Bonn-Strasbourg Mini-Symposium

Spin Centers in Life and Materials Sciences

Bonn, July 09, 2015

Venue: Institute for Physical and Theoretical Chemistry
Wegelerstrasse 12, 53115 Bonn
Opening at 8:45 am

Speakers:
Eric Beaurepaire (Strasbourg)
Thomas Bredow (Bonn)
Gregor Hagelüken (Bonn)
Arne Lützen (Bonn)
Pierre Rabu (Strasbourg)
Bertrand Vileno (Strasbourg)
Peter Vöhringer (Bonn)
Jean Weiss (Strasbourg)

Organizers:
Jean Weiss (Strasbourg)
Peter Vöhringer (Bonn)

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Bonn-Strasbourg Mini-Symposium

“Spin Centers in Life and Materials Sciences”

of the Collaborative Research Center 813 “Chemistry at Spin Centers”

July 09, 2015

Venue: Lecture Hall, Institute for Physical and Theoretical Chemistry, Wegelerstrasse 12, 53115 Bonn

Scientific Program:

08:50 Welcome
09:00 – 09:45 Jean Weiss (Université de Strasbourg)
Self-assembly of molecular wires: Examples of morphology control
09:45 – 10:30 Arne Lützen (Universität Bonn)
Self-assembly of metallosupramolecular aggregates and π-conjugated materials
10:30 – 11:00 Coffee Break
11:00 – 11:45 Bertrand Vileno (Université de Strasbourg)
Biophysical applications of electron paramagnetic resonance: From free radical investigation to molecular and structural biology
11:45 – 12:30 Gregor Hagelüken (Universität Bonn)
Structural and functional analysis of the ferrous iron transporter FeoB from Escherichia coli BL21 via X-ray crystallography, UV/Vis- and EPR spectroscopy
12:30 – 14:00 Lunch Break
14:00 – 14:45 Eric Beaurepaire (Institut de Physique et Chimie des Matériaux de Strasbourg)
Antiferromagnetic interactions and exchange anisotropy in MnPc films deposited on Co
14:45 – 15:30 Pierre Rabu (IPCMS and icFRC, Strasbourg)
Hybrid interfaces in layered hydroxides: Magnetic and multifunctional superstructures by design
15:30 – 16:00 Coffee Break
16:00 – 16:45 Peter Vöhringer (Universität Bonn)
Ultrafast solvated electron dynamics in liquids and supercritical fluids
16:45 – 17:30 Thomas Bredow (Universität Bonn)
Excited states of water and ammonia: From molecules to the condensed phase
17:30 Award Ceremony “Sigrid Peyerimhoff Nachwuchspreis”
17:30 Conclusion of the scientific program
Abstracts

Scientific Presentations
Self-assembly of molecular wires: Examples of morphology control

Jean Weiss

Institut de Chimie, UMR 7177 CNRS-University of Strasbourg, 4 rue Blaise Pascal 67000 Strasbourg, France.

Among the challenges of nanomaterial design, the design of functional electroactive components that self-assemble in one dimension to form linear molecular wires in soft deposition conditions remain a challenge. The self-assembly of molecular wires is generally achieved through a dominant interaction that ensures the intermolecular association and a set of weaker interactions that is responsible for the fine tuning of the organization in the solid state.

Electron rich molecules possessing a mobile π-electron density are mostly used as building blocks. Among the candidates, porphyrins and polyaromatics have been extensively exploited. The use of neutral species excludes the use of electrostatic and electronic effects as primary intermolecular interactions but offers the advantage of a full chemical control on the set of weak interactions employed, whereas the use of charged species increases the panel of weak interactions with a tool highly depending on the role of counter ions.

In all cases, the incorporation of molecular wires into devices involves their deposition or formation on surfaces which requires the taking into account the role of molecule/surface interactions and their control.

A first example utilizing geometrically well-defined axial coordination in a neutral phenanthroline strapped zinc porphyrin structure (Figure 1 left) to perform the surface assisted formation of self-assembled porphyrin wires (Figure 1 right) will illustrate the fine tuning of molecule/surface interaction to control the morphology of self-assembled species. A second example based on the use of radical cationic hosts and guests will illustrate the importance of counter anion on self-assembled organic wires and their properties.
Self-assembly of metallosupramolecular aggregates and π-conjugated materials

Arne Lützen

Kekulé-Institute for Organic Chemistry and Biochemistry
Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany

The design and synthesis of molecular structures is the domain of the preparative chemist. However, the formation of a single bond in the Ångström-regime poses different challenges than a deliberate synthesis of a nano-sized object or even the fabrication of an optoelectronic device. These are areas where supramolecular chemistry can make valuable contributions as will be discussed on the basis of some of our recent results.
Biophysical applications of electron paramagnetic resonance: From free radical investigation to molecular and structural biology

Bertrand Vileno

POMAM Lab - Institut de Chimie UMR 7177 CNRS / Université de Strasbourg, 4, rue Blaise Pascal / CS 90032 F-67081 Strasbourg FRANCE

Electron Paramagnetic Resonance (EPR) is a spectroscopic tool for studying paramagnetic, ferromagnetic and antiferromagnetic spin systems. It covers a broad range of fields from solid state physics and chemistry to medicine and molecular biology. Noteworthy, advanced methods such as pulsed-EPR spectrometry are nowadays well established for the investigation of molecular and structural properties of biomolecules. In this talk, I will illustrate some biophysical applications of EPR such as free radical detection and distance measurements.

Reactive and free radicals are intrinsic to numerous essential and/or extremely deleterious mechanisms in everyday life. In the EPR spin trapping process, a diamagnetic probe (the trap) reacts specifically with the targeted short lived free radical to give a more persistent paramagnetic molecule, which is subsequently detected and characterized.

Double Electron Electron Resonance (DEER) affords distance measurements at a nanoscale level. The great majority of biomolecules being diamagnetic, one cannot probe them directly via EPR. Hence, a paramagnetic spin probe, known as a Spin Label (SL), is used to covalently label proteins, RNA/DNA molecules, phospholipids, etc. SLs are very efficient reporter of mobility, dynamic and structural changes. Inter-SL distances can be estimated in the 5 to >70Å range between 2 SLs targeted at selected positions within biomolecules.
The ferrous iron transporter FeoB is an important factor in the iron metabolism of various bacteria. As a membrane bound GTPase it also represents an interesting evolutionary link between prokaryotic and eukaryotic membrane signalling pathways. To date, structural information for FeoB is limited to the cytosolic GTPase domain and many of its structural and functional features such as the oligomeric state of the transporter in the membrane or its regulation are unknown. Based on peptide screening assays, we have found that FeoB contains a short (9-mer) peptide sequence, which (in isolation) strongly binds to the spin center heme. This indicates a possible regulation of the protein via a FeoB/heme interaction. To investigate this, we overexpressed and purified the full-length membrane protein FeoB from *Escherichia coli* BL21. Heme binding assays using UV/Vis- and cw-X-band EPR spectroscopy indicate that the interaction is also present on the protein level. This was confirmed by site directed mutagenesis of the heme binding site. X-ray crystallography and PELDOR distance measurements were used to analyse the oligomeric state of FeoB, and if the heme interaction leads to conformational changes of the protein, which might regulate iron transport. As a prerequisite for the PELDOR experiments, we spin labelled FeoB with the unnatural amino acid para-acetylphenylalanine (pAcF). Our results provide new insights into the structure and function of this intriguing protein.
Antiferromagnetic interactions and exchange anisotropy in MnPc films deposited on Co

Eric Beaurepaire¹, Manuel Gruber^{1,2}, Samy Boukari¹, Fadi Choueikani³, Philippe Ohresser³, Wulf Wulfhekel², Fabrice Scheurer¹, Wolfgang Weber¹, Mebarek Alouani¹, and Martin Bowen¹

¹ Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS-UdS UMR 7504, Strasbourg, France
² Physikalisches Institut, Karlsruhe Institute of Technology, Karlsruhe, Germany
³ Synchrotron SOLEIL, L’Orme des Merisiers, Gif-sur-Yvette, France

Spin dependent hybridization at the interface between a molecular layer and a ferromagnetic metal (FM) leads to outstanding spintronics response for FM/molecule/FM contacts [1]. We address here the exchange anisotropy that results from exchange interaction at the interface between a ferromagnet and an antiferromagnet. An important consequence is the occurrence of exchange bias, a cornerstone of spintronics, since it allows the stabilization of the “hard” magnetic layer in magnetoresistive devices, but is still overlooked as far as organic spintronics is concerned. We present results showing that an organic molecular film can be at the origin of a bias experienced by an inorganic material. For this purpose, we considered manganese phthalocyanine (MnPc) thin films deposited on ultrathin Co layers epitaxially grown on Cu(001). Previous works on this system have shown that a strong interfacial exchange interaction leads to a high magnetic polarization of the adsorbed molecule [2]. This leads to a high degree of spin polarization of the electronic density of states at the vicinity of the Fermi energy for the interface, as probed by direct and inverse photoemission and in agreement with band structure calculations [3]. We’ll present XMCD measurements, performed at the Co and Mn L_{2,3} edges, which clearly show antiferromagnetic correlations up to room temperature for in situ grown multilayers MnPc on Co(001), i.e. at a temperature much larger than in purely molecular films [4]. Exchange bias is observed at temperatures below 100K by MOKE magnetometry for such films with 50 MnPc monolayers. Ab initio DFT calculations provide further insight into mechanisms of exchange interactions and magnetic anisotropy that are key ingredients for the occurrence of exchange bias in thin films. The implications of this finding for organic spintronics will be discussed.

Hybrid interfaces in layered hydroxides: Magnetic and multifunctional superstructures by design

Pierre Rabu,1,2 Emilie Delahaye1,2 and Guillaume Rogez1,2

1 Institut de Physique et Chimie de Strasbourg, IPCMS, UMR 7504 CNRS - University of Strasbourg, 23, rue du Loess, 637034 Strasbourg, cedex 2, France
2 International Center for Frontier Research in Chemistry (icFRC), 8 Allée Gaspard Monge, F-67000, Strasbourg, France

Our presentation consists in a brief review on layered hybrid organic-inorganic functional structures. We specially discuss series of results concerning the design of magnetic and multi-property systems derived from hybridization of layered transition metal hydroxides. Series of hybrid materials showing original magnetic properties are reviewed, which were prepared by functionalization of layered simple hydroxides (LSH) of general formula $M_2(OH)_3A$ (M = Co, Cu, Ni, Zn, ... and A = NO$_3^-$, OAc$, alkylcarboxylates, peptides, metal complexes...). To make the point on this vast family of hybrid compounds, we present first the work investigating the mechanism of interaction and the structural factors influencing the magnetic properties of hybrid materials based on LSH. Then we detail how even more complex anions can be immobilized and grafted into the inter-lamellar space giving rise to new functionalities. These systems are very good models for understanding the correlations between the structure of hybrid systems and the physical properties brought by the inorganic host and by the molecular moieties grafted onto the inorganic metal network. The interface between the organic and inorganic components, i.e. chemical bonding, together with charge density, spin dimensionality or local pressure, is essential for the control of the properties of multifunctional hybrid systems. Some conclusions will be drawn on the future of this approach, useful for developing new two-dimensional functional systems.

Some references:
P. Rabu, E. Delahaye, G. Rogez, Nanotechnology Reviews, in press
http://dx.doi.org/10.1039/C0CS00159G
http://dx.doi.org/10.1002/adem.200310082
Ultrafast solvated electron dynamics in liquids and supercritical fluids

Peter Vöhringer

Institute for Physical and Theoretical Chemistry, University of Bonn, Germany

The solvated electron is the “mother of all spin centers”. Formally, it constitutes an unpaired negative elementary charge embedded in a condensed-phase matrix where it is self-stabilized by polarizing its surroundings. In the language of solid-state physics, the electron moves together with its polarization cloud as a quasi-particle, the so-called “polaron”. In the context of solvated electrons in liquids, a heavily debated issue is the motif of electron binding. Is the electron trapped in a localized cavity within the liquid or do we have to regard it as a solvated radical anion cluster in which the spin density is diffusely smeared across a larger number of solvent molecules? How does the binding mode affect the physico-chemical properties of the system and is the reactivity of a “cavity electron” different to that of a “radical cluster electron”?

To address some of these issues, we have recently studied extensively the ultrafast spectroscopy of solvated electrons in H-bonded solvents like water, alcohols, and ammonia [1]. The electrons were generated chemically (e.g. in metal-ammonia solutions) or photolytically via multi-photon ionization of the neat solvent. The solvent was studied over a wide range of thermodynamic conditions ranging from the tightly packed cryogenic liquid all the way over to the supercritical fluid with gas-like densities. In this talk, we will describe some of the progress we have made to understand the chemical reactivity of solvated electron with a particular emphasis on the dynamics of geminate recombination following an ultrafast ionization with energies above and below the band gap of the solvent. Such studies will be discussed in terms of Onsager’s seminal theory for the initial recombination of ions in condensed media and in terms of detailed Monte-Carlo simulations to account for the molecular-level mechanisms that bring about an annihilation of the excess charge and spin densities.

Excited states of water and ammonia: From molecules to the condensed phase

Thomas Bredow, Vafa Ziaei, Daniel Püschner

Institute for Physical and Theoretical Chemistry, University of Bonn, Germany

The formation of solvated electrons in liquid ammonia was first observed more than hundred years ago, and their electric and spectroscopic features are well known. More recently, also the relaxation dynamics of excess electrons in water and liquid ammonia have been studied. However, despite the large number of experimental studies detailed knowledge of the formation mechanism of solvated electrons and the geometric and electronic structure of the solvation shell is still scarce. Theoretical studies can provide additional and complementary information on the atomic level. Due to the methodological and computational advances achieved in the last decades, it is now possible to study these complex phenomena with increasingly accurate quantum-chemical approaches, applied to more and more realistic models. In the first part of the talk, recent theoretical work on spectroscopy and dynamics of water clusters, liquid water and ice taken from the literature will be summarized. Our own work starts with the hydrogen bond dissociation in small water and ammonia clusters in electronically excited states. More accurate but computationally demanding multi-reference configuration interaction methods will be compared with more efficient methods based on time-dependent density-functional theory (TD-DFT). The optical spectra of crystalline phases of ice and solid ammonia were calculated with a combination of Green-function and Bethe-Salpeter approaches (GW-BSE) based on periodic models and plane waves. The experimentally observed shifts of the optical excitation energies with respect to the gas phase were reproduced quantitatively. Combining the GW-BSE approach with first-principles molecular dynamics simulations, optical spectra of water and liquid ammonia were obtained. The observed low-energy tails of the optical bands were correlated with the distortions of solvent geometries. Excited-state molecular dynamics simulations at plane wave TD-DFT level were performed for the first few hundred femtoseconds after the photoexcitation in order to study the formation process of the solvated electrons generated by photodissociation.
LIST OF SPEAKERS:

DR Dr. Eric Beaurepaire
Institut de Physique et Chimie de Materiaux de Strasbourg (IPCMS, CNRS)
23, rue de Loess
BP 20CR
F-67037 Strasbourg
phone: (+33) 3 88 10 70 08
eric.beaurepaire@ipcms.unistra.fr
http://www.ipcms.unistra.fr/?page_id=9314

Prof. Thomas Bredow
Mulliken Center for Theoretical Chemistry
Institut für Physikalische und Theoretische Chemie
Rheinische Friedrich-Wilhelms Universität
Beringstrasse 4
D-53115 Bonn
phone: (+49) 228 73 3839
bredow@thch.uni-bonn.de
http://www.thch.uni-bonn.de/tc/

Dr. Gregor Hagelüken
Institut für Physikalische und Theoretische Chemie
Rheinische Friedrich-Wilhelms Universität
Wegelerstrasse 12
D-53115 Bonn
phone: (+49) 228 73 3839
hagelueken@pc.uni-bonn.de
http://www-schiemann.thch.uni-bonn.de/hagelueken/

Prof. Arne Lützen
Kekulé-Institut für Organische Chemie und Biochemie
Rheinische Friedrich-Wilhelms Universität
Gerhard-Domagk-Straße 1
D-53121 Bonn
phone: (+49) 228 73 7533
arne.luetzen@uni-bonn.de
http://www.chemie.uni-bonn.de/oc/forschung/arbeitsgruppen/ak_lue

DR Dr. Pierre Rabu
Institut de Physique et Chimie de Materiaux de Strasbourg (UMR 7504)
CNRS and Université de Strasbourg
23, rue de Loess
F-67034 Strasbourg, Cedex 2
phone: (+33) 3 88 10 71 35
pierre.rabu@ipcms.unistra.fr
http://www.ipcms.unistra.fr/
Dr. Betrand Vileno
Institut de Chimie de Strasbourg (UMR 7177, CNRS)
Université de Strasbourg
4 rue Blaise Pascal, CS90032
F-67000 Strasbourg
phone: (+33) 3 68 85 16 31
vileno@unistra.fr
http://www-chimie.u-strasbg.fr/~pomam/

Prof. Peter Vöhringer
Institut für Physikalische und Theoretische Chemie
Rheinische Friedrich-Wilhelms Universität
Wegelerstrasse 12
D-53115 Bonn
phone: (+49) 228 73 7050
p.voehringer@uni-bonn.de
http://www.chemie.uni-bonn.de/pctc/voehringer

DR Dr. Jean Weiss
Institut de Chimie de Strasbourg (UMR 7177, CNRS)
Université de Strasbourg
1 and 4 rue Blaise Pascal
F-67000 Strasbourg
phone: (+33) 3 68 85 14 23
jweiss@unistra.fr
http://www-chimie.u-strasbg.fr/~lclac/
ORGANIZERS:

DR Dr. Jean Weiss
Institut de Chimie de Strasbourg (UMR 7177, CNRS)
Université de Strasbourg
1 and 4 rue Blaise Pascal
F-67000 Strasbourg
phone: (+33) 3 68 85 14 23
jweiss@unistra.fr
http://www-chimie.u-strasbg.fr/~lclac/

Prof. Peter Vöhringer
Institut für Physikalische und Theoretische Chemie
Rheinische Friedrich-Wilhelms Universität
Wegelerstrasse 12
D-53115 Bonn
phone: (+49) 228 73 7050
p.voehringer@uni-bonn.de
http://www.chemie.uni-bonn.de/pctc/voehringer