementary technique like synchrotron-based X-ray absorption near edge-fine structure spectroscopy (XANES) at the C- and N *K*-edges, is strongly recommended. Advances in the method developments in C- and N-XANES will be summarized [2], and it will be shown, how Py-FIMS and XANES complement in the characterization of soil organic matter. Current research issues requiring the application of both methods in conjunction are the characterization of heat-affected transformations in soil organic matter (PhD Kristian Kiersch), systematic modifications of soil organic matter functional groups as a precondition for disclosing the mechanisms of xenobiotic-organic matter bonds at the molecular scale (PhD Ashour Ahmed) and mechanisms of organic matter-metal-mineral surface bonds (PhD Chunmei Chen at the Delaware Environmental Institute, University of Delaware). The outlook will highlight ongoing method improvements and new instrumentation in spectroscopy applied to these types of samples.

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Interaction of soil organic matter with xenobiotics: Pyrolysis mass spectrometry (Py-FIMS), X-ray absorption near-edge fine structure spectroscopy (XANES) and theoretical modeling

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Binding of chlorinated organic pollutants by soil can be studied experimentally and theoretically. Experimentally we investigated the adsorption of hexachlorobenzene (HCB) on different soil samples. In these samples the soil organic matter (SOM) composition was changed systematically as prerequisite to disclose the contribution of various functional groups to the adsorption process. First we removed hot water-extractable organic matter because these substances originate mostly from plant and microbial metabolites and contain oxygen-containing and, thus polar, functional groups (e.g. in sugars and amino acids). Then we added this hot water-extracted organic matter in increasing amounts to the original soil samples. Finally, we pyrolyzed a native soil sample under N₂ atmosphere at 400°C in order to decrease the polar character of SOM. In this way we obtained soil samples with similar mineralogy but gradual differences the SOM content and polarity. We checked the success of these gradual alterations by Py-FIMS and XANES at the C and N *K*-edges. The experimentally determined adsorption data of HCB were fitted to the Freundlich equation, yielding squares of the correlation coefficients from 0.978-0.996. The adsorption of HCB became stronger in the order native soil < soil + 3 HWE < soil + 6 HWE \approx pyrolyzed soil. Explanation of these results with the mass and X-ray spectroscopic data indicated that the adsorption became stronger as the proportions of carbohydrates, peptides, N-heterocyclic compounds and/or phenols + lignin building blocks increased. These experimental data were tested theoretically by modeling the SOM by small molecules that contain the most interesting SOM functional groups. The binding energy for HCB with each molecule was calculated in the gas phase. These calculations revealed that the binding energy increased in the presence of polar functional groups, which confirmed the experimental results.

Abstracts of the posters

Determination of Some Pesticides in Soils by Shaking Extraction Combined with Gas Chromatography - Mass Spektrometer

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Increasing production and application of pesticide (herbicides, insecticides, fungicides, etc.) loadings on agricultural soils have caused air, ground and surface water pollution [1]. This pollutants in soils have resulted erosion and tillage, reducing the quality of the soils and posing important environmental and toxicological threats. Fungicides are widely used in viticulture for vine and grape protection. Vineyard soils are usually highly degraded soils in terms of biochemical properties and are thus more susceptible to contamination [2]. The behavior, persistence and mobility of pesticides are closely associated with different processes occurring in soils; sorption-desorption, volatilization, chemical and biological degradation, up-take by plants and leaching. Extraction procedures of pesticide residues from soil samples depend on the chemical and physical properties of the pesticides as well as the type of sample matrix [3]. The aim of the research was to work out the analytical procedures of pesticides in soil samples. we used shaking extraction procedures for pesticides (Chloropyriphos, Fhention, penconazol, triadimenol and mayclobutanil) extraction from the soil samples. We selected methanol for extraction solvent, 2 hours for extraction time and 900 rpm shaking speed. The extracts were enriched and performed in gaz chromatography-mass spektrometer for analaysis. Detection limit; 51-228 ng/L, enrinchment factor; 92.6-114.8 was obtained. The results were analyzed statistically (Duncan's test, Pearson correlation, ANOVA etc.).

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Investigation of cell nuclei in human brain tissue section using Raman spectroscopic imaging

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Raman spectroscopic imaging is a powerful technique which provides image contrast based on material's intrinsic vibration spectroscopic signature without the use of stains. It has been used to characterize tissue sections and to diagnosis tumors. Different chemometric tools such as: vertex component analysis (VCA), principal component analysis, K-means cluster analysis, fuzzy C-means cluster analysis, and hierarchical cluster analysis were applied to extract important information from the Raman images of brain tissue sections. Cell nuclei that are characterized by the spectral contributions of nucleic acids and histone protein were clearly identified by all methods. Chemical images were constructed using nucleic acids (DNA) spectral bands to identify cell nuclei in the tissue section. Based on the results and comparisons to microscopy image of the hematoxylin and eosin (H&E) stained brain tissue section, spectral unmixing VCA gives better information about the structures of the tissue section. In addition, it was shown that VCA identifies nuclei of tumor cells in the brain tissue section.

Theoretical study of charge-transfer processes in $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ based system for photocatalytic water splitting

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Photocatalytic water splitting into hydrogen and oxygen is a very attractive direction in the search for new energy sources. One of the schemes for a homogeneous water splitting solar cell involves an Ir(III) containing photo-sensitizer (IrPS), a Fe(II) catalyst, and the sacrificial reductant triethylamine (TEA) [1]. In present work, we focused on the first stage of the process involving the structure of the ground and lowest excited electronic states of IrPS ($[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (ppy = phenylpyridine and bpy = bipyridine)) in oxidized and reduced form and its interaction with TEA. Based on the results of TDDFT (LC-BLYP) and CASSCF/CASPT2 calculations we reassigned the bands in the UV-Vis absorption spectrum (Fig. 1a) and proposed a scheme for the photophysical and photochemical process involving the lowest excited states of IrPS.

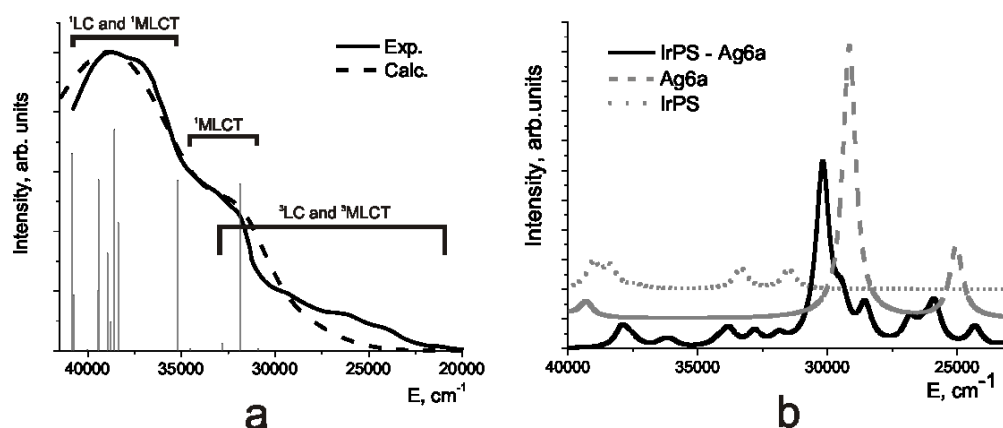


Fig. 1. (a) The experimental and calculated absorption spectra of IrPS; (b) Theoretical absorption spectrum of IrPS-Ag₆ system.

One possible way to increase the sun light absorption is through the surface plasmonic and/or field enhancement effects which occur upon binding of PS to small metal nanoparticles. We studied the changes in nature and order of the excited states under the physisorption of IrPS on Ag_n ($n = 2\div 20$) particles (Fig. 1b). Our results indicate the increase in efficiency of charge separation in the excited states that could favour the overall process efficiency.

Literature

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Smoking a cigarette under nitrogen atmosphere? Pyrolysis and combustion experiments with a cigarette combustion simulator.

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Analysis of complex and dynamic substance mixtures such as tobacco smoke which is a mixture of particles and vapours containing thousands of compounds that are harmful and can undergo rapid changes in concentration require a suited analytical method. The application of on-line measurement methods such as time-of-flight mass spectrometry (TOF-MS) combined with a soft ionisation technique is expedient to analyse such difficult mixtures with a high time resolution. Single and resonance enhanced multi photon ionisation (SPI/REMPI) are soft ionisation techniques with almost no fragmentation. Their energy is insufficient to ionise matrix constituents such as nitrogen and CO₂. In this regard, a cigarette combustion simulator is used for pyrolysis and combustion of tobacco. The simulator is designed to incinerate and pyrolyse a sample in close approximation to the burning conditions experienced by a lit cigarette. It allows variation and control of parameters such as smouldering and puff temperature as well as combustion rate and puffing volume. The objective of the study was to compare chemical composition of smoke generated by the simulator and a real cigarette, respectively. The smoking simulator was coupled to the mass spectrometer by a specially designed adapter that enables the analysis of pyrolysis and combustion gases of tobacco and tobacco products (e.g. 3R4F reference cigarette) with almost no aging. The measurements are not influenced by dead volume or memory effects. This facilitates investigation of several toxicants' formation under different puffing conditions (e.g. based on ISO regime) and other parameters (e.g. change of puff and smouldering temperature, nitrogen atmosphere). The measurement enables distinction between the different smoking conditions on the basis of the corresponding mass spectra and the results of their statistical evaluations (e.g. difference spectra, principal component analysis). The formation of six selected substances are monitored in more detail: NO, acetaldehyde, 1,3-butadiene, benzene, phenol and nicotine.

Gravimetric and Spectrophotometric studies of adsorption behavior and corrosion inhibitive potential of *Cordia Sebestena* extracts on mild steel/sulphuric acid interface

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ABSTRACT

The inhibition of *Cordia Sebestena* (COSEB) extracts on the corrosion of mild steel in 0.2M Sulphuric acid was studied by gravimetric and UV-visible Spectrophotometric methods at 303-333K. Results obtained show that COSEB extracts act as inhibitor of mild steel in 0.2M H₂SO₄ solution. The inhibition efficiency was found to increase with increase in COSEB concentration but decrease with increase in temperature. Activated parameters and Gibb's free energy for the adsorption process using Statistical physics were calculated and discussed. The UV-visible absorption spectra of the solution containing the inhibitor after the immersion of the mild steel specimen indicate the formation of COSEB-Fe complex. The adsorption of COSEB extracts on the mild steel surface obeys Langmuir and Kinetic thermodynamic models.

Keywords: *Cordia Sebestena* extracts, Inhibitor, Mild steel, Sulphuric acid, Langmuir, Thermodynamics.

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Luminescence Quenching of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ by Triethylamine in a Photocatalytic Model System

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The efficient hydrogen generation due to photocatalytic water splitting is an ambitious challenge in the renewable energy field. We investigate an active, photocatalytic model system consisting of an iridium-photosensitizer (PS), an iron-catalyst, and triethylamine (TEA) as a sacrificial reductant.^[1] So far, little is known about the individual reaction steps and possible loss mechanisms. Here, we focus on the primary photochemical reaction steps including the relaxation dynamics of the iridium-complex following excitation and its reaction with triethylamine in different solvents.

Luminescence quenching by triethylamine has been studied by steady-state and time-resolved luminescence measurements employing a streak camera with a 30 ps time resolution. Figure 1 shows the luminescence lifetimes and quantum yields of the iridium-PS as τ_0/τ and ϕ_0/ϕ vs. the concentration of TEA. For the luminescence quantum yields a linear dependency is found even for high TEA concentration, yielding a quenching rate constant of $k_q = 5.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$. At low concentration the same correlation could be found for the lifetime. However, at higher TEA concentration τ_0/τ rises remarkably pointing to non-exponential electron transfer dynamics.

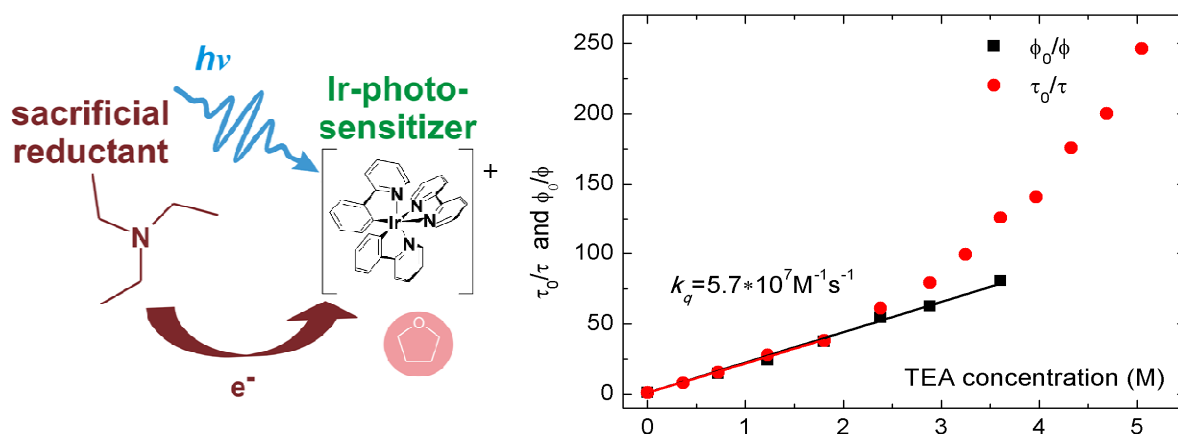


Figure 1. Luminescence quenching of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ by TEA in tetrahydrofuran.

Similar experiments performed in presence of water reveal a linear dependency of both τ_0/τ and ϕ_0/ϕ as TEA concentration is increased. Presumably, intermolecular interaction between the Ir-complex and the water molecules hinder direct interaction between the Ir-PS and the sacrificial reductant TEA.

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Can large Ni particles be beneficial in CH₄ reforming by CO₂ ?

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Introduction

Ni catalysts have attracted considerable attention in dry reforming (DR) of CH₄ to syngas due to their high initial activity, selectivity and low cost. In general, small metallic nickel (Ni⁰) nano particles are highly active but suffer from deactivation due to sintering and carbon deposition. In this work, we demonstrate by applying different characterization techniques (i.e. Ferromagnetic resonance (FMR), TEM and TPO) that large Ni particles can be also beneficial in the target reaction in spite of large amount of carbon deposits.

Results and discussion:

SiO₂- and γ -Al₂O₃ supported nickel (1 and 5 wt.% Ni) catalysts were prepared by impregnation and tested in the DR reaction at 673 K. The catalysts showed different activity, stability and different type and amount of carbon deposits (Table 1). For the less stable catalysts, i.e 1%Ni/SiO₂, the particle size was too small to be detected by TEM.

Additionally, only a slight change in the spectral behaviour was observed by FMR after 100 h time on stream (TOS) indicating that sintering is not the main reason for deactivation of the catalyst. TEM and TPO measurements indicate the

Table 1 Results of catalysts characterization by TEM, and TPO as well as of catalytic testing in the DR reaction.

Catalysts	Mean particle size, (TEM)	Initial H ₂ yield %	Activity loss % (32 h)	Type of coke deposits	TPO (CO ₂ conc ./g cat)*
5%Ni/ γ -Al ₂ O ₃ (1)	5-20 nm	5.5	23.6	Graphene	0.147
5%Ni/ γ -Al ₂ O ₃ (2)	Very small	5.8	12.1	CNTs	0.097
5%Ni/SiO ₂	up to 50 nm	6.1	4.9	CNTs	1
1%Ni/SiO ₂	Very small	4.7	42.6	Amorphous	0.015

* normalized

formation of a small amount of amorphous carbon on the surface of the catalyst leading to blockage of the active sites and deactivation of the catalyst. This was also true for 5%Ni/ γ -Al₂O₃ (1). For the most active and stable catalysts i.e 5%Ni/SiO₂, the Ni particle size was large (up to 50 nm) and inhomogeneously distributed. The FMR measurements of the used catalyst showed several spectral changes in the shape, line-width, g values, and in the Curie temperature indicating the aggregation of Ni(0) particles. Moreover, high amount of carbon deposits was detected by TPO. However, TEM images showed that carbon nanotubes (CNTs) were formed during reaction with Ni particles located on the tip of these tubes. This could be the reason for the stability of the catalyst since Ni(0) particles remains accessible to the reactants. The reason for deactivation of 5%Ni/ γ -Al₂O₃ (2), which also showed CNT deposition, was attributed to the aggregation of the support itself during the DR reaction as evident from TEM images.

Conclusions

In conclusions, we found that small Ni(0) particles showed high initial activity but suffered from deactivation due to carbon deposition. On the other hand, large Ni particles can be also active and stable in DR reaction as long as the nature of the carbon deposits is CNTs and the Ni particles remain accessible to the reactants.

Fresh grain flow, analyzed at line, by near infrared instrument

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Every year, the breeding companies have to harvest thousands of experimental plots in many locations. During maize grain harvest, daily collect can reach more than 400 plots. To compute the dry yield, moisture of fresh grain samples is usually done by electric conductivity devices, either with on line (on harvester) or at line (in laboratory) instruments. Some samples of reference are dried (below 40°C with 48 hours air flow) and laboratory analyses are carried out on biochemical parameters (glucids, lipids, proteins and minerals) and physical characteristics (vitreousness, properties of starch). The breeding companies and the team of E. I. Purpan decided to join in an attempt to reduce the costs of harvesting. We worked on a near infrared (NIR) instrument, directly used on experimental harvesters, to measure water content, as well as physical and chemical composition of fresh grains. Measuring a flow of grain by the mean of NIR spectrometry is very different from usual laboratory analysis (static or semi static). The grain must pass as quickly as possible in a dense concentration with a weak dilution. The target is to measure the NIR absorbance of a concentrated flow of grain, with a quality close to what can be made in static mode.

During the summer and the autumn 2009, we built, tested and validated a prototype and the flow parameters, in order to simulate grain flow in a hose. Its specifications corresponded exactly to the constraints of an experimental harvester.

By the end of maize harvest 2009, we collected fresh maize grain samples. Water content was measured at E. I. Purpan laboratory by oven reference method, the day after the NIR measurement. All the basic NIR spectra collected (a hundred cycles of measurement for each spectrum) were filtered with minimum and maximum limits established by the study of databases from similar devices. PCA, PLS, MLR calibration and mathematical treatments were achieved with Foss Infracore International Package.

We assume that a correct measurement on a flow of wet grain can be simulated at line with a special device, in order to test the feasibility of doing the measures and then to develop a model of prediction. Perfect NIRS spectra acquisition and cycle filtering are important steps to manage before on line use. With a SEP around 0.60 on 18 samples of wet grain, the prediction is not far from an acceptable level for breeding purposes. The simultaneous analysis of moisture, protein and starch contents, and also vitreousness, could be a very useful tool for breeders.

The special designed hose, with trap and counter weight system, must now be tested on breeder's experimental harvester during maize harvest, in order to collect thousands of references spectra. Then, more emphasis will be put on NIRS modeling and validation.

Comparision of Remazol Brilliant Blue Removal by Two Different Immobilized Organisms

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Reactive dyes are important chemical pollutants from textile industries. For this purpose, is to investigate the biological treatment of synthetic dyes, at a low cost and in the shortest possible time, which are used expecially dye and textile industries and are an important polluting agent in the waste water dumped into the environment by these industries. For this purpose, in this study, of Remazol Brilliant Blue was researched to remove with immobilized *Pleurotus ostreatus* and *Coprinus plicatilis*. This dye was removed 100% (dye concentration; 10.0 mg L⁻¹) by both immobilized organisms. Laccase and MnP enzyme activities were also monitored. There was an attempt to identify metabolites with FT-IR at the end of the decolorization. These results indicate that the samples did not include any detectable metabolite.

Key words: Remazol Brilliant Blue, *Pleurotus ostreatus*, *Coprinus plicatilis*, Immobilized White rot fungi, FT-IR

Preparation and in situ spectroscopic characterization of Cu-clinoptilolite catalyst for the oxidative carbonylation of methanol

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Dimethyl carbonate (DMC) is an important gasoline additive and chemical, which is normally produced by phosgenation of methanol [1]. One alternative environmentally benign process could be the oxidative carbonylation of methanol to dimethyl carbonate. Several Cu-contained zeolites catalysts have been applied for DMC synthesis finding promising results Cu⁺-Y zeolites [2-4]. Following the idea of use zeolites, clinoptilolite which is the most abundant natural zeolite was studied in this reaction.

Cu-modified clinoptilolite samples were prepared by wetness impregnation and cation exchange. The samples were comprehensively characterized by different spectroscopy methods such as ATR, XRD and mainly by *in situ* FTIR and *operando* DRIFT/UV-vis-DRS/MS measurements.

In situ FTIR investigations were made with aid of the probe molecules CO and NO in order to evaluate the species in different oxidation state of copper. Thus, CO was used to analyze the Cu⁺ sites and NO to look at the Cu²⁺ sites. Finding Cu²⁺ ions could be located at isolated sites or at strongly associated sites on clinoptilolite samples, depending of the nature of the catalyst and the preparation procedure.

The oxidative carbonylation of methanol was monitored by *in situ* FTIR and *operando* DRIFT/UV-vis-DRS/MS for observing reactions intermediates, reaction products and possible changes on the catalyst. During the reaction monitoring, formation of CO₂, methoxide, formate (COO⁻) and methyl formate (MF) adsorbed on the surface were detected by *in situ* FTIR, while changes of the coordination sphere of Cu²⁺ were observed in *operando* experiments. The main reaction products identified by MS analysis were dimethoxy methane (DMM) and MF. In contrast to the Cu-Y catalyst system no DMC is formed, therefore Cu-clinoptilolite catalysts seem to be not suitable for DMC production.

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A μ -probe sampling device for on-line PI-TOFMS analysis of pyrolysis/combustion gases within cigarettes and coffee beans

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A microprobe sampling device (μ -probe) was constructed for in-situ on-line mass spectrometric analysis of volatile chemical species within fuel particles (e.g. biomass or coal pieces), burning objects (e.g. cigarettes) or roasted food products (e.g. coffee beans). Thus the occurring processes during heating, pyrolysis, combustion and charring can be studied as they occur in the local environment. First applications of this measuring method comprised mainstream smoke analysis inside the burning coal of a cigarette and the investigation of a roasted single coffee bean. Recently, on-line sampling methods coupled with time-of-flight mass spectrometry with photon ionisation (PI-TOFMS) have proven to be useful to allow the detection of many organic smoke constituents in real time. The main advantages of the PI-TOFMS technique are its soft and sensitive ionisation without fragmentation as well as high time resolutions. Results obtained from this microprobe linked with PI-TOFMS will be presented to demonstrate the puff resolved on-line analysis of (semi-)volatile species (e.g. acetaldehyde, 1,3-butadiene, isoprene, acetone, benzene, toluene, phenol, indol, and phenanthrene) inside the burning cigarette coal. The gas mixture reveals different dynamic behaviour in the coal as compared to mainstream smoke yields at the filter. Statistical methods allow the research of mechanistic formation processes of the smoke compounds and can differentiate between pyrolysis and combustion conditions. Furthermore the roasting process outside and inside a single coffee bean was analysed for the behaviour of selected volatiles (e.g. acetaldehyde, pyrazine, vinylguaiacol and caffeine). By means of principle component analysis it is possible to classify between the two measurement kinds. Hence an insight results in the formation processes of flavouring.

Multidimensional vibrational Hamiltonian and wave packet dynamics of $\text{Mn}_2(\text{CO})_{10}$

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We investigated the wave packet dynamics of dimanganese decacarbonyl ($\text{Mn}_2(\text{CO})_{10}$) driven by circularly polarized (CP) light in the IR regime. The electronic structure of $\text{Mn}_2(\text{CO})_{10}$ has been studied using density functional theory and geometric parameters as well as harmonic frequencies are found to be in a good agreement with experimental work. Two degenerate IR active normal modes are selected for CP laser excitation and treated beyond the harmonic approximation. They are coupled to a set of harmonic modes within a seven dimensional potential energy surface (PES). For this model the time-dependent vibrational Schrödinger equation is solved and it is shown that a CP IR laser pulse in the femtoseconds domain can trigger a vibrational excitation which propagates around the symmetry axis of the molecule. Further, a two-dimensional PES suitable for dissociative of an equatorial CO group is discussed.

In situ (HP)-FTIR-spectroscopy coupled with applied chemometrics for studying kinetic and mechanistic aspects of the rhodium catalyzed hydroformylation

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In order to study mechanistic aspects of catalytic reactions, heterogeneous as well as homogeneous, one approach is to couple kinetic investigations with spectroscopic techniques. Nowadays this is more often accompanied with a chemometric treatment of the data obtained [1]. We perform selected homogeneous hydroformylation reactions in a semi-batch reactor which is coupled with a high pressure IR cell and an automated sampling device for ex situ gas chromatographic analysis. This allows us to study the organometallic catalyst species time resolved under real reaction conditions by FTIR spectroscopy as well as the often complex educt/product mixture by GC [2]. The spectroscopic data obtained contain the information of the particular catalyst species in form of the absorbance spectra and the respective concentration at a definite time. The software tool PCD (pure component decomposition) which is based on matrix factorization performs a recovery of the pure component spectra and their associated concentration profiles [3]. For the hydroformylation of 3,3-dimethyl-1-butene with the monodentate phosphite TDTBPP as ligand performed at 20 bar, 30 and 70 °C we extracted the pure component spectra of the respective acyl and hydrido complex and their normalized concentrations. Comparative analysis of the concentration profiles of the organometallics and of the educt/product shows that the reaction rate is controlled by the late hydrogenolysis. This is expressed by a shift from an intermediate regime of saturation kinetics to pseudo 1st order with respect to the olefin and a linear dependence between reaction rate and concentration of the acyl complex.

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**Strong doped ion segregation in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$
nanocrystals detected by spectroscopic techniques**

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Spectra and decay curves of $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals clearly demonstrate the decreasing of $^1\text{D}_2 \rightarrow ^3\text{H}_4$ concentration quenching threshold as compared to $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ bulk crystals. The analysis of luminescence decay curves and excitation spectra revealed the presence of considerable amount of Pr ion pairs even at 0.5 at.% Pr^{3+} concentration.

Experimentally observed abnormal quantity of Pr ion pairs even at low doped ion concentrations has been explained from the viewpoint of surface-induced doped ion segregation. Strain gradient determined by nanocrystal surface stimulates the uphill diffusion of doped ions leading to the non-uniform Pr^{3+} distribution, Pr^{3+} pair's formation and as consequence to the low threshold of luminescence concentration quenching. Variation of temperature treatment parameters allows us to trace the processes of Pr^{3+} segregation and to estimate the main characteristics of this process.

The effect observed for $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ nanocrystals could be exploited as a very effective tool to design and to tune the cooperative processes (up-conversion, cross-relaxation, frequency summation) within RE ensemble that allows controlling of the nanophosphors luminescence properties.

Hierarchy Approach to Multi-Exciton Dynamics in Molecular Aggregates

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The theoretical simulation of the exciton dynamics in multichromophoric system is of vital importance for understanding the function of natural and synthetic light harvesting complexes [1]. Perylene bisimide based aggregates are typical man made excitonic systems whose structural and electronic properties can be tuned over a wide range [2]. At high excitation intensities multi-exciton states have been observed in these systems using ultrafast pump-probe spectroscopy [3]. Among the limiting factors for establishing high exciton densities is exciton-exciton annihilation, that is an effect which originates from the breakdown of the Born-Oppenheimer approximation.

This study will focus on the dissipative laser-driven multi-exciton dynamics in a perylene bisimide like model system. To this end the hierarchy equation approach [4–6] is adopted to the case of multi-exciton dynamics in the presence of exciton-exciton annihilation.

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Conference Program

time	Wednesday June 15	time	Thursday June 16	time	Friday June 17
		8.00	Stefan Krause <i>Single Molecule Studies of Surface and Soft Matter Interaction of Functionalized Perylene Diimides</i>	8.00	Janina Kneipp <i>Modern Raman-spectroscopic methods for investigations of complex bioorganic samples</i>
		8.40	Juliane Kleeblatt <i>Investigation of medically relevant substances using Photoionization-Time of Flight Mass Spectrometry</i>	8.45	Virginia Joseph <i>Development and characterisation of new planar SERS sensors for detection of catalytic activity and other applications for investigations of complex bioorganic samples</i>
		9.00	Coffee break	9.00	Coffee break
		9.30	Hergen Breitzke <i>NMR, Peptides and the catalytic cycle, an approach</i>	9.30	Tim Conrad <i>Proteomic fingerprinting: an example for information-based medicine</i>
		10.10	Dhanya Murali <i>Human Hemoglobin detection by using AgO thin films as Surface Enhanced Raman scattering (SERS) substrates</i>	10.00	Stephan Aiche <i>Capturing Proteolytic Activity in Mass Spectrometry Measurements</i>
		10.30	Iryna Fylymonova <i>Features of exciton migration in cyanine dye J-aggregates</i>	10.25	Ionela Radu <i>FT-IR Spectroscopy of Membrane Proteins</i>
		10.50	Kseniya Korobchevskaya <i>Ultrafast Spectroscopy Investigation of Au-FexOy Hetero-nanostructures</i>	11.10	Alois Fendt <i>Soft photo ionization mass spectrometry for the analysis of biomass flashpyrolysis gases within the Karlsruhe bioliq® - Biomass to Liquid - Project</i>
		11.15	Wameath Abdul Majeed <i>Study the atomization of the generated hydride species in a dielectric barrier discharge atomizer</i>	11.35	Anna Wcislo <i>New 9,10-Anthraquinone derivatives in terms of Molecular Recognition</i>
12.00	Registration with soft drinks	11.35	Lunch Break with Postersession	12.10	Lunch Break with Postersession
13.00	Udo Kragl <i>Welcome Note</i>	13.00	Regine von Klitzing <i>Neutron and x-ray reflectometry for characterisation of polymer coated surfaces</i>	13.30	Jakob Anderasson Nic Timneanu <i>Spectroscopy at the extremes with x-ray lasers: from structural sciences to fusion physics</i>
13.15	Angelika Brückner <i>Spectroscopic Viewing: A Way to Watch Catalysis at Work</i>	14.10	Wilfried Wurth <i>Free electron lasers – the brightest x-ray sources</i>	14.15	Bianca Iwan <i>Spectroscopy at the extremes with x-ray lasers: from structural sciences to fusion physics</i>
14.05	Christiane Janke <i>Elucidating Structure-Reactivity Relationships for V-Containing Oxynitrides VMON in the Ammoxidation of 3-Picoline..</i>	14.55	N.N.	14.40	Peter Leinweber <i>Pyrolysis-field ionization mass spectrometry and x-ray absorption near edge structure spectroscopy of complex biomaterials</i>
14.25	Leif Knöpke <i>Coupled ATR-IR / UV-vis in situ-spectroscopy supported by ex situ Raman spectroscopy..</i>	15.15	Kerstin Thurow <i>Automated Analysis in Life Science Research</i>	15.30	Ashour Ahmed <i>(Py-FIMS), X-ray absorption near-edge fine structure spectroscopy (XANES) and theoretical modeling</i>
14.50	Jana Engeldinger <i>Operando DRIFTS/UV-vis/MS studies of oxidative carbonylation..</i>	16.00	Heidi Fleischer <i>High Throughput Determination of Amino Acids using Mass Spectrometry</i>	15.50	Udo Kragl <i>Farewell Speech</i>
16.00	Guided Tours			16.00	departure
		18.45	Come Together Dinner at the Harbor Cruise with special talk Martin Rösel		

