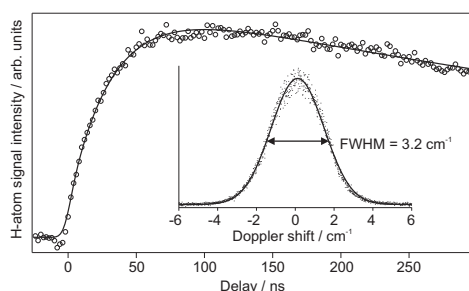


Spectroscopy and Dynamics of the A-State of the 1-Methylallyl Radical

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A detailed description of the deactivation pathways of optically excited hydrocarbon radicals is a pivotal prerequisite for modeling their reaction kinetics. A common reaction channel of such excited radicals is the loss of a hydrogen atom and the corollary formation of a closed shell molecule. We recently published a study on the 2-methylallyl radical. [1] The excited states of the 1-methylallyl radical have been scarcely investigated spectroscopically so far. Callear and Lee reported a series of absorption bands between 42 000 cm^{-1} and 43 950 cm^{-1} . [2]



In this work we focus on the identification and spectroscopical characterization of the so far unknown low-lying π -state with the help of 1+1' REMPI, H-atom photofragment and depletion spectra. Additionally, we investigated the hydrogen fission dynamics under jet-cooled conditions after excitation by time- and frequency-resolved detection of Hydrogen atoms.

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Test of nuclear spin symmetry conservation in partially deuterated methane-isotopomers in the expansion of a molecular supersonic jet

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The conservation of nuclear spin symmetry represents a relatively strong selection rule for radiative transitions, bimolecular collisions and reactions on short time scales [1]. This led to the separation of para- and ortho- H_2 already in 1929 through cooling in the presence of a magnetic catalyst [2]. The violation of this selection rule can have both de facto and de lege origins [3]. The possibility of intramolecular and intermolecular nuclear spin symmetry interconversion has been demonstrated in a number of experiments at longer time scales [4–6]. On the other hand on short time scales in supersonic jet expansions nuclear spin symmetry is found to be conserved for CH_4 [7]. We have extended these investigations to CH_3D and CHD_3 in a diode laser experiment with slit jet supersonic expansion. A temperature below 10 K was reached for both molecules. Detailed analysis of the R_2 -line intensities shows that nuclear spin symmetry relaxation plays only minor role if any under the conditions given.

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Transition wave numbers from the $EF\ 1\Sigma_g^+$ ($v=0, N=0, 1$) state to selected np Rydberg states ($n \approx 60$) below the $X+2\Sigma_u^+$ ($v^+=0, N^+=0, 1$) ionization threshold have been measured in H_2 [1], HD and D_2 [2] at a precision better than 10 MHz. By modelling the measured Rydberg series using multichannel quantum defect theory including fine and hyperfine effects and combining the results with previous experimental and theoretical data for other energy level intervals, the ionization and dissociation energies of H_2 , HD and D_2 could be determined at an absolute accuracy of better than 20 MHz. These new results are more precise by over an order of magnitude than any other experimental value of the dissociation and ionization energies reported so far in a molecular system and offer therefore an excellent opportunity of a comparison with theoretical values. In particular, our results will be compared to the latest *ab initio* calculations [3] which include nonadiabatic, relativistic and radiative effects. The comparison indicates that relativistic and radiative quantum electrodynamics corrections of order up to α^4 are needed to account for the experimental results.

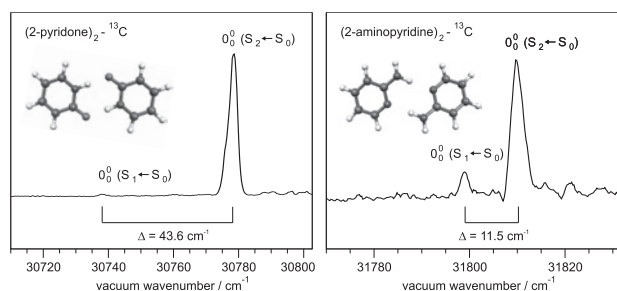
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Exciton Splittings in Molecular Dimers

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We have interpreted the optical spectra of the supersonically cooled molecular dimers (2-pyridone)₂ [1] and (2-aminopyridine)₂ [2] in terms of delocalized excited states with experimentally determined S_1/S_2 excitonic splittings of 44 and 11 cm^{-1} , respectively. High-level *ab initio* calculations predict excitonic splittings that are too large by a factor of 5–40. These purely electronic splittings are quenched by vibronic coupling to the optically active intramolecular vibrations. Quenching factors determined from experiment and calculations on the corresponding monomers are in good agreement with the observed S_1/S_2 origin splittings. The effect of vibronic coupling also has to be taken into account for other symmetric doubly hydrogen bonded complexes such as (cyanophenol)₂, (benzoic acid)₂ or (benzonitrile)₂. This point has been widely overlooked in previous work.

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Chiral Selection of [4]Helicene in Binding to DNA

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Chirality plays an important role in the recognition processes between biological molecules such as protein – DNA interaction, enzymatic catalysis, antibody activity, etc. Therefore the molecular mechanisms involved in these specific interactions attract strong interest. Cationic helicene derivatives have a polycyclic aromatic and positively charged structure (Figure 1), these properties make them attractive chiral DNA binding agents.

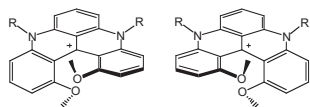


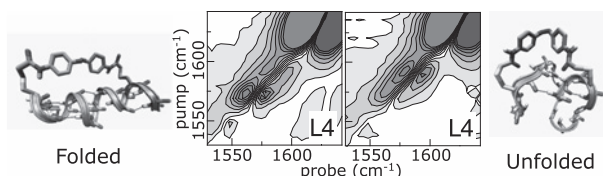
Figure 1. Structure of [4]helicene (R = CH₃ (Hel-Me) and R = (CH₂)₂CH₃ (Hel-Pr))

Using steady state and ultrafast time resolved fluorescence methods, we can observe a different behavior for [4]helicenes in water and organic solutions. This effect is due to the presence of H-aggregates in the former, which dramatically changes the photophysical properties of the investigated compounds.

Beyond that, absorption and fluorescence change significantly upon addition of DNA, e.g. the fluorescence quantum yield increases in parallel with the amount of [4]helicene intercalated into DNA. Using a fluorescence titration method, we observe that they bind to DNA in a stereoselective way: the (*M*)-enantiomer interacts more efficiently with salmon sperm DNA than the (*P*)-enantiomer independently of the substituents on the aromatic rings. On the other hand, it reveals that one dye unit of Hel-Me interacts with two base pairs of DNA, whereas the ratio for Hel-Pr is one to one. The origin of these effects will be discussed in detail.

2D-IR Study of a Photoswitchable Isotope-Labeled α -Helix [1]Robbert Bloem¹, Ellen Backus², Peter Hamm¹¹University of Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland²FOM, Science Park 104, 1098 XG Amsterdam, The Netherlands

Understanding folding and folding dynamics of biomolecules is necessary to understand the functioning of the biomolecules. Two-dimensional infrared spectroscopy (2D-IR) has a high time resolution and shows, among others, the frequency of vibrations and the coupling between vibrations, making it ideal to study dynamics. However, to do this, vibrations have to be isolated from the main band using isotope labeling. In this study an α -helical peptide was labeled with single (¹³C/¹⁸O) isotopes at various positions in the helix. A single label gives rise to two distinct bands while no coupling is visible. These bands have been assigned to the hydrogen-bonded (either internally or to the solvent) and non-hydrogen-bonded state. Using the photoswitch, we could switch between the folded and unfolded state of the helix. The relative intensity of the peaks for the two states gives an indication of the fraction of molecules that are hydrogen-bonded at a certain location along the sequence. For most sites, unfolding the helix resulted in a shift of intensity from the hydrogen-bonded peak to the non-hydrogen-bonded peak. The shift in intensities shows us where in the helix the hydrogen bonds are created or broken when switching between the two states. In future transient 2D-IR experiments we hope to observe these hydrogen-bond switching events during the folding process in greater detail.



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Ultrafast Dynamics of Horse Heart Cytochrome c by mean of pump – UV-broadband probe spectroscopy

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An important issue in protein functionality is the transmission of information between different sites inside the protein. It has been shown that the interplay between different residues could be strongly related to the redistribution mechanisms of local electronic and vibrational excess energy, that can be generated during biological functions.[1]

Horse heart cytochrome c (hh cyt c) is a haem protein whose haem iron is 6-fold coordinated and axially ligated to a Methionine (Met) and Histidine (His) in both its ferric and ferrous redox states. It is known that upon excitation with visible light, the reduced state undergoes Met photolysis while in the oxidized state, only cooling dynamics has been reported. [2] The possibility to induce or not the photolysis by changing the oxidation state makes this system suitable to disentangle electronic and cooling dynamics and to study their dependence on the excess of vibrational energy and on the Fe oxidation state.

We present the results of our study on both oxidation states of cyt c by the mean of pump – UV-VIS broadband probe spectroscopy spanning the range from 270 to 680 nm. The UV extension of the probe spectrum permits us to follow simultaneously the response of the haem and of a Trp cofactor close to it. By tuning the excitation from 530 nm to 287 nm we investigate not only the effects of the remarkable increase in the time-zero haem temperature but we also directly measure for the first time the Trp – Haem energy transfer, demonstrating that it induces the same haem dynamics as observed upon photoexcitation.

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Activity and Stability of PtCo_x Catalysts for Oxygen Reduction in Polymer Electrolyte Fuel Cells

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Commercialization of polymer electrolyte fuel cell (PEFC) technology requires two achievements: significant cost reduction and improved stability of PEFC components [1]. In this regard, the platinum based cathode catalysts are playing a key role, due to their high cost and moderate stability.

Previous work demonstrates that Pt-alloy nanoparticles like PtCo_x (0.33 ≤ x ≤ 1) show improved stability [2] and catalytic activity [1, 3] towards the oxygen reduction reaction. These PtCo_x nanoparticles may consist of different crystalline phases including Pt₃Co, PtCo or PtCo₃ [3]. It is not obvious which of these phases offer the highest catalytic activity or stability for PEFC applications.

We developed preparation routes where one of these phases is preferentially produced. The catalytic activity of these nanoparticles was tested using cyclic voltammetry and rotating disc electrode measurements before and after stability tests. New electron microscopic techniques as well as XRD and ICP-OES were applied to follow the degradation of the catalysts during accelerated ageing tests.

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Activation strategies for LaFe_{0.95}Pd_{0.05}O₃ towards Improved oxidation of methane

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LaFe_{0.95}Pd_{0.05}O₃ is currently used as a component of automotive three-way catalysis for the emission control of stoichiometric gasoline engines. It is known that LaFe_{0.95}Pd_{0.05}O₃ is able to segregate metallic palladium to its surface when reduced and to re-incorporate it to form a solid solution when re-oxidized, which is described as the self-regenerating property [1]. Consequently, reduction-reoxidation treatments are one route to activate the catalyst. Catalytic activity measurements during methane combustion (1%CH₄, 4%O₂/He) were performed on 2wt% Pd-doped LaFeO₃ catalysts, with Pd either incorporated into the lattice (LaFe_{0.95}Pd_{0.05}O₃) or impregnated (Pd/LaFeO₃). Highest CH₄-conversion rates were observed for the impregnated material, where most of the Pd exists in the oxidation state 2+ and as well dispersed nano-particles on the surface [2], where it is accessible to the reactants. However, after reaction up to 900°C and subsequent cooling, LaFe_{0.95}Pd_{0.05}O₃ exhibits improved catalytic activity comparable to that of Pd/LaFeO₃. This phenomenon is well known in literature and described as activation route through high temperature treatment [3]. For better understanding of the structural changes of palladium during such pre-treatments and the consequence for the catalytic activity, we have performed in-situ XANES measurements on fresh and aged Pd/LaFeO₃ and LaFe_{0.95}Pd_{0.05}O₃ catalysts followed by reaction.

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Femtosecond Pump-Probe Experiments for the Investigation of Intramolecular Vibrational Energy Redistribution in Methane Derivatives After Overtone Excitation of the CH-Stretching Vibration

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Intramolecular vibrational energy redistribution (IVR) is essential for our understanding of intramolecular dynamics and for the theory of chemical reactions. One can derive the time evolution of the wavefunction theoretically from ab initio calculations and experimentally from high resolution IR-spectroscopy [1-3] or the intramolecular dynamics can be measured directly in femtosecond pump-probe experiments in the gas phase [3-6], where after near-IR excitation the time dependence of the population of the initially excited level is obtained from the absorption of a delayed IR or UV probe pulse. If a single excited molecular level is coupled to a dense set of background states a simple decay signal is obtained. However, in more complex cases oscillatory signals are measured and a decay may be superimposed. Using a hollow waveguide [5, 6] we have newly investigated the IVR process for differently deuterated methyl iodides and fluorides and we have observed the time dependent population for different vibrational levels of the Fermi resonance coupled CH-manifold.

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Dissociative Electron Attachment Cross Section of HCN: Isotope Effect

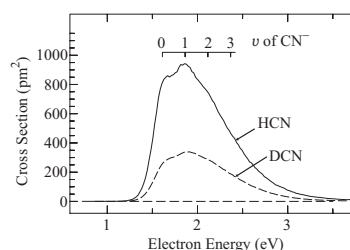
Dušan Kubala, Olivier May, Michael Allan

Department of Chemistry, University of Fribourg, Chemin du Musée 9, Fribourg 1700, SWITZERLAND

We present measurements of absolute partial cross sections for formation of the CN⁻ anion by dissociative electron attachment (DEA) to hydrogen cyanide (HCN) and its deuterated analogue:



The study is motivated by the current interest of theory [1] in this process and by its possible role as an initiator of abiotic synthesis of complex organic molecules in interstellar media and atmospheres of extraterrestrial bodies [2,3].



The absolute cross sections were measured with a recently constructed TOF-MS/trochoidal electron monochromator (TEM) [4]. Relative yields of the CN⁻ anions were then recorded under 60 meV resolution with standard TEM/QMS instrument and normalized to the absolute values (see Figure).

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Quantum mechanical processes at very high quantum numbers: Ion-pair states of Cl₂ at principal quantum numbers beyond 1000

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Ion-pair states of Cl₂ with principal quantum number $n > 1800$ have been observed by high-resolution vacuum ultraviolet spectroscopy. Ion-pair states are vibrationally and electronically highly excited states that consist of a cation and an anion bound by the Coulomb interaction. In the case of the homonuclear diatomic molecule Cl₂, the ion-pair Cl⁺-Cl⁻ consists of two nearly equally heavy ions leading to a qualitatively similar, but quantitatively completely different behaviour compared to Rydberg states [1], which consist of an electron bound to a positively charged ion core. The size of the reduced mass $\mu_{\text{Cl}^+\text{-Cl}^-}$ leads to a Rydberg constant $R_{\text{ion-pair}} = R_{\infty} \cdot \frac{m_{\text{Cl}}}{2m_0}$ for the ion-pair state that is ≈ 32000 times larger than R_{∞} .

In the present study, ion-pair states have been mainly investigated in the region of the Cl⁻(¹S₀) + Cl⁺(³P₂) dissociation threshold by laser excitation to the energy region around $\tilde{\nu} \approx 95'440 \text{ cm}^{-1}$ above the Cl₂ ground state and subsequent detection of the Cl⁺ or Cl⁻ fragments.

In this energy region, a regularly spaced spectral pattern could be observed, corresponding to predissociating ion-pair states of principal quantum around $n = 1850$ converging to the Cl⁻(¹S₀) + Cl⁺(³P₀) dissociation threshold. Application of different static and pulsed electric fields also enabled us to study the electric field ionisation and lifetime of these states. In particular, we observe the behaviour that one expects for long-lived Rydberg or ion-pair states. These states are coupled to a pseudocontinuum of high ion-pair states with principal quantum numbers in the range $n > 35000$, localised just below the Cl⁻(¹S₀) + Cl⁺(³P₂) dissociation threshold.

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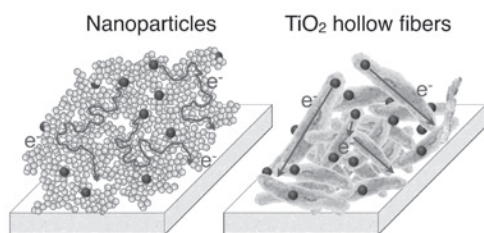
Enhanced Electron Collection Efficiency in Dye-Sensitized Solar Cells Based on Nanostructured TiO₂ Hollow Fibers

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Nanostructured TiO₂ hollow fibers have been prepared using natural cellulose fibers as a template. This cheap and easily processed material was used to produce highly porous photoanodes incorporated in dye-sensitized solar cells and exhibited remarkably enhanced electron transport properties compared to mesoscopic films made of spherical nanoparticles [1].



Photoinjected electron lifetime, in particular, was multiplied by 4 in the fiber morphology, while the electron transport rate within the fibrous photoanode was doubled. A nearly quantitative absorbed photon-to-electrical current conversion yield exceeding 95% was achieved upon excitation at 550 nm and a photovoltaic power conversion efficiency of 7.2 % reached under simulated AM 1.5 (100 mW cm⁻²) solar illumination.

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Making EXAFS surface sensitive? Red-ox cycles on Rh/Al₂O₃

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Automotive catalysts operate under severe conditions of temperature and atmosphere. They experience fast transients and periodic reaction conditions that are challenging to reproduce for mechanistic studies. Improved data evaluation is required to isolate the contribution of intermediate species. This can be achieved by a demodulation technique [1], that has been applied here to EXAFS, a typical bulk technique in an effort to capture the behaviour of noble metals at ca 4Hz, thus under conditions relevant to automotive catalysis. The time-resolved energy dispersive-EXAFS spectra collected at the Rh K-edge during a modulation experiment (CO vs. NO) on 2 wt% Rh/Al₂O₃ display only subtle changes in the absorption spectra. It is obvious from the spectra that Rh remains essentially reduced throughout the experiment. The demodulation algorithm generates a set of phase-resolved spectra in which the absorption jump is filtered out as well as all other features responding at a different frequency than that of the external stimulation. This processing considerably reduces the noise in the spectra. Small features in the EXAFS region can be then greatly resolved. From the demodulation envelopes the temporal behavior of the structural changes is precisely assessed from the averaged time-resolved spectra. The whole approach provides surface sensitivity to the EXAFS method: the data reveal that during the CO-NO pulses a likely thin oxidic layer is periodically formed and reduced [2]. The data allow recognizing that the observed subtle changes occur at different rates thus uncovering the detailed structural-dynamic behaviour of the system.

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New methods in Nuclear Magnetic Resonance to measure transverse relaxation rates in homonuclear *J*-coupled systems

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Measuring transverse relaxation rates in systems with homonuclear scalar-coupled spins is a challenge because the envelopes of spin echoes obtained with trains of refocusing pulses are normally modulated. These echo modulations can be quenched by cumulative pulse errors that arise after many refocusing pulses with moderate radiofrequency amplitudes, as long as some narrow "recoupling" conditions are avoided. This method was applied to systems with a large number of coupled protons [1]. Resonances of overlapping protons were analyzed by magnetization transfer to neighboring heteronuclei or using a heteronuclear two-dimensional experiment. The study of C^α in the three-spin system of alanine enriched in carbon-13 showed that the variation of the carrier frequency can be an additional tool to obtain modulation-free echo decays [2]. By changing the pulse angles from π to multiples of 2π, the "recoupling" conditions can be eliminated, while the refocusing property gets lost.

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Aluminum zoning in ZSM-5 crystals: its origin and characterization

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Aluminum zoning is an important phenomenon not only for the physicochemical characterization of the zeolite crystals, but also from the point of view of their application. It affects the catalytic properties of the zeolites and impacts post-synthesis treatments, such as dealumination and desilication.

We studied the spatial aluminum and silicon distribution in tetrapropylammonium-templated Al-ZSM-5 at different stages of the crystal growth, for crystals of different morphology and Si/Al ratio. Zeolite crystals were cut with focused ion beam and EDX mapping of the smooth cut was performed (Figure 1a). Aluminum was preferentially located in the shell. The base-assisted desilication showed that aluminum zoning was present in crystals of different size obtained after various crystallization times (Figure 1b).

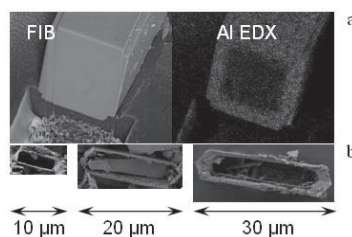
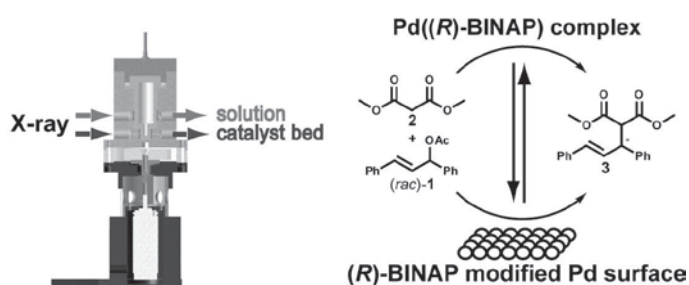


Figure 1. (a) SEM of the FIB cut of a ZSM-5 crystal and Al EDX mapping along it; (b) SEM of base-treated ZSM-5 crystals at different stages of the synthesis.

Asymmetric C-C bond formation reaction with Pd: How to favor heterogeneous or homogeneous catalysis?Sven Reimann¹, Jan-Dierk Grunwaldt², Tamas Mallat¹, Alfons Baiker¹¹ETH Zurich, Wolfgang-Pauli-Str. 10, 8093 Zurich (Switzerland)²KIT, Kaiserstr. 12, 76128 Karlsruhe (Germany)

Recently, we developed a readily accessible catalyst system using Pd/Al₂O₃ modified by chiral diphosphines for the asymmetric allylic substitution of (*rac*)-**1** with dimethyl malonate (**2**) [1]. However, determining the true nature of the active sites is a demanding task. Here we report a combined approach using *in situ* XANES spectroscopy and catalytic experiments to clarify the heterogeneous or homogeneous character of the Pd/Al₂O₃ – (*R*)-BINAP catalyst system. The study led to some surprising observations concerning the role of reaction components and conditions in preserving the metallic state of Pd or promoting metal leaching and molecular catalysis.

[1] S. Reimann, T. Mallat, A. Baiker, *J. Catal.* **2008**, *254*, 79–83.**Combined *in situ* FTIR and Raman microscopy of electrode materials – a new tool for battery scientists**Holger Schneider¹, Andreas Hintennach¹, Pascal Maire¹, Petr Novák¹¹Paul Scherrer Institute, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

We developed a new experimental setup which enables us to record *in situ* spatially resolved FTIR and Raman spectra of battery electrodes.

In situ Raman microscopy has been used with great success to elucidate the processes occurring both at battery cathodes and anodes while cycling with high spatial resolution on the order of (4 μm)³ [1]. *In situ* FTIR spectroscopy has proven to be a useful tool to follow changes occurring at the electrode materials while cycling as well. Like Raman microscopy, it is a surface sensitive method, i.e., it does not provide any information about the bulk structure. The information which can be drawn from the FTIR spectra is complementary to the insights from Raman experiments. However, in contrast to Raman microscopy, to the best of our knowledge all *in situ* FTIR electrochemical experiments performed so far have not made use of a microscope.

In our group, we designed a new cell for combined *in situ* Raman and FTIR microscopy, which allows for both *in situ* FTIR and *in situ* Raman microscopy characterization of the same spot of the electrode. (The resolution in the infrared range is not as good as for the Raman microscopy [sample sizes on the order of 10 μm–100 μm]). For instance, the growth of the SEI layer on a single graphite particle can be monitored, potentially even distinguishing between basal and edge planes, while the lithium intercalation can be followed by Raman spectroscopy on the same grain. First promising tests in these directions have been performed in our laboratory, including recording infrared spectra from the surface of a graphite electrode while cycling.

[1] R. Baddour-Hadjean, J.-P. Pereira-Ramos, *Chem. Rev.*, **2010**, *110*, 1278**Hard-X-ray photon-in-photon-out spectroscopy for the characterization of functional materials**E. Kleimenov¹, E. Alayon¹, J. van Bokhoven^{1,2}, A. Eliseev³, M. Janousch¹, N. Verbitskij³, A. Vinogradov⁴, and M. Nachttegaal¹¹ Paul Scherrer Institut, 5232 Villigen PSI² Institute for Chemical and Bioengineering, ETH Zurich, 8093 Zürich³ Moscow State University, 142432 Moscow, Russia⁴ St. Petersburg State University, 198504 St. Petersburg, Russia

Our recent instrumentation developments [1] at the SuperXAS beamline of the Swiss Light Source allowed the implementation of a row of new hard-X-ray spectroscopic techniques: X-ray emission spectroscopy (XES), high-energy-resolution fluorescence detected (HERFD) XAS, resonant inelastic X-ray scattering (RIXS), and X-ray Raman spectroscopy (XRS). A combination of these techniques delivers information on the density of occupied and unoccupied electronic states, symmetry of the chemical compound, and interatomic distances of a chemical compound investigated at ambient or reaction conditions. Two examples of the application of the techniques to functional materials will be presented.

The electronic and geometric structure of single-wall carbon nanotubes filled with copper halides have been found to depend strongly on the halogen atom type (Cl, Br, I). Variation in the interaction strength of the fill material with the walls result in the variation in the order and chemical state of copper atoms in the one-dimensional structure.

Electronic structure of a copper-zeolite catalyst for methane conversion was followed by HERFD XAS while changing the gas atmosphere and temperature between non-reactive and reactive conditions. The pronounced changes in the spectra were related to the changes in the type of the ligands and oxidation state of copper. The catalytically active state of the material has been characterized.

[1] Kleimenov E, Bergamaschi A, van Bokhoven J, Janousch M, Schmitt B, Nachttegaal M, *J. Phys.: Conf. Ser.* **2009**, *190*, 012035**EXAFS studies of leached Pt_xCo_x PEMFCs**L. Klüpfel^{1,2}, H. Schulenburg², M. Nachttegaal²¹ETH Zurich, Wolfgang Paulistrasse 10, 8093 Zurich, Switzerland²Paul Scherrer Institute, 5232 Villigen, Switzerland

In order to reduce the required amount of costly Pt in proton exchanged membrane fuel cells (PEMFCs), Pt-alloy catalysts were investigated. Several Pt-alloy catalysts, amongst Pt-Co alloys, exhibited an enhanced activity compared to pure Pt catalysts. The mechanism for this enhancement is still not fully understood [1]. However, the durability of these Pt-alloy catalysts is limited, as the non-noble elements have been shown to leach out over time [2].

The objectives of this study were to evaluate the influence of the synthesis pathway and the Pt:Co stoichiometry on the local geometric structure and thereby the durability of the Pt-alloy catalyst. Leaching experiments were conducted in 0.1M HClO₄, mimicking the acidic electrolyte in PEMFCs. The Pt-Co alloy catalysts were synthesized with the stoichiometries Pt:Co 3:1, 1:1, 1:3 applying three different synthesis pathways for each. Subsequently, by analyzing the extended X-ray absorption fine structure (EXAFS) spectra of the samples, the change in the local geometric structure from the unleached to the leached samples was investigated. The activity of the PEMFC before and after leaching was measured using voltametry.

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Scavenging Free Radicals to Extend Longitudinal and Transverse Relaxation Times in NMR using Hyperpolarization by Dissolution Dynamic Nuclear Polarization

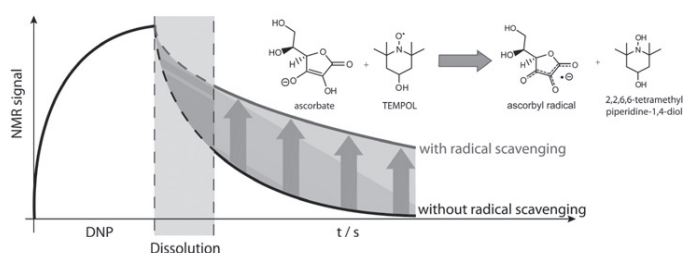
Pascal Miéville¹, Puneet Ahuja¹, Riddhiman Sarkar¹, Sami Jannin^{*1}, Paul R. Vasos¹, Sandrine Gerber¹, Mor Mishkovsky¹, Arnaud Comment¹, Rolf Gruetter¹, Olivier Ouari², Paul Tordo², and Geoffrey Bodenhausen^{1,3}

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Vitamin C extends lifetimes of hyperpolarized spin states and long-lived coherences: We demonstrate herein how nitroxide radicals that are widely used for DNP can be reduced by scavengers like sodium ascorbate (vitamin C) during the dissolution process, thus extending transverse and longitudinal relaxation times in NMR.



Long-lived coherences for homogeneous line-narrowing in spectroscopy

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Line-broadening, which arises either from inhomogeneous samples or from incoherent homogeneous relaxation effects, is the Achilles' heel of NMR spectroscopy. It turns out that coherent broadening may be considerably reduced by exploiting long life-times associated with superpositions of quantum states with different symmetry, termed long-lived coherences (LLC's). Very highly-resolved spectra can thus be obtained, with homogeneous line-widths that are much narrower than in conventional spectroscopy. The effect is illustrated by proton nuclear magnetic resonance spectroscopy of proteins in isotropic solution, where the slow oscillatory decays of LLC's yield spectra with considerably improved resolution compared to classical coherences, which decay with the spin-spin relaxation time constant, T_2 .

If external contributions to relaxation may be neglected, the gain in resolution obtained for a pair of coupled spins follows the calculated ratio of transverse relaxation times, i.e. $T_{LLC}/T_2 = 3$ in small molecules to $T_{LLC}/T_2 = 9$ in macromolecules or viscous media [3]. This should facilitate NMR experiments in viscous environments such as ionic liquids or inside the cell.

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[2] R. Sarkar, P. Ahuja, P. R. Vasos, and G. Bodenhausen, *Phys. Rev. Lett.* **2010**, 104, 053001.

Applications of Dynamic Nuclear Polarization in Solid-State NMR

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Dynamic Nuclear Polarization (DNP) can achieve increases in polarization of 2 orders of magnitude with respect to the Boltzmann equilibrium for proton NMR. The resulting increase in signal-to-noise ratios can reduce the time needed for signal averaging for many NMR experiments, thus reducing the acquisition times considerably. Following the pioneering work of Griffin and co-workers [1,2], Bruker Biospin has commercialized a system using DNP with Solid-State Magic Angle Spinning (MAS) NMR. The system operates at temperatures near 100 K, with sample rotation frequencies of up to 17 kHz. DNP is achieved by transferring polarization from highly polarized radicals via high power (~5 W) microwave irradiation from a gyrotron source. Molecules of interest are typically prepared in a solvent containing the radicals such as TEMPO which forms a glass on freezing.

We are currently applying DNP to new systems and developing new applications that take advantage of the greatly increased signal-to-noise.

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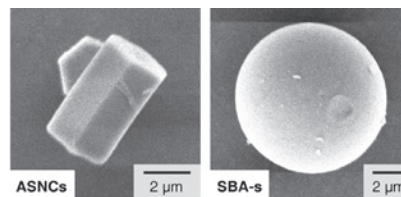
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Functional Group Distributions on Mesoporous Silica

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The control of the distribution of functional groups on mesoporous silica is essential for applications of these materials in various fields, including catalysis, drug delivery, adsorption, and sensing. The placement of functional groups on specific regions of the mesoporous silica surface (external particle surface, pore walls, pore entrances) is particularly challenging.^[1] We have developed methods that allow the independent functionalization of external surfaces and channel walls in arrays of silica nanochannels (ASNCs) and mesoporous silica spheres (SBA-s).^[2] The distribution of the functional groups was studied as a function of reaction parameters, such as solvent polarity or the presence of trace water, and analyzed by confocal laser scanning microscopy and nitrogen sorption.^[1,2,3]



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Adsorption of surface ions at liquid/liquid interfaces studied by time-resolved surface second harmonic generation

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We will report on the effect of salts added to the aqueous phase of an alkane/water interfacial system probed by the time-resolved surface second harmonic generation technique (TRSHG), which is known to be a powerful spectroscopic method for selectively probing the excited-state dynamics of molecules at the interfaces¹. The physical properties of the interfacial region have been investigated by measuring excited-state relaxation dynamics of malachite green (MG)^{1,2} dissolved in the lower phase of the interfacial system. The excited-state lifetime of MG is known to be strongly environment sensitive varying from 0.5 picoseconds (in water) to hundreds picoseconds (in more viscous solvent). Moreover, the excited-state lifetime increases strongly with the formation of MG aggregates.

The addition of salt to the bulk causes a reduction of the MG solubility and stimulates an attraction of MG cations to the interface changing the equilibrium constant between MG molecules adsorbed at the interface and those being dissolved in the bulk. A modified Frumkin-Fowler-Guggenheim (FFG) model³ has been proposed to describe the observed relation between the number of MG molecules and the bulk salt concentration.

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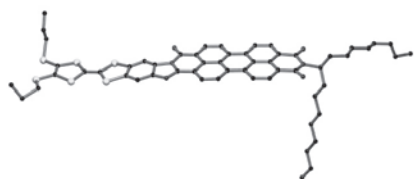
Annulated Donor-Acceptor Systems Incorporating Tetrathiafulvalene and Perylenebisimide Subunits

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Organic, electrochemically amphoteric compounds and charge-transfer (CT) systems have been attracting much attention due to their potential applications in organic (opto)electronic devices. Research efforts have been directed towards the design of molecular donor-acceptor (D-A) systems. The work at hand focuses on compactly fused, conjugated D- π -A assemblies comprising tetrathiafulvalene (TTF) and perylene-tetracarboxydiimide (PDI) moieties. Thus far, these two units have been combined using linkers and spacers,^[1] resulting in only weak coupling between the donor and the acceptor. Our type of annulated TTF-PDI systems exhibits strong interaction between the D and A moieties. The resulting electronic excited CT states lead to strong optical absorption over a wide spectral range.^[2]

The photophysical properties and redox-behaviour of two TTF- π -PDI systems (see Figure for single crystal structure of one example) will be presented.



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Oriental effects in time-resolved surface second harmonic generation studies of liquid/liquid interfaces

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Organic dye molecules adsorbed at an interface may lead to a significant rise of the intensity of the second harmonic light generated at this interface due to resonant enhancement of the nonlinear susceptibility $\chi^{(2)}$ [1]. In a time-resolved surface second harmonic generation experiment, optical excitation of the dye molecules usually leads to a decrease of the second harmonic intensity due to depopulation of the dye ground state. In certain cases however, when the evolution of individual components of the nonlinear susceptibility tensor is recorded, an increase of the second harmonic intensity may be observed. The presence and magnitude of this rise at liquid/liquid interfaces depend on the liquids constituting the interface and are correlated with the orientation of the molecules at the interface.

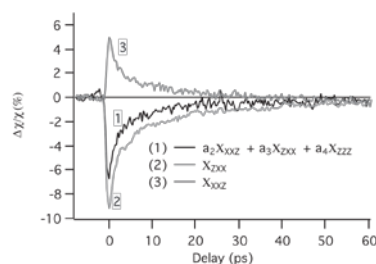


Fig. 1. Temporal evolution of various components of the nonlinear susceptibility tensor measured at a liquid/liquid interface.

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Study of the sympathetic cooling of molecular ions in a surface-electrode ion trapI.M. Georgescu¹ and S. Willitsch¹¹Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

Due to their open geometry, Surface Electrode (SE) ion traps are now being used in various experiments such as: quantum computation [1], the study of cold collisions between ions and neutrals [2] or cold-chemistry experiments [3]. We study both numerically and experimentally ensembles of laser-cooled atomic ions and sympathetically-cooled of molecular ions in SE traps.

We investigate the dynamics of trapped ions using molecular dynamics simulations based on numerically calculated electrical potentials. These molecular dynamics simulations allow us to study the shape and structure of the crystallized atomic and molecular species as well as their sympathetic cooling and heating.

We constructed a new type of SE electrode trap with large electrodes and small inter-electrode gaps. The trap is laser-cut in thin gold-coated stainless-steel foil mounted on a small insulator frame, which is fixed on a gold-plated circuit board with the RC-filter electronics. The key feature of this design is the elimination of exposed dielectric surfaces that due to the accumulation of stray charges cause unwanted electric fields. Atomic Ca⁺ ions are loaded by photoionization of neutral Ca in the trapping zone and laser cooled. Cold molecular ions are produced by photoionization and sympathetic cooling by the Coulomb interaction with the laser-cooled Ca⁺ ions.

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A new experiment to study ultracold ion - molecule reactions

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A new experiment for the study of chemical reactions between molecular ions and atoms at ultralow temperatures ($T \leq 1$ mK) has been conceived and developed, allowing to probe chemical processes at energies three orders of magnitude lower than previously investigated [1]. Ultracold molecular ions are produced by sympathetic cooling with a Ca^+ coulomb crystal in a linear rf quadrupole trap. Ultracold atoms are generated in a magneto-optical trap. The combination of both traps completely *in vacuo* leads to a highly flexible apparatus, enabling the study of molecular interactions in a regime where quantum mechanical effects may dominate reactions. The design and construction of the experiment are discussed and prospects for future investigations are highlighted.

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MANIPULATING COLD RYDBERG ATOMS AND MOLECULES

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The development of methods to decelerate and manipulate the translational motion of Rydberg atoms and molecules in the gas phase using static and time-varying inhomogeneous electric fields [1] has led to the experimental realisation of Rydberg atom optics elements including a lens [2], a mirror [3] and two- and three-dimensional traps [4,5]. These experiments make use of the very large electric dipole moments associated with Rydberg Stark states. Recently, we have demonstrated the possibility to extend these techniques to molecules by stopping a seeded, pulsed, supersonic beam of H_2 travelling with an initial velocity of 500 ms^{-1} within 3 mm in approximately $15 \mu\text{s}$ using electric fields of a few kVcm^{-1} [6].

The cold samples are well suited to applications in precision spectroscopy, in studies of slow predissociation and in investigations of inelastic collisions involving Rydberg atoms and molecules at low collision energies. In experiments in which the Rydberg atoms and molecules are trapped, trap losses can be caused by transitions induced by blackbody radiation, by collisions between Rydberg states and collisions with the background gas. To study these different processes, we have developed a new deceleration and trapping scheme with which the Rydberg atoms and molecules are deflected from the supersonic beam during deceleration prior to trapping.

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Generation and Charge-transfer Spectroscopy of State-Selected and Translationally Cold N_2^+ Molecular Ions

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The generation and study of translationally cold molecules and ions represents one of the most recent and exciting new developments in physical chemistry. Although the complex internal structure of molecules has precluded the application of laser cooling, molecular ions can be cooled and Coulomb crystallised by exchanging kinetic energy with laser cooled atomic ions by means of the Coulomb interaction ("sympathetic cooling").

Sympathetically cooled molecular ions are translationally cold, however their internal degrees of freedom are generally in thermal equilibrium with the environment because of the coupling to the ambient black-body radiation (BBR) field. For a number of applications it is essential to prepare internally state-selected species which has only very recently been achieved in polar molecular ions using optical pumping methods. However, these techniques are not applicable to non-polar ions of fundamental interest like H_2^+ and N_2^+ . We presently develop a new experimental setup which will allow for the first time to produce Coulomb crystals of state-selected non-polar molecular ions based on the combination of threshold-photoionization with sympathetic-cooling methods.

In our current experiment, molecular N_2^+ ions are produced in a well-defined rotational quantum state by resonance-enhanced multiphoton ionisation (REMPI) of neutral N_2 molecules inside an ion trap. Rovibronic state selection is achieved by ionizing only slightly above the required rotational *ionization threshold* accessible from a selected rovibronic *intermediate level* used in the excitation process. Such state-selected ions are then sympathetically cooled by the Coulomb interaction with laser-cooled Ca^+ atomic ions. State-selective preparation and the lifetimes of the prepared rotational states are studied using a spectroscopic scheme based on the laser induced charge transfer reaction: $\text{N}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2$.

Cold atomic and molecular samples by multistage Zeeman deceleration

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Multistage Zeeman deceleration exploits the interaction of open shell atoms and molecules with inhomogeneous magnetic fields to manipulate the translational motion of pulsed supersonic beams [1-5] and allows the production of cold samples of species that cannot be laser cooled. We report on the development of our latest generation of multistage Zeeman decelerators. A new modular design enables us to easily adapt the length of the decelerator to the mass and magnetic moment of the species of interest. Typical relative translational temperatures of samples prepared in this way are in the range of 10-100 mK and are therefore ideally suited for applications in precision spectroscopy and studies of cold reactive collisions. We have employed multistage Zeeman deceleration to stop ground state hydrogen and deuterium atoms in the lab frame and load the atoms into a magnetic quadrupole trap [4,5]. The implementation of an accurate three-dimensional particle trajectory simulation program has been essential to achieve a complete interpretation of the dynamics of the deceleration and trap loading processes. In this contribution we shall also present studies of the transverse and longitudinal phase-space stability during the deceleration process and their implications on the design of optimal pulse sequences for extended multistage Zeeman decelerators.

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Rotationally resolved spectroscopy and potential energy curves of the X 0⁺ ground state and excited C 1 and D 0⁺ states of ArXe and of the low-lying electronic states of ArXe⁺

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ArXe and ArXe⁺ play an important role in ion lasers and excimer lasers and their electronic spectrum has been studied by high resolution spectroscopy [1,2,3]. However, the rotational and hyperfine structures of the electronic spectra has not been observed yet. A narrow-bandwidth VUV laser system [4] has been used to measure rotationally resolved spectra of the D 0⁺ ← X 0⁺ and C 1 ← X 0⁺ transitions of selected isotopomers of ArXe. Rotationally resolved photoelectron spectra have been recorded from selected rovibrational levels of the D 0⁺ and C 1 states. These spectra provide information on the potential energy curves of the X 0⁺, D 0⁺ and C 1 states of ArXe and of the low-lying electronic states of ArXe⁺. The analysis of the rotational structures enabled the characterization of the dissociation pathway from the C 1 state of ArXe [5]. In the case of Ar¹²⁹Xe and Ar¹³¹Xe the hyperfine structure could also be resolved and analyzed. These results significantly extend the current knowledge on ArXe and ArXe⁺.

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Photophysics of human lens UV filters in biological environment

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Kynurenine (KN) and its derivatives act as UV filters in the human lens, protecting eye tissues from harmful UV radiations. The mechanism of this effective UV protection has been recently explored [1]; it has been shown that intermolecular hydrogen bonds are responsible for the fast radiationless S₁→S₀ transition in protic solvents. Unfortunately, kynurenines are unstable under physiological conditions and the decomposition products can covalently bind to lens proteins. UV filter-modified lens proteins exhibit a higher photochemical activity than unmodified kynurenines. This may be a contribution to the development of cataract.

We present here the study of the photophysics and photochemistry of KN covalently bound to the amino acids cysteine, histidine and lysine and to the protein lysozyme. The goal is to examine the influence of a model biological environment on the photoactivity of KN.

The femtosecond time-resolved measurements reveal a two-fold increase of the S₁ state lifetime of KN after the attachment to amino acids; the nanosecond-resolved experiments have shown similar increase of the triplet state yield. The binding to a more bulky substituent – a lysozyme protein – leads to a 7-fold increase of the fluorescence quantum yield as compared to free KN. The obtained time profiles of the excited-state dynamics reveal a multiphase decay, which corresponds to KN attached at different positions of the protein. The weakening and/or blocking of intermolecular hydrogen bonds between KN and solvent molecules should be responsible for the changes in the photochemical properties of KN.

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Excited State Dynamics of Wurster Salts

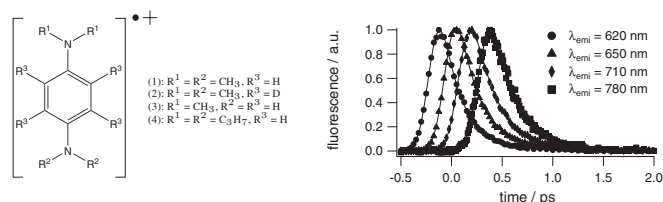
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One of the key-steps in the harvest of sunlight by photovoltaics is the electron transfer (ET) reaction. Despite intensive theoretical [1] and experimental [2] efforts, many basic questions that concern this fundamental reaction remain subject of debate, among them the photophysics of the direct products formed upon ET.

We present femtosecond time-resolved fluorescence up-conversion and transient absorption results for the cations of various *p*-phenylenediamine derivatives. These ions show up in many ET studies since their neutral parent compound are excellent electron donors [2, 3]. By derivatization at both, the amino groups and the phenyl core, we gain experimental insight into the internal coordinate that is responsible for the ultrafast excited state decay found for all of them. The excited state lifetime of the famous Wursters Blue radical cation (1), for example, was found to be only 200 fs at room temperature (see Figure). A detailed picture is obtained by extensive D₀-D₁ energy mapping done *via* CASPT2/CASSCF//Amber quantum mechanical calculations performed for this radical cation.



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Periodical-DFT studies of pressure effects on solids

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The pressure effect on solid state materials is analyzed with periodical DFT calculations, performed within Local Density Approximation (LDA)[1] and Generalized Gradient Approximation (GGA)[2].

Variations of cell parameters dimensions and vibrational frequencies shifts (Raman and IR modes) as function of pressure are calculated and from this bulk moduli and Grüneisen parameters are obtained; when possible, the comparison with experimental data is reported.

For BaFCl physical and chemical pressure effects are studied: the physical pressure is suppose to be isotropically applied; the chemical pressure is studied considering the Ba_{1-x}Sr_xFCI solid solutions with 0<x<1. The solid solutions calculations are performed in the Virtual Crystal Approximation.

The characterization of BaFCl and Ba_{1-x}Sr_xFCI allows to make a correlation between physical and chemical pressures.

Ternary metal hydride systems were also treated with this approach.

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The rotational structure and large-amplitude motion in the PFI-ZEKE photoelectron spectra of the ground state of $C_3H_6^+$ and $C_3D_6^+$

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The pulsed-field-ionization zero-kinetic-energy photoelectron spectra of the origin band of the $\tilde{X}^+ 2A'' \leftarrow \tilde{X} 1A'$ transition of propene (C_3H_6) and perdeuterated propene (C_3D_6) have been recorded at high resolution using a narrow bandwidth vacuum ultraviolet (VUV) laser system [1] and optimized electric field pulse sequences [2], allowing for the partial resolution of the rotational structure. The analysis of the spectra in the realm of the orbital ionization model for rigid-rotor asymmetric-top molecules [3] enabled the determination of the adiabatic ionization energy of propene and the rotational constants of $C_3H_6^+$ and $C_3D_6^+$. The tunneling splittings resulting from the hindered rotation of the methyl group could not be resolved and the analysis was therefore carried out in the C_s molecular symmetry group. Angular momentum contributions of p_π , d_π and d_σ character were included in the single-center expansion describing the molecular orbital out of which ionization occurs, leading to the selection rules $|\Delta N| = |N^+ - N''| \leq 2$ and $\Delta K_a = K_a^+ - K_a'' = \pm 1, \pm 2$ and to photoelectron partial waves with angular momentum quantum number up to $\ell = 3$. The observation of a strong spectral feature associated with $\Delta K_a = 0$ indicates the importance of vibronic interactions which are also implied by the observation of vibrational bands of A'' symmetry in the photoelectron spectra of the $\tilde{X}^+ 2A''$ state of $C_3H_6^+$ and $C_3D_6^+$. The spectra reveal an anharmonic progression associated with the internal rotation of the methyl group [4]. The assignment of the complex vibrational structure can be achieved by investigating partially deuterated isotopomers.

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Femtosecond Degenerate Four-Wave Mixing of Cyclohexane and Deuterocyclohexane

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Obtaining precise structural information of nonpolar cycloalkanes is of great interest for chemistry. The technique of femtosecond degenerate four-wave mixing (fs-DFWM) is very well suited to fulfill this task [1]. In the present poster, we report the use of fs-DFWM for the measurement of highly accurate rotational and centrifugal distortion constants of the nonpolar cycloalkanes cyclohexane (C_6H_{12}) and deuterocyclohexane (C_6D_{12}). We compare the molecules, which both can be treated as symmetric tops [2], in terms of their rotational and centrifugal distortion constants.

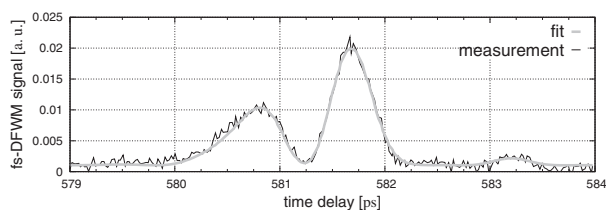


Figure 1: Selected fs-DFWM transient of cyclohexane. Black: experimental data, gray: fit to the data. The fit allows to determine the rotational and centrifugal distortion constants.

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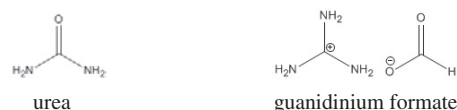
Guanidinium formate as novel ammonia precursor compound for the selective catalytic reduction of NO_x in engine exhaust gas

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Future emission limits are focusing on a strong decrease of nitrous oxides (NO_x) in the exhaust gas of diesel engines. This can be achieved by applying the selective catalytic reduction (SCR) process to reduce the NO_x with ammonia over a catalyst.^[1]

Nowadays, an aqueous solution of urea (AdBlue[®]) is used as safe ammonia precursor for mobile applications. Due to the poor temperature stability and low ammonia releasing potential of the solution, novel ammonia precursor solutions have been investigated.^[2]



Mixtures of guanidinium formate with urea and water exhibit improved temperature stability and release up to 1.5 times more ammonia than AdBlue[®].^[3] Due to the more complex structure of guanidinium formate, the optimum conditions for catalytic hydrolysis had to be investigated.

In a new laboratory SCR test stand, aqueous solutions of either up to 60% guanidinium formate or a mixture of 38% guanidinium formate and 15% urea could be decomposed on commercial catalysts without significant side-product formation. The decomposition was monitored by real time gas analysis utilizing FTIR spectroscopy and aerosol analysis employing HPLC.

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Analysis of the Accuracy of the Raman Femtosecond Degenerate Four-Wave Mixing Technique

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The accuracy of the femtosecond degenerate four-wave mixing (fs-DFWM) technique is statistically analyzed using the model molecule CO_2 . To reliably estimate the measurement errors, the profile likelihood method is applied to obtain the confidence intervals of the multi-parameter fit.

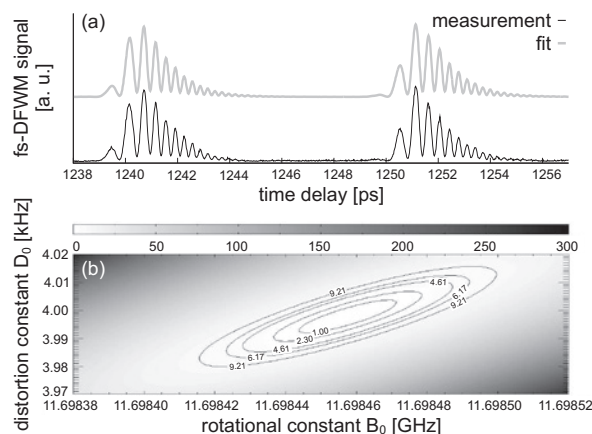


Figure 1: (a) Selected fs-DFWM transient with corresponding model fit. (b) Profile likelihood estimation. The χ^2 is expressed as a gray scale. The narrower the ellipses, the more accurate the rotational and centrifugal distortion constants.

Chemo-selective hydrogenation of substituted nitro aromatics

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Substituted aromatic amines are important intermediates in chemical industry for the production of pharmaceuticals, fine chemicals, herbicides and polymers. Usually they are prepared via catalytic reduction of the corresponding nitro compounds. While simple nitro compounds are easily reduced over a wide range of commercial catalysts, the selective hydrogenation of nitro groups in the presence of other reducible functional groups is a more difficult task. The employed catalytic systems exhibit major drawbacks such as the formation of by-products and limited reusability [1]. Recently Corma et al. [1] discovered that supported gold catalysts catalyzed the liquid phase hydrogenation of substituted nitro compounds under mild conditions. Nitro aromatics containing additional functional groups such as double bonds, carbonyl, amide or nitrile groups were converted to the corresponding amines with very high selectivities (> 95 %). Goal of our work is to design highly active and selective catalysts for the development of new, clean and sustainable industrial processes. To achieve that the origins of the factors that influence the catalytic performance and the reaction mechanism have to be understood. Our focus lies on the selective hydrogenation of 4-nitrobenzaldehyde to 4-aminobenzaldehyde over supported gold catalysts. In particular the effect of particle size, gold loading, support material, pre-treatment conditions and the addition of radical initiators are being investigated.

[1] A. Corma, P. Serna, *Science* **2006**, 313, 332.**Elucidating the reaction mechanism of the hydrogenation of nitro benzenes over Au/MeOx catalysts**

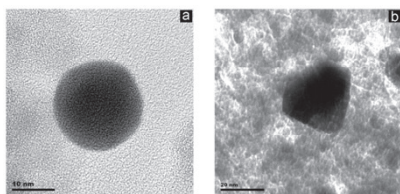
Martin Makosch and Jeroen A. van Bokhoven

ETH Zürich, Wolfgang Pauli Strasse 10, 8093 Zürich, Schweiz
Paul Scherrer Institut, Energy and Environment, 5232 Villigen, Schweiz

Chemo-selective hydrogenation is of fundamental importance in the production of fine chemicals, agrochemicals, and pharmaceuticals. State of the art catalysts contain often supported nickel, palladium or platinum and more or less toxic modifiers to increase selectivity[1]. Recently Corma et al. discovered that Au/MeO_x catalysts show very high activity and chemo-selectivity in the liquid/solid phase hydrogenation of nitrobenzene even without modification[2]. Especially Au/TiO₂ catalysts showed high chemo-selectivity without accumulating explosive intermediates and thus could be an environmental friendly alternative to state of the art catalysts used so far. Although many proposals about how the reaction takes place on the catalyst have been made, it is still not clear what the reaction pathway on the catalyst is and how the different components of the catalyst interact with the substrate. Goal of our work is to get mechanistic insights into the hydrogenation of nitro benzenes over supported gold catalysts and to improve the performance of those catalysts regarding the activity as well as the selectivity. Our approach is to correlate combined *in situ* X-ray absorption spectroscopy (XAS) and attenuated total reflection infra red spectroscopy (ATR IR) measurements with kinetic measurements. With the resulting structure/performance relationships we will investigate which parameters influence the reaction and how they can be improved. For this an *in situ* XAS/ATR IR cell is designed and Au/MeO_x catalysts are synthesized. The reaction will be examined with those catalysts and different nitro benzene derivatives to see the influence of the support and the influence of the functional groups as a function of the position on the ring.

[1] H.U. Blaser, H. Steiner, M. Studer *ChemCatChem* **2009**, 1, 210-221.[2] A. Corma, P. Serna, *Science* **2006**, 313, 332.**Influence of phosphorous aging on automotive catalysts**A. Winkler¹, D. Ferri², M. Santhosh Kumar², M. Aguirre²¹Empa, Internal Combustion Engines Laboratory, CH-8600 Dübendorf, Switzerland²Empa, Laboratory for Solid State Chemistry and Catalysis, CH-8600 Dübendorf, Switzerland

Increasingly stringent emission regulations for the automotive sector (upcoming Euro 6) in combination with high durability demands for the catalyst require detailed knowledge of the catalyst aging phenomena. Whereas thermal aging occurs due to high temperature induced sintering, chemical aging results from combustion products of motor oil based additives (e.g. zinc dialkyldithiophosphates) accumulating on the catalyst.



Phosphorous based combustion products strongly influence the morphology of the catalytically active platinum particles of an engine aged automotive catalyst. In the presence of phosphorous, smaller spherical platinum particles are formed (HR-TEM, Figure a) whereas in the absence of phosphorous sintering results in larger, polyhedral platinum particles (Figure b). With regard to the catalytic activity, the smaller spherical platinum particles show significantly lower NO oxidation activity than the polyhedral platinum particles [1]. Similar results have been obtained after synthetic aging at lab scale revealing that the effect of phosphorous on particle size and shape is general.

[1] A. Winkler, D. Ferri, M. Aguirre, *Appl. Catal. B* **2009**, 93, 177.**Methane combustion on Pd catalysts: structure activity studies by operando XANES under genuine conditions**M. Santhosh Kumar, M. H. Aguirre, A. Weidenkaff and D. Ferri
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The combustion of methane is essential to diminish its impact on global warming [1-3]. Although Pd based catalysts are the most effective for this reaction, the intriguing behaviour of Pd is not yet completely understood and is still a subject of debate [2,3]. In this study, the behaviour of Pd supported on γ -Al₂O₃ was monitored by operando X-ray absorption spectroscopy during combustion of methane between ca. 350 and 1123 K (during both heating and cooling) in a lab scale fixed bed reactor coupled with a mass spectrometer. This setup enabled us to overcome the intrinsic limitations of *in situ* reaction cells and thus obtain accurate and reliable data on structure activity relationships. The results indicate that Pd oxide species are the active sites, in particular below 950 K and above this temperature metallic Pd can also catalyze the reaction. The improved combustion activity of the catalyst below 650 K while cooling is attributed to decreased Pd dispersion and increased Pd oxide particle size as evidenced by EXAFS, STEM and CO chemisorption studies on the fresh and used catalysts.

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Tracking Ultrafast Cis-Trans Isomerization with Transient Infrared Anisotropy Measurements

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Cis-Trans isomerization is an elementary reaction of wide importance and is involved in many reaction steps in nature. Following Cis-Trans isomerization in time is a challenging target for spectroscopists, and could be of great importance in aiming to understand the critical steps to get it fast and efficient.

Here, we discuss on how polarization sensitive time-resolved mid-infrared spectroscopy can be used to directly observe the structural changes occurring during ultrafast cis to trans photo-isomerization. We applied our method on a zwitterionic N-alkylated indanylidene pyrroline photoswitch (Z-NAIP). Previous work on this photoswitch [1, 2] showed that it undergoes ultrafast isomerization by passing through a conical intersection with a wavepacket behavior in the sub picosecond timescale.

Our results suggest that the isomerization is mostly due to the rotation of the pyrroline moiety, which carries a 15D permanent dipole moment, and not the much larger indanylidene moiety. We discuss the possibility of detecting unidirectional rotation during the isomerization process.

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Heterodyne-detected photon echo measurements using a frequency doubled cavity dumped femtosecond oscillator

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The aim of the project is a detailed comparison of the heterodyne-detected photon echo technique and related population spectroscopy techniques based on transient absorption (TA) and time resolved fluorescence (TRF) detection for investigating polar solvation dynamics and energy transfer processes.

The photon echo experiment is a four-wave-mixing technique, which allows a full control of the four fields involved in a third order nonlinear optical process. It removes the inhomogeneous contribution to the electronic dephasing and permits thereby to study solvent fluctuation and relaxation in real time. The heterodyne detection scheme provides information about both amplitude and phase of the signal field as a function of time by an interference with a secondary field used as known reference and commonly called local oscillator. The experimental set-up consists of a cavity dumped Ti:Sapphire oscillator which provides sub 20 fs pulses at 800 nm with an energy per pulse of up to 50 nJ. Dispersion control by two separate prism compressors permits to obtain bandwidth-limited pulses at 400 nm with a conversion efficiency up to 40%. The same laser system can be used as a source for an all-reflective up-conversion set-up, which allows studying the same sample under identical excitation conditions using two different experimental methods.

First results of the examination of solvation dynamics by means of a heterodyne-detected photon echo experiment with 400 nm excitation will be presented.

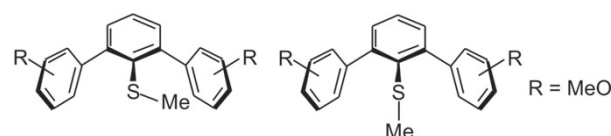
Radical cations of thioanisole derivatives.

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It is known that the thioethers side chains of proteins containing methionine are susceptible to oxidation by reactive oxygen species. [1] It is postulated that cataract formation and neurodegenerative diseases such as Parkinson's and Alzheimer's are the consequence of this process. [2] It has also been reported that the radical cations of thioethers are stabilized by arenes that are not directly connected to them, forming S $\cdots\pi$ interactions. [3] We therefore decided to study the effect of flanking aryl groups on the properties of the radical cation of thioanisole. In particular we were interested in the conformation of the S-Me in relation to the centred phenyl moiety (in parent thioanisole radical cation these are coplanar, with a high rotational barrier). We employed low-temperature spectroscopy and quantum chemical calculations to address this question.



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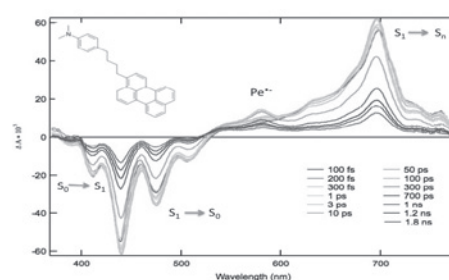
The excited-state dynamics of a Perylene-Dimethylaniline bridged system

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The excited state dynamic of a donor-bridge-acceptor system consisting of N, N dimethylaniline (DMA) as electron donor and Perylene (Pe) as electron acceptor has been investigated in different solvents various time resolved spectroscopic techniques.

The time constants obtained to reproduce the fluorescence decay evidence the occurrence of an electron transfer process in all the solvents used, with a quenching efficiency that increases with the solvent polarity. Transient absorption spectra confirmed the existence of charge-separated state and the intensity of its absorption band shows a dependence of the solvent polarity. The weak intensity of this band centered at 587 nm relative to that at 700 nm due to S₁ absorption of perylene points to a very small population of the charge separated state. This can be explained by a charge recombination that is faster than the initial charge separation, a phenomenon known as inverted kinetics. The origin of such dynamics will be discussed.



The formation of PdZn alloy and its catalytic activity in the hydrogenation of 1-pentyne

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The potential of PdZn alloy to replace the conventional catalyst in several important catalytic reactions has been explored. Improved thermal stability and selectivity were reported in various reactions [1-3]. X-ray diffraction showed that the extent of alloy formation increases at elevated temperatures [4]. It was postulated that during the reduction, hydrogen spills over from palladium metal to reduce the ZnO and forms the Pd-Zn intermetallic phases. The zinc metal which decorates palladium sites significantly decreases the available palladium sites and, consequently, suppresses the catalytic activity. To optimize the potential of PdZn alloy in various catalytic reactions, it is necessary to establish how exactly it is formed during reduction, its stability under reaction condition and if the structure-performance relationship exists. Results from in situ XRD and XAS showed that the formation of alloy started from the surface at a temperature as low as 100°C, under reducing condition. This affects the catalytic performance as the full hydrogenation was completely suppressed.

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Pulsed-Field-Ionization Zero-Kinetic-Energy (PFI-ZEKE) Photoelectron Spectroscopic Study of the $\tilde{X}^2\Pi \rightarrow \tilde{X}^+ 1\Sigma^+$ ($v = 1$) Transition of NO

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The pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectrum of NO in a cold supersonic beam has been measured in the region of the $\tilde{X}^2\Pi \rightarrow \tilde{X}^+ 1\Sigma^+$ ($v = 1$) band between 77040-77100 cm^{-1} . The PFI-ZEKE spectra were obtained with a resolution of better than 0.07 cm^{-1} and full rotational resolution was obtained. Additionally, Rydberg-state-resolved (RSR) PFI-ZEKE spectra were obtained for the same band. This variant of PFI-ZEKE allows for the determination of the position of ionic energy levels at an accuracy limited by the bandwidth of the tunable photoexcitation source and for the study the interactions between different rotational ionization channels of NO. The high resolution of the PFI-ZEKE experimental setup can be used to study large amplitude motions in larger molecular cations.

In Search of the Marcus Inverted Region using Femtosecond Spectroscopy

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The Marcus Inverted Region (MIR), i. e. the slowdown of the rate of electron transfer (ET) upon increasing its driving force, for intramolecular forward ET in linked donor-acceptor systems [1] and intermolecular back ET [2] could be unambiguously established in the mid-eighties. However, since Rehm's and Weller's pioneering work in the late sixties the MIR for photoinduced intermolecular electron transfer has "escaped" observation until today.[3] This apparent absence of the MIR in this type of reactions has puzzled and inspired the scientific community at least as much as its Nobel prize rewarding prediction in 1956.[4]

Contrary to intramolecular and back ET, where the reaction partners are in close contact, intermolecular forward ET requires the diffusive approach of the reactants prior to the reaction thus masking the *per se* much faster elementary reaction. Previous attempts to extract the intrinsic electron transfer rate from the diffusion influenced kinetics failed, however, due to their limited time resolution (ps-regime).[5] Fortunately, the recent advent of femtosecond spectroscopic techniques allows for probing the pure initial electron transfer dynamics prior to the onset of their diffusive perturbation.

We are confident, that a femtosecond time-resolved "Rehm-Weller plot" will provide a more definite answer to the long lasting enigma of the apparent lack of the MIR in photoinduced forward electron transfer reactions.

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Jahn-Teller effect and spin-orbit coupling in the electronic ground state of CH_3I^+ and CD_3I^+ from rotationally resolved photoelectron spectra

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We present the high-resolution PFI-ZEKE photoelectron spectra of the $X^+ 2E$ ground states of both CH_3I^+ and its deuterated isotopomer, CD_3I^+ . The spectral resolution of better than 0.15 cm^{-1} allowed full rotational resolution of the lower spin-orbit components $^2E_{3/2}$ for the first time.

CH_3I^+ and CD_3I^+ experience a very strong spin-orbit coupling and consequently have to be treated in the corresponding spin-double group, $C_{3v}^2(M)$: Their rotational structures are reproduced with spectroscopic accuracy using a rovibronic Hamiltonian [1], which incorporates the effects of the spin-orbit as well as the Jahn-Teller coupling on the rotational structure. In addition, a set of rovibronic photoionization selection rules was derived which describes Hund's case (b) to Hund's case (a) ionizing transitions in polyatomic molecules and account for the experimental observations.

Deuteration of CH_3I^+ does not affect the purely electronic properties and therefore provides the opportunity to unambiguously determine all relevant spin-orbit coupling parameters (a and ζ_e) and the linear Jahn-Teller coupling constants d_H and d_D . Finally, the ionization energies E_I and rotational constants along with the ground state structures of the methyl iodide cation and its deuterated isotopomer are derived with better accuracy than previously possible [2,3].

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Rovibrational Spectroscopy of Small Organic Molecules in the THz Frequency Region

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The fundamental bands of the CCl₃ asymmetric deformation modes of selected isotopomers of chloroform (CHCl₃) and freon-11 (CFCl₃) have been measured between 7 and 8 THz in a static cell at ambient temperature using a laser-based source of tunable radiation in the terahertz region (0.1-10 THz) of the electromagnetic spectrum [1]. Simulation of the rotational contour of the ν_6 fundamental transition of ¹²CH³⁵Cl₃ confirmed previously suggested values for C_6 and $C_6\zeta_6$ [2]. The fundamental frequencies were derived with a precision of 2 GHz for all compounds except CF³⁵Cl₃, where the precision amounted to 3 GHz. The frequencies are in agreement with values calculated *ab initio*.

Development of an experimental setup with which it is possible to partially resolve the rotational structure of these molecules is in progress. In this experiment, the vibrational excitation will be followed by photoionization of the upper vibrational level using another laser source. By tuning the frequency of the THz source and detecting the photoions, this double-resonance scheme should enable sensitive, background-free and isotopomer-selective absorption measurements.

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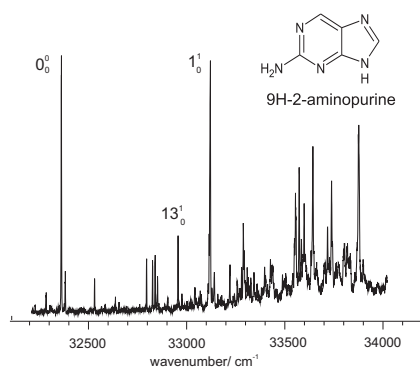
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Supersonic Jet Spectroscopy of the Adenine Analogue 2-Aminopurine

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The chemical structure of 2-aminopurine (2AP) differs from adenine (6-aminopurine) only in the position of the amino group, but the lifetime of its S_1 state is significantly longer (2.1 ns) than that of adenine (10 ps). Jet-cooled 2AP has been previously studied [1, 2]. We have investigated the vibronic spectrum and excited-state nonradiative processes of supersonic jet-cooled 2AP and d₃-2AP by prompt and delayed two-color resonant two-photon ionization spectroscopy. The rotational contour of the 0_0^0 band shows that the transition is $^1\pi\pi^*$. Excitation is followed by rapid intersystem crossing to a $^3\pi\pi^*$ state.



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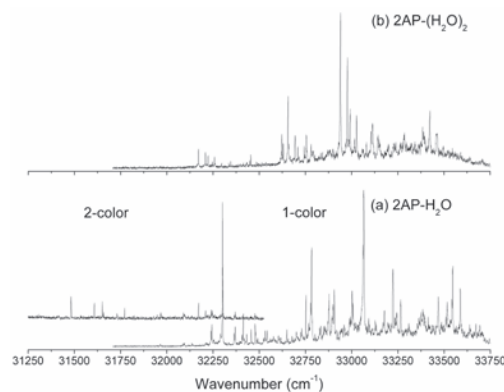
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Excited state spectroscopy of jet cooled 2-aminopurine-(water)_{1,2} clusters

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2-aminopurine (2AP) is a purine base analogous to the nucleobase adenine, differing in the position of the -NH₂ group. The resonant two photon ionization (R2PI) spectrum of 2AP has been reported earlier [1]. Here, we present the one and two-color R2PI (1C-R2PI, 2C-R2PI) spectra of 2AP-H₂O and 2AP-(H₂O)₂ clusters. The effect of microhydration on the electronic $^1\pi\pi^*$ origin [2] and other vibrational fundamentals of 2AP is investigated on the basis of observed changes in the R2PI spectra of these species. Several isomers of 2AP-H₂O cluster are identified and studied using 2C-R2PI experiments.



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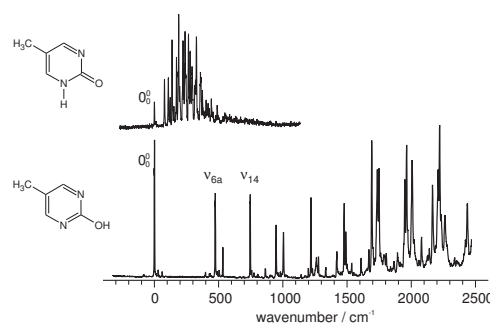
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Jet Spectroscopy of the Deoxythymine Tautomers 5-Methyl-2-Hydroxypyrimidine and 5-Methyl-2-Pyrimidinone

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We have investigated the absorption spectra of jet-cooled 5-methyl-2-hydroxypyrimidine (5M2HP) [1] and 5-methyl-2-pyrimidinone (5M2P), the two tautomeric forms of deoxythymine, using two-color resonant two-photon ionization (R2PI) spectroscopy. Unlike uracil and thymine, which exhibit structureless optical spectra [2], the vibronic spectra of 5M2HP and 5M2P are well-structured with narrow vibronic bands, allowing to probe the excited state of a thymine analogue. The spectrum of 5M2HP shows strong in-plane benzene-type vibrations, extended progressions and combination bands up to $> 3\ 600\ \text{cm}^{-1}$ whereas the spectrum of 5M2P breaks off $\sim 500\ \text{cm}^{-1}$ above the electronic origin.



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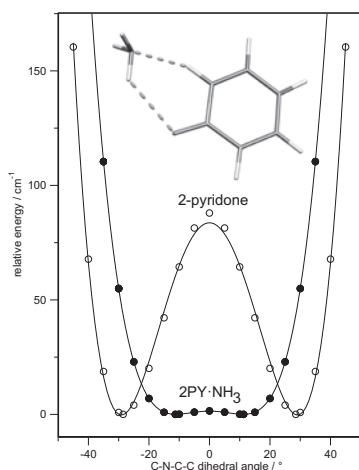
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Intermolecular vibrations of 2-pyridone-(NH₃)_n (n=1–3) clusters

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We reinvestigated the 2-pyridone-(NH₃)_n and *d*₁-2-pyridone-(ND₃)_n (n=1–3) clusters, which have been studied before [1,2], by resonant two photon ionisation spectroscopy and carried out detailed assignments of the vibronic bands. Due to complexation of the 2-pyridone with ammonia the out-of-plane ν_1 twist of the N–H and C=O groups is hindered and the S_1 state ν_1 potential changes from a pronounced double minimum potential for bare 2-pyridone to a flat-bottomed single minimum potential for 2-pyridone-NH₃.



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Synchrotron based highest resolution FTIR spectroscopy of naphthalene (C₁₀H₈) and rovibrational analysis in the 17-30 THz rangeS. Albert¹, K.K. Albert¹, Ph. Lerch², M. Quack²¹Physical Chemistry, ETH Zuerich, CH-8093 Zuerich
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One of the great challenges of astronomical infrared spectroscopy is the identification of the Unidentified Infrared Bands (UIBs) found in several interstellar objects. Polycyclic Aromatic Hydrocarbons (PAHs) have been proposed to be the carrier of the UIBs [1]. For that reason we have started to investigate the rotationally resolved FTIR spectrum of the bicyclic naphthalene as a simple prototypical spectrum for a PAH infrared spectrum. Extending our previous setup [2], we have interfaced an eleven chamber interferometer, the ETH-SLS Bruker prototype 2009, to the infrared port available at the Swiss synchrotron, the Swiss Light Source (SLS) located at the Paul-Scherrer-Institute. Due to the high brightness of the synchrotron radiation, which is effectively 5 to 10 times brighter than conventional thermal sources in the spectral region between 500 and 900 cm⁻¹ (17-30 THz), and the high resolution of the new interferometer (unapodized resolution of 0.00053 cm⁻¹, 18 MHz), it was possible to analyze the newly rotationally resolved infrared spectrum of naphthalene (C₁₀H₈). Previously, this has been recorded only at modest resolution in the IR [3] and at high resolution in the UV [4]. Here, we present a rovibrational analysis of the strongest band, consisting of *c*-type transitions of naphthalene in this region, the out-of-plane mode ν_{46} . We can simulate this band at different resolutions based on our analysis. Due to the unique band shape of a *c*-type band we propose a simple check for the UIBs to determine whether planar PAHs can be the carriers of these bands.

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Non-Equilibrium Population of CH₄ Nuclear Spin Species in the Gas Phase at 16 KH. M. Niederer¹, S. Albert¹, S. Bauerecker^{1,2}, M. Quack¹, G. Seyfang¹¹ETH Zürich, CH-8093 Zürich, Switzerland
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The principles of approximate parity and nuclear spin symmetry conservation in molecular processes are among the most useful insights in molecular dynamics and spectroscopy [1]. Attempts to find their violations have been suggested and undertaken in practice [2,3], including an early FTIR-study of CH₄ in supersonic jets [4] and studies by cw-cavity ring down spectroscopy of supersonic jets [5]. We study here again methane CH₄ in the gas phase at very low temperature for the understanding of the spin conversion mechanism and energy transfer within excited quantum levels with a new experimental technique in this context. Methane was cooled down to at most liquid Helium temperature using a collisional cooling cell [6,7] connected to the Zürich prototype Bruker 125 FTIR spectrometer [8,9]. Transitions to the isolated ν_3 band around 3000 cm⁻¹ have been observed with a wavenumber accuracy better than 10⁻⁵ cm⁻¹. Due to a rapid cooling process, non-equilibrium intensity ratios have been observed. The spectra could be simulated with effective rotational temperatures of about 16 and 27 K under different conditions, and assuming conservation of nuclear spin symmetry upon cooling. An upper bound for the conversion rate between A, E and F nuclear spin isomers can be estimated from the residence time of the molecules in our experimental setup.

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High Resolution Spectroscopy of Small, Chiral Heterocyclic Molecules

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Small, chiral precursor molecules of evolution [1] are very interesting because of the possibility of their astrophysical observation using spectroscopic methods [2,3]. Particularly interesting also in this regard is the discussion of molecular parity violation in terms of early biochemical evolution [3,4]. The chiral molecules oxiranecarbonitrile (C₃H₃NO) and aziridine-2-carbonitrile (C₃H₄N₂), for these reasons, are excellent objects of study [3-5]. We report results of an experimental high resolution infrared spectroscopic investigation of these two molecules and monodeuteriooxirane [6] (C₂DH₃O) a simple chiral molecule for which the undeuterated species has been detected in interstellar space [7]. Results include detailed examination of several rovibrational bands in each molecule, including the ν_{12} ($\nu_0 = 915.2565$ cm⁻¹) band of C₃H₃NO, analyzed using the ground state constants of Behnke et al [8], and the ν_8 ($\nu_0 = 896.02524$ cm⁻¹) band of C₂DH₃O, and a comparison of the spectra of these three molecules in the region 800 – 1000 cm⁻¹.

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Intramolecular vibrational energy redistribution (IVR) in CHD₂I studied by high resolution spectroscopy

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CHD₂I is an appropriate candidate for the investigation of Intramolecular Vibrational energy Redistribution (IVR) after excitation in the region of the CH-stretching overtone to the low frequency CI modes. We have used two fundamental approaches to study IVR; (i) the time resolved fs pump-probe approach and then (ii) the high resolution spectroscopic approach without time resolution (for a critical discussion and comparison see [1]). Recent fs pump-probe experiments in our group [2] have shown that CHD₂I has different IVR-times from fs to ps, revealing different intramolecular coupling mechanisms. On the other hand, our spectroscopic work at modest resolution has already highlighted the strong Fermi-resonance coupling between the CH-stretching and bending modes in CHD₂I, demonstrating very fast redistribution times on the order of 100 fs [3]. The present work will newly focus on the rovibrational analysis of the very high-resolution spectra of fundamentals [4]: a systematic investigation should make it possible to establish weaker couplings between the modes and to understand the slower redistribution times in the fs-pump-probe experiment. We discuss our new results in relation to our recent work on the overtone spectra and dynamics and to the femtosecond pump-probe results.

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Probing nuclear spin symmetry conversion in water in a supersonic-jet expansion by cavity ring-down (CRD) spectroscopy

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Supersonic expansion is a well-suited technique to investigate the possible conversion of nuclear spin isomers in a molecule. In the case of nuclear spin symmetry conservation, the various nuclear spin isomers keep their relative populations set at room temperature before the expansion and one observes a Boltzmann redistribution for the population of the rotational levels of each nuclear spin isomer. Conversely, in the case of nuclear spin symmetry relaxation, the nuclear spin states are allowed to change during the collisional process of the expansion and the relative populations should represent the global thermal equilibrium among all states at low temperatures.

In our group, the interconversion of nuclear spin isomers has already been investigated for CH₄ and its isotopomers in a supersonic-jet expansion and in collisional cooling cells with FTIR [1,2] and diode laser spectroscopy [3] and nuclear spin conservation has been observed. H₂O is another interesting candidate already discussed in a different context [4]. We present here our initial results of H₂O expansions in seeded jets probed by cavity ring-down spectroscopy in the region of the 2ν₃ overtone at temperatures below 30 K.

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Reinvestigation of the overtone icosad of ¹²CH₄ in a supersonic-jet expansion using cavity ring-down (CRD) spectroscopy

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Methane (¹²CH₄) plays a key role in various fields such as geosciences, reaction kinetics and combustion science, biotechnology, astrophysics, atmospheric and environmental science, to name but a few. In all these cases infrared spectroscopy is generally the best diagnostic tool and has been studied for a long time in order to model methane absorption precisely. The number of interacting vibrational levels within a polyad increases rapidly with the polyad quantum number, rendering the line-by-line assignment analysis more and more difficult. The ν₂ + 2ν₃ subband of the N = 2.5 icosad of ¹²CH₄ has been first assigned in 1933 at low resolution [1]. The CRD measurements performed in our group some years ago [2] using supersonic expansions provided first high resolution analyses and an accurate location of the vibrational level ν₂ + 2ν₃ at 7510.3378 cm⁻¹. Following additional, more recent studies [3,4], we have reinvestigated this spectral region at lower temperatures [5] and present here a new assignment of the Q branch and a more detailed assignment of the R branch. While the first series of measurements were performed with an expansion of pure methane at 54 K, we can now detect signal of ¹²CH₄ in a 1 % Ar-expansion cooled at 28 K with our improved setup. We also discuss the investigation of interconversion of nuclear spin isomers.

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Isotope Selective Overtone Spectroscopy (ISOS) of the NH-stretching vibration in substituted anilines measured in a molecular beam

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The investigation of the vibrational structure and dynamics in aniline has a long history. The inversion motion of the NH₂ group over the plane of the phenyl ring can be described by a double well potential with a saddle point of the potential hypersurface at the planar geometry. An early determination led to a barrier of about 450 cm⁻¹ [1]. The tunneling process through the barrier splits the ground state and also many vibrationally excited states into two tunneling components. In the chiral isotopomers R-NHD the splitting can be used to derive stereomutation times between the enantiomers on the ps and sub ps timescale. The dependence of the inversion tunneling process upon the excitation of other vibrational modes was approximately treated using the quadiabatic channel reaction path Hamiltonian (RPH) [2] and shows a strong mode selectivity. Room temperature FTIR spectroscopy and supersonic jet ISOS spectroscopy has been used in our group to investigate the dependence of the tunneling process on the NH-stretching excitation of the normal and deuterium substituted anilines, showing the NH-stretching to be an inhibiting mode [2,3,4]. The main goal of the present experiments is to extend the measurements up to the second NH(ND)-stretching overtone and to fluorine substituted anilines using FTIR spectroscopy at room temperature and the ISOS method [3,4] at very low temperature in a molecular beam. The comparison of the assignment for C₆D₅NH₂ and normal aniline C₆H₅NH₂ confirmed the applicability of the restricted normal mode model to the NH₂-chromophore in aniline.

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Wave packet dynamics of a model of Cl-O-O-Cl under laser excitation including parity violation

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The quantum dynamics of the torsional vibrational modes of chlorine peroxide is studied in terms of populations, time dependent absorbed energy (multiphoton spectra) and wave packets of stereomutation processes. Torsional modes are calculated using the quasideiabatic channel Reaction Path Hamiltonian (RPH [1,2]) treatment. The time-dependent Schrödinger equation including coherent radiative excitation is solved in the Quasi Resonant Approximation (QRA [3-6]). The following dynamical limiting situations are studied:

i) stereomutation during laser excitation, ii) stereomutation after laser excitation of an excited state of well-defined chirality, and iii) time evolution under parity violation.

Finally we simulate the time evolution for a possible measurement of parity violation based on the schemes proposed in [7,8].

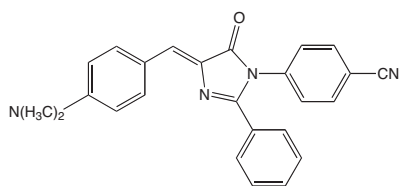
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Photoinduced intramolecular charge transfer dynamics in GFP-chromophore derivatives

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A new class of organic compounds with great promise for optoelectronic application are biologically inspired **1H-imidazol-5(4H)-derivatives** and more particularly their dimethylamino derivatives.

Introducing strong electron donating dimethylamino group in the benzylidene moiety changes substantially the nature of the excited-state, namely charge transfer (CT) state. This effect is stronger when an electron-withdrawing substituent presents in the imidazolone part of the molecule. CT state is characterized by an ultrafast intramolecular charge separation dynamics and large emission wavelength dependence in polar solvents. Thus, controlling the CT character of the excited state of these molecules should in principle allow a rather fine-tuning of their emission wavelength even in rigid media, where their emission quantum yield is very large.

Herewith carrying out detailed studies on the ultrafast photoinduced intramolecular charge transfer processes of these new synthetic *p*-benzylidene substituted imidazolones using time-correlated single photon counting and fluorescence up-conversion, as well as transient absorption spectroscopy in the femtosecond time domain our aim is to employ the obtained knowledge in order to rationalize their optoelectronic properties in more details.

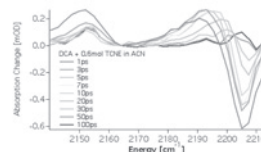
Bimolecular electron transfer beyond Marcus theory

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Photo-induced electron transfer (ET) between donor-acceptor (DA) pairs, often considered as the simplest of chemical reactions, plays an important role in chemistry and biology. In general, the classical Marcus theory is applied to rationalize the kinetics of ET reactions though the predicted inverted region has never been observed experimentally for bimolecular photo induced electron transfer [1,2]. Since long it has been speculated that ET to an excited state could account for this by shifting the reaction to the normal region.



Analysing the hot ground state contribution upon ultrafast ET quenching and subsequent charge recombination, we can estimate the amount of heat which is released to the reaction partners. Comparing DA pairs where an excited state of the ion is energetically accessible with pairs where this is not the case, we observe a clear trend which strongly supports the mentioned hypothesis. In cases where an excited electronic state of the ion is accessible, the hot ground state contribution of that reaction partner indicates largely increased heat release due to the relaxation from the excited electronic state to the ground state where the corresponding excess energy is released exclusively to that reaction partner.

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Morphology and Optical Properties of Cyanine Dye / PCBM Blends

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Today a plethora of soluble cyanine dyes absorbing from the ultra-violet to the near-infrared range are available owing to more than a century of research and development, mostly in photographic industry. Numerous properties of cyanine dyes suggest that this material class can be interesting for organic opto-electronic devices. Most importantly, the unparalleled absorption coefficients allow using very thin films for harvesting solar photons. Secondly, dye molecules are capable of self-assembling into aggregates where charge and excited states are delocalized over hundreds of molecules.

Here we exploit the phenomenon of spinodal dewetting during spin coating of blends of PCBM and a cyanine dye for the design of well defined phase separated morphologies. AFM snapshots of as-prepared films and after selective dissolution suggest that the solution separates into transient bilayers, which destabilize due to long-range intermolecular interactions [1]. Highly organized H-aggregates form spontaneously during phase separation [2], their formation can be controlled through the parameters that influence film formation.

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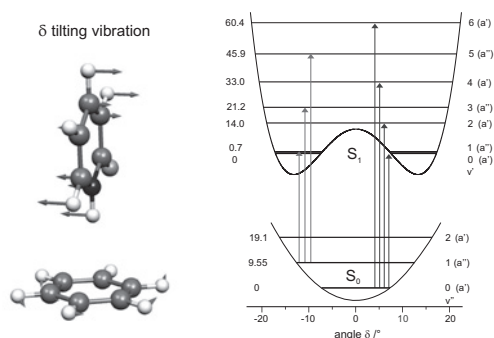
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Large-Amplitude Vibrations of an N-H... π Hydrogen Bonded Cis-Amide - Benzene Complex

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We have investigated the large-amplitude vibrations of supersonically cooled 2-pyridone-benzene in the S_1 state, using two-color resonant two-photon ionization spectroscopy. RI-CC2 and SCS-RI-CC2 calculations of the S_1 state predict a tilted T-shaped structure with an N-H... π hydrogen bond to the benzene ring, similar to the S_0 state [1]. The vibronic band structure up to 60 cm^{-1} above the electronic origin is dominated by large-amplitude δ tilting excitations, reflecting a change in the tilt angle. The S_0 and S_1 state δ potentials were fitted to experiment, yielding a single minimum in the S_0 state and a double-minimum S_1 potential with $\delta_{\min} = \pm 13$ degrees. Weaker excitations of the second large-amplitude vibration, the θ twisting or benzene internal-rotation mode, are also observed.



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ABSORPTION OF VISIBLE LIGHT BY PROTONATED NILE RED IN THE GAS PHASE

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Due to its highly sensitive fluorescence behavior to environmental factors, Nile Red (NR) is a widely used probe for the investigation of many chemically important systems [1, 2]. According to calculations reported by Tuck, et. al., the absorbance maximum of neutral NR in solution exhibits a blue shift from 518 nm to 502 nm as the solvent is changed from acetonitrile to benzene [2]. When the relative blue shift (16 nm) is compared to the experimentally determined value (13 nm, 549 nm to 536 nm) relatively good agreement is observed. It is of great importance to determine the behavior of such an important fluorescent probe in the limit of no environmental effects, i.e. the gas phase. Calculations by Tuck also predict a further blue shift to 463 nm when neutral NR is transferred from the non-polar benzene solution into the gas phase [2]. The electronic nature of protonated NR in the gas phase can be probed thanks to the combination of a modified Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) and a line-tunable continuous wave Ar⁺ laser located in the Zenobi laboratory at ETH. Depending on the site of protonation, calculations at the TD B3LYP/6-311+G level predict either a blue or a red shift in the absorption maximum when neutral NR is compared to protonated NR. Upon irradiation with 50mW laser light for 5 seconds, the fragmentation behavior of the trapped protonated NR indicates that protonation occurs at the nitrogen found on the central ring, since fragmentation, and hence absorption, occurs more efficiently at 514 nm than at 488 nm.

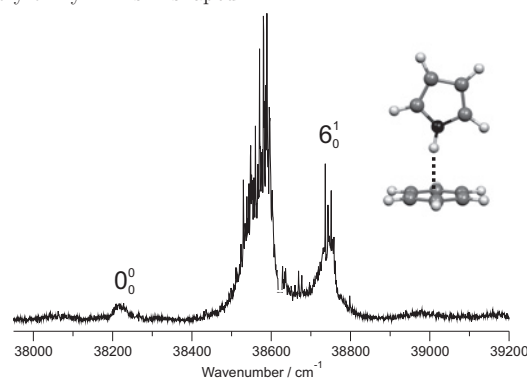
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Supersonic jet spectroscopy of unconventional N-H... π hydrogen bonded complexes and clusters

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In order to understand the secondary stabilization of proteins and polymers the spectroscopic analysis of N-H... π unconventional hydrogen bonds is of great importance. The 2-pyridone-benzene complex shows an unconventional T-shaped structure similar to the benzene dimer[1]. We investigate the $S_1 \leftarrow S_0$ spectrum of the supersonically cooled pyrrole-benzene (Pyr-Bz) complex and Pyr_mBz_n clusters (m,n = 1,2) using resonant two-photon ionization spectroscopy and ab initio calculations. The S_0 state is analyzed by IR-depletion spectroscopy. The SCS-MP2 S_0 state geometry of Pyr-Bz is T-shaped.



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Single enantiomorphism due to chiral conflict in 2D crystals

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In order to investigate chiral recognition at the molecular level, we studied the effect of chiral conflict between different chiral entities in monolayers on Cu(110) with scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). As reported earlier, doping of achiral succinic acid (Fig. 1b) with small amounts of chiral tartaric acid (Fig. 1a) installs homochirality on the entire surface (sergeants-and-soldiers effect) [1].

Here we present now a cross-contamination experiment of tartaric acid (TA) and malic acid (MA, Fig. 1c). The mixture of left and right handed TA (*rac*-TA) shows a superposition of the two homochiral enantiomorphs in LEED. Adding one enantiomer of MA to the mixture suppresses formation of one of the two enantiomorphs. (*R*)-MA allows thereby only the formation of the structure known for pure (*R,R*)-TA, while (*S*)-MA leads to the (*S,S*)-enantiomorph.

Our STM investigations suggest that in the *rac*-TA/MA experiment nucleation of one enantiomorph is suppressed by a disordered MA/TA quasiracemate.

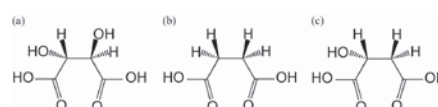


Figure 1 a) (*R,R*)-tartaric acid, b) succinic acid, and c) (*R*)-malic acid.

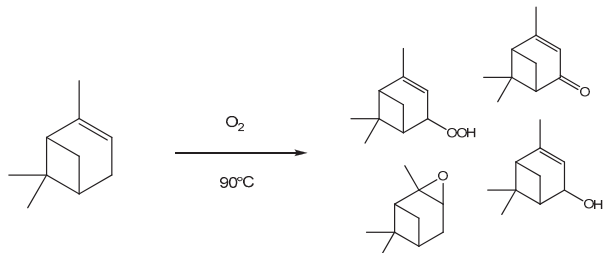
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Aerobic Oxidation of alpha-Pinene

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A combined experimental and theoretical approach was used to study the aerobic oxidation of the renewable olefin α -pinene [1]. Four regioisomeric peroxy radicals are generated, the verbenyl peroxy radical being the most abundant one. All four peroxy radicals can react in two distinct types of propagation steps, i.e. the abstraction of allylic H-atoms, and the addition to the unsaturated C=C bond; the efficiency for both pathways appears to depend on the structure of the peroxy radical. The observed product selectivities are used to determine the oxidation mechanism.



The selectivity as well as the overall reaction rate of propagation is affected by the oxygen pressure [2]. This unusual behavior is a consequence of further oxygen-involving elementary steps.

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NO_x storage and reduction over M/MgAl₂O₄ (M = Pt, Pd, Rh, and Ir): Comparison of performances of noble metals in terms of Oxidation, Storage and Reduction

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NO_x storage and reduction (NSR) catalysis is an efficient technique to remove NO_x from the exhaust of lean-burn gasoline or diesel engines [1,2]. Under lean conditions of engines, when oxygen is in excess, NO_x is oxidized and adsorbed on the catalyst, and under rich conditions, when the reductants evolve, the stored NO_x is reduced. Earlier we have shown, that flame-made Pt/MgAl₂O₄ had superior dynamic NSR performance at short regeneration times (< 30s) compared to a standard 1%Pt-20%Ba/Al₂O₃ reference catalyst. However, the better NSR performance at short regeneration times of Pt/MgAl₂O₄ was limited to the use of hydrogen as reductants, whereas with other reductants, like CO or C₃H₆, the NSR performance was similar for both catalysts [3].

In this contribution we present the comparison of different noble metals (Pt, Pd, Rh and Ir) dispersed on MgAl₂O₄, in terms of oxidation, storage and reduction in NSR catalysis. The reduction ability of the stored NO_x by different noble metals was dependent on the (i) regeneration time, (ii) nature of reductants, and (iii) temperature.

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NO_x adsorption and release properties of MgAl_{2-x}Co_xO₄ spinel-like oxides

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Recent research by our group has identified flame-made MgAl_{2-x}M_xO₄ (M = Mn, Fe, Co, x = 0.1, 0.5, 1 and 2) spinel-like oxides as active catalysts in the catalytic combustion of methane [1]. Currently we are investigating the applicability of these materials in other processes, especially those centered on the abatement of NO.

In this contribution we present the adsorption and release properties of NO on MgAl_{2-x}Co_xO₄ spinel-like oxides. Under oxygen-rich conditions, NO is oxidized and subsequently strongly adsorbed on the catalyst surface. Upon switching to reducing atmosphere, NO is released from the material. A possible application of these materials might therefore be in NO_x abatement from diesel or gasoline exhaust gas as noble metal free adsorbent. The NO_x reduction can then take place on a downstream noble metal based catalyst. This spatial de-coupling has the advantage that storage and reduction can be optimized independently.

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SrO:Al₂O₃ composite materials: A new efficient catalyst class for oxidative coupling of methane

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Oxidative coupling of methane (OCM) with molecular oxygen to produce higher hydrocarbons has been a subject of research since three decades [1-3]. In search of a new catalyst for OCM, a series of xSrOyAl₂O₃ composite oxide materials have been prepared by hydroxide precipitation method and characterized by various analytical techniques. These catalysts contain a mixture of a crystalline and non-crystalline phase as determined by XRD and solid state NMR. The mixed oxides show maximum conversion of 28 % with selectivity toward C₂₊ products of 63 %. The non-crystalline phase containing materials outperformed the crystalline single phase reference compounds. It was observed that the relative extent of non-crystalline phase in the composite materials increased with Sr/Al ratio and this was well correlated with the conversion of methane. The specific activity with respect to surface area of the catalyst increased with increasing Sr/Al ratio up to 1.25. These catalysts show comparable activity to the well-known reference catalyst 1.9%Mn-4%Na₂WO₄/SiO₂ [4].

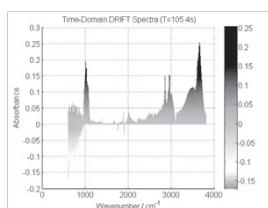
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TG and FTIR investigation on the adsorption behavior of alcohols, water and CO on Cu-BTC

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Due to their exceptionally high specific surface areas, large pore volumes and high crystallinity MOFs have been utilized in gas storage, gas separation, sensor and catalysis applications. Since all these processes require an interaction of target molecules with the framework, a proper understanding of the adsorption of substrate molecules at the active sites is an important prerequisite for the successful design of functional MOF materials. In the present study we have used time-resolved DRIFTS as well as TG experiments to study the adsorption behavior of several alcohols at the accessible Cu²⁺ sites of Cu-BTC.



It could be shown that two species were present after MeOH adsorption (3500 and 3650 cm⁻¹). TG experiments revealed that the amount of chemisorbed MeOH corresponds to the number of Cu²⁺ centers in the structure.

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Molecular engineering of organic molecules for dye-sensitized solar cells

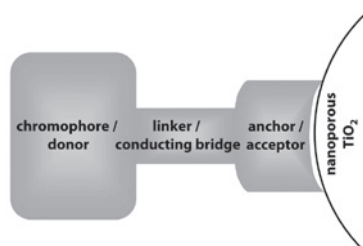
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Organic molecules have been shown to be highly efficient sensitizers in dye-sensitized solar cells (DSC)[?]. Usually, they consist of three parts: a chromophore (donor), a linker (conducting bridge) and an anchoring group (acceptor). In order to fine-tune the properties of the dyes (like photon-to-electron conversion efficiency, potential, etc.), a theoretical and experimental study of the influence of changes in the molecular structure on each of the three moieties has been performed.



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A Peptide Capping Layer over Gold Nanoparticles

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We use time-resolved femtosecond infrared spectroscopy to study vibrational energy transport through a capping layer of short peptide helices over gold nanoparticles. Energy transport is initiated by exciting the plasmon resonance of spherical gold nanoparticles, which are covalently linked to and completely covered by 3₁₀-helical peptides. The subsequent flow of vibrational energy through the applied peptide layer is monitored by employing C=O probes at various distances from the gold surface as local thermometers.

The measured transport properties qualitatively agree with our previous studies of energy transport in 3₁₀-helices after UV excitation of a covalently attached Azoswitch [1] and IR excitation of C-D modes in a Leu-d₁₀ residue [2]. The fact that the transport rate does not depend on how exactly vibrational energy is deposited means that it is not mode selective, and hence, vibrational energy must be completely randomized on the picosecond time scale.

We discuss the advantages of using gold nanoparticles as an alternative heater for energy transport experiments.

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Electronic dephasing processes of non-polar solutes in both polar and non-polar solvents studied by UV 3-pulse photon echo measurements

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Photon echo techniques are powerful methods to investigate intramolecular dephasing processes as well as solvation dynamics by tracking the transition frequency correlation function of the chromophore probe. They have successfully been employed in the visible and infrared ranges. However, these techniques have been less developed in the ultraviolet (UV) region; although there are much interest such as fluctuation dynamics in biological systems and non-polar solvation dynamics.

In a series of articles [1-3], we investigated the electronic dephasing of nonpolar solutes, p-terphenyl and diphenylacetylene, in various solvents by 3-pulse photon echo measurements in the UV. In all of these cases, we observed sub-100 fs electronic dephasing times for both polar and non-polar solvents. This is in contrast to previous theoretical work where the electronic dephasing for non-polar solute in non-polar solvent was primarily related to slight rearrangement of the first solvation shell around the chromophore and was estimated to be in the order of hundreds of femtoseconds [4]. Our results reveal a much faster solvent independent dephasing mechanism and suggest that the primary mechanisms for the electronic dephasing in non-polar solution are intra-molecular processes, namely internal conversion or internal vibrational redistribution.

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Electron injection into semiconductor thin films studied with time-resolved fluorescence

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Dye sensitized solar cells (DSSC) are based on the use of metal-based molecular complexes adsorbed onto a semiconductor substrate. Upon absorption of visible light by the singlet metal-to-ligand-charge-transfer ($^1\text{MLCT}$) states of the dye, injection of an electron into the substrate occurs, provided the excited state of the dye lies above the conduction band of the substrate. The detailed understanding of the mechanism and time scale of electron injection is crucial for the optimization of DSSCs. So far, it is accepted that injection occurs from the triplet $^3\text{MLCT}$ state, but several studies have pointed out an efficient sub-100 fs injection from $^1\text{MLCT}$. We observed an extremely fast (≤ 30 fs) $^1\text{MLCT}$ to $^3\text{MLCT}$ intersystem crossing in Ru- and Fe(bpy) $_3$ complexes in solution using femtosecond-resolved broad-band fluorescence up-conversion.^{1,2} We also found that intramolecular relaxation (Internal conversion (IC) and Internal Vibrational Redistribution (IVR)) occurs in ≤ 10 fs. We found similar results for RuN3 and RuN719 dyes in solution. We compared them with results of the RuN719 dye adsorbed on TiO $_2$ (which favours electron injection) and on Al $_2$ O $_3$ (which does not allow electron injection). While the kinetic behaviour we observe is identical for the two substrates and for the solution data, we found a ~ 3 fold decrease in intensity of the short-lived fluorescence on TiO $_2$ compared to the Al $_2$ O $_3$ substrate. This points to an injection that competes with the ultrafast IVR/IC, and from the intensity decrease we estimate a Quantum Yield of singlet state injection of 66 %, and an injection time of ≤ 3 fs.

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Comparison of microscale measurement of residual stress in silicon using EBSD cross-correlation technique and confocal Raman microscopy

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Residual stresses have been measured by electron backscatter diffraction (EBSD) cross-correlation technique [1,2] and confocal Raman microscopy [3] on laser-crystallized polycrystalline silicon thin film on glass substrate for solar cells, and around indents in Si wafers. EBSD gives information on the full strain and stress tensor and confocal Raman microscopy measures the total stress. A good agreement was found between the two techniques, but larger residual stress values are generally measured with the EBSD technique, as previously observed by Vaudin et al. around wedge indents in Si [4]. This is interpreted to be mainly due to the difference of probing depth between the two techniques. The residual stress in laser-crystallized polycrystalline Si on glass substrate is complex due to a progressive intergranular lattice misorientation linked to the laser process. The main residual stress occurs close to grain boundaries and in areas where the lattice bending is strong, and can reach GPa values. High residual stresses can influence the mechanical integrity of the solar cell device. It is also directly associated to multiple defects such as dislocations, which can act as recombination centers for electron-hole pairs and hence deteriorate the solar cell performance.

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Excited state dynamics of tetraphenyl- and octaethyl-metalloporphyrins studied with time-resolved fluorescence

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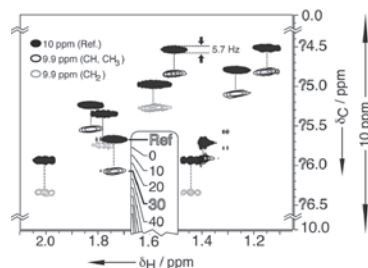
Metalloporphyrins are paradigm molecules for many biological systems, such as hemoproteins, and are at the center of an intensive research aimed to design functional and scalable artificial photosystems. Despite this growing interest, the understanding of their photocycle is still not complete, mainly because previous time-resolved studies were limited to a resolution of several hundreds of fs. Thanks to our sub-100fs resolution fluorescence set-up with broadband detection, we have carried out studies on metalloporphyrins having a partially filled metal 3d shell and found a photocycle for the Zn and free base porphyrins more complex than previously reported. Exciting the Soret band (corresponding to the S_2 excited state), we obtain a biphasic internal conversion (IC) with time constant of 370 fs and 2 ps, from this state to hot levels of the S_1 state (corresponding to the so-called Q-bands), followed by an IVR/cooling dynamics spanning from 300 fs to 20 ps. We also observed that the energy structure of the empty states on the central atom speeds up all dynamics by almost two orders of magnitude. We also investigate the effect of the porphyrin ring terminations by comparing the tetraphenyl- and octaethyl-porphyrins (TPP and OEP) analogs. Interestingly we found a dramatic effect on the Q band emission both in terms of band profile and lifetime (~ 30 fs for TPP and ~ 100 fs for OEP). Our results confirm that in these systems there is no dependence of the relaxation dynamics on the specific metal, but only on the presence of empty metal d orbitals. Conversely the electronic structure of the porphyrin ring plays a dramatic role both on the excited state lifetime and on the electron-phonon couplings.

High-resolution 2D NMR Experiments Using 10&9.9 ppm or Differential Evolution in Carbon to Resolve Ambiguities in Aliased HSQC Spectra

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The overlap of two HSQC spectra recorded with 10 ppm¹ and 9.9 ppm carbon spectral windows gives rise to highly resolved signals with a pattern providing unambiguous precise and accurate chemical shifts. The quantized shifting of signals in the 9.9 ppm spectrum relative to those of the 10 ppm spectrum allows one to determine the full six-digit chemical shift using a correction ruler for the high-order digits. Alternatively to the overlap of spectra, the new DENA-HSQC pulse sequence takes advantage of a differential evolution of carbon chemical shifts to do the same in a single experiment. Combined with multiplicity edition, the DENA-HSQC experiment advantageously replaces commonly used 1D DEPT-135 spectra.



The correction ruler indicate that the full chemical shift of the relevant signal is $5.67 + 30 = 35.67$ ppm.

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A molecular dynamics study of vibrational energy relaxation of the cyanide ion in water

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The exchange of vibrational energy between solute and solvent molecules is important in the understanding of chemical reactions in solution. As a simple model system to study the exchange of vibrational energy, we chose the vibrational energy relaxation of cyanide ion in water, which has been investigated by experiments [1-2] and by computer simulations [3-4] previously. In this work, the vibrational relaxation of the cyanide in H₂O, D₂O, and T₂O is studied using classical molecular dynamics (MD) simulations with multipole moments on the cyanide ion [5] and flexible water model [6].

When the cyanide ion in water is vibrationally excited, it relaxes back to the ground state, releasing energy to the surrounding water molecules. The efficiency of this process relies to some extent on the coupling between inter- and intramolecular degrees of freedom. In order to compare with the experimental results, the vibrational relaxation time T_1 was computed from multiple classical MD trajectories. By comparing T_1 values obtained from the simulations with and without multipole moments on the cyanide ion, it is shown that multipole moments play an important role in the simulation of vibrational energy relaxation.

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Reactive Molecular Dynamics study of sulfuric acid (H₂SO₄) Photodissociation

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In the troposphere, sulfur is emitted mainly as sulfur dioxide (SO₂), which is oxidized to form sulfuric acid (H₂SO₄) [1]. This cycling between SO₂ and H₂SO₄ has been studied mainly because it plays an important role in the troposphere aerosol layer formation [2] which is related to the global atmospheric chemistry, including cloud condensation altering the chemical composition and influencing the course of aqueous reactions in clouds. The mechanism and pathway involved in the photodissociation of H₂SO₄ have not been characterized yet. Studies by Crim [3-4] and Vaida *et al* suggest that dissociation of H₂SO₄ is possible mainly by highly excited OH-stretching vibrational overtone in H₂SO₄. Thus, excitation of the higher OH-stretching vibrational overtone should provide sufficient energy for photodissociation to take place. Here we use a Reactive Molecular Dynamics (RMD) [5] to investigate vibrationally induced H₂SO₄ decomposition. The results show that once ~ 32 kcal/mol is deposited in internal degrees of freedom, decomposition of H₂SO₄ to form SO₃ and H₂O takes place on picosecond time scale. This results agrees with experimental data which for the third overtone excitation (36 kcal/mol) leads H₂SO₄ dissociation.

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Heteronuclear Double-Resonance Methods in NMR as probes for fast dynamics in biomolecules

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Biological processes are often governed by local dynamics occurring on μ s timescales, which can result in chemical-exchange contributions to relaxation. In particular, chemical-exchange-induced cross-relaxation between multiple-quantum (MQ) coherences can provide a wealth of information about fast local dynamics as well as thermodynamical and structural parameters [1]. We have designed new Heteronuclear Double-Resonance (HDR) methods [2] based on well-known decoupling schemes, applied simultaneously to two scalar-coupled spins, to preserve MQ coherences, so that the interconversion between them can occur only through cross-relaxation. An analytical expression for the MQ cross-relaxation rate under HDR irradiation was obtained extending the approach of Podkorytov and Skrynnikov [3]. Experiments carried out on ubiquitin have led to the characterization of the fast exchange process occurring on a timescale of ~40 μ s, in agreement with Massi *et al.* [1]. Results obtained on KIX are complementary to [4] and may reveal the presence of an additional faster process.

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Simultaneous gas- and condensed phase investigations in multiphase atmospheric chemistry at low temperatures

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An experimental study of thin ice films doped with atmospheric relevant trace gases will be presented.

Pure ice films, representative of PSCs, are grown at temperatures relevant for the atmosphere (170-210 K) in a high vacuum reactor [1] by deposition of water onto a Si optical support. A known amount of dopant can be injected through an independent line in order to contaminate the ice.

IR Fourier transform spectroscopy is employed to monitor the solid phase and two configurations are available: transmission and grazing incidence transmission reflection spectroscopy (RAIRS), at an angle of incidence of around 75°. HeNe interferometry at 632.8 nm is also used for observation of the changes of the film thickness. The gas phase products are also studied using a residual gas MS analyzer and an absolute pressure gauge.

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UV laser micropatterning of silicone nanofilaments

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Initially superhydrophobic surfaces were fabricated using a versatile and inexpensive technique by which a dense layer of silicone nanofilaments grows onto various substrates [2]. Performing a refunctionalization step with 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) the coating becomes non-wetting for both polar and non polar liquids [3]. The coated surfaces were then patterned in order to create regions of contrasting wettabilities. This was achieved by exposing regions of the surface to a nanosecond Nd:YAG laser operating at 355 nm and causing ablation of nanofilaments coated surface. Applied aqueous and oily solutions wet only ablated domains while the rest of the sample remains dry. The straightforward patterning procedure enables the creation of superhydrophilic/superoleophilic patches of arbitrary shape (e.g. channels, circles, squares) with micron precision embedded into superhydrophobic or superoleophobic background.

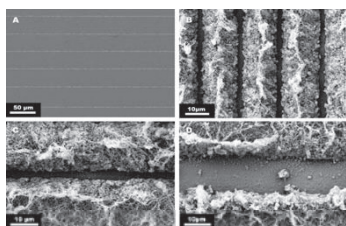


Figure 1. SEM images of hydrophilic channels created by laser ablation of superhydrophobic silicone nanofilaments.

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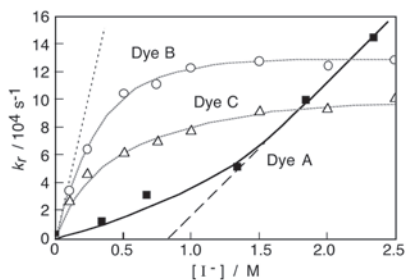
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Kinetics of Light-Induced Oxidation of Iodide by Dye-Sensitizers Adsorbed on the Surface of Nanocrystalline TiO₂ Films

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Photo-excited dye-sensitizer molecules (S) adsorbed on the surface of TiO₂ readily inject an electron into the conduction band of the oxide. Sustainable charge separation and regeneration of the dye is achieved by reducing the resulting oxidized dye species (S⁺) by iodide. Oxidation of iodide to iodine atom S⁺ + I⁻ → S + I[•] is slow. A fast alternative one-electron transfer reaction path involves the formation of I₂^{-•} radical-anions: S⁺ + 2 I⁻ → S + I₂^{-•}.



The dependence of the pseudo first-order rate constant (k_r) of the regeneration of various inorganic and organic dyes adsorbed on nanocrystalline TiO₂ films upon I⁻ concentration was studied. Results indicate that a fast pre-equilibrium S⁺ + I⁻ ⇌ (S⁺-I) establishes with sulfur atom-containing dye molecules, which is followed by the reaction with a second iodide anion: (S⁺-I) + I⁻ → S + I₂^{-•}. Depending on the dye's structure, an associative or repulsive interaction of iodide contained in the solution with the sensitized surface is observed to strongly influence the kinetics of electron transfer.

Conductivity in Dye sensitized TiO₂ probed by Optical Pump THz Probe SpectroscopyJan C. Brauer¹, Joël Teuscher¹, Angela Punzi¹, Jacques-E. Moser¹¹Ecole Polytechnique Fédérale de Lausanne Institute of Chemical Science and Engineering, CH-1015 Lausanne Switzerland

Dye sensitized solar cells (DSSCs) have shown to be an promising alternative to traditional silicon based solar cells. DSSCs consists of a porous network of TiO₂ sensitized by a dye molecule and an electrolyte or hole transporter material sandwiched between two electrodes. Effective transport of the injected charges in the TiO₂ and the electrolyte is essential to the functioning of the cell.

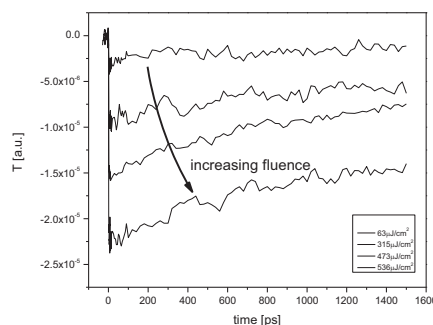


Fig1 Photo-induced change of THz transmission in dye sensitized mesoporous TiO₂ layers

We have investigated the charge transport dynamics and especially the effect of dye aggregation on the TiO₂ surface using Optical Pump THz Probe spectroscopy in mesoporous anatase layers using a RuL₂(SCN)₂ complex (N3) as sensitizer.

Classical and Quantum Simulations of Proton Dynamics in Acetylacetone

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Acetylacetone (AcAc) is a prototype system for studying intramolecular proton transfer (PT). It is also important in coordination chemistry for its anion being a common bidentate ligand to many transition metals. Although AcAc has been studied experimentally and computationally over the years, some fundamental properties are still not fully understood. For example, it is still a matter of debate whether its ground state assumes an asymmetric (C_s) structure with a double-minimum potential [1] or a symmetric (C_{2v}) structure with a single-minimum potential [2].

Here we discuss classical and quantum simulations of AcAc on a globally valid, accurate and reactive potential energy surface (PES). The PES is based on molecular mechanics with proton transfer (MMPT) [3] and allows to reproduce structures, energetics and vibrational features predicted by electronic structure calculations at MP2/aug-cc-pVTZ level. Molecular dynamics simulations of AcAc and deuterated AcAc in both gas phase and solution are carried out, and the computed IR spectra reproduce the experimental ones very well. This reactive force field is transferable to other β-diketones.

Proton tunneling and proton dynamics are then explored by solving a harmonic bath average (HBA) Hamiltonian [4]. As an analogy to the reaction path Hamiltonian [5], HBA hamiltonian is constructed by explicitly including the couplings between the PT coordinate and other vibrational modes. Our results might help explain the experimental observations in Ref. [1] and [2].

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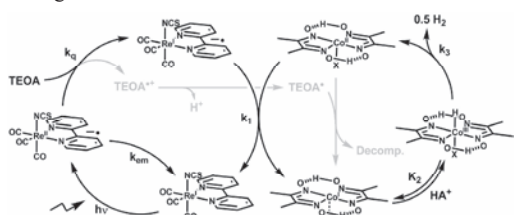
Time resolved infrared spectroscopy of a homogeneous Rhenium and Cobalt based system for the photocatalytic production of H₂

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We use time resolved infrared spectroscopy from pico- to milliseconds to elucidate mechanism and kinetics of the photocatalytic H₂ production from transition metal complexes, namely Re^I(CO)₃ based photosensitizers in combination with Co(dmgh)₂ type water reduction catalysts.^{1,2} Experiments were performed in DMF as well as H₂O, whereas the latter constitutes a major step towards a full water splitting system.³ A typical example of such a water reducing system, together with its catalytic cycle in DMF, is shown in the following scheme:



After excitation of the photosensitizer [ReNCS(CO)₃bipy], the reaction proceeds via reductive quenching with triethanolamine (TEOA) and subsequent electron transfer to the water reduction catalyst [Co(dmgh)₂], which then produces H₂.

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High Resolution Cavity Enhanced Lamb-Dip Spectroscopy of NH₃

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Investigation of parity violation in chiral molecules is of great interest in physics and chemistry [1,2,3]. Several experiments are discussed in relation either to measure frequency shifts [4,5,6,7] or to measure the energy difference between enantiomers $\Delta_{\nu\nu}E$ directly in a time-dependent measurement [8], which uses an excited state with well defined parity and seems to be most promising. In preparation for this experiment a stimulated emission setup with a cw-OPO as pump laser was realized. Nonlinear spectroscopic techniques are useful to resolve the hyperfine structure and lines, otherwise congested by inhomogeneous broadening. We report Lamb-dip spectra of a number of lines of the ($\nu_1 + \nu_3$)-state of NH₃ at about 6600 cm⁻¹. Some of these lines are (partially) hyperfine resolved. We estimate a quadrupole coupling constant for the ($\nu_1 + \nu_3$)-vibrational level and analyse the pressure and laser intensity dependence of the Doppler-free linewidth. This leads to an estimation of the transition-dipole moment and of the elastic and inelastic collisional cross sections.

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Doppler free Spectroscopy of the CH-Stretching Fundamental of C₂H₂ through Stimulated Emission

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The investigation of parity violation in chiral molecules is of great interest in physics and chemistry [1,2]. Several high-resolution experiments were proposed and performed to measure the very small parity violating frequency shift between IR bands of two enantiomers of CHFClBr [3-5]. However, this shift is calculated to be extremely small [6]. Another promising experiment is to observe the time evolution of an initially prepared state with well-defined parity [7,8]. In this time resolved method the excited state with well-defined parity has to be populated in a multi-step preparation process [7,8]. In preparation for this experiment, a system with one stabilized OPO-laser and a second tuneable OPO was set up for a stimulated emission experiment. Such double resonance techniques allow also for Doppler free spectroscopy and states are accessible, to which direct transitions from the vibrational ground state are forbidden, through the population of an intermediate level. We report the high-resolution rovibronic analysis of the vibrational level ν_1 of C₂H₂ using the $\nu_1 + \nu_3$ vibrational state as an intermediate level. This provides a proof of principle of the preparation step in the aforementioned pumping scheme.

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Cross section of protein ions in the gas phase probed by electron impact ionization and dissociation mass spectrometry

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Electron impact ionization/dissociation (EII/EID) is a classical mass spectrometrical technique used in structure analysis of organic molecules. However, recent development of mass spectrometry made it possible to study structures of larger molecules, including peptides and proteins. On the contrary to EII/EID applied to neutral organic molecules, ionization and fragmentation of peptides and proteins is performed on typically multiply charged species. Irradiating positively charged peptides and proteins with high energy (50-100 eV) electrons leads to single and multiple electron emission and formation of radical ions with the higher charge states. The described process has only recently been discovered and presented in the first publications. Here we present results of the measurements of two main characteristics of this process as a function of ion charge state – electron-ion collision cross section and ionization energy. The EII/EID experiments were performed on a high performance Fourier transform ion cyclotron resonance mass spectrometer (12T FT-ICR MS at EPFL, Lausanne) equipped with ion-electron interaction cell located in a high magnetic field. Preliminary results show the non-linear increase of ionization energy with ionic charge state. In addition, we evaluate the possibility of using EII experiments as a “gas phase electronic microscope”. Keeping both precursor and product ions trapped before detection allows accurate measuring of relative electron-ion ionization cross-section. Selection of peptides and proteins for the cross section measurements was performed to allow a comparison with protein ion gas phase cross sections previously suggested by other methods. For example, the EII/EID data was correlated with the known ion mobility mass spectrometry data coupled to replica exchange molecular dynamics (REMD) simulation performed in collaboration with group of Prof. Dugourd, University of Lyon, France.

Thermodynamic Cycles Involving at least one Source or Sink with Finite Heat CapacityYves Carraux¹¹Gravure Myl SA, R&D Department, Rue Charles-Perrier 1, CH-2074 Marin-Epagnier, Switzerland

For many years, thermodynamic cycles involving at least one source or sink with finite heat capacity were studied in finite time thermodynamics, using an infinite number of endoreversible, Carnot cycle stages. We present the conventional study of three thermodynamic cycles using a new physical model that describes an elementary, ideal gas transformation in perfect thermal contact with part of a source of finite heat capacity [1]. The first cycle is called a "Polycycle" and works between an initially hot source with finite heat capacity and a sink with infinite heat capacity [2]. The second cycle has already been evoked in the literature but does not have a name [3]. It works between a heat source with infinite heat capacity and a reservoir with finite heat capacity, which is initially at a cold temperature and finally at the same temperature as the heat source. This cycle has the particular feature of recovering the heat usually lost in the heat sink. The third cycle is the generalized Carnot cycle working between two sources or sinks with finite heat capacity. The notion of maximum adiabatic work (without any exchange of heat with the environment) which can be produced from different reservoirs of finite heat capacity is introduced and must be distinguished from exergy. Systematic study of this cycle demonstrates a new result: the temperature (K) finally reached by extracting the maximum adiabatic work of different reservoirs with finite heat capacity, is the geometric mean of the initial temperatures (K) weighted by the corresponding heat capacities.

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Solvation Dynamics of the Hexacyanoferrate(II) Ion Probed with Ultrafast Laser and X-ray Absorption Spectroscopy

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Reactant charge-transfer processes are of particular interest in chemistry and biochemistry. They most often take place in solution where the solvent medium influences the reaction energetics and dynamics. One method of probing the reaction coordinates is to investigate the charge-transfer-to-solvent (CTTS) states which are populated after photo-excitation of the solute with photons close to the ionization threshold. These states represent a sharing of electron density between the solvent and solute and are very sensitive to the intermolecular potential. Using a combination of ultrafast x-ray and laser spectroscopy we have investigated the solvent perturbation around the aqueous iodide anion after photoexcitation of an electron into a CTTS state [1]. Our current studies extend this to the more complicated molecular system of aqueous hexacyanoferrate(II) ($[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$). Our particular interest is to obtain a complete picture of the ongoing dynamics after photoexcitation into a CTTS state [2] and the subsequent relaxation processes, including intramolecular electronic relaxation and electron solvation dynamics. Applications of cyanoferrates are found in photoswitching, energy conversion and biologically related fields.

Ultrafast laser spectroscopy is capable of resolving the dynamics of the electronic states involved in these processes, it does not, however, directly provide structural information. Ultrafast x-ray absorption (XAS) is the ideal technique to resolve both electronic and structural changes around the absorbing atom [3]. In this case the iron atom will represent the local probe at the center of the molecule, and will be sensitive to both the change in oxidation state to Fe(III), and the structural rearrangement of both the CN ligands and the surrounding solvent. Ultrafast laser experiments have been performed and x-ray experiments are in preparation, the details of which will be presented.

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Conformational dynamics of single G protein-coupled receptors trapped in solutionAlexandre Fürstenberg¹, Samuel Bockenhauer¹, Quan Wang¹, Xiao-Jie Yao², Brian Kobilka², W. E. Moerner¹¹Department of Chemistry and ²Department of Molecular and Cellular Physiology and Medicine, Stanford University, Stanford, CA 94305, USA

In single-molecule studies, one would ideally like to observe each biomolecule in its native or in a close-to-native environment for as long a time as possible, which means without the molecule diffusing away from the observation volume and without chemically attaching it to a surface which might impair its function. The Anti-Brownian Electrokinetic (ABEL) trap developed in the Moerner group solves this issue by using electrokinetic forces which can be very strong on single fluorescent nanoscale objects so as to suppress Brownian motion in solution using real-time feedback control. Compared to diffusion through a Gaussian focal spot, the time-averaged optical intensity is uniform in the ABEL trapping volume, so that useful amplitude information can be extracted from each molecule. We demonstrate how this device can be used to trap single biological objects such as G protein-coupled receptors (GPCRs) in order to extract information on the dynamics of single biomolecular systems.

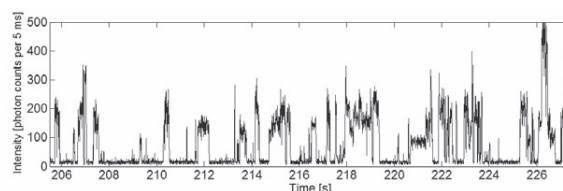


Figure 1. Trapping of single GPCRs in solution. Every fluorescence burst corresponds to a single protein trapped in solution for up to ~1 second.

Copper-zeolites for the conversion of methane to chemicalsE.M.C. Alayon^{1,2}, M. Nachtegaal², J.A. van Bokhoven^{1,2}¹ETH Zurich, Wolfgang Paulistrasse 10, 8093 Zurich, Switzerland²Paul Scherrer Institute, 5232 Villigen, Switzerland

A reaction route for the conversion of methane to chemicals at mild conditions as a highly economical and environmentally attractive alternative to the energy-intensive steam-reforming process is explored. This requires an active and selective catalyst to activate the strong C-H bond without total oxidation. Infrared spectroscopy data showed that methanol was formed on Cu-MOR and Cu-ZSM5 during methane interaction at 150°C. However, the catalytic process is hindered by the strong sorption of methanol on the catalyst surface [1]. The adsorbed species was extracted and detected by gas chromatographic analysis as methanol, and its desorption as CO₂ during heating the catalyst in helium was seen through mass spectroscopic measurements. Pre-adsorbed methanol on Cu-MOR and Cu-ZSM5 dehydrated to dimethyl ether upon heating in helium. Conversion of methanol to dimethyl ether and dimethyl carbonate has also been shown to occur on similar copper-exchanged zeolites [2,3]. Thus, a route of converting methane directly to chemicals is envisioned to be possible by performing these successive reactions on the same catalyst.

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New Ruthenium Sensitizer With Carbazole Antennas For Efficient And Stable Thin-Film Dye-Sensitized Solar Cells

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A new heteroleptic ruthenium complex, coded CYC-B13, incorporating an antenna ligand composed of the sequential connection of a conjugated segment and carbazole hole-transport moiety was prepared. This new sensitizer exhibits the lower energy Metal to Ligand Charge Transfer (MLCT) band centered at 547 nm with a high molar absorption coefficient of $1.93 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Thin-film cells based on this new sensitizer show good conversion efficiency (>8%) and excellent durability under light soaking at 60°C in simulated sunlight for 1000 h. An all-solid state device based on CYC-B13 is also demonstrated to have a conversion efficiency of 3.8%. The photovoltaic data of DSCs sensitized with CYC-B13 suggested that carbazole is a photostable hole-transporting moiety to be used in dye-sensitized solar cells.

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High rate capability of graphite anodes in lithium-ion batteries

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Graphite is one of the most used anode materials of today's lithium-ion batteries. It has several advantages compared to other anode materials including safety, a low potential versus lithium metal, high coulombic efficiency, and reasonable specific charge of 372 mAh/g.

For LiFePO₄ cathodes high rate capability of 400C have already been achieved [1]. Such fast cathodes require also fast anodes. Therefore, our group investigates graphite with regard to its high rate capability. The diffusion coefficient should not limit the rates in graphite [2]. Previous results proposed that loading, electrode thickness and porosity influences the possible rates. Therefore, we prepared electrodes with different thicknesses and porosities which have been cycled versus lithium metal. Medium thicknesses of 50 µm can be discharged at 20C while single layers of graphite particles of about 1-2 µm can be discharged at very high rates. Unfortunately, the charge process is much more limited with 2C for medium and 5C for thin thicknesses, respectively. The rate limiting step seems to be electrolyte diffusion or exchange currents at the solid electrolyte interphase. In this work, the dependency of the rate capability to electrode thickness and charge/discharge rate will be presented.

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Adsorption of Ethylene on Pd(111) surface: a first-principles periodic density calculation

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We present and discuss results of the calculations of the adsorption of Ethylene (C₂H₄) at different sites on Pd(111) surface using ab initio method based on Density Functional Theory (DFT) formalism with generalized gradient approximation (GGA.PW91) for exchange and correlation. These calculations provide information about geometries, stabilities, and reactivities of adsorbed species on various surfaces. We compare our result with previous experimental and theoretical studies of the ethylene adsorption on Pd(111) surface.