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TERAHERTZ TIME-DOMAIN SPECTROSCOPY STUDY OF THE CONDUCTIVITY OF HOLE-TRANSPORTING MATERIALS

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Redox-active ionic liquids, organic liquids and amorphous solids containing electron donating moieties, and conductive polymers can efficiently transport positive electrical charges. These hole-conducting media find increasing applications in bulk heterojunction solar cells and organic light-emitting diodes.

Appropriate methods are required to unravel the detailed conduction and trapping mechanisms in these materials and fully understand the interplay of molecular vibrations and charge transport processes. Terahertz time-domain spectroscopy (THz-TDS) was used as a powerful technique, allowing for the direct determination of the complex conductivity of hole transporting materials in a contactless, purely optical manner. Beyond the measurement of the conductivity of solid and liquid materials, THz (far infrared) spectroscopy also provides direct information on the librational and vibrational modes coupled to charge transport processes and therefore is invaluable in the study of the mechanism of polaronic transport in matter and light-induced electron transfer reactions coupled to low-frequency phonons.

Application of this technique is illustrated by examples provided by the study of the redox-active ionic liquid 3-methyl-1-propylimidazolium iodide (PMII) and that of the molecular liquid hole conductor 10-methylphenoxazine. Both systems are of particular interest, as both are successfully used as alternatives to solvent-based electrolytes in dye-sensitized solar cells.

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Chiral modification of Platinum using Peptides: asymmetric induction in hydrogenation reactions

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The potential of tryptophan-based peptides as chiral surface modifier of Pt/Al$_2$O$_3$ has been explored, due to the structural similarity of tryptophan with cinchonidine.[1] A full class of peptidic modifiers can be easily created via addition of natural amino acids to the tryptophan starting unit via peptidic bond, thus affording a large number of modifiers and a broad chemical and tridimensional variety of the chiral moiety. A preliminary screening of a relatively limited set of peptides in the asymmetric hydrogenation of the model substrate ketopantolactone shows enantioselectivities up to 30%. The catalytic data have been correlated to structures calculated using density functional theory in order to get insights into the topology of the asymmetric environment produced (Fig.1). Significant information has been gained concerning adsorption geometries, properties of the chiral pocket and mechanistic aspects of the hydrogenation.[2]

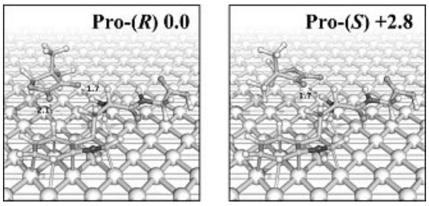

Fig. 1- Relative energies of the Pro-(*R*) and Pro-(*S*) complexes between ketopantolactone and Trp-Gly adsorbed on Pt(111) surface.

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High Open-circuit Voltage Solid-State Dye-Sensitized Solar Cells with Organic Dye

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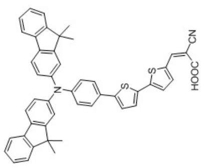
Solid-state dye-sensitized solar cells were fabricated using an organic dye, 2-cyanoacrylic acid-4-(bis-dimethylfluoreneaniline)dithiophene (a), which exhibit more than 1 V open-circuit potential (V$_{oc}$). To scrutinize the origin of high voltage in these cells transient V$_{oc}$ decay measurements and DFT calculations of the interacting dye/semiconductor surface were performed. A negative conduction band shift was observed due to the favorable dipolar field exerted by the organic sensitizer to the TiO$_2$ surface, at variance with heteroleptic Ru(II)-dyes for which an opposite dipole effect was found, providing an increased V$_{oc}$.[1]



(a)

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Local viscosity of binary water+glycerol mixtures at liquid/liquid interfaces studied by time-resolved second harmonic generation

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We studied local viscosity of mixtures of water and glycerol at an interface with a liquid alkane by means of time-resolved second harmonic generation [1]. A dye such as malachite green (MG) or brilliant green (BG) was dissolved in the water+glycerol phase. Dye molecules adsorbed at the interface enhance the yield of second harmonic (SH) generation when they are in the ground state and do not contribute to the signal after optical excitation by an ultrashort laser pulse. Therefore the intensity of the SH recorded as a function of the delay between the excitation and the probe (fundamental) pulse reflects the repopulation of the ground state of the dye. The nonradiative relaxation of the dyes involves large amplitude structural motion, thus they can be used as probes of the local viscosity [2, 3, 4].

We compared the deactivation of MG and BG in bulk solutions and at the interface for various proportions of water and glycerol in the mixture. In the bulk as well as at the interface lifetimes of the excited state follow a power dependence, $\tau(\eta) \sim \eta^{\alpha}$, where η is the macroscopic viscosity of the mixture. The influence of glycerol is however lower at the interface than in the bulk solution. Additionally, anomalous behaviour of the decay time for specific proportions of the mixture has been observed at the interface.

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State-Resolved Reactivity of $CH_4(2\nu_3)$, $CH_4(2\nu_2+\nu_4)$ and $CH_4(\nu_1+\nu_4)$ on Pt(110)-1x2: maximizing the projection on reaction coordinates from transition state structure

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The key step in steam-reforming, which converts CH_4 and H_2O into H_2 and CO, is the dissociative chemisorption of CH_4 on a transition metal catalyst surface. Design of metal catalysts generally focuses on activation barrier optimization [1]. One might also pay attention to the transition state structure, as suggested by our recent comparative study on Ni(111) and Pt(111) [2]. Transition state structure calculations for Pt(110)-1x2 show that CH_4 needs to be both stretched and bent to access the lowest energy path to dissociation [3]. In order to study the role of the transition state geometry, we performed state-resolved reactivity measurements for CH_4 on the corrugated Pt(110)-1x2 single crystal surface. The reactivity enhancement relative to the ground state were measured for three different vibrational eigenstates of CH_4, containing either C-H stretch ($2\nu_3$), C-H bend ($2\nu_2+\nu_4$) or stretch plus bend ($\nu_1+\nu_4$) amplitude. We find vibrational energy to be most efficient in promoting the dissociation for the state containing both stretch and bend excitation followed by the stretch overtone and the bend overtone. The observed mode specificity shows that prepared states of the incident methane are not completely scrambled by the surface impact. Comparison with the calculated transition state structure indicates that vibrational states with geometry similar to the transition state provide the most efficient activation.

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New methods in Nuclear Magnetic Resonance: application of relaxation phenomena to the study of local dynamics in biomolecules

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Nuclear Magnetic Resonance (NMR) spectroscopy offers many ways to study dynamic properties of biomolecules [1]. Many biological processes involve μs to ms time scale conformational motions that can give rise to *chemical-exchange* contributions to relaxation. In particular, in two-spin systems, correlated chemical exchange leads to *cross-relaxation* phenomena which can provide important kinetic, thermodynamic, and structural information [2]. We have designed new Heteronuclear Double-Resonance (HDR) methods based on well-known decoupling pulse sequences, applied simultaneously to two coupled spins, for the investigation of chemical-exchange-induced cross-relaxation processes [3]. We have carried out a theoretical study of the dynamics of a two-spin system under HDR in the framework of a so-called product-operator formalism, using average Hamiltonian and average Liouvillian theories to treat coherent effects and relaxation, respectively. This theoretical analysis, supported by experiments, has provided a deep insight into the physics of the system. We can present now the first applications of the HDR methods, which have permitted the quantification of the time scale of chemical-exchange processes in the protein ubiquitin. Applications to other biological systems will also be discussed.

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Solvation dynamics study on aqueous iodide using picosecond and femtosecond hard X-ray absorption spectroscopy

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A rearrangement of water molecules surrounding photodetached aqueous iodide has been studied for the first time using femtosecond hard X-ray absorption spectroscopy (XAS). The dynamics of resonant 2s 5p transition in the radical iodine strengthen our finding from previous picosecond XAS on the back electron donation of water molecules to the nascent iodine atoms [1]. The data show that the resonant peak is reduced by ~50% at 50 ps, while almost no reduction has been found at 300 fs. The solvent structure at 50 ps was inferred by refining pair radial distribution function g(r) [2] of iodine and oxygen with the L3 edge transient EXAFS at 50 ps. The refined g(r) shows two peaks at 2.6 and 4.5 Å which is in fairly good agreement with a DFT simulation. The transient structure at 300 fs can be visualized by an analysis that combines the femtosecond transient absorption and DFT simulation.

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Retrieving photochemically active structures by ultrafast optical and X-ray spectroscopies

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Observation of the making and transforming of chemical bonds in the course of a chemical reaction is the dream of every chemist. The recent implementation of X-ray absorption spectroscopy in the ultrafast time domain allows studying the electronic and structural dynamics of photochemically active molecules in solutions. In this study we present the structural determination of the photoexcited $[Pt_2(P_2O_5H_2)_4]^{4-}$ anion. This molecule plays an important role in photocatalytic chemical conversions and its photochemical properties are a manifestation of the newly formed Pt-Pt bond in its excited triplet state. X-ray pulses of 70 ps width from the Swiss Light Source are used to probe the transient structure after excitation with a femtosecond laser pulse tuned to the excited state absorption at 380 nm. A rigorous model-based statistical analysis of the difference (excited minus unexcited) X-ray absorption spectrum shows a large contraction of 0.31(5) Å of the Pt atoms and a ligand expansion of 0.010(6) Å. [1,2] Complementary to the time-resolved X-ray measurements, optical fs transient absorption measurements have shown wavepacket dynamics in the impulsively excited singlet state. In addition, the results allow us to propose a model for intersystem crossing.

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Energy Transport in Peptide Helices after IR Excitation of Leucine-D10

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We have recently introduced a new experimental concept to study vibrational energy transport through peptide helices [1]. Vibrational energy is locally deposited at the one end of a peptide 3_{10} helix by UV excitation of an azobenzene moiety. The subsequent energy flow through the helix is detected at various distances from the heat source as a function of time by employing vibrational pump-probe spectroscopy. For this purpose certain amide I vibrations are singled out from the main amide I band by site-selective isotope labeling.

In order to investigate the influence of the amount of energy initially deposited, we repeat this experiment after low energy excitation with IR photons. As an alternative heat source for IR pumping [2] we incorporate a decadeuterated Leucine residue into the molecular chain and excite its C-D vibrations. We report on the progress of the project.

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The cooperative effect of the hydrogen-bonded chains in the environment of a π → π* chromophore

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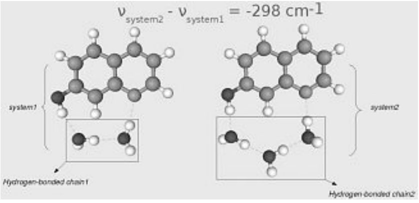
Laser resonant two-photon ionization UV spectra provide clear evidence that the effect of increasing the length of the hydrogen-bonded chain consisting of such molecules as NH_3, H_2O, or CH_3OH bound to the chromophore on the $\pi \rightarrow \pi^*$ excitations of 7-hydroxyquinoline (cis-7HQ) is strongly cooperative [1]. A theoretical analysis of the experimental data usinge the orbital-free embedding formalism [2] is provided to identify the origin of this cooperativity for four chains.

It is concluded, that the electronic coupling between the molecules at the ends of the chain,which are hydrogen bonded to cis-7HQ, rather than changes of the geometry lies at the origin of this cooperativity.



Keywords: electronic excitations, orbital-free embedding

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High Resolution Infrared Spectroscopy of Oxirane Carbonitrile

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Precursor molecules of evolution like oxirane carbonitrile [1] are of interest in relation to possible astrophysical observation using spectroscopy [2,3]. As a chiral molecule, the heterocyclic molecule CH_2OCHCN (cyanooxirane or in systematic nomenclature oxirane carbonitrile) is also of potential interest when relating biomolecular evolution and molecular parity violation [3,4]. We report here results of a high resolution infrared spectroscopic study of the ν_{13} and ν_{12} bands (ν_o = 849.11 cm^{-1} and ν_o = 915.27 cm^{-1}, respectively). In general, the highly resolved infrared spectra of chiral molecules are difficult to assign because of their complex structure. Many of the high resolution infrared studies of these molecules available to date have been performed in our group [5,6], including those of the three-membered heterocyclic ring compounds d1-oxirane and fluoro-oxirane [7,8]. The work reported here expands importantly upon this foundation.

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Determination of the ionization and dissociation energies of the hydrogen molecule

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The transition wave number from the $EF\ ^1\Sigma_g^+(v=0, N=1)$ energy level of ortho-H_2 to the $54p1_1(0)$ Rydberg state below the $X^+\ ^2\Sigma_g^+(v^+=0, N^+=1)$ ground state of ortho-H_2^+ has been measured to be $25209.99756\pm(0.00022)_{\mathrm{statistical}}\pm(0.00007)_{\mathrm{systematic}}$ cm^{-1}. Combining this result with previous experimental and theoretical results for other energy level intervals, the ionization and dissociation energies of the hydrogen molecule have been determined to be 124417.49113(37) cm^{-1} and 36118.06962(37) cm^{-1}, respectively, which represents a precision improvement over previous experimental and theoretical results by more than one order of magnitude. The new value of the ionization energy can be regarded as the most precise and accurate experimental result of this quantity, whereas the dissociation energy is a hybrid experimental-theoretical determination. Experiments on D_2 and HD are in progress.

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Vibronic structure of the 3s and 3p Rydberg states of the allyl radical

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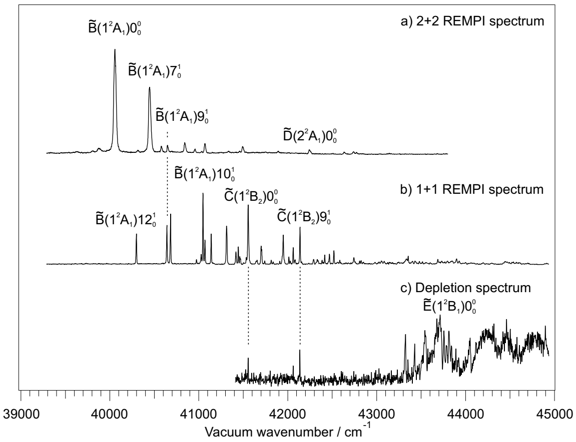
Vibronic spectra of supersonically cooled allyl radical were recorded. The allyl radical was generated via photolysis. This leads to a colder expansion than the pyrolysis applied in former studies. [1] Several bands earlier ascribed to fundamentals proofed to be hot-bands, which lead to a complete reinterpretation of the observed vibrational spectra. The band origins of the Rydberg 3s, $3p_y$ and $3p_z$ states were identified at 40 046, 41 556 and 42 230 cm^{-1}, respectively. The only fully allowed Rydberg $3p_x$ state depletes efficiently to the ground state via a three state conical intersection. Therefore it has to be detected via UV/UV-depletion.



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Population transfer spectroscopy of protonated biological molecules in cold ion trap

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One major goal for gas-phase spectroscopy of is to explore the potential energy surface that governs the stable conformations. Important objectives of this work are to provide information on the conformational minima and the barriers between the stable conformations of gas phase biomolecules. We first determine the potential minima by infrared spectroscopy and then evaluate their fractional abundances, using population transfer spectroscopy.

Biomolecular ions are produced in the gas phase via nanospray and cooled in a 22-pole ion trap[1] where we use a variety of laser techniques to study them spectroscopically. We initially performed our population transfer experiments using protonated phenylalanine. As a first step, the electronic and infrared spectroscopy of the protonated molecule was studied using single- and double-resonance photofragmentation methods. Comparison of the experimental infrared spectrum with DFT calculations allows assignment of the conformation. Having identified different conformers[2,3], we then performed population transfer experiments in protonated phenylalanine and a seven amino acid helix Ac-Phe-(Ala)5-Lys using IR excitation of the NH and the CO stretch vibrations .

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Modeling of Vibrational Relaxation and the Vibrational Stark Shift in Protein Electric Fields

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Vibrational spectroscopy is a powerful technique that is used in all areas of chemistry to explore molecular structure and dynamics. Photoexcitation can be used to target an individual bond, adding a measured amount of energy and yielding valuable information from subsequent vibrational relaxation rates and pathways. Accurately modeling bond vibrational frequencies while adequately sampling available phase space, however, quickly becomes prohibitive using full *ab initio* calculations. Traditional force field methodologies, employing harmonic bonded potentials and simple point charges, are not sufficiently detailed to obtain realistic vibrational responses. In this work we demonstrate that vibrational coupling can be successfully modeled within a classical force field framework by using anharmonic bonded potentials. Vibrational relaxation after photoexcitation of CO in bound carbonmonoxy myoglobin is used as an example by comparison with experimental pump-probe results, and possible cooling mechanisms are described. We additionally present separate work to show that realistic vibrational frequency shifts can be achieved in an applied non-uniform electric field by using a fluctuating multipolar force field. This result has implications for interpretation of Stark shift measurements, complementing new techniques that are being developed to probe electric fields in protein active sites.

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Partially oxidized platinum generates high activity for CO oxidation

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High activity for CO oxidation over Pt/Al_2O_3, Pt/TiO_2, and Pt/SiO_2, was obtained over partially oxidized platinum, as probed by in-situ x-ray absorption spectroscopy. The high activity state occurred at high temperature and low CO concentration. CO poisoned the metallic surface. Ignition, which is the switch from low to high activity, was characterized by an abrupt increase in CO conversion, accompanied by oxidation of the catalyst as seen in the increasing intensity of the XANES [1]. EXAFS analysis showed a dynamic platinum particle structure consisting of a metal core and a strongly defected surface oxide [2]. The amount of surface oxide depended on the local concentration of the reactants in the gas phase and on the temperature that it formed. Complimentarily, linear- and bridged-CO species abruptly decreased during ignition as observed in in-situ infrared measurements. With the sudden decrease in CO conversion during extinction, the partially oxidized catalyst became reduced and CO-covered. Small particles of Pt/Al_2O_3 reached high activity at lower temperature than larger particles. Pt/TiO_2 and Pt/SiO_2 reached high activity at the lowest and highest temperature, respectively, and in the same order, were least and most oxidized.

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Heat and Light Resisting Organic Sensitizer for Solar Cell Applications

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The conversion of sunlight to electricity using dye-sensitized solar cells (DSCs) represents one of the most promising methods for future large scale power production from renewable energy sources. In these cells, the sensitizer is one of the key components, which harvest the solar radiation and convert it to electric current. Ruthenium complexes have exhibited remarkable efficiency and stability. However, there are several challenges limiting their development for large-scale applications. Therefore several groups have developed metal free organic sensitizers and obtained relatively low efficiencies compared to the ruthenium sensitizers. In this work, we report a meticulously engineered organic sensitizer, 3-(5-(5-(4-(bis(4-(hexyloxy) phenyl)thiophene-2-yl)thiophene-2-yl)-2-cyanoacrylic acid [1] that exhibit not only comparable efficiency to the ruthenium sensitizers but also unprecedented stability under light and heat soaking conditions where the overall efficiency of dye-sensitized solar cell remained at 90% of the initial value after 1000 hrs.

[1] J.-H. Yum, D. P. Hagberg, S.-J. Moon, K. M. Karlsson, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem., Int. Ed.* **2009**, *48*, 1576.

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Chemisorption of methyl mercaptane on supported Au nanoparticles: A way for Au surface area determination?

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Supported gold nanoparticle catalysts have attracted tremendous attention during the last decade. Many reactions are effectively catalyzed by gold, and much research on expanding the scope of these catalysts is still ongoing [1]. Clear is that since bulk gold is not (or hardly) active, small particles are needed to perform catalysis, typically in the range of 1 -10 nm in diameter. Clearly, this places emphasis on the controlled synthesis of such particles and their characterization. Two techniques commonly employed in the characterization of supported noble metal catalysts are chemisorption (by probe molecules such as CO and H_2) and electron microscopy (typically STEM). However, due to the nobility of (even) Au nanoparticles, no suitable probe molecules are which probe the entire surface, although low coordinated sites are possible to probe with CO [2] and H_2 [3]. Additionally, STEM analysis of supported Au nanoparticles becomes difficult in those cases where there is little contrast with the support (i.e. small particles, heavy support, etc.).

In this contribution we present the results of adsorption of methyl mercaptane on Au/TiO_2 catalysts. Strategies for optimal sample preparation are presented and the feasibility of using these measurements for Au chemisorption measurements are discussed.

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State-averaged Density Matrix Renormalization Group Calculations for Unsaturated Organic Molecules

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Since its development by White in 1992 [1], the Density Matrix Renormalization Group (DMRG) algorithm has been used in ab initio quantum chemistry calculations where a large active space was required [2-4]. Indeed, this method enables one to treat a large number of active orbitals which is not feasible with CASSCF due to the factorial scaling. The DMRG approach is therefore interesting to study highly delocalized systems like ¯-carotene [4] or chlorophyll. In a pioneering work, DMRG was successfully applied to calculate sufficiently accurate relative energy between ground states of different spin and between isomers of binuclear transition metal clusters on the same potential energy surface [5].

In this study, we have elaborated on a sound strategy for the efficient and accurate calculation of excited states, i.e. accurate excitation energies. In order to prevent root flipping or loosing states due to the numerical Davidson subspace iteration technique, the state-averaged (averaged reduced density matrix) approach proposed by Garnet G.-L. Chan and coworkers [6] was implemented in our DMRG code. Our program is then applied on polyene systems for which accurate reference data are available [4]. Different effects on the relative energies such as the number of DMRG states, the number of roots in the state-averaged approach, different weighting of the reduced density matrix of the excited states, levelshift, noise, . . . are tested on five polyene of increasing size (ranging from C8H10 to C24H26). While for the small systems, reference CASSCF calculations can be conducted, the largest systems benefit from the polynomial scaling of the DMRG algorithm. Moreover, our results are compared to TDDFT and CC2 calculations on the bases of the energy and the spatial symmetry ordering of the states.

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Ultrafast Infrared Spectroscopy of New Biomimetic Photoswitches Driven by Z/E Isomerization

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Molecular switches based on Z/E isomerization constitute examples of systems able to convert light into mechanical motion at the molecular level. The design and preparation of novel building blocks mimicking various aspect of the photoisomerization of the visual pigment rhodopsin has led to the synthesis of a new family of switches based on the N-alkylated indanilidene-pyrroline (NAIP) framework [1]. These systems undergo ultrafast, efficient and reversible isomerization in solution [2]. The present work reports on the ultrafast infrared characterization of these photoswitches.

Our data reveal a sub-picosecond isomerization in both trans-to-cis and cis-to-trans directions. A subsequent cooling process is completed in 20ps suggesting that a two photon induced rotary motion is possible in the gigahertz range. Results are compared with simulations and perspectives are given for the application of NAIP's as unidirectional rotors.

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Photocatalytic Degradation of Selected Organic Pollutants under Visible Light Irradiation with $BiVO_4$ Nanoparticles

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Activity of $BiVO_4$ nanoparticles as a photocatalyst was tested against three types of organic pollutant under visible light irradiation. These powdered photocatalysts were prepared by a Flame Spray process described elesewhere [1]. Band edge positions and surface properties are key parameters influencing the reactivity of a heterogeneous photocatalyst for the degradation of organic pollutants. The as-prepared powders exhibited a band-gap of 2.5 eV and an isoelectric point (IEP) of 2.3. Unlike TiO_2, $BiVO_4$ requires the presence of H_2O_2 as an electron acceptor in order to achieve the photocatalytic reaction involving both hole and electron charge transfer. In heterogeneous photocatalysis, phenol is known to be degraded by the electophilic attack of $^{\cdot}$OH radical [2]. Dichoroacetate anion is degraded by direct hole attack [3]. Imidazolium and methylene blue are cationic species with more complex chemistry. The interaction of these model pollutants with $BiVO_4$ and H_2O_2 in aqueous media wil be discussed.

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Infrared Laser Photofragment Spectroscopy of Biomolecules

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The combination of mass spectrometry and laser spectroscopy is used to investigate properties of biological ions in the gas phase. Closed-shell biomolecular ions are produced by a nanoelectrospray source, mass-selected by a quadrupole mass filter and guided into a 22-pole ion trap where they are cooled down, by collisions with helium buffer gas, to less than 10 K. While stored inside the trap, the ions interact with laser light and dissociate upon absorption. The spectra are obtained monitoring the fragmentation signal as a function of the laser wavelength.

We recently measured highly resolved electronic and infrared spectra of peptides of up to 17 amino acids, containing one or two chromophores, using infrared laser-assisted photofragment spectroscopy (IRLAPS) [1]. The fragmentation yield of UV excited molecules increases by as much as 2 orders of magnitude when they further interact with the CO_2 laser. This approach can be also applied in a IR-UV double resonance scheme, allowing measurements of conformer specific infrared spectra of protonated peptides.

The fragmentation channel, which is always greatly enhanced by IRMPE of UV preexcited molecules, is the loss of the neutral, aromatic side chain via cleavage of the C_α-C_β bond, independently of the chromophore excited in the peptide. We will discuss here the possible mechanisms which lead to the formation of the observed photofragment.

[1] M. Guidi, U. J. Lorenz, G. Papadopoulos, O. V. Boyarkin, and T. R. Rizzo, *J. Phys. Chem. A* **2009**, *113,* 797.

396

Conformational analysis of metal complexes by direct observation of DNP-enhanced NMR of Yttrium-89 , Ag-107 and Ag-109.

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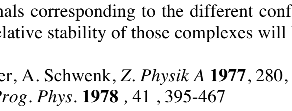
It is challenging to analyze organometallic complexes using NMR techniques due to the existence of various conformations in equilibrium. To overcome this issue, a possibility is to measure the NMR signal of metallic ions. It is known that their NMR signals depend on the symmetry of the ligand field surrounding the metal atom [1]. Hence, different conformations lead to different NMR signals of the same metallic ion. Metallic nuclei with spin S = ½, such as yttrium (^{89}Y) and silver (^{107,109}Ag), allow one to carry out straightforward NMR experiments, but they suffer from two majors drawbacks: poor gyromagnetic ratios ($\gamma / \gamma_{^1H} = 6 \cdot 10^{-5}$ - $1.18 \cdot 10^{-4}$) and extremely long T_1 (100-400 s). This makes the acquisition of their NMR spectra technically challenging. The aim of our work is to use the Dynamic Nuclear Polarization (DNP) [2-3] to enhance the signal of the metallic nuclei and obtain a one-shot NMR measurement of complexed the metallic ions spectra. We investigate the complex $[Y(DOTAM)(H_2O)](ClO_4)_3$ which is known to have two well characterized conformations (M- and m-isomers) with a relatively slow exchange rate [4-5].



We intend to assign the signals corresponding to the different conformations and establish their relative weights. The relative stability of those complexes will be determined.

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PFI-ZEKE measurements of the Allyl Radical C_3H_5 via the B [1^2A_1] 3s Rydberg state

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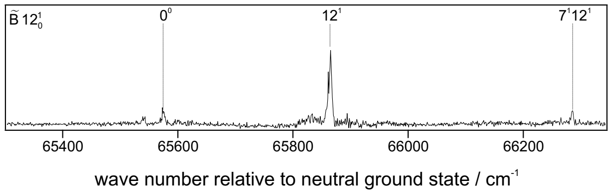
The value of the ionization potential of the allyl radical was discussed intensively in the last decade [1,2]. With our pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of jet-cooled allyl radicals (C_3H_5) recorded following resonant multiphoton excitation, we have resolved this ambiguity. The analysis of the rotational contours of the photoelectron spectra yielded values of the first adiabatic ionization energy of allyl of 65581.3(80) cm^{-1}. More than 30 transitions to vibrational levels of the cation were identified and assigned on the basis of predictions from *ab initio* calculations [3].



The Figure above shows the 1+1′ PFI-ZEKE photoelectron spectra obtained via the $\tilde{B}\ 12^1$ intermediate state. The dominant peak at 65865 cm^{-1} corresponds to the $\Delta\nu = 0$ transition. This is in agreement with the small change in geometry between the intermediate state and the cationic structure. A second weaker peak is visible at +422 cm^{-1} that we assign to a transition to the $7^1 12^1$ vibrational level of the cation.

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398

Rotationally resolved spectroscopy and potential energy curve of the X 0^+ electronic ground state of ArXe

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Rotationally resolved (1 + 1') resonance-enhanced two-photon ionization spectra of the D 0^+, C 1 ← X 0^+ band systems of several isotopomers of ArXe were recorded at high resolution in the wave number range from $77\,000\,\mathrm{cm}^{-1}$ to $77\,300\,\mathrm{cm}^{-1}$ using a near-Fourier-transform-limited vacuum-ultraviolet laser system [1] . The rotational structure of the $v'' = 0, 1$ vibrational levels of the X 0^+ ground state of ArXe could be fully resolved and assigned, leading to a complete set of spectroscopic parameters that enabled the determination of the potential energy function describing the van der Waals interaction [2] in the ground state of ArXe using a semiempirical fitting procedure [3]. The internuclear separation, the first vibrational energy interval and the bond dissociation energy were determined to be $R_\mathrm{e} = 4.092(1)$ Å, $\Delta G_{v+1/2} = 23.447(5)$ cm^{-1} and $D_\mathrm{e} = 131.498(60)$ cm^{-1}, respectively.

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Controlled release of volatile molecules from block copolymer micelles in ethanol-water mixtures

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Phase diagrams of various block copolymers, made of ethylene glycol and propylene glycol (Pluronic®), with different compositions and molecular weights (Mw), were determined by dynamic light scattering in ethanol-water mixtures. Pluronic® P-103 formed micelles up to 40 wt% of ethanol, whereas copolymer L-43 (with a similar composition and lower M_w) stayed in solution as free chains. Phase diagrams of both copolymers with five perfumery raw materials (PRMs, ethyl butyrate (EB), Manzanate, Triplal®, Romascone®, and Citral) were studied at 40 wt% of ethanol. A significant micelle growth was detected with P-103 and Romascone®, in contrast to EB. Partitioning of Romascone® or EB between L-43 or P-103 phases and solvent was then measured by diffusion NMR spectroscopy. Both PRMs were present in the solvent phase with L-43. On the other hand, a majority of Romascone® was located in the P-103 micelle, in contrast to EB, as expected based on their thermodynamic compatibility. The impact of P-103 micelles on the evaporation of both PRMs, compared to L-43 solutions, is determined by static headspace analysis at the equilibrium and by measuring mass losses as a function of time by thermogravimetry. P-103 micelles significantly reduced the evaporation rate of Romascone®, confirming the drastic effect of micellisation on release profiles of volatile molecules.

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Bridge Effect on Electron Transfer through Oligofluorenes

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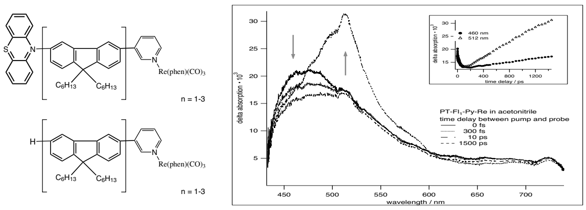
Oliver Wenger[b*], Eric Vauthey[a*]

University of Geneva, [a]Department of Physical Chemistry
[b]Department of Inorganic, Analytical and Applied Chemistry

Studies on electron transfer (ET) reactions are still gaining interest due to their implications on fields of upmost practical impact like artifical photosynthesis, the design of solar cells, or light emitting diodes, to name a few. Despite the great advances made in the last decades, the parameters that govern the rate constant of an ET reaction are still subject of animated discussion[1].

The improvements made in ultrafast spectroscopy, both, in terms of time resolution as well as spectral quality, enable us to identify the short lived species that occur in the (often stepwise) course of ET of complex systems like, e.g., the photosystem of plants.

We report on photoinduced ET of a series of model dyads composed of a rhenium(I) tricarbonyl diimine photosensitizer, a variable bridge, and a phenothiazine moiety as electron donor. The effect of length and chemical nature of the bridge is discussed in the light of their electrochemical and electronic properties.



Left: Structure formula of the investigated dyads. Right: Transient absorption spectra showing the appearance of a positively charged phenothiazine subunit after photo–excitation at 400 nm

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Ultrafast Photoinduced Charge Separation in Multichromophoric Systems

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Creation of smart artificial photosystems, which would convert solar energy into chemical energy with high efficiency attracts increasing attention. Multichromophoric systems consisting in amino naphthalene diimides (NDIs) covalently attached to a *p*-octaphenyl (POP) scaffold have been shown to self-assemble in lipid bilayer membranes and on gold surfaces. The photo- and electro- chemical properties of the NDIs systems can be tuned by varying the substituent on the NDIs core. Moreover NDIs chromophores have substantial π-acidity and *n*-semiconductivity, which allows organizing them in an ordered and oriented "zipper" assembly. Using femtosecond time-resolved spectroscopy, we evidence the formation of a charge-separated state upon photoexcitation of rBrNDIs (Figure 1) chromophores attached to POP and oligophenylene-ethynylene (OPE) scaffolds. We found that the pathways of the charge separation and the lifetime of the charge-separated state depend on the scaffold. The origin of these effects will be discussed in detail.

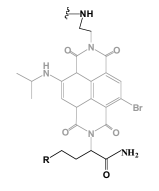

Figure 1. rBrNDI chromophore

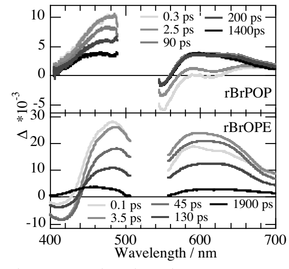

Figure 2. Transient absorption spectra measured with rBrPOP and rBrOPE in MeOH at various time delays after 520 nm excitation

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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 three-pulse photon echo peak shift (3PEPS) 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 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 μJ. 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 3PEPS experiment with 400 nm excitation will be presented.

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Elucidating the particle-size effect on the hydrogenation of 1-pentyne over oxide-supported palladium nanoparticles

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The complete elimination of alkynes from hydrocarbon mixtures rich in olefins and hydrogen via selective hydrogenation is industrially important for the production of polymers [1]. The effect of particle size of the catalysts on the hydrogenation of long-chain alkynes is poorly understood. We determined the reactivity and selectivity of the hydrogenation of 1-pentynes over oxide-supported palladium nanoparticles as a function of particle size. The reactivity and selectivity of the reaction are strongly particle size dependent. Large particles are more reactive and more selective to the formation of n-pentene, while smaller particles have higher selectivity to n-pentane. Possible reasons for such trend are discussed.

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Effect of salts at the liquid/liquid interface investigated by time-resolved second harmonic generation spectroscopy

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We present time-resolved second harmonic generation experiments in order to investigate the effect of salts on the ground state recovery (GSR) of malachite green oxalate (MG) adsorbed at the alkane/water interface.
Experiments were first carried out on alkane/pure-water interfaces with four alkanes of different viscosities. These studies did not show any significant change in the GSR of the MG at the interface. In contrast, addition of NaCl and NaSCN salts to the aqueous phase seemed to markedly slow down the GSR of the MG at the interface (fig.1).

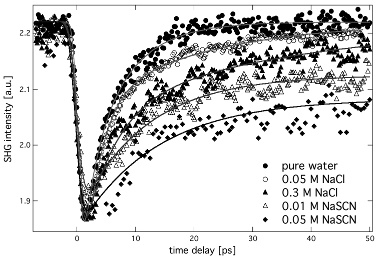

Figure 1: GSR of MG at pentadecane/salty-water interface.

The dependence of the dynamics on the sodium salts as well as on the nature of the alkane (odd and even) was investigated. Moreover, dynamics at the interface was also compared with that in bulk salty-water [1].

[1] Punzi A. et. al., J. Phys. Chem. C, 2008, accepted

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Laterally interacting organic sensitizers for solar cell applications

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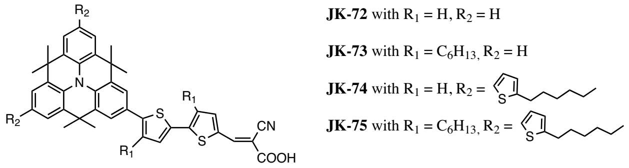
[c]Università di Perugia, 06123 Perugia, Italy

As an alternative to Ru-based sensitizers for DSC, some organic molecules can also be used for this application. One class of highly efficient sensitizers consists of a bis-dimethylfluoreneaniline moiety acting as electron-donor and a cyano-acrylic acid moiety acting as electron-acceptor, the two functions being connected by conducting thiophene units.[1] By modifying the donor unit, dyes showing lateral interactions on TiO_2 surfaces have been engineered (**JK-72** and **JK-74**). In case of additional hexyl moieties (**JK-73** and **JK-75**), this lateral interaction is inhibited, resulting in narrowed IPCE. With this series of organic dyes, stable DSC with over 6% efficiency under AM 1.5 conditions have been assembled.



JK-72 with $R_1 = H$, $R_2 = H$

JK-73 with $R_1 = C_6H_{13}$, $R_2 = H$

JK-74 with $R_1 = H$, $R_2 =$

JK-75 with $R_1 = C_6H_{13}$, $R_2 =$

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A Novel Method for Producing State-Selected and Translationally Cold 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 not been achieved up to date. We presently develop a new experimental setup which will allow for the first time to produce state-selected molecular Coulomb crystals based on the combination of threshold-photoionisation with sympathetic-cooling methods.

In our experiment, molecular ions will be produced state selectively by resonance-enhanced multiphoton ionisation (REMPI) of suitable neutral precursor molecules inside an ion trap using the output of two Nd:YAG-pumped dye lasers. Rovibronic state selection will be achieved by preparing the precursor in its lowest rovibronic levels using cooling in a supersonic expansion and ionising only slightly above the lowest rovibronic ionisation threshold accessible from a selected intermediate state. Such state-selected ions will be sympathetically cooled by the Coulomb interaction with laser-cooled Ca^+ atomic ions. The lifetime of the initially prepared quantum state which is usually limited by BBR-induced optical transitions will be increased by cryogenic cooling of the trap environment.

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Molecular engineering of organic sensitizers for solar cell applications

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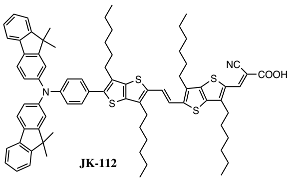
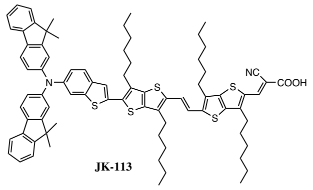
Organic molecules have been shown to be highly efficient sensitizers in dye-sensitized solar cells (DSC). One class of these dyes consists of a bis-dimethylfluoreneaniline moiety acting as electron-donor and a cyano-acrylic acid moiety acting as electron-acceptor, the two functions being connected by conducting thiophene units.[1] In order to increase the photon-to-electron conversion efficiency by broadening the absorption spectrum, the dyes shown below (**JK-112** and **JK-113**) have been developed. In these sensitizers, the thiophene units have been replaced by alkylated thieno(3,2-b)thiophenes. DSC based on these dyes have been assembled, reaching up to 59% (solid-state DSC) and 87% (liquid DSC) incident photon-to-current conversion efficiency (IPCE),corresponding to overall conversion efficiencies of over 4% (solid-state DSC) and over 7% (liquid DSC) under standard AM1.5 conditions.



JK-112



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Synthesis and Nanosoldering of Silver Nanowires on AFM Cantilevers for Tip-Enhanced Raman Spectroscopy (TERS)

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Surface enhanced Raman spectroscopy (SERS) is based on the absorption of light by nanometer-sized metal particles, resulting in large enhancement of the Raman signal. By replacing the metal particles by a metallic nanotip, the enhancement can be localized. The resulting tip-enhanced Raman spectroscopy (TERS) is capable of measuring Raman spectra with high spatial resolution, effectively overcoming the diffraction limit. A successful TERS experiment depends heavily on the ability to fabricate tips of a definite metal with the appropriate shape and size, which is still a challenging process. We show that silver nanowires attached to atomic force microscope (AFM) cantilevers produce a strong, localized enhancement of the Raman spectroscopy intensity. The nanowires are synthesized by electrochemical deposition inside the pores of an alumina membrane. By subsequently dissolving the alumina membrane, freestanding nanowires are obtained, with an approximate diameter of 200 nm. In the next step, the silver nanowires are attached onto AFM tips by using the electron beam of a scanning electron microscope (SEM) to perform localized electron impact-induced dissociation and deposition, a process which we refer to as nanosoldering. We tested these functionalized probes with our homemade TERS setup, based on the combination of a unique ultraflat atomic force microscope in dynamic mode fitted in a reflective-type micro-Raman spectrometer. We observed large and reproducible TERS enhancement factors. TERS tips made of other metals (gold, copper) and of smaller dimensions (down to 50 nm) can also be produced with our technique. These probes could improve the feasibility and reproducibility of the TERS technique.

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Colloid-derived Pt nanoparticles: different poisoning effect of the stabilizer at the solid/gas and solid/liquid interface

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Precipitation of metal colloids on a high surface area support affords heterogeneous model catalysts. The organic stabilizer, however, may not be fully removed from the metal surface due to the strong interactions required for the synthesis of stable colloids. We have investigated the poisoning effect of the stabilizer on the example of poly(acrylic) acid (PAA)-capped Pt nanoparticles with well defined shape distributions (Fig. 1).

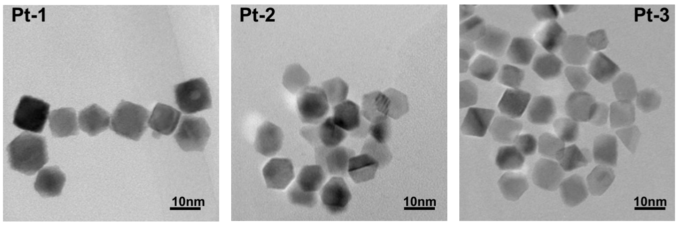

Fig. 1: Representative TEM images of PAA stabilized Pt colloids

Gas phase CO chemisorption revealed that the Pt surface sites were almost completely covered by the stabilizer. In the hydrogenation of cyclohexene from liquid phase at 1 bar H_2 pressure, however, a reasonable activity was observed. The strong anomaly of the CO chemisorption data and the catalytic activity of Pt nanoparticles is attributed to the different mobility of the stabilizer at the solid/gas and solid/liquid interface. Further investigations on the impact of the stabilizer on the chemoselectivity of liquid phase hydrogenations are in progress.

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Shape selective enantioselective hydrogenation on Pt nanoparticles

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Supported Pt nanoparticles of different shape distributions [1] have been synthesized, characterized by electron microscopy, and tested in the enantioselective hydrogenation of activated ketones. In the presence of a cinchona-type modifier a remarkable rate enhancement and enantiomeric excess (ee) of up to 92% were achieved in the hydrogenation of ethyl pyruvate (Fig. 1 top).

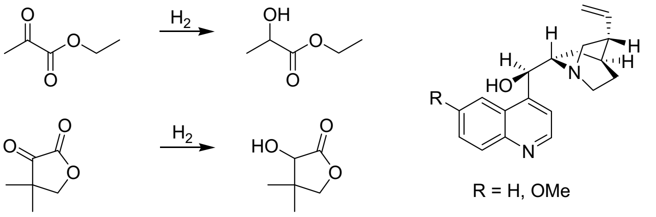

Fig. 1: Hydrogenation of activated ketones

Correlation of the rate acceleration and ee to the Pt nanoparticle shape revealed significant structure sensitivity. Analogous results for the hydrogenation of ketopantolactone (Fig. 1 bottom) revealed that aldol-type site reactions were not the origin of the observed shape-dependent activity. The reason for structure sensitivity was investigated by modeling the modifier adsorption on different Pt surfaces by DFT as well as spectroscopic studies.

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Pd/Al_2O_3-catalyzed asymmetric allylic substitution: a combined theoretical-spectroscopic study

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Enantioselective allylic substitution over chirally modified Pd is a new and highly successful route in heterogeneous asymmetric catalysis [1]. We extended the application range to conventional supported Pd (e.g. Pd/Al_2O_3) and various chiral diphosphines as modifiers [2, 3]. The new catalytic systems show enantioselectivity (*ee*) up to 88% and offer high yields (up to 94%). The heterogeneity of the system was confirmed by catalytic tests and *in situ* XANES measurements.

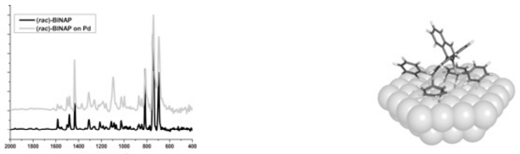

Figure 1: Spectra of BINAP adsorbed on Pd (left) and the probable adsorption mode of BINAP on a Pd (111) surface derived from theoretical calculations (right).

However, the origin of the observed rate acceleration as well as the temperature independence of the *ee* are not yet fully understood. In order to clarify the structure of the active sites, the adsorption behavior of the modifier has been studied by ATR-IR spectroscopy using Pd nanoparticles modified with (*rac*)-BINAP as a model system. The spectroscopic results are supported by theoretical calculations.

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Red-ox behavior of $Pd/LaFeO_3$ and $LaFe_{0.95}Pd_{0.05}O_3$ catalysts in methane combustion

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Catalytic activitiy measurements of methane combustion (1%CH_4, 4%O_2/He) were performed on 2wt% Pd-loaded $LaFeO_3$ catalysts, with Pd either incorporated into the lattice ($LaFe_{0.95}Pd_{0.05}O_3$) or impregnated ($Pd/LaFeO_3$). Results [1] showed highest CH_4-conversion rates for the impregnated material, were most of the Pd is accessible to methane, which is required for high catalytic activity. As $LaFe_{0.95}Pd_{0.05}O_3$ is known to show segregation of palladium in reductive atmosphere [2], reductive pretreatments may provide a way to prepare a better catalyst.

Temperature programmed reduction (H_2-TPR, 5mol%H_2, r.t.-900°C) revealed that palladium is stabilized against reduction up to 150°C in $LaFe_{0.95}Pd_{0.05}O_3$, whereas $Pd/LaFeO_3$ is reduced already at room temperature. In-situ XANES during reduction and CO adsorption measurements on reduced samples (300°C) indicated that palladium exists as small and finely dispersed Pd particles in $LaFe_{0.95}Pd_{0.05}O_3$. Preliminary activity tests performed after reduction at 300 and 500°C reveal that the activity is not improved, and that Pd is immediately incorporated within $LaFeO_3$ after admittance of $CH_4 + O_2$. Reduction at higher temperatures (>700°C) appear to be a better strategy to improve the catalytic activity of $LaFe_{0.95}Pd_{0.05}O_3$.

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Generalized Reactive Force Field for Proton Transfer and Application to Liver Alcohol Dehydrogenase

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Hydrogen bonding and transfer are of fundamental importance in a wide variety of processes in physical chemistry and biochemistry. However an accurate description of hydrogen transfer reactions is still highly challenging. In this work we generalize a force field to characterize both linear and nonlinear hydrogen transfer reactions based on previous investigations on molecular mechanics with proton transfer (MMPT) [1]. The required parameters have been obtained according to *ab initio* calculations for hydrogen transfer in malonaldehyde. This model force field has been embedded into the CHARMM program [2] and long time molecular dynamics (MD) simulations (10 ns) for malonaldehyde have been performed. The calculated hydrogen transfer rates in both gas phase and condensed phase compare well with previous work ranging from short time QM/MM simulations to model rate equation simulations, which implies its applicability to other hydrogen bonds. After establishing its validity for malonaldehyde, the modified MMPT potential is used to investigate proton transfer reactions around the active site of liver alcohol dehydrogenase (LADH) [3] with proper morphing transformations. Long time MD simulations (10 ns) with stochastic boundary conditions have been performed. The direct simulations of proton transfer processes provide more details about the mechanism.

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The role of support acid-base properties on the Pt-catalyzed enantioselective hydrogenation of ketones

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It is well known from former studies [1, 2] that the catalyst support may have a great impact on the chemoselectivity in the hydrogenation of (multifunctional) compounds. The support effect has also been investigated in enantioselective hydrogenations but no clear correlation has been found. For the present study we have selected the hydrogenation of α-ketoesters as the most understood heterogeneous enantioselective transformation. In this reaction the best catalysts are Pt supported on Al_2O_3, but no scientific explanation has been provided yet. We prepared by flame synthesis a series of Pt/Al_2O_3 catalysts, where the acid/base properties of the support were systematically varied via introduction of SiO_2 (5-80 wt.%) or Cs_2O (0.25-10 wt.% loading). The catalysts were characterized by various physic-chemical techniques and tested in the hydrogenation of α-ketoesters in the presence of cinchonidine as chiral modifier. Introduction of SiO_2 increased the support acidity and the enantioselectivity; the opposite effect was observed in the presence of Cs_2O. The probable explanation is that the Pt - support interaction varies with the support ionicity and affects the adsorption of the substrate-modifier complex on the metal surface.

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Vibrational studies of potential hydrogen storage material

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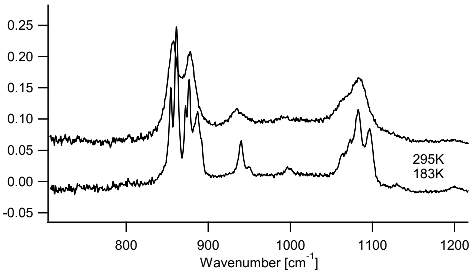
Metal borohydrides are very interesting materials for the hydrogen storage for their large gravimetric and volumetric hydrogen density.

In this work we have studied IR and Raman spectra of several systems, in particular $Ca(BH_4)_2$ and its decomposition products, $Mn(BH_4)_2$, alkali zinc borohydrides and the selectively labeled $NaBD_3H$. For the last compound, the analysis was made varying the temperature; the IR spectra at 295 K and 183 K shown below illustrate the changes due to the structural phase transition.



The experiments were supported by DFT calculations. In these calculations we optimized and calculated the frequencies of $(BD_xH_{4-x})^-$ ions where $0 \leq x \leq 4$.

We used Gaussian03 program at OLYP/TZVP and B3LYP/6-31g(d,p) levels.

This work is supported by Swiss National Science Foundation.

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Luminescence of Sm^{2+} doped in BaFBr

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Alkaline earth fluoride halides (MFX) doped with divalent lanthanide ions show a wide range of spectroscopic properties with many practical applications. Sm^{2+} in those crystals can be used as pressure sensors [1] and has been shown to be the first compound which allows room temperature hole burning [2]. BaFBr doped with Sm^{2+} presents rich luminescence spectra. In this work we studied the effect of pressure and temperature on the CF energy levels of Sm^{2+}doped BaFBr. Sharp Sm^{2+} crystal field (CF) f-f emission bands are observed. At high temperature (more than 450K) we observed broad emission originating from the lowest $4f^5 5d^1$ state. The CF energy levels were determined from the $^5D_{0,1,2} \rightarrow {}^7F_j$ (where j=0-4) transitions. The CF parameters were refined to reproduce the experimental CF energy levels within error less than 10 cm^{-1} using the program written by S. Edvardsson et al.[3]. The pressure up to 8 GPa results red shift of luminescence bands. $^5D_{0,2} \rightarrow {}^7F_0$ band shift with pressure showed very good linear dependence with pressure. The $^5D_0 \rightarrow {}^7F_0$ shift is three times stronger than R_1 lineshift of ruby and the shift increases with temperature. The pressure induced study also revealed the reduction of the splitting between the two $^7F_1$ CF energy levels (A_2 and E). The radiative lifetimes of $^5D_{0,1,2}$ state decrease with temperature, the radiative lifetime of $^5D_1$ decreases much faster than $^5D_0$. The energy of the lowest excited state of the configuration $4f^5 5d^1$ was determined by fitting the lifetime values of $^5D_1$ state.

This work is supported by the Swiss National Science Foundation.

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Isotope effect in dissociative electron attachment cross sections in acetylene

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We present absolute partial cross sections for dissociative electron attachment to C_2H_2 and C_2D_2 which have been measured using a new time-of flight ion spectrometer combined with a trochoidal electron monochromator.

For C_2H_2 the new data is in good agreement with the total cross sections measured previously in our laboratory using the total ion collection principle [1]. The present measurement on deuterated acetylene reveals a pronounced isotope effect at the first dissociative electron attachment band at 3 eV, with the cross section for C_2D^-/C_2D_2 being 14.7 times smaller than that for C_2H^-/C_2H_2. The dramatic magnitude of the effect is attributed to slower motion of the D atom as compared to H atom, combined with unfavorable competition of the dissociation with autodetachment. The recent calculations by Chourou and Orel are in good agreement with our experimental values for C_2H^-/C_2H_2 but underestimate values for C_2H_2/C_2D_2, their ratio $\sigma(C_2H^-)/\sigma(C_2D^-)$ being 28.9 [2].

A second band is observed at around 8 eV corresponding to the light fragments H^- or D^- which dominate above the C_2^- fragment, in contrary to previous assignment. These bands exibit much weaker isotope effects, in agreement with their assignment to Feshbach resonances with narrow autodetachment widths.

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Kinetic oscillations of CO oxidation: space and time resolved structure of a supported platinum catalyst in a catalytic reactor

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Kinetic oscillations of CO oxidation have been observed on supported platinum catalysts [1] and single crystals [2]. On single crystals and under high vacuum conditions, these oscillations originate from switching between different surfaces after reconstruction, which have different rates [3]. Oscillations under high pressure originate from changes in surface structure, which can be reduced, respectively oxidized, resulting in distinct rates [4]. We elucidated the structural changes that occur during the kinetic oscillations of CO oxidation over a real supported catalyst by combining in situ space and time resolved X-ray absorption spectroscopy, infrared spectroscopy, and kinetic measurements. CO oxidation occurred in two distinctive regimes: a low-activity regime characterized by adsorbed carbon monoxide that poisons the surface and a high-activity regime characterized by the presence of surface oxidized platinum [5]. The structure of the catalyst varied over time and differed as function of position in the plug flow reactor. Kinetic oscillations, also confirmed by infrared spectroscopy, occur because of local changes in the catalyst structure inside the reactor.

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Combustion of methane over Pd/Ce-ZrO$_2$ and Pd/LaFeO$_3$: A physico-chemical characterization

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Methane is a greenhouse gas with a greater global warming potential than carbon dioxide. Therefore, its total oxidation is essential before being emitted from its sources (e.g., compressed natural gas (CNG) vehicles). Pd-based catalysts are reported to be the most active for this purpose [1]. Pd based Ce$_{1-x}$Zr$_x$O$_2$ and perovskites have got a great deal of attention due to their combustion activity and thermal stability especially to treat CNG vehicle exhaust [2]. Interestingly, a hysteresis (a decrease in the reaction rate) has been typically observed between 600 and 800°C over different Pd catalysts, however it is not completely understood. The present work aims to comprehend this phenomenon on Pd/Ce$_{1-x}$Zr$_x$O$_2$ and Pd/LaFeO$_3$.
The catalyst Pd/Ce$_{1-x}$Zr$_x$O$_2$ exhibits much higher activity than Pd/LaFeO$_3$. Surprisingly, it maintained most of its activity even up to 750°C and while cooling down. In contrast, a known hysteresis was observed between 580 and 750°C on Pd/LaFeO$_3$, which was more pronounced while cooling down (a loss of 25% activity at 657°C) than heating up (ca. 5% activity loss). The contradictory behavior of Pd/Ce-ZrO$_2$ and Pd/LaFeO$_3$ was monitored by in situ XANES spectroscopy during the reaction. The results revealed that in the temperature range where the hysteresis was observed, a fraction of PdO was reduced in both the catalysts but to different extents indicating the importance of PdO in methane combustion (at least up to 730 °C).

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Optical Pump-Probe Spectroscopy Study of the Parameters Influencing Electron Injection Dynamics in DSSC

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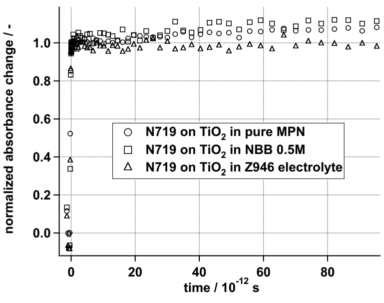
Sensitization of titanium dioxide with ruthenium dyes is at the basis of dye-sensitized solar cells (DSSC) with promising performances.
Light-induced charge separation involves, as the first step, the injection of an electron from the excited state of the sensitizer into the conduction band of the semi-conductor.



Electron injection dynamics heterogeneities have been reported with time components ranging from tens of fs to hundreds of ps, in particular for N719 (cis-Ru(II)(dcbpy)$_2$(NCS)$_2$) dye. The goal of this study is to approach the working conditions of a solar cell [1], with a direct measurement of the electron injection. Influence of a light bias, as well as the composition of the electrolyte are investigated on the ultrafast time-scale. Measurements on a real working cell have also been performed.

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Exciton splitting in the excited state of the jet-cooled 2-aminopyridine dimer

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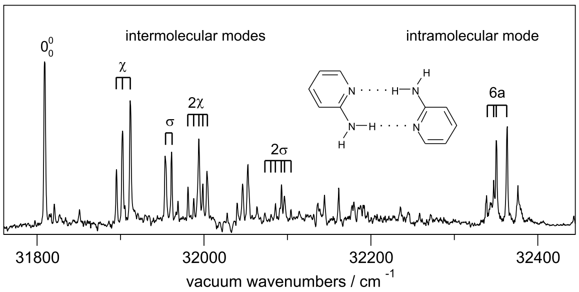
2-aminopyridine (2AP) is a hydrogen-bond mimic of the Watson-Crick binding site of adenine. Hence, 2AP and its selfdimer (2AP)$_2$ have been employed as models for doubly hydrogen bonded DNA base pairs in the gas phase [1]. We have investigated the S_1/S_2 excitonic splitting in (2AP)$_2$ and its ^{13}C- and d$_1$-isotopomers. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ vibronic band structure is analyzed based on the vibronic coupling model for a symmetric homodimer [2]. While these treatments focus on the exciton coupling to *intra*molecular modes, we find that the low-energy part of the UV spectrum is dominated by the coupling to two *inter*molecular vibrations.



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Spinel-based materials as NSR catalysts

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Reduction of NO_x from lean-burn engines (air-to-fuel ratio > 14.7) requires catalysts with NO_x storage and reduction capabilities. During lean-burn operation, the nitrogen oxides are stored and during a subsequent short pulse of a rich gas mixture reduced to nitrogen and carbon dioxide. The current Nitrogen Storage and Reduction (NSR) catalysts generally employ barium as a storage compound [1]. Barium however can react with several supports and even noble metals [2] forming ineffective storage compounds. Additionally, cost and poisonousness of the Ba-salts employed drive research into alternative storage concepts.

Recent research in our labs has showed that high surface area $Pt/MgAl_2O_4$ is an excellent candidate for Ba-free NSR catalysis. Tests revealed a comparable to better storage behavior compared to a standard Ba-containing catalyst, although the selectivity of the reduction step was lower (relatively more NH_3 formed). This contribution will demonstrate the steps taken to improve the selectivity of this novel catalytic system by doping the B-position of the spinel with transition metals such as Mn, Fe and Co.

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UV 3-pulse photon echo experiments on diphenylacetylene solution

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Photon Echo techniques have been extensively and successfully used in the visible and infrared region to study solvation dynamics. However, these techniques have been less developed in the UV region due to several obstacles such as typically very short homogeneous dephasing times (<50fs), strong solvent related non-resonant signal, scattered light, etc.; although there are much interests such as fluctuation dynamics in biological systems and non-polar solvation dynamics [1,2].

We recently developed a UV 3-pulse photon echo set-up in the range of 270-300 nm with a time resolution of about 50 fs, which allowed us to investigate the solvation dynamics in different molecular solutions. Here, we present the results of Photon Echo Peak Shift (PEPS) experiments on diphenylacetylene (DPA) solution in ethanol. DPA is reported to have longer dephasing times (in the order of a few hundred femtoseconds) compared to the typical values in the UV range [1,2]. After eliminating the strong non-resonant signal of the solvent at time-zero, we could detect for the first time a dynamics of $\tau \approx 50 \pm 10\, fs$ in the PEPS trace that should be related to solvation dynamics. In addition, we directly measured the homogeneous dephasing time of DPA solution to be about 500 fs in zero population time $(T_{23} = 0)$.

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Jet Spectroscopy of the Cytosine Analogue 5-Methyl-2-Pyrimidinone

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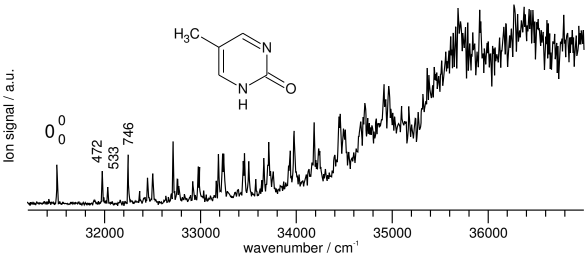
The fluorescent nucleic acid base analog 5-methyl-2-pyrimidinone (5M2P) has been calculated to have excited state decay pathways similar to cytosine [1]. There are no gas-phase spectra of 5M2P and the calculations [1] were compared to room-temperature solution data. We have measured two-color resonant two-photon ionization spectra of supersonically cooled 5M2P. The 0_0^0 band at 31'529 cm^{-1} is in good agreement with the vertical excitation energy calculated at the RI-CC2/aVDZ level. The low energy bands correspond to in-plane ring deformation vibrations. Extended progressions and combinations of these fundamentals extend to 3600 cm^{-1} above the 0_0^0 band. Broadening of the rotational band contours signals the onset of ultrafast excited-state nonradiative processes already at 1700 cm^{-1} vibrational excess energy.



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Intermolecular vibrations of 2-pyridone$\cdot(NH_3)_n$ (n=1,2) clusters in the S_1 state

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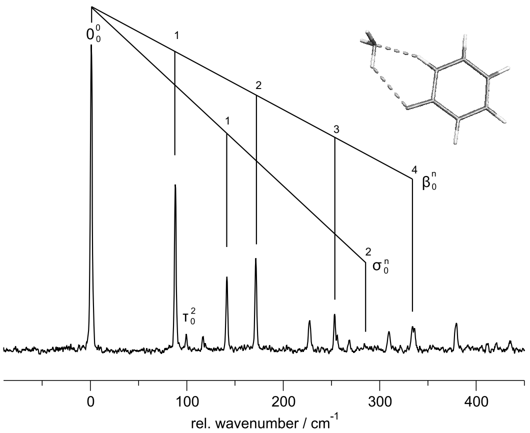
2-pyridone$\cdot(NH_3)_n$ (n=1,2) complexes have been studied experimentally by Nimlos et.al.[1] and Held et.al.[2]. We have reinvestigated the 2-pyridone$\cdot(NH_3)_n$ and d_1-2-pyridone$\cdot(ND_3)_n$ (n=1,2) complexes by resonant two photon ionisation spectroscopy and carried out detailed assignments of the vibronic bands. We identified two in-plane intermolecular vibrations (in-plane wag β and hydrogen-bond stretch σ) and the torsional excitation τ.



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Neutron and Light Scattering Study of the Adsorption of a Strong Polyelectrolyte onto Oppositely Charged Particles

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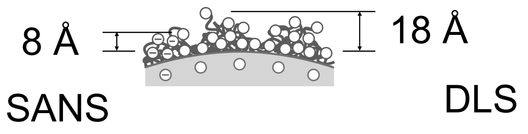
The structure of a cationic polyelectrolyte, poly (diallyldimethyl-ammonium) chloride (PDADMAC) adsorbed onto negatively charged colloidal latex particles was investigated by small-angle neutron scattering (SANS) and dynamic light scattering (DLS). SANS gives a layer thickness of 8 ± 1 Åand a polymer volume fraction of 0.31 ± 0.05 within the film. DLS gives a somewhat larger thickness of 18 ± 2 Å, and the discrepancy is most likely caused by to the inhomogeneity of the layer and the existence of polymer tails or loops protruding into solution. These results show that a highly charged polyelectrolyte adsorbs on an oppositely charged colloidal particle in a flat configuration due to the attractive forces acting between the polyelectrolyte and the substrate.



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Simultaneous Investigation of Gas and Surface Species during NO_x Storage-Reduction by *In Situ* Polarization-Modulation Infrared Reflection-Absorption Spectroscopy

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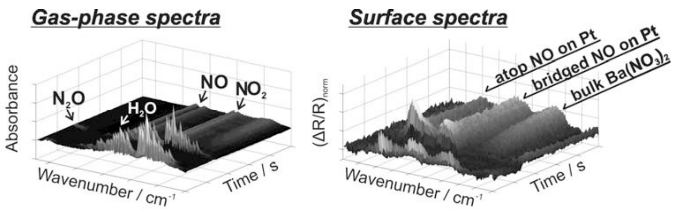
In situ polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS) was employed to investigate NO_x storage-reduction catalysis, which is one of the key technologies in the abatement of NO_x in automotive exhaust. As a model catalyst system, a BaO film with 20 nm thickness was deposited on a polished aluminium plate, followed by wetness-impregnation of Pt precursor. This model film catalyst proved to be well-suited for the simultaneous detection of gas-phase, surface species on Pt particles, and bulk Ba species. During rich (H_2)-lean (NO + O_2) cycles, PM-IRRA surface spectra showed three major absorption bands, which are assigned to atop and bridged NO on Pt surface and bulk $Ba(NO_3)_2$. Their anti-parallel evolution demonstrated that NO is oxidized to NO_2 on Pt particles, followed by the NO_2 storage reaction by its spillover to the Ba surface to form bulk $Ba(NO_3)_2$. Based on the temporal evolutions of the involved gaseous and surface species, detailed insight on reaction mechanisms could be gained.



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Ultrafast spectroscopic investigations of zwitterionic dyes: Interplay between torsional angle and excited-state properties

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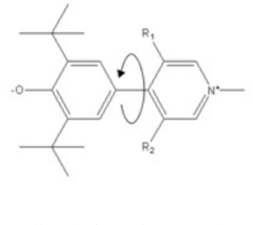
The excited-state dynamics of a series of pyridinium phenolates derivatives has been investigated using steady-state and femtosecond-resolved spectroscopies. These dyes are characterized by a very large dipole moment in the ground state. Optical excitation leads to a substantial decrease of the polarity of theses molecules. Therefore, relaxation to the ground state can be considered as intramolecular charge separation process.



In this series of dyes, the dihedral angle around the central bond has been increase by controlling the steric hindrance. A substantial influence of this torsion angle on the steady-state and dynamic properties has been measured. All these effects can be rationalized in terms of the coupling between the phenolate and pyridinium moieties.

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Optimisation of the strength of biopolymeric gels: Insights from the plant cell wall

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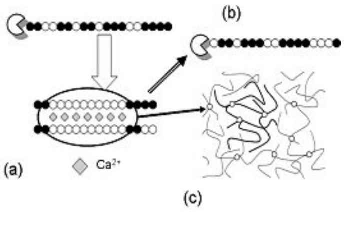
The polysaccharide pectin is found in the cell walls of all land plants where it has considerable mechanical utility, predominantly mediated by the amount and pattern of calcium-binding sugar residues occurring on a co-polymeric backbone. This backbone consists of galacturonic acid and its methylesterifed counterpart. The amount and pattern of the former, which is responsible for the calcium cross-linking of the chains, is controlled in-vivo by the action of an enzyme, pectinmethylesterase (PME).

The ionotropic gelling behaviour of pectin has been investigated with a light scattering technique, using different polymeric architectures that have been designed to be realistic bio-mimetic models of in-vivo structures. The work clearly suggests which polymeric fine structure maximises the strength of calcium-induced networks, and shows how Nature might be tailoring such architectures by using PMEs of optimised processivity or controlling the local calcium concentration. Further, it is interesting to see that studying the physics of resultant networks can yield conclusions regarding the action patterns of remodelling enzymes.



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Ionization energy of propene and investigation of the torsional motion of the propene cation by high-resolution PFI-ZEKE photoelectron spectroscopy

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Pulsed-field-ionization zero-kinetic-energy photoelectron spectra of the $\tilde{X} \rightarrow \tilde{X}^+$ transition in propene and propene-d_6 have been measured following single-photon excitation from the neutral ground state. The spectra reveal very anharmonic vibrational progressions associated with the low frequency methyl and CH_2 torsional modes ν_{21} and ν_{20}, respectively [1]. Using a narrowband vacuum ultraviolet laser system [2] and optimized electric field pulse sequences, we have been able to partially resolve the rotational structure of several vibrational bands with a spectral resolution between 0.15 cm^{-1} and 0.25 cm^{-1} depending on the pulse sequence. The ionization energy of propene and propene-d_6 have been determined to be 78600.96(10) cm^{-1} and 78759.93(15) cm^{-1}, respectively. The rotational structures have been analyzed using the orbital ionization model [3].

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Revealing the Functional Competition for Ligand Binding in Neuroglobin

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Neuroglobin (Ngb), a recently discovered heme-protein [1] of the globin family, shows an interesting feature earlier found in several plant hemoglobins and cytoglobin. In the absence of an exogeneous ligand at the sixth coordinating position of the heme iron, the distal His64 can bind in a competitive fashion with gaseous ligands, like CO, NO and O_2 to the heme iron. In this work we analyze the mechanism of His64 hexacoordination directly after dissociation of CO from the heme prosthetic group using Reactive Molecular Dynamics Simulations [2]. Computationally determined hexacoordination rates in wt Ngb, V109L, V109P and V109W Ngb revealed a reduced or even non-existent binding affinity for systems having larger sidechains at position 109. This is in good agreement with earlier [3] and ongoing experimental results. Furthermore, we investigate the process of heme-sliding taking place after a dissociation of the heme bound His64. The pentacoordinatedheme group moves ≈ 1 Å towards the proximal cavity within 160 ps. Heme-sliding was found to trigger several rearrangements within the close proximity of Ngb's active site which might be crucial for migration and subsequent binding of external ligands like CO.

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Efficient preparation of vibrationally excited methane by rapid adiabatic passage for the study of steric effects in methane chemisorption

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Quantum state resolved reaction cross section measurements are central to the study of chemical reaction dynamics for bimolecular reactions in the gas phase and more recently also for gas/surface reactions. In the past, our group has focused on experiments using pulsed laser excitation because suitable tuneable cw-infrared laser sources with sufficient power were not commercially available.

This situation has changed dramatically with the development of a cw-IR-OPO system using periodically poled lithium niobate, which led to a commercially available, widely tuneable, single mode infrared source with an output power >1 Watt. We have added this new light source to our state-resolved surface reaction dynamics experiment and will describe our new setup, including frequency locking of the infrared source to a Lamb Dip. Using rapid adiabatic passage of a molecular beam through an appropriately focused excitation laser beam, we are able to excite essentially 100% of the reagent molecules from a given ground state to a single quantum state.

The availability of intense, quantum state prepared molecular beams opens many interesting possibilities for studies of gas/surface reaction dynamics. We are exploring the incident angle dependence and surface temperature dependence of methane's state resolved reactivity on a Ni(100) surface. Furthermore, we can use the excitation via linearly polarized light to control the spatial alignment of the reagents' angular momentum vector and vibrational transition dipole moment in the laboratory frame for the first studies of steric effects in gas-surface reactions with quantum state resolution. First results from these studies for CH_4 and CD_3H on Ni(100) will be presented.

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Stimuli-Responsive Dendrimer Surface Nanopatterns

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Since their synthesis in the late 1970s, dendrimers have been the subject of intensive investigations. They consist of a core to which repeat units are sequentially added to form hyperbranched and topologically regular macromolecules. One of the most interesting possible applications is to use them as molecular cage in host-guest complexes. For these reasons, significant effort has been dedicated to experimentally characterize the changes in volume of these macromolecules in solution[1-2]. In particular, small angle neutron scattering experiments showed that poly(amido amine) (PAMAM) dendrimers do not change shape in solution as the pH and the ionic strength are varied [2]. However, no information is available about conformational changes of dendrimers adsorbed on a charged surface.

In this work, we studied the effect of pH and ionic strength on the conformation of poly(amido amine) (PAMAM) G10 dendrimers adsorbed on silica surfaces.

Dendrimers were pre-adsorbed on silica at pH 4 and subsequently exposed to solutions having different pH and ionic strengths values. The changes in shape of adsorbed dendrimers were directly measured via atomic force microscopy and indirectly observed by combining quartz crystal microbalance and reflectometry techniques.

Our results show for the first time that adsorbed G10 dendrimers shrink and swell as the surface charge is increased and decreased respectively. Thus, by weakening the strength of the attractive interactions, via the addition of salt, swelling is promoted.

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Millimetre wave spectroscopy of high Rydberg states of xenon: Stark effect and hyperfine structure

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In the range 0–45 cm^{-1} below the ionisation limit, the separation between adjacent electronic states (Rydberg states with principal quantum number $n > 50$) of atoms and molecules is smaller than 2 cm^{-1}. In order to resolve the fine or hyperfine structure of these states, it is necessary to combine high-resolution vacuum ultraviolet (VUV) laser radiation, which is required to access the Rydberg states from the ground state, with millimetre wave radiation [1].

Millimetre wave transitions (240–350 GHz) between $n\ell$ ($52 \leq n \leq 64, \ell \leq 3$) Rydberg states of different xenon isotopes were detected by pulsed field ionisation followed by mass-selective detection of the cations. Because of the high polarisability of high-n Rydberg states ($\propto n^7$, $\sim 10^4$ MHz cm^2 V^{-2} for $n \approx 50$), it is necessary to reduce the electric stray fields to values of the order of 1 mV/cm (or less) to minimise the (quadratic) Stark shift of the millimetre wave transitions. Several p and d Rydberg states of Xe are nearly degenerate and efficiently mixed by small stray fields, making it possible to observe transitions forbidden by the $\Delta\ell = \pm 1$ selection rule and transitions exhibiting the linear Stark effect characteristic of degenerate high-ℓ Rydberg states.

Multichannel quantum defect theory (MQDT) [2] was used to analyse the millimetre wave data and to determine the hyperfine structure of the $^2P_{3/2}$ ground electronic state of ^{129}Xe$^+$ and ^{131}Xe$^+$.

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High-resolution spectroscopy of np Rydberg states of He$_2$

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A supersonic beam of metastable He$_2^*$ a $^3\Sigma_u^+$ molecules was generated using a pulsed discharge at the exit of a pulsed valve prior to the gas expansion into vacuum. Transitions to high np Rydberg states were recorded using photoionization and Rydberg-state-resolved threshold ionization spectroscopy. Overview scans at moderate resolution (0.3 cm^{-1}) were obtained with ionization fields ranging from 1.3 to 133 V/cm, lowering the ionization thresholds by 5.5 and 55 cm^{-1}, respectively. Using a solid-state UV laser system with a 20 MHz bandwidth, high-resolution spectra of Rydberg series with n up to 150 and with resolved fine structure of the initial He$_2^*$ a $^3\Sigma_u^+$ (N'') state were recorded. The threshold ionization spectra of He$_2$ (a $^3\Sigma_u^+$) reveal a dense structure of very sharp features that can be attributed to transitions to Rydberg states converging on the first ($N^+ = 1-7$) rotational levels of the X$^+$ $^2\Sigma_u^+$ ($v^+ = 0$) ground ionic state. Many of these states associated with rotationally excited levels of the ion core (rotational quantum number N^+) are embedded in the ionization continua associated with the $N^+ - 2$ and $N^+ - 4$ ionization channels. The rotational autoionization dynamics is complex and is strongly influenced by the application of weak electric fields. Several series are immune to ionization and the corresponding states are metastable. The extrapolation of the observed Rydberg series to their limits enabled the determination of the ionization energy of the a $^3\Sigma_u^+$ state and the rotational structure of the He$_2^+$ ion with a precision of better than 20 MHz. The energy level structure and the rotational autoionization dynamics have been analyzed by multichannel quantum defect theory (MQDT). An interpretation of the effects of the electric fields on the autoionization dynamics is proposed.

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Spin cross-over in Fe(II)-based molecular complexes studied by visible-pump/UV-probe femtosecond transient absorption

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Fe(II) molecular complexes have been intensively studied due to the spin cross-over (SCO) phenomenon, among others, because of potential applications in magnetic data storage devices. In the aqueous [Fe^{II}(bpy)$_3$]$^{2+}$, light excitation from the singlet low spin (LS) ground state to the singlet metal-to-ligand-charge-transfer states (^{1}MLCT) leads to population of the lowest high spin (HS) excited quintet $^5T_2$ state by non-radiative relaxation with unitary quantum yield.[2] The details of the intermediate steps going from the ^{1}MLCT state to the $^5T_2$ state were not clearly resolved, with a debate between different possible photocycles.[2] In previous studies we have shown that the ^{1}MLCT state relaxes in ~30 fs to the ^{3}MLCT manifold, which then decays in ~130 fs.[3] However the lack of spectroscopic observables in the spectral region > 350 nm did not allow the observation of the relaxation pathway to the $^5T_2$ state. Furthermore, the issue of vibrational energy storage and relaxation in the quintet state was still unsolved. To this purpose we have developed a visible pump/broadband UV-probe setup to directly follow the rise, cooling and decay of the population in the quintet state, confirming a direct passage from the ^{3}MLCT to the $^5T_2$ state,[4] and showing that it leads to vibrational wave packet dynamics in the HS state. We also determined the time scales of the vibrational relaxation providing the final elements to describe the full photocycle of aqueous [Fe^{II}(bpy)$_3$]$^{2+}$.

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Femtosecond UV spectroscopic studies of cytochrome c dynamics

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Analysis of time resolved fluorescence allows investigation of solvation relaxation, cooling processes and Förster energy transfer in biological macromolecules. In this respect, we want to probe the local dynamics of wild-type hemoproteins at very short times, by means of ultrafast broad-band emission detection of optically active amino acids, as tryptophan (Trp), or prosthetic group, as the heme. Cytochrome c, a hemoprotein involved in electron transfer process and apoptosis, undergoes geminate recombination of the methionine (Met80) side chain after photodissociation from the reduced heme iron [1, 2]. Thanks to this simple photocycle, Cyt c is an excellent molecular system to carry out an extensive study with our recently implemented UV-fluorescence up-conversion [3] and transient absorption set-ups, exciting at 285 nm and probing at 250-380 nm, where the Trp neighboring the heme absorbs and emits. Indeed, we are interested in the ultrafast photodynamics of this Trp in a view to use it as a probe for the earlier times heme local dynamics, after a pre-pulse photolysis of Met80. The influence of the oxidation state on the primary photoprocesses has been investigated and we will present results of the ultrafast photodynamics of oxidized and reduced form of Cytochrome c. The ultrafast Trp fluorescence decay due to Förster energy transfer to the porphyrin ring was found to be slowed down in the oxidized form (500 fs) compared to the reduced form (400 fs).

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Exploring hydrogen bonding interactions in proteins by MD simulations with MMPT potential

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A computational procedure to carry out molecular dynamics (MD) simulations with explicit hydrogen bonding potentials (MMPT potentials) has been established, which allows better prediction of scalar couplings across hydrogen bonds [1] in a set of six proteins than customary molecular mechanics force fields [2]. The orientation-dependent potentials are based on a zeroth-order *ab initio* PES of $H_3N–H^+ \cdots OH_2$ and morphed to describe hydrogen bonding patterns in proteins [3]. In general "morphing" depends on the chemical environment of hydrogen bonding motif $D–H \cdots A$ and is achieved by adjusting parameters in the PES. A set of suitable morphing parameters will not only lead to closer agreement between calculated and measured couplings but also reveal geometrical and dynamical features of certain hydrogen bonding interactions.

From MD trajectories where a unified MMPT potential was used, we find out the best morphing parameters are those that make D–A distance equals average N–O distance in the x-ray structure and H–A distance equals 1.933Å. The later value is reminiscent of the hydrogen bond geometry parameter δ_{HA} calculated from a statistical analysis of 52 proteins [4]. MMPT/MD simulations with hydrogen bonds in different secondary structures morphed separately have also been carried out and analyzed, which will help us understand their difference in geometry and strength.

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Nanostructured and nanoscopic p-type oxides for photoelectrochemical water splitting

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Direct photolysis of water on a semiconductor surface is an appealing route to get hydrogen without using any other energy supply than sunlight. P-type ternary oxides with delafossite crystal structure are promising candidates for photocathode application. $CuAlO_2$, $CuCrO_2$, $CuFeO_2$ have an optimal value of band gap, conduction band edge position, conductivity and stability in an aqueous environment. The metastability of these compounds at room temperature as well as the need to have nanoscaled materials imply synthetic challenges to get a high surface-to-volume ratio, which is required both to increase the surface for H_2 evolution and to shorten the distance the photogenerated electrons have to travel to reach the electrolyte, thus diminishing recombination losses. Different synthetic approaches have been attempted and are presented here. Among them, coprecipitation from inorganic salts and sol-gel route have fulfilled the requirement of high surface area, whereas hydrothermal reaction employing the FEP Teflon pouch technique[1] needs to be combined with the use of a carbon template in order to limit the crystal growth. The next challenge lies now in transferring the nanoscaled powders on a suitable substrate to make a photocathode for hydrogen evolution in a photoelectrochemical cell.

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Nanostructured Hematite Photoanodes For Solar Hydrogen Production

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Dihydrogen is often seen as a very promising energy vector in a carbon-neutral market. Photoinduced water splitting is certainly the most natural and sustainable dihydrogen production method. Indeed it uses only light from the Sun as the energy input, our sole truly renewable and infinite energy source.

To achieve low-cost water splitting, iron oxide (α-Fe_2O_3, or hematite) is especially attractive as a photoanode[1]. It has a very favorable band gap of 2.0 – 2.2 eV, is very stable, and its abundance makes it a very inexpensive material. However solar-to-hydrogen production with hematite has been limited in efficiency by poor light absorption and a small hole diffusion length. These drawbacks can be overcome by nanostructuring a thin film photoanode, e.g. using a high surface area host to support a thin layer of hematite in a "Host-Guest" configuration. Thus photogenerated holes will be likely produced in high proximity to the semiconductor-liquid junction, and electrons can flow through a high conductive material to the cathode, evolving H_2. The interface between the iron oxide and the electron conducting substrate is of great importance to minimize losses in such system.

After discussing the electronic phenomena involved, the presentation will detail the state-of-the-art for photoanodes, and especially the APCVD deposited hematite thin films[3]. Then the new "Host-Guest" concept[3], which should improve the photoelectrochemical performance of hematite, will be introduced and recent results on hematite/SnO_2 interface modification will be shown.

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Adsorption-Desorption Induced Structural Changes of Cu-MOF Evidenced by Solid-state NMR and EPR Spectroscopy

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MOFs as catalysts possess properties of both homogeneous and heterogeneous catalysts.[1] Our work presents that adsorption-desorption induced structural changes of the Cu-MOF $[Cu(bpy)(H_2O)_2(BF_4)_2(bpy)]$ have been evidenced by combined MAS NMR and CW EPR spectroscopy.[2] Upon adsorption of CH_3CN even at a few mbar, EPR spectra show that they are activated to form complexes at Cu(II) sites, which results in a change of the Cu-MOF's structure as indicated by a high-field shift of the ^{11}B MAS NMR. After desorption, both EPR and ^{11}B MAS NMR spectra evidenced that the structure of the Cu-MOF reversibly shifted to the original state. This observation indicates that MOFs can undergo structural changes during adsorption-desorption are involved such as gas storage, separation, and catalysis.

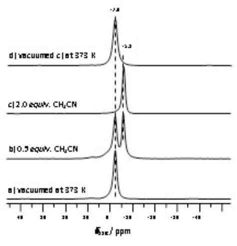

Fig. 1 ^{11}B MAS NMR spectra of Cu-MOF vacuumed at 373 K (a), loading 0.5 equiv. CH_3CN (b), and 2.0 equiv. CH_3CN(c), and vacuumed c (d).

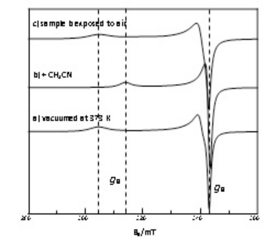

Fig. 2 CW EPR spectra of the Cu-MOF vacuumed at 373 K (a), after loading 2.0 *equiv.* CH_3CN (c), and sample b exposed to air (d).

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UV absorption spectroscopy of 2-pyridone·benzene

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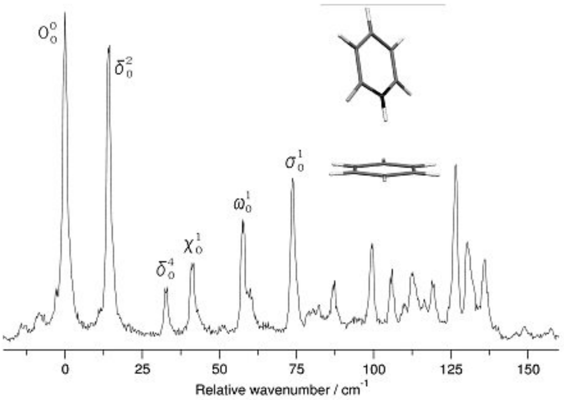
Among the weak intermolecular interactions found in proteins, the amide N-H $\cdots\pi$ interaction has been widely observed but remains poorly characterized. Previously, we have experimentally and theoretically studied the S_0 state of the complex of the nucleobase analogue and cis-amide 2-pyridone (2PY) with benzene [1]. We have now investigated the S_1 state of supersonically cooled 2PY·benzene using two-color resonant two-photon ionization (2C-R2PI) spectroscopy and ab initio calculations. The SCS-CC2 S_1 state geometry is a slanted T-shaped structure, similar to the S_0 state. The 2C-R2PI spectrum shows excitations in the tilting (δ), shearing (χ), opening (ω) and stretching (σ) intermolecular vibrations.



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Surface Design in Solid-State Dye Sensitized Solar Cells: Effects of Zwitterionic Co-adsorbents on Photovoltaic Performance

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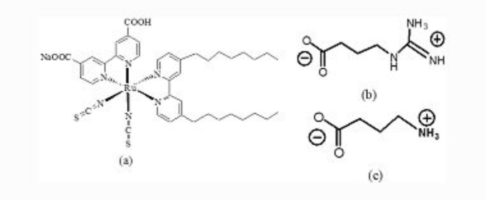
In solid-state dye sensitized solar cells (SSDSCs) charge recombination at the dye-hole transporting material interface plays a critical role in the cell efficiency. For the first time we report on the influence of dipolar co-adsorbents on the photovoltaic performance of sensitized hetero-junction solar cells. In the present study, we investigated the effect of two zwitterionic butyric acid derivatives differing only in the polar moiety attached to their common 4 carbon-chain acid, i.e., 4-guanidinobutyric acid (GBA) and 4-aminobutyric acid (ABA). These two molecules were implemented as co-adsorbents in conjunction with Z907Na dye on the SSDSC. It was found that a Z907Na/GBA dye/co-adsorbent combination increases both the open circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) as compared to using Z907Na dye alone. The Z907Na/ABA dye/co-adsorbent combination increases the J_{sc}. Impedance and transient photovoltage investigations elucidate the cause of these remarkable observations.



(a) Z907 dye (b) GBA (c) ABA

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Electron capture dissociation for peptide structure analysis: role of amino acid properties and ion internal energy

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Quantitative description of product ion abundances (PIA) in electron capture dissociation (ECD) and activated ion (AI) ECD based tandem mass spectrometry of peptides and proteins is a possible route toward development of a predictive model for ECD tandem mass spectrometry with possible applications in proteomics. Here, influence of amino acid properties as well as internal peptide energy in the gas phase is under investigation for model synthetic peptides H-Arg-$(Ala)_4$-Xxx-$(Ala)_4$-Lys-OH and H-Arg-$(Gly)_4$-Xxx-$(Gly)_4$-Lys-OH. ECD and AI-ECD experiments performed on 12 T and 7 T LTQ FT-ICR MS with ion activation by IR laser.

Our recent study on ECD PIA of poly-Ala peptide series revealed 3 groups of amino acids distinguished by their properties to form hydrogen bonds, attract proton and participate in radical migration. We will further demonstrate that ECD PIA scale for poly-Ala correlates well with ECD PIA scale for poly-Gly build backbone for all amino acids. The dependencies of PIA on peptide ion internal energy in AI-ECD show competition between *c* and *b* fragment ion formation. Observed dependencies will be rationalized in terms of amino acid property influence on ECD PIA versus conformation effect. A kinetic ECD model consisting of two independent steps (a reorganization to match the appropriate conformations followed by either the dissociation or relaxation into other conformations) will be employed to qualitatively explain ECD PIA ion internal energy dependence. Implications for practical utility of these data in peptide and protein sequencing as well as related fundamental advances of gas phase radical ion chemistry will be outlined.

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Radical ion chemistry of β peptides

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Understanding peptide and protein structural changes induced by incorporation of β-amino acids is of a primary interest in beta-peptide based drug discovery. Recently developed electron induced tandem mass spectrometry applied to β-peptides may not only provide structural information but also could advance the current understanding of radical ion chemistry in the related ion-electron interactions. Here, we apply, for the first time, electron capture dissociation (ECD) and electron transfer dissociation (ETD) for characterization of β-peptides in the gas phase.

Beta-peptide variants of model alpha-peptides as well as β-turn mimicking peptides were synthesized at EPFL, UNIL and Paris VI University, France. ECD was performed on a 7T Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer, whereas ETD was realized on a Paul ion trap MS. Vibrationally induced fragmentation techniques were employed to validate peptide sequences and provide complementary MS/MS data.

Preliminary data reveals first characteristic features of ECD/ETD of β-peptides as compared to similar alpha-peptides: shift of the average product ion mass to upper m/z values, change in the charge neutralization site, and substantial decrease of backbone bonds rupture efficiency within beta amino acids. Presumably radical properties of beta-Phe residue are manifested through efficient fragmentation of its N-Ca bond, not observed for non-aromatic amino acids. Presence of C=O group in beta amino acid residues may be necessary for corresponding amino acid cleavage and thus may be responsible for success of ECD/ETD implementation in peptide and protein deamidation studies. Further investigation of amino acid side chain properties and peptide conformational flexibility dependence in beta peptides are currently being performed in a systematic approach.

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Passivation of Nanocrystalline TiO_2 Junctions by Surface Adsorbed Phosphinate Amphiphiles Enhances the Photovoltaic Performance of Dye Sensitized Solar Cells

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We report a new class of molecular insulators that electronically passivate the surface of nanocrystalline titania films for high performance dye sensitized solar cells (DSC). [1] Using electrical impedance measurements [2] [3] we demonstrate that co-adsorption of dineohexyl bis-(3,3-dimethyl-butyl)-phosphinic acid (DINHOP, Figure 1), along with the amphiphilic ruthenium sensitizer Z907Na increased substantially the power output of the cells mainly due to a retardation of interfacial recombination of photo-generated charge carriers. The use of phosphinates as anchoring group opens up new avenues for modification of the surface by molecular insulators, sensitizers and other electro-active molecules to realize the desired optoelectronic performance of devices based on oxide junctions.

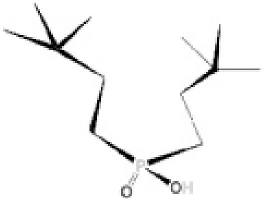

Figure 1 Molecular structure of dineohexyl phosphinic acid (DINHOP).

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Ar(np', $J = 0, 1, 2$) autoionization dynamics probed by photoionization spectroscopy and velocity map imaging

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Two-step excitation experiments using a high-resolution XUV laser system [1] were carried out to measure spectra of even np' autoionizing Rydberg states (ARS) of argon. The three excited levels Ar(4s'$[1/2]_1$, 3d$[1/2]_1$, 5s$[3/2]_1$) were prepared from the Ar ground state by a pulsed XUV laser source (bandwidth 12 GHz) and further excited by Fourier-transform limited laser radiation (bandwidth 100 MHz). The second laser was continuously tuned to record the Ar(np', nf') autoionization spectra of interest. The linear polarization vectors of both light beams were chosen to be either parallel or perpendicular to each other resulting in very different spectral intensity distributions and photoelectron angular distributions.

The experimental results will be discussed in the context of multi-channel quantum defect theory (MQDT) and configuration interaction Pauli-Fock including core polarization (CIPF CP) calculations [2,3].

Support by the Swiss National Science Foundation and by the Deutsche Forschungsgemeinschaft (Ho427/30) is gratefully acknowledged.

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Ultrafast Dynamics of Hemin in Water vs. Ethanol probed by Time Resolved Absorption Spectroscopy

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Porphyrins are basic constituents of many molecular devices, due to their remarkable photophysical, photochemical and electrochemical properties. Hemin is used for the detection of (toxic and reactive) ligand vapors because of its open coordination sites for axial ligation and the large spectral shifts and the intense colour change it undergoes upon ligand binding. Studying the mechanism of ligation can be done by pump-probe techniques, where a first pulse photodissociates the ligand from the porphyrin, and a second continuum pulse probes the evolution of the system, as a function of pump- probe time delay. In this work we investigate the relaxation dynamics of the detached ligand from chloro-hemin complex, where Cl atom is a coaxial ligand on one side, and the other side is complexed with a solvent molecule. Femtosecond time-resolved absorption studies of this complex were investigated in water and in ethanol using pump- probe techniques exciting its Soret band, at 400 nm and probing in the 320 – 700 nm range.

The results showed different kinetics for hemin in the investigated solvents. At low fluence, three decay times of ~ 500 fs, 5 ps and 1ns were observed for hemin in water while in ethanol no presence of the ns component was shown. We propose the following model to describe the results. Upon 400 nm excitation, electron from a π^* orbital of porphyrin macrocycle is transferred to the metal ion. This process is followed by a charge back transfer from a low lying d metal orbital to an empty orbital of the macrocycle within 500 fs which leads to an excited state (*d,d**) localized on the metal. The relaxation of these states seems to depend on the solvent. In ethanol, the system relaxes to the GS within 5 ps while in water, the relaxation process was found to be biexponential. This could be explained by a detachment of the Cl ligand from the hemin after charge back transfer due to the strong interaction between the Fe and the water molecule which weaken the Fe-Cl bond. Experiments at high pump fluence on hemin in ethanol showed the same behavior as the hemin in water at low fluence. This supports our proposed model about photodissociation of the Cl ligand.

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Fs-Rotational Raman Four-Wave Mixing of CO_2 in a Pulsed Molecular Beam

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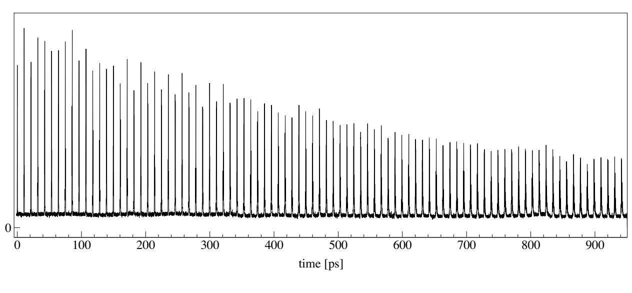
Gas phase femtosecond time-resolved rotational Raman four-wave mixing (fs-RRFWM) is a method that yields highly accurate molecular rotational and centrifugal distortion constants [1], from which structural information can be derived. In a gas cell, signal intensity decreases in time due to J- and M_J-changing intermolecular collisions [2]. The figure below shows a ∼1 ns long transient of CO_2 in a gas cell at 12 mbar and 293 K.



To avoid collisional decoherence effects, we introduced a 330 Hz repetition rate pulsed molecular beam, which yields a beam at ∼100 K rotational temperature. Both signal and temperature remain constant over time delays up to 6 ns.

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Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer

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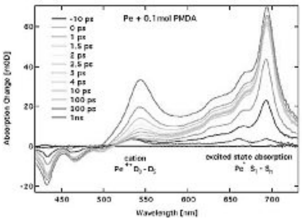
Recently, we showed that ultrafast mid-infrared spectroscopy permits to directly observe tight and loose ion pairs (TIPs and LIPs) as primary reaction products of photo-induced bimolecular electron transfer, providing insight into structure and dynamics of these ion pairs [1]. Improving the photometric resolution allowed us since then to identify spectral signatures of TIPs and LIPs also in the visible spectral domain for several different donor-acceptor (DA) pairs.



As overall features we observe two distinct spectral signatures of TIPs at short time delays < 10ps and LIPs at longer time delays > 50ps, respectively, resembling closely what we obtained in the IR spectral domain with the DA pair methylperylene-tetracyanoethene (MePe-TCNE). These findings indicate that obtaining TIPs and LIPs as primary reaction products is indeed a more general feature to be observed with highly exergonic electron transfer reactions.

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