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A dive into the Cytochrome b_6f complex via ultrafast spectroscopy.

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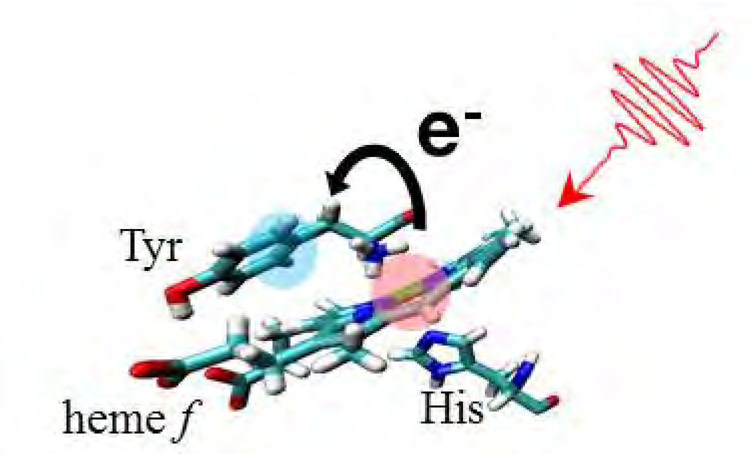
The Cytochrome (Cyt) b_6f complex is a key element of the photosynthetic apparatus in plants. It serves as the mediator of electrons between Photosystem II and Photosystem I and as a results, participates in the creating of an electrochemical potential across the membrane. It is therefore one of the driving force of ATP synthesis. As a dimer, it is comprised of pair of heme *f* and two pairs of *b*-hemes (b_h and b_l), therefore structurally similar to its homologue Cyt bc_1. However the Cyt b_6f has the particularity of having additional constituents such as a Chlorophyl (Chl) and a Caroten (Car) molecule that have up to now no known function in the physiological mechanisms of this Cyt. Their presence in the Cyt b_6f will be discussed.

The ferrous (Fe^{2+}) centers of the heme *f* is shown to photo-dissociate with it tyrosine ligand after excitation by a short laser pulse (~50 fs). This “instantaneous” cleavage is then followed by the ligand recombination within 6 ps. Interestingly, via the heme’s transient signal, we can follow the structural rearrangement of the heme binding pocket with a time constant of 2 ps.



The*b*-hemes give rise to signals that differs drastically from the Cyt*bc*1signals (1), certainly due to their proximity with the Chl and Car molecule. Their interaction is here discussed.

The effects of molecular oxygen on the different relaxation mechanisms of Chl and Car have also being investigated. In the light of our data, oxygen seems to only have affected the spectral signatures while living the early fs-ps dynamics of the chromophores unchanged.

To our knowledge, this is the first ultrafast heme-analysis of the Cyt*b*6*f*. Such unique behaviors shine light on the still intriguing electron-coupled-proton transfer mechanism of the complex.

(1) Adrien Chauvet, Andre Al Haddad, Wei-Chun Kao, Frank van Mourik,Carola Hunte and Majed Chergui;Photo-induced dynamics of the heme centers incytochrome bc1; PCCP; 2014

Revealing conformers of protonated tryptophan by IR-IR-UV triple resonance spectroscopy of cold ions.

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Infrared (IR) laser spectroscopy in the gas phase is a powerful technique for structural determinations of small to large polyatomic molecules and ions. A combination of IR spectroscopy with UV photodissociation (IR-UV double resonance) often allows the identification of conformers of the same species, and it has been demonstrated on species as large as decapeptides [1]. In this approach one uses specific UV transitions to dissociate only one conformer of cold molecules or ions, while measuring the change of UV fragmentation yield in function of IR laser wavelength.

Tryptophan (Trp) is the largest amino acid and building block of proteins and peptides. Despite all the advances in ion spectroscopy, the protonated form of this benchmark species remained the last aromatic amino acid, for which the conformations could not be determined. A particular property of the protonated tryptophan that forbids these determinations by IR-UV double resonance is a very short (tens of femtoseconds) lifetime of the $TrpH^+$ electronic excited state. This short lifetime makes the UV spectrum of the ions extremely broad and, essentially, the same for all the conformers [2]. We have implemented an IR-IR-UV triple resonance approach [3] to solve this problem. The method allows us to measure conformer-selective IR spectra by tagging different conformers with their vibrational frequencies, rather then by using electronic transitions. In the present work the IR-IR-UV triple resonance technique was applied to protonated tryptophan cooled to T= 10 K. The measured IR spectra reveal the presence of two main conformers of $TrpH^+$. These conformer specific IR signatures can now be used for unbiased validations of the structures, calculated for protonated tryptophan.

[1] N.S. Nagornova, T.R. Rizzo, O.V. Boyarkin, *Angew. Chem.,* **2013**, 52, 6002-6005.
[2] O.V. Boyarkin, S.R. Mercier, A. Kamariotis, T.R. Rizzo, *J. Am. Chem. Soc.,* **2006**, 128, 9, 2816-2817.
[3] V.A. Schubert, T.S. Zwier, *Phys. Chem. A.,* **2007**, 111, 13283-13286.

Ultrafast Electro-modulated Differential Absorption Spectroscopy of Methylammonium Lead Iodide Perovskite Thin Films: Evidence for Carriers Trapping and Accumulation at the Surface

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Electro-modulated differential absorption (EDA) spectroscopy allows us to investigate the dynamic interaction between an electric field, photo-generated charge carriers and the active material itself. For photovoltaic applications, the photo-generation of charge carriers and the presence of an field are basic conditions for operation Consequently, the technique enables us to study photovoltaic materials under environments that more closely mimic their operating environment and hence it makes possible to observe phenomena that uniquely arise under these conditions

The ultrafast electro-modulated differential absorbance technique (EDA) relies on the application of an external bias voltage. Upon illumination, charge carriers are generated, whose separation and drift induces an electric field opposed to the applied bias. The dynamics of the electric field felt locally by the perovskite material can be monitored by recording the time evolution of Stark shifts.

Here we present results obtained from the EDA investigation of thin films of $CH_3NH_3PbI_3$ perovskites. Our results demonstrate that there is an accumulation of photo-generated carriers prior to carrier extraction within the perovskite film in planar heterojunction architecture that could be related to the hysteresis effect observed in I-V curves[1]. Under pulsed photo-excitation, carrier migration across crystalline domains is hindered due to the cyclic population and depopulation of interfacial trap states as carriers drift across the film. By correlating the dynamics associated with carrier accumulation in insulated perovskite films and in perovskite | TiO_2 bilayers, where carrier extraction is taking place, we were able to demonstrate spectroscopically that carrier extraction at the heterojunction is rather slow in planar device architectures and occurs over hundreds of picoseconds.

Cold ion spectroscopy reveals the exact structure of protonated helical peptides in the gas-phase.

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The helix is one of the most common secondary structure motifs in proteins[1] and since decades significant scientific effort has been expended in order to shed light on its folding mechanism and stability. The main goal of this project is to apply IR-UV double resonance spectroscopy to the study of cold, helical peptides in the gas-phase. This technique is able to provide conformer-specific infrared spectra of gas-phase ions that can be directly compared with theoretical calculations to reveal structures[2]. The application of this technique to ions at low temperature allows us to drastically increase the spectra resolution compared to room temperature experiments[2].

This poster reports our most recent results on singly protonated peptides of the sequence Ac-Phe-Ala_n-Lys. It is well established that the presence of the charged lysine amino acid at the C-terminus of a polyalanines chain is responsible for the helical structure of the peptide[3]. Ion mobility experiments have provided the collisional cross sections for similar systems[3], but in order to determine their exact structure, we add a spectroscopic dimension to these measurements. Applying IR-UV double resonance spectroscopy, we show that each peptide of the sequence Ac-Phe-Ala_n-Lys-H^+ exhibits primarily two stable conformations. The UV band origins are close to that of protonated phenylalanine, indicating that the Phe side-chain is relatively isolated from the protonation site as well other polar groups[1], and this is confirmed by the comparison with calculations[1,4]. From the analysis of the IR spectra we demonstrate that the conformers have similar hydrogen-bonding patterns[1], confirming the central role of this interaction in determining the stability of this structure in the gas-phase. Furthermore, we show that it is possible to form helical peptides by replacing the Lys at the C-terminus of the sequence with a metal cation, but in this case not all of the conformers present in the gas-phase are helical.

[1] J. A. Stearns, O. V. Boyarkin, T. R. Rizzo, *JACS*. **2007**, 129, 13820 - 13821
[2] T. R. Rizzo, J. A. Stearns, O. V. Boyarkin, *Int. Rev. in Phys. Chem*. **2009**, 28, 481 - 515
[3] R. R. Hudgins and M. F. Jarrold, *JACS.* **1998**, 121, 3494 - 3501
[4] A. Zabuga. *EPFL – Lausanne* PhD Thesis. **2014**b

Photoinduced charge transfer mechanism in Diketopyrrolopyrrole(DPP) dye-sensitiezed solar cell

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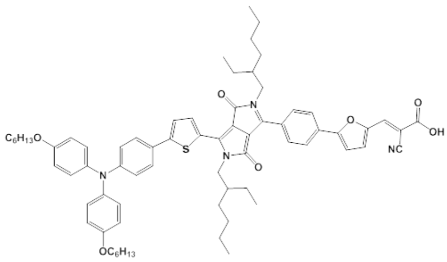
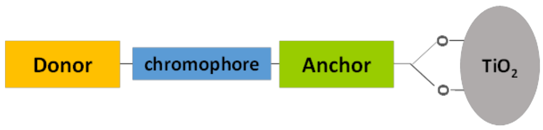
Dye-sensitized solar cell (DSSC) has been reported as powerful alternative energy source since its potential for high conversion efficiency and low cost of production.[1] Especially, the use of organic
sensitizer such as blue DPP-based dyes which is synthetically accessible, with high photostability, starts to receive attention as DSSC sensitizer by using donor-chromophore-anchor(D-C-A) concept.[2] Here, we explore photoinduced charge transfer pathways in blue-colored DPP based sensitizer adsorbed onto mesoporous wide-bandgap semiconductor, titanium oxide.





As kinetic competition between forward charge transfer and recombination processes greatly influences efficiency in DSSC, it is crucial to reveal the dynamics of holes and electrons following light excitation. By using time-resolved transient absorption spectroscopy, we monitor charge separation such as electron and hole injection at the sensitizer-semiconductor heterojunction probing the fs-ps time domain, and reveal the pathway of charge recombination at longer timescale up to the ms.

[1] O'Regan, B.; Gräztel, M. *Nature* **1991**, 353, 737.
[2] Holcombe, T. W.; Yum, J. H.; Kim, Y.; Rakstys, K.; Gräztel, M; *J. Mater. Chem. A*, **2013**, 1, 13978-13983.

Spectroscopic studies of kinetically trapped conformations in the gas phase: the case of triply protonated bradykinin

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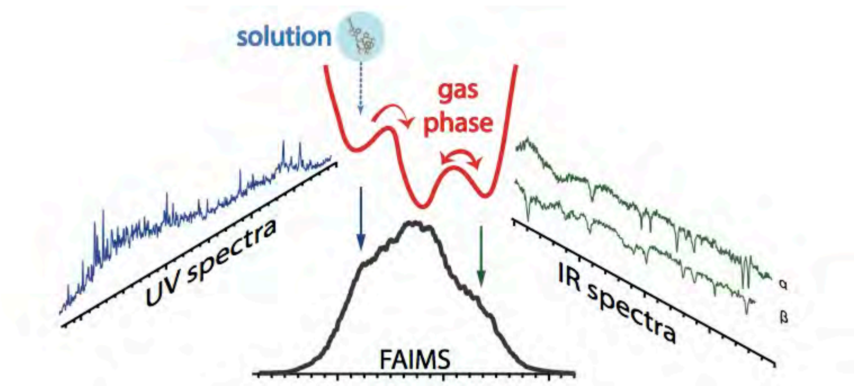
Understanding the relation between the gas-phase structure of biological molecules and their solution-phase structure is important when attempting to use gas-phase techniques to address biologically relevant questions. Directly after electrospray ionization, molecules can be kinetically trapped in a state that retains some “memory” of its conformation in solution and is separated from the lowest-energy gas-phase structure by barriers on the potential energy surface. In order to identify and characterize kinetically trapped structures, we have explored the conformational space of triply protonated bradykinin in the gas phase by combining field-asymmetric ion mobility spectrometry (FAIMS) with cold ion spectroscopy. We isolate three distinct conformational families and characterize them by recording their UV-photofragment spectra and vibrational spectra. Annealing of the initial conformational distribution produced by electrospray reveals that one of the conformational families is kinetically trapped, while two others are stable, gas-phase structures. We compare our results to previously published results obtained using drift-tube ion mobility spectrometry (IMS) and propose a correspondence between the conformational families separated by FAIMS and those by IMS.



State-to-state scattering of $CH_4(\nu_3)$ from Ni(111) and LiF(100) surfaces.

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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] Through the use of state-selective vibrational excitation, effects such as bond selectivity, mode specificity and alignment dependent reactivity have been uncovered. In these dissociation studies, it was observed that typically a large fraction of the incident methane molecules does not dissociate but scatters inelastically from the surface even if their incident energy is significantly higher than the minimum barrier height of ≈0.8 eV for a Ni(111) surface.

Such inefficient dissociation can either be explained by a very narrow transition state, causing very steep rise of the reaction barrier for anything but the optimal orientation of the dissociating molecule with respect to the surface and the dissociation site. Alternatively, fast vibrational relaxation of the incident vibrationally excited methane might be competing with dissociation. Efficient relaxation of vibrational energy in a gas/surface collision is possible via electron-hole pair excitation in the metal surface and has been observed for NO and HCl on Au(111)[5,6] but never before for CH_4 on Ni(111). Knowledge about the existence of electronically nonadiabatic relaxation channels and possible breakdown of the Born-Oppenheimer approximation is of great importance for the development of realistic theoretical models of gas/surface reactivity.

In order to study the fate of vibrational excited CH_4 in a scattering collision, we have developed a state-to-state molecular beam/surface scattering experiment by equipping an existing machine with a cryogenic bolometer detector combined with state-specific laser tagging. This setup allows us to prepare the incident molecular beam in a specific rovibrational state before collision and to state-selectively detect the scattered molecules after collision with the surface. We present first data obtained with this setup, for the scattering of CH_4 from Ni(111) and LiF(100) surfaces.

1 Smith, R. R., Killelea, D. R., DelSesto, D. F. Utz, A. L. Preference for vibrational over translational energy in a gas-surface reaction. *Science* **304**, 992-995, doi:DOI 10.1126/science.1096309 (2004).
2 Beck, R. D. *et al.* Vibrational mode-specific reaction of methane on a nickel surface. *Science* **302**, 98-100, doi:DOI 10.1126/science.1088996 (2003).
3 Nave, S., Tiwari, A. K. Jackson, B. Dissociative Chemisorption of Methane on Ni and Pt Surfaces: Mode-Specific Chemistry and the Effects of Lattice Motion. *J Phys Chem A* **118**, 9615-9631, doi:Doi 10.1021/Jp5063644 (2014).
4 Dâiez Muiäno, R. Busnengo, H. F. *Dynamics of Gas-Surface Interactions Atomic-level Understanding of Scattering Processes at Surfaces*. (Springer Berlin Heidelberg, 2013).
5 Cooper, R. *et al.* Efficient translational excitation of a solid metal surface: State-to-state translational energy distributions of vibrational ground state HCl scattering from Au(111). *J Vac Sci Technol A* **27**, 907-912, doi:Doi 10.1116/1.3071971 (2009).
6 Huang, Y. H., Rettner, C. T., Auerbach, D. J. Wodtke, A. M. Vibrational promotion of electron transfer. *Science* **290**, 111-114, doi:DOI 10.1126/science.290.5489.111 (2000).

Infrared spectroscopy of mobility-selected H$^+$-Gly-Pro-Gly-Gly (GPGG)

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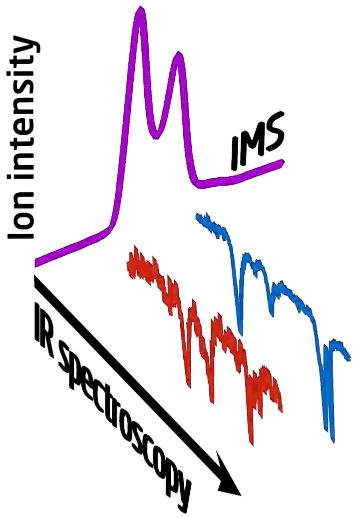
We report results from a new instrument capable of acquiring infrared spectra of mobility-selected ions. This demonstration involves using ion mobility to first separate the protonated peptide Gly-Pro-Gly-Gly (GPGG) into two conformational families with collisional cross-sections of 93.8 and 96.8 Å^2. After separation, each family is independently analyzed by acquiring the infrared predissociation spectrum of the H_2-tagged molecules. The ion mobility and spectroscopic data combined with Density Functional Theory (DFT) based molecular dynamics simulations confirm the presence of one major conformer per family, which arises from *cis*/*trans* isomerization about the proline residue. We induce isomerization between the two conformers by using collisional activation in the drift tube and monitor the evolution of the ion distribution with ion mobility and infrared spectroscopy. While the *cis*-proline species is the preferred gas-phase structure, its relative population is smaller than that of the *trans*-proline species in the initial ion mobility drift distribution. This suggests that a portion of the *trans* -proline ion population is kinetically trapped as a higher energy conformer and may retain structural elements from solution.



Electronic energy transfer in model peptides

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Electronic energy transfer (EET) is an important solution-phase technique in structural biology because it allows one to measure the distance between donor and acceptor chromophores in a protein, thus providing structural information.[1] We investigate the principles that govern EET in the gas phase and calibrate the technique utilizing model helical peptides with general formula $AcFA_nYKH^+$. These molecules adopt a well-defined structure.[2] The specific IR-UV double resonance spectroscopy of cold molecules [3] allows us to investigate different conformers, and as a result, to have a fixed distance and relative orientation between chromophores. This is important because both distance and orientation play key roles in dictating whether EET occurs by Förster resonance energy transfer (FRET) or Dexter exchange transfer. We will present our recent results on the dependence of electronic energy transfer efficiencies on the peptide chain length.

[1] Single particle tracking and single molecule energy transfer. Edited by C. Bräuchle, D. C. Lamb, J. Michaelis, Wiley, **2010**, 343 p.
[2] J. A. Stearns, O. V. Boyarkin, T. R. Rizzo, *J. Am. Chem. Soc.,* **2007**, 129, 13820–13821
[3] T. R. Rizzo, J. A. Stearns, O. V. Boyarkin, *Int. Rev. Phys. Chem.*, **2009**, 28, 481–515

Pushing the limits of cold ion spectroscopy: structural characterization of protonated ubiquitin in the gas phase

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Over the last decade spectroscopy of cold, gas-phase biomolecular ions as large as decapeptides[1] has been extensively used to characterize their three-dimensional (3D) structure. Here we report for the first time on the use of ultraviolet (UV) spectroscopy for elucidation of structural features of a small protein in its native-like and unfolded states.
Ubiquitin is a 76-residue protein, found in almost all eukaryotic cells. It has been extensively studied both in solution and in the gas phase using a variety of techniques[2-4]. For instance, it has been shown that in aqueous solution ubiquitin remains in its highly structured native form, while an addition of methanol induces the formation of partially unfolded structure[3]. Electrospray ionization (ESI) technique enables transferring biomolecules from solution into the gas phase and, consequently, studying them in well-defined environments. In particular, it has been shown that ubiquitin ions formed by ESI under different source conditions adopt a multitude of partially interconvertible conformations[4]. Furthermore, the fact that the conformational distribution of gas-phase ions is sensitive to solvent composition indicated that some of them are likely to retain their solution structures.
We use UV photofragmentation spectroscopy[5] for structural investigation of cold, gas-phase protonated ubiquitin under various ESI source conditions. Cooling the ions to cryogenic temperatures greatly suppresses thermal congestion of UV spectra and reveals their vibronic structure[6], which is very sensitive to local environment of the chromophores (one tyrosine and two phenylalanines). Changes in UV photofragmentation spectra therefore allow us to monitor the evolution of ubiquitin's 3D structure. The spectra, in particular, suggest the presence of at least three different types of microenvironment of the tyrosine residue, which can be assigned to the native-like, partially and fully unfolded states, while the spectral changes observed upon increasing the charge state are clearly the signatures of protein unfolding. The effect of solvent composition is significant only for the +7 charge state. This observation suggests that in this state the protein structure is metastable, such that ubiquitin retains its solution structure only under the gentle ESI source conditions.

[1] Nagornova, N. S.; Guglielmi, M.; Doemer, M.; Tavernelli, I.; Rothlisberger, U.; Rizzo, T. R.; Boyarkin, O. V. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 5383.
[2] Vijay-kumar, S.; Bugg, C. E.; Cook, W. J. *J. Mol. Biol.* **1987**, *194*, 531.
[3] Wilkinson, K. D.; Mayer, A. N. *Arch. Biochem. Biophys.* **1986**, *250*, 390.
[4] Wyttenbach, T.; Bowers, M. T. *J. Phys. Chem. B* **2011**, *115*, 12266.
[5] Kopysov, V.; Nagornova, N. S.; Boyarkin, O. V. *J. Am. Chem. Soc.* **2014**, *136*, 9288.
[6] Boyarkin, O. V.; Mercier, S. R.; Kamariotis, A.; Rizzo, T. R. *J. Am. Chem. Soc.* **2006**, *128*, 2816.

Photoassociation of cesium atoms upon Rydberg excitation in a dense ultracold gas

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Ultracold cesium atoms are excited to $np_{3/2}$ Rydberg states with narrow-band UV laser radiation. Detuned from the atomic transitions we observe additional resonances in the photoexcitation spectra that are attributed to the photoassociation of Cs atoms to Cs_2 molecules. Depending on the intensity of the UV laser radiation, two types of Cs_2 molecular states are observed.

The first type of molecular states correspond to Cs_2 dimers, in which both atoms are excited to high Rydberg states. These dimers of Rydberg atoms are called macrodimers and are observed in our experiments following Rydberg excitation with an intense, pulsed UV laser. The interactions between the two Rydberg atoms giving rise to these macrodimers are modeled using a long-range multipole expansion, the relevant terms being the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole contributions [1]. The different molecular resonances can be assigned clearly as arising from one of these three contributions in the multipole expansion.

The second type of molecules are Cs_2 molecules, in which one of the atoms is in a high Rydberg state and is bound to a ground-state atom located inside the Rydberg-electron orbit. We observe these molecules by photoassociation with a continuous-wave UV laser. The binding mechanism does not fit into one of the known categories of bonds (covalent, ionic, metallic, or van der Waals) but results from the scattering of the slow Rydberg electron off the ground-state atom. Among the unusual properties of these molecules are huge bond lengths exceeding 1000 Bohr radii at n=30 and extremely low binding energies (typically much less than 1 GHz, i.e. much less than 1 J/mol) [2]. These molecules nevertheless have sharp vibronic levels and high-resolution spectroscopy reveals all details of their structure and dynamics. The binding energies of the vibronic ground states are reproduced in a model based on a Fermi pseudopotential to account for the interaction of the Rydberg electron with the ground-state atom, including singlet and triplet s-wave scattering channels.

[1] Johannes Deiglmayr, Heiner Saßmannshausen, Pierre Pillet, and Frédéric Merkt, Physical Review Letters **2014**, 113, 193001.
[2] Heiner Saßmannshausen, Frédéric Merkt, and Johannes Deiglmayr, Physical Review Letters **2015,** 114, 133201.

Precision Spectroscopy in Cold Molecules: The First Rotational Intervals of He^+_2 by High-Resolution Spectroscopy and Rydberg-Series Extrapolation

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Having only three electrons, He^+_2 represents a system for which highly accurate ab initio calculations are possible. The latest calculations of rovibrational energies in He^+_2 do not include relativistic or QED corrections but claim an accuracy of about 120 MHz [1]. The available experimental data on He^+_2, though accurate to 300 MHz, are not precise enough to rigorously test these calculations or reveal the magnitude of the relativistic and QED corrections. We have performed high-resolution Rydberg spectroscopy of metastable He_2 molecules and employed multichannel-quantum-defect-theory extrapolation techniques [2] to determine the rotational energy-level structure in the He^+_2 ion. To this end, we have produced samples of helium molecules in the *a* $^3\Sigma^+_u$ state in supersonic beams with velocities tunable down to 100 m/s by combining a cryogenic supersonic-beam source with a multistage Zeeman decelerator [3]. The metastable He_2 molecules are excited to *n*p Rydberg states using the frequency-doubled output of a pulse-amplified ring dye laser. Although the bandwidth of the laser system is too large to observe the reduction of the Doppler width resulting from deceleration, the deceleration greatly simplifies the spectral assignments because of its spin-rotational state selectivity (see Fig. 1). Our approach enabled us to determine the rotational structure of He^+_2 with unprecedented accuracy, to quantify the size of the relativistic and QED corrections by comparison with the results of Ref. [1] and to precisely measure the rotational structure of the metastable state for comparison with the results of Focsa et al. [4].

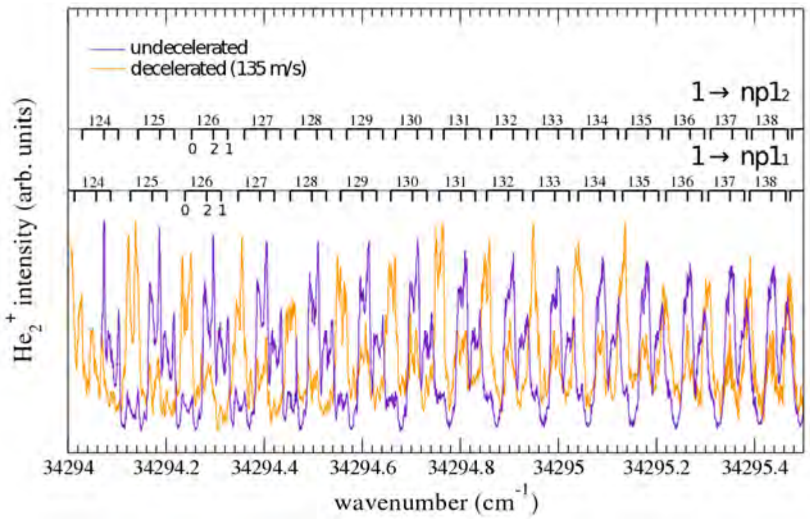

Figure 1. Rydberg series of metastable He_2 molecules in the Q1 region of the spectrum for undecelerated and decelerated beams.

[1] W.-C. Tung, M. Pavanello, L. Adamowicz, *J. Chem. Phys.* **2012**, 136, 104309.
[2] D. Sprecher, J. Liu, T. Krähenmann, M. Schäfer, and F. Merkt, *J. Chem. Phys.*, **2014**, 140, 064304.
[3] M. Motsch, P. Jansen, J. A. Agner, H. Schmutz, and F. Merkt, *Phys. Rev. A*, **2014**, 89, 043420.
[4] C. Focsa, P. F. Bernath, and R. Colin, *J. Mol. Spectrosc.*, **1998** 191, 209.

Continuous trap loading of Rydberg-Stark decelerated metastable helium using overlaid electric and magnetic traps

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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)* $^3S_1$ can be trapped magnetically following Rydberg-Stark deceleration.

The He Rydberg atoms are prepared in a selected Rydberg-Stark state using a home-built narrow-bandwidth (160 MHz) pulsed tunable laser. The Rydberg atoms are then decelerated and deflected off the atomic beam axis and trapped electrostatically. Once they decay to the metastable state, they are trapped in a quadrupole magnetic trap produced by two permanent magnets. A detection scheme using two-photon ionisation with the second harmonic of a Nd:YAG laser is employed to ionise the trapped helium atoms and the ions are detected using a micro-channel plate detector. The experimental setup is also used to study the radiative processes (spontaneous emission, stimulated emission, and absorption induced by blackbody radiation) that limit the lifetimes of the Rydberg-Stark states.

[1] S. D. Hogan, and F. Merkt, *Phys. Rev. Lett.* **100**(4), 043001, (2008.)
[2] P. Allmendinger, J. A. Agner, H. Schmutz, and F. Merkt, *Phys. Rev. A* **88**(4), 043433, (2013.)

MQDT-assisted high-resolution spectroscopy of the Rydberg states of H_2 - ionization energy of $H_2$and rovibrational structure of H_2+

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H_2^+ and H_2 are the simplest of all molecules and as such are important molecules for the development of molecular quantum mechanics. The rovibrational energy-level structure of H_2^+ and H_2 can be calculated extremely precisely by quantum chemical methods which include the determination of relativistic and quantum-electrodynamic effects [1,2]. Because the rotational and vibrational transitions of H_2^+ are electric-dipole forbidden, the experimental data on its energy-level structure are limited.

We present studies of multiphoton transitions to Rydberg states of H_2 belonging to states converging to a wide range of rovibrational levels of H_2^+ X^+ ($^2\Sigma_g^+$; v^+ = 0 - 12, N^+ = 0 - 6) at high spectral resolution.

By extrapolating the Rydberg series using multichannel quantum-defect theory the vibrational, rotational, fine- and hyperfine-structure intervals of H_2^+ can be determined precisely [3,4]. The same data can also be used to determine the ionization and dissociation energies of H_2 [5].

Using a home-built pulsed near-infrared laser with Fourier-transform-limited linewidth and adjustable pulse duration, in combination with an improved multiphoton-excitation scheme, we have recently improved the accuracy of these measurements. To this end, systematic errors originating from ac and dc Stark shifts, from pressure shifts, and from the frequency shifts and chirps accompanying the generation of the NIR laser pulses were quantified and minimized.

[1] V. I. Korobov, Phys. Rev. A **73**, 024502 (2006).
[2] K. Piszczatowski et al., J. Chem. Theory Comput. **5**, 3039 (2009).
[3] A. Osterwalder et al., J. Chem. Phys. **121**, 11810 (2004).
[4] Ch. Haase et al., J. Chem. Phys. **142**, 064310 (2015).
[5] J. Liu et al., J. Chem. Phys. **130**, 174306 (2009).

High-Resolution VUV-Absorption Spectroscopy using Phase Modulation

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High-resolution absorption spectroscopy in the vacuum (λ≤200 nm; VUV) and extreme (λ≤105 nm; XUV) ultraviolet ranges of the electromagnetic spectrum is notoriously difficult. VUV radiation from synchrotron sources needs to be monochromatised, which limits the bandwidth of the radiation to at best 0.1 cm^{-1} [1]. VUV-FT absorption spectroscopy, as recently extended to the XUV range offers the multiplex advantage, but so far the best resolution achieved with this method is 0.33 cm^{-1} [2]. Pulsed VUV laser systems based on four-wave mixing enable a higher resolution [3], but the large pulse-to-pulse fluctuations resulting from the non-linearity of the VUV generation process limits the sensitivity of absorption measurements, so that only very few laser VUV absorption spectra of atoms and molecules in supersonic beams have been reported [3,4].

To improve the low sensitivity resulting from the large pulse-to-pulse fluctuation of the VUV radiation, Sommavilla *et al.* [5] have used a dispersion grating and exploited the beam diffraction in the negative first order to normalise the VUV laser intensity pulse by pulse and were able to reliably measure absorption signals of 10^{-4}.

We present here an alternative method to record absorption spectra with high sensitivity that relies on frequency modulation techniques. The VUV radiation is produced by two-photon resonance-enhanced ($\nu_{VUV}=2\nu_1\pm\nu_2$) four-wave mixing in Kr using the $^1S_0 \rightarrow 4p^5\ 5p[1/2](J=0)$ resonance at $2\nu_1$=94092.96 cm^{-1} using the output of two FT-limited pulsed lasers (pulse length 5 ns, obtained by pulse amplification of cw ring laser radiation). The modulation of the VUV laser frequency is achieved by generating side bands on the output of the second laser (ν_2) using an electro optical modulator. These side bands are automatically transferred to the VUV because the four-wave mixing process is linearly dependent on the intensity of the second laser.

The poster will present spectra of atomic and molecular transitions to demonstrate absorption experiments in the VUV range of the electromagnetic spectrum with this new method in supersonic beams.

[1] Laurent Nahon, Christian Alcaraz, Jean-Louis Marlats, Bruno Lagarde, François Polack, Roland Thissen, Didier Lepère and Kenji Ito, *Rev. Sci. Instr.*, **2001**, 72, 1320.
[2] N. de Oliveira, D. Joyeux, D. Phalippou, J. C. Rodier, F. Polack, M. Vervloet and L. Nahon, *Rev. Sci. Instr.*, **2009**, 80, 043101.
[3] P. C. Hinnen, S. Stolte, W. Hogervorst and W. Ubachs, *J. Opt. Soc. Am. B*, **1998**, 15, 2620.
[4] T. P. Softley, W. E. Ernst, L. M. Tashiro and R. N. Zare, *Chem. Phys.*, **1987**, 116, 299.
[5] M. Sommavilla, U. Hollenstein, G. M. Greetham and F. Merkt,*J. Phys. B: At. Mol. Opt. Phys.*, **2002**, 35, 3901.

Mapping the electronic states of small transition metal clusters by nonlinear spectroscopy

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To gain a deeper understanding on the photochemistry and catalytic activity of transition metal dimers and clusters, detailed knowledge of the chemical bonding and electronic structure is needed. However, conventional spectra of such species, such as those recorded using absorption and laser-induced fluorescence (LIF) techniques, are often difficult to analyze. The high density of states yields complex spectra displaying overlapping transitions that originate from neighboring electronic states. Also, a closely spaced pattern of numerous isotopologues might occur. In addition, one-photon dipole selection rules prevent the direct observation of many excited states. Even computation offers no solution as the high density of states renders current methods too expensive.

To overcome these difficulties, we utilize a nonlinear technique to perform optical-optical double-resonance (OODR) spectroscopy. Transient species containing transition metals are generated in the cold and collision-free environment of a molecular beam by combining laser ablation of a metal target and subsequent supersonic expansion of the products into vacuum. OODR experiments are then performed in the molecular beam by using the Two-Color Resonant Four-Wave Mixing (TC-RFWM) technique. TC-RFWM is intrinsically background-free and generates a laser-like signal beam that can be remotely detected. The fully resonant process yields spectra of high-resolution, with a sensitivity approaching that of LIF. TC-RFWM has proven advantageous to disentangle complex spectra. A signal is only obtained if two transitions involving a common state are addressed simultaneously [1]. At the same time the doubly-resonant nature of the technique enables the observation of states that are stringently forbidden for one-photon transitions. Furthermore, perturbations between energetically close-by states result in mixing of their characters, which may exhibit different spin multiplicity. Pumping such states provides access to transitions within otherwise optically inaccessible manifolds. Such experiments have recently been demonstrated within our laboratory, where initial deperturbation studies on triplet transitions of the carbon dimer led to the first detection of a quintet-quintet band [2].

In this work, we report on the initial steps towards TC-RFWM spectroscopy of heterogeneous transition metal dimers/clusters and reacted versions thereof. A new laser-vaporization disc source that yields a stable pulse to pulse reproducibility is under development. Initial rotationally resolved TC-RFWM spectra of the copper dimer will be presented. The results demonstrate the potential to gain insight into the complex electronic structure of metal dimers and clusters, including heterogeneous and reacted species.

[1] P.P. Radi, M. Tulej, G. Knopp, P. Beaud, and T. Gerber,*Journal of Raman Spectroscopy*, **2003**, 34, 1037.
[2] P. Bornhauser, R. Marquardt, C. Gourlaouen, G. Knopp, M. Beck, T. Gerber, J.A. van Bokhoven, and P.P. Radi, *The Journal of Chemical Physics*, **2015**, 142, 094313.

Dissociation dynamics of dissolved CH_3I studied with time-resolved resonant inelastic X-ray scattering

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The aim of this study is to theoretically and experimentally investigate structural and dynamical properties of dissolved CH_3I with static and time-resolved resonant inelastic X-ray scattering (RIXS). The C-I bond breakage in dissolvedCH_3I and the subsequent chemical reaction of the resulting fragments with an active metal, such as Rh or Ir, represents a fundamental reaction step in the commercial synthesis of acetic acid (CH_3COOH) from methanol, known as the Monsanto process. The substance is one of the world's most important chemicals and serves as an intermediate in the production of a vast range of products, such as polymers, pharmaceuticals, adhesives, etc. Dissociation in CH_3I can be triggered by a resonant laser UV excitation to A-band states, corresponding to promotions of non-bonding p-electrons to the σ* orbital, and probed several ps later with a delayed x-ray pulse tuned around the iodine L_1 and L_3 absorption edges. Such measurements provide information about the character of unoccupied (absorption) and occupied (emission) molecular orbitals which are in turn sensitive to the local chemical environment. In order to simulate RIXS on liquids the spectra have to be computed and summed for several different geometries of solvent and solute molecules, to cover a sufficient part of the phase space. We have performed *Car-Parrinello* molecular dynamics (MD) simulations [1] at finite temperature for iodomethane surrounded by different number of solute molecules. The calculated (static) high energy resolution fluorescence detected (HERFD) X-ray absorption spectra, which are taken as horizontal slices from RIXS maps, indicate a strong changes in the post-edge features in comparison with the gas phase (see figure). In following step we will perform MD simulations in which CH_3I is excited to the dissociative A-band states and calculate HERFD spectra as a function of time in order to extract dynamical information and compare them with future experimental data.

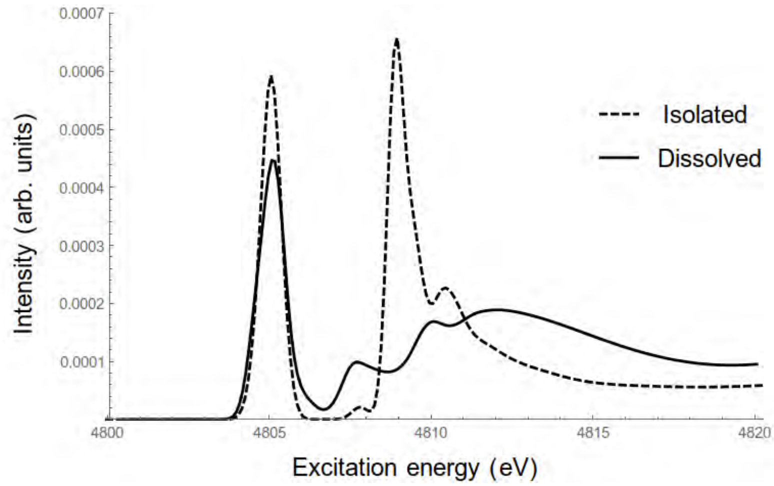

Figure: A comparison between theoretical iodine L_1 HERFD spectra of an isolated CH_3I molecule (dashed line) and CH_3I molecule surrounded with 16 water molecules (full line).

[1] Dahlia K. Remler, Paul A. Madden, Molecular Physics, 1990, 70, 921-966

Femtosecond Time-resolved Spectroscopy in the Extreme Ultraviolet Spectral Range

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Owing to recent advances in extreme ultraviolet (EUV) and soft x-ray (SXR) light sources, ultrafast time-resolved spectroscopy, it is nowadays possible to probe the electronic structure of a molecule in a site-selective way on an ultrafast time-scale. A large variety of photoinduced processes of molecular samples have been followed by time-resolved photoelectron spectroscopy (PES), including electronic relaxation [1], core-level shifts [2], photoinduced bond breaking [3], and bond formation [4]

In this contribution we will show recent advances in EUV PES of molecular samples in room-temperature liquid solution studied in our laboratory. The setup employed is characterized by high photon flux and energy, high temporal and outstanding spectral resolution [5]. The wealth of information contained in the full valence electron spectrum paired with the simultaneous observation of core levels mitigates many problems inherent to the more common ultrafast techniques. The temporal evolution of PES bands that stem from iron 3d molecular orbitals serve as unequivocal reporters for their oxidation state and coordination after absorption of light.

[1] M. Probst, R. Haight, Appl. Phys. Lett. 71 (1997) 202; A. Makida, H. Igarashi, T. Fujiwara, T. Sekikawa, Y. Harabuchi, T. Taketsugu, J. Phys. Chem. Lett. 5 (2014) 1760
[2] H. Dachraoui, M. Michelswirth, P. Siffalovic, P. Bartz, C. Schäfer, B. Schnatwinkel, J. Mattay, W. Pfeiffer, M. Drescher, U. Heinzmann, Phys. Rev. Lett. 106 (2011) 107401
[3] L. Nugent-Glandorf, M. Scheer, D. Samuels, A. Mulhisen, E. Grant, X. Yang, V. Bierbaum, S. Leone, Phys. Rev. Lett. 87 (2001), 193002; P. Wernet, M. Odelius, K. Godehusen, J. Gaudin, O. Schwarzkopf, W. Eberhardt, Phys. Rev. Lett. 103 (2009) 013001; M. Fushitani, A. Matsuda, A. Hishikawa, Opt. Lett. 19 (2011) 9600
[4] M. Bauer, C. Lei, K. Read, R. Tobey, J. Gland, M. Murnane, H. Kapteyn, Phys. Rev. Lett. 87 (2001) 025501
[5] J. Ojeda, C. Arrell, J. Grilj, F. Frassetto, L. Mewes, H. Zhang, F. van Mourik, L. Poletto, M. Chergui, submitted (to Structural Dynamics)

Quantum-Logic Spectroscopy for Single Trapped Molecular Ions

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The recent application of quantum techniques to the spectroscopy of single trapped particles has enabled the determination of atomic properties at unprecedented levels of precision. "Quantum-logic spectroscopy" (QLS) has enabled the next generation of atomic clocks and new precision tests of fundamental physical theories[1]. Thus, we would like to extend the scope of quantum techniques for frequency measurements to spectroscopically probe the properties of single isolated molecules and establish a quantum toolbox for the non-destructive interrogation of single molecules by coupling to a single atom. These developments will pave the way for molecular precision spectroscopic measurements to study, e.g., a possible time variation of particle masses[2-8]. The experiments will focus on $^{14}N_2^+$ which has recently been identified as a promising candidate system for precision spectroscopy[2].

[1] P. O. Schmidt *et. al.*, *Science*, **2005**, 309, 749.
[2] M. Kajita *et. al.*, *Phys. Rev. A*, **2014**, 89, 032509.
[3] S. Willitsch, *Int. Rev. Phys. Chem.*, **2012**, 31, 175.
[4] S. Schiller, V. Korobov, *Phys. Rev. A*, **2005**, 71, 032505.
[5] M. Schnell, J. Küpper, *Faraday Discuss.*, **2011**, 150, 33.
[6] S. Schiller *et. al.*, *Phys. Rev. Lett.*, **2014**, 113, 023004.
[7] P. Jansen *et. al.*, *J. Chem.* Phys., **2014**, 140, 010901.
[8] M. Shi *et. al.*, *New Journal of Physics*, **2013**, 15, 113019.

Towards hybrid trapping of cold molecules and cold molecular ions

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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 RFion 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.

[1] S. Willitsch, *Ion-atom hybrid systems*, **2014**, arXiv:1401.1699v1 [physics.atom-ph].
[2] S.Y.T. van de Meerakker, H. L. Bethlem, N. Vanhaecke, G. Meijer*, Chem. Rev.*, **2012**, *112*, 4828.

Cold Ion-Neutral Reactions in Next-Generation Ion-Atom Hybrid Traps

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Recent studies of chemical reactions at extremely low temperatures using laser-cooled, co-trapped ions and atoms in hybrid traps showed the ability of such systems to be used for investigation of the quantum character of reactive collisions [1-4]. Details of the mechanism of chemical reactions and the nature of molecular interaction potentials can be studied. But so far, insufficient control over the collision energy magnitude and distribution impeded the study of effects with narrow dependencies on collision energy such as shape resonances [5]. Here we present results from the extension of our hybrid trap setup with increased control over the collision energies.

Our hybrid trap consists of a linear Paul trap for atomic and molecular ions overlapped with a magneto-optical trap for neutral rubidium atoms. Initial experiments focused on interactions between Ca^+ + Rb [1,2] and Ba^+ + Rb [3], in which both systems have been laser cooled. Recently, chemical reactions of sympathetically cooled N_2^+ molecular ions with Rb atoms have been studied as well [4].

In the original setup, control over the energy of the ion-atom collisions was achieved by changing the number of ions and shape of the ion crystal. Heating of the ions due to micromotion lead to large spreads of the collision energies, averaging out the effect of narrow resonances. In a new approach, we use a modified magneto-optical trap which allows the use of a dynamic atom cloud. Radiation pressure differences in the cooling laser beams along one axis create atom clouds in off-center positions. On-resonance push beams accelerate the atoms through the ion crystal after which the atoms are recaptured in the opposite off-center position. By carefully tuning the cooling and push beam sequence and intensities we are able to produce moving atom clouds with well-defined velocities in the lab frame. Using this approach with ion strings on the rf null line of the ion trap, the collision energy resolution could be greatly improved.

Following our pioneering study to introduce molecular species in the hybrid trap [4], we now have coupled the setup with a molecular beam machine to allow the state-selective generation and sympathetic cooling of molecular ions [6]. We are now implementing sympathetic cooling of vibrationally state-selected O_2^+ ions to study vibrational effects in cold molecule-atom collisions.

[1] Felix H.J. Hall et al; *Phys. Rev. Lett.* **2011**, 107, 243202
[2] Felix H.J. Hall, Pascal Eberle et al; *Mol. Phys.*, **2013**, 111, 14-15, 2020-2032
[3] Felix H.J. Hall et al; *Mol. Phys.* **2013**, 111, 12-13, 1683-1690
[4] Felix H.J. Hall et al; *Phys. Rev. Lett.* **2012**, 109, 233202
[5] Humberto da Silva Jr. et al; *New J. Phys.* **2015**, 17, 045015
[6] Xin Tong et al; *Phys. Rev. Lett.* **2010**, 105, 143001

Ionic Liquids based on crown ether as electrolytes for batteries

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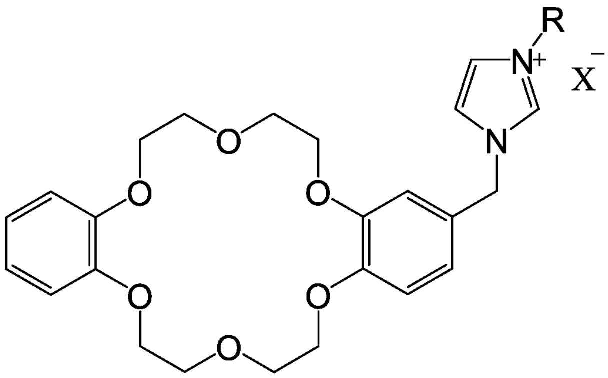
Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and are usually composed of an asymmetrical organic cations and large charge anion delocalized which are poorly coordinated. Their unique properties make them very interesting for many applications, including catalysis and electrolytes for ionic and electronic devices[1].

The strong interest of increasing the conductivity of the electrolyte generated a significant interest for crown ether which exhibit the property to strongly interact with alcali metal cation (Li^+, Na^+, K^+) and being good reagent to prevent electrolyte decomposition[2].



R = C_4H_9, C_5H_{11}, C_6H_{13}, ….
X^- = $CF_3CO_2^-$, $CF_3SO_2^-$, BF_4^-, PF_6^-, $^-N(SO_2CF_3)_2$

Fig. 1. New Ionic liquids based crown on ether

However there not many works about the using of crown ether in the field of electrolytes. So we propose to use them as an alkali cation carrier in the ionic liquid system. The aim of the project is to design new ionic liquids (RTILs) based on crown ether with enhanced properties (high ion concentration and conductivity, low viscosity, high chemicaland electrochemical stability) that can be applied as electrolyte for rechargeable batterieswith higher theoretical energy density such as metal-water or metal-air batteries.

[1] H. Ohno, *Electrochemical aspect of ionics liquids*, **2005**, John Whiley sons, Inc.
[2] Xu, W et al, *Crown Ethers in non aqueous Electrolyte for Lithium/Air Batteries*, Eletrochemical and Solid –State Letters, **2010**. 13(4): p.A48-A51.

Electrons and ionic liquids - a novel approach to study electron scattering from nonvolatile compounds

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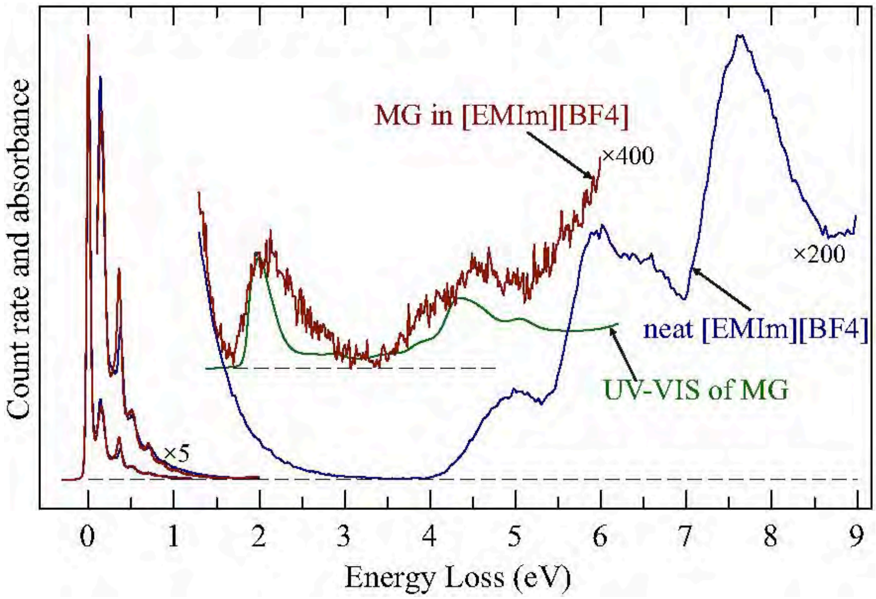
The technique of low-energy electron impact spectroscopy, originally developed for gas phase molecules [1], is applied to room temperature ionic liquids. For the purpose of the present study a droplet of an ionic liquid, suspended by a molybdenum wire, was placed in the electron beam and scattered electrons were collected at an angle of 135° with respect to the incident beam.

Excited states of four representative ionic liquids were characterized by electron energy-loss spectra (EELS) and DFT/MRCI calculations, with good agreement.

Energy-loss spectrum of a saturated solution of methylene green (MG) in 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIm][BF_4] showed a methylene green band at 2 eV (see Figure 1), demonstrating that ionic liquids may serve as hosts for nonvolatile compounds. Surprisingly, the methylene green band was missing in the energy-loss spectrum when it was dissolved in a different IL, 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [BMPipe][TFSI] - this may indicate that it is displaced from the surface and cannot be reached by electrons as they have a limited penetration depth.

This study demonstrates power of EELS to investigate surface structure.



[1] M. Allan, *J. Phys. B: At. Mol. Opt. Phys.*, **2007**, 40, 3531-3544.

Ligand exchange reactions with Palladium, Platinum doped Au25(SR)18 clusters

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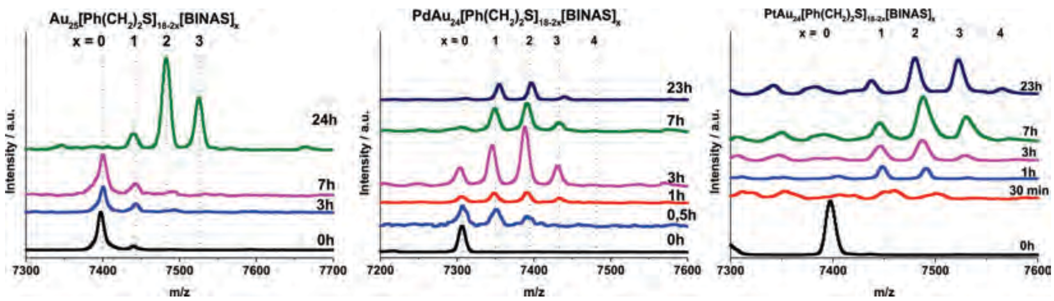
Thiolate protected gold nanoclusters $Au_n(SR)_m$ have gained substantial interest in recent years.[1] They are a well-studied topic because of their exceptional size-dependent physical, chemical and optical properties, related with their discrete molecular-like electronic structure. Recently, hetero-atom doping of the gold clusters was found to be an efficient method to alter the clusters properties, like e.g. stability and reactivity.[2] Another method for post-synthetic modification of the clusters is to perform ligand exchange (LE) reactions.

The effect of Pd/Pt doping on structure and reactivity of $Au_{25}(SR)_{18}$ was studied by performing LE reactions. An interesting chiral bidentate ligand, BINAS (1,1-binaphthyl-2,2-dithiol) was chosen, hence it is expected to induce chirality on achiral $Au_{25}(SR)_{18}$. Following the reported procedure,[3] LE reactions were performed with a 100 fold excess of ligand. Aliquots were taken at defined times and analysed by UV-VIS, MALDI and CD.

The kinetics of the LE reaction reveals a significant increase in reactivity for the doped clusters. MALDI analysis confirms that Pd doping doubles the reactivity of the ligand exchange, while Pt doping increases this reactivity 50 times. (Figure 1) Surprisingly, both monometallic Au25(SR)18 as well as the doped clusters exchange maximum 3 bidentate BINAS ligands in 24h.

It can therefore be stated that Pd and Pt doped Au25(SR)18 samples show a clear enhancement in the ligand exchange reactivity in comparison with monometallic Au25(SR)18.



[1] Kurashige W., Niihori Y., Sharma S., Negishi Y., *J. Phys. Chem. Lett,* **2014**, *5*, 4134
[2] Negishi, Y.,Kurashige W., Niihori Y., Iwasa T., Nobusada K., *Phys Chem Chem Phys,* **2010**, 12, 6219-25.
[3] Knoppe, S., T. Burgi,. *Phys Chem Chem Phys,* **2013**, 15, 15816-20.

Tracking Solvent Controlled Photoinduced Electron Transfer Using Broadband Fluorescence Up-Conversion

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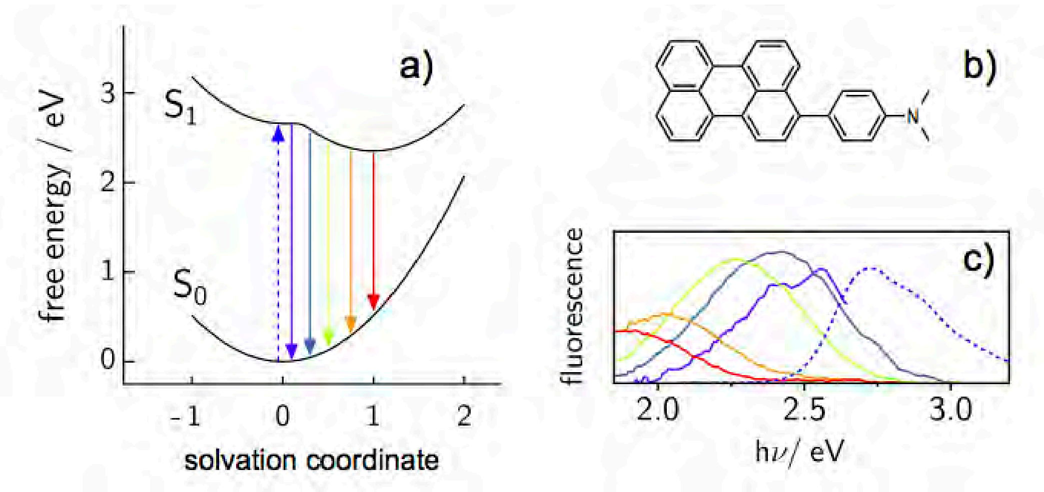
Solvation dynamics is crucial for understanding charge transfer reactions in liquids.[1] Here we revisit the kinetics of a donor-acceptor molecule [2] in several solvents of varying static and dynamic dielectric properties, harnessing the power of femtosecond broadband fluorescence up-conversion [3] and a theoretical model based on the Generalized Smoluchowski Equation approach.[4] By doing so we combine unprecedented photometric resolution, which sheds light on otherwise inaccessible data, with a proper and well-grounded physical description of the phenomenon.



a) Free energy surface for the LE/CT of b). c) Broadband fluorescence spectra at consecutive times allowing to track the reaction progress.

[1] H. Heitele, Angew. Chem. Int. Ed. **1993**, 32, 359.
[2] N. Banerji, G. Angulo, I. Barabanov, and E. Vauthey, J. Phys. Chem. A **2008**, 112, 9665.
[3] K. Tominaga, G. C. Walker, W. Jarzeba, and P. F. Barbara, J. Phys. Chem. **1991**, 95, 10475.
[4] X. X. Zhang, C. Würth, L. Zhao, U. Resch-Genger, N. P. Ernsting, and M. Sajadi, Rev. Sci. Instr. **2011**, 82, 063108.

Ligand exchange reaction of chiral $Pd_2Au_{36}(SR)_{24}$ cluster

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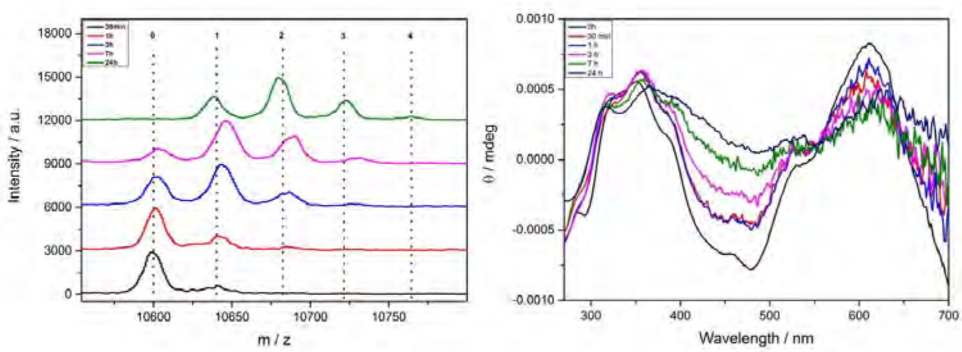
Thiolate-protected gold clusters and heteroatoms doped gold clusters have attracted increased attention by their well-defined structure and size-dependent properties.[1] Among them, the $Au_{38}(SR)_{24}$ cluster bears intrinsically chiral features, which can be altered by ligand exchange reaction.[2] Enhanced stability and catalytic activity of gold nanoclusters have been achieved by Pd doping.[3]In order to study the Pd doping effect on the ligand exchange reaction of $Pd_2Au_{36}(SR)_{24}$ (-SR= 2-Phenylehanethiol), the clockwise enantiomer and chiral ligand R-1,1'-Binaphthyl-2,2'-dithiol (R-BINAS) reaction mixture was monitored by MALDI, UV and CD. MALDI confirmed the presence of the second exchange product after one hour (Figure 1 left), while the second exchanged product of $Au_{38}(SR)_{24}$ clockwise enantiomer has not been observed after 48h. This suggests a greatly enhanced ligand exchange reactivity of $Pd_2Au_{36}(SR)_{24}$. High reactivity offers the possibility to study the chiral properties of multiple exchanged products. Slight change of the anisotropic factor of the ligand exchange mixture was observed after 7h (Figure 1 right), indicating some distortion of the $Pd_2Au_{36}(SR)_{24}$ structure upon ligand exchange.



The ligand exchange reaction of the racemized cluster was followed in-situ by HPLC at reduced reaction rate to compare the ligand exchange reactivity of both enantiomers of $Pd_2Au_{36}(SR)_{24}$. A preference of R-BINAS for the anti-clockwise enantiomer of $Pd_2Au_{36}(SR)_{24}$ is observed.

[1] Jin, R.; Nobusada, K. *Nano Res* **2014**, 7, 285.
[2] Knoppe, S.; Michalet, S.; Burgi, T. *J Phys Chem C* **2013**, 117, 15354.
[3] Niihori, Y.; Kurashige, W.; Matsuzaki, M.; Negishi, Y. *Nanoscale* **2013**, 5, 508.

Chiral Recognition in Bimolecular Photoinduced Electron Transfer

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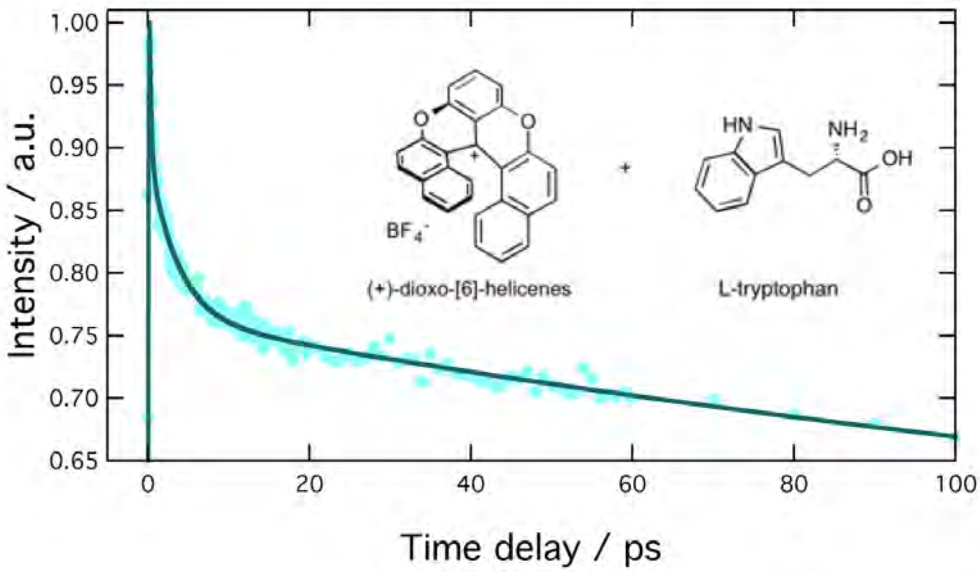
Electron transfer (ET) is one of the simplest and most investigated photochemical reactions[1]. Whereas the influence of many parameters, such as solvent polarity, driving force, on the ET dynamics is rather well understood, the effect of the chirality of the reactants is still unclear. Previous investigations on the ET quenching of chiral fluorophores, such as binaphthyl[2] or metal complex[3] by chiral amines, point to a small effect in weakly polar solvents and did not evidence a significant difference in polar solvents. However, in most of these studies, ET was diffusion controlled, and thus, the effect of chirality might have been hidden.

We will report on our investigation of chiral recognition in bimolecular photoinduced ET in polar solvents using ultrafast spectroscopy. This approach enables the observation of the first stages of the ET quenching where it is dominated by the static and non-stationary regimes, and not influenced by diffusion[4]. The ultrafast quenching dynamics of the two enantiomeric forms of chiral [6]-helicenes fluorophores by has been compared and the differences, which reflect chiral selectivity, will be discussed.



[1] Rosspeintner A., Vauthey E., *Phys. Chem. Chem. Phys.*, **2014**, 16, 25741
[2] Irie M., Yorozu T., Hayashi K., *J. Am. Chem. Soc.*, **1978**, 100, 2236.
[3] Riesgo E. C., Credi A., De Cola L., Thummel R. P., *Inorg. Chem.*, **1998**, 37, 2145.
[4] Rosspeintner A., Angulo G, Vauthey E., *J. Am. Chem. Soc.*, **2014**, 136, 2026

Excited-state dynamics of radical ions

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[1]University of Geneva

Radical ions are of interest for multiple reasons: they are found to be of importance in biochemical and chemical synthesis, organic solar cells, and biological complexes.[1][2][3] They are also of interest due to their role in photoinduced bimolecular electron transfer (ET). Marcus ET theory predicts a decrease of the rate constant with increasing driving force (the Marcus Inverted Region, MIR) and this has been observed for all types of ET reactions save photoinduced bimolecular ET reactions.[4] A hypothesis as to why the MIR is unobserved is that excited radical ion states are first generated, leading to a lower driving force and hence non-MIR behaviour. This was recently given credence with energy redistribution based evidence, however direct observation of generated radical excited states remains elusive.[5]

Using classical methods for radical ion generation, characterisation of the radical excited states using state of the art ultrafast UV-Vis transient absorption (TA) and fluorescence upconversion is possible and enables us to gain novel insight into this important class of ubiquitous though highly transient species. The excited state properties of radical ions of cyanoanthracenes (common electron acceptors) and napthalenediimide derivatives (potentially useful subunits in artificial photosynthesis mimics) will be presented.

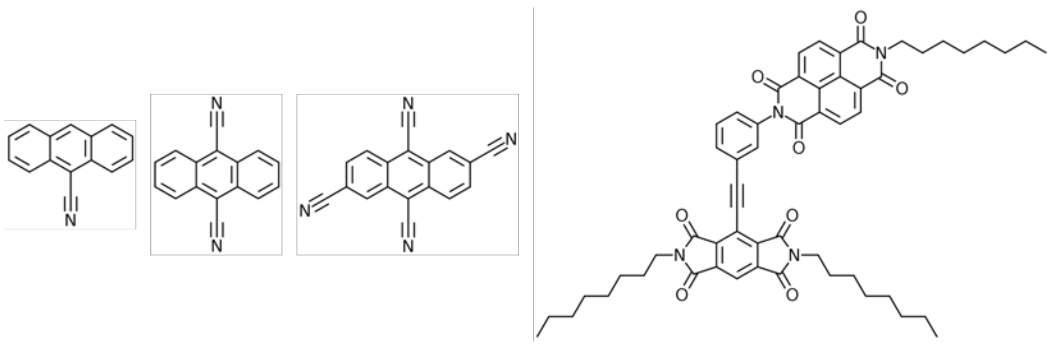

Figure 1: Molecules studied.

[1] L. Ford, U. Jahn, *Agnew. Chem. Int. Ed.,***2009**, 6386-6389
[2] W. Lubitz, F. Lendzian, R. Bittl, *Acc. Chem. Res.,***2002**, 313-320
[3] J. L. Segura, N. Martin, D. M. Guldi, *Chem. Soc. Rev.,***2005**, 31-47
[4] A. Rosspeintner, E. Vauthey, *Phys. Chem. Chem. Phys.,***2014**, 25741-25754

[5] M. Koch, A. Rosspeintner, K. Adamczyk, B. Lang, E. J. Nibbering, E. Vauthey, *J. Am. Chem. Soc.,***2013**, 9843-9848

Separation of chemical shifts and J-couplings using homodecoupled-DIAG spectra

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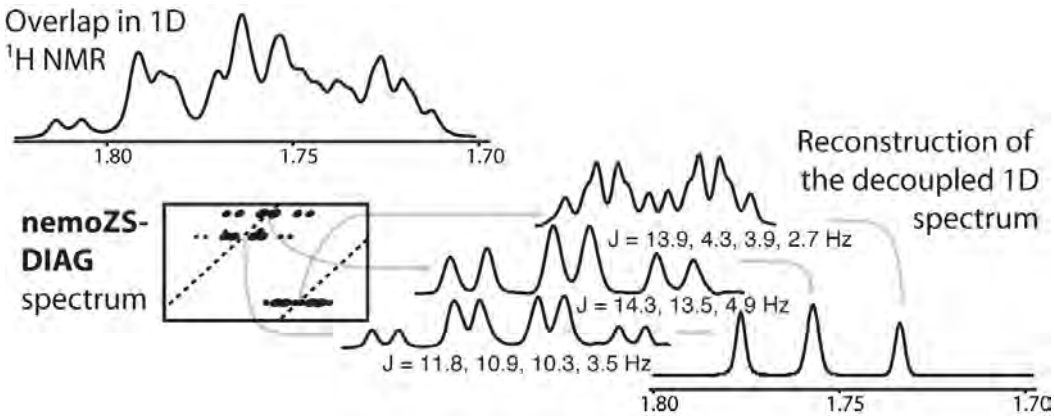
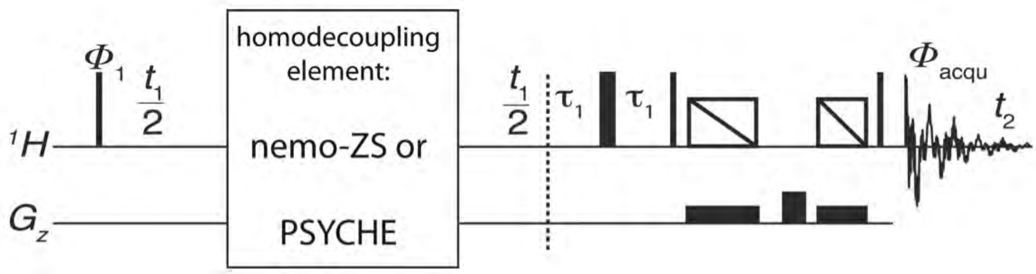
1D ^{1}H NMR spectra containing only singlets can be reconstructed using 2D-DIAG spectra. These two-dimensional homonuclear spectra contain only diagonal signals with singlet structure in F1 and the normal J-coupling multiplets in F2 dimension, respectively.[1]



This experiment uses indirect homodecoupling based on the nemo-ZS or PSYCHE[2] decoupling schemes.

The presence of only narrow signals makes possible applying 100x aliasing to reach very high resolution in a few t1 time increments. The spectra are therefore recorded in a few minutes and provide scalar coupling constants in weakly-coupled systems.



[1] Axelle Cotte, Damien Jeannerat,*Angew. Chem. Int. Ed.*,**2015**,54, 6016-6018.
[2] Mohammadali Foroozandeh, Ralph W. Adams, Nicola J. Meharry, Damien Jeannerat,Mathias Nilsson, Gareth A. Morris,*Angew. Chem. Int. Ed.*,**2014**,53, 6990-6992.

Ultrafast Intersystem-crossing Dynamics and Breakdown of the Kasha-Vavilov's Rule of Naphthalenediimides

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[1]University of Geneva

One of the most important rules in organic photophysics and photochemistry is the Kasha-Vavilov's rule that states that emission takes place from the lowest electronic excited state only, namely the S_1 and T_1 states for closed-shell molecules, and that the emission quantum yields do not depend on the excitation wavelength.

We will report on a red core-substituted naphthalenediimide dye, r(ed)NDI, whose fluorescence quantum yield decreases by a factor of almost 2 by going from $S_1 \leftarrow S_0$ to $S_2 \leftarrow S_0$ excitation. Time-resolved spectroscopic measurements reveal that this deviation from the Kasha-Vavilov's rule is due to an ultrafast, ‹ 200 fs, intersystem-crossing (ISC) from the S_2 state to the triplet manifold, due to the $\pi\pi^* \rightarrow n\pi^*$character of the transition and to the presence of the heavy Br atom. In non-core substituted naphthalenediimide (pNDI), ISC is slower, ~2 ps, and was found to be reversible on a timescale shorter than that of vibrational cooling. The fluorescence and triplet quantum yields of rNDI can thus be substantially changed by a simple variation of the excitation wavelength.

rNDI and pNDI can be used as building blocks for constructing elaborate molecular architectures that show photovoltaic properties (1, 2). The excited-state dynamics of these systems will also be presented.

[1]OleksandrYushchenko, DiegoVillamaina, NaomiSakai, StefanMatile, EricVauthey(submitted).
[2]Naomi Sakai, Marco Lista, Oksana Kel, Shin-ichiro Sakurai, Daniel Emery, Jiri Mareda, Eric Vauthey, Stefan Matile, *J. Am. Chem. Soc.,* **2011,** *133*, 15224-15227.

Time Resolved infrared spectroscopy of Ruthenium(II) tris-bipyridyl complexes

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[1]University of Geneva

The ^{3}dd state is considered to be the dark quenching state for the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ in solution. The energy of the ^{3}dd state can be successfully controlled by adjusting the ruthenium-bipyridyl ligand bond length via ligand substitution.[1] $[Ru(mbpy)_3]^{2+}$ (mbpy = 6-methyl-2,2'-bipyridine) was designed to achieve this function. Ultrafast transient electronic absorption spectroscopy reveals that in this complex the ^{3}MLCT decays within 1.6 ps, while the return to the ground state takes 450 ps.[1] The intermediate state was assigned as ^{3}dd with a lifetime 450 ps. In order to further characterize this intermediate state, we performed time resolved infrared (TRIR) spectroscopy. The C=C double bond is very sensitive to the excess charge.[2] Therefore, the TRIR spectra of the bipyridyl ligand can be used as electron location indicator.[3] One can expect a significantly different TRIR spectrum for the ^{3}MLCT state with the electron localized on the ligand compared to the TRIR spectrum of the ^{3}dd state with the electron localized on ruthenium. This is borne out by the TRIR spectra shown in Figure 1 for $[Ru(bpy)_3]^{2+}$ in the ^{3}MLCT state and for $[Ru(m\text{-}bpy)_3]^{2+}$ in the ^{3}dd state.

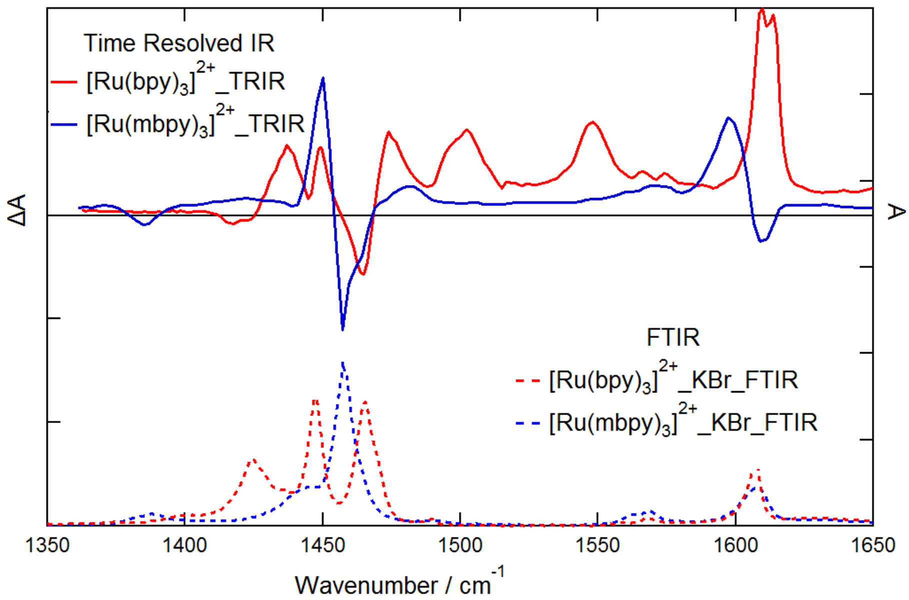

Figure 1. Species-associated difference spectra of $[Ru(bpy)_3]^{2+}$ and $[Ru(mbpy)_3]^{2+}$ in CD_3CN (l_{ex}=400nm) for the long lifetime components. The ground state IR spectra are given for comparison.

References

[1] Q. Sun, S. Mosquera-Vazquez, L. M. L. Daku, L. Guénée, H. A. Goodwin, E. Vauthey, A. Hauser, J. Am. Chem. Soc. 135 (2013) 13660.

[2] T. Mukuta, N. Fukazawa, K. Murata, A. Inagaki, M. Akita, S. Tanaka, S. Koshihara, K. Onda, Inorg. Chem. 53 (2014) 2481.

[3] K.M. Omberg, J.R. Schoonover, A. Treadway, R, M. Leasure, R. B. Dyer, T. J. Meyer, J. Am. Chem. Soc. 119 (1997) 7013.

Structural investigation of the HS toLS relaxation dynamics on the porous coordination network $[Fe(pz)Pt(CN)_4]\cdot xH_2O$

T. Delgado, C. Besnard[1], L. Guénée[1], A. Hauser[1]*

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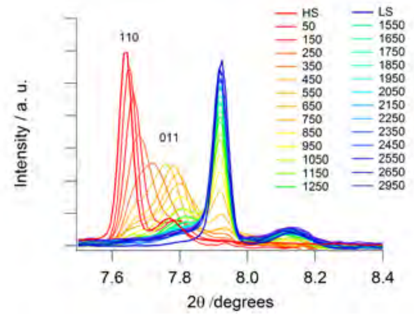
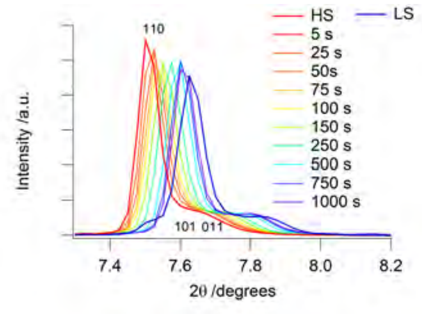
Spin transitions are associated with large structural changes [1]. The metal-ligand bond lengths difference in iron(II) complexes of ~0.2 Å creates elastic interactions between the centres, resulting in cooperative effects that influence the thermal and light-induced spin crossover [2]. Synchrotron X-Ray 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 $[Fe(pz)Pt(CN)_4]\cdot xH_2O$ (pz = pyrazine) [3]. Time-resolved measurements evidence that the HS-to-LS relaxation depends on the particle size. For 1.2 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, whereas by reducing the size to 383 nm no nucleation is observed. In the following figure the time evolution of the (110) and the (011) diffraction peaks during the photo-induced HS→LS relaxation of 1.2 µm (top) and 383 nm particles (bottom) is displayed.





[1] Philippe Guionneau, *Dalton Trans,***2014**, *43*, 382-393.
[2] PhilippeGütlich, Andreas Hauser, Hartmut Spiering, *Angew. Chem. Int. Ed.* **1994**, *33*, 2024-2054.
[3] Teresa Delgado *et al.*, *Chem. Eur. J.* **2015**, *21*, 3664-3670.

Marangoni flow driven maze solving

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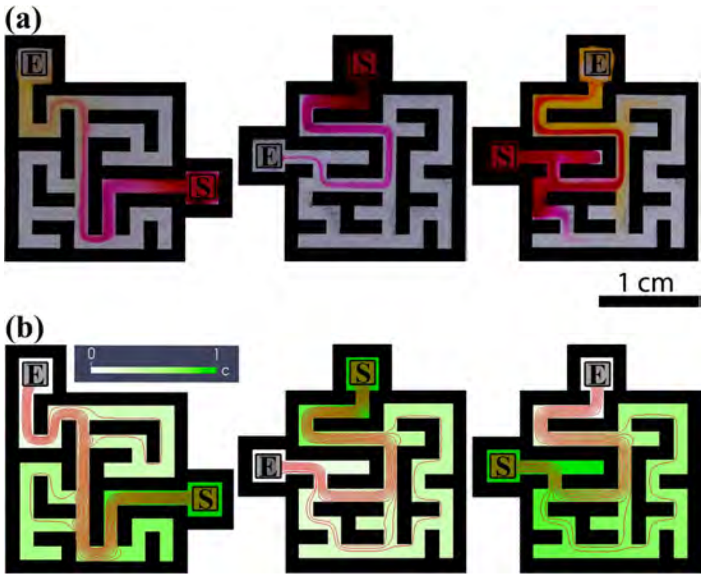
Solving maze problems and finding the shortest path sometimes can be challenging for mathematical algorithms. In this talk we aim to show two chemical methods to solve a maze. We show how the pH- and temperature-induced Marangoni flow can be of utility for finding the shortest path and all possible paths in a maze. The pH or temperature gradient applied between the entrance and exit of the maze creates a surface tension gradient. This surface tension gradient induces the flow of the fatty acid solution in the maze in the direction of the exit at the liquid-air interface. When dye particles are placed at the entrance of the maze on the surface of the solution, they make the shortest path visible by dissolving during their motion to the exit. The longer paths are shown later by the less intense flow. The pH or temperature gradient are the largest along the shortest path indicated by the most intense colour of the dissolved dye particles.



Kohta Suzuno, Daishin Ueyama, Michal Branicki, Rita Tóth, Artur Braun, and István Lagzi, Langmuir, **2014**, 30, 9251

Identification of Gas-Phase-Active Reactive Intermediates in Thermal Decomposition of Organophosphorus Compounds

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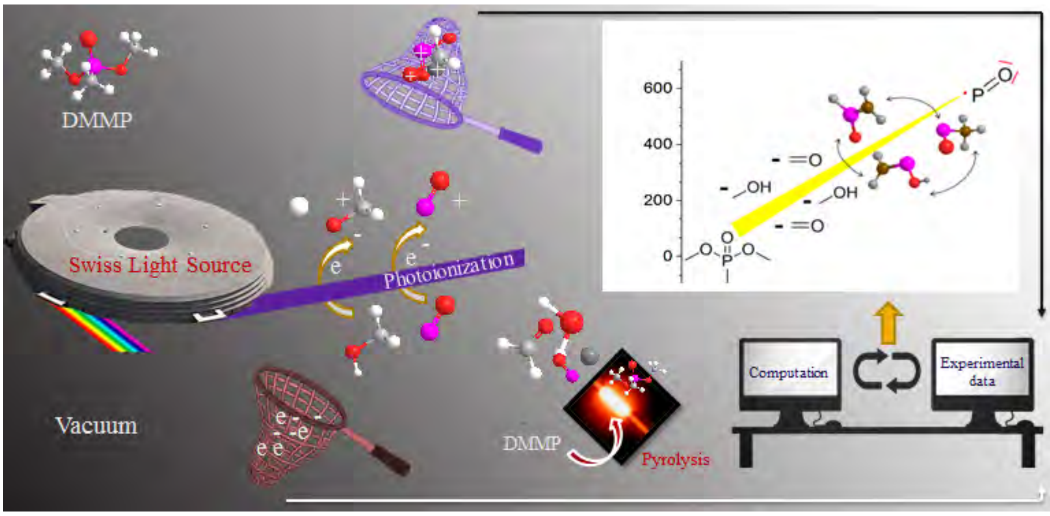
[1]EMPA, [2]Paul Scherrer Institute, Villigen, [3]ETH Zurich, [4]EMPA

The production of phosphoryl species such as PO, PO_2 is believed to be of great importance for efficient flame retardant action in the gas phase [1, 2]. In this study we carry out a detailed investigation on identifying the gas-phase-active reactive intermediate formed in thermolysis of organophosphorus compounds using vacuum ultraviolet (VUV) synchrotron radiation and imaging photoelectron photoion coincidence (iPEPICO) spectroscopy (Fig. 1)[1,2]. This technique provides a timely snapshot of the decomposition process and direct evidence of how the reactive phosphoryl species are generated during heat exposure. One of the key findings of this work is that only PO is formed in high concentration upon DMMP decomposition at elevated temperatures, whereas PO_2 is absent. It can be concluded that the formation of PO_2 needs an oxidative environment. Bolstered by DFT and CBS-QB3 computations and based on the identification of decomposition products such as methanol, formaldehyde and PO, as well as intermediates like O=P-CH_3, H_2C=P-OH and H_2C=P(=O)H, we propose the predominant pathways leading to active phosphoryl species during the thermal decomposition of DMMP (Fig. 1) [3]. Moreover, new data for another important molecule, dimethyl phosphoramidate (DMP), will be further presented and discussed.



[1] Twarowski, A. Combustion and Flame, 1993. 94(1–2): p. 91-107 [2] Liang, S.; Neisius, M.; Mispreuve, H.; Naescher, R. and Gaan, S. Polymer Degradation and Stability, 2012, 97, 2428-2440 [3] Bodi, A.; Johnson, M.; Gerber, T.; Gengeliczki, Z.;Sztáray, B. and Baer, T. Review of Scientific Instruments, 2009, 80, 034101 [4] Liang, S.; Hemberger, P.; Neisius, M.; Bodi, A.; Grützmacher, H.; Levalois-Grützmacher, J. and Gaan, S. Chemistry – A European Journal 2015, 21, 1073-1080.

Exact versus approximate methods for nonadiabatic quantum molecular dynamics induced by the interaction with the electromagnetic field

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We have implemented a general split-operator/Magnus integrator algorithm of arbitrary order in accuracy for exact nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. Then, we have derived and implemented analogous geometric integrators of arbitrary order of accuracy for several approximations of treating the molecule-field interaction: the time-dependent perturbation theory, Condon, rotating-wave, and ultrashort pulse approximations. Our general and efficient implementation permits every possible combination of these basic approximations, allowing testing the validity of each approximation under the experimental conditions independently. The algorithms are applied to one-dimensional harmonic systems and to the multidimensional vibronic coupling model of pyrazine in order to compare the exact and approximate descriptions of the photoexcitation process with a single laser pulse of finite length as well as nonadiabatic quantum dynamics induced by pump and probe laser pulses.

Hyperpolarized para-ethanol

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[1]ISIC, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland., [2]Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Gif-sur-Yvette, France, [3]Département de Chimie, École Normale Supérieure, 24 rue Lhomond, 75005 Paris, France

Two of the major limitations of Nuclear Magnetic Resonance (NMR) are the low intrinsic sensitivity (normally governed by Boltzmann's law) and the short lifetime of nuclear magnetization (usually limited by the longitudinal relaxation time constant T_1).

Dissolution Dynamic Nuclear Polarization (DNP)[1] is a powerful technique to enhance NMR or Magnetic Resonance Imaging (MRI) signals by up to five orders of magnitude. DNP provides a unique way to study biological systems *in-vitro* and *in-vivo*: the main drawback is that DNP-enhanced states rapidly decay with the time constant T_1. Long-Lived States (LLS)[2] are nuclear spin states with lifetimes T_{LLS} that can be much longer than T_1. In a two-spin system, they correspond to a "Triplet/Singlet Imbalance" (TSI)[3], induced by perturbing the equilibrium between the average of the populations of the three triplet states and the population of the singlet state. *Para*-hydrogen is the prototypical molecule with a large TSI, made observable by using chemical reactions such as additions onto double bonds that break the symmetry of the two hydrogen nuclei[4].

We have shown[5] that it is possible to create a TSI by D-DNP in a pair of magnetically equivalent protons in partly deuterated ethanol $CD_3{}^{13}CH_2OD$ because the population of the singlet state is depleted at very low spin temperatures on the order of 10 mK at 6.7 T. Unlike *para*-hydrogen, no further preparation methods are required: the TSI can be observed because cross-relaxation leads to population differences across observable transitions of either ^1H or ^{13}C spins, in natural abundance. In our experiments we used DNP at T = 1.2 K and transferred the sample through a magnetic tunnel (B = 0.9 T) to a 500 MHz NMR spectrometer at room temperature. We observed non-binomial ^{13}C triplets and anti-phase ^1H doublets. These signals are enhanced by up to two orders of magnitude (with respect to Boltzmann's polarization in thermal equilibrium) and their lifetimes are longer than T_1. Simulations using *SpinDynamica* confirmed that these enhanced and long-lived non-binomial multiplets indeed result from TSI.

Our experimental scheme is applicable to virtually any molecule comprising a $^{13}CH_2$ group in natural abundance, without requiring any chemical reaction prior to detection. This technique could be used as a tracer to obtain biochemical and biophysical information in NMR or MRI when the molecules of interest have short-lived signals that are too weak to be studied by conventional methods.

(1) Ardenkjaer-Larsen, J. H.; Fridlund, B.; Gram, A.; Hansson, G.; Hansson, L.; Lerche, M. H.; Servin, R.; Thaning, M.; Golman, K. Increase in Signal-to-Noise Ratio of 10,000 Times in Liquid-State NMR. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100* (18), 10158–10163.
(2) Carravetta, M.; Johannessen, O. G.; Levitt, M. H. Beyond the T-1 Limit: Singlet Nuclear Spin States in Low Magnetic Fields. *Phys. Rev. Lett.* **2004**, *92* (15), 153003.
(3) Meier, B.; Dumez, J.-N.; Stevanato, G.; Hill-Cousins, J. T.; Roy, S. S.; Hakansson, P.; Mamone, S.; Brown, R. C. D.; Pileio, G.; Levitt, M. H. Long-Lived Nuclear Spin States in Methyl Groups and Quantum-Rotor-Induced Polarization. *J. Am. Chem. Soc.* **2013**, *135* (50), 18746–18749.
(4) Bowers, C. R.; Weitekamp, D. P. Transformation of Symmetrization Order to Nuclear-Spin Magnetization by Chemical Reaction and Nuclear Magnetic Resonance. *Phys. Rev. Lett.* **1986**, *57* (21), 2645–2648.
(5) Mammoli, D.; Vuichoud, B.; Bornet, A.; Milani, J.; Dumez, J.-N.; Jannin, S.; Bodenhausen, G. Hyperpolarized *para* -Ethanol. *J. Phys. Chem. B* **2015**, *119* (10), 4048–4052.

Excitonic Effects and Optical Spectra of Single Walled Carbon Nanotubes for Biosensor Applications in Life Sciences and Medicine

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Single Walled Carbon Nanotubes (SWCNTs) are rolled up sheets of graphene that yield long, nanoscale cylinders. The sheets can be rolled in different directions, and the specific angle with which the sheet is rolled determines nanotube properties such as diameter and band gap [1]. Semiconducting SWCNTs produce photo-stable, near-infrared fluorescence emissions that are sensitive to the nanotube's environment, allowing these nanostructures to be used as optical nanosensors. In these nanosensors, the SWCNTs are coated with a polymer wrapping that controls the sensor's selectivity by modulating the surface coverage of the nanotube in the presence of an analyte (Figure 1). The optical response of the polymer-wrapped SWCNTs is governed by the exciton states. The 1D quantum confinement of photogenerated excitons in the SWCNTs can amplify the detection of adsorption and desorption events, realising sensors with single-molecule sensitivities [2]. Single-molecule adsorption and desorption events on the nanotube surface result in stochastic changes in SWCNT fluorescence [3].

This presentation explores the exciton dynamics of single-molecule SWCNT sensors. Random walk analysis of the fluorescence emissions is used to provide a quantitative and physical assessment of reversible binding events [4]. The quantum efficiency of light emission is computed as a function of both radiative and non-radiative, environmentally dependent, exciton life-times. Based on many-body effects in the dielectric function, we further explore exciton dynamics in polymer-wrapped nanotubes as a quasi-1D system, challenging conventional underlying assumptions of uni-dimensionality.

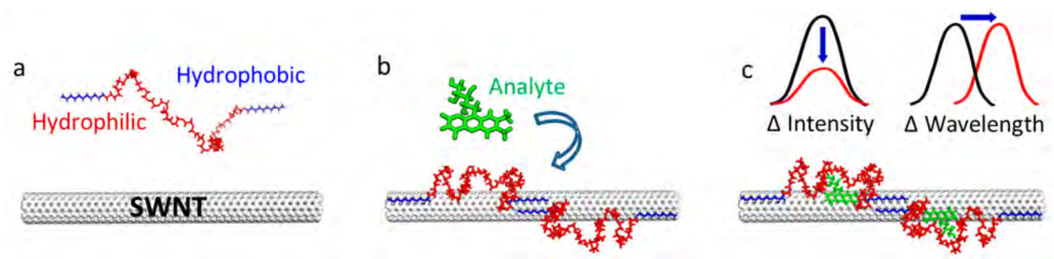

Figure 1 Polymer consisting of hydrophobic and hydrophilic parts (**a**) with a specific conformation when (**b**) adsorbed to SWCNT to allow analyte binding. Selective binding of the analyte (**c**) results in a wavelength and/or intensity alteration in SWCNT fluorescence (borrowed from [5]).

[1] S. Iijima, Nature **354**, 56 (1991).
[2] J. Zhang, A. A. Boghossian, P. W. Barone, A. Rwei, J. H. Kim, D. Lin, D. A. Heller, A. J. Hilmer, N. Nair, N. F. Reuel, and M. Strano, J. Am. Chem. Soc. **133**, 567 (2011).
[3] A. A. Boghossian, J. Zhang, F. T. Le Floch-Yin, Z. W. Ulissi, P. Bojo, J. H. Han, J. H. Kim, J. R. Arkalgud, N. F. Reuel, R. D. Braatz, and M. Strano, J. Chem. Phys. **135**, 084124 (2011).
[4] D. M. Harrah and A. K. Swan, ASC Nano **5**, 647 (2011).
[5] J. Zhang, M. P. Landry, P. W. Barone, J. Kim, S. Lin, Z. W. Ulissi, D. Lin, B. Mu, A. A. Boghossian, A. J. Hilmer, *et al*. Nature Nanotechn. **8**, 959 (2013).

Studying Xe Migration in Truncated Hemoglobin with Molecular Dynamics Simulations

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In metalloproteins, the physicochemical characterization of the network that allows the migration of gas molecules towards the active site is essential for obtaining a better understanding of their function. For such a study, xenon is experimentally considered to be an appropriate analogue of ligands like O_2 and NO, due to its solubility in hydrophobic environments and its Van der Waals radius. Recently, the migration of Xe atoms in cytochrome *bα3* oxidase was investigated through crystallographic studies ([1], [2]), which allowed both the identification of the binding sites and their occupancy, as well as the determination of the kinetic rate constants for transitions between these sites. In the present work, we investigate the migration of Xe in truncated hemoglobin N (TrHbN), through classical molecular dynamics simulations. The main Xe binding sites in this protein have been determined experimentally [3], [4]. The resulting kinetic model, as well as the occupancy of the binding sites, will be compared to the results obtained from previous computational studies on the migration of NO and O_2 in TrHbN [5]-[8]. Mutations will also be considered, in order to assess the extent to which they affect Xe migration.

[1] V.M. Luna, Y. Chen, J.A. Fee, C. D. Stout, *Biochem.*, **2008**, *47*, 4657
[2] V.M. Luna, J.A. Fee, A.A. Deniz, C. D. Stout, *Biochem.*, **2012**, *51*, 4669
[3] M. Milani, A. Pesce, Y. Ouellet, P. Ascenzi, M. Guertin, M. Bolognesi, *EMBO J.*, **2001**, *20*, 3902
[4] M. Milani, A. Pesce, Y. Ouellet, S. Dewilde, J. Friedman, P. Ascenzi, M. Guertin, M. Bolognesi, *J. Biol. Chem.*, **2004**, *279*, 21520
[5] S.Mishra, M. Meuwly, *Biophys. J.*, **2009**, *96*, 2115
[6] S.Mishra, M. Meuwly, *Biophys. J.*, **2010**, *99*, 3969
[7] P.A. Cazade, M. Meuwly, *Chem. Phys. Chem.*, **2012**, *13*, 4276
[8] P.A. Cazade, W. Zheng, D. Prada-Gracia, G. Berezofska, F. Rao, C. Clementi, M. Meuwly, *J. Chem. Phys.*, **2015**, *142*, article no 025103

Tunneling in molecules probed by high-resolution photoelectron spectroscopy

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Removal of an electron from a stable and rigid neutral molecule often results in less stable and semi-rigid singly-charged cations which are subject to large-amplitude motion and quantum-mechanical tunneling. High-resolution photoelectron spectroscopy provides access to the structure and geometry of such cations. Moreover, the distribution of Franck-Condon factors favors the observation of the vibrational modes most strongly a ffected by the electron removal.

We use pulsed-field ionization zero-kinetic-energy photoelectron spectroscopy to study large-amplitude motion in cations such as butatriene in which photoionization is induced out of double bonds. The photoionization process in these molecules is of particular interest as it introduces torsional flexibility and quantum-mechanical tunneling between equivalent structures along the torsional coordinate.

Spectroscopy of Rydberg Helium in Electric and Magnetic Fields

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The deceleration and trapping of atoms and molecules attracted great attention in recent years [1,2]. Currently, a higher phase-space density of trapped atoms and molecules is desirable to allow further study of these trapped atoms, for example by high-resolution spectroscopy. One of the proposed mechanisms is to decelerate and trap triplet helium in a Rydberg state using electric fields. These Rydberg states are short lived (~µs) and they decay into the metastable triplet state, which is trapped using a magnetic field. This cycle will be repeated for several gas pulses to increase phase-space density of trapped He atoms. Since the trap consists of combined electric and magnetic fields, the effects of these fields on Rydberg states of helium need to be characterized. We measured the spectra of transitions to Rydberg states of He 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. The spectra were also calculated by diagonalization of the Hamiltonian matrix. If a pure electric or a pure magnetic field is applied, the orbital angular momentum quantum number, l, is no longer a good quantum number. Only the projection of the orbital angular momentum onto the axis of the field, $\hbar m$, is a constant of motion. The same is true for parallel electric and magnetic fields. However, when the fields are not parallel, the cylindrical symmetry is broken and m is not a good quantum number any more. As the symmetry of the problem is reduced, the complexity of the spectra is increased and the theoretical description becomes challenging. Our study indicates a scheme for continuous trap loading of helium in a combined electric and magnetic trap.

[1] Hogan Stephen D., Motsch Michael, and Merkt Frédéric, *Physical Chemistry Chemical Physics,* **2011,** 13, 18705-18723.
[2] van de Meerakker Sebastiaan Y. T., Bethlem Hendrick L., Vanhaecke Nicolas, and Meijer Gerard, *Chemical Reviews,***2012,** 112, 4828-4878 .

Kinetics of platinum oxidation

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Supported platinum nanoparticles are widely used as oxidation catalysts in industry. For any oxidation process using oxygen as the oxidant, its activation is a crucial step in the reaction. The activation of oxygen over platinum single crystals is relatively well understood and recently both experimentally and theoretically described. How nano-sized particles, which are the commercially applied catalysts, behave is much less known. To investigate how the kinetics of platinum oxidation depends on the oxidation state of platinum, the oxidation of platinum was studied by *in situ* XANES on a Pt/Al_2O_3 catalyst under catalytically relevant oxygen partial pressures.

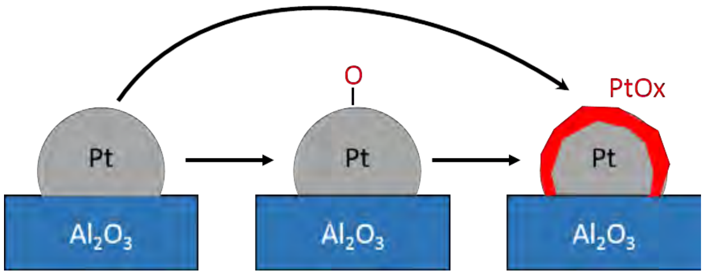

Figure 1: Possible mechanism for platinum nanoparticle oxidation. The oxidation can either proceed through a chemisorbed oxygen intermediate, or directly lead to the formation of a platinum surface oxide.

Time resolved XANES measurements of the platinum catalysts revealed that the oxidation of platinum particles cannot be well described by a single rate law over its entire range, indicating that the oxidation of platinum nanoparticles proceeds in multiple stages. The oxidation proceeds initially faster, but overall more slowly, on a completely reduced sample compared to a slightly pre-oxidized one. These results show that the oxidation of a platinum nanoparticle is a complex process involving the possible formation of intermediates (Figure 1), depending on the sample pretreatment history. These results have important implications for catalysis, since it suggests that oxygen activation rates are highly dependent on catalyst oxidation state. In fact, we observed a strong effect of catalyst pretreatment on its oxidation behavior.

Single walled Carbon nanotubes-based composites for hybrid organic photovoltaic application

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Keywords: Carbon nanotubes; Photovoltaic; Optoelectronic properties; Conjugated polymers.

We report on the incorporation of carbon nanomaterials (CNMs) such as single-walled carbon nanotubes (SWCNTs) into organic PV (OPV) cells for efficiency optimization. Although CNMs have been used before in OPVs, the focus is put here to elucidate the effect of the structural properties of the CNMs on OPV performance, which is poorly understood. More specifically, we address the issue of improving the performance of a new hybrid OPV device by combining the physical and chemical characteristics of light-sensitive conjugated polymers (CP), e.g. P3HT, with the high electrical conductivity of SWCNTs by blending the both in a composite photoactive layer. The focus is put on exploring in depth the electronic and optoelectronic properties of the composite material in an OPV scheme and exploring its corresponding photo-conversion capability. The root-mean-square roughness, photoluminescence and optical absorption were found to increase with increasing SWCNTs content and a non linear correlation between the nanotubes loads and the open circuit voltage V_{OC} was clearly pointed-out. Our best performances were obtained with 2.5 wt. % SWCNTs concentration, with a V_{OC} of 0.78 V and a power conversion efficiency of 3.65 %.

Gas-phase Microsolvation of an Adenine Analogue

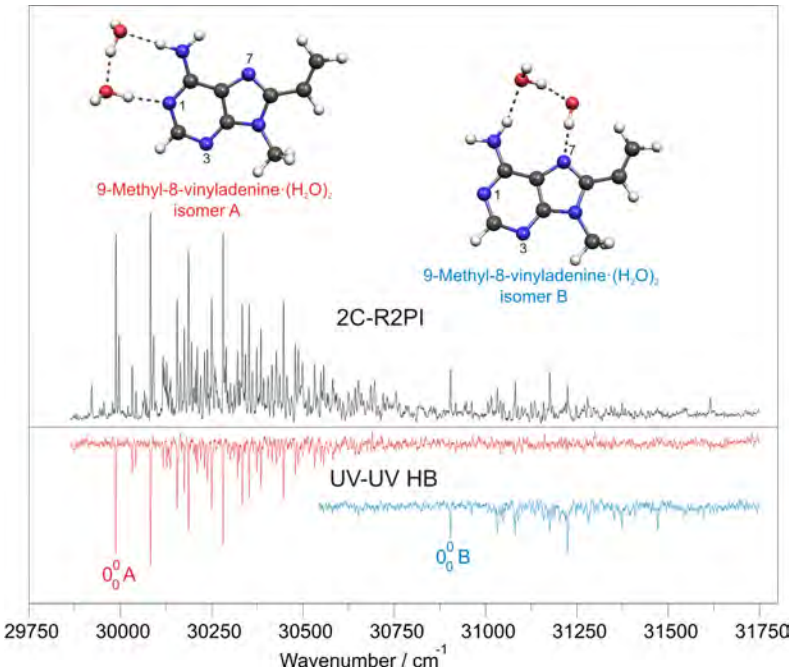
L. Siffert[1], S. Lobsiger[1], S. Leutwyler[1]*

[1]University of Bern

Understanding the excited state relaxation pathways of nucleobases is of great importance to understand the underlying protection mechanisms of the DNA radiation-induced damage.[1] Lobsiger et al. have shown for another adenine analogue that the site specific hydration is of great importance.[2]

The mass-selective two-color resonant two-photon ionization (2C-R2PI) and UV-UV hole-burning (UV-UV HB) spectra of supersonic jet-cooled 9-methyl-8-vinyladenine·$(H_2O)_n$ clusters (9M8VA·$(H_2O)_n$) with n=0-3 have been measured to investigate the hydration pattern of an adenine analogue. Our results show several isomers for each cluster size, the cis orientation of the vinyl group is more stable than the trans. Most microhydrate isomers involve H-bonds to the N(1) position and 2-amino group, a less stable isomer exhibits an analogous H-bond pattern at the N(7) position, as shown in the figure.

Delayed ionization measurements of 9M8VA as well as of the different water clusters have been recorded to investigate the excited state lifetimes and deduce the relaxation pathways.



[1] K. Kleinermanns, D. Nachtigallova, M. S. de Vries, *Int. Rev. Phys. Chem.*, **2013**, 32, 2, 308-342
[2] S. Lobsiger, S. Blaser, R. K. Sinha, H.-M. Frey, S. Leutwyler, *Nature Chemistry*, **2014**, 6, 998-993

Jet-Cooled UV-Spectra and Nonradiative Relaxation Dynamics of N1-Substituted Cytosines

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

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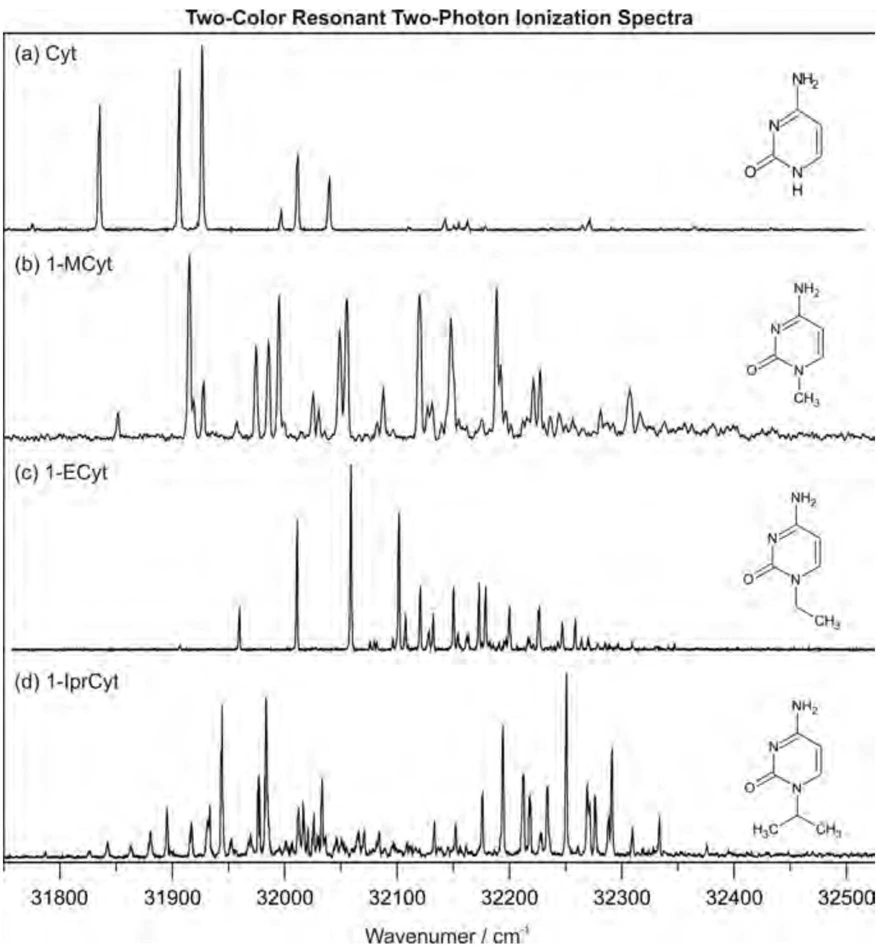
In the biological context cytosine occurs in the form of (deoxy)cytidine, which carries a (deoxy)ribose substituent at the N1 atom of cytosine. In order to mimic cytidine, we have investigated a series of cytosine derivatives substituted at the N1 position that increasingly resemble the biologically relevant nucleoside. We have measured the vibronically resolved two-color resonant two-photon ionization (2C-R2PI) spectra of jet-cooled cytosine (Cyt), [1] 1-methylcytosine (1-MCyt), 1-ethylcytosine (1-ECyt), 1-isopropylcytosine (1-IprCyt) and 1-(2-tetrahydrofuranyl)cytosine (1-THFCyt).

Picosecond pump / ionization delay measurements of 1-ethylcytosine revealed a surprisingly long lifetime of τ_{fl} ~1.1 ns. The vibronic lifetimes decrease with increasing vibrational excess energy.



[1] S. Lobsiger, M. A. Trachsel, H.-M. Frey, S. Leutwyler, *J. Phys. Chem. B*, **2013**, 117, 6106-6115.

Unusually long-lived transient negative ion of c-C_4F_8O formed by electron impact ionisation

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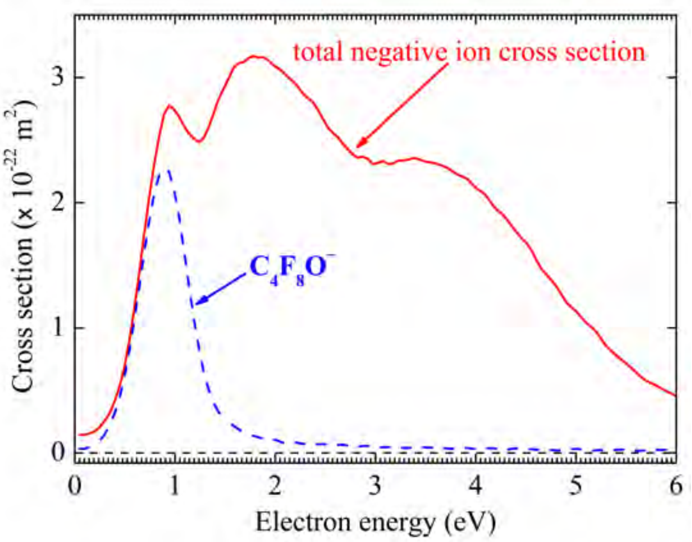
The cyclic ether perfluorotetrahydrofuran (octafluorotetrahydrofuran, c-C_4F_8O) recently attracted considerable attention due to its electron attachment properties with many practical applications. This molecule promises to be a suitable alternative for plasma processing gasses. It has already been applied in Cherenkov radiation detectors [1], and it might effectively replace the high voltage insulating gasses (primarily SF_6) as it is environmentally more acceptable [2]. Since the fundamental electron driven processes of c-C_4F_8O are not well known, we have performed a detailed experimental study.
The experiment has been performed using a quantitative dissociative electron attachment (DEA) spectrometer with trochoidal electron monochromator in combination with ion time-of-flight (TOF) analyzer [3]. The measurements for absolute cross sections have been executed in a mixture of studied molecule c-C_4F_8O together with CO_2 and HCOOH used as calibration gasses with known cross sections and positions of resonances [4].



Dissociative and non-dissociative electron attachment to octafluorotetrahydrofuran (c-C4F8O) has been experimentally investigated.We present the partial absolute cross sections for negative-ion formation from electron attachment to c-C_4F_8O in the energy range 0-6 eV. We have observed rich fragmentation pattern from dissociative electron attachment at electron energies ~1.7 eV, ~2.5 eV and ~3.4 eV. We have recorded an extraordinarily long-lived (parent) negative ion (m/z = 216) formed at at non-thermal incident electron energy of 0.9 eV. We have explained the unusually long lifetime of the parent anion ($C_4F_8O^-$) as a consequence of very different geometries of the neutral molecule and the anion, and of high vibrational level density due to low frequencies of C-F vibrations. The long lifetime accounts for effective three-body attachment and it is thus crucial for the interpretation of high pressure electron transport data.

[1] M. Artuso et al, Nucl. Instrum Meth. A, **2006**,558
[2] K. J. Kim et al, J. Vac. Sci. Technol. B,**2004**,22
[3] O. May et al, Phys. Rev. A, **2009**,80
[4] R. Janečková et al, Phys. Rev. Lett., **2013**,111

Directional Energy Migration in Nanoparticles of Crystalline Transition Metal Complexes

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[1]University of Geneva, [2]University of California Berkeley, [3]Université de Versailles

A reverse micelle technique was used to prepare size-controlled tetrahedral nanocrystals of 140 and 670 nm and microcrystals of 2.5 mm edge lengths of $[Ru(bpy)_3][NaCr(ox)_3]$, ox = oxalate, bpy = 2,2'-bipyridine, where $[NaCr(ox)_3]^{2-}$ forms a three-dimensional network. The photophysical properties of the Cr^{3+} chromophores in these systems were investigated by high-resolution optical spectroscopy at low temperature and compared to the energy migration properties of Cr^{3+} in 4 mm microparticles [1] prepared by fast precipitation. Significant differences in the luminescence spectra of nanoparticles are observed compared to the luminescence spectrum of the 4 mm microparticles after laser excitation at 532 nm at 4 K (see Figure 1). For the larger particles the luminescence originates from the R_1 line of the ^2E emission of bulk $[Cr(ox)_3]^{3-}$ chromophores. Time-resolved fluorescence line narrowing techniques demonstrate that for the smaller particles, the luminescence of the lower energy broad band originates from chromophores at or near the surface having their ^2E state at lower energy. These are excited via directional energy transfer from the initially excited chromophores in the bulk of the particles [2].
b

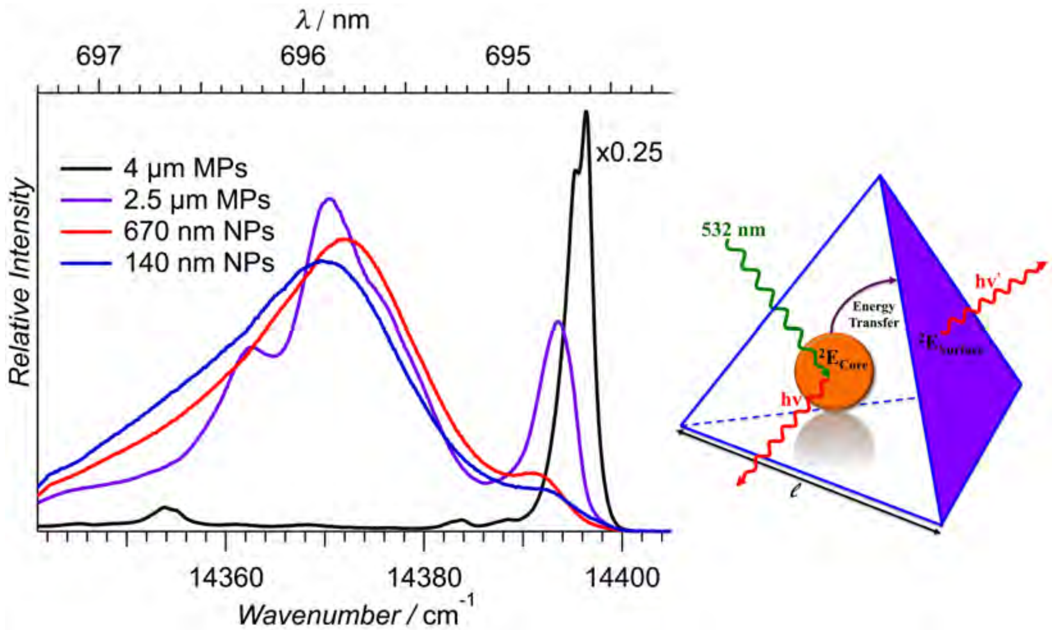

Figure 1. Luminescence spectra in the region of the ^2E-$^4A_2$ transition of Cr^{3+} in particles of $[Ru(bpy)_3][NaCr(ox)_3]$ of different size at 4.2 K on excitation at 532 nm.

[1] M. Milos, S. Kairouani, S. Rabaste, A. Hauser, *Coor. Chem. Rev.* **2008**, *252*, 2540.
[2]. E. Previtera, A. Tissot, R. W. Johns, A. Hauser, *Adv. Mater.* **2015**, *27*, 1832-1836.

Nanoparticle – polyelectrolyte composites: Enhanced IR absorption and electron transfer upon visible light illumination

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[1]University of Geneva

Attenuated total reflection infrared (ATR-IR) spectroscopy and scanning electron microscopy (SEM) are used to study the enhancement and the properties of nanoparticle-polyelectrolyte composites on a Ge internal reflection element. First the Ge ATR crystal is functionalized by a positively charged polyelectrolyte poly (allylamine hydrochloride) (PAH). Then negatively charged citrate-stabilized nanoparticles (gold, silver) are adsorbed onto the modified Ge ATR crystal. The layer-by-layer growth of polyelectrolytes (PAH and PSS; poly (sodium 4-styrenesulfonate)) on top of the nanoparticles is followed in situ. It is observed that enhancement is more pronounced for larger nanoparticles and it decreases with increasing distance from the particles surface. Furthermore at high nanoparticle coverage the signal from the first polyelectrolyte layer is particularly enhanced and the signal increases slowly with time compared to subsequent layers. We assign this to polyelectrolyte adsorption within narrow gaps between nanoparticles, where the electric field is enhanced (Figure 1). Furthermore enhanced absorption was observed in the gap between the nanoparticles and the Ge internal element, which was confirmed by polarized measurements. This enhancement is more pronounced for silver particles and it represents a promising route for analysis of surfaces by infrared spectroscopy. On the other hand, upon illumination of gold nanoparticles adsorbed on PAH-functionalized Ge with visible and near infrared light, a strong infrared absorption has been observed, which can be traced to intervalence band transitions in Ge. This reveals the existence of holes in the Ge near its valence band edge. The effect develops with a peculiar kinetics, which may indicate the development of an interfacial layer between germanium and gold that allows efficient electron transfer upon illumination.

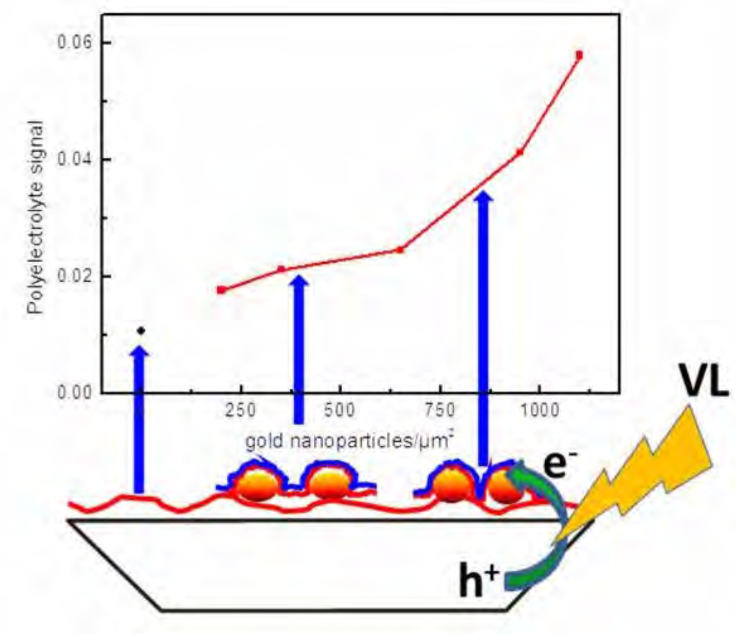

Figure 1. Enhancement of polyelectrolyte signal from nanoparticles surface and electron transfer upon visible light illumination.

1. Ghosh H., Bürgi T., J. Phys. Chem. C 2013, 117, 26652–26658.
2. Ghosh H., Bouhekka A., Bürgi T., Phys. Chem. Chem. Phys. 2014, 16, 19402-19407.

Concentration dependent kinetic model of the energy transfer of Eu^{2+} in $SrAl_2O_4$ including thermal quenching processes

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[1]University of Geneva, [2]EMPA

$SrAl_2O_4$ doped with Eu^{2+} and other rare earth ions is one of the best persistent phosphors known [1]. The Eu^{2+}-ions are located on the two different sites of the Sr^{2+}-ions [2], leading to 2 emission bands at 430 and 520 nm respectively. The energy transfer from one site to the other in this material is studied as a function of Eu^{2+} concentration (0.01% to 3 % relative to Sr^{2+}) with temperature dependent lifetime measurements and luminescence spectra. A quantitative kinetic model including thermal quenching consistent with the experimental data is presented.

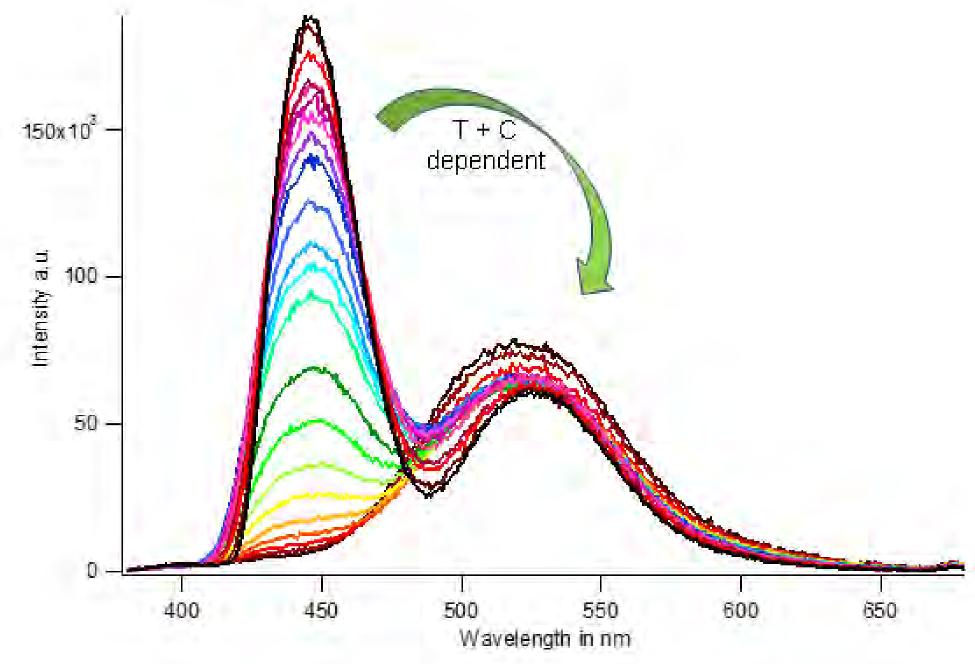

Figure 1 Temperature dependent emission Spectra of $SrAl_2O_4$ doped with Eu^{2+} from 8K to 300K

This work is supported by the Swiss National Science Foundation.

[1]T. Matsuzawa et. al., *J. Electrochem. Soc*. **1996**, 143, 2670-2673.
[2] S.H.M. Poort, W.P. Blokpoel G. Blasse, *Chem. Mater*. **1995**, 7, 1547-1551.

Gold nanowire fabrication with lipid nanotubes

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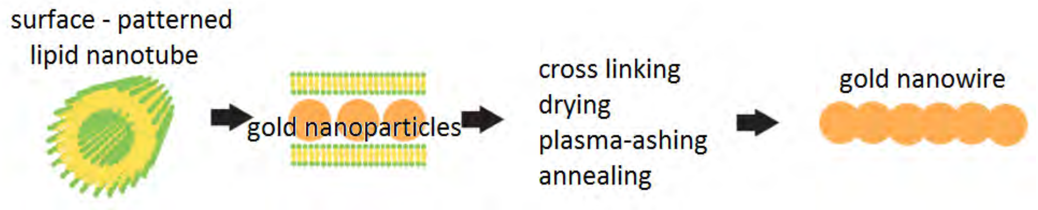
[1]Geneva University, [2]University of Geneva

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. It is well recognized that gold is a highly stable metal at the nanometer scale and because of its unique properties various research have been focused on the fabrication of one-dimensional gold nanostructures. Gold nanowires in particular have many advantages such as large surface area, excellent electrical conductivity and biocompatibility. Here we demonstrate a technique to convert self-assembled lipid nanotubes (LNTs) into gold nanowires using lipids as an organic template. First, lipid blocks in inverted hexagonal phase are formed with 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE) in a buffer solution with gold nanoparticles (GNPs), enabling GNP encapsulation inside the lipid blocks. Second, GNP-encapsulated lipid blocks are adsorbed on a polyethyleneimine (PEI)-coated surface. Upon application of a shear force, it has been previously found that LNTs self-assemble from the lipid blocks. Subsequently, the GNP-encapsulated LNTs are cross-linked by chemical fixation and dried. Third, lipid templates are removed by plasma-ashing, and final annealing melts the GNPs into connected nanowires. This method is simple and offers the possibility to nano-pattern gold nanowires without using expensive electron-beam lithography.



Raman optical Activity of chiral (6,5) Single Walled Carbon Nanotubes

M. Magg[1], Y. Kadria-Vili[2], S. Luber[3], B. R. Weisman[2]*, T. Bürgi[1]*

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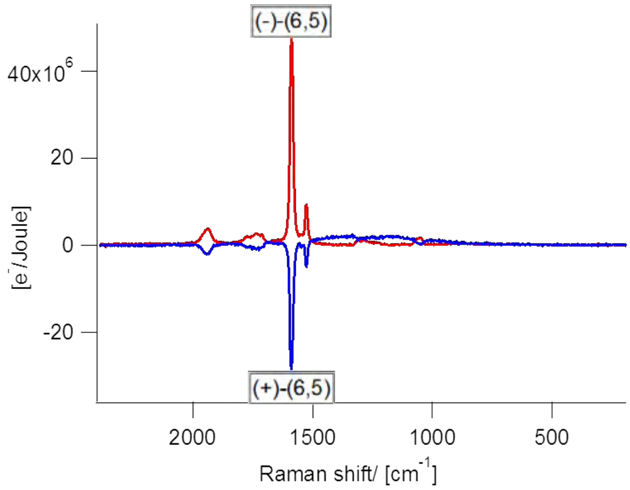
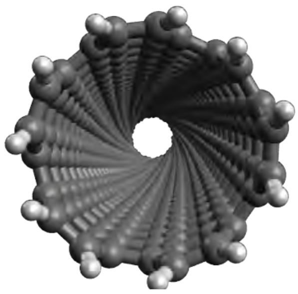
Single walled carbon nantotube (SWCNTs) exhibit helical chirality which is described by the indeces (n,m) of the chiral vector. The chirality of SWCNTs has a strong influence on their structure related properties, e.g, the band gab in semiconducting SWCNTs. The separation of SWCNTs according to their chiral vector has become feasable. Enantioseparation by nonlinear density gradient ultracentrifugation (DGU) has been achieved on a micrograms scale. In this study we will present resonance ROA spectra of (-)-(6,5)-[SWCNT] and (+)-(6,5)-[SWCNT] which were prepared from HiPco nanotubes and separated in one step in a nonlinear gradient of iodixanol. Sodium cholate was used as a chiral surfactant. Our ROA instrument uses an excitation wavelength of 532 nm, which is near the E_{22} transition of (6,5)-[SWCNT] at 570 nm. The tangential G-band is strongly enhanced which results in a remarkably intense ROA spectrum. This is particularly interesting as it allows measuring SWCNTs at small concentrations. While CD has previously been used to investigate the optical activity of chiral SWCNTs, this is to our knowledge the first study which uses ROA.





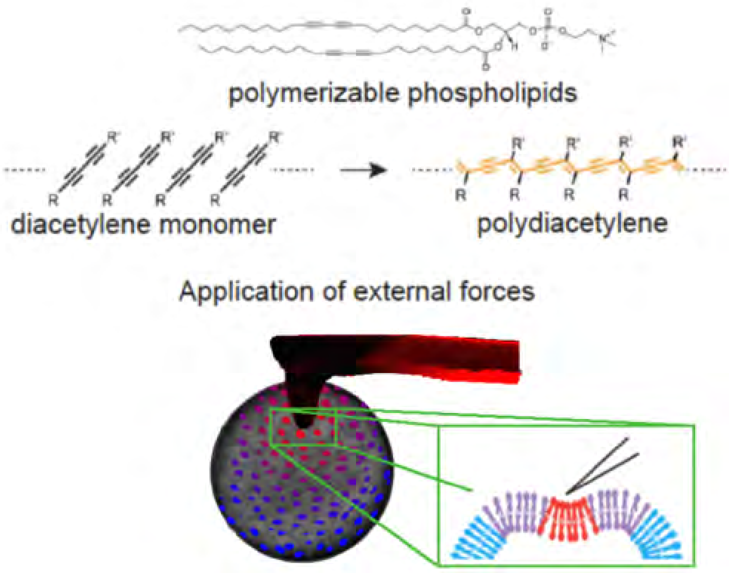
[1] S. Ghosh, S. M. Bachilo, R. B. Weisman, *Nat. Nanotechnol.* **2010**, *5*, 443–450.
[2] A. A. Green, M. C. Hersam, *Adv. Mater.* **2011**, *23*, 2185–2190.
[3] S. Ghosh, S. M. Bachilo, R. B. Weisman, *Fullerenes, Nanotubes, Carbon Nanostructures* **2013**, *22*, 269–279

Development of membrane mechanosensors with characterization in giant unilamellar vesicles.

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

[1]University of Geneva

The mechanical properties of cells as well as the cells' ability to interpret and respond to mechanical signals are increasingly recognized as playing critical roles in biological processes such as cancerous mutation and stem cell differentiation. Soft pillar substrates are commonly used to study the acto-myosin cell contractility. Atomic force microscope (AFM) is employed to determine the biding forces between molecules. However, no technique to date allows for monitoring the force distribution in lipid membranes. In this work, we develop a mechanosensitive fluorescence probe capable of mapping forces within lipid bilayers. The probe is based on a mechanochromic polymer polydiacetylene (PDA), which changes its color and the fluorescence intensity upon force applications. As a proof of principal, we incorporate the probe into giant unilamellar vesicles (GUV) as an artificial cell model. The first challenge is to incorporate PDAs into the phospholipid bilayers without disturbing the electroformation of GUVs. The combined AFM and fluorescence microscopy setup enables the calibration of the probe by correlating the fluorescence intensity and the applied forces on GUVs via AFM. The probe can be used in living cells in future for studying Membrane-molecular interactions and cell motility.



Charge transfer processes in a molecular pentad

M. Orazietti[1], M. Kuss-Petermann[2], O. S. Wenger[2], P. Hamm[1]*

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

A better understanding of single and multiple electron transfer (ET) is needed in order to design systems able to mimic natural photosynthesis. Thus, triad systems capable of forming photoinduced charge-separated state with single ET have been extensively studied.
We focused our research on a different system, a new linear pentad (fig.1), formed by two triarylamines, acting as electron donors (D), two ruthenium-trisbipyridine as photosensitizers (PS) and anthraquinone as acceptor (AQ). Due to its design and to the ability of AQ of accommodating two electrons, it has the unique capability of performing a double intramolecular ET, thus forming a long-living charge-separated state where two negative charges are located in the final electron acceptor.
Using VIS-pump IR-probe ultrafast spectroscopy, we are following the formation of the charge-separated state and the charge-recombination processes, discriminating between the different intermediates. Preliminary data show the presence of a band in the transient spectrum corresponding to $AQ^{\bullet -}$ (1483 cm^{-1}). Furthermore, if we compare the spectrum to the one of the reference triad (D-PS-AQ), where the second ET cannot occur, one band (1365 cm^{-1}), corresponding to the $AQ^{=}$, can be clearly distinguished, confirming the double ET (fig.2). The kinetics of the $AQ^{\bullet -}$ show that both pentad and triad form a photoinduced charge-separated state that lives for hundreds of nanoseconds and that when an acid is present in solution, it stabilizes the charge-separated state, protonating the reduced AQ, leading to shorter kinetics (fig.3).
A double-pulse experiment will be performed to selectively excite both PSs and follow both ETs.

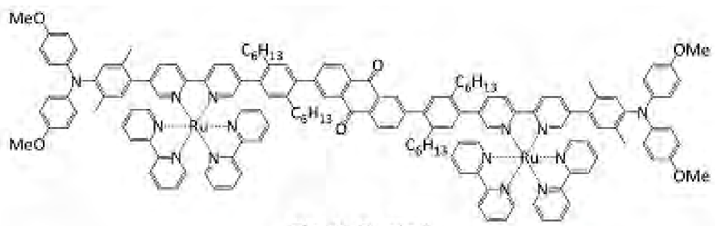


Fig.1: Pentad

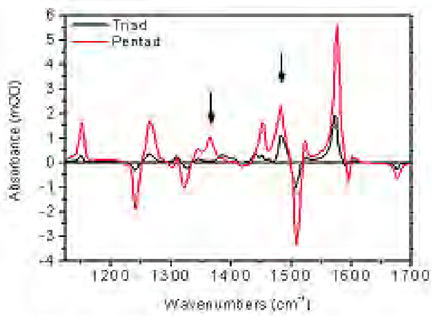


Fig.2 – Transient IR spectra of triad and pentad, 0.5 ns after the pump pulse

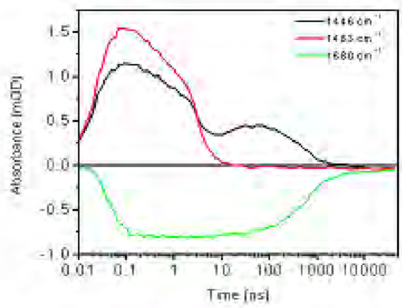


Fig.3 – Kinetics for different AQ species

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Unraveling the Photophysical Properties of Organic Semiconductors(Grammaticakis-Neumann Award Lecture 2015)

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[1]University of Fribourg, Chemistry Department, Chemin du Musée 9, CH-1700 Fribourg

Organic semiconductors offer numerous advantages compared to their inorganic counterparts, such as low-cost manufacturing, flexibility and lightweight. One important application is their use in new generation solar cells (Figure 1). The active layer of such photovoltaic devices often consists of a conjugated polymer, blended with a fullerene derivative in a solid-state thin film. In order to understand how those solar cells work and to improve their performance, it is important to investigate the light-matter interactions of the organic materials. We have done so by using a palette of experiments, spanning from ultrafast spectroscopy, via Stark effect methods, terahertz techniques, photocurrent measurements, to mobility characterization.

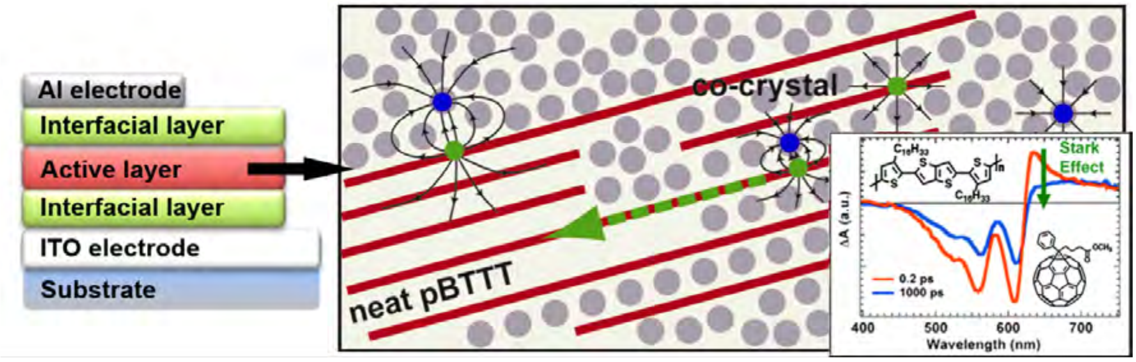

Figure 1: Typical organic solar cell, with zoom on the active layer nanoscale structure, and transient absorption spectra of polymer pBTTT blended with fullerene PCBM, showing a Stark signature due to photogenerated charges

In the first part of the talk, I will present our insights about the excited-state properties of conjugated polymers, which display a fascinating behavior in-between that of small molecule systems and that of bulk semiconductors [1,2]. I will then move on to discuss the correlation between the phase-morphology of polymer:fullerene blends and the photogeneration of free charge carriers [3-5]. Indeed, our work has shown that this essential step in solar cell functioning is largely determined by the way in which the polymer and fullerene arrange at the nanoscale (Figure 1). Finally, I will give an overview of our most recent studies about organic and hybrid semiconductors, not just applied to photovoltaics, but also to transistors and biological sensors.

[1] N. Banerji, *J. Mater. Chem. C.* **2013**, *1*, 3052.
[2] M. Scarongella, A. Laktionov, U. Röthlisberger, N. Banerji, *J. Mater. Chem. C.* **2013**, *1*, 2308.
[3] M. Scarongella, J. De Jonghe-Risse, E. Buchaca-Domingo, M. Causa', Z. Fei, M. Heeney, J.-E. Moser, N. Stingelin, N. Banerji, *J. Amer. Chem. Soc.* **2015**, *137*, 2908.
[4] M. Scarongella, A. A. Paraecattil, E. Buchaca-Domingo, J. D. Douglas, S. Beaupre, T. McCarthy-Ward, M. Heeney, J.-E. Moser, M. Leclerc, J.-M. Fréchet, N. Stingelin, N. Banerji, *J. Mater. Chem. A*. **2014**, *2*, 6218.
[5] A. A. Paraecattil, N. Banerji, *J. Amer. Chem. Soc.* **2014,** *136*, 1471.

Kinetic Isotope Effects on Exchange Rates of H^N and D^N in Tryptophan

E. Canet[1,2], P. Kadeřávek[1,2], P. Pelupessy[2], G. Bodenhausen[1,2]*

[1]EPF Lausanne, [2]ENS Paris

We have quantified the exchange rates between indole protons in tryptophan with the protons of the aqueous solvent, and compared the exchange rate of the analogous process when hydrogen is replaced by deuterium, so that we could determine the H/D kinetic isotope effect (KIE).

$$H^N + H' \rightarrow H'^N + H$$

$$D^N + D' \rightarrow D'^N + D$$

The measurement of H/H and D/D exchange rate constants of H^N and D^Non the indole ring in tryptophan is of obvious interest. The isotope effect is considered to be one of the most sensitive tools for the study of reaction mechanisms as it can give insight into free energies and other thermodynamic parameters that describe the stability of hydrogen-bonded structures in different environments.

We have extended our method originally designed for measuring very fast proton exchange rates[1,2,3] to deuterium exchange rates. The effects of scalar relaxation caused by the exchanging H^N or D^N nuclei is determined by detecting the decay of the coherence of a ^{15}N nucleus that has a scalar coupling $^1J(^{15}N, ^1H)$ or $^1J(^{15}N, ^2D)$ to the exchanging nuclei under a multiple-refocusing CPMG pulse train in the presence or absence of proton or deuterium decoupling.

The exchange rates were found to lie in the range from 17 to 10 000 s^{-1} for pH from 2.2 to 11.8 and temperature from 290 to 320 K. The logk_D vs. pH plot indicates a combination of specific base catalysis at high pH, un-catalyzed exchange at intermediate pH, and specific acid catalysis at low pH, which becomes more important at higher temperatures.

The kinetic isotope effect k_H/k_D was found to lie in the range from 0.22 to 14.99 for pH from 6.3 to 10.5 and temperature from 300 to 320 K. The kinetic isotope effect increases with increasing pH and temperature.

Altogether we can say that in the base-catalyzed mechanism the rate-limiting step of the exchange is the removal of the proton or deuteron from the amide, while for the acid-catalyzed mechanism it is the donation of a proton or deuteron by H_3O^+, respectively D_3O^+. From the small values of the kinetic isotope effect we can conclude that the H^N/D^N bonds are elongated, and not totally broken in the transition state, the H/D atom being more tightly bound to the donor N atom of tryptophan than to the acceptor D_2O or OD^-.

[1] F. Kateb, P. Pelupessy, G. Bodenhausen, *J. Magn. Reson*. **2007**, 184, 108-113.
[2] A. A. Sehgal, L. Duma, G. Bodenhausen, P. Pelupessy, *Chem. Eur. J.* **2014**, 20, 6332-6338.
[3] T. Segawa, F. Kateb, L. Duma, G. Bodenhausen, P. Pelupessy, *ChemBioChem*, **2008**, 9, 537-542.

Photoinduced Stark effect in colloidal systems: a case study with $MAPbBr_3$ and AQU/nC_{60}

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Understanding the mechanisms of charge carrier generation and transport in photovoltaic systems is a key to get to efficient devices. The primary step towards such an understanding is a thorough analysis of the electronic structure and properties of those systems, yielding more targeted designs. Among several effects, the electronic modifications arising from the presence of an electric field is of great interest in such a framework: indeed, optical excitations tend to generate excitons, and those excitons create a transient electric field. This excitonic field in turn perturbs the electronic structure of the surrounding species, yielding a shift in their optical properties: it is a case of photoinduced (optical) Stark effect.

Ideal systems for the study of such optical Stark shifts are colloidal suspensions. Nanoparticles actually allow an extensive delocalization of the created exciton compared to molecules in solution, which creates a favorable environment for observation of a photoinduced Stark effect. Moreover, control on nanoparticle size is another advantage of the system compared to solid-state films.

Herein, we aim at studying those electro-optical shifts in two colloidal systems: methylammonium lead-bromide perovskites ($MAPbBr_3$) and hydrated fullerene C_{60} (AQU/nC_{60}), using ultrafast transient absorption (TA) and electroabsorption (EA) measurements. Via the application of an external electric field, the latter method gives a direct insight into the features of the Stark signal for a given sample (electroabsorption spectrum). Then, on the basis of EA results, transient absorption experiments allow to directly assess the presence or absence of Stark-related features in our systems. As well, it gives us the associated dynamics, which informs us about delocalization of excitonic states.
EA measurements were performed on the solid-state film counterparts of our two colloidal systems. We show that both MAPbBr3 and AQU/nC60 colloids exhibit significant Stark shifts in their transient absorption spectra. As well, hints at a possible system size dependence of such a signal were obtained, that should be thoroughly considered in further studies.

High resolution infrared spectroscopy and theory of parity violation and tunneling for dithiine as a candidate for measuring the parity violating energy difference between enantiomers of chiral molecules

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In the framework of ordinary “electromagnetic” quantum theory the ground states of the enantiomers of chiral molecules are energetically equivalent. However, with the electroweak quantum chemistry and parity violation, one predicts a small “parity violating” difference $\Delta_{PV}E$ on the order of 100 aeV, typically, depending on the molecule, corresponding to a reaction enthalpy of stereomutation of about 10^{-11} J mol^{-1} [1,2]. So far, this effect has never been observed experimentally. In our paper, we report exploratory spectroscopy and theory in view of a possible use of the chiral C_2-symmetric molecule dithiine ($C_4H_4S_2$) for detecting molecular parity violation using a current experimental setup in our laboratory [3]. Using high resolution FTIR spectroscopy [4] we were able to provide a first rovibrational analysis of two bands, one centered at 623.3121 cm^{-1} consisting of c-type transitions and the second centered at 1308.8724 cm^{-1} consisting of a-type transitions. The assignments have been verified by combination differences. In parallel we calculated parity violating potentials using our recent coupled cluster approach [5] and tunneling using our quasiadiabatic channel reaction path Hamiltonian approach [6] . The implication of our results for the study of molecular parity violation will be discussed.

[1] M. Quack, *Fundamental symmetries and symmetry violations from high resolution spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 1, (Eds. M Quack and F Merkt), Wiley, Chichester (**2011**), 965-1021.
[2] M. Quack, *Angew. Chem.-Int. Edit. Engl.* **1989**, *28*, 571-586.
[3] P. Dietiker, E. Milogyadov, M. Quack, A. Schneider and G. Seyfang, in *Proceedings of the 19th Symposium on Atomic, Cluster and Surface Physics (SASP 2014), University center Obergurgl, Austria, 8th to 14th February 2014*, edited by D. Stock, R. Wester and R. Scheier (Innsbruck University Press, Innsbruck, 2014), pp. 226–229. ISBN: 978–3–902936–26–4.
[4] S. Albert, K. K. Albert and M. Quack, *High Resolution Fourier Transform Infrared Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2, (Eds. M Quack and F Merkt), Wiley, Chichester (**2011**), 965-1021. S. Albert and M. Quack, *ChemPhysChem*., **8**, 1271 – 1281 (2007).
[5] L. Horny and M. Quack, *Mol. Phys*. (2015) in press.
[6] B. Fehrensen, D. Luckhaus, M. Quack, *Chemical Physics* **2007**, *338*, 90-105.

Symmetry-Breaking Phenomena Detected with Ultrafast Time-Resolved Infrared Spectroscopy

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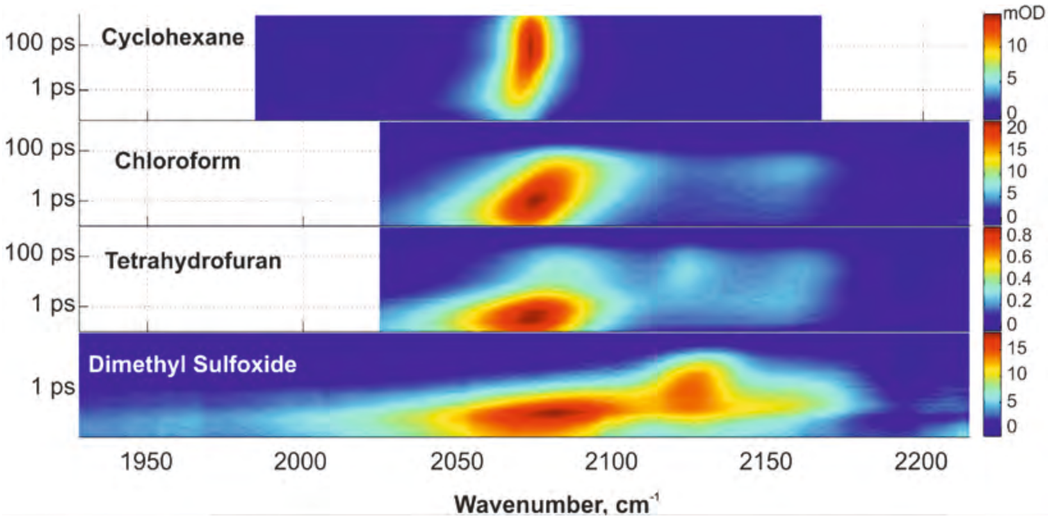
Quadrupolar molecules with a D-π-A-π-D molecular architecture are known to show large cross-sections for two-photon absorption processes. A search for such systems is stimulated by a growing need of photointitiators for two-photon initiated photopolymerization. This field has been intensively developing in the last decade. Such molecules possess a small net dipole moment due to symmetry reasons, but the solvent dependence of their emission shows that they behave like highly dipolar molecules in polar environment. This remarkable behavior points to a localization of the optical excitation on one side of the molecule, i.e. to symmetry-breaking. Whereas electronic transient absorption of such molecules does not provide wealth of information about this phenomenon, a rich insight can be obtained by ultrafast time- resolved infrared spectroscopy. Using this technique we have monitored excited-state vibrational modes located on both branches of a D-π-A-π-D molecule. Directly after the optical excitation the same frequency is observed for both branches independently on the solvent polarity. At later time in polar solvents new bands develop reflecting the localization of the charge-transfer excited state on one side of the molecule. To the best of our knowledge it is the first spectroscopic visualization of such symmetry-breaking process in quadrupolar molecule.



Vibrational Optical Acitivity (VOA) of Chiral Ionic Liquids (CILs)

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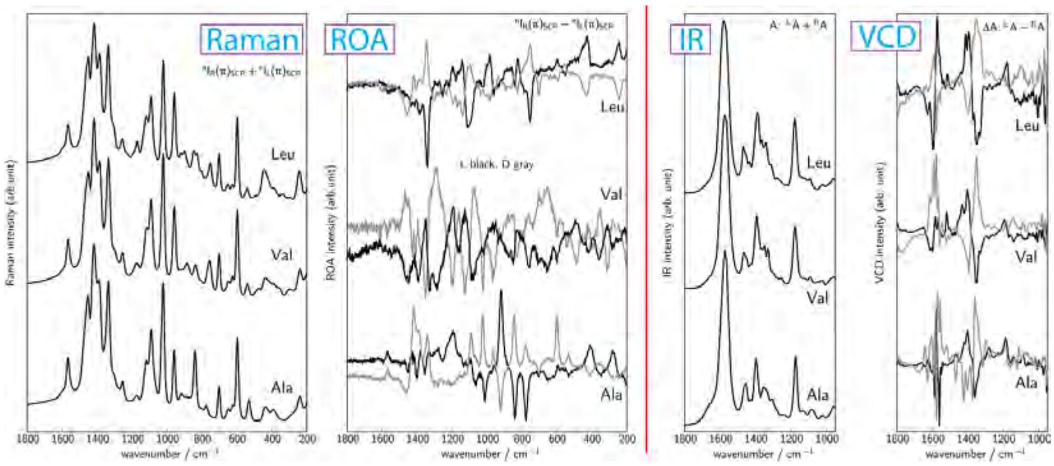
The synthesis of CILs from amino acids with 1-ethyl-3-methyl- imidazolium ([Emim]) as cation was presented a decade ago[1]. We have synthesized and recorded the Raman scattering and absorption spectra, and their optical activity for both techniques, for the L-/D-pairs of alanine, valine, and leucine ([L-/D-Ala][Emim], [L-/D- Val][Emim], and [L-/D-Leu][Emim]), see Figure below.



The spectra are analyzed by comparison to literature[2], and with the support of new calculations for both the anions and the cation.

Additional insight into the origin of observed spectral bands was obtained for the sample case of [L- Ala][Emim] through a Born-Oppenheimer molecular dynamics (BOMD) simulation[3]. The simulation box comprises 20 [L- Ala][Emim] pairs. In total three different sets of four [L-Ala][Emim] pairs and five different sets of one [L-Ala][Emim] pair were used to investigate the influence of the conformation on the optical activity of this CIL.

The emphasis is set on the dependence of molecular conformation and effects of the anion/cation interaction in regard to the generated optical activity.

[1] Fukumoto, K., Yoshizawa, M., Ohno, H. (2005). Journal of the American Chemical Society, 127(8), 2398–2399.
[2] Kiefer, J., Fries, J., Leipertz, A. (2007). Applied Spectroscopy, 61(12), 1306–1311.
[3] Luber, S., Iannuzzi, M., Hutter, J. (2014). The Journal of Chemical Physics, 141(9), 094503.

Characterization of Gd(III) chelators and combination of paramagnetic NMR with Gd(III)-nitroxide DEER in studies of biomacromolecules

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We applied the double electron-electron resonance (DEER) technique with Gadolinium(III) ions and nitroxide radicals as spin labels to measure nanometre-range distances on proteins [1] and peptides [2]. This relatively new approach [3] utilizes two spectroscopically and/or chemically orthogonal (non-identical) tags. It allows to benefit from extended spectroscopic information content, and from the combination with further techniques in studies of biomacromolecules.

We characterized several Gd(III) macrocycle chelators as labels for dipolar spectroscopy applications and observed an effect of the hyperfine interaction on their performance. [4] As an example of orthogonal labelling, we show that the pairs of non-identical spin labels could be introduced into an enzyme (hCAII) using an inhibitor derivative for the nitroxide and cysteine chemistry for the lanthanide label. The labelled hCAII of known X-ray structure was used to test the combination of paramagnetic relaxation enhancement and pseudo contact shift NMR with DEER measurements for structure determination. Correspondences between NMR and EPR constraints are analyzed and a guideline for a joint use of those data is presented. Noteworthy, orientation selection experiments were sufficient to extract the nitroxide orientation with respect to the protein at 35 GHz (Q-band). This example reveals that Gd(III)-nitroxide DEER is a versatile tool in studies of bio-macromolecules and potentially allows for addressing more complex biological systems than before.

[1] Luca Garbuio, Enrica Bordignon, Evan K. Brooks, Wayne L. Hubbell, Gunnar Jeschke, Maxim Yulikov, *Journal of Physical Chemistry B*, **2013**, 117, 3145-3153.
[2] Luca Garbuio, Bartosz Lewandowski, Patrick Wilhelm, Ludmila Ziegler, Maxim Yulikov, Helma Wennemers, Gunnar Jeschke, *Chemistry, a European Journal*, **2015**, *In print*.
[3] Petra Lueders, Gunnar Jeschke, Maxim Yulikov, *Journal of Physical Chemistry Letters*, **2011**, 2, 604−609.
[4] Luca Garbuio, Kaspar Zimmermann, Daniel Häussinger, Maxim Yulikov, *Submitted*, **2015**.

Experimental study of the ion-molecule reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ at low collision energies

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H_2 molecules in a skimmed supersonic beam are excited to nonpenetrating n = 30, M_J = 3 Rydberg-Stark states belonging to series converging to a selected rotational level (N^+= 0,1,2 or 3) of the $X^{+2}\Sigma^+{}_g$ (v^+= 0) ground state of H_2^+. The beam of Rydberg molecules is then deflected and velocity selected using a bent surface decelerator [1] and merged with another supersonic beam of ground state H_2. In n = 30, M_J= 3 Rydberg-Stark states, the Rydberg electron is completely decoupled from the H_2^+ ion core motion and acts as a spectator when the H_2^+ ion core reacts with an H_2 molecule located within the Rydberg-electron orbit [2]. The experimental apparatus has been conceived so that the relative velocities of the two beams can be adjusted, making the study of the reaction at collision energies below 10 meV possible.The reaction products are monitored on an imaging microchannel-plate detector following extraction with a pulsed electric field. The information contained in the ion time-of-flight (TOF) distributions and in the distributions of H_3^+ product ions on the images are used to determine the relative cross section in dependence of the collision energy and the selected rotational state of the H_2^+ion core. A typical TOF spectrum showing H_3^+ ions formed from the reaction of H_2^+(v^+= 0, N^+= 0) at a collision energy of 6 meV is displayed in the Figure as illustration.

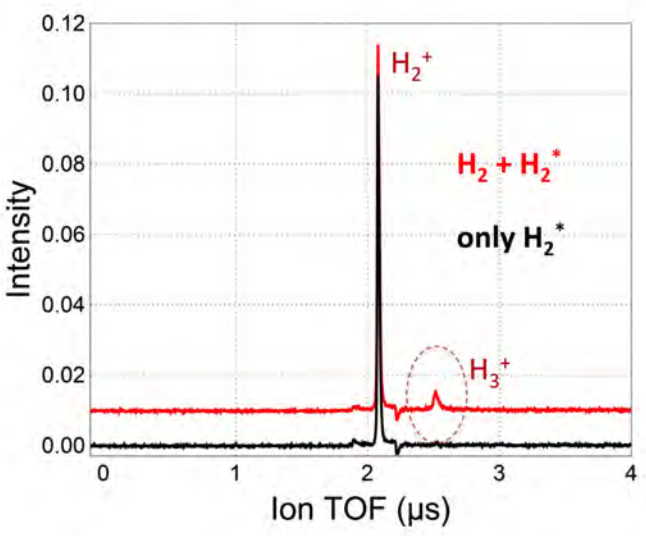

Figure 1: TOF spectrum showing H_2^+ ions (main peak) produced by pulsed field ionization of the initially prepared n = 30, M_J = 3 Rydberg states and H_3^+ ions resulting from the $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction at 6 meV collision energy.

[1] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, Phys. Rev. A.,2014, 90,043403
[2] P. M. Dehmer, W. A. Chupka, J. Phys. Chem.,2005,99,1686

$ClHO_3S$ as a prototype system for studying photo-dissociation induced by OH stretching overtone excitation

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Sulphur containing compounds play an essential role in atmospheric chemistry. Especially the photo-dissociation of sulphuric acid into water and sulphur trioxide is of interest, due to its role in tropospheric aerosol layer formation.[1] It was found that this reaction can be induced by excitation of OH stretching overtones, rather than by absorption of ultra violet radiation.[2] Experimental analysis of this reaction is experimentally difficult. This is due to the fact that H_2SO_4 is, in gas phase, in equilibrium with its two fragments (H_2O + SO_3) and it possesses an extremely low vapour pressure.[3]

For that reason related compounds were considered as a model system. It was suggested to use $ClHO_3S$ as a prototype system for the experimental investigation of vibrationally induced photo-dissociation.[4]Using several thousands points at the MP2/6-311G++(2d,2p) level of theory and fitting to a parameterised force field, extensive reactive MD simulations were run. For the analysis of the photo-dissociation of sulfurochloridic acid multi-surface adiabatic reactive molecular dynamics (MS-ARMD)[5] simulations were performed. This method enables us to follow the H transfer, as well as the HCl elimination after the excitation of the OH-stretching mode. Final state analysis of several thousands of trajectories of the two fragments show distinct distributions for translational, rotational, and vibrational degrees of freedom.[6]

[1] David J. Hofmann, James M. Rosen, *Nature*, **1982**, 297, 120-124.
[2] Veronica Vaida, Henrik G. Kjaergaard, Paul E. Hintze, D. James Donaldson, *Science*, **2003**, 299, 1566–1568.
[3] James B. Burkholder, Mike Mills, Stuart McKeen, *Geophysical Research Letters*, **2000**, 27, 2493–2496.
[4] Priyanka Gupta, Joseph R. Lane, Henrik G. Kjaergaard,*Physical Chemistry Chemical Physics*, **2010**, 12, 8277-8284.
[5] Tibor Nagy, Juvenal Yosa Reyes, Markus Meuwly, *Journal of Chemical Theory and Computation*, **2014**, 10, 1366–1375.
[6] Juvenal Yosa Reyes, Tibor Nagy, Sebastian Brickel, Markus Meuwly, *in preparation*.

Cold Chemistry on a multi-functional ion trap chip

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Chip-based trapping techniques present novel possibilities for precise experiments with cold, quantum-state controlled particles with potential applications in mass spectrometry, chemistry, quantum information science, and spectroscopy [1-7]. We have designed and characterized a multi-functional monolithic miniaturized device for shuttling and manipulation of sympathetically cooled molecular ions [8-9] using accurately shaped electric fields above the surface of the chip. The chip consists of quadrapolar and octupolar surface-electrode RF traps featuring a few experimental sites that are connected via two optimized junction structures. The experiment aims to shuttle translationally cold N_2^+, CaH^+, and CaO^+ with laser-cooled $^{40}Ca^+$ions in the milikelvin range. However, our design based on a mass-independent normalized optimization presents a universal surface pattern structure applicable to any other mass as well as trapping parameters.

This compact, flexible technology will progressively impact on experiments with hybrid quantum systems [10-11] as well as highly integrated experiments with molecular ions combining various tasks such as chemistry and spectroscopy, which have thus far been in the domain of costly and complex guided-ion beam machines [12].

[1] J. Chiaverini, et al., Quantum Inf. Comput., **2005**, 5, 419.
[2] S. A. Meek, H. Conrad, and G. Meijer, Science, **2009**, 324, 1699.
[3] M. D. Hughes, et al., Contemp. Phys., **2011**, 52, 505-529. and R. C. Sterling, et al., Nat. Commun., **2013**, 5, 3637.
[4] D. T. C. Allcock, et al., New J. Phys., **2010**, 12, 053026.
[5] R. Schmied, et al., Phys. Rev. Lett., **2009**, 102, 233002.
[6] J. M. Amini, et al., New J. Phys., **2010**, 12, 033031.
[7] A. Mokhberi and S. Willitsch, Phys. Rev. A, **2014**, 90,023402.
[8] S. Willitsch. Int. Rev. Phys. Chem., **2012**, 31,175.
[9] A. Mokhberi and S. Willitsch, New J. Phys., **2015**, 17, 045008.
[10] S. Willitsch, et al., Phys. Rev. Lett., **2008**, 100, 043203.
[11] F. H. J. Hall and S. Willitsch, Phys. Rev. Lett., **2012**, 109, 233202.
[12] D. Gerlich, in Advances in Chemical Physics, **1992**, Vol. 82, edited by C.-Y. Ng and M. Baer (Wiley, New York).

(Benzonitrile)$_2$ and (meta-Cyanophenol)$_2$: Influence of a Hydroxy Group on the Excitonic Splitting

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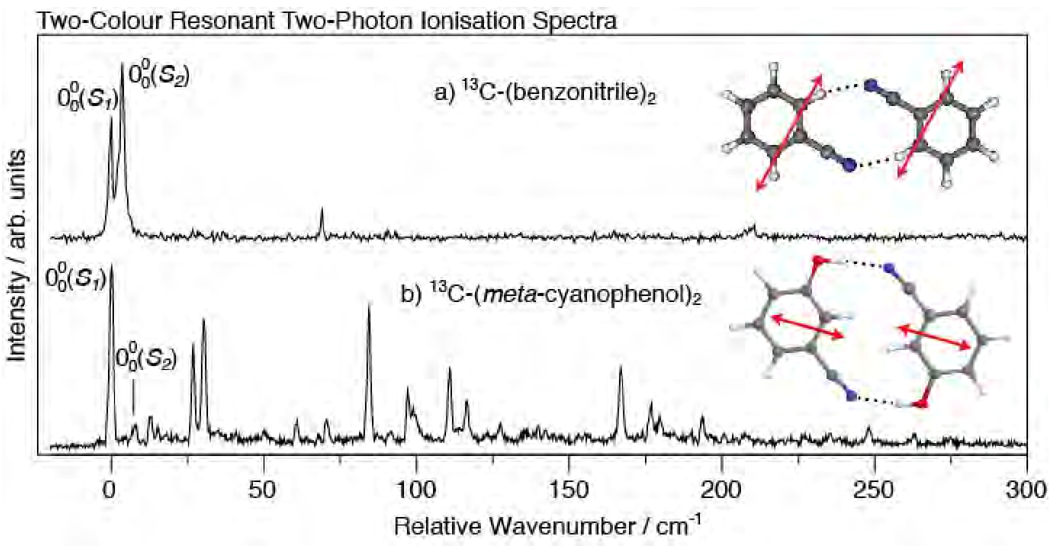
The benzonitrile dimer (BN)$_2$ is C_{2h}-symmetric with two antiparallel CN···H bonds. Its $S_0 \rightarrow S_1$ ($^1A_g \rightarrow {}^1A_g$) transition is inversion-symmetry forbidden, and only the $S_0 \rightarrow S_2$ ($^1A_g \rightarrow {}^1B_u$) transition is observed. In the ^{13}C-isotopomer the monomers are inequivalent, rendering both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition allowed as shown in Figure (a). The S_1/S_2 splitting of the ^{13}C-isotopomer is 3.9 cm^{-1} and consists of an excitonic contribution (Δ_{exc}=2.0 cm^{-1}) and a ^{13}C-isotope effect (Δ_{iso}=3.3 cm^{-1}). [1]

Substituting the H-atom at the *meta*-position of benzonitrile (BN) with an OH-group changes the H-bond pattern, see Figure (b). The presence of the hydroxy-group also rotates the transition dipole moments within the mCP unit by 40° to an almost collinear/anti-collinear alignment in the dimer, leading to an allowed $S_0 \rightarrow S_1$ ($^1A_g \rightarrow {}^1A_u$) transition and a forbidden $S_0 \rightarrow S_2$ ($^1A_g \rightarrow {}^1A_g$) transition. ^{13}C-substitution renders both transitions allowed and the excitonic S_1/S_2 splitting was determined to be Δ_{exc}=7.1 cm^{-1}.



[1] F. Balmer, P. Ottiger, S. Leutwyler, *J. Phys. Chem. A*, **118**, 11253-11261 (2014).

Aqueous Catholyte for Rechargeable Li-O_2 and Li-Water Batteries

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Lithium is the lightest metal with the most negative potential (-3 V vs. SHE). Combining oxygen and water as a cathode as well as an electrolyte with lithium, the resulting rechargeable Li-O_2 and Li-water batteries provide 10-20 times higher energy densities than the conventional Li-ion batteries.

However, the reversibility of the redox reactions and hence the cyclability of those batteries are far below the requirements. Among several structures of Li-O_2 batteries, using an aqueous electrolyte provides a higher efficiency and cyclability due to the high ionic mobility and the solubility of discharge products [1]. A schematic of hybrid (organic/solid/aqueous) electrolyte-based Li-O_2 cell is shown in Fig. 1. During charging and discharging, the pH value changes so extremely that current membranes are damaged [2,3]. It was also reported that the saturated discharge product (LiOH) blocks the pores of the membrane, where Li^+ ions should be able to pass through [4].

To avoid such extreme change of pH in an aqueous electrolyte, buffer solutions (PO_4^{3-} and SO_4^{2-}) are useful. The pH values, the discharge products and ionic conductivity are evaluated in the process of charging and discharging. Accordingly, the electrochemical reactions are monitored to investigate the properties of electrolyte.

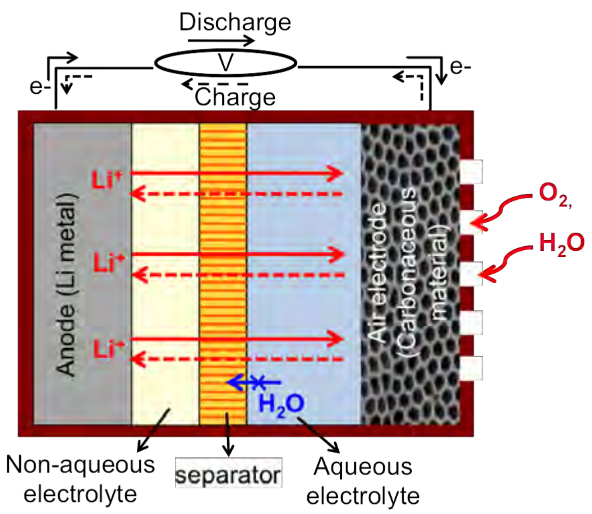

Fig. 1. Schematic of hybrid (organic/solid/aqueous) electrolyte-based Li-O_2 cell.

[1] X. Wang, Y. Hou, Y. Zhu, Y. Wu, R. Holze, *Scientific Reports* 2013, *3*, 1401, doi:10.1038/srep01401.
[2] D.-J. Lee, O. Yamamoto, D.-M. Im, Y. Takeda, N. Imanishi, 2012, Patent Application No. 13/191769.
[3] J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, *J. Electrochem. Soc.* 2012, *159*, R1-R30.
[4] Y. Wang, H. Zhou, *J. Power Sources* 2010, *195*, 358-361.

Quantifying Equilibrium Binding Affinity using 2D IR Spectroscopy and Non-native Amino Acids

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Azidohomoalanine (Aha) is a very versatile label that can be incorporated into proteins. It absorbs in the non-congested part of protein IR spectra and the center frequency is sensitive to the environment [1]. The combination of ultrasensitive 2D IR spectroscopy and Aha labelling of proteins gives rise to new possibilities of investigating biological structures and their dynamics with very low sample demands. With voice coil flexure guided delay stages and automated exchange of buffer and protein samples it is possible to measure Aha labelled proteins down to a concentration of 0.5 mM with good signal to noise ratio. This is demonstrated with equilibrium binding studies of Aha-labelled peptide with its associated wild-type protein binding domain PDZ2. Upon binding, the Aha band redshifts by ~ 15 cm^{-1} and can clearly be resolved from the unbound fraction. For a fixed ligand concentration of 0.5 mM, analysis of fractional binding recovered from 2D IR spectra collected at various protein concentrations allows for the direct observation of the binding affinity.

[1] Robbert Bloem, Klemens L. Koziol, Steven A. Waldauer, Brigitte Buchli, Reto Walser, Brighton Samatanga, Ilian Jelesarov, Peter Hamm, *J. Phys. Chem. B*, **2012**, 116, 13705-13712