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Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
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Structure-Activity Relationship of Photoinitiators for Two Photon Polymerisation

J. S. Beckwith[1], A. Rosspeintner[1], G. Licari[1], M. Lunzer[2], J. Fröhlich[2], E. Vauthey[1]*

[1]University of Geneva, [2]Technical University of Vienna

Donor-Acceptor-Donor molecules are of interest due to their two-photon absorption, symmetry breaking, solvatochromism and in their potential application as photoinitiators for polymerisation reactions. [1] The photoinitation process for polymerisation commonly occurs from the triplet state,[2] and thus for efficient photoinitiators high two photon cross sections, intersystem crossing rate constants and triplet yields irrespective of environment are desireable.

In our contribution we will outline a structure-activity relationship of a new series of photoinitiators (the building blocks of which are shown below). Using steady-state absorption and fluorescence spectroscopy, TCSPC, fluorescence upconversion and transient absorption we have investigated a series of structurally similar systems, in which the donor and acceptor groups have been varied systematically. This enables us to observe clear trends.

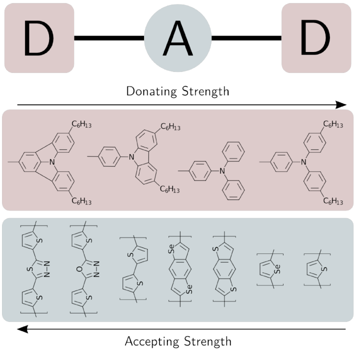

Figure 1: Building blocks of the series of photoinitiators, as well as a scheme of their general structure.

With these techniques we can quantify how efficiently the triplet state is reached and what impact this has on the photoinitiator efficiency. For example, the figure below shows that the investigated selenium based chromophores (which structuring tests have found to be the most efficient photoinitiators) have much higher intersystem crossing rate constants and triplet yields than any of the other sulfur based systems due to the heavy atom effect.

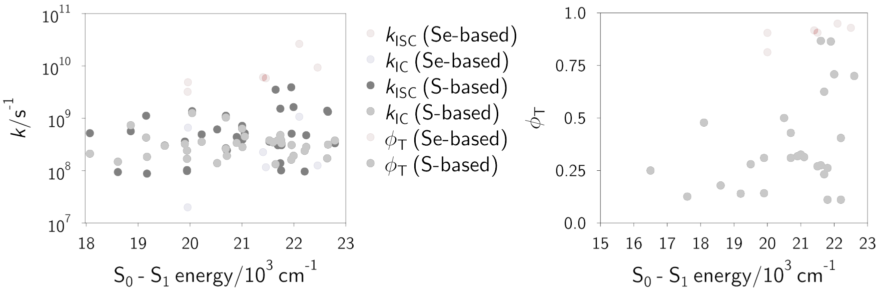

Figure 2: Intersystem crossing, internal conversion rate constants and triplet yields plotted vs S_0-S_1 energy.

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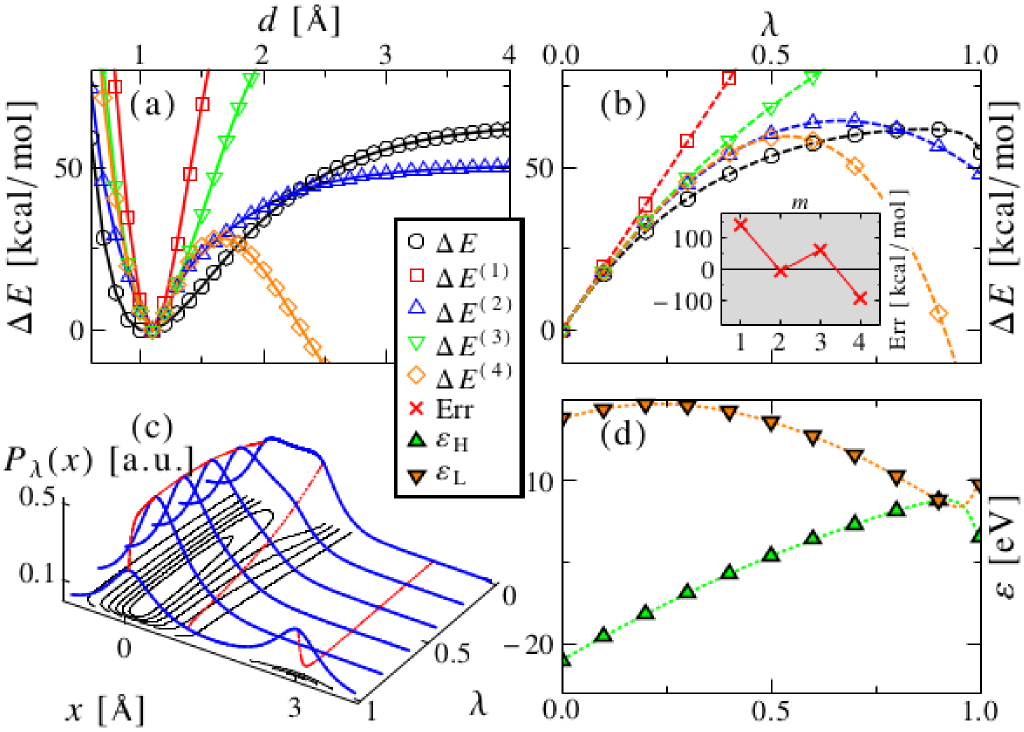
Fast and accurate prediciton of covalent bonds in chemical space.

K. Y. S. Chang[1], S. Fias[2], R. Ramakrishnan[1], O. A. von Lilienfeld[1,2]*

[1]University of Basel, [2]Free University Brussels

We assess the predictive accuracy of perturbation theory based estimates of changes in covalent bonding due to linear alchemical interpolations among molecules. We have investigated σ bonding to hydrogen, as well as σ and π bonding between main-group elements, occurring in small sets of iso-valence-electronic molecules with elements drawn from second to fourth rows in the p-block of the periodic table. Numerical evidence suggests that first order Taylor expansions of covalent bonding potentials can achieve high accuracy if (i) the alchemical interpolation is vertical (fixed geometry), (ii) it involves elements from the third and fourth rows of the periodic table, and (iii) an optimal reference geometry is used. This leads to near linear changes in the bonding potential, resulting in analytical predictions with chemical accuracy (~1 kcal/mol). Second order estimates deteriorate the prediction. If initial and final molecules differ not only in composition but also in geometry, all estimates become substantially worse, with second order being slightly more accurate than first order. The independent particle approximation based second order perturbation theory performs poorly when compared to the coupled perturbed or finite difference approach. Taylor series expansions up to fourth order of the potential energy curve of highly symmetric systems indicate a finite radius of convergence, as illustrated for the alchemical stretching of H2+. Results are presented for (i) covalent bonds to hydrogen in 12 molecules with 8 valence electrons (CH4, NH3, H2O, HF, SiH4, PH3, H2S, HCl, GeH4, AsH3, H2Se, HBr); (ii) main-group singlebonds in 9 molecules with 14 valence electrons (CH3F, CH3Cl, CH3Br, SiH3F, SiH3Cl, SiH3Br, GeH3F, GeH3Cl, GeH3Br); (iii) main-group double bonds in 9 molecules with 12 valence electrons (CH2O, CH2S, CH2Se, SiH2O, SiH2S, SiH2Se, GeH2O, GeH2S, GeH2Se); (iv) main-group triple bonds in 9 molecules with 10 valence electrons (HCN, HCP, HCAs, HSiN, HSiP, HSiAs, HGeN, HGeP, HGeAs); and (v) H_2^+single bond with 1 electron.



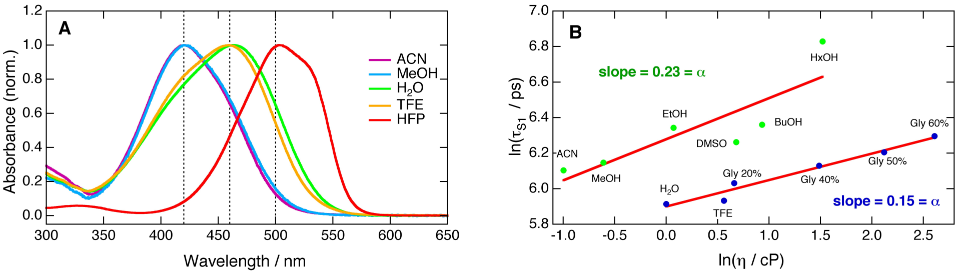
Ultrafast excited-state dynamics of the azo dye methyl orange

C. Nançoz[1], B. Dereka[1], O. Yushchenko[1], J. Beckwith[1], R. Letrun[1], A. Rosspeintner[1], S. Richert[1], E. Vauthey[1]*

[1]University of Geneva

Azobenzenes and their derivatives are well known for their trans-cis photoisomerisation properties[1] that can be used for various applications as molecular information storage devices[2], photoswitch in biology[3] or light-driven molecular shuttels[4]. The exact photoisomerisation mechanism is the object of intense research. It is known to depend on different factors such as excitation wavelength, solvent polarity, pH, and substituents on the azobenzene.

In this study, we will focus on the methyl orange azobenzene in a wide range of solvents using several steady-state and time-resolved techniques: fluorescence up-conversion, transient electronic absorption, transient infrared absorption, Fourier transform infrared spectroscopy and time resolved surface second harmonic generation.



A) Absorption spectra of methyl orange in acetonitrile (ACN), methanol (MeOH), water (H2O), trifluoroethanol (TFE), hexafluoropropanol (HFP).
B) Viscosity dependence of the S1 state lifetime of methyl orange in solvents with weak (green) and strong (blue) hydrogen-bond donating ability. The empirical relationship between the lifetime and the viscosity is described by $\tau \propto \eta^{\alpha}$

The decay of the excited state population is ultrafast, below one picosecond in all solvents. The decay time increases with viscosity as expected for a trans-cis isomerisation, but this dependence is rather weak and depends on the hydrogen-bond donating ability of the solvent (figure B). The effect of the hydrogen bond is also visible in the steady state absorption spectra with a red shift on the absorption band in the most solvents (figure A). This reveals hydrogen bonding between the solvent and methyl orange in the ground state has a substantial impact on its excited state dynamics and on the photoisomerisation.

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Development of membrane mechanosensor

R. D. Ortuso[1], K. Sugihara[1]*

[1]University of Geneva

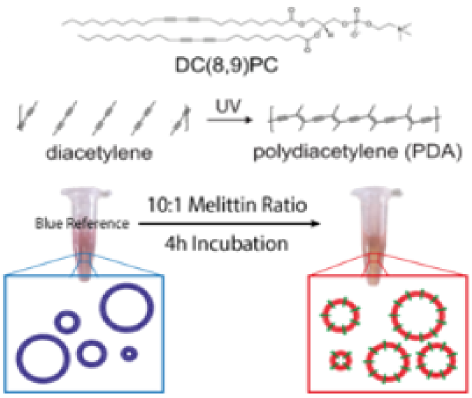
Membrane forces play pivotal roles in numerous physiological processes such as endocytosis, cell mutations and calcium signaling.

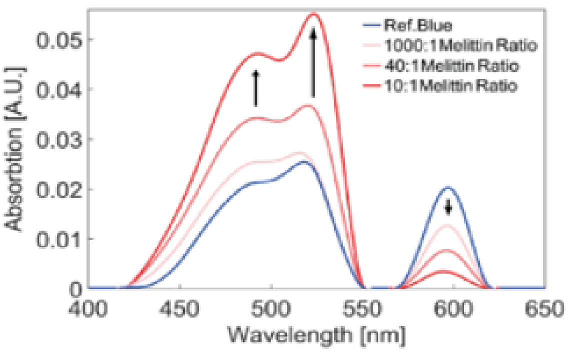
Currently used characterization methods such as atomic force microscope (AFM) or optical tweezers allow for the controlled force application but not for the detection of the forces applied to the bilayers. Micro-aspiration of giant unilamellar vesicles (GUV) enables the quantification of surface tension, however, its conversion into local forces is difficult.

We are developing a mechanosensitive membrane probe that enables direct measurement of molecular forces applied within lipid bilayers. We employ a mechanochromic polymer polydiacetylene that changes its color and fluorescence intensity upon application of forces. As a first step, we demonstrated a PDA vesicle assay that detects melittin, a transmembrane peptide from bee venom. First we fabricated PDA vesicles by self-assembling the lipid monomer and subsequently crosslinking by UV. These spectra overlap, suggesting no colorimetric response due to the addition of melittin. However, we found that the spectra shifted over the next several hours. After 4 hours, the shape of the spectra changed completely, as the color change was clearly visible also by naked eyes. The slow response from our PDA sensor against melittin is different from what has been reported with other types of PDA sensors[1][2].

In this work, we further analyze the unexpectedly slow interaction kinetics, fluorescence spectra of PDAs, and discuss possible origin of the slow kinetics and calibrate the system to peptide concentration [3].

The developed assay proved that DiynePC PDA is sensitive to mechanical stimuli. The advantage of our PDA sensor is that it has a phosphocholine head group that mimics cell membranes. Its combination of sensitivity and the biocompatibility will allow us to incorporate this probe in live cells in future, providing us a further possibility to investigate force distribution during mitosis, cell migration, and interactions with medical implants etc.





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Rechargeable Dual Electrolytes Li-Air and Li-Water Batteries

N. H. Kwon[1], Y. Sheima[1], K. Fromm[1]*

[1]University of Fribourg

Lithium is the lightest metal with the most negative potential (-3 V vs. SHE). Combining oxygen or water as a cathode and an electrolyte with lithium as anode, rechargeable Li-air and Li-water batteries potentially provide higher energy densities than the conventional Li-ion batteries.

However, the redox reversible reactions and cyclability of those batteries remain a challenge. Among the several structures of Li-air batteries, using an aqueous electrolyte provides a higher efficiency and cyclability due to the high ionic mobility and the solubility of discharge products [1]. However, water must not contact the lithium metal anode to avoid a violent reaction, producing heat and gas evolution. Thus, we apply an organic electrolyte on the lithium anode to protect the metal and an aqueous electrolyte on the cathode side to allow reversible electrochemical reactions.

During discharging, the value of pH increases due to the formation of LiOH, which damages the membranes [2,3] and leads upon saturation to LiOH precipitation [4].

In the Li-air system, the solubility of O_2 in the aqueous solution is a key parameter to obtain highly reversible electrochemical reactions and a high energy density.

We studied the O_2 solubility in terms of the concentration of LiOH aqueous solution and other mixed salt solutions by means of the electrochemical techniques. Fig. 1 shows that the O_2 solubility decreased with increasing concentration of LiOH. We will show the behavior of the O_2 solubility of different aqueous mixed salt solutions and the charge/discharge behaviors in dual electrolytes systems.

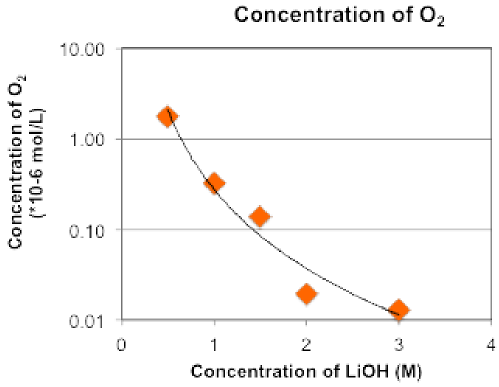

Fig. 1. The concentrations of O_2 as a function of the various concentrations of LiOH in the aqueous electrolyte.

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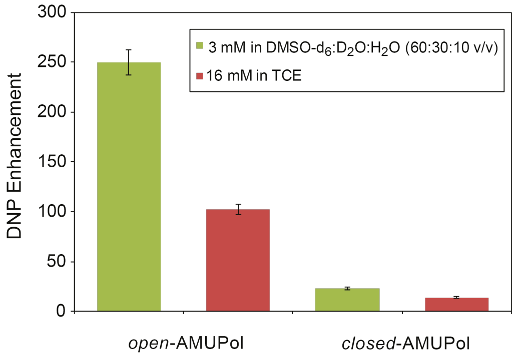
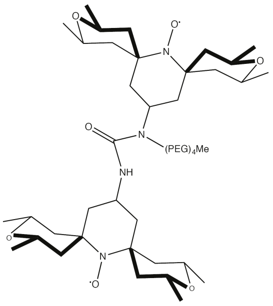
Effects of Steric Hindrance and Electron Relaxation on DNP Enhancement at High Field

D. J. Kubicki[1], C.E. Avalos[1], B. Náfrádi[2], M. Yulikov[3], G. Casano, S. Abel, C. Sauvée, K. Ganesan[4], G. Jeschke[3], P. Tordo[4], A. Lesage[5], O. Ouari[4]*, L. Emsley[1]*

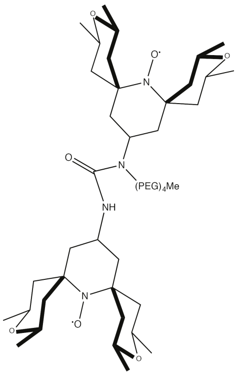
[1]Institut des sciences et ingénierie chimiques, [2]Laboratoire de Physique de la Matière Complexe , [3]ETH Zurich, [4]Institut de Chimie Radicalaire, Aix-Marseille Université / CNRS, [5]Centre de RMN à très hauts champs

Dynamic nuclear polarization (DNP) methods can boost the sensitivity of magic-angle spinning (MAS) solid-state NMR experiments at low temperatures by several orders of magnitude. For experiments at 80 K or above, typically the samples are dissolved or impregnated with a solution of stable biradicals, acting as polarizing agents capable of transferring the electron polarization to surrounding nuclei through the cross-effect. In order to maximize sensitivity it is important to understand the factors that affect the magnitude of the DNP enhancement. From previous work, we found that a two-fold improvement in DNP enhancements can be achieved by simply incorporating solid particles into the sample, with enhancements up to $\varepsilon_H = 515$ [1]. We also found that the DNP enhancement appears to be strongly correlated with the electron and nuclear spin relaxation times, with longer longitudinal relaxation times (T_1) leading to better enhancements. Heavier, more bulky radicals have longer electronic relaxation times, and we have shown that this leads directly to better DNP enhancements with the introduction of TEKPol and AMUPOL [2]. However, we guessed that the extent of crowding created by functional groups adjacent to the unpaired electron(s) could also significantly affect the DNP enhancement.





open-AMUPol



closed-AMUPol

We recently measured the electron relaxation times of `Open' and `Closed' forms of AMUPOL at 94 GHz and found that the electron relaxation times of both species are similar, yet the DNP enhancement using these radicals is an order of magnitude different. In this presentation we will review the origin of some of these enhancement effects as well as present some new high field relaxation data of commonly used DNP radicals at temperatures of 100 K and magnetic fields up to 16 T.

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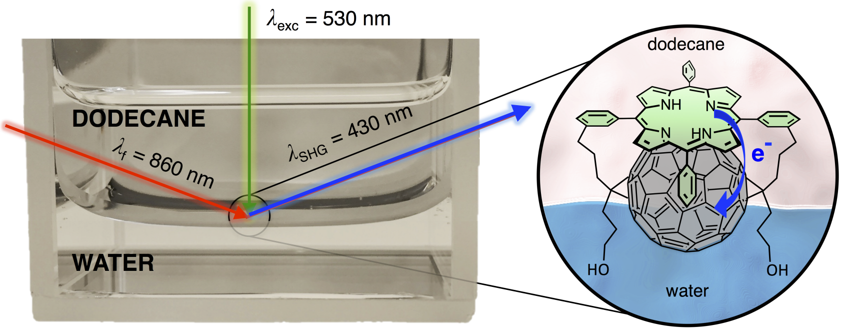
Electron-Transfer Dynamics at Water-Dodecane Interface Probed by Surface Second Harmonic Generation

T. Kumpulainen[1], G. Licari[1], A. Efimov[2], E. Vauthey[1]*

[1]University of Geneva, [2]Tampere University of Technology

Increasing global energy consumption and limited reserves of fossil fuels have driven industrial and academic research towards renewable energy resources. Organic photovoltaics (OPVs) and dye-sensitized solar cells (DSCs), devices that convert solar energy into electricity, have gained increasing attention during the past decades due to their low cost and easy fabrication. Both approaches rely on absorption of photons by small π-conjugated molecules, metal complexes or polymers followed by electron transfer to an acceptor. In the case of OPVs the acceptor is typically also an organic molecule such as fullerene (C_{60}), whereas in DSCs it is often a semiconductor such as TiO_2.[1,2] The common feature for both is that the electron transfer process occurs at the interface of two materials with different dielectric properties. Therefore understanding of the charge-separation process at interfaces is of paramount importance for the future development of superior devices.

We approach this problem in an innovative way using a donor-acceptor dyad deposited on a water-dodecane interface. The dyad consists of a covalently bound porphyrin donor and a fullerene acceptor coupled to two hydrophilic arms to orient the dyad perpendicular to the interface.[3] We use Surface Second Harmonic Generation (SSHG) to investigate the spectral properties and the orientation of the molecules at the interface. Secondly, a pump-probe approach gives us direct access the interfacial electron-transfer dynamics. The experimental approach is depicted in the figure below. This opens up new possibilities to selectively change the properties of the donor and the acceptor medium contrary to bulk solution measurements. In our contribution, we will present our preliminary results on the water-dodecane interface.



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Bimolecular Charge Separation and Recombination in Dipolar and Ionic Environments

A. Rosspeintner[1], G. Angulo[2], M. Koch[1], E. Vauthey[1]*

[1]University of Geneva, [2]Polish Academy of Sciences

The last decade has seen room temperature ionic liquids (RTIL) gain notoriety as „panacea-solvents“ in so diverse areas as biomass processing, gas chromatography or batteries and solar cells.[1] This widespread use is mostly owed to the exceptional physical properties of RTILs compared to conventional solvents.[2]

Here we investigate how the different nature of a solvent - either dipolar or ionic - affects the dynamics of bimolecular charge separation (CS) and recombination (CR). Studies on CS have shown that the kinetics are mostly governed by viscosity, regardless of the electronic nature of the solvent, which is of minor importance.[3,4] Investigations on CR, however, have so far not been reported. Thus the question of how an itself ionic environment - compared to a dipolar one - influences the fate of photochemically generated ionic species is still unresolved.

We compare a simple donor-acceptor model system in three different solvent environments (low viscous organic / high viscous organic / RTIL), by following the population of all involved species from the sub-ps to the sub-μs range using broadband pump-probe spectroscopy in the visible. Taking recursion to the unified version of the encounter theories we are able to obtain a quantitative description of all involved species (including spin evolution) for the entire geminate reaction stage.[5]

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Rydberg-Stark deceleration of metastable triplet helium atoms in a magnetic field

M. Zesko[1], O. Tkáč[1], F. Merkt[1]

[1]ETH Zürich

The technique of Rydberg-Stark deceleration has provided a means to decelerate and trap Rydberg atoms and molecules at a temperature of around 100 mK. This technique relies on the very large electric-dipole moments of Rydberg-Stark states (up to 3000 D at n=30), which enable one to exert large deceleration forces on atomic and molecular beams using inhomogeneous electric fields.

In the case of atomic hydrogen and helium at n=30, the trapped Rydberg atoms decay by fluorescence on a time scale of around 100 µs [1,2]. This decay opens up the possibility to trap paramagnetic atoms in their ground state or a metastable state using an overlaid electric and magnetic trap. Such a trap would offer the advantage of increasing the phase-space density of the trapped atoms by accumulating population in the ground state in successive experimental cycles. To achieve this goal, we have designed and constructed a new experimental setup with which metastable He (1s)(2s) $^3S_1$ (He* hereafter) can be trapped magnetically following Rydberg-Stark deceleration.

The first major step is studying how the deceleration process is affected by the magnetic field. In a previous study, we examined how the energy levels of excited He* behave in electric and magnetic fields of arbitrary orientation [3]. The findings allowed us to choose the optimal state for the deceleration process. We present the experimental realisation of deceleration of He* in a magnetic field. The experimental result is compared to the deceleration measurements in a magnetic-field-free setup and with a particle-trajectory simulation of the deceleration process in a magnetic-field-free case and in the presence of the magnetic field.

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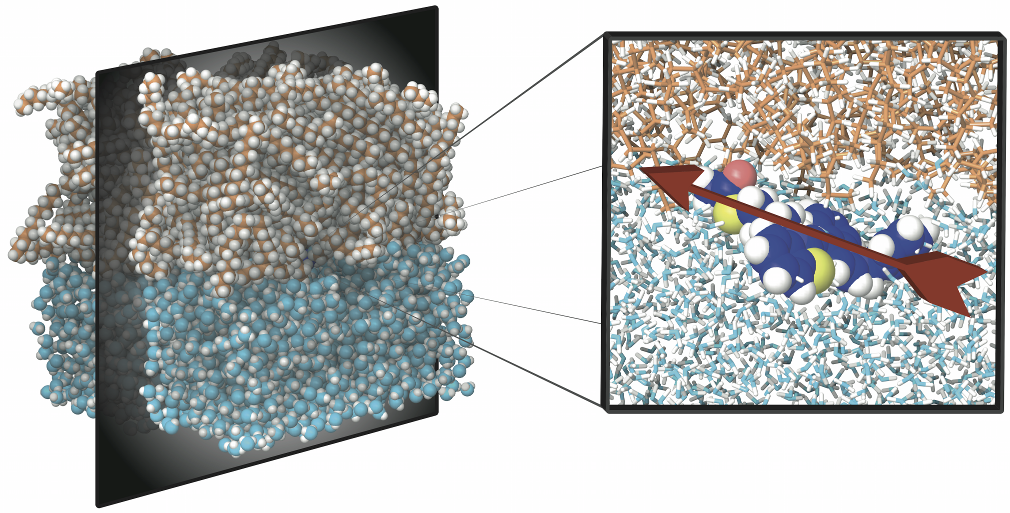
Orientation of a DNA probe at biological-like interfaces

G. L. Licari[1], L. Cwiklik[2], P. Jungwirth[2], E. Vauthey[1]*

[1]University of Geneva, [2]Academy of Sciences of the Czech Republic, Prague

Biological interfaces such as cell membranes fulfill prominent tasks in a cell and are of fundamental interest for life science. The membranes are constituted mainly by phospholipid bilayers and function as gates to the cell interior being selectively permeable to ions and organic molecules. Such an environment is difficult to probe because the membrane (or in general any other interface) represents a small portion of the cell and its properties are buried by the response of the bulk phase. To overcome this problem, specific techniques must be employed, one of which is Surface Second Harmonic Generation (SSHG).[1] The dipolar origin of SSHG technique forbids generation of the signal from medium with inversion symmetry and therefore can be used to answer fundamental questions concerning interfaces.

We are currently employing SSHG to study DNA molecular probes at the interface between dodecane and water in the presence of a phospholipid monolayer to simulate the environment of a cell membrane. Our results suggest that the orientation of the cyanine dye TOSAC-bz, belonging to the YO family,[2,3] changes dramatically in the presence of the phospholipid monolayer at the interface. Thank to this effect TOSAC-bz could be used as an orientational probe to track structural changes in the membranes and in the cell shape. In this contribution we will discuss our measurements in this regard as well as Molecular Dynamics simulations (MD), which allows direct insight into the microscopic system and give additional information on the origin of the changes of the dye orientation.



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Calorimetric and Spectroscopic Studies on the Solvation Energetics for H_2 Storage in the CO_2/HCOOH System

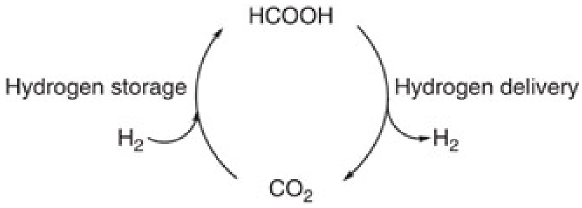
C. Fink[1], G. Laurenczy[1]*

[1]EPF Lausanne

Fossil fuels account for the majority of our energy needs, such as heat, electricity, and transportation.[1] The exploitation of these energy reserves by simple combustion processes releases vast amounts of carbon dioxide gas into the atmosphere, with the well-known consequences (greenhouse effect). Formic acid (FA) can contribute to a solution to our current energy crisis: By capturing some part of the anthropogenic CO_2 and reducing it with hydrogen, obtained from readily available renewable energy sources (wind or sun), is an elegant way to surpass the fluctuating nature of these energy sources since formic acid dehydrogenation allows to provide electricity by fuel cell combustion on demand.[2]

Solvents play a crucial role in the catalytic formic acid/carbon dioxide cycle and additives can be used to shift the reaction equilibrium towards higher yields. We studied the enthalpy of mixing for selected solvents and basic additives (amines, aqueous KOH).[3] Total formic acid yields are highest when produced FA is “removed” effectively from the reaction equilibrium. Clearly, the usage of basic chemicals - or solvents - yields higher total FA concentrations, but the liberation of hydrogen is in return more energy consuming. Therefore, the enthalpy of mixing is a valuable parameter for designing hydrogen storage devices because it allows to estimate the energy balance for the CO_2 hydrogenation/H_2 liberation cycle.

The highest formic acid concentrations in direct catalytic CO_2 hydrogenation under acidic conditions were reached in DMSO.[4] DMSO exhibits considerably stronger interactions with formic acid than water as was observed in calorimetric measurements. The difference can be ascribed to the formation of stronger hydrogen bonds between FA and DMSO than FA - water. The phenomenon was examined more closely with in-silico methods, ATR-FTIR -and NMR spectroscopy (^{1}H, ^{13}C). We found that 1:1 aggregates are predominating in DMSO - FA solution in a broad concentration range, while the stoichiometry and the number of the FA - water aggregates essentially depends on the concentration.



Formic acid/carbon dioxide cycle for hydrogen storage and delivery

Acknowledgments: The Swiss Competence Center for Energy Research (SCCER), Commission for Technology and Innovation (CTI), and EPFL are thanked for financial support.

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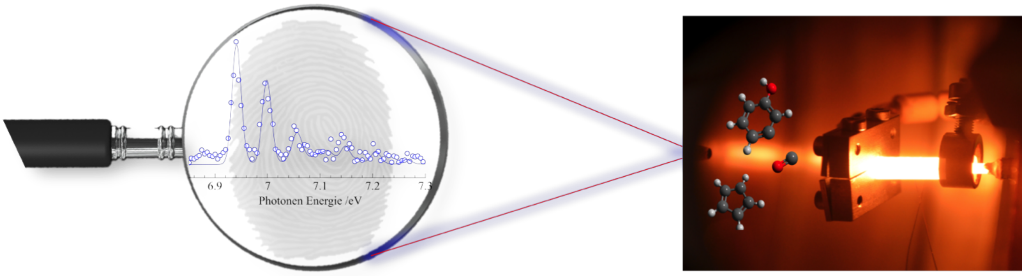
Threshold Photoelectron Spectroscopy to trace Chemistry in Combustion, Pyrolysis and Catalysis

P. Hemberger[1]

[1]Paul Scherrer Institute, Villigen

In the last two decades soft photoionization with tunable vacuum ultraviolet (VUV) synchrotron radiation has evolved into a versatile workhorse for the identification and quantification of reactive intermediates and stable molecules in processes of energy conversion such as combustion. Photoionization mass spectra (PIMS), which can be obtained by scanning the photon energy and recording the ion signal, can be useful to distinguish between constitutional isomers, when compared with calculated or experimental data.
However, this approach is limited if the ionization energies of different isomers are close, since PI spectra do not show sharp peaks and vibrational fine structure as conventional photoelectron spectra do.
Photoelectron photoion coincidence (PEPICO) spectroscopy is an excellent extension to mass spectrometry, since it allows measuring (threshold) photoelectron spectra mass-selectively. These spectra show selective vibrational transitions into ion states, which mostly follow the Franck-Condon principle and thus serve as vibrational fingerprints (see Figure) to identify complex composition of isomers. We will show several examples, which profited greatly from this additional analytical dimension, which is implemented in the PEPICO endstation located at the VUV beamline of the Swiss Light Source:

Hydroxyphenylradicals (HPR) produced selectively in a glowing microtubular reactor (see Figure) decompose to form soot precursor molecules such as propargyl and cyclopentadienyl radicals. Although HPRs were selectively synthesized, they are shown to rearrange to phenoxy radicals, the global minimum on the potential energy surface, prior to decomposition.[1]



In a *m*-xylene oxygen flame ($\Phi = 1.8$) we were able to identify up to four different isomers of the composition C_9H_{10} and $C_{10}H_{10}$, which are important findings in terms of soot formation chemistry.[2] In Addition, we have identified *m*-xylyl as the most abundant fuel radical and found a similar decomposition mechanism as previously identified in a hot microreactor.[3]

Most recently we have carried out experiments in the field of catalytic pyrolysis of lignin model compounds. Zeolites like HUSY were tested towards their capabilities to form reactive molecules when exposed to guaiacol. Compared to bulk phase catalytic pyrolysis fulvene and methyl-cyclopentadienyl were identified, which might provide insight of the mechanisms taking place on the catalyst surface.

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Precision Spectroscopy in Cold Molecules: The Rotational Intervals of He_2^+ by High-Resolution Spectroscopy and Rydberg-Series Extrapolation

L. Semeria[1], P. Jansen[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich, CH-8093, Switzerland

He_2^+ is an interesting system both from a theoretical and experimental point of view. It has only three electrons, therefore highly accurate *ab initio* calculations are possible. Claiming an accuracy of 120 MHz, the latest calculations of the rovibrational energies of He_2^+ do not include relativistic and quantum electrodynamics (QED) effects [1]. High-resolution Rydberg spectroscopy of metastable He_2 molecules has allowed us to determine the rotational energy-level structure of He_2^+ [2] through Rydberg-series extrapolation by multichannel-quantum-defect-theory [3]. To this end, helium molecules in the $a\ ^3\Sigma_u^+$ state are produced in supersonic beams with velocities tunable down to about 100 m/s by combining a cryogenic supersonic-beam source with a multistage Zeeman decelerator [4]. The metastable He_2 molecules are then excited to high *n*p Rydberg states using the frequency-doubled output of a pulse-amplified ring dye laser. The Zeeman decelerator greatly simplifies the spectral assignment because of its spin-rotational state selectivity. The deceleration also reduces the systematic uncertainty arising from a possible Doppler shift, even if the bandwidth of the laser system is too large to observe the reduction of the Doppler width resulting from deceleration. The unprecedented accuracy of 18 MHz that we have obtained for the lowest rotational intervals of He_2^+ (with $N^+ \leq 5$) enables the quantification of the relativistic and QED corrections by comparison with the results of Ref. [1]. Moreover, the rotational structure of the metastable state has been measured precisely for comparison with the results of Focsa [5]. In our poster, we present an extension of these measurements and their MQDT analysis to higher rotational intervals of He_2^+ up to $N^+ = 17$. We have also replaced our pulsed UV laser by a cw UV laser, improving the resolution of the spectra by a factor of more than five.

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Modifying peptides and proteins for quantum interference experiments

J. Schaetti[1], U. Sezer[2], L. Mairhofer[2], J. Cotter[2], M. Arndt[2], V. Köhler[1]*, M. Mayor[1]*

[1]University of Basel, [2]University of Vienna

The current world mass record for matter-wave interference experiments relies on the careful design of the analyte molecules, i.e. chromophores decorated with highly fluorinated tags.[1] The experiments require slow molecular beams and accordingly postionization of the neutral analyte in the gas phase for manipulation and detection. Thermal evaporation of peptides without decomposition is notoriously difficult due to the thermal lability and strong intermolecular interactions of the analytes.[2] In addition their postionization by VUV (vacuum ultra violet radiation) is hampered if the peptide sequence displays a low tryptophan content.[3] A range of model compounds were prepared to i) reduce intermolecular interactions and thereby improve their volatility ii) investigate photoionization of peptides in the gas phase. The intermolecular interactions can be reduced by the removal of charges (through acylation and amidation) and hydrogen bond donors (through methylation) and the decoration with fluorinated alkyl chains.

The decoration of a small peptide (Ala-Trp-Ala) with fluorinated alkyl chains led to promising evaporation results. It was possible to produce a slow molecular beam and measure the first ever interference pattern of a peptide by mass detection after electron impact ionization.

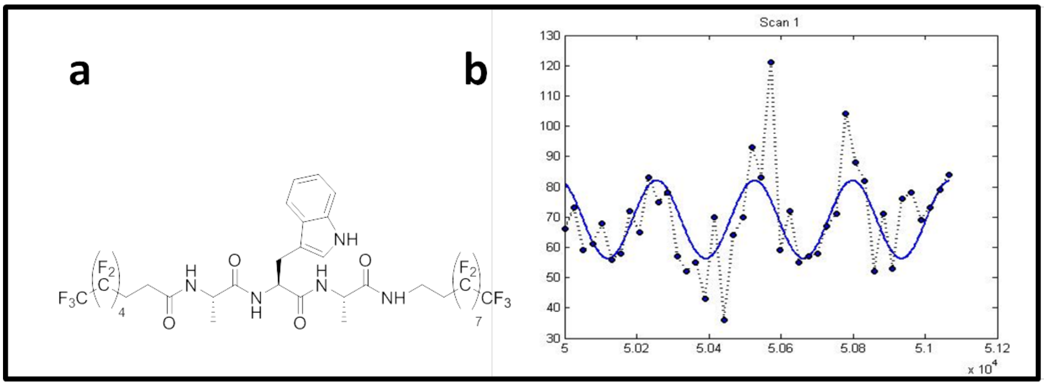

Fig 1: (a) The tripeptide Ala-Trp-Ala with fluorinated alkyl chains attached to its C- and N-termini. (b) Interference pattern of the tripeptide; X-axis : position (nm), Y- axis : counts/s. The blue line is a guide for the eye.

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Gold nanowire fabrication with lipid nanotubes

K. Jajcevic[1], K. Sugihara[1]

[1]University of Geneva

The fabrication of conductive nanostructures is the key technology in semiconductor industry and has gained importance in biology for applications such as biosensors and drug delivery.
We have demonstrated a high-throughput approach to fabricate gold nanowires on surfaces with a lipid nanotube template. Biotin-tagged lipid nanotubes are formed from lipid blocks in inverted hexagonal phase adsorbed on polymer-coated surfaces upon application of shear force. Streptavidin-coated gold nanoparticles were attached to the biotin-tagged lipid nanotubes and gold nanoparticle-encapsulated lipid nanotubes were cross-linked by chemical fixation. Samples were dried and treated with oxygen plasma to remove the organic template and connect the particles. The created nanowires were characterized by cryo-transmission electron microscopy, atomic force microscopy and electrical measurements.

Determining Nano to Micro Structures from Relayed DNP NMR

A. C. Pinon[1], J. Schlagnitweit[2], P. Berruyer[2], A. Rossini[2,3], A. Lesage[2], C. Copéret[4]*, L. Emsley[2]*

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), [2]Centre de RMN à très hauts champs, [3]Iowa State University, [4]ETH Zurich

The characterization of the architecture materials on the nano to micro scale is of great importance today.

However in many cases, where the sample is either for example opaque or made of many mixed components, determining micro structures still remains an unsolved analytical problem. Since there are very few direct methods to probe the inside of these types of materials, solid-state NMR would be an attractive approach to look at these solid-state structures.[1,2,3] Here, we show how, combined with a model for spin diffusion, DNP NMR can be applied to determine domain sizes in such materials.

Using an approach where we selectively dope a source component with radicals (usually by impregnating the material with a radical containing solution), and where another target component remains undoped, we show how polarization builds up in the target component in a manner that is characteristic of the size and geometry of the target component.

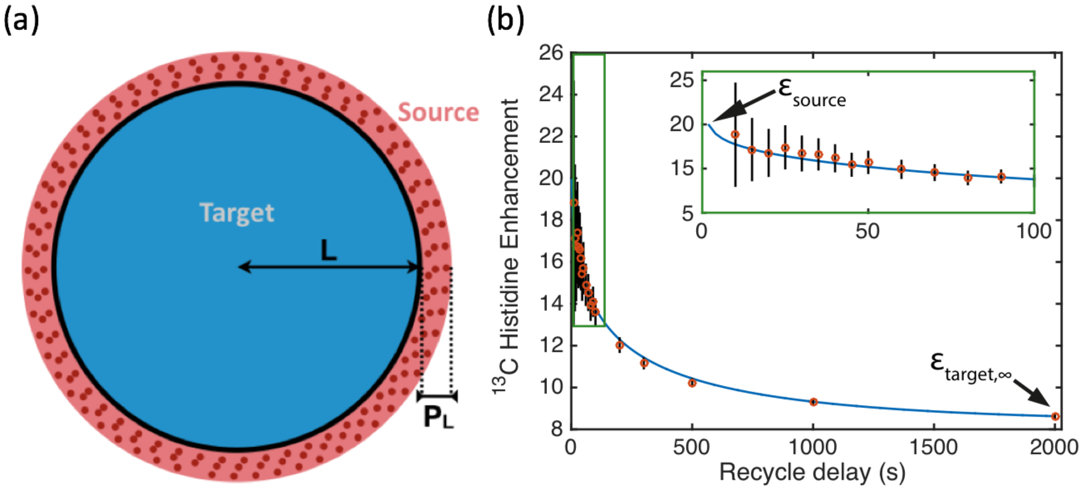

Figure (a): Representation of the model for micro-particulate materials (blue) impregnated with a polarizing liquid (pink) containing radicals (red). The particle is polarized by spin diffusion.
(b) Experimental DNP enhancement for micro-crystalline histidine particles as a function of the polarization time compared to a simulation of the diffusion of polarization for a 9 µm particle radius.

For several pertinent types of geometry, we calculate the heterogeneous distributions of polarization as a function of position at steady state. We then show the variation of the integrated DNP enhancement (ε) as a function of the polarization time. **The curves are seen to be characteristic of the domain sizes in all cases.** Finally, we compare the prediction of the enhancement at steady state (ε_∞) as a function of the size of the object to an analytical expression from the numerical result.

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Long-range molecules correlated to electronically highly excited states in Cs

H. Saßmannshausen[1], F. Merkt[1], J. Deiglmayr[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich

We present the observation of weakly bound, long-range Cs_2 molecular states in singly or double excited Rydberg states [1]. Rydberg states are electronically highly excited states, *i.e.* states with large values of the principal quantum number n.

The experiments are performed on ultracold gas-phase samples of Cs atoms which are released from a magneto-optical trap at a temperature of 40 µK and a density of about 10^{11} cm^{-3}. The Cs atoms are photoexcited to $np_{3/2}$ Rydberg states in one-photon transitions using UV laser pulses with wavelengths of about 320 nm. Close to the intense atomic $np_{3/2} \leftarrow 6s_{1/2}$ transitions we observe additional molecular resonances that are attributed to the photoassociation of two ultracold Cs atoms into long-range molecular states. Two different types of molecular resonances are identified.

The formation of the first type of long-range molecules is a result of the interaction of a Cs Rydberg atom with a single ground-state atom which is located within the extended orbit of the Rydberg electron [2,3]. The molecular potentials are modelled by taking into account the low-energy scattering of the Rydberg electron off the ground-state atom. The exotic molecular levels are bound by only about 0.0002 kJ/mol, much less that the thermal energy at room temperature. We present the results of spectroscopic measurements of the binding energies at different values of the principal quantum number (n between 26 and 34), of the Stark effect in external electric fields and of the lifetime. The consequences of the hyperfine interaction of the ground-state atom on the molecular binding are also discussed [4].

The second type of molecular resonances reveals the long-range interactions between two Cs Rydberg atoms. These interactions are van der Waals interactions. The observed resonances are a result of the dipole-dipole, dipole-quadrupole [5] and higher-order [6] contributions in the multipole expansion of the long-range electrostatic interaction. To observe these doubly excited Rydberg-atom-pair states, we employ either a one-colour two-photon excitation scheme [7], which requires high-intensity laser pulses, or a two-colour two-photon scheme of the type $nl_j n'l'_{j'} \leftarrow 6s_{1/2} nl_j \leftarrow 6s_{1/2} 6s_{1/2}$. The two-colour excitation scheme relies on the resonant excitation of a few atoms to Rydberg states (called seed atoms) and enables the observation of bound Rydberg-atom pairs and of Rydberg-atom aggregates.

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Cold and controlled mechanistic studies of conformer selected ionic cycloadditions

A. Kilaj[1], D. Rösch[1], H. Gao[1], J. Küpper[2,3]*, S. Willitsch[1]*

[1]Departement Chemie, Universität Basel, Klingelbergstrasse 80, 4056 Basel, [2]Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, [3]Department of Physics, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Despite their significance in organic synthesis, the mechanistic details of Diels-Alder cycloadditions, in which a diene and a dienophile react to form a cyclic product, still remain an unsolved and extensively discussed question. It has proven difficult to determine whether these reactions favor a synchronous concerted or a stepwise mechanism. In case of a concerted pathway, only the s-cis conformer of the involved diene reacts to form the cyclic product while in a stepwise mechanism also the s-trans conformer adds to the formation of the product. Due to their high stereo- and regioselectivity, a concerted mechanism is generally assumed [1]. For polar Diels-Alder reactions, however, where one of the reactants contains a charge, the reaction does not necessarily proceed via a concerted pathway but may instead favor a stepwise mechanism.

In order to shed light on these questions we investigate the reactivities of individual conformers by employing molecular beam technology [2]. Owing to their different dipole moments, conformers can be spatially separated in an inhomogeneous electric field. Directing a molecular beam of spatially separated conformers into a cloud of sympathetically cooled molecular ions in an ion trap allows us to study highly conformationally selective reactions such as Diels-Alder cycloadditions. Previously, this method has been successfully applied to study reactive collisions of 3-aminophenol with a Coulomb crystal of Ca^+ ions [3][4].

As a representative example, we want to study the conformationally resolved ionic cycloaddition reaction of 2,3-dibromo-1,3-butadiene (diene) which exhibits two different conformers, s-cis and s-trans, with ionic maleic anhydride (dieneophile). Here, the dieneophile is ionized via a femtosecond laser pulse and sympathetically cooled into a linear quadrupole ion trap through a Coulomb crystal of Ca^+ ions. Then, a molecular beam of neutral conformer-selected diene species is directed into the trap center where it collides with the dieneophile. Finally, the products of the reactive collisions can be analyzed by an integrated high-resolution time-of-flight mass-spectrometer. The performance of this setup was recently confirmed by measuring the rate constant of the reaction between laser cooled Ca^+ ions with N_2O which was in good agreement with existing literature [5]. This advancement will enable us to trace the complex mechanistic pathways of Diels-Alder reactions.

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Towards Continuous Trap Loading of Helium in Rydberg States

O. Tkáč[1], M. Zesko[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland

We present experiments on triplet helium Rydberg states carried out to fully characterize the joint effects of electric and magnetic fields. We measured the high-resolution spectra of transitions from the $(1s)(2s)^3S_1$metastable state of He to Rydberg states around n = 30 in pure electric (Stark effect) and magnetic (Zeeman effect) fields as well as in combined electric and magnetic fields at various relative angles and strengths [1]. The spectra were also calculated by diagonalization of the Hamiltonian matrix. The avoided crossings between Rydberg states in the range of electric- and magnetic-field strengths relevant for Rydberg-Stark deceleration and magnetic trapping were characterized. In particular we discuss the effect of the successive reduction of the spatial symmetry from isotropic under field-free conditions (l and m_l are good quantum numbers) through cylindrical in a homogeneous electric or magnetic field (m_l is still a good quantum number) to situations where even m_l is lost as a good quantum number.

These experiments are carried out in the context of efforts to develop a continuous trap-loading scheme for Rydberg atoms and molecules, the trap-loading being realized by Rydberg-Stark deceleration [2, 3] and the long-term storage being achieved with a magnetic trap. A prerequisite for this trap-loading scheme is that the trap centre is displaced from the propagation axis of the beam. The poster will also describe experiments in which the He Rydberg atoms have been deflected and loaded in an electric trap located 4 mm away from the beam propagation axis. This enabled ameasurement of the decay of He atoms initially excited to n = 20 Rydberg states from the off-axis electrostatic trap operated in a range of blackbody radiation temperatures between 5 and 300 K.

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Dynamic Nuclear Polarization Method as a Probe of Lipid Nanoparticles Structure

J. Viger-Gravel[1], A. Schantz[2], A. Rossini[3], A. C. Pinon[1], S. Schantz[2]*, L. Emsley[1]*

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), [2]AstraZeneca R&D, [3]Iowa State University

Lipid nanoparticles (LNPs) are used as drug carrier systems to achieve cellular internalization of hydrophilic bioactive molecules such as small interfering RNA (siRNA) and messenger RNA (mRNA).[1] The structure of LNPs and the mechanism of encapsulation of siRNA or mRNA by LNPs is still unknown. Several propositions for LNPS structures have been made on the basis of modelling or diffraction results, including multilamellar vesicle or nanostructure type structures, but there is currently no consensus.

In this work, we develop and apply dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS)to characterize structural features of LNPs in the presence and absence of siRNA. The LNPs used here are composed of cationic lipid (DLin-MC3-DMA), a phospholipid (DSPC), cholesterol and PEG (DMPE-PEG 2000), also sulphonated-siRNA is used to mimic mRNA.[2] We present for the first time the successful application of ^{1}H, ^{31}P and ^{13}C DNP SENS to these systems. By studying the DNP enhancement (ε) as a function of polarization time in terms of a relayed spin diffusion model we are able to determine the architectures of the LNPs. In particular the various chemical components of the LNPs are well resolved in the NMR spectra and we can establish their relative positions with respect to the LNP surface. In addition, slow CP magic angle turning (CPMAT) experiments in the presence and absence of siRNA allow measurement of the chemical shift anisotropy (CSA) of the sulphonated siRNA and the lipid components of the LNP (PEG and DSPC).

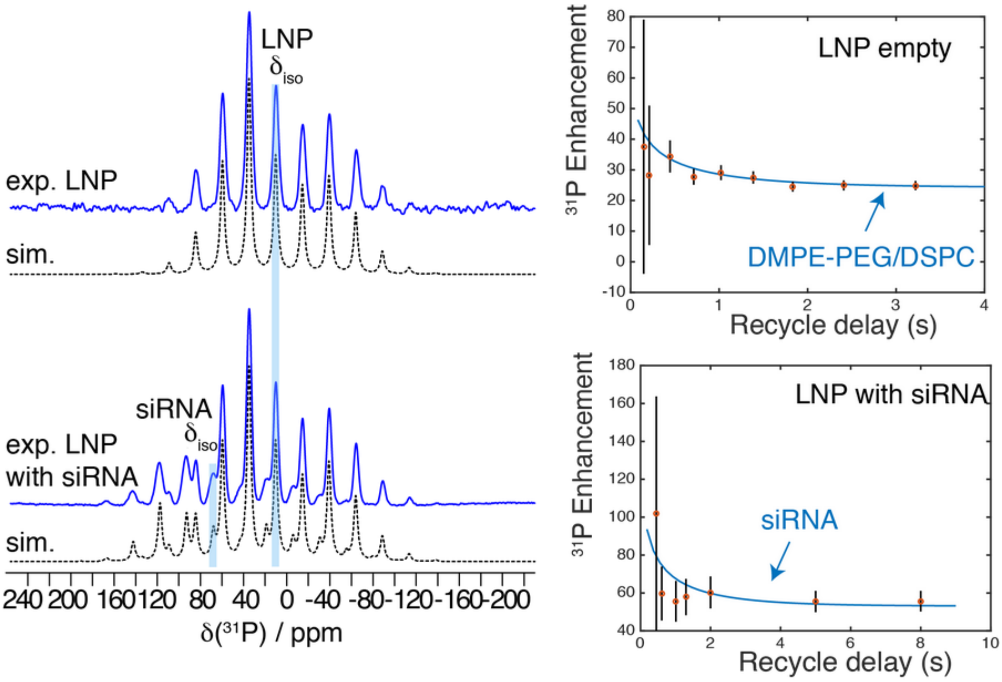

Figure 1. ^{31}P DNP SENS (9.4T) spectra of LNPs in the presence and absence of siRNA as well as ε(^{31}P) as a function of polarization time.

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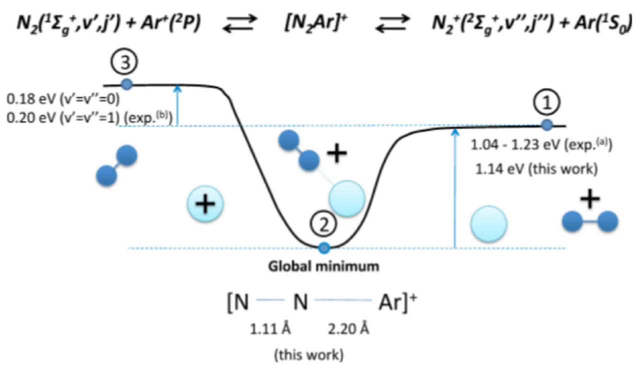
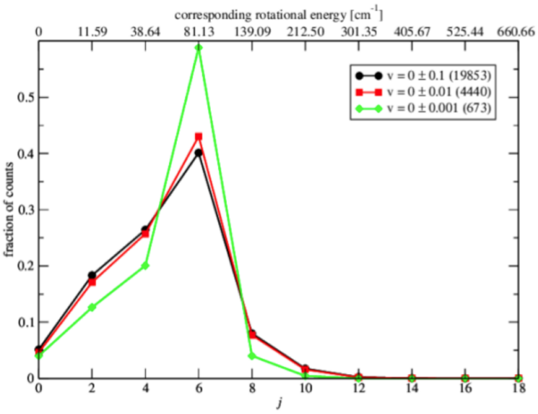
Collision-Induced Rotational Excitation in N_2^+-Ar: Comparison of Computations and Experiment

O.T. Unke[1], J. C. Castro-Palacio[1,2], M. Meuwly[1]*

[1]University of Basel, [2]Imperial College of London

The collisional dynamics of N_2^+ cations with Ar atoms is studied using quasiclassical simulations. N_2^+-Ar is a proxy to study cooling of molecular ions and interesting in its own right for molecule-to-atom charge transfer reactions. An accurate potential energy surface (PES) is constructed from a reproducing kernel Hilbert space (RKHS) interpolation based on high-level ab initio data. The global PES including the asymptotics is fully treated within the realm of RKHS. From several ten thousand trajectories, the final state distribution of the rotational quantum number of N_2^+ after collision with Ar is determined. Contrary to the interpretation of previous experiments[2] which indicate that up to 98 % of collisions are elastic and conserve the quantum state, the present simulations find a considerably larger number of inelastic collisions which supports more recent findings[3].





Quasi-classical molecular dynamics simulations of the nonreactive collision between the N_2^+ cation and Ar atoms at two different temperatures show that inelastic rotational excitation of the ion in the product channel is important and occurs more frequently than previously assumed. The simulations use an RKHS PES based on UCCSD(T)/aug-cc-pVTZ electronic structure calculations and correct handling of the asymptotics within the RKHS framework. Analysis of the results for j'' = 6 using a strict filtering criterion for the vibrational energy suggests that inelastic collisions occur in at least 17 % of the cases, which is one order of magnitude larger than reported in earlier experiments (2 %).[2] However, it can not be ruled out that subtle quantum mechanical effects affect the quantitative conclusions of the present work. Converged close-coupling calculations using the present PES will be a desirable complement to the present considerations, but challenging due tothe deep well and the large anisotropy of the PES.

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Conformational effects in neutral and ionic Diels-Alder reactions

U. Rivero[1], M. Meuwly[1]*, S. Willitsch[1]*

[1]Universität Basel

The Diels-Alder reaction is one of the most important reactions in organic chemistry in which a diene reacts with a dienophile forming a cyclic product. Despite its prominence in text books and the large body of literature existing on this reaction, there are many mechanistic details that are still not well understood. For example, the synchronicity of the reaction is not clear in asymmetric systems [1] or it has not yet been proven under single-collision conditions that only the s-*cis*-conformer can react to form the cyclic product as required by the postulated concerted reaction mechanism.

Y.-P. Chang et al. [2] have recently achieved conformational separation of isomers by electrostatic deflection of a molecular beam based on their different dipole moments. With this technique, it would be possible to separate the s-*cis* and s-*trans* conformers of a diene if they have sufficiently different dipole moments.

Our goal is to explore the detailed mechanism of Diels-Alder reactions using both experimental and theoretical techniques. In this part of the work, we theoretically study the reaction between conformationally selected 2,3-dibromo-1,3-butadiene and supersonically cooled neutral and cationic maleic anhydride. For this purpose, we calculate the potential energy surface of both systems as a basis for reactive molecular dynamics simulations [3] for a theoretical characterization of the reaction dynamics.

The theoretical results obtained will be presented in the context of the relevant experiments. Also, the ionic and neutral results will be contrasted in order to gain insight into the role of charge in this important reaction.

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Unraveling the electronic states of transition metal species by optical spectroscopy

M. Beck[1], B. Visser[1], P. Bornhauser[1], G. Knopp[1], J. A. van Bokhoven[2,1], P. P. Radi[1]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich

Within the main groups of the periodic table, the excited states of small molecules and clusters are usually well accessible by both spectroscopy and computation. For transition metals on the contrary, both approaches are hindered by the high density of states found in such systems. Absorption spectra of transition metal clusters are typically characterized by a quasi-continuum of densely packed lines from overlapping states, making assignments almost impossible. Computing these states by *ab initio* quantum chemistry, multi-referenced methods are required. However, a few transition metal atoms are already sufficient to reach the limits of available computing capacity. In this work we apply double-resonant, non-linear spectroscopy in a molecular beam environment to characterize a so far overlooked low-energy state in the copper dimer, contesting a common assumption used in recent computational works.

The applicability of two-color resonant four-wave mixing spectroscopy for isotopologue-selective studies in a mixed cluster beam as well as our experimental setup was already described in [1]. Utilizing this method in search of an unknown high-lying state in dicopper by double-resonance excitation, we instead found and characterized a state slightly below the so far lowest-lying known excited singlet state. As the spin-orbit coupling in copper is much weaker than for the isolobal gold, Hund’s case (a) was considered to be a good assumption for computational treatment of the copper dimer. But since the newly found state would not exist in that case, it is shown that significant jj-coupling has to be taken into account.

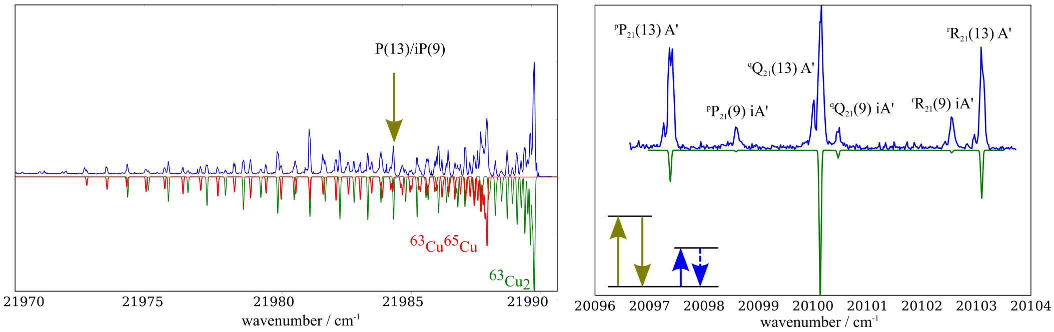

Figure 1: On the left, a one-color scan of the rotational lines within the B-X (1,0) transition of Cu_2 is shown over simulations of the most abundant isotopologues. The arrow indicates the pump wavelength for the two-color scan shown to the right. There, only lines originating in the “pumped” rotational levels of the ground state are visible. i indicates the heavier species.

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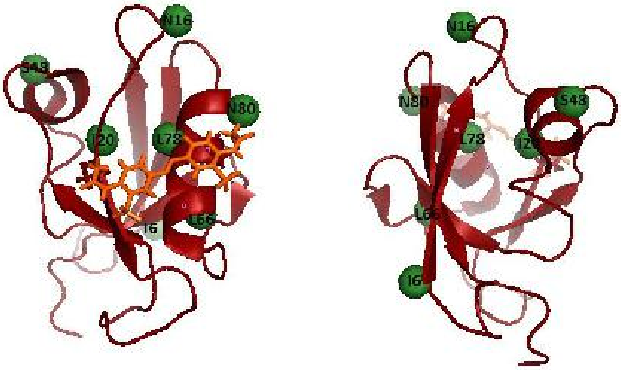
Two-dimensional infrared spectroscopy of a site-specifically labeled photoswitchable allosteric protein

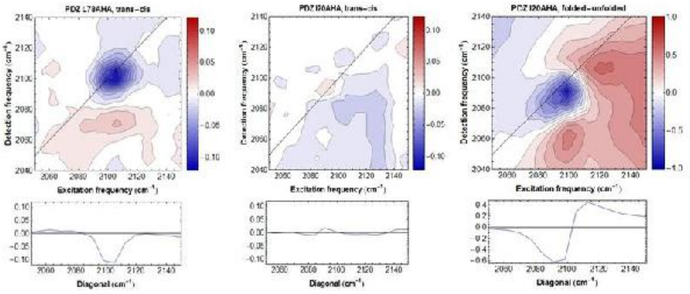
O. Bozovic[1], B. Stucki-Buchli[1], P. J. Johnson[1], K. L. Koziol[1], P. Hamm[1]*

[1]University of Zurich

It has been shown that azidohomoalanine is a good vibrational label that can be inserted site-specifically into proteins, can serve as a reporter for the changes in local environment and it is possible to measure azidohomoalanine labelled proteins down to a sub-millimolar concentration, with good signal to noise ratio[1, 2]. In order to investigate the signal propagation upon a conformational change of protein, we have incorporated azidohomoalanine as a site-specific label into the photoswitchable PDZ2 domain, previously used as a model system for investigating allosteric proteins[3].



Our results show that azidohomoalanine is suitable as a label for reporting large changes, e.g., moving the label from a hydrophobic environment to a solvent exposed surrounding, as it happens upon thermal unfolding. One of the mutant PDZ2 domain has shown a significant change in azidohomoalanine absorption upon conformational switching. When the label is placed at other positions in the protein, the changes in surrounding are too small to observe a difference in absorption. Therefore, we have been investigating additional labels, with larger oscillator strength, which may allow us to gain sensitivity to very small variations in surrounding.



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Ultrafast and Nanosecond Transient Absorption and Photoluminescence Spectroscopy Enlightens the Pathway towards Perovskite Electronic and Photovoltaic Devices

N. Droseros[1], G. Longo[2], H. J. Bolink[2], N. Banerji[1]

[1]University of Fribourg, [2]Universidad de Valencia

Solid-state photovoltaic cells and light emitting diodes are the most promising solutions for the modern, global energetic needs. Furthermore, the constantly developing electronics and telecommunication technology needs new electronic elements such as field effect transistors (FET) and lasers based on new generation materials. The on-going research has shown promising applications, and the role of many physical mechanisms has been revealed, but many new questions have been raised.

The optoelectronic properties of recently developed solid-state devices containing organic/inorganic hybrid Perovskites, seem to be highly dependent on the synthetic conditions and the subsequent film morphology. In the pathway towards the application of these materials into complete devices, many interfacial and bulk mechanisms have been found to play a crucial role. Upon photo-excitation, most of these mechanisms, which govern the deactivation of the excited state and the fate of free carriers, are in kinetic competition.

Ultrafast spectroscopy and in particularly transient absorption on the femtosecond timescale is a key characterization technique, which reveals the deactivation pathways and provides information about their kinetic competition. Moreover, supported by other time-resolved techniques, such as transient absorption and time-resolved photoluminescence in the nanosecond to millisecond timescale, the influence of the microstructure on the free carriers can be investigated and useful information about the synthetic and processing of the materials can be provided.

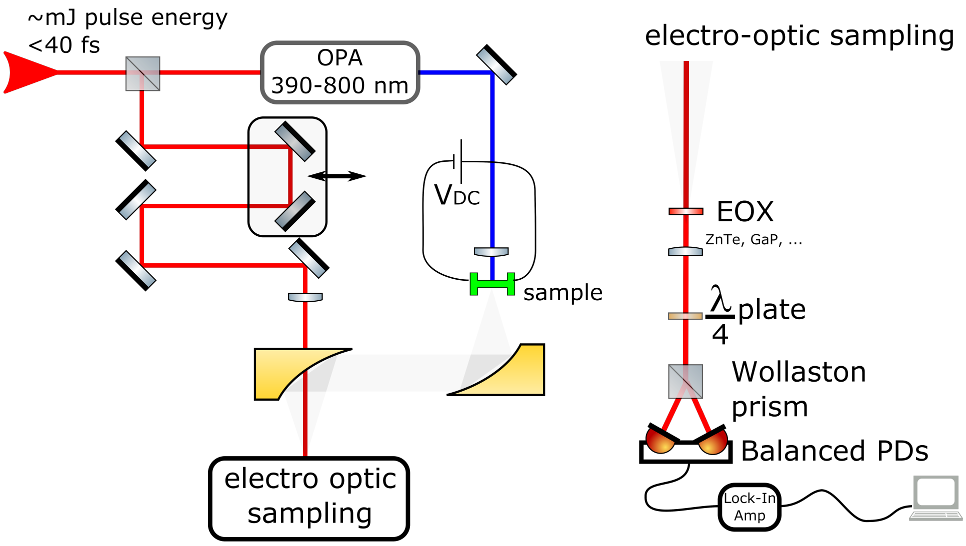
Terahertz Emission Spectroscopy on Thin Films

P. Krauspe[1], D. Tsokkou[1], N. Banerji[1]*

[1]University of Fribourg

In the terahertz emission spectroscopy, ultrashort laser pump pulses are focused on the gap between two metal electrodes deposited on top of the thin film samples of interest. For our experiments, a photoconductive switch configuration known as Auston switch [1] will be used. Pulses with photon energy higher than the band gap of the investigated semiconductor cause the photo-generation of carriers via interband transitions, which are subsequently accelerated by an external static electric field V_{DC} applied via the electrodes.

Using free space electro optic sampling the immediate electric field of the terahertz waveform is measured. From the electric field, we can obtain information about the generation and recombination rate of photoexcited carriers in the investigated sample on a femtosecond (1^{-15} s) timescale [2].



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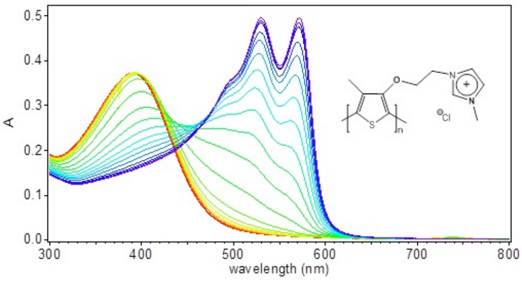
Photophysical study of a water-soluble cationic polythiophene derivative

L. Peterhans[1], J. C. Brauer[1], E. Alloa[2], M. Leclerc[3], S. C. Hayes[2], N. Banerji[1]*

[1]University of Fribourg, [2]University of Cyprus, [3]Laval University

Here we present a spectroscopic study of a water-soluble cationic polythiophene (CPT) derivative. CPT has a conjugated backbone, providing it with favorable optoelectronic properties, and positively charged side chains, allowing water-solubility. It has been used as a biosensor for DNA oligomers because of its interesting optical properties[1-2]. In aqueous solution, CPT can adopt different conformations depending on the temperature and on the assembly with single-strand DNA oligomers (ssDNAs). With a combination of stationary absorption and resonance Raman spectroscopy, we have observed that the polymer backbone has more torsional disorder at high temperature and that the chains are well dissolved, while CPT becomes more planar at low temperature and can form aggregates. In the presence of ssDNAs, another situation occurs: the backbone can become very planar (depending on the DNA sequence), but the complexation to ssDNA prevents backbone aggregation and we are in presence of the isolated polymer with elongated chains. The excited-state behavior of CPT in these different cases has been investigated using transient absorption spectroscopy.



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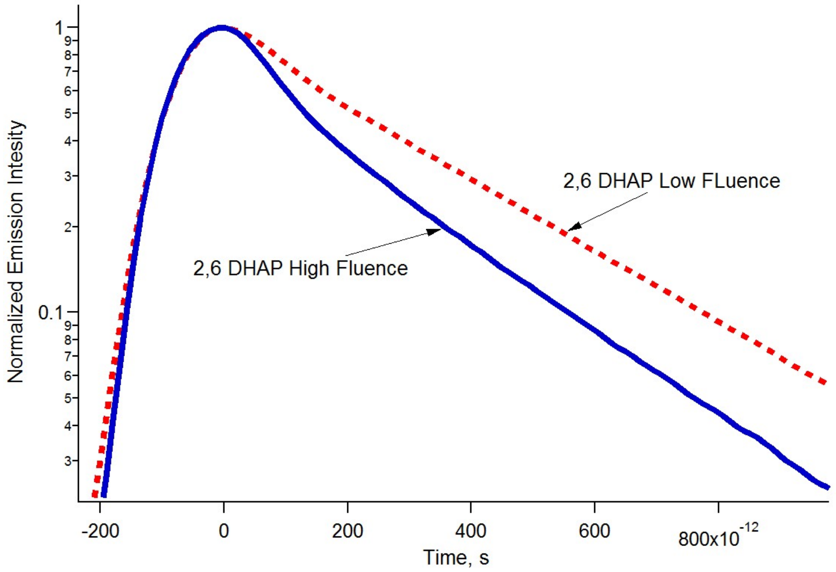
Possible role of triplet states in matrix-assisted laser desorption ionization investigated by time resolved decay measurements

P. Steffen, R. Knochenmuss[1], S. Leutwyler[1]*

[1]University of Bern

While matrix assisted laser desorption ionization (MALDI) is a technique which is widely used, primary ionization processes are still controversial. Evidence exists that for some MALDI substances ionization occurs via triplet states, possibly including multicentre processes including exciton pooling [1]. In order to investigate these physical processes the frequently used MALDI matrix 2,4,6-trihydroxyacetophenone (THAP) and various analogues like 2,6-dihydroxyacetophenone (2,6 DHAP) were examined. The fluence dependent decay curves of the matrices at different excitation wavelengths were analysed using a streak camera. At different excitation density the time dependent emission changes. A faster decrease in emission at high fluence is consistent with pooling as shown in the figure below. The measurements were done in solution at different concentrations and also in the solid state. Non time resolved emission and excitation spectra were also measured, changes as a function of concentrations including the solid state phase were observed. These results will be analysed in the context of pooling and other MALDI ionization models [2]. Further experiments including MALDI/MS to measure the performance and ion yield of the matrices are planned.



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Structural studies on mixed shell thiolate-protected gold clusters

A. Sels[1], N. Barrabes[2], T. Bürgi[1]*

[1]University of Geneva, [2]Institute of Materials Chemistry, Technical University of Vienna

Thiolate protected gold nanoclusters are a promising group of atomically precise nanostructures which gained great importance in the last decades due to their unique size-dependent physical, chemical and optical properties.[1] Their atypical structure and challenging crystallization impedes the structural determination, hence X-ray absorption spectroscopy has been proven a very reliable identification method.[2] The surrounding ligands play an important role in the stability of the cluster. Recently, exchange of ligands was found to be a straightforward and efficient post-synthetic functionalization method. Targeting several biomedical and sensing applications, incorporation of the requested functionalities requests a thorough understanding of this exchange mechanism.

Previous XAFS measurements focus on the influence of doping on the clusters structure, yet our interest lies towards the effects of incoming ligands on the sulfur environment. In this study we performed ligand exchange reactions on $PdAu_{24}(2\text{-PET})_{18}$ with enantiopure R-BINAS as substituting ligand.[3] Using this dithiol ligand limits the number of isomers and results in a stable exchanged product.

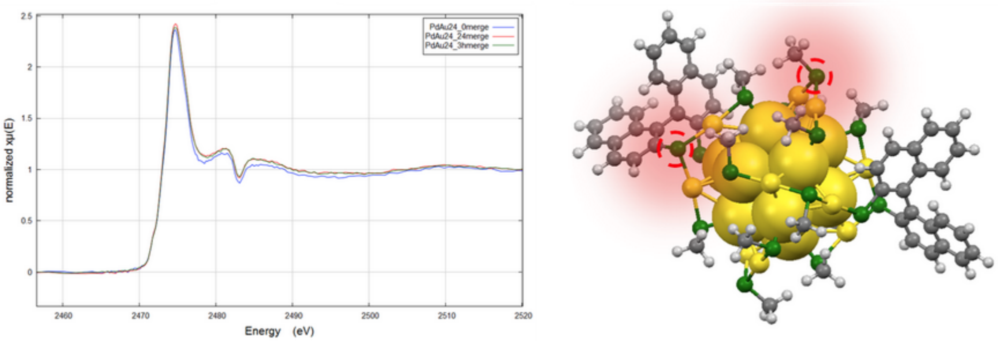

Figure 1: S K-edge XANES spectra (left); $PdAu_{24}(CH_3)_{14}(R\text{-BINAS})_2$ with different sulfur environments labelled (right)

Figure 1 presents the S K-edge XANES spectra of $PdAu_{24}(2\text{-PET})_{18-2x}(BINAS)_x$ at several reaction time intervals. XANES measures the average sulfur environment of the cluster, therefore obvious changes are difficult to observe at first sight. Preliminary data shows interesting results, however theoretical fittings are currently in progress as they are absolutely necessary when stating conclusions on the experimental data. We expect that the exchange of ligands will not drastically influence the Au-S framework of the $PdAu_{24}(2\text{-PET})_{18-2x}(BINAS)_x$ cluster. Additional XAFS measurements on Au LIII-edge are expected to shed more light on this issue.

Although sulfur XANES measurements are highly challenging, we are optimistic this method will open new insights into thiolate protected clusters and their behaviour upon ligand exchange.

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Ag doped Au38(SC2H4Ph)24 nanocluster: metal migration and chiroptical properties

B. Zhang[1], T. Bürgi[1]*

[1]University of Geneva, [2]Université de Genève

Thiolate-protected gold clusters and heteroatoms doped gold clusters have attracted increased attention by their well-defined structure and size-dependent properties. [1] Among them, the $Au_{38}(SCH_2CH_2Ph)_{24}$ cluster bears intrinsically chiral features due to the arrangement of the protecting ligands on the surface of the cluster. [2] Enhanced stability and surface flexibility of gold nanoclusters have been achieved by doping two Pd atoms inside Au_{38}. [3] However,theeffect of the number of dopant atoms on the nanocluster stability and chiral properties has not been studied. Multiple Ag atoms were doped inside Au_{38} by time-dependent metal exchange. Spontaneous Ag migration between Ag_xAu_{38-x} and Au_{38} nanoclusters was also observed by MALDI. The enantiomers of selected $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ samples (average x=6.5 and 7.9) have been separated by HPLC. Doping changes the electronic structure, as is evidenced by the significantly different CD spectra (Figure 1). The temperature required for complete racemization follows Au_{38} › Ag_xAu_{38-x} (x=6.5) › Ag_xAu_{38-x} (x=7.9) (Figure 1), which shows an increased flexibility of the cluster with increasing silver content. The weaker Ag-S bonds compared to Au-S, is proposed to be at the origin of this observation.

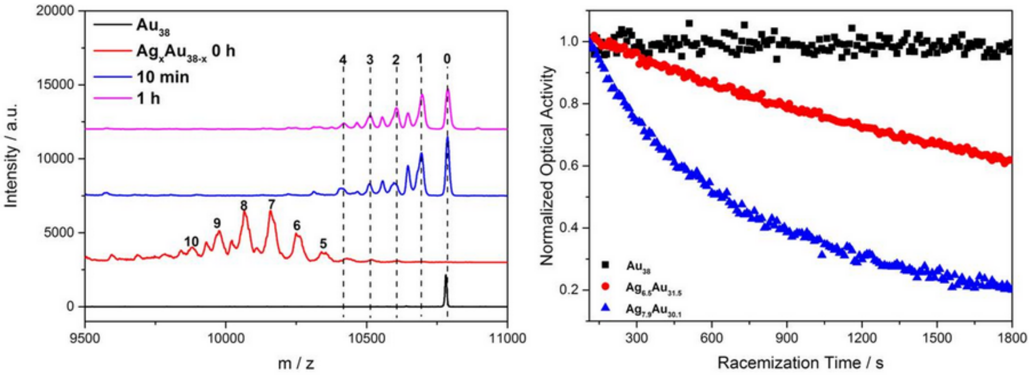

Figure 1: left: MALDI spectra of $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ before and after mixing with $Au_{38}(SCH_2CH_2Ph)_{24}$ in toluene solution, dopantnumber is marked above corresponding peaks; right: First enantiomer of $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ nanoclusters (x=0, 6.5 and 7.9), CD response as a function of time at 40˚C in racemization experiment.

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Wood filter technology for waste water treatment

S. Vitas[1], I. Burgert[1], E. Cabane[1]

[1]ETH Zürich

The removal of heavy metals is still a crucial step in the treatment of waste water. Actual strategies often imply the use of chemical coagulants, salts of aluminium or iron that bind the heavy metal to form a floc [1]. The flocculation has to be combined with a filtration step and the filtrate will undergo further treatments before entering the water supply [2]. The scope of this project is to develop a filter able to strip the heavy metal directly from a contaminated flow.
Wood is a readily available natural material with anisotropic porosity [3]. Its natural ability to transport water throughout its hierarchical structure makes it a material of choice for the development of innovative filters based on renewable resources.
However, wood cell wall components (cellulose, lignin, and hemicelluloses) mainly offer hydroxyl groups as reactive or binding sites. In order to improve the affinity of the filter towards heavy metals, we propose to increase the carboxylic content of wood (beech) through an esterification reaction with succinic anhydride (see Figure A) [4]. The modification succeeded in a direct step consisting in mixing the wood with the reactant and a catalyst in DMF.

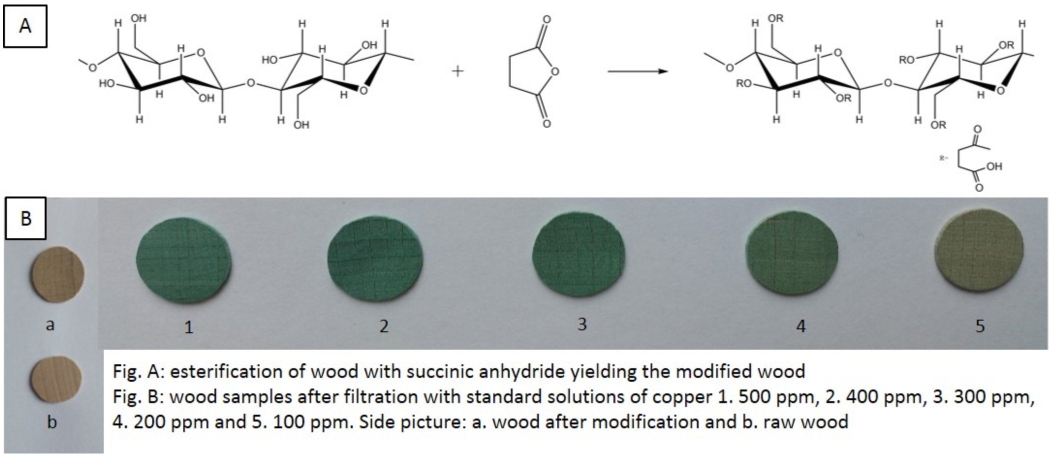

Fig. A: esterification of wood with succinic anhydride yielding the modified wood
Fig. B: wood samples after filtration with standard solutions of copper 1. 500 ppm, 2. 400 ppm, 3. 300 ppm, 4. 200 ppm and 5. 100 ppm. Side picture: a. wood after modification and b. raw wood

The capacity of the filter to remove heavy metal was assessed by filtering standard solutions of copper ranging from 100 ppm to 500 ppm, through gravity filtration (see Figure B). The filtrates were analysed using UV-Vis spectroscopy and AAS to confirm copper removal. Our preliminary results show that the concentration of copper is significantly decreased in the filtrate and there are indications that the filters do not reach saturation after a single filtration event. This indicates that wood can be used as a functional material with tuneable properties which allow for its use in the field of water treatment and can provide cheap and robust alternatives to actual systems.

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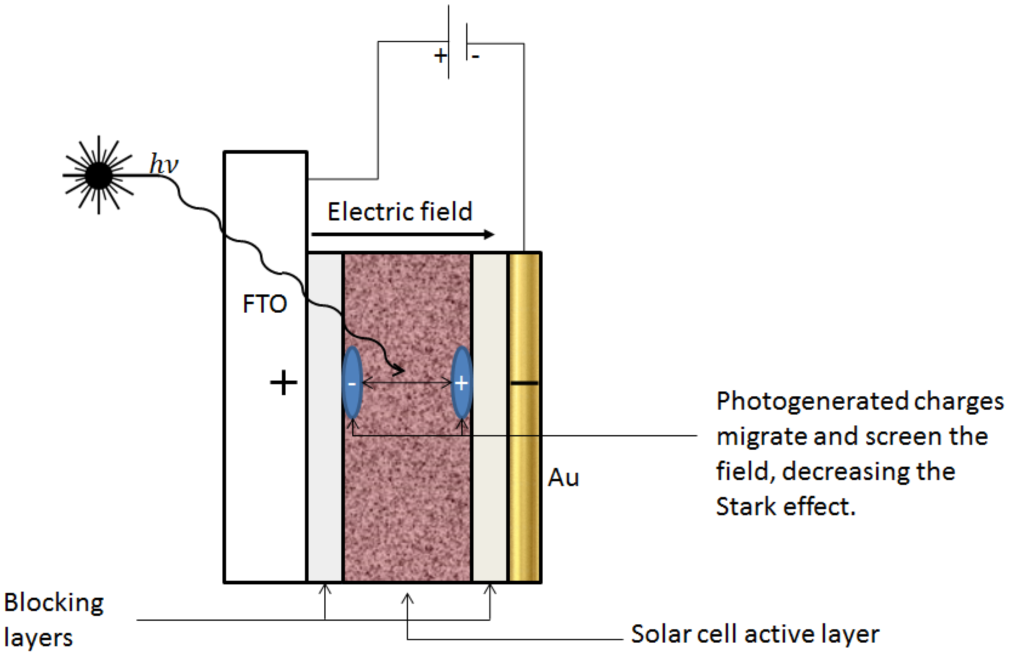
Charge Carrier Dynamics in Dye-Sensitized Solar Cells Investigated by Ultrafast Electromodulated Differential Absorption Spectroscopy

A. Burgos[1], J.-E. Moser[1]*

[1]Photochemical Dynamics Group, Institute of Chemical Sciences & Engineering, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Dye-sensitized solar cells (DSSCs) are one of the earliest third-generation photovoltaic technologies. Introduced by Grätzel et al. in the 90’s, devices based on nanocrystalline mesoporous TiO_2 anode and a liquid electrolyte have reached a maximum power conversion efficiency (PCE) of 13%, while solid-state cells see their efficiency level off at 9%.[1] A majority of research efforts in the field have turned nowadays towards perovskite solar cells, whose PCE now exceeds 22%.[2] A number of lessons learned from the latter technology with regard to carrier transport and extraction could be used for solid-state DSSCs, where plenty of room for improvement still exists. As for perovskite photovoltaics, ultrafast spectroscopy techniques can prove very useful to further understand limiting factors and point out the way forward.



Photogenerated charges migrate and screen the field, decreasing the Stark effect.

We present novel insights into photogenerated charge carrier dynamics in DSSCs using ultrafast electromodulated differential absorption (EDA) spectroscopy. This technique is based on the time-resolved monitoring of the screening by drifting photocarriers of an external electric field-induced Stark effect.[3] It allows to characterize several dynamic processes, such as interfacial charge transfer states dissociation, carrier separation and migration, and trapping-detrapping. In addition, we present the fabrication steps for special devices designed to selectively study various components and processes.

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Structural models of calcium silicate hydrate nanoparticles from NMR constraints

B. J. Walder[1], A. Kumar[2], A. Mohamed[2], B. Srinivasan[2], A. Hofstetter[1], A. Rossini[3], P. Bowen[2], K. Scrivener[2], L. Emsley[1]*

[1]Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, [2] Institut des Matériaux, Ecole Polytechnique Fédérale de Lausanne, [3]Department of Chemistry, Iowa State University, USA

Numerous structural models for cementitious calcium silicate hydrate (C-S-H) materials have been proposed, but lack of detailed experimental constraints for model validation has led to conflicting results and continuing debate about C-S-H structure. This is particularly true near the industrially important ratio Ca:Si = 1.8. We have conducted a series of dynamic nuclear polarization enhanced solid-state NMR experiments to obtain structural constraints on C-S-H nanoparticle gels with Ca:Si ratios between 1.0 and 2.0; specifically, variable contact time $\{^{1}H\}^{29}Si$ CP, $\{^{1}H\}^{29}Si$ HETCOR, and $\{^{29}Si\}^{29}Si$ scalar INADEQUATE experiments at 100 K. Using the constraints provided from the *Q* species quantification, ^{29}Si connectivities, and ^{1}H NMR lineshapes, we propose a structural model consistent with the NMR results.

Spectroscopy of$H_2^+$and HD^+Near the Dissociation Threshold: Shape and Feschbach Resonances

M. Beyer[1], F. Merkt[1]*

[1]ETH Zurich

We use high Rydberg states to measure the properties of H_2^+ and HD^+ in the vicinity of their dissociation limits H^++H, H^++D and H+D^+, with particular emphasis on quasibound rovibrational levels above the dissociation threshold of the $X^+\ ^2\Sigma_g^+$ ground state. Although the existence of these quasibound levels has been predicted a long time ago [1], they have never been observed. Given the role that such states play in the three-body and radiative recombination of H(1s) and H^+ to form H_2^+ , this lack of data may be regarded as one of the largest unknown aspects of this otherwise accurately known fundamental molecular cation. We present measurements of the positions and widths of the lowest-lying quasibound rotational levels (shape resonances) of H_2^+ , located close to the top of the centrifugal barriers and which decay by quantum-mechanical tunneling [2]. For HD^+ we present measurements of rovibrational levels of the $A^+\ ^2\Sigma_u^+$ state, located between the two dissociation limits. Because of the g-u-symmetry breaking in HD^+, these levels are coupled to the H^++D continuum by nonadiabatic interactions (Feshbach resonances). The experimental results will be compared with the positions and widths we calculate for these levels using a potential model for the X^+ and the A^+ state of H_2^+ and HD^+ which includes adiabatic, nonadiabatic, relativistic and radiative corrections to the Born-Oppenheimer potential energies.

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Encoding of chemical shifts using multiple indirect evolution in Homo- and Heteronuclear NMR experiments

E. Sistaré[1], D. Jeannerat[1]*

[1]University of Geneva

We propose a new general approach for chemical shift encoding based on the introduction of an additional evolution time period in heteronuclear (HSQC) and homonuclear (DQF-COSY) [1] pulse sequences. The additional evolution time period (t_1’) results in a signal splitting along F1 as a function of the difference between the corresponding signal’s resonance and the carrier’s resonance during that period. The “low-precision” chemical shift measured in the signal split combined with the ambiguous but “high-precision” chemical shift of aliased signals, [2,3] makes it possible to reconstruct full 2D spectra with high resolution in F1. [4]

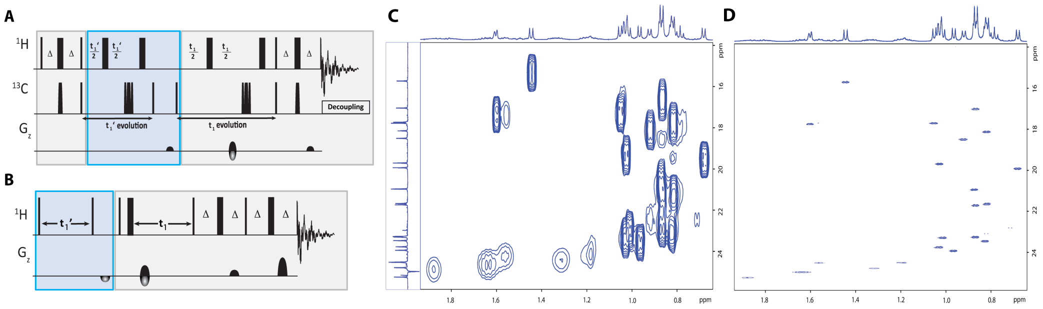

Figure 1. *HSQC (A) and DQF-COSY E/A (B) pulse sequences including the additional t_1’ evolution time to produce chemical shift dependent splitting of signals. Comparison of a normal HSQC (C) recorded with 256 time increments in 28 min, and a reconstructed spectrum (D), obtained from an experiment using the same number of increments.*

[1] Mark Rance, Ole W. Sørensen, Geoffrey Bodenhausen, Gerhard Wagner, Richard R. Ernst and Kurt Wüthrich. *Biochem. Biophys. Res. Comm*. **1983**, *117*, 479.
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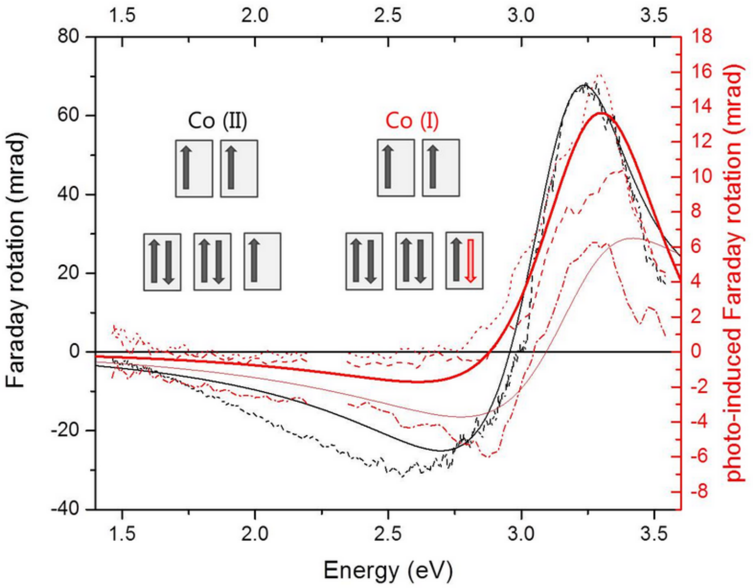
Evidence of spin state changes in homogeneous solar water splitting

S. Oh[1,2], D. Bleiner*[1], A. Borgschulte[1,2]

[1]Empa Materials & Technology, [2]University Zürich

The concept of homogenous solar water splitting follows the idea that photo-excited molecules in aqueous solution induce charge carriers. The electrons and holes, respectively, are then transferred to the water reduction and oxidation catalysts (WRC and WOC), which oxidize and reduce water to hydrogen and oxygen, respectively [1]. UV-VIS spectroscopy is an established spectroscopy to study the electronic structure of matter and its changes upon chemical reaction. The spectroscopy is thus compatible to investigate materials for solar energy harvesting, because the UV-VIS properties serve as the analytical fingerprint, and are the sought properties of the light harvesting devices as well. However, the UV-VIS properties are usually optimized for one compound (the light absorbing complex, photosensitizer, dye, or semiconductor), while the other parts should not disturb the light flux to the light harvesting part. Accordingly, these parts are difficult to detect by UV-VIS spectroscopy. To overcome this challenge, we developed a Faraday spectrometer, which is compatible to the technical setup of a light harvesting device. The magneto-optical Faraday Effect describes the change of light transmitted through a medium exposed to a magnetic field and is particularly large in molecular spin states [2]. We demonstrate the change of magneto-optical properties upon illumination of a polypyridyl-based Co-complex as WRC evidence for a change of the spin state due to electron transfer. From an analysis of the Faraday spectra we derive that the electron transfer from the dye to the WRC oxidizes the Co(II)-complex to a Co(I)-complex, which is less paramagnetic.



The figure shows the Faraday rotation spectra of a homogeneous solar water splitting system consisting of a Re-complex, a polypyridyl-based Co-complex as WRC, and ascorbic acid as sacrificial electron donor, with, and without light (plotted as difference spectra).

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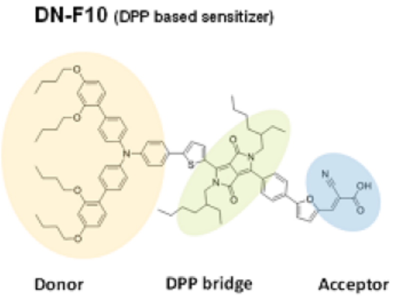
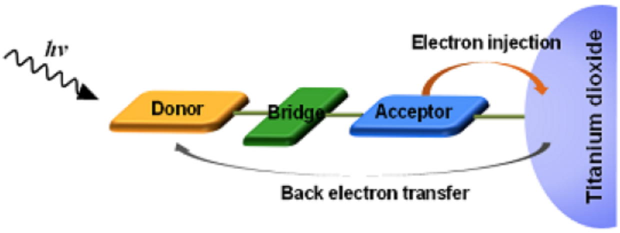
Excited state and light-induced electron injection dynamics in diketopyrrolopyrrole-based push-pull organic dye-sensitized solar cells

H.Bahng[1,1], J.-E. Moser[2]*

[1]Heewon Bahng, [2]EPF Lausanne

DN-F10 is a blue-colored push-pull dye, where the conjugated bridge between an electron donor moiety and the acceptor part is constituted by a diketopyrrolopyrrole (DPP) chromophore. This molecule is an attractive redox sensitizer for solid-state dye-sensitized solar cells (ss-DSSCs) based on mesoporous TiO_2 anodes, as it encompasses high-performance and aesthetic properties.[1] Despite its successful use in practical devices, much has still to be understood regarding the detailed mechanisms and dynamics, by which charge separate upon photoexcitation, within the molecule and across the dye-semiconductor junction. In particular, it is still unclear if the electron-hole pair is resonantly split in the excited state between the acceptor and donor moieties or the process takes place in sequential steps. Detailed investigation in this field involve the use of ultrafast transient absorption and fluorescence spectroscopies.





The complex dynamics of electronic excited states of the (D-p-A)-structured dye in solution and adsorbed on a redox-inactive metal-oxide surface, such as Al_2O_3, were scrutinized by femtosecond pump-probe laser spectroscopy. Lateral intermolecular energy- and charge transfer reactions between adsorbed molecules were evidenced. Photo-induced interfacial electron injection and charge recombination dynamics were monitored in dye-sensitized nanocrystalline TiO_2 transparent films.

Since kinetic competition between various electron transfer, charge transport, and recombination processes controls the photon-to-electron conversion efficiency in DSSCs,[2] these observations are expected to help determine the crucial factors that still limit the photovoltaic performances of organic dye-based solar cell systems and foster new, improved designs.[3]

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Ultrafast Electromodulated Absorption Spectroscopy of Perovskite Solar Cells: Investigating Charge Carrier Separation Dynamics under Externally-Applied Electric Field

A. A. Paraecattil[1], M. Bouduban[1], J. De Jonghe[1], A. Ajdarzadeh[1], J. Teuscher[1], J.-E. Moser[1]*

[1]EPF Lausanne

Record power conversion efficiencies now exceeding 22 % have been achieved with single-junction perovskite solar cells.[1] Ultrafast electromodulated differential absorption (EDA) spectroscopy was applied for the first time to methylammonium lead triiodide perovskite ($MAPbI_3$) thin films under reverse bias to unravel the mechanisms of light-induced charge separation and transport across the semiconductor. The technique consisted in monitoring optically the dynamics of the local counter electric field produced by the drift of photo-generated electrons and holes in opposite directions. Free charge carriers were produced by a femtosecond pump laser pulse, while the time-evolution of the Stark shift of the absorption spectrum of the material caused by carrier separation and ensuing screening of the externally applied electric field was probed by a delayed broadband pulse.

Studying the dynamics of photocarrier separation in an insulated, polycrystalline, vapor deposited, 300 nm-thick films of $MaPbI_3$ with EDA, we extracted an intra-grain averaged DC charge mobility value $m_{\pm}$ = 23 $cm^2\ V^{-1}\ s^{-1}$. Carrier trapping-detrapping processes at grain boundaries were observed to slow down the migration of electrons and/or holes through the entire film. A blue shift of the perovskite absorption edge caused by their eventual accumulation at insulated surfaces took place within tens of picoseconds, yielding a decreased carrier mobility m = 5 $cm^2\ V^{-1}\ s^{-1}$. [2]

The powerful EDA spectroscopy technique was also applied to state-of-the-art devices based on mixed-ions perovskites[3]. In this case, the active absorber layers were quite homogeneous and respective electron and hole mobilities $m_e \approx 22\ cm^2\ V^{-1}\ s^{-1}$ and $m_h \approx 3\ cm^2\ V^{-1}\ s^{-1}$ were calculated for drift across the entire film thickness. When the photovoltaic device is illuminated through the transparent electron-extracting electrode (SnO_2/ FTO glass) these results show that negative carriers must reach the perovskite/acceptor interface significantly faster than do holes at the opposite surface.

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Electron Transfer within $MAPbBr_3$ Perovskite Colloidal Nanoparticles

M. E. Bouduban[1], A. Burgos[1], R. Ossola[2], J.-E. Moser[1]*

[1]EPF Lausanne, [2]ETH Zurich

Unravelling the mechanisms of light-induced charge carrier generation, separation, transport, and collection in photovoltaic systems is key to the development of efficient devices. The primary step towards such an understanding is a thorough analysis of the electronic structure and properties of the active semiconducting material, yielding more targeted designs.

This is even more important in the context of hybrid lead halide perovskite solar cells : Further improvement of their power conversion efficiency and stability requires now a clearer vision of the dynamics of electron transfer occurring at heterojunctions. Indeed, the main limitation towards reaching the theoretical Schockley-Queisser efficiency limit in these perovskite systems arises from parasitic phenomena hindering charge separation and transfer at crystal grain boundaries and interfaces. The dynamics of photogenerated electron-hole pairs and those of the related interfacial phenomena, thus, need to be scrutinized to ensure further progresses.

Ideal systems for the study of such processes are nanoparticle colloidal suspensions : Colloids exhibit a large surface/ volume ratio, which creates a favorable environment for the observation of interfacial phenomena. Here, we characterized the electronic structure of methylammonium lead bromide perovskites ($MAPbBr_3$) nanoparticles as well as their interactions in solution. In addition, we investigated the kinetics of interfacial charge transfer for suspensions in chlorobenzene and two different electron donors: N,N,N',N'-tetrakis(4-methoxyphenyl)benzidine and 1,4-bis(diphenylamino)benzene.

Ultrafast transient absorption and nanosecond flash photolysis experiments have been performed, a necessary combination of techniques allowing for getting insights into the very different timescales of interest. Furthermore, Stern-Vollmer analyses and time-resolved fluorescence measurements have shed light on the nature of the donor-acceptor interaction and the long photoluminescence lifetime.

We show that the prepared nanoparticles were heterogeneous mixtures of 3D and multi-layered perovskite platelets. The latter exhibited highly efficient energy transfer towards bulk (3D) domains. Hole transfer from the valence band of the perovskite to donors at the surface was observed to take place on an unusually long timescale, which was rationalized by the particular structure of the interface.

Experimental studies of the ion-molecule reactions $H_2^+ + H_2$ and $H_2^+ + D_2$ at low collision energies with a merged beam apparatus

K. Höveler[1], P. Allmendinger[1], J. Deiglmayr[1], F. Merkt[1]*

[1]ETH Zurich

Experimental studies of ion-molecule reactions at very low temperatures are essential for the understanding of the chemical processes in interstellar clouds. The temperatures in these clouds range from 10 K to 50 K, corresponding to energies below 5 meV. So far, such low collision energies for ion-molecule reactions could not be obtained in the laboratory because of the inevitable heating of ions by space-charge effects and stray electric fields. These effects can be avoided by studying reactions involving molecules in nonpenetrating high-*n*, high-*l* Rydberg states instead of electrically charged ions. As demonstrated experimentally, the high-*n* Rydberg electron does not influence the ion-molecule reaction occuring within its extended orbit [1], but effectively shields the reaction against external fields.

We have implemented this approach in a merged beam experiment. Two neutral-gas beams are generated by pulsed supersonic expansion. The two beams initially propagate in directions seperated by an angle of 10°. Merging of the two beams is archieved by photoexcitation of the molecules of one beam to high-*n* Rydberg-Stark states followed by trapping and deflection in the inhomogeneous field of a curved chip-based surface decelerator [2]. Reactions between the positively charged ion cores of the Rydberg molecules in the deflected beam and the neutral molecules in the other beam take place in an about 3cm-long flight region. Ionic reaction products are detected in a time-of-flight mass spectrometer. The average collision energy can be controlled by de- or ac-celeration of the Rydberg molecules or by changing the temperature of the pulsed valve used to generate the neutral-reactant beam. High energy resolution is achieved by exploiting the spatial dispersion of velocity components in the neutral-reactant beam resulting from the very short opening times of a home-built valve as was already sucessfully exploited in neutral-neutral reactions [3].

The performance of this approach to study ion molecule reactions is demonstrated using the exothermic barrierless reaction $H_2^+(v^+ = 0, N^+ = 0) + H_2(v = 0, N = 0,1) \rightarrow H_3^+ + H$. This reaction is the initial step of the reaction cycles forming many molecules in the interstellar medium [4]. Collision energies as low as E/k_B = 100 mK could be reached. In this range, the observed reaction cross sections hardly deviate from classical Langevin capture model cross sections, in accord with theoretical predictions [5,6]. The reaction $H_2^+ + D_2$ provides the possibility to distinguish between charge transfer, D atom transfer, and H^+ ion transfer, and first results in this reaction system will be presented.

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Computational study onthe O_2 formation on Amorphous solid water in cold interstellarclouds

M. Pezzella[1], O.T. Unke[1], M. Meuwly[1]*

[1]Universität Basel

It is believed that pristine water can be formed and grows on the icy dust grains in interstellar clouds from hydrogen and oxygen atoms. At present, however, little is known about the mechanisms underlying water formation in and on dust grains. Two possible channels are identified in interstellar space: one involving atomic oxygen and the other through molecular oxygen (O_2) and ozone (O_3).

In all these scenarios, oxygen mobility is essential. In the present work it is shown that oxygen atom diffusion on amorphous water surfaces is possible down to low temperatures (50 K) and that recombination to form O2 is possible in cavities of the amorphous ice matrix [1]. The recombination process is studied through reactive molecular dynamics and establishes that O_2 can be stabilized by energy transfer between the energized molecule and the environment. Previous experimental studies shows that the for lower temperature quantum effects could be considered [2].

The diffusion behavior of O is studied using Monte Carlo simulations and then the time evolution is investigated using classical and quantum methods. For temperatures lower then 50 K diffusion barriers are be found between 0.3-0.9 kcal/mol. The inclusion of quantum effects for calculating the diffusion distribution show only a slight deviation from the classical simulations (2.6 %).

The formation of O_2 is then investigated inside a water cavity using Reactive Molecular Dynamics using for the bound state an interpolation of high quality potential energy curve [3]. Formation of O_2 is occurs on time scale of 100-200 ps and partial vibrational relaxation of of 20 kcal/mol is observed during 1 ns simulation.

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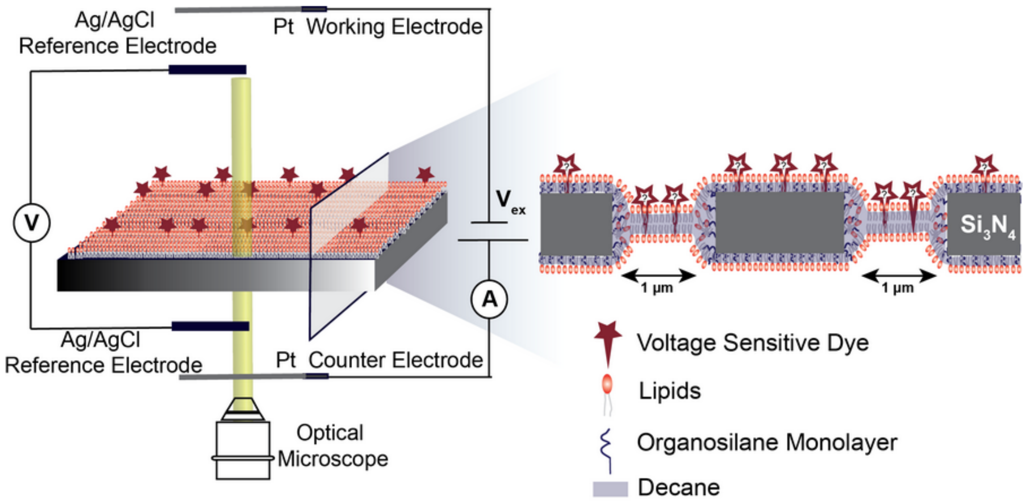
Simultaneous Optical and Electrochemical Characterization of Voltage Sensitive Dyes in Lipid Membranes

M. Tsemperouli[1], K. Sugihara[1]

[1]University of Geneva

Voltage sensitive dyes (VSDs) are powerful tools for cell membrane potential monitoring. The main characteristic of VSDs is the change in their inherent fluorescence upon membrane potential changes. The characterization of VSDs is commonly performed either directly with living cells or with vesicles where the membrane potential is established by incorporating ion selective channels. However, both characterization methods lack the possibility to precisely control the voltage sequences, thus are unable to study the kinetics of the dyes. In this work, a new approach for the mechanistic and kinetics studies of VSDs in lipid membranes is proposed. First, pores (φ = 1 µm) were fabricated in silicon nitride thin (200 nm) membranes by focused ion beam (FIB). Second, the membrane with pores was mounted in a home-made electrochemical cell where both sides of the membrane are electrically accessible. Third, free-standing lipid bilayers were formed over the pores either by preparation of black lipid membranes (BLMs) or by giant unilamellar vesicle (GUV) rupture. After the incorporation of VSDs (*e.g*. di-4-ANEPPS), the fluorescence signal from the bilayer is monitored by fluorescence microscopy while applying different voltage sequences with a four electrode system. The electrochromic dye di-4-ANEPPS appears a voltage-dependent shift in the excitation or emission spectrum where the dye is assumed to be bound to the extracellular surface of the membrane and undergo charge distribution in its excited state. The magnitude of the spectral shift is linearly related to the change in the potential. The proposed platform offers the possibility 1) to apply any voltage sequences, 2) to modify bilayer composition freely, and 3) to acquire two-dimensional mapping of the VSD activities, allowing more detailed studies of VSDs.



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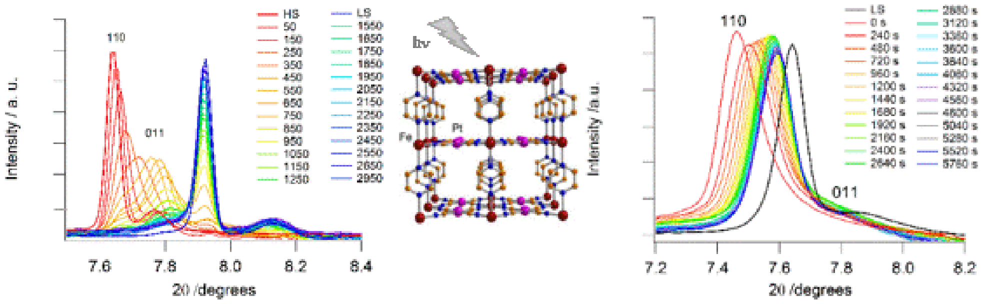
Structural investigation of the HS to LS relaxation dynamics on [Fe(pz)Pt(CN)$_4$] spin crossover nanoparticles

T. Delgado[1], A. Tissot[2], L. Guénée[1], P. Pattison[3], A. Hauser[1]*, C. Besnard[1]*

[1]University of Geneva, [2]Université de Versailles, [3]Swiss-Norwegian Beamline, ESRF, Grenoble

The investigation of the LS to HS photo-excitation and subsequent relaxation dynamics in the solid state is of particular importance for understanding the underlying physics associated with cooperative effects. In our studies Synchrotron X-Ray powder diffraction reveals a quantitative photo-induced LS-to-HS conversion based on Light-Induced Excited Spin State Trapping at 10 K on microcrystalline and nanocrystalline powders of [Fe(pz)Pt(CN)$_4$]·xH$_2$O (pz = pyrazine) [1]. Time-resolved measurements evidence that the HS-to-LS relaxation depends on the particle size. For 1.3 µm particles, the relaxation proceeds by a two steps mechanism: a random HS to LS conversion at the beginning of the relaxation followed by a nucleation-growth process. When reducing the size to 50 nm no nucleation is observed due to the lower rigidity of the lattice with respect to the bulk material which prevent the cooperativity between centers through long range interactions. In order to better understand the limit size above which long-range interactions become more important intermediate particles sizes have been analysed. In the case of 400 nm particles the relaxation proceeds mainly though a random distribution with correlations only appearing towards the end whereas in the case of 140nm particles only a random distribution is observed. The relaxation rates of all the samples depends thus on the size, that’s say, on the mechanism they follow and on the way they interact with the surrounding medium.



Time evolution of the (110) and the (011) diffraction peaks during the photo-induced HS→LS relaxation of 1.3 µm (left) and 50 nm particles (right)

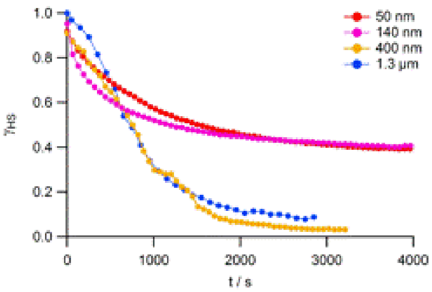


Figure 2. Comparison of the HS fraction relaxation curves at 15 K of the different sample sizes after photoexcitation with 532 nm laser during LIESST experiment.

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Solvent Suppression in DNP-Enhanced Solid State NMR

J. Yarava[1], S. R. Chaudhari[2], A. Rossini[3], A. Lesage[2], L. Emsley[1]*

[1]Institut des Sciences et Ingènierie Chimiques, Ecole Polytechnique Fèdèrale de Lausanne , [2] Universitè de Lyon, Institut des Sciencse Analytiques, Centre de RMN à très hauts champs (CRMN/ENS Lyon/UCB Lyon1), Villeurbanne, France, [3]Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Solid state NMR is a powerful analytical tool for the characterization of structure and dynamics of a broad range of chemical and biological materials. However, the intrinsic low sensitivity of NMR limits many applications. Dynamic nuclear polarization (DNP), in which large electron polarization can be transferred to nuclear spins under the effect of microwave irradiation, allows a sensitivity gain of two orders of magnitude and is currently revolutionizing the field. However, unpaired electrons are usually introduced to the sample in the form of stable organic radicals in a bulk solution that is used either to impregante the system under investigation or to dissolved the target analyte. In both cases this results in a large solvent signal that can potentially obscure both proton and carbon-13 spectra.

Here we show how the solvent resonances can be efficiently suppressed in either frozen solutions or in impregnated solids. This can be achieved by (i) exploiting the short relaxation times of the solvent compared to longer relaxation times of impregnated solids, or (ii) by using short cross-polarization contact times to transfer hyperpolarization to only directly bonded carbon-13 nuclei in frozen solutions. Finally, we show how this allows for the acquisition of high-resolution proton-proton correlation experiments without interference from the solvent signals.

On the formation of H_2^+ by radiative recombination

L. Möller[1], M. Beyer[1], F. Merkt[1]*

[1]ETH Zurich

Recently shape resonances of the $X^+\ ^2\Sigma_g^+$ ground electronic state of H_2^+ have been observed [1]. These shape resonances represent a possible pathway for the recombination reaction $H^+ + H(1s) \rightarrow (H_2^+)^* \rightarrow H_2^+(v^+,N^+)$. Electric-dipole-allowed transitions connect the $^2\Sigma_g^+$ shape resonances to the $A^+\ ^2\Sigma_u^+$ state. However, only bound levels with $N^+ \leq 2$ exist in the A^+ state and the lowest-N^+ shape resonance has $N^+=4$, which precludes electric-dipole transitions because of angular-momentum selection rules. For this reason, it is generally assumed that the radiative recombination takes place through electric-dipole transitions connecting the A^+ continuum to the rovibrational bound levels of the X^+ state [2,3,4].

We discovered that electric-quadrupole transitions connecting the $X^+\ ^2\Sigma_g^+$ shape resonances to bound X^+ levels represent an alternative mechanism by which H_2^+ can be formed. We present a complete theoretical model of these electric-quadrupole recombinations and calculations of the thermal recombination rate as a function of the temperature. We discuss the astrophysical implications of our results.

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NMR Studies of Hierarchical Protein Dynamics

B. Busi[1], J. Yarava[1], A. Hofstetter[1], M. Blackledge[2], L. D. Emsley[1]*

[1]Ecole Polytechnique Federale De Lausanne, EPFL, [2]Université Grenoble Alpes, Institut de Biologie Structurale (IBS)

A fundamental challenge in biology is to understand the complex interaction between protein motion and protein function. Recently, Lewandowski and coworkers have shown that temperature dependent magic angle spinning multinuclear solid state NMR relaxation measurements at temperatures ranging from 105 to 280K can provide a window into the hierarchy of dynamic processes in prioteins.[1] Since it is likely that the quantitative description of motions reporting on different components of the system are dependent on a well-controlled experimental conditions, here we evaluate the reproducibility of such measurements, and extend the measurements to additional probes and to other magnetic fields.

We measured at 11.7T (500 MHz) the same set of thirteen different NMR observables as the previous study twice for each of nineteen different temperatures in the range from 105 to 280 K in the fully hydrated crystalline protein GB1 (^{1}H,^{13}C,^{15}N). Our measurements are interpreted using the same analysis as previously and we find excellent reproducibility between the three measurements. We have also recorded data sets at 9.4 and 18.8 T.

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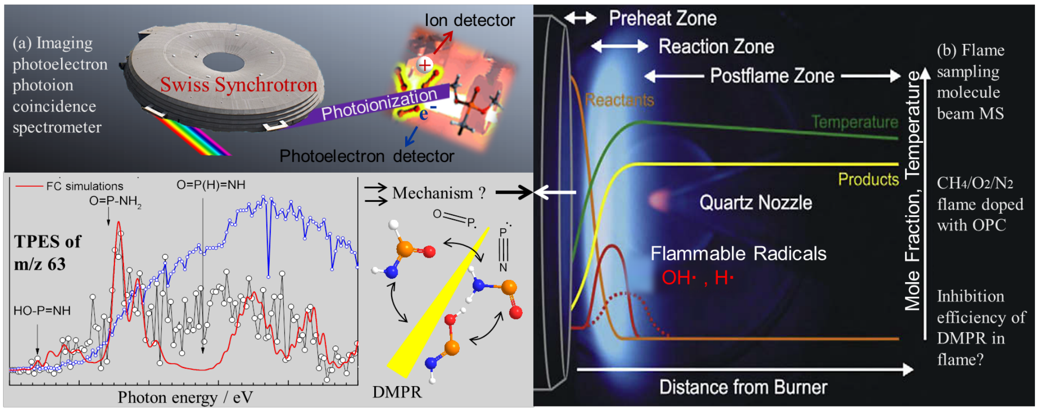
Complex thermolysis mechanism of phosphoramidate: Formation of PN based gas phase active phosphorus species

S. Liang[1,5], P. Hemberger[2], J. Levalois-Grützmacher[3], O. Korobeinichev[4], H. Grützmacher[3]*, S. Gaan[6]*

[1]ETH Zürich, [2]Paul Scherrer Institute, Villigen, [3]ETH Zurich, [4]Siberian Branch Russian Academy of Sciences Russia, [5]Empa, [6]EMPA St. Gallen

P-N containing organophosphorus compounds have received increasing attention in different domains, such as biology, catalysis and in particular as flame retardant additives [1]. However, due to the complexity of the flame chemistry and the lack of proper analytical technique allowing for simultaneous snapshots of the thermolysis process under different conditions, their corresponding inhibition mechanism in the flame still remains open. This study aims to make a valuable contribution towards a better understanding of decomposition mechanism of the yet unstudied phosphoramidate category and thereby provides a foundation for the targeted design of new molecules. Taking advantage of the tunability of VUV synchrotron radiation, the thermolysis process of dimethyl phosphoramidate was elucidated by imaging photoelectron photoion coincidence (iPEPICO) spectroscopy, which allows for isomer-resolved species identification, by recording temperature dependent mass spectra as well as threshold photoelectron spectra (TPES) for each relevant species (Fig. 1 (a)). To correlate the probed decomposition mechanism of DMPR with the corresponding inhibition efficiency under fire conditions, we performed further experiments with a laminar premixed methane-air flame, in which the formation of H and OH responsible for maintaining flames was monitored using a molecular beam mass spectrometry (MBMS, Fig. 1 (b)) [2].



Based on these synchrotron experiments, a number of species such as methanimine, ethylene and different phosphoryl species were unequivocally identified, including the commonly known PO, OPOH [3] as well as the yet unknown species PN. More interestingly, the signal intensity in the MS proves a significant preference on PN formation than other phosphoryl species. Different computational chemistry approaches have been applied to develop a comprehensive reaction mechanism, while the most dominant pathways will be presented and discussed. Besides, by further investigating the efficiency of radical inhibition in flame sampling MBMS experiments, the promising roles of PN in poisoning the flame will be addressed.

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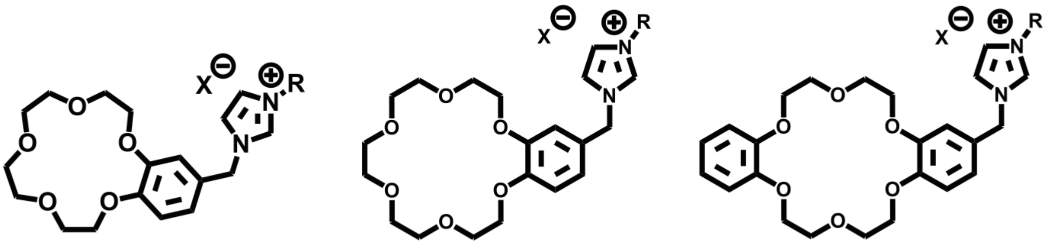
Ionic Liquids based on Crown Ethers as electrolytes for batteries

H. Yao[1], K. M. Fromm[1]*

[1]University of Fribourg

Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and that are usually composed of an asymmetrical organic cation and a large charge-delocalized anion which is poorly coordinated. They are non-flammable, and thermally as well as electrochemically stable. These properties make them very interesting for many applications including green solvents for synthesis, catalysis, and electrolytes for ionic and electronic devices[1]. Crown ethers are able to strongly interact with alkali metal cations (Li+, Na+, K+) and have been used as additives in battery electrolytes in order to increase the ionic conductivity of the latter and to prevent electrolyte decomposition[2-3]. However, few studies have been done on crown ethers in the field of electrolytes.



R= C_nH_{2n+1}, n=1-6 ;X^-= PF_6^-, BF_4^-, $CF_3SO_3^-$, $^-N(CF_3SO_2)_2$

Figure 1: New Ionic liquids based on crown ether building blocks

This is why we propose to integrate them covalently as an alkali cation carrier[4-5] in the ionic liquid system. The aim of the project is thus to design and synthesize new Room Temperature Ionic Liquids (RTILs) based on crown ether moieties, to investigate their properties (flammability, thermal and electrochemical stability, conductivity, Li/Na-ion diffusion) and then to use them as electrolytes for rechargeable batteries. We will present their synthesis, structures and properties in this contribution.

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Time-resolved THz spectroscopy of Rhenium complex solvation in water.

S. N. Ahmed[1], A. Shalit[1], P. Hamm[1]*

[1]University of Zurich

The solvation dynamics of photoexcited water-soluble Rhenium complex $[Re^{I}(py)(CO)^{3}bipy]^{+}$ is investigated by means of ultrafast near-UV pump, THz probe spectroscopy. Excited electronic state of Rhenium complex created by near-UV excitation (400nm) has a dipole moment which differs significantly from that in the ground state [1]. The dynamics of low frequency modes of water interacting with a dipole configuration of the excited Rhenium complex is probed by THz pulse. Figure 1 shows the pump-induced changes in the amplitude of THz pulse transmitted through 1 mM solution of Rhenium complex in water. The data shows how the excitation affects the surrounding water molecules which solvate a photo-excited Re-complex within few picosecond. Such a time scale is consistent with typical dielectric relaxation time of 8 ps obtained for a bulk water [2].

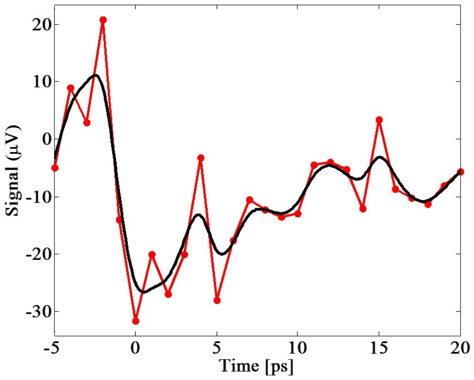

Fig.1 Pump-probe signal (red) obtained for a 1 mM solution of Rhenium complex in water. No signal was observed in the absence of complex.

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Evaluating the magneto-crystalline anisotropy constant of (SPIONs) systems

J.C. Martinez Garcia[1], F. Crippa[1], C. A. Monier[1], A. M. Hirt[2], A. P. Fink[1], M. Lattuada[1]

[1]Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland, [2]Institute of Geophysics, ETH Zürich, Sonneggstrasse 5, 8092 Zürich, Switzerland

Magnetic hyperthermia (MH) is a promising technique in cancer treatment because it causes less damage than chemotherapy or radiotherapy. Active research is being done to improve the specific adsorption rate (SAR), i.e., the amount of heat released per unit mass of MNPs, which could permit the treatment of tumors of small size [1]. The specific absorption rate is extremely sensible to the change of the magneto-crystalline anisotropy constant (K_V) which is so far for the case of magnetic nanoparticles assumed as an independent temperature parameter. By applying a model free route approach [2,3] we have determined K_V in superparamagnetic iron-oxide-magnetic-nanoparticles (SPIONs) systems directly from the magnetic susceptibility data. We found a strong dependence between K_V and T as well as a strong discrepancy with the assumed universal value of infinity relaxation time.Our results show a new way to estimate the specific adsorption rate (SAR) directly from the magnetic susceptibility data without any model assumption. This can have a direct impact to evaluate the magnetic hyperthermia in a more assertive way [4].

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Interrogating Weakly Bound Complexes by Velocity Map Imaging Photoelectron Photoion Coincidence

A. Bödi[1]

[1]Paul Scherrer Institut

Summary: Internal energy selection makes photoelectron photoion coincidence (PEPICO) a versatile tool to study unimolecular reaction mechanisms and energetics. When applied to hydrogen bound complexes, unfavorable Franck–Condon factors at the ionization energy and the multicomponent nature of the sample make data analysis challenging. In such cases, photoion velocity map imaging (VMI) contributes significantly to tracing the reactive flux, as will be shown in mixed water–acetic acid adducts. Thanks to its sensitivity, PEPICO has revealed a new, C–C bond formation pathway in methanol dimers, as well.

When monochromatic vacuum ultraviolet radiation ionizes isolated neutral species, only photoelectrons may remove energy from the parent ion, and internal energy selection can be achieved by electron kinetic energy analysis. Time-of-flight analysis of the coincident parent and fragment ions as a function of photon energy has so far yielded hundreds of accurate dissociative photoionization thresholds in covalent molecules. These can be used in thermochemical cycles to derive new energetics and thermochemical quantities.

Negligible Franck–Condon factors close above the ionization energy are the first obstacle to studying energetics in weakly bound species by PEPICO. In the energy range the nuclear wave function overlap allows for ionization, the clusters may already have enough excess energy to fragment. This is very often the case in H-bonded species that also exhibit intriguing intracluster reactions. Nevertheless, intact dimers are sometimes seen, and, as will be shown for the water dimer, appearance energies have the potential to yield very accurate experimental proton affinities, too. Methanol dimer cations have been studied multiple times, but the water-loss channel, yielding ethanol or perhaps dimethyl ether cations, has never been observed before. Thanks to internal energy selection, minor but interesting reaction paths can be studied quantitatively. This also puts ab initio potential energy surfaces to the test.

Unfortunately, neutral cluster sources are rarely monodisperse. Clusters of different size often yield the same fragments, which complicates signal apportioning and constitutes the second main limitation. As will be shown in the case of mixed water–acetic acid clusters, velocity map imaging photoions in double imaging coincidence experiments offers a way to tell translationally cold parent species apart from the products of fragmentation processes, as only the latter are subject to kinetic energy release. The energy correlation map between the total energy and the photoion kinetic energy can be obtained by the simultaneous reconstruction of coincidence double imaging data. Our novel approach hinges on the separation of the near-orthogonal kinetic energy distribution and angular anisotropies in the VMI projection.

Halide Free $M(BH_4)_2$ (M= Sr, Ba and Eu): Single Route Synthesis

M. Sharma[1], L. Daku[1], R. Černý[1], H. Hagemann[1]

[1]University of Geneva

Borohydrides have attained high interest in last few years due to their high volumetric and hydrogen content. Synthesis of di-tri metallic borohydride is a way to alter the thermodynamics of hydrogen release from borohydrides. Presence of halide ions in borohydrides change their physical and chemical properties. Halide free monometalic borohydrides may be used as precursors for synthesizing di or tri metallic borohydrides. In this paper we present a way to synthesize halide free alkaline earth metal (Sr, Ba) and Europium borohydride starting with respective hydrides as precursors.

Mechanism of the cooperativity in antimicrobial peptides

E.B. Drab[1], K. Sugihara[1]

[1]Department of Physical Chemistry, Univeristy of Geneva, Geneva, Switzerland

In this study we aim to elucidate the fundamental mode of action of antimicrobial cooperativity. To investigate the cooperativity between two different human peptides defensin and cathelicidin we synthesized artificial lipid bilayer onto highly doped p-type silicon electrode covered by naturally formed silicon dioxide as a clean platform to separate peptide-peptide and peptides-bilayer interactions from influence of other components within cell. Lipid bilayer was obtained by fusion of unilamellar vesicles from buffer solution and investigated mainly by impedance spectroscopy which is non-destructive and sensitive technique. In addition we performed Fluorescence Recovery After Photobleaching measurements as a complementary technique to confirm the bilayer formation by its recovery in photobleached region.

Next step in our investigation is to inject peptides and elucidate how they influence on the lipid bilayer and moreover what is the mechanism of cooperativity of two different peptides. The change in the resistance and the capacitancence will be studied at different peptide concentrations.

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Time-resolved X-ray absorption spectroscopy indicates a new photodissociation mechanism of dissolved CBr_4

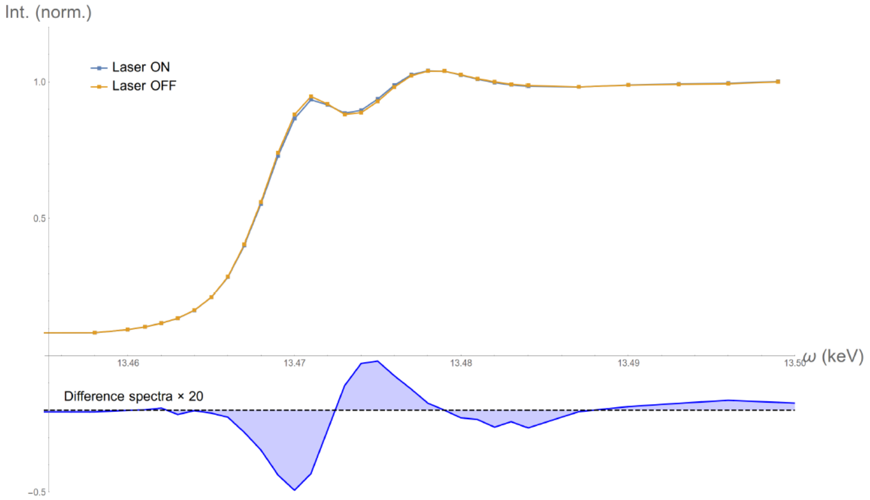
R. Bohinc[1], A. Schneider[1], G. Smolentsev[2], M. Nachtegaal[2], J. A. van Bokhoven[4]*

[1]Paul Scherrer Institute, [2]Paul Scherrer Institute, Villigen, [3]ETH Zurich, [4]ETH Zurich/PSI Villigen

Commercial catalytic reactions can be improved by optimizing the slowest reaction step in the catalytic cycle. Nucleophilic substitution, in which one bond is broken and another bond is created, often represents the rate determining reaction step, as for instance in the Monsanto process in which acetic acid is synthesized from carbon monoxide and methanol. Understanding the initial carbon-halogen bond breakage of halogenated methanes in such reactions is therefore of utmost importance.

Photodissociation of dissolved CBr_4- a prototype bond breaking reaction - has been extensively investigated innumerous time-resolved studies. As the reaction mechanisms involves several intermediates and final products, the identification of individual species represents a challenging problem. In particular, previous studies have shownsomewhat contradictory results regarding the formation of final products [1, 2]. In order to elucidate the dissociation mechanism of dissolved CBr_4 on the ns - µs time scale, associated with the formation of final states,we have performed time-resolved X-ray absorption spectroscopy (XAS) measurements. Because XAS is only sensitive to the specific element probed and consequently to its chemical environment, it is often the preferred method for determining reaction mechanisms of photo-initiated chemical reactions [3].

In our study we have found that Br_2, formed ns after the UV excitation, is not stable in the solvent (methanol) and reacts within the first 1 µs upon photodissociation of CBr_4. On the other hand C_2Br_6, previously considered to be an intermediate decaying into Br_2 and C_2Br_4 [2], is found to be the final decay product. These findings are well supported by our ab initio DFT calculations which also indicate that other decay products are likely to contain HBr and CH_3Br in agreement with other studies [4]. Finally, we have extracted recombination rate constants from the experimental data and with this the missing ns - µs part of CBr_4photodissociation kinetics.



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Reaction-detected infrared spectroscopy of state-selected molecular ions

U. Jacovella[1], J.-A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]ETH Zurich

First results are presented obtained using an experimental setup developed to record IR spectra of rotationally state-selected ions. The method we use is a state-selective version of a method developed by S. Schlemmer, D. Gerlich and coworkers (Int. J. Mass. Spec. **185**, 589 (1999); J. Chem. Phys. **117**, 2068 (2002)) to record IR spectra of ions.

Ions are produced in specific rotational levels using mass-analysed threshold ionisation spectroscopy combined with single-photon excitation of neutral molecules in supersonic expansions with a vacuum-ultraviolet laser. The ions generated by pulsed-field ionisation of Rydberg states of high principal quantum number ($n \approx 200$) are extracted toward an octupole ion guide containing a neutral target gas. Prior to entering the octupole the ions are excited by an IR laser. The target gas is chosen so that only excited ions react to form product ions. These product ions are detected mass selectively as function of the IR laser wavenumber.

To illustrate this method, we present IR spectra of $C_2H_2^+$ in selected rotational levels of the $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ spin-orbit components of the electronic ground state.

From non-relativistic pre-Born-Oppenheimer theory to molecular structure

A. Muolo[1], M. Reiher[1]

[1]ETH Zurich

The central paradigm of present day theoretical and computational chemistry consists in treating the nuclei as distinguishable particles in the Born and Oppenheimer (BO) approximation[1], as they define a framework geometry unambiguously even if formally dentical. Electrons, however, are described by an antisymmetric wavefunction, as it is appropriate for indistinguishable fermions. There are no doubts that the BO approximation can be considered as the backbone of modern quantum chemistry but, although it proved to be satisfactory for many purposes, the fundamental questions about the very concept of molecular structure for an isolated molecule prevals.[2] Essentially there are no reasons to believe that the probabilities for all possible nuclear configurations are the same and maxima of radial and angular densities may be taken as an indication for some underlying structure.[3] However, when nuclear permutation symmetry is not ignored, the undistinguishability of nuclei becomes the main obstacle toward the reconstruction of the classical structure.[4,5] While trying to translate those traditional chemical notions, such as molecular structure, chirality and isomerism, into the formalism of quantum mechanics, calculations in the pre-BO regime also provide highly accurate energy levels[6,7] that contribute to a deeper understanding of different phenomena in molecular physics.

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Towards hybrid trapping of cold molecules and cold molecular ions

D. Haas[1], C. von Planta[1], D. Zhang[1], S. Willitsch[1]*

[1]University of Basel

Hybrid systems of cold atoms and ions have been studied intensively in recent years. The simultaneous trapping of atoms with ions has opened up new possibilities for the investigation of interactions between the two species and has greatly contributed to the understanding of collisional and chemical processes at low temperatures [1].

Here, we report on the development of an advanced hybrid trapping technique which aims at trapping neutral molecules and molecular ions simultaneously. A translationally cold package of neutral molecules is produced by means of Stark deceleration. This deceleration technique exploits the Stark effect experienced by polar molecules in switched inhomogeneous electric fields, thereby producing a molecular package at translational temperatures T_{trans} › 1 mK [2]. During the last deceleration stage, the molecular package is loaded into a magnetic trap, which is incorporated into an RF ion trap. With this set-up, the superposition of cold neutral molecules with molecular ions allows for quantum-state selective investigations of elastic, inelastic and reactive collisions at low translational energies. Initial experiments will focus on $OH + Ca^+$, $OH + N_2^+$ and $OH + H_2O^+$ as collision systems.

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State-to-state scattering of methane from Ni(111) and epitaxial graphene on Ni(111)

M. van Reijzen[1], J. Werdecker[1], R. Beck[1]*

[1]EPF Lausanne

In recent years the dissociation reaction of CH_4 on Ni(111) has been studied extensively both by quantum state resolved experiments and by first principles theory.[1-4] In these dissociation studies, it was observed that typically a large fraction of the incident methane molecules does not dissociate but scatters from the surface even if their incident energy is significantly above the minimum barrier of ~0.8 eV.

Such inefficient dissociation can be explained either by a very narrow transition state, requiring a specific deformation of the reactant, or by fast vibrational energy transfer between the incident reactant and the metal surface through electron-hole pair excitation in the metal which competes with the dissociation reaction. Efficient vibrational energy transfer in gas/surface collisions has been reported for NO and HCl on Au(111)[5, 6] but has never been investigated for collisions of methane with transition metal surfaces .

To study ro-vibrational energy transfer in methane/surface collisions, we have developed a state-to-state molecular beam/surface scattering machine. The experiments use infrared laser excitation to prepare methane incident on a Ni(111) surface sample in a specific rovibrationally excited quantum state and probes the quantum state distribution of the scattered molecules by a cryogenic bolometer detector in combination with infrared laser tagging.

Using this setup, we have prepared incident methane with one quantum of antisymmetric C-H stretch vibration $CH_4(\nu_3)$ and measured the rovibration state distributions of the scattered molecules. We detect both vibrationally elastic and inelastic scattering of CH_4 and quantify the probabilities for the different channels. Efficient vibrational energy transfer is observed for incident $CH_4(\nu_3)$ leading to scattered $CH_4(\nu_1)$ and CH_4 (v=0).

Through chemical vapor deposition of hydrocarbons, a well ordered monolayer of carbon (graphene) can be grown on the Ni(111) surface. Scattering of a state prepared beam of $CH_4(\nu_3)$ from this C/Ni(111) surface shows a distinctly different scattering probability for both vibrationally elastic and inelastic scattering than for the clean Ni(111) surface. These new results, as well as the developed method, will be discussed.

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Study of the $N(^4S)+NO(^2\Pi)$ reactive collision at extreme temperatures relevant to the hypersonic flight regime.

O. Denis-Alpizar[1], R. Bemish[2], M. Meuwly[1]*

[1]University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, [2]Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, New Mexico 87117, USA

The NO molecule plays a major role in the chemistry near the surface of vehicles for atmospheric re-entry in the hypersonic flight regime. Therefore, the reactions of this system with the most common atmospheric gases, e.g. N and O, must be considered in the design of spacecraft. At the extremely high temperature typical of this regime, the experiments are difficult and expensive. Consequently, the theoretical studies became vital for the correct comprehension of the energy transfer of such molecular collisions. This work focuses on the study of the $N(^4S)+NO(^2\Pi)$ reaction using classical and quantum methods to describe the nuclear dynamics, which occur entirely in the triplet manifold. Most studies of the dynamics of this collision [1,2] have used the $^3A'$ and $^3A''$ potential energy surfaces (PESs) computed at the CASPT2 level [3]. Only very recently, new $^3A'$ and $^3A''$ PESs have been presented at the MRCI level [4]. However, these surfaces only could be used for the reverse $N_2(^1\Sigma)+O(^3P) \rightarrow N(^4S)+NO(^2\Pi)$ channel because they do not have the correct long-range behavior. Here, we develop PESs for the two lowest triplet states at the MRCI+Q level, where the correct R^{-6} asymptotic behavior is taking into account in the fitting procedure. Quasi-classical trajectory calculations have been carried out for the $N(^4S)+NO(^2\Pi)$ reaction using both PESs. Then thermal rate coefficients are determined in the 100-20000 K temperature range. Furthermore, time-independent quantum reactive scattering calculations were performed. The probabilities of reaction at several energies are reported. Finally, the results using both, classical and quantum methods, are compared.

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Spectroscopic separation of ^{13}C NMR spectra of complex isomeric mixtures by the CSSF-TOCSY-INEPT experiment

A. Moreno[1], H. Sommer[2]

[1]Bruker BioSpin AG, [2]Firmenich SA

Among the most critical parameters for NMR experiments are spectrometer stability and sensitivity. The spectrometer hardware for optimal results will depend strongly on the application used. The presentation will cover probe choice and probe design for high resolution NMR applications. The impact of the sensitivity gain by CryoProbes[1] for ^{13}C detection will be illustrated with an example of a complex mixture analysis using the CSSF-TOCSY-INEPT experiment[2].

This experiment uses the resolving power of a chemical shift selective filter (CSSF) to separate strongly overlapped ^{1}H NMR signals in complex mixtures. The selectivity of the CSSF is then amplified via magnetization transfer from the excited proton(s) to all other protons within the same coupling network during TOCSY isotropic mixing. Subsequent refocused INEPT transfer from proton to carbon spins allows then the acquisition of proton-decoupled ^{13}C sub-spectra.

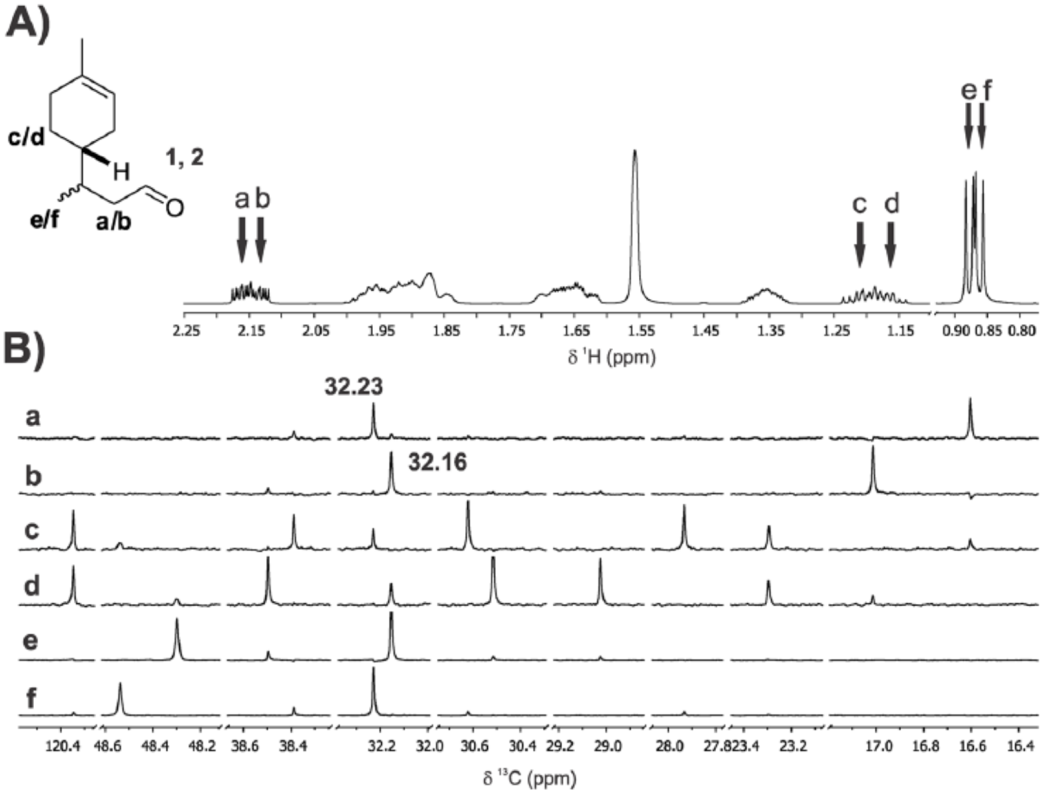

Figure: Spectroscopic separation of a 1:1 mixture of diastereomers **1** and **2** (~360mM each). (A) Selection of ^{1}H chemical shifts for selective excitation. (B) CSSF-TOCSY-INEPT experiments with ^{1}H selective excitation of a–f generate six ^{13}C NMR sub-spectra.

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Ultrafast spectroscopy as a tool to investigate the microstructure of donor-acceptor blends for organic photovoltaics

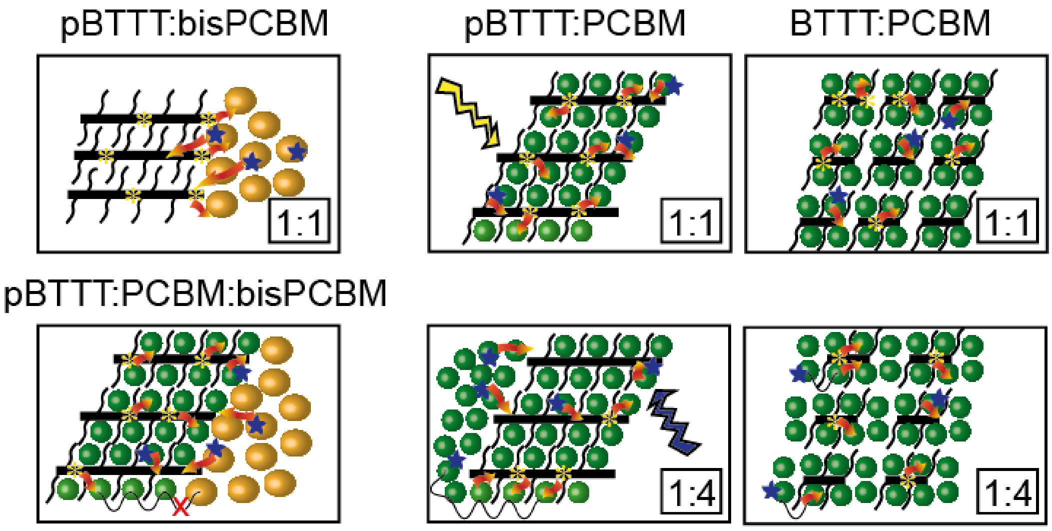
M. Causa, E. Buchaca-Domingo[1], B. P. Cherniawski[2], M. Heeney[1], A. L. Briseno[2], N. Stingelin[1], N. Banerji[3]*

[1]Imperial College London, [2]University of Massachusetts, [3]University of Fribourg

The active layer of organic solar cells consists of blends of an electron donor and an electron acceptor, known as the bulk heterojunction (BHJ). Understanding he phase morphology, i.e. the co-existence of an intermixed donor-acceptor phase with neat donor and neat acceptor domains, is important in view of its significant impact on the photovoltaic performance. In this respect, results from time-resolved spectroscopy do not only allow following charge transfer dynamics between the donor and the acceptor and the charge generation process, but, additionally, they provide information on the BHJ microstructure, which is necessary to optimise organic solar cells.

We have monitored ultrafast processes at the interface between the donor component (poly- and oligothiophene derivatives, pBTTT and BTTT respectively) and a range of fullerene acceptors (PCBM, bisPCBM and ICBA), which are different with respect to size, conjugation and electron accepting properties. Moreover, different fullerene concentrations in the blends (D:A ratio of 1:1 or 1:4 by weight) and combinations of two fullerene units with the donor in ternary systems have been investigated, in order to further address the effect of donor-acceptor phase separation.

Femtosecond transient absorption data demonstrates distinct spectral features and evolutions for the different blends, which we correlate to the diverse phase morphologies of each system. Our observations highlight how alternative acceptors and, in particular blend composition, have a specific impact on the miscibility of the acceptor with the donor and on the tendency to form fullerene domains that act as energetic sinks. The latter favours the spatial charge separation of photo-generated electron-hole pairs, playing a key role during the charge generation and collection processes.



Surface-Enhanced 2D Attenuated Total Reflectance IR Spectroscopy for Studying Surface-Sensitive Ultrafast Vibrational Dynamics

J. Kraack[1], P. Hamm[2]

[1]University of Zürich, [2]University of Zurich

Dynamics and structures of molecules at solid-liquid interfaces are of significant importance in chemistry and physics. To study ultrafast vibrational properties of samples near solid-liquid interfaces, we recently developed two-dimensional attenuated total reflectance infrared spectroscopy (2D ATR IR)[1-4]. 2D ATR IR spectroscopy is a third-order nonlinear method which employs short-range (sub-µm) evanescent fields at reflecting planes of an ATR crystal, guaranteeing maximum light intensity at the interface and the well-known surface-sensitivity of the ATR technique. We focus on the two most recent major developments of 2D ATR IR. Firstly, we use ultrathin (~nm) noble metal layers to immobilize molecules at the ATR interface and to enhance the weak nonlinear signals[3] from sub-monolayer surface coverages[2]. Using polarization-dependent 2D ATR IR signals, we clarify the mechanisms of signal enhancement and evaluate contributions from electromagnetic and chemical contributions[3]. We demonstrate that s-polarization (solid lines, Fig. 1 (a)) optimally enhances 2D ATR IR signals from voids between metal nanoparticles (NPs, Fig. 1 (b) – (c)), while p-polarization (dashed lines, Fig. 1 (a)) enhances signals from outside the voids with different degrees of enhancement. Secondly, we report on a combination of 2D ATR IR spectroscopy with spectroelectrochemistry (SEC), using the ultrathin conductive layers at the ATR interface as electrodes [4]. We outline experimental key-points in the development of 2D ATR IR SEC and use vibrational Stark-shift spectroscopy of carbon monoxide (CO) adsorbed to platinum (Pt) NPs to demonstrate the electrochemical performance of the electrode surfaces (Fig. 1 (d) – (g)). Furthermore, we characterize potential-dependent ultrafast vibrational relaxation as well as spectral diffusion of surface-bound CO (Fig. 1 (h)).

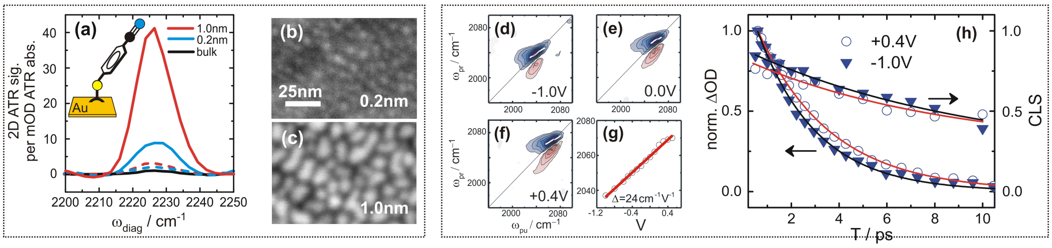


Figure 1. (a) – (c) Characterization of surface-enhancement mechanisms with diagonal 2D ATR IR signals (a) and electron-microscopy analysis (b) – (c) of different surfaces from Gold NPs. (d) – (f) 2D ATR IR SEC signals of CO adsorbed ot Pt NPs at different electrode potentials. (g) Ground-state bleach vibrational Stark-shoft signals of CO. (h) Potential-dependent vibrational relaxation (left scale) and spectral diffusion (CLS, right scale) of surfacebound CO. In (g) and (h), open symbols are experimental data, solid lines represent linear- or exponential fits.

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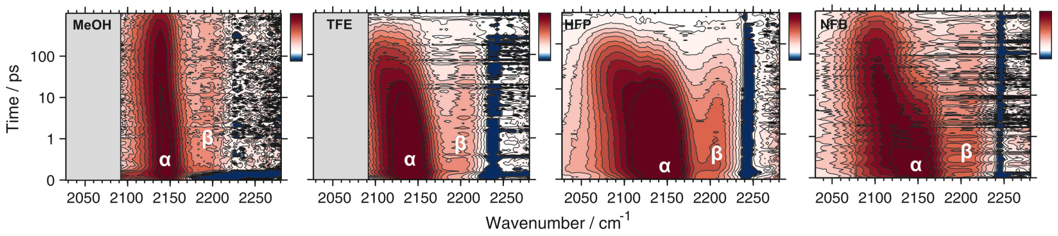
Direct visualization of excited-state symmetry breaking by ultrafast time-resolved infrared spectroscopy

B. Dereka[1], A. Rosspeintner[1], E. Vauthey[1]*

[1]University of Geneva

An overwhelming majority of quadrupolar and octupolar charge-transfer molecules designed for various two-photon absorption applications behave in the electronic excited state as if they were dipolar although they demonstrate the expected multipolar character in the ground state. We show that femtosecond time-resolved infrared spectroscopy spectacularly reveals symmetry breaking occurring in the excited state. This breaking leads to a rapid transformation from an initially prepared quadrupolar excited state with evenly distributed electronic excitation to a symmetry-broken state where the density of electronic excitation is different in the identical branches of the molecule. This transformation is driven by the solvent fluctuations and the rearrangement of the polar environment during the solvation of excited chromophore. We demonstrate that in highly polar solvents the process proceeds even further causing the complete localization of the electronic excitation on a single branch of the molecule. TRIR unveils the disparate spectral signatures of symmetrical, symmetry-broken and localized states and provides an unprecedented accuracy in following its dynamics. This effect is general and originates from non-specific interaction with the solvent molecules. However, we demonstrate that specific hydrogen-bonding interactions with the solvent can be utilized to enhance it even further. The dynamics of these interactions is slower than of non-specific ones and it provides an easier way to follow this process in real time. When H-bonding to the solvent is very strong it can cause the reactivity of the different identical branches within a single molecule to be vastly different. This provides means of controlling the photochemical reactivity at the different sites of the same molecule.



TRIR contour maps of the quadrupolar probe molecule in H-bonding solvents (MeOH - methanol, TFE - trifluoroethanol, HFP - hexafluoroisopropanol, NFB - nonafluorotert-butanol). Band designations are shown for early pump-probe delays. Symmetry-breaking enhancement as well as formation of stoichiometrically bound H-bonded complex are clearly seen.

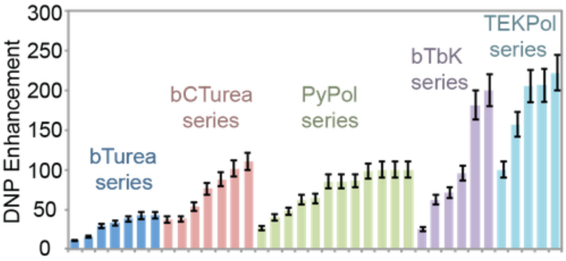
Rational Design of Nitroxide Biradicals for Efficient Cross-Effect Dynamic Nuclear Polarization

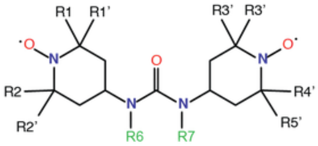
D. J. Kubicki[1], G. Casano, S. Abel, C. Sauvée, K. Ganesan[2], M. Schwarzwälder[2], M. Yulikov[3], A. Rossini[1], G. Jeschke[3], C. Copéret[3], A. Lesage[4], P. Tordo[2], O. Ouari[2]*, L. Emsley[1]*

[1]Ecole polytechnique fédérale de Lausanne, [2]Institut de Chimie Radicalaire, Aix-Marseille Université / CNRS, [3]ETH Zurich, [4]Centre de RMN à très hauts champs

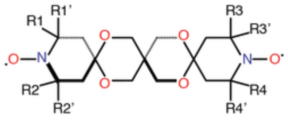
Dynamic nuclear polarization (DNP)[1-3] currently attracts considerable attention as one of the most efficient methods to increase the sensitivity of NMR experiments.

In particular, it can boost the sensitivity of magic-angle spinning (MAS) solid-state NMR experiments at low temperatures by several orders of magnitude.[4] Typically, the samples are dissolved or impregnated with a solution of stable biradicals, acting as polarizing agents capable of transferring the electron hyperpolarization through the cross-effect. Here, a series of 41 bi-nitroxide radicals has been prepared and their performance studied as polarizing agents in cross-effect DNP NMR experiments at 9.4 T and 100 K in bulk solution. We observe that in this regime the DNP performance is strongly correlated with the electron and nuclear spin relaxation times, with longer relaxation times leading to better enhancements. We observe that deuteration of the radicals generally leads to better DNP performance. One of the new radicals introduced here provides the best performance obtained so far under these conditions. In similar conditions we show that over a two-fold improvement in DNP enhancements can achieved be simply incorporating solid particles into the sample. Enhancements up to $\varepsilon_H = 515$ are obtained in this way, corresponding to 78% of the theoretical maximum.[5]





bTurea, bCTurea and PyPol series backbone



bTbK and TEKPol series backbone

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Microhydration of N1-Cytosine Derivatives

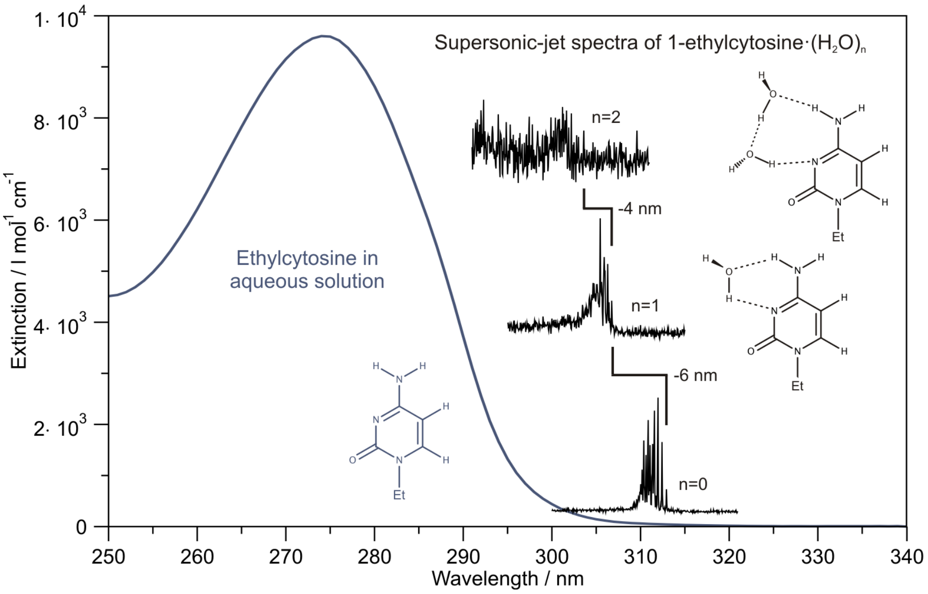
L. Siffert[1], M. A. Trachsel[1], T. Wiedmer[1], S. Leutwyler[1]*

[1]Department of Chemistry and Biochemistry, University of Bern

The $S_0 \rightarrow S_1$ electronic transition of cytosine as well as different N1-substituted derivatives in the gas phase, 1-methylcytosine, 1-ethylcytosine and 1-isopropylcytosine, are between 313 and 315 nm [1,2]. In contrast the red edge of the UV absorption of cytosine and N1-substituted cytidines in solution are blue shifted by ~15 nm to ~300 nm [3].

To investigate the influence of stepwise microhydration on the $S_0 \rightarrow S_1$ electronic transitions, we measured the mass-selective two-color resonant two-photon ionization and UV-UV hole-burning spectra of supersonic jet-cooled 1-ethylcytosine·$(H_2O)_n$ and 1-methyl-5,6-trimethylenecytosine·$(H_2O)_n$ with n=0-2. The n=1 clusters shift by -6 nm compared to the monomers, the n=2 clusters shift further to the blue (-4 nm) resulting in a blue shift of -10 nm compared to the bare N1-cytosines.

The most stable isomers of 1-ethylcytosine·$(H_2O)_n$ calculated at the SCS-CC2/aVDZ level are shown in the figure. Their calculated $S_0 \rightarrow S_1$ electronic origins are blue-shifted relative to the monomer and are in very good agreement with the experimental values.



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