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Physical Chemistry **345**

Ultrafast Time-Resolved Infrared Studies on Photoinduced Bimolecular Electron Transfer

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Although photoinduced bimolecular electron transfer (ET) has been studied over several decades, the question of the nature of the direct reaction product remains still open. Transient absorption and time-resolved Raman measurements have shown that the electronic absorption spectra and the high frequency vibrational modes of the transient species do not change upon separation of a contact ion pair into free ions [1]. A major difficulty in these studies is the overlap of different spectral contributions in the visible domain. To overcome this limitation we employed perylene (Pe) as donor and 1,4-dicyanobenzene (DCB) as acceptor in acetonitrile and recorded the band shape of the asymmetric CN strech vibration of DCB$_-$ as a function of delay time after phototriggering ET,
i.e. as a function of the "age" of the ion pair, using ultrafast infrared transient absorption. The observed band narrowing on a time-scale of 200-400ps permits for the first time a direct spectral insight into the separation process of an ion pair into free ions. Further support comes from a novel pump-pump-probe experiment [2] which shows that the relaxation dynamics of the excited radical DCB anion generated by ET undergoes a significant change on the same time scale. With tetracyanoethylene as acceptor, large spectral broadenings of Pe vibrational modes within the first picoseconds after ET show that an important part of the released free energy in highly exergonic ET is dumped into intramolecular vibrational modes, opposed to solvent reorganisation as has been supposed by applying classical Marcus theory.

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Physical Chemistry **346**

Fast Redistribution of Vibrational Energy in Methyl Iodides

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Intramolecular vibrational redistribution of energy (IVR) within a molecule is essential for understanding intramolecular dynamics [1]. Mode selective chemistry might be expected, if the time scale for IVR is comparable to or slower than the time scale for unimolecular reaction. The IVR process can be studied directly in femtosecond pump-probe experiments. Alternatively the time evolution of the vibrational wavefunction can be obtained from high-resolution IR-spectra. Both methods have been applied successfully in our research group to different classes of molecules [1-3]. In our contribution we present femtosecond pump-probe experiments (near-IR pump, UV-absorption probe) on the intramolecular redistribution of vibrational energy in the gas phase after near-IR overtone excitation in different methyl iodides (^{12}CH$_3$I, ^{13}CH$_3$I, CH$_2$DI, and CHD$_2$I). For ^{12}CH$_3$I two significantly different processes with relaxation times of $\tau_1 = 0.3$ ps , $\tau_2 = 6$ ps and $\tau_3 = 400$ ps have been measured [3,4]. The ultra-fast relaxation process with τ_1 is only detected for a near-IR excitation around 5900 cm^{-1}, whereas the IVR process for an excitation around 6100 cm^{-1} shows exclusively the slow relaxation process with τ_3. A similar behavior is found for ^{13}CH$_3$I. No ultra-fast relaxation process was measured within our detection limits for CH$_2$DI and CHD$_2$I. The strong frequency dependence of the IVR process is explained by means of different couplings of the initially excited vibrational levels to the remaining levels, especially to the CI-stretching states.

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Physical Chemistry **347**

Direct Spectroscopic Measurement of Water Dissociation Energy

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We have performed a direct measurement of one of the most fundamental thermochemical values—the O-H bond energy of water. Using a triple-resonance laser excitation scheme, we excite the molecule through a series of rotationally-resolved vibrational overtone transitions to access directly the onset of the dissociative continuum. The value of D_0= 41145.94±0.15 cm^{-1} determined from our experiments is orders of magnitude more accurate than all previously reported and accepted results and has important implications for other thermochemical quantities linked to the bond energy of water.

Physical Chemistry **348**

The Jahn-Teller effect in CH_4^+ characterized by high-resolution photoelectron spectroscopy

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The methane cation is one of the simplest molecules possessing a triply degenerate electronic ground state that is subject to a strong Jahn-Teller effect. The rotationally resolved pulsed-field ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectrum of methane was first reported in 1999 [1] but an assignment of the rotational structure has not been possible so far because of the complex large-amplitude tunneling motion. Combining sources of infrared (IR) and vacuum-ultraviolet (VUV) radiation in two complementary double-resonance experiments has enabled us to assign nuclear spin-symmetries and rotational quantum numbers for the lowest rovibronic levels of CH_4^+. Narrow-band infrared radiation at 3.3 μm was generated by difference-frequency-mixing and used to excite selected rovibrational transitions of the antisymmetric stretch vibration of the neutral molecule. In the first experiment a selected IR transition was saturated and the depletion of PFI-ZEKE photoelectron signal was monitored. In the second experiment photoelectron spectra were recorded from single rotational levels prepared by IR excitation.
These results provide a complete energy level diagram of the ground vibronic state of the methane cation including rovibronic symmetries and an ionization energy of $IE/hc = 101753 \pm 1$ cm^{-1}.
A new theoretical analysis of the Jahn-Teller effect in CH_4^+ has been performed which predicts the symmetries and energetics of the vibronic states resulting from large-amplitude pseudorotational dynamics. The ground vibronic state is described as a tunneling doublet with a splitting on the order of the rotational constant. Its rotational structure is described in terms of a simple rotation-tunneling Hamiltonian developped for this purpose. These predictions will be presented and compared to the experimental results.

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Physical Chemistry **349**

Towards a Molecular Movie: Real Time Observation of Hydrogen Bond Breaking by Transient 2D-IR Spectroscopy in a Cyclic Peptide

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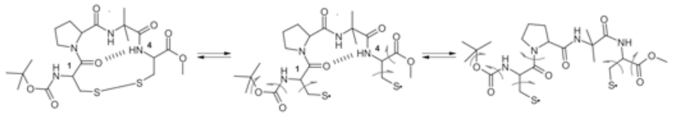
We used transient 2D-IR spectroscopy (T2D)[1] to investigate the opening of a β-turn in a small cyclic peptide[2]. The β-turn is stabilized by an intramolecular hydrogen bond and clasped by a disulfide bridge, providing a predetermined "breaking point", which can be cleaved by UV light generating *non-equilibrium* conditions[3]. In the 2D-IR spectra we observed a set of crosspeaks that arises from coupling of the nearest neighbors and a crosspeak influenced by the intramolecular hydrogen bond. Extending our investigations to the *non-equilibrium* we observed bleaching of a transient crosspeak in the T2D-spectra, indicating that the β-turn is falling apart. The time of disappearance of the crosspeak is in perfect agreement with the times scales extracted from the pump-probe experiments and MD-simulations.



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Physical Chemistry **350**

Radical Ions of N-Nitrosoamines and Their Fragmentation

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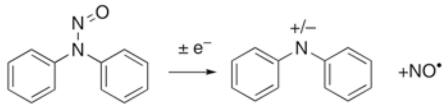
This talk will focus on an investigation where matrix isolation complements pulse radiation studies in solution to investigate radical ions of N-nitroso compounds and their fragmentations, in view of the generation and investigation of nitrenium cations and anions.



On X-irradiation of N-nitrosodiphenylamine in the presence of an electron scavenger, a procedure that usually gives rise to radical *cations*, we observed, however, several spectroscopic features that could not be assigned to the targeted species or its possible fragmementation products.

Eventually we discovered that, even in the presence of electron scavengers, we obtained substantial quantities of the *radical anions* of these species in Ar matrices. There are several reports in the literature, in particular from the group of Kasai,[1] on matrix isolation studies of radical anions by the very sensitive ESR technique, but we found only a single previous report on attempts to record UV/Vis spectra of radical anions in Ar matrices.[2]

We have extended these investigations to other species with positive electron affinities and found that radical anions generated in Ar matrices can often be selectively bleached, which allows to record their full IR spectra for the first time.

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Physical Chemistry **351**

The highly resolved FTIR spectrum of pyrimidine: Analysis of the B_1 modes ν_{10b} and ν_4 and B_2 mode ν_{6b}

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Recently developed techniques in high resolution Fourier transform infrared (FTIR) spectroscopy [1] now make it possible to record and analyse rotationally resolved spectra of relatively heavy molecules containing numerous vibrational modes. We have started to measure and analyse systematically the FTIR spectra of aromatic (fluoro- and chlorobenzene [2], phenol and benzaldehyde) and heterocyclic molecules (pyridine [3] and pyrimidine) in the region 600-1300 cm^{-1}. Here we present new results for the molecule pyrimidine ($C_4H_4{}^{14}N_2$) which has important implications for biopolymers such as DNA. We have recorded the spectrum of pyrimidine ($C_4H_4{}^{14}N_2$) in the region 600-1300 cm^{-1} with our Zürich Bruker 2001 prototype Fourier transform infrared spectrometer with an instrumental resolution of 0.0008 cm^{-1}, essentially Doppler limited, with Doppler widths ranging from 0.0008 to 0.0015 cm^{-1}. The analysis of the bands located at $\tilde{\nu}_c = 714.54106\ \mathrm{cm}^{-1}$ (ν_4) and $\tilde{\nu}_c = 803.97947\ \mathrm{cm}^{-1}$ (ν_{10b}) will be discussed. In addition, the ν_{6b} band rotationally assigned by Kisiel et al. [4] was analysed ($\tilde{\nu}_c = 620.54976\ \mathrm{cm}^{-1}$). Based on our FTIR analysis a search for extraterrestial pyrimidine will be discussed in the context of a probable successful detection of interstellar pyridine [5] in the infrared region.

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Physical Chemistry **352**

Rovibrational Analysis of the High Resolution Infrared Spectrum of $CH^{35}ClF_2$ involving the Vibrational Levels ν_4, $2\nu_6$, $\nu_6 + \nu_9$ and $2\nu_6$: Experiment and Theory

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$CHClF_2$ is of considerable interest as a trace gas in the earth's atmosphere and in this context we have recently studied in much detail the "atmospheric window" bands ν_3 and ν_8 around 1100 cm^{-1} (see [1] and refs. cited therein). The molecule has also been successfully used in infrared laser chemistry in view of ^{13}C laser isotope separation (e.g. [2]) and it is also an important prototype molecule for the study of intramolecular rovibrational redistribution processes (e.g. [3]).

The present investigation [4] aims at completing our knowledge of the rovibrational parameters of the fundamental bands of $CHClF_2$. High resolution FTIR spectra of the $\nu_4/2\nu_6$ band system in the region 750-850 cm^{-1} were measured for $CH^{35}ClF_2$ and $CH^{37}ClF_2$ with our Bruker IFS 125 HR Zurich prototype (ZP2001) spectrometer (instrumental resolution <0.001 cm^{-1} (FWHM)). The spectra were analysed by means of a polyad Hamiltonian built up from the $\nu_4/2\nu_6$ Fermi dyad and the $2\nu_6$, $\nu_6 + \nu_9$, $2\nu_9$ Coriolis triad which share the level $2\nu_6$. We also report *ab initio* calculations for this band system.

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Physical Chemistry **353**

Rydberg Stark deceleration of atomic hydrogen

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In recent years considerable efforts have been invested to produce slow, cold samples of atoms and molecules in the gas phase [1]. Supersonic gas beams are a convenient starting point to create such samples because the particles in supersonic beams are already translationally and internally cold. However, the particles move with a high velocity in the laboratory frame. Therefore to bring such cold particles to rest in this frame, they must be decelerated.

I shall present a method to slow down Rydberg particles in a supersonic beam using inhomogeneous electric fields. The deceleration mechanism relies on the large dipole moments (ea_0n^2) of Rydberg particles that arise as a result of the linear Stark effect [2, 3]. At n values between 20 and 30 the dipole moments are more than three orders of magnitude larger than those typically found in dipolar molecules. This can be used to apply forces on these particles causing accelerations of up to 10^8 m/s^2 and deceleration path lengths of only a few mm [4]. Measurements on atomic hydrogen will be presented in which deceleration to zero velocity in the laboratory frame and subsequent trapping for over 100 μs was achieved.

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Physical Chemistry **354**

Adsorption of Acridine Orange at C_8/water/acetonitrile interface

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Liquid chromatography is one of the most widely used separation techniques but there is still many questions concerning the organization and dynamics of the stationary phase structure. Acridine orange (3,6-dimethylaminoacridine) is a fluorescent adsorbate that has been well characterized at chromatographic interfaces. Its adsorption behavior at the hydrocarbon/solvent interface is investigated using Molecular Dynamics simulations. For different initial positions of the molecule with respect to the silica surface, the displacement of the acridine is analyzed from surrounding solvent density and distance from bare silica. For initial positions close to the silica surface, the acridine orange diffuses away from the silica surface and stays close to the terminal group of the C_8 alkyl chains. For initial positions in the bulk solvent, the acridine orange remains in the solvent phase. The transport behavior of the acridine orange is discussed in view of experimental data in water[1]. It is found that the transport of the acridine orange is mostly driven by the water gradient concentration in the water/acetonitrile mixture.

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Physical Chemistry **355**

Dimensionality of Energy Transfer in Dye-Loaded Zeolite L Host-Guest Materials

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The key process in a photonic antenna is Förster type radiationless energy transfer. We used pyronine,oxonine-loaded zeolite L material to explore this phenomenon, where pyronine works as a donor and oxonine as an acceptor. Donors and acceptors are randomly distributed inside the channels of zeolite L. We investigated series of samples were the ratio of the number of donor and acceptor molecules is constant (1:1) but the mean distance between them is decreasing. By selectively exciting pyronine at 460 nm, energy transfer from pyronine to oxonine takes place. The higher the loading of the sample, the smaller the donor-acceptor distance, the higher the rate of energy transfer.

In time-resolved fluorescence experiments both donors and acceptors identify energy transfer. The acceptor intensity first builds up before it starts to decay. This intensity increase becomes faster with increasing loading. The intensity decay of the donor decreases with increasing loading. It follows a stretched-exponential model where δ (or β in Klafter-Blumen formalism) is the parameter of dimensionality. It is equal to ½, 1/3 and 1/6 for three, two and one dimensions, respectively. A remarkable fact in our series is that δ decreases from 0.46 (for the lowest loading) to 0.23 (for the highest loading). In the packed sample energy is transported mostly in one direction, along the channel, and not between the channels [1]. This is a big advantage for photonic antennae, as anisotropic transport of the electronic excitation energy is important for efficient energy migration. Mono-directional antenna materials will be discussed [2].

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Physical Chemistry **356**

Switch of Enantioselectivity on a Chirally Modified Metal Surface Induced by Conformational Changes

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Different substituents at the phenyl ring of *O*-phenyl-cinchonidines exhibit intriguing enantioselective switching properties in the hydrogenation of activated ketones on chirally modified Pt/Al_2O_3. Catalytic data[1] show that *O*-phenyl-cinchonidine (PhOCD) affords the opposite enantiomer compared to cinchonidine (CD) that produces the (*R*)-enantiomer, despite having the same absolute configuration. Substitution at the phenyl ring by two CF_3 groups (CF_3PhOCD) inverts again the sense of enantioselection (*R*). The adsorption of CD, PhOCD, CF_3PhOCD and *O*-3,5-dimethyphenyl-cinchonidine (CH_3PhOCD) has been investigated using ATR-IR spectroscopy combined with density functional theory (DFT) calculations of the adsorbed species on Pt clusters. The spectroscopic data suggest that beside similar adsorbed species concerning the anchoring to the metal, the orientation and position of the phenyl ring strongly affect the position of the quinuclidine moiety with respect to the surface plane, and therefore the shape of the chiral pocket, a crucial factor for the final configuration of the product. The structure of the observed surface conformers is obtained by DFT calculations. Monitoring the orientation of the quinuclidine moiety of the modifiers responsible for the interaction with substrates, the origin of the enantioselective switch can be attributed to a conformational change imposed by the affinity of the *O*-substituent to the metal surface.

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Physical Chemistry **357**

High resolution rovibrational spectroscopy of halogenated aromatic compounds

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The low resolution vibrational spectra of fluorobenzene (C_6H_5F) and chlorobenzene (C_6H_5Cl), molecules which have C_{2v} symmetry, were previously assigned by Smith et al. [1] and Whiffen [2]. While benzene and monodeuterated benzene has been studied at high resolution including work from our group [3] there exists only one rovibrational analysis of the ν_{19a} band of chlorobenzene [4] and fluorobenzene [5]. As part of our ongoing investigation of highly resolved rovibrational spectra of aromatic compounds [6] we have measured the infrared spectra of these two halobenzenes with our Bruker IFS 125 HR (ZP2001) Fourier transform spectrometer [7] at room temperature in a 3 m glass cell and in a White-type cell with an effective optical path length of 9.6-19.6 m. The spectra were recorded with a resolution of 0.0008-0.0015 cm^{-1} in the range 600-1300 cm^{-1} and were analysed in the ν_{10b} (B_1 symmetry) regions of C_6H_5F ($\tilde{\nu}_c = 754.90374$ cm^{-1}) and $C_6H_5^{35}Cl$ ($\tilde{\nu}_c = 741.22393$ cm^{-1}). An analysis of the rovibrational spectrum of chlorobenzene might offer more insight into the combustion chemistry of polychlorinated biphenyls (PCBs).

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Physical Chemistry **358**

High Resolution Rovibrational Spectroscopy Of Halogenated Aromatic Compounds

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The low resolution vibrational spectra of fluorobenzene (C_6H_5F) and chlorobenzene (C_6H_5Cl), molecules which have C_{2v} symmetry, were previously assigned by Smith et al. [1] and Whiffen [2]. While benzene and monodeuterated benzene has been studied at high resolution including work from our group [3] there exists only one rovibrational analysis of the $\nu_{19\alpha}$ band of chlorobenzene [4] and fluorobenzene [5]. As part of our ongoing investigation of highly resolved rovibrational spectra of aromatic compounds [6] we have measured the infrared spectra of these two halobenzenes with our Bruker IFS 125 HR (ZP2001) Fourier transform spectrometer [7] at room temperature in a 3 m glass cell and in a White-type cell with an effective optical path length of 9.6-19.6 m. The spectra were recorded with a resolution of 0.0008–0.0015 cm^{-1} in the range 600–1300 cm^{-1} and were analysed in the ν_{10b} (B_1 symmetry) regions of C_6H_5F ($\nu,\tilde{}_c$ = 754.90374 cm^{-1}, d_{rms} = 0.00017 cm^{-1}) and $C_6H^{35.5}Cl$ ($\nu,\tilde{}_c$ = 741.22393 cm^{-1} d_{rms} = 0.00021 cm^{-1}). An analysis of the rovibrational spectrum of chlorobenzene might offer more insight into the combustion chemistry of polychlorinated biphenyls (PCBs).

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Physical Chemistry **359**

New Peptide-Based Organogelators and Their Use for The Preparation of Inorganic Materials

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Self-organizing molecules are of prime interest for the development of nanoscale organized materials. Low molecular weight organogelators are small molecules (molecular weight < 5000 Da) which can gel organic solvents and adopt various structures like fibers or tubes thanks to weak intermolecular interactions [1]. Beside the interest in self assembly, there is also in the material science community a constant interest in smart template which can be transcripted into inorganic materials via sol-gel technology [2].

We here present a new family of organogelators [3] (figure 1) based on l-valine which are available on a multi-gram scale. They are efficient organogelators and can be used as a (bioinspired) template for inorganic materials. Using the versatility of tetraethoxysilane and metal alkoxides in general, we were able to translate the nanoscale information to materials like amorphous silica nanorods or anatase based textured materials. A better understanding of these simple systems will lead to the better comprehension of the mechanism leading to the more complex structures synthesized by Nature.

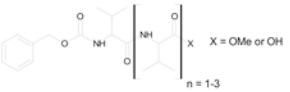

Figure 1: Structure of the organogelators

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Physical Chemistry **360**

Absolute Angle-Differential Cross Sections for Excitation of Rare Gas Atoms by Electrons near threshold

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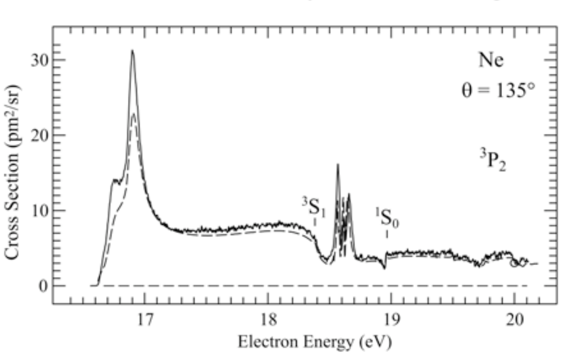
The knowledge of the absolute cross sections for the electronic excitation of rare gases by electron impact is essential for the understanding and optimization of various technological plasmas used for lighting and materials processing, but – except for helium – both the theoretical description and the measurement of these processes has remained a substantial challenge. Recently, however, significant progress has been made in theory by means of the *B*-spline *R*-matrix method and in the low-energy and wide angular range capacity of the experiment. This work presents the results for neon [1], argon and xenon. (Dashed line shows theory, continuous line experiment.)



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Physical Chemistry **361**

Silicone Nanofilaments as Surface Coating

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We present a chemical vapour deposition method for growing silicone nanofilaments onto surfaces by the reaction of trichloromethylsilane and water. The diameter of the flexible silicone nanofilaments ranges from 20 nm to 150 nm and their length up to a micrometre. Several technological important materials such as glass, polymers or silicon can be coated. The coating is optically transparent, even anti-reflective and renders coated surfaces superhydrophobic. With water contact angles range up to 163° and sliding angles below 20°. Electron microscopy and scanning force microscopy data, contact angle measurements and UV/Vis-spectra are presented.

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Physical Chemistry **362**

Spontaneously Absorped Molecularly Flat Films of the Redox [Os(bpy)$_2$(PVP)$_5$Cl]Cl Complex at HOPG Electrodes

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Well-defined polymeric structures featuring pendant redox groups have generated a great deal of attention due to their possible applications on molecular electronics. In the present contribution, the redox properties of the [Os(bpy)$_2$(PVP)$_5$Cl] complex, where bpy = 2,2'-bipyridyl and PVP = poly(4-vinyl pyridine), self-assembled at highly oriented pyrolitic graphite (HOPG) surfaces was studied by cyclic voltammetry and scanning probe microscopies.

The morphology and electrochemical properties of redox active films obtained by spontaneous adsorption of [Os(bipy)$_2$(PVP)$_5$Cl]Cl, bpy = 2,2´-bipyridyl and PVP = poly(4-vinylpyridine), at HOPG electrodes are reported. Two growth regimes with distinctive topographies are observed as a function of the adsorption time from diluted aqueous solution of the complex. [Os(bpy)$_2$(PVP)$_5$Cl]Cl exhibits a strong affinity to the clean HOPG surface leading to the formation of compact layers with well defined electrochemical properties. It is demonstrated that spontaneous adsorption of the complex allows the formation of redox polymer phases with some of the smoothest surfaces ever reported from solution phase deposition process.

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Physical Chemistry **363**

The Dynamics of Photoinduced Intramolecular Charge Transfer in Linked Perylene/N,N-Dimethylaniline Systems

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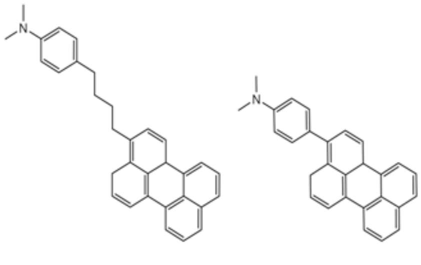
We report here on the dynamics of photoinduced intramolecular charge transfer within linked Perylene/N,N-Dimethylaniline systems, studied by time-resolved absorption and emission techniques. Bimolecular electron transfer (ET) from N,N-Dimethylaniline (DMA, electron donor) to photoexcited Perylene (Pe, electron acceptor) occurs with a driving force of -0.44eV in acetonitrile. To overcome the limitations of diffusion-controlled encounter between the donor and acceptor molecule, the ET dynamics of Pe in pure DMA has been investigated. We now go further by linking the two molecules, for example by a four-membered carbon chain (**1**), or directly (**2**). In the first case, a *quasi* bimolecular ET takes place between the locally excited Pe acceptor-moiety and the totally decoupled DMA donor-moiety in polar solvents, as evidenced by the appearance of the transient absorption peak of Pe$^{\cdot-}$. In the directly linked system, local excitation of Pe (decoupled from DMA in the ground state) leads to the ultrafast population of a charge transfer state (CT state) in acetonitrile, with substantially different spectroscopic properties than the Pe$^{\cdot-}$ state populated upon full charge transfer. It is probable that the CT state has a planar geometry allowing for electron delocalization, while the ground state is twisted.



Physical Chemistry **364**

New Fulvenium Derivatives: Diphosphafulveniums Cations. EPR and DFT Studies.

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Fulvene derivatives have been widely studied in chemistry of molecular conductors, semi-conductors and super conductors (tetrathiafulvalene…). Their electronic and structural properties explain enthusiasm for this kind of molecule: generally, it consists of neutral specie which gives a persistent paramagnetic planar cation when oxidized.

We present new cationic fulvalene derivatives with two phosphines. Paramagnetic species have been generated by reduction process and studied by EPR spectroscopy. Reductions change dramatically the geometry. DFT calculations are in good agreement with experiment.

Physical Chemistry **365**

ATR-IR spectroscopy of chiral self-assembled monolayers at solid-liquid interfaces

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In situ attenuated total reflection infrared (ATR-IR) spectroscopy is used to study the self-assembly of chiral thiols, such as L-glutathione and N-acetyl-cysteine on gold surfaces. Time-dependent spectral changes provide information about the self-assembly process and molecule-surface interactions. Furthermore, the relative intensities of selected signals of adsorbed and randomly oriented molecules (liquid phase) give information on the average orientation of the adsorbed species within the SAM.

We have recently combined ATR-IR with modulation excitation spectroscopy (MES). MES selectively reveals the periodically changing signals stimulated by an external parameter [1]. Specifically, we have shown that an L-glutathione monolayer self-assembled on gold undergoes reversible structural changes upon acid-base stimuli (pH-modulation) [2]. By periodically changing the absolute configuration of a probe molecule (absolute configuration modulation) at the chiral SAM interface, enantiospecific interactions can be spotted. Conventional infrared spectroscopy has the disadvantage that also nonspecific interactions give rise to signals. In contrast, signals in the ME spectra exclusively arise due to the different interactions of the two enantiomers with the chiral interface, revealing the functional groups responsible for enantiodiscrimination. The method was successfully applied to study the chiral discrimination between an L-glutathione [3] and an N-acetyl-L-cysteine SAM, respectively, and the amino acid proline [4].

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Physical Chemistry **366**

Molecular Structure of Cyclooctatetraene

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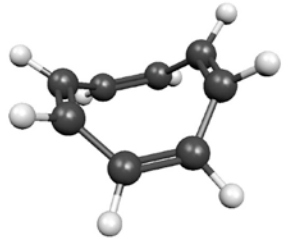
Femtosecond degenerate four-wave mixing and *ab initio* calculations are used to redetermine the accurate molecular structure of 1,3,5,7-cyclooctatetraene (C_8H_8) which is a paradigmatic antiaromatic (and non-planar) molecule [1].



This rotational coherence method yields very accurate ground state rotational as well as centrifugal distortion constants [2][3]. By combining these with CCSD(T) anharmonic structure calculations we are able to extract C=C, C-C and C-H geometry parameters for the D_{2d} structure of C_8H_8.

[1] P. M. Thomas and A. Weber, *J. Raman. Spec.*, **1978**, *7*, 353 .
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Physical Chemistry **367**

Striking a Helix with a Hammer

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Proteins are the building bricks of the living cells and consequently are an ubiquitous element of life. The functionality of a protein is conditioned by its structure and the most common secondary structure motifs in the folded proteins are the β sheets and helices. As of now there is no clear model for the efficient transport of vibrational energy through proteins helices. In order to address this question we designed a molecule that consists of a stable 3_{10}-helix (Aib_8) with a chromophore attached (Azobenzene). In order to investigate how vibrational energy travels through the helix we synthesized molecules in which we isotopicaly label different CO oscillators along the helix.

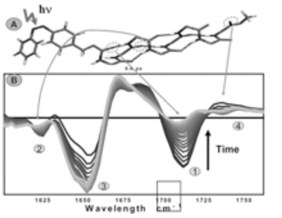

Figure 1: A) Sketch of the Aib helix and the attached chromophore B) UV-pump IR-probe transients in the Amide I spectral region at delay times varied from 500 fs to 30 ps.

By comparing the kinetics of the label band in molecules where the label is close to the dye and in molecules where the label is further away from the dye we infer information about the efficiency of the vibrational energy transport in a 3_{10} helix.

Physical Chemistry **368**

Time-Resolved Infrared Measurements of the Dynamics of Aib Containing Thiopeptides

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To investigate dynamics of a peptide during a conformational change, photo switches integrated into the backbone of the peptide can be used as a trigger. Here we use a substitution of an oxygen atom in one peptide bond by a sulphur atom, which shifts the $\pi \rightarrow \pi^*$ excitation red with respect to the one of a non-substituted peptide bond and can be excited selectively. Significant isomerization for N-Methylthioacetamide (the simplest isomerizing molecule with a substituted peptide bond) and thiopeptides up to 20 amino acids has been reported[1][2]. A series of thiopeptides, Z-Gly(S)-Aib-Ile-OMe, Z-Ala(S)-Aib-Ile-OMe and Z-Ile(S)-Aib-Gly-OMe, are investigated by time-resolved UV-pump/IR-probe and IR-pump/IR-probe spectroscopy, steady-state FTIR-spectroscopy and ^{1}H-NMR. All of these compounds contain Aib, which aids the formation of 3_{10}-helices and stabilizes β-bends. On the other hand, Aib is relatively bulky and may perturb the isomerization efficiency. We have found very similar isomerization dynamics and quantum efficiencies for all three thiopeptides, while the larger sidechains of the substituted amino acid destabilizes the cis-ground state. Additionally, structural parameters have been determined by polarization-dependent measurements for the thiopeptides in thermal equilibrium and show similar rigid structures in the inner part of the three thiopeptides, while the tails are more flexible.

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Physical Chemistry **369**

High Resolution Diode Laser IR-Spectra Measured in a Pulsed Slit Nozzle Supersonic Jet Expansion

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Rotationally resolved high resolution IR-spectra are of fundamental importance to understand intramolecular dynamics in polyatomic molecules [1,2] and to model IR-absorption spectra in the atmosphere [3] and in interstellar space [4]. Due to the population of low lying vibrational states and small rotational constants (resulting in a large number of rotational lines), often IR-spectra of medium sized molecules measured at room temperature are too congested to be rotationally resolved, even with state of the art high-resolution IR-absorption techniques. The spectra are strongly simplified if the rotational and the vibrational degrees of freedom are cooled down efficiently in a molecular beam. The molecular beam technique is also ideally suited to investigate the IR-spectra of small clusters like dimers, trimers, or tetramers.

We have set up an IR-diode laser spectrometer and have combined it with a pulsed molecular beam. To increase the optical absorption length a slit nozzle has been used and rotational temperatures below 10 K could be reached. Resolved IR-spectra of CF_4, CF_3CCH and other molecules will be presented and their analysis discussed.

[1] M.Quack, *Annu. Rev. Phys. Chem.* ***1990,*** *41, 839*

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Physical Chemistry **370**

Transient 2D-IR spectroscopy of thiopeptide isomerization

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Two dimensional IR spectroscopy allows one to measure coupling and relative orientation of Amide I transition dipole moments in peptides. This information can be used to determine the dihedral angles between neighboring peptide units and yields structural information of the system in equilibrium on a subpicosecond time scale [1]. Recent works [2,3] have shown an extension of this technique to non equilibrium systems. Here the isomerization of a small thiopeptide, Boc-Ala-Gly(=S)-Ala-Aib-OMe, is followed using pump-probe and transient 2D-IR spectroscopy. The two techniques yield complementary information on the dynamics. New properties of transient 2D spectroscopy are explored. Of great interest is the possibility to use this technique for resolving bands that are not resolved in the 1 D manner. Indeed the additional frequency axis allows us to individually address single IR bands. Moreover we also observe cross peaks in the transient 2 D spectra. Cross peaks in the transient 2 D spectra open us the possibility to gain structural information during the conformation change of a peptide.

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Physical Chemistry **371**

A multiphase investigation of the HCl/ice system in the temperature range 170-200 K

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An experimental study of thin ice films (in the micron range), both pure and doped with HCl, will be presented. Films are grown in a chamber [1] under high vacuum conditions by deposition of water vapour onto a temperature controlled substrate, which is a gold coated quartz crystal microbalance (QCMB). The latter allows to monitor mass changes in the deposited film. A known amount of dopant, HCl in this case, can be injected though an independent line in order to contaminate the ice. IR Fourier transform spectroscopy is employed to monitor the solid phase: the optical arrangement allows to perform grazing incidence transmission reflection spectroscopy (RAIRS), at an angle of incidence of around 75°. The gaseous phase in the reactor is also studied, using an absolute pressure gauge and a residual gas MS analyzer.

Depending on the growth temperature (around 190 K and 170 K respectively), two different phases of the H_2O/HCl system have been found, which have been assigned to an amorphous and an hexahydrate crystalline phase. Growth conditions and spectroscopic properties of the samples will be illustrated. In addition, the stability of the crystalline phase as a function of the temperature will be taken into account. Possible implications for cirrus clouds and polar stratospheric clouds will finally be discussed.

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Physical Chemistry **372**

Millimetre-wave spectroscopy and multichannel quantum defect theory of the high-n Rydberg states of para D_2

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Millimetre-wave spectra of transitions between hyperfine components of high-n Rydberg states located below the $X\,^2\Sigma_g^+$ ($v^+ = 0$, $N^+ = 1$) threshold of para D_2^+ will be reported. A double-resonance VUV-UV excitation scheme, $X\,^1\Sigma_g^+\ (v'' = 0,\ J'') \rightarrow B\,^1\Sigma_u^+\ (v' = 3,\ J') \rightarrow ns\,/\,nd,\ X\,^2\Sigma_g^+\ (v^+ = 0,\ N^+)$, was used to populate nd Rydberg states with $n = 51 - 53$. A millimetre-wave source ($120 - 180$ GHz) was then used to excite transitions to neighbouring nf Rydberg states with $n = 54 - 57$. A spectral resolution of 1 MHz was achieved, which enabled the resolution of the hyperfine structure of the initial and final Rydberg states. The hyperfine structure of the f states is dominated by the hyperfine interaction between the nuclear spin and the core-electron spin. In contrast, the exchange interaction is dominant in the more penetrating d states. However, some evidence of weak singlet-triplet mixing induced by the hyperfine interaction is observed in the d states.

Multichannel-quantum-defect-theory calculations on the hyperfine structure of the d and f Rydberg states of para D_2 were carried out using the methodology developed by Osterwalder *et al.* [1]. A fit to the experimental data permitted the extraction of the hyperfine coupling constants of the $X\,^2\Sigma_g^+$ ($v^+ = 0$, $N^+ = 1$) state of the D_2^+ ion.

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Physical Chemistry **373**

Photocatalytic Degradation of Dicarboxylic Acids On Tio$_2$ Studied by Operando ATR-IR Spectroscopy

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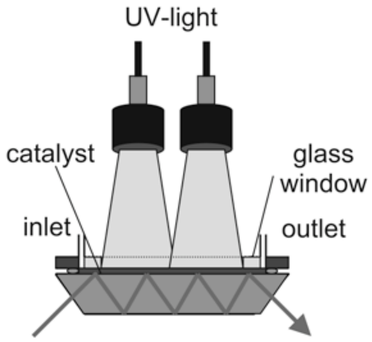
Switzerland

In situ Attenuated Total Reflection Infrared (ATR-IR) spectroscopy is used to study the solid-liquid interface of a TiO_2 (P25) photocatalyst during band gap irradiation (see Figure). In particular the photocatalytic mineralization, i.e. decomposition to carbon dioxide and water, of malonic acid is studied. Upon illumination the coverage of adsorbed malonic acid is decreasing and oxalic acid is observed on the TiO_2 surface. Oxalate is a major intermediate in the mineralization of malonic acid. However, the observed transient kinetics of adsorbed malonic and oxalic acid indicates additional pathways not involving oxalate. The rate constant of oxalic acid is slightly larger than the one for malonic acid. During band-gap illumination a large fraction of the surface is not covered by acid. The modulation of the light flux and a phase-sensitive detection yields even more details about the processes occurring and the species present at the catalytic solid-liquid interface [1]



[1] I. Dolamic, T. Bürgi, submitted for publication.

Physical Chemistry **375**

Ultrafast long distance excitation energy transfer in tri-chromophoric donor-bridge-acceptor molecules

Guillaume Duvanel[1], Albert Gossauer[2], Anne Schuvey[2], and Eric Vauthey[1]

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[2] Département de chimie, Université de Fribourg

The excited state dynamics of a tri-chromophoric donor-bridge-acceptor (DBA) where D is Zn tetraphenylporphine (ZnTPP), and A is a free base tetraphenylporphine (FbTPP) has been investigated. The centre to centre distance between A and D is larger than 45 Å.

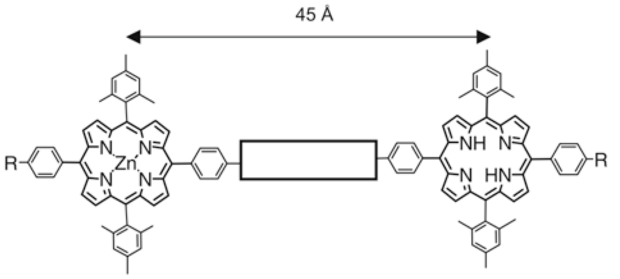

Figure 1: Schematic structure of the DBA molecule

The excited state energy of the bridge depends on its structure. When the bridge excited state is above the S_2 state of ZnTPP, ultrafast excitation energy transfer (EET) to both A and D is observed. On the other hand, if the bridge excited state is lower, EET from the S_2 state of the ZnTPP to the bridge takes place within a few picoseconds. This is followed by another EET from the spacer to A and D. Globally, this corresponds to a EET over more than 45 Å within a few picoseconds.

Physical Chemistry **374**

The Influence Of Hydrogen Bonding On The Raman And ROA Spectra Of(2S)-2-Fluoro-Propionic Acid

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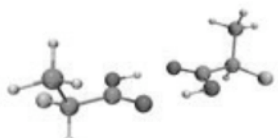
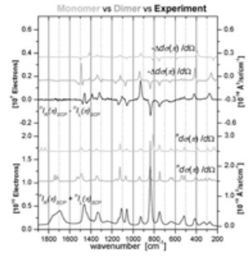
We have exploited the sensibility of Raman and Raman Optical Activity (ROA) spectra to hydrogen bonding for studying the formation of hydrogen bonded clusters of carboxylic acids in the liquid phase. To this end, the spectra of small clusters of the title compound were calculated and compared with measured spectra. The results show that the dimer makes the dominant contribution to the observed spectra.





The geometry optimization and the force field calculations were done at the DFT-B3PW91/6-31+G** level with Gaussian03, while the electronic tensors were obtained by TDHF/rDPS [1] with Dalton. The spectra, shown above, are in substantial agreement with results obtained by using a geometry and a force field obtained by DFT-B97-1/rr-pc-2 [2].

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Physical Chemistry **376**

Spectroscopic discrimination of active sites during liquid-phase alcohol oxidation on Pd/Al_2O_3 using ATR-IR spectroscopy

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Alcohol oxidation over Pd is reported as structure insensitive reaction based on UHV studies [1], whereas carbonyl product degradation to CO is structure sensitive [2]. ATR-IR measurements during liquid-phase oxidation of benzyl alcohol on a commercial Pd/Al_2O_3 at 50°C reveal the adsorption of CO predominantly on three-fold bridge sites upon benzaldehyde decarbonylation. CO coexists to some extent with dissolved oxygen before being fully oxidized, at which point catalyst deactivation starts [3]. Pre-equilibration of the supported Pd catalyst with CO retards benzyl alcohol dehydrogenation, by about 2 h. During this time, CO is removed from Pd from on-top and two-fold sites under the flow of the benzyl alcohol solution. When reaction can occur again, the surface is occupied by CO on three-fold sites. Identical experiments with ^{13}C-labeled benzyl alcohol at the benzyl carbon atom reveal that no further decarbonylation occurs when these sites are blocked by CO. Additionally, CO formation is strongly inhibited on three-fold sites during reaction on Pd-Bi/Al_2O_3, where Bi is predominantly deposited on the Pd particles.

The data indicate that sites where CO adsorbs in a three-fold mode are responsible for benzaldehyde degradation reactions, whereas alcohol dehydrogenation occurs indistinctly on on-top, two-fold and three-fold sites.

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[3] C. Keresszegi, D. Ferri, T. Mallat, A. Baiker *J. Phys. Chem. B* **2005**, 109, 958.

Physical Chemistry **377**

Photophysics of Oxazole Yellow Derivatives in Presence of Different DNA Conformations

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Monomeric and especially dimeric oxazole yellow (YO) and thiazole orange (TO) derivatives have become widely popular fluorescent DNA stains because of their high sensitivity to detect B-DNA and the fact that they virtually do not fluoresce when they are free in solution. The high difference in the fluorescence quantum yield between the free and the bound form has been shown to be governed by two mechanisms: inhibition of an ultrafast isomerization process within the cyanine dye and disruption of intra- (for dimers) or intermolecular (for monomers) aggregates upon intercalation into DNA [1,2].

Although DNA mainly exists under its B conformation, the A and Z helices have been shown to be physiologically relevant. The size and depth of the grooves significantly differ from one DNA isoform to the other. It is thus expected that the exposure of any DNA-bound probe to the surrounding solvent molecules varies, which should in turn influence the conformation and the photophysics of the bound dye. We present here our investigations of the photophysics of YO derivatives in presence of A, B and Z-DNA.

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Physical Chemistry **379**

Investigation of Open Shell Organic Ions in Solution Using Ultrafast Spectroscopy

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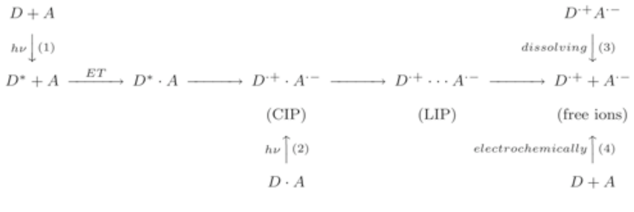
The structures of the different radical ion pairs formed upon photoinduced electron transfer (ET) are still essentially unknown and subject of contradictory debate [1]. The following scheme shows the proposed species which differ in ion distance and solvation: The counter ion pair (CIP), the loose ion pair (LIP, also called solvent separated ion pair) and the free ions.



We present transient absorption and fluorescence up–conversion experiments testing ion pairs resulting from (1) bimolecular photoinduced electron transfer, (2) excitation of Donor–Acceptor–Complexes ($D \cdot A$) [2, 3], (3) persistent radical cations and (4) radicals created by electrochemical oxidation in a home–built electrochemical flow–through cell.

Employing such distinct ways of generation, we test the different radical ion pairs mentioned above.

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Physical Chemistry **378**

Light-Induced Spin Transition Probed via Time-Resolved X-Ray Absorption Spectroscopy

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Electronic structure changes are at the origin of chemical reactivity, which drive the making and breaking of bonds. We have developed and applied a novel time-resolved X-ray Absorption Spectroscopy (XAS) technique to probe photoinduced structure changes of both electronic, via XANES, and geometric nature, via EXAFS. We use an ultrashort laser pump/X-ray probe scheme at a 3rd generation synchrotron (Swiss Light Source, Villigen). The iron(II)-tris-bipyridine complex, $[\mathrm{Fe(bpy)_3}]^{2+}$ is a typical example of light-induced spin-crossover compounds, in which excitation with light leads to population of the ligand-field split e_g level with parallel spins, thus generating a high spin (HS) complex with quintet ($\Delta S=2$) multiplicity. Both theoretical and experimental studies on compounds that undergo temperature-induced spin-cross over, predict an elongation of the Fe-N bond distance by ca. 10% of the low-spin bond length.

In this study, we have successfully employed and measured for the first time the picosecond time-resolved XAS in order to capture the transient molecular structure of the photoexcited HS state of $[\mathrm{Fe(bpy)_3}]^{2+}$ at ca. 50 ps time delay after the laser excitation. The structural analysis of the results in both XANES and EXAFS regions points towards a symmetric Fe-N bond length elongation of ca. 0.15 Å, which is considerably less than the values predicted by theory ($\Delta r_{HL} = r_{HS} - r_{LS} \approx 0.2$ Å). Up to date, no experimental measurement of the local HS structure of this complex has been reported.

Physical Chemistry **380**

2D-Mapping of the catalyst structure inside a fixed-bed reactor: Partial oxidation of methane over Rh/Al$_2$O$_3$

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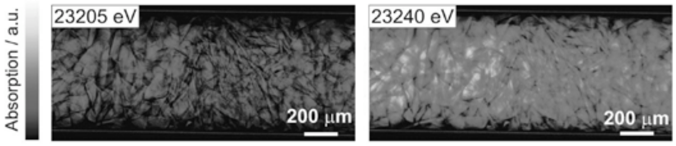
In situ X-ray absorption spectroscopy is a well-suited technique to gain information on the structure of heterogeneous catalysts. In certain cases a variation of the catalyst structure can occur inside a catalytic reactor as a result of temperature or concentration gradients. This requires spatially resolved molecular information on a microscale. Here, we have used a position sensitive X-ray camera to record XANES spectra from inside the catalytic reactor with a spatial resolution on the scale of a few micrometers [1]. The catalytic performance was determined using mass spectrometric analysis.

Partial oxidation of methane over Rh/Al$_2$O$_3$ catalyst is used as an example. For recording locally resolved the absorption of the sample inside the catalytic microreactor, a CCD camera was installed behind the *in situ* cell and X-ray absorption images were recorded around the Rh K-edge (23220 eV) as shown in the Figure. In total, 170 absorption images were taken that allowed the reconstruction of the full Rh K-edge XANES spectra at each pixel. The measurements uncovered tremendous changes of the structure of the Rh particles along the catalyst bed within less than 100 µm.



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Physical Chemistry **381**

π-Extended-Tetrathiafulvalene with Metal-Ion Binding Ligand

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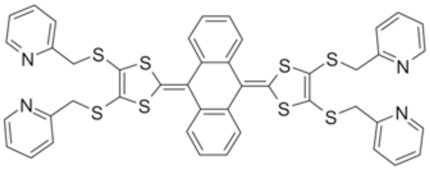
π-Extended Tetrathiafulvalene in which the 1,3-dithiole rings are connected through a conjugating spacer group or a *p*-quinodimethane moiety are versatile building blocks in supramolecular and materials chemistry [1]. In order to prepare materials with multiphysical properties, functionalization with ligating groups such as pyridine of the well-known redox-active unit TTF have been performed in our group [2]. Contrary to the parent TTF, π-Extended TTF with anthracene core exhibit some structural change upon oxidation.



Herein, we will describe the synthetic pathway and properties of this compound and exploit its coordination chemistry with a variety of transitions metal ions.

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Physical Chemistry **382**

Rovibrational analysis of the ν_{9a}, ν_{15} and ν_{18a} modes of pyridine

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Pyridine is a prototype of heterocyclic aromatic molecules. It is of astrophysical interest and can be related to other nitrogen-containing aromatic systems important for biopolymers. Therefore, a complete understanding of its rovibrational resolved infrared spectrum is of fundamental interest. We have conducted a detailed analysis of its highly resolved infrared spectrum between 600-1300 cm^{-1} [1] based on an extended analysis of its submillimeter spectrum [2]. This work is part of our effort to understand the rovibrational spectroscopy of aromatic systems [3]. The assignment of the ν_{11} mode leads probably to the first detection of pyridine in interstellar space [4]. The spectrum was recorded with our Zürich Bruker 2001 prototype Fourier transform infrared spectrometer [5] at the essentially Doppler limited resolution of 0.0008 cm^{-1}. A detailed analysis of different resonance systems of pyridine $\nu_{15}/\nu_4 + \nu_{16b}$ ($d_{rms} = 0.00027$ cm^{-1}) and ν_{18a}/ν_{18b} ($d_{rms} = 0.00024$ cm^{-1}) will be given. In addition, we will discuss the assignment of the ν_{9a} mode ($d_{rms} = 0.00022$ cm^{-1}) which is relatively free of interactions.

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Physical Chemistry **383**

A 3D electrostatic trap for Rydberg atoms

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Recent progress in our group on the deceleration and subsequent manipulation of clouds of dipolar Rydberg particles in time-dependent inhomogeneous electric fields has led to the experimental realisation of several components with optical analogues, including Rydberg particle mirrors, lenses and two-dimensional (2D) traps [1-3]. This work takes advantage of the large Stark shifts experienced by Rydberg states in electric fields of moderate strength. Having achieved full 2D control over the motion of Rydberg particles, we now aim to control the velocity distributions of Rydberg atom clouds in three dimensions (3D) and to perform high-resolution spectroscopy on the cold, trapped particles.

We report on the development of a novel 3D electrostatic trap for Rydberg particles. The trap design includes access for mm-wave radiation along the coldest trapping dimension allowing measurements to be made with the minimum Doppler broadening. It also permits the possibility of having a non zero electric field at the trap minimum. With a non zero electric field at the minimum of the trap, losses arising from the Rydberg electron moving to an untrapped Stark state when a particle passes through the zero-field point may be avoided.

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Physical Chemistry **384**

Near-threshold photoionisation studies of the isotopomers of N_2^+

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The photoionisation spectrum just above the first ionisation limit of N_2 is dominated by a broad feature in the range of 126 200 cm^{-1} to 126 500 cm^{-1}, the so called "cathedral". Several different assignments of the strongest lines in this range have been published previously [1, 2, 3, 4, 5].

For the first time, the photoionisation spectra of the isotopomers of molecular nitrogen ($^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$) are recorded simultaneosly using a narrow bandwith vacuum ultraviolet laser system [6].

The analysis of the recorded photoionisation spectra is presented together with a comparison to earlier assignments [5, 4] and calculations [4].

This work is supported by the ETH Zürich.

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Physical Chemistry **385**

Site and state selective chemistry in dissociative electron attachment to 1-amino-2-hydroxyethane.

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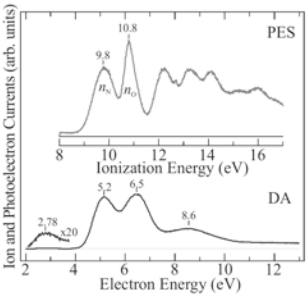
Both the amino and the hydroxyl groups are ubiquitous in living organisms. Inspired by the discovery that low-energy electron-induced chemistry is decisive in radiation damage to living organisms [1], we decided to gain insight into the electron-induced chemistry of compounds containing these functional groups by recording dissociative electron attachment (DEA) spectra of simpler model compounds containing both groups [2][3][4].



We discovered an interesting case of site and state selective chemistry in 1-amino-2-hydroxyethane (1) and related compounds. Two bands, at 5.2 and 6.5 eV, are observed in the yield of the (M-1) anion (loss of a hydrogen atom) from (1). They correspond to Feshbach resonances whose grandparent cations are ionized from the nitrogen and the oxygen lone electron pairs, respectively – indicating site-localized excitation.

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Physical Chemistry **386**

Folding and Unfolding of a Photoswitchable Peptide

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Protein folding remains one of the most demanding tasks of biophysical chemistry. One ultimately wishes to be able to predict a protein structure solely from its amino acid sequence, which would open unprecedented possibilities in treating diseases and drug design. The major goal of this project is to observe all crucial dynamic events of folding and unfolding processes of a photoswitchable peptide, from pico-seconds to micro-seconds. We have performed sets of 1-D-(transient UV-pump IR-Probe)-absorption experiments on photoswitchable peptide with site-selectively isotope labeled amino acids and observed clear differences (almost an order of magnitude) in helix formation rates at various positions in the amino acid sequence, the N-terminal being the faster site of the helix-formation.

In order to set experimental benchmarks for computational protein dynamic simulations, both the folding and the unfolding processes of an α-helix has been studied by using the same technique (UV-pump IR-probe). By studying both processes in a large temperature range, free energy landscape(s) of folded and unfolded states can be investigated in very detailed manner. This approach allows more detailed comparison between different folding models, which is not solely possible when a folding or unfolding process, alone, or at specific temperature, is studied. We observed that at room temperature the unfolding rate is about five times higher than that of folding and that the spectral kinetics is rather complex in both processes, which puts high demands on determination of the free energy landscape of conformational dynamics of α-helices (proteins).

Physical Chemistry **387**

REMPI spectroscopy of Ne_2

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Autoionization of Rydberg states of the rare-gas dimers provides intensity to the pulsed field ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectrum in the region where the Franck-Condon factors for direct ionization are negligible [1]. In this way, the determination of the electronic structure of the ions becomes possible. We present a study of the electronic and vibrational autoionization and predissociation dynamics of Ne_2 Rydberg states located below the dissociation limit of the ground I(3/2u) electronic state of Ne_2^+. The Rydberg states are excited in a resonant two-photon (VUV+UV) excitation from the X 0_g^+ electronic ground state of Ne_2 via the C $0_u^+(v'=0\text{–}3)$ intermediate levels. Decay of the Rydberg states by autoionization and predissociation is observed, and in the latter case the measurement of the kinetic energy of the fragments provides information on the predissociation mechanism. Strong and sharp autoionization resonances are observed in the region above 167000 cm^{-1} that are attributed to Rydberg states belonging to series converging on electronically excited states of Ne_2^+. Their intensity suggests that these ionic states should be observable by PFI-ZEKE photoelectron spectroscopy.

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Physical Chemistry **388**

Optical Detection and Tracking of Single Gold Nanoparticles for Biophysical Studies

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We show that scattering of gold nanoparticles down to a size of 5nm can be detected at the water-glass interface in a simple interferometric detection scheme. Gold nanoparticle labels are superior to fluorescent labels because 1) they do not photobleach, and 2) allow fast (100kHz-1MHz) detection and tracking.

Gold nanoparticles are interesting candidates for labeling in biophysical single particle-tracking experiments as they are bio-compatible and easily attached to the object of interest using thiol-chemistry. The scattered field from a weak scatterer can be interfered with the reflected light from an interface. The resulting interference cross term is detected more easily for small particles than the pure scattering contribution as it does not scale with sixth but rather the third power of the particle diameter so that 5nm gold nanoparticles are detectable at the water-glass interface. We discuss a number of issues which are important for the application in particle tracking. We show that the dispersion of the plasmonic excitation of the particle can be used to distinguish gold particles from dielectric scattering objects present in a biological sample. Furthermore, because the scattering of a gold nanoparticle does not saturate with light intensity, we are able to reduce detection time down to a microsecond level. Moreover, the detection can be done also in a wide-field microscope, enabling simultaneous observation of many particles in large systems. We show first results obtained after developing and constructing a laser beam scanning microscope for fast particle tracking in 2D. Acousto optical deflectors are used for fast beam scanning. The detection is assured by a 4 quadrant diode, which gives us an information about the direction the tracked particle is moving into. By using an analog feedback loop we can then follow the particle easily.

Physical Chemistry **389**

Excited state reactivity of 2-pyridone: the role of out-of-plane vibrations

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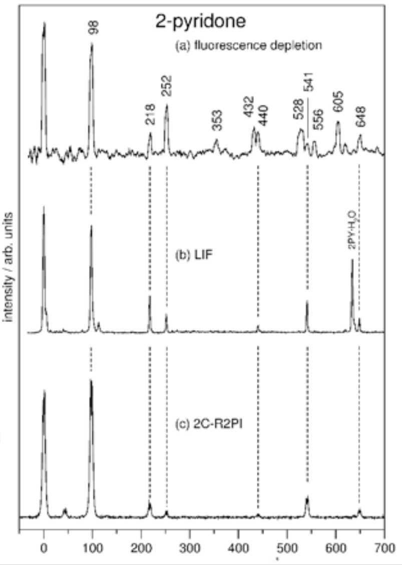

2-Pyridone (pyridin-2-one; 2PY) is a "minimal" nucleobase analogue containing a *cis*-amide group and has been employed as a DNA-base mimic in both biochemical and spectroscopic studies. Unlike the canonical pyrimidine nucleobases, 2PY fluoresces from its S_1 $\pi\pi^*$ state.We have measured the $S_1 \leftarrow S_0$ vibronic spectra by laser-induced fluorescence, resonant two-photon ionization and fluorescence depletion spectroscopies. The low-frequency S_1 state vibrations show progressions in two out-of-plane vibrations ν_1' and ν_2'. Above $350\,\mathrm{cm}^{-1}$, the out-of-plane levels are "dark", as can be seen from spectrum (a) relative to with (b,c). These levels lie above a S_1 state barrier which leads towards a S_1/S_0 state conical intersection, calculated to have a pre-fulvenic geometry. This enhancement of the non-radiative relaxation rate by low-lying S_1 vibrations may also be important for uracil,

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Physical Chemistry **390**

Fluorobenzene-Nucleobase Interactions: Hydrogen bonding, no π-stacking

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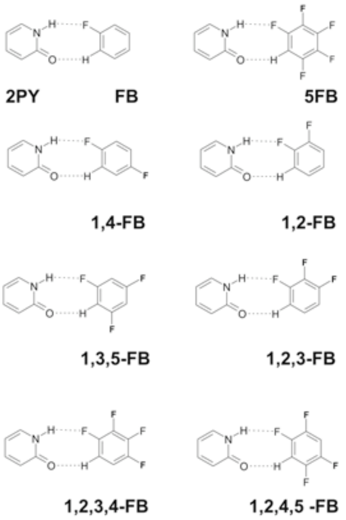
Current research on modified DNA oligomers has shown that nucleobases can exhibit stable and even selective pairing with shape-complementary fluorinated nucleobases. Because of the poor propensity of F to form hydrogen bonds, the DNA stability has been attributed to π-stacking and shape-complementarity only.

Using resonant two-photon ionization and fluorescence spectroscopies, we show that supersonically cooled complexes of the nucleobase analogue 2-pyridone with eight substituted fluorobenzenes are hydrogen-bonded and **not** π-stacked[1]. The vibronic spectra show ground and excited state intermolecular vibrational frequencies that are characteristic for doubly hydrogen bonded complexes. With increasing F-substitution the 0_0^0 bands shift to the blue, in excellent agreement with the *ab initio* calculated shifts. These are linearly correlated with the calculated hydrogen-bond dissociation energies D_0=5.86 - 6.5 kcal/mol[2].



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[2] J. A. Frey, R. Leist and S. Leutwyler *J.Phys.Chem.A*, **2006**, *110, 4188*

Physical Chemistry **391**

The Nature of the Chemical Process. 2. Mixing and Separation

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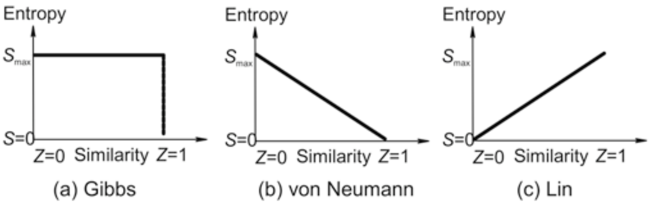
Entropy of mixing (ΔS) has been expressed as free energy ($\Delta G = -T\Delta S$) under the typical isothermal and isochoric conditions, which is a fundamental flaw in thermodynamics. Mixing or separation has nothing to do with energy (including free energy); it is exclusively related to information loss ($\Delta I = -\Delta S$, where information I is defined as the amount of data after compression). Information theory has been applied to the structural stability and process spontaneity consideration and the new higher (information theory) entropy-higher symmetry and more generally the new higher entropy-higher similarity-higher stability relationship have been set up [1], see figure c:



(a) Gibbs (b) von Neumann (c) Lin

(Information theory) entropy of mixing (ΔS) at solid state is a negative value ($-\Delta S = \Delta I > 0$). At solid state, separation process has an increase in the entropy value, and solid phase separation is always a spontaneous process.

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Physical Chemistry **392**

Molecular Dynamics Calculations of Predissociation Lifetimes and Absorption Spectra of The Dimer $(HF)_2$

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The dynamics of hydrogen bond formation and breaking is of fundamental importance for understanding many biophysical-chemical processes. We use hydrogen fluoride dimer $(HF)_2$ as prototype system to better understand and describe dynamics in hydrogen bonded systems. The particular simplicity of this dimer allows for high-resolution rotational-vibrational spectroscopy[1-5], and full dimensional quantum dynamical calculations on accurate potential hypersurfaces[6-7]. The predissociation lifetime τ_{PD} of the dimer is highly mode specific. For instance, using highly resolved pulsed jet CW cavity-ring down experi-ment[5], we have shown that the lifetime of the 2_1 state involving two quanta of the bonded HF stretching mode is only ~50 ps whereas that of the 2_2 state involving two quanta of the free HF stretching mode is more than 1 ns. The 2_3 state which involves one quantum in each of the stretching modes exhibits an intermediate behavior (τ_{PD}~ 200 ps)[5].

In order to obtain a more detailed understanding of the dynamics in this dimer and to provide a benchmark system for classical dynamics simulations, we have performed molecular dynamics calculations using the accurate fully 6-dimensional SO-3 electronic potential hypersurface $(HF)_2$ established previously in our group[6] to estimate lifetimes and absorption spectra. We present here our first results for $N=2$ triad of the first HF stretching overtone region and compare them with experimental results[5].

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CHIMIA **2006**, *60*, No. 7/8

Physical Chemistry **393**

Potential Energy Hypersurface for Ammonia

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We aim at obtaining realistic potential energy surface (PES) for ammonia which can be used both for the calculation of spectroscopic transitions in the infrared to visible region as well as for the simulation of the reaction dynamics related to large amplitude motions such as the dissociation, recombination and the inversion reactions. Recently, in our group, we have studied high resolution IR spectra of isotopically substituted ammonia, the related potentials and wave packet dynamics in some details [1,2]. Single reference CCSD(T)[3] and Multi Reference CI approaches are used and "merged" to obtain a global ab-initio PES for ammonia that includes several low lying dissociation channels and including also fitting to experimental data. Specially devised fitting functions[4] are used to allow for a robust and compact analytical representation of the global PES. The robustness of the fitting functions including the experimental dissociation energy have played a key role in the smooth merging of the two ab-initio numerical PES. The conical intersection between the $NH_3 \rightarrow (^2A_1)NH_2+H$ and $NH_3 \rightarrow (^2B_1)NH_2+H$ the dissociation channels is described approximately with the PES representing a truly adiabatic ground state. Results from the variational calculation of vibrational levels are promising and determine the first global PES for ammonia in its electronic ground state that is close to spectroscopic accuracy.

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Physical Chemistry **394**

Chiral switch by on-stream replacement of chiral modifiers on Pt/Al_2O_3 in a continuous flow reactor

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Chiral modification of a catalytically active metal surface by adsorption of a chiral modifier is a powerful strategy for heterogeneous enantioselective hydrogenation[1]. The most prominent example is the platinum-cinchona system successfully applied for the hydrogenation of α-keto esters. The environment created upon adsorption of the modifier on Pt can induce opposite enantioselection according to the modifier structure[2]. The pseudoenantiomeric pair cinchonine (CN) and cinchonidine (CD), as well as quinidine (QD) and CD have been used in this study to induce the formation of the opposite enantiomer of the product in a continuous process. A solution of ethylpyruvate and chiral modifier, 308 ppm, in acetic acid was continuously fed to a fixed bed flow through reactor under 15 bar H_2. On-stream exchange from QD to CD led to a chiral switch from 57 % ee to (S)-ethyl lactate to 89 % ee to the (R) enantiomer. The time necessary to reach the racemic mixture was dependent on the modifier adsorption strength. The switch from CN to CD changed the ee of ethyl lactate from 86 % (S) to 82 % (R). The turnover frequency increased from 544 h^{-1} to 9435 h^{-1} by adding CD to the stream, indicating that also in the continuous system chiral modifiers generate rate acceleration. In-situ ATR-IR spectroscopy gave insight into the modifier interchange at the molecular level.

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Physical Chemistry **395**

Spectral Diffusion Due To Resonant Excitation Energy Transfert Inside The Electronic Origin Of The $^4A_2 \rightarrow ^2E$ Transition in $[Ru(bpy)_3][NaCr(ox)_3]$

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In the 3D oxalate network $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ the resonant excitation energy transfer between the zero-field split components of the electronic origin of the $^4A_2 \rightarrow ^2E$ transition of the Cr^{3+} chromophore at 1.4 K manifests itself in the form of a multi-line pattern in the fluorescence line narrowing (FLN) spectrum [1]. At higher temperatures phonon assisted processes become dominant and the energy selective multiline pattern is lost. In $[Ru(bpy)_3][NaCr(ox)_3]$ static FLN spectra show no evidence for resonant energy transfer. However, the time-resolved FLN spectra in Fig. 1 show strong spectral diffusion. In contrast to the Rh containing system, this is due to efficient quasi-resonant energy transfer within the same component of the $^4A_2 \rightarrow ^2E$ transition. This is directly correlated to the smaller inhomogeneous line width of 1.3 cm^{-1} as compared to the 4.4 cm^{-1} for the latter, and thus the higher concentration of species which are truly resonant within the homogeneous line width of 0.02 cm^{-1} at 1.4 K.

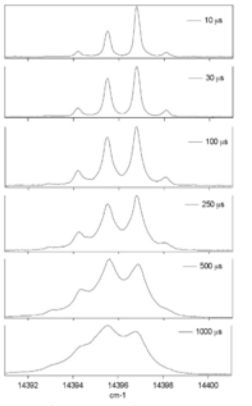

Fig. 1: Time-resoved FLN spectrum of the $^4A_2 \rightarrow ^2E$ electronic origin of $[Ru(bpy)_3][NaCr(ox)_3]$ at 1.4 K.

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Physical Chemistry **396**

Femtosecond Mid-Infrared Spectroscopic Studies of Aqueous Bimolecular Acid-Base Neutralization Reactions

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Bimolecular acid-base neutralization reactions are of fundamental importance in chemistry and biology. We investigate this fundamental acid-base neutralization reaction by use of femtosecond mid-infrared spectroscopy. We use a photoacid, to optically trigger proton transfer reaction, to be neutralized by carboxylate bases. We follow the dynamics in real time by inspection of vibrational marker modes of the proton donor, proton acceptor as well as of the hydraten proton species. With this approach we have explored three different types of acid-base reaction pathways in aqueous solution, by adjusting the base concentration: (a) "tight" acid-base complexes, (b) "loose" complexes, and (c) uncomplexed acid and base. For low base concentrations pathway (c) dominates and the dynamics is governed by diffusion. For pathway (a) we observe a full transfer within our time resolution of 150 fs [1]. More importantly, pathway (b) has been monitored to occur through a von Grotthuss hopping mechanism, where the proton/deuteron first transfers to the water bridge, followed by a second transfer to the base [2].

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Physical Chemistry **397**

Distance Dependence of the Ultrafast Dynamics of Photoinduced Interfacial Electron Transfer in the Dye-Sensitization of Titanium Dioxide Nanoparticles

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The effect of electronic and nuclear factors on the dynamics of dye-to-semiconductor electron transfer (ET) was studied employing Ru(II) polypyridyl complexes grafted onto mesoporous transparent films made of nanocrystalline metal oxide particles.

Two different approaches were strived to understand the dependence of the kinetics of charge injection and recombination processes upon the distance separating the dye molecules and the redox active surface:

A series of bridged sensitizers containing *p*-phenylene spacers of various lengths and phosphonic anchoring groups were adsorbed onto TiO_2 films. The kinetics of both forward- and back-electron transfer were recorded by use of time-resolved spectroscopy in the fs-ps and µs-ms time domains. The ultrafast electron injection was found to be biphasic with a clear exponential distance dependence of the fast kinetic component. A damping factor of $\beta = 0.2$ Å^{-1} was obtained for the distance dependence of charge injection, while a value of $\beta = 0.5$ Å^{-1} was measured for the charge recombination of conduction band electrons with oxidized sensitizer molecules.

In a second approach, we investigated the kinetics of interfacial ET across a thin layer of insulating Al_2O_3 deposited onto TiO_2 nanocrystalline particles. In this case efficient charge injection was observed over distances up to 60 Å and an upper limit for the distance parameter $\beta < 0.3$ Å^{-1} was estimated. In contrast, the half-lifetime for back ET decreased exponentially with the thickness of the alumina layer with $\beta = 0.15$ Å^{-1}.

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Physical Chemistry **398**

Probing the hydrogen binding sites of cytosine in the gas phase

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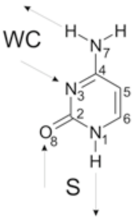
Lactam-lactim and amino-imino tautomerism lead to a total of six cytosine tautomers. Three of them have been identified in the gas phase. The conformers of those three tautomers offer a total of 11 double hydrogen binding sites, depicted below (WC=Watson-Crick, S=Sugar-Edge, W=Wobble). Cytosine (Cyt) and 1-methylcytosine (1MCyt) as well as their H-bonded complexes with 2-pyridone (2PY) were investigated by dispersed laser fluorescence and IR/UV depletion spectroscopy. One isomer of 1MCyt·2PY and two isomers of Cyt·2PY have been found upon two color resonant two photon ionisation (2C-R2PI). To identify the observed complexes, the binding energies and frequencies of all possible dimers have been calculated by density functional theory (DFT) and correlated *ab initio* (RI-MP2) methods.



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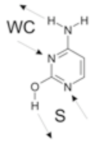

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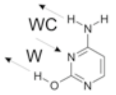

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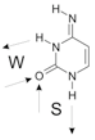
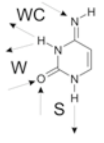


3a



3b

Physical Chemistry **399**

A New Spectrometer for Measurements on Very High Atomic and Molecular Rydberg States

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A new spectrometer for high resolution spectroscopic measurements in the VUV wavelength region has been developed based on ultra-high vacuum technology. The apparatus has been designed such as to fully exploit the FT-limited bandwidth (50 MHz) of our new all-solid-state VUV laser system [1]. Polar molecules in the background gas of conventional high-vacuum chambers, as well as external sources of electric and magnetic stray fields commonly restrict observation of Rydberg states to below n=200. By optimizing the geometry of the electrodes and by reducing the background gas pressure to below 5×10^{-10} mbar, it is possible to alleviate substantially some of the apparative limitations associated with stray electric fields within the photoexcitation region and to observe Rydberg series up to n»200. Minimization of the supersonic probe gas beam divergence in the experimental setup by means of a double skimmer arrangement allows us to diminish the extent of Doppler broadening to below the VUV laser bandwidth. High-resolution spectra of krypton in the autoionizing region between the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds have been recorded by single-photon VUV excitation. The performance and specifications of the spectrometer as well as the analysis of the spectra will be presented.

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Physical Chemistry **400**

Sm^{2+} as a probe of crystal field in fluorides and fluorohalides : effect of pressure and temperature

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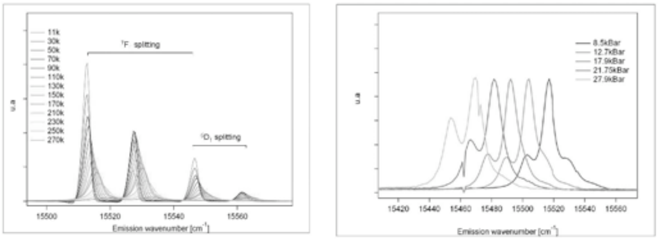
The luminescence of Sm^{2+} ($4f^6$ like the well studied Eu^{3+}) is very sensitive to the crystalline environment. In this work, we want to study the effect of pressure and temperature on the crystal field and electronic structure of Sm^{2+} not only in higher symmetry hosts such as tetragonal SrFBr, but also in low symmetry crystals such as $BaMgF_4$ and $SrAlF_5$ which are potential hosts for UV laser components. The study of the entire range of the $^5D_0$-^7F_j transitions of Sm^{2+} in $SrAlF_5$ and specially the $^5D_0$-$^7F_0$ transition permits to observe the luminescence of the 4 different substituted sites and to suggest a phase transition at "negative" pressure in agreement with the crystal structure of the $Ba_{0.43}Sr_{0.57}AlF_5$[1] The ratio of the splitting of the $^7F_1$ and $^5D_1$ levels in SrFBr : Sm^{2+}(which are related to the crystal fields parameter B^2_0) changes dramatically with increasing pressure : this behavior is discussed in comparison with spectra in other crystals.



Effect of pressure and temperature on the $^5D_1 \rightarrow {}^7F_1$ transition in SrFBr : Sm^{2+}

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Physical Chemistry **401**

Ultrafast Second Harmonic Generation at Liquid Interfaces

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Investigating the structural and dynamic properties of molecules adsorbed at the interface between two immiscible liquids represents one of the more challenging spectroscopic problems. Because of the complexity of fluid interfaces and the difficulty to experimentally access these buried regions, their spectroscopic features are essentially unknown.

In order to investigate ultrafast dynamics at liquid/liquid interfaces, the first experimental method developed in our group was the evanescent transient grating technique [1]. However, the interfacial selectivity of this method was limited by the depth of the evanescent optical field generated upon total internal reflection at the boundary region.

On the contrary, the second harmonic generation (SHG) spectroscopy has been shown to have a greater surface-specificity, since the inversion symmetry is broken only in the interfacial region between the two centrosymmetric media. Moreover, the success of this technique comes from performing SHG measurements under total internal reflection conditions (TIR-SHG), thus obtaining much greater sensitivity than the normal SHG [2].

We are developing a time-resolved second harmonic generation (TR-SHG) experiment at liquid interfaces with a typical pump and probe geometry, optimizing the SH generation and detection as a function of the polarizations, the incident angle, the dye concentration etc. Preliminary time-resolved measurements, using a femtosecond near-infrared laser and a NOPA output between 480 and 700nm as pump/probe beams and malachite green (MG, high hyperpolarizability) as the interfacial dye, will be presented.

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Physical Chemistry **402**

Resorufin in the Channels of MCM-41: In Situ Detection of Release Profiles

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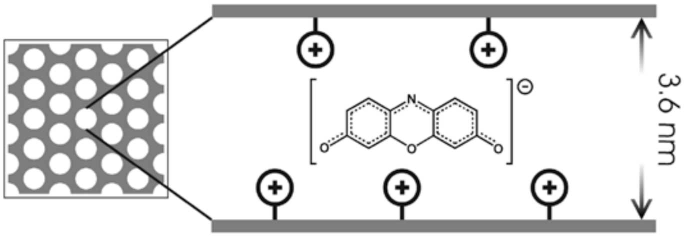
Controlled release of guest molecules from functionalized mesoporous silica is of interest for the development of novel drug delivery systems [1]. A general problem in the design of such materials is the quantification of the actual release profile. We have devised an in situ method using the strongly luminescent resorufin anion as a drug model. Adsorption of resorufin in the channels of MCM-41 is accomplished by functionalization of the pore surface with tetraalkylammonium cations. In agreement with results reported for resorufin in zeolite L [2], luminescence quenching occurs upon incorporation of resorufin into the host material. The significant luminescence intensity difference between resorufin in MCM-41 and free resorufin enables sensitive monitoring of the release process.



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Physical Chemistry **403**

Study of metastable states of rare gases

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Metastable electronically excited states of atoms and molecules are produced in a pulsed discharge at the exit of a pulsed nozzle and cooled to a translational temperature of $\sim 1\,\mathrm{K}$ in a supersonic expansion. The metastable atoms are characterised by time-of-flight mass spectrometry following photoionisation with visible and UV laser radiation. Transitions from the metastable states to higher-lying electronic states, primarily Rydberg states, have been measured and analysed. The metastable states were also characterised by high-resolution photoelectron spectroscopy and information on the energy level structure of the cations could be derived. Spectroscopic measurements on metastable states provides access to atomic and molecular states not easily accessible from the ground state as will be shown with the example of He, He_2, and other rare gas atoms and dimers.

Physical Chemistry **404**

Self-Assembly of Azure A Molecules on a Gold Substrate Investigated by Scanning Tunneling Microscopy

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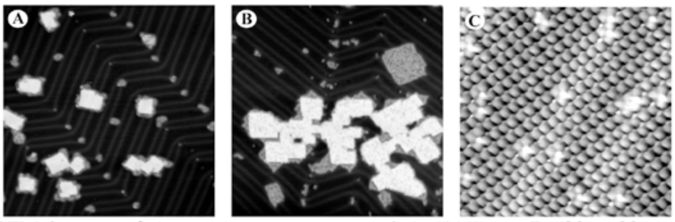
Nanostructures, CH-1015 Lausanne, Switzerland

Molecular self-assembly at surfaces is governed by the subtle balance between intermolecular and molecule-surface interactions. Understanding supramolecular aggregation starting from these basic interactions is a prerequisite to control the self-assembly for future use in mass fabrication of nanoscale devices. The Scanning Tunneling Microscope (STM) is an extremely efficient tool for such studies revealing in situ the resulting molecular arrangement. In particular, experiments performed under ultra-high vacuum (UHV) elucidate the intermolecular interactions and offer control of the coverage. Here we have investigated the self-assembly of Azure A molecules on the herringbone reconstructed (111) surface of gold using a Low-Temperature STM in UHV. We prepared the sample by sublimation in UHV onto a cold substrate (50K), followed by a brief thermal annealing. Depending on the amount of deposited molecules, various microscopic patterns (Fig. A and B: 0.15 and 0.30 monolayer coverage, respectively) exhibiting an internal order (Fig. C) were observed.



STM images of Azure A on reconstructed Au(111): A, B (80 x 80 nm); C (10 x 10 nm).

Physical Chemistry **405**

MQDT Calculations of Rydberg States of Krypton: μ versus η Defect and the Hyperfine Structure of $^{83}\mathrm{Kr}^+$

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A phase-stabilised backward wave oscillator (BWO) in the 260–380 GHz range was combined with a VUV laser system to record high-resolution spectra of high-n Rydberg states of krypton (^{84}Kr and ^{83}Kr) at sub-MHz resolution and with mass selection.[1]
A multichannel quantum defect theory (MQDT) treatment of the hyperfine structure [2] was used to analyse the millimetre wave data in combination with recent high-resolution VUV laser data [2] and the available data from the literature in order to obtain improved MQDT parameters and hyperfine structure data of the ^{2}P ground electronic state of $^{83}\mathrm{Kr}^+$. The results using either μ or η defects [3] are discussed.

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Ch. Jungen, pers. commun.

Physical Chemistry **406**

A HIGH-RESOLUTION STUDY OF THE METHYL CATION

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We present high-resolution photoionisation and pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of CH_3, CD_3, CH_2D and CD_2H recorded near the adiabatic ionisation thresholds. The radicals where produced by 193 nm photolysis in a quartz capillary and cooled in a supersonic expansion to temperatures below 40 K. Nitromethane was selected as the photolysis precursor molecule and offers clear advantages over other precursor molecules such as CH_3I, CH_3Br, $(CH_3)_2S$, $(CH_3)_2CO$. In CH_3^+ rotational autoionisation mediated by the quadrupole of the ion core was observed in the photoionisation spectrum as Rydberg series of principal quantum numbers $n = 30 - 50$ converging on higher rotational levels. The photoelectron spectra provide detailed information on the photoionisation dynamics of methyl and can be understood semi-quantitatively in the realm of the direct orbital ionisation model of Reference [1]. However, the intensity distribution can only be fully accounted for by taking rotational channel interactions into account. Improved values for the adiabatic ionisation potentials were found to be: 79356.2(15) cm^{-1} for CH_3, 79338.8(15) cm^{-1} for CD_3, 79319.1(15) cm^{-1} for CH_2D and 79296.4(15) cm^{-1} for CD_2H.

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Physical Chemistry **407**

Assessment of Particulate Exposure and Surface Characteristics in Association with Urinary Levels of Biomarkers of Oxidative Stress

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The increase of exposure to PM_{10} and $PM_{2.5}$ (particulate matter with aerodynamic diameter smaller than 10 µm and 2.5 µm) has been found to be associated with a range of adverse health effects. Surface characteristics (chemical reactivity, surface area) are considered of prime importance to understand the mechanisms which lead to harmful effects. A hypothetical mechanism to explain these adverse effects of particulate matter is the ability of some components (organics, metal ions) adsorbed on these particles to generate reactive oxygen species (ROS), and thereby to cause oxidative stress in biological systems. ROS can attack almost any cellular structure, leading to the formation of a wide variety of degradation products which can be used as a biomarker of oxidative stress.
The aim of the present research project is to demonstrate an association between the exposure to Diesel exhaust particulate (DEP) and the oxidative stress status. For that purpose, a survey is conducted in real occupational situations where workers are exposed to DEP (bus depots). Several biomarkers of oxidative stress have been determined either in urine or serum of volunteers, and levels will be discussed in relation to exposure variables.
In order to bring some insight into the relation between the particulate surface characteristics and the formation of ROS by-products, different exposure variables have been considered: particulate number, distribution and surface (SMPS); particulate mass (gravimetry); elemental and organic carbon (coulometry); total adsorbed heavy metals (atomic absorption); surface functional groups present on particles (Knudsen flow reactor).

Physical Chemistry **408**

High Resolution Diode Laser IR-Spectra Measured in a Pulsed Slit Nozzle Supersonic Jet Expansion

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Rotationally resolved high resolution IR-spectra are of fundamental importance to understand intramolecular dynamics in polyatomic molecules [1,2] and to model IR-absorption spectra in the atmosphere [3] and in interstellar space [4]. Due to the population of low lying vibrational states and small rotational constants (resulting in a large number of rotational lines), often IR-spectra of medium sized molecules measured at room temperature are too congested to be rotationally resolved, even with state of the art high-resolution IR-absorption techniques. The spectra are strongly simplified if the rotational and the vibrational degrees of freedom are cooled down efficiently in a molecular beam. The molecular beam technique is also ideally suited to investigate the IR-spectra of small clusters like dimers, trimers, or tetramers.
We have set up an IR-diode laser spectrometer and have combined it with a pulsed molecular beam. To increase the optical absorption length a slit nozzle has been used and rotational temperatures below 10 K could be reached. Resolved IR-spectra of CF_4, CF_3CCH and other molecules will be presented and their analysis discussed.

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Physical Chemistry **409**

On the Possibility of Stable Nuclear Spin Symmetry Isomers in H_2O

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The separation of the stable nuclear spin symmetry isomers para- and ortho-H_2 has been known already in 1929 through a cooling process in the presence of a magnetic catalyst [1]. It is also known that nuclear spin symmetries may even be preserved in chemical reactions [2]. The preparation of stable spin isomers in H_2O is of great potential importance in NMR experiments. Recently it was claimed that para- and ortho-H_2O could be separated by adsorbing it to a charcoal adsorbant and could be stored for months at 255 K [3,4]. Probing the $3_{0,3}$ -ortho and the $0_{0,0}$-para rotational transitions by THz- and IR-absorption these authors found a deviation from the statistical 3:1 ortho-para ratio after desorption.

We have applied two different infrared spectroscopic methods, high resolution FTIR-spectroscopy in a long path absorption cell and highly sensitive near-IR cavity ring down spectroscopy, in trying to reproduce the results from [3,4]. However, we could not detect any preparation of stable, long lived para- and ortho-H_2O by adsorption on Purolite Macronet MN-200 or silica gel. From the signal to noise ratio of our experiments we conclude that we should have seen deviations from the statistical 3:1 ratio larger than 5-10 %, if any, but no such deviation was found in the IR-spectra [5].

The nuclear spin conversion of water on the surface of porous materials has also been recently reviewed by Limbach et al. [6]

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Physical Chemistry **411**

Ultrafast Dynamics in Pentacene Crystals and Films

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Pentacene, with one of the highest mobilities of organic semiconductors, has in recent years experienced an intensive research effort due to its potential for use in organic electronics. In pentacene, the excitonic fission process from the lowest singlet exciton to a pair of lowest triplet excitons S_1□$2T_1$ is energetically allowed, while in the other polyacenes this process is prohibited [1].

Here we present a comparative study of the ultrafast dynamics in pentacene crystals, undoped pentacene films and C_{60}-doped pentacene films using optical pump-probe spectroscopy, measuring the photoinduced (PI) changes in the reflectivity $\Delta R/R$ and transmissivity $\Delta T/T$. The processes involved include singlet exciton recombination, singlet-triplet fission, triplet state absorption, and charge-transfer dynamics. In pentacene crystals the dynamics is dominated by triplet production which occurs on a sub-picosecond time scale, and displays as a very broad and long-lived PI absorption centered at 1.4 eV. In pentacene thin films, undoped or C_{60}-doped, this feature is heavily suppressed, and the dynamics becomes strongly temperature dependent in contrast to crystals which display no temperature dependence. This is attributed to competing ultrafast processes by trapping in the undoped films and electron transfer onto C_{60} in the doped films. Furthermore, the temperature dependence of both films at 1.83 and 1.93 eV shows signatures of a PI structural phase transition which is currently under investigation.

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Physical Chemistry **410**

A theoretical determination of the excited states dynamics of nitric acid (HNO_3)

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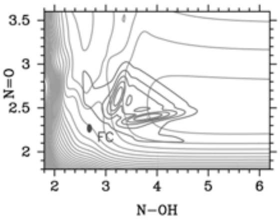
The photochemistry of nitric acid (HNO_3) [1] is of interest due to its role in atmospheric chemistry, particularly to the ozone–governing processes. Additional to the vertical excitation energies, the potential energy surfaces (PES) of the four lowest lying states of HNO_3 S_0(A'), S_1(A"), S_2(A"), and S_3(A'), were calculated with the ab initio MCSCF–CI method to understand the excited state dynamics. It is shown that the behavior of the important bifurcation dissociation process:

$$HNO_3(S_3) \longrightarrow OH + NO_2$$
$$HNO_3(S_3) \longrightarrow O + HONO$$

is governed by the PES topology in 2 coordinates: $R(N\ddot{-}O)$ and R(N–OH).



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Physical Chemistry **412**

Excited-state proton/H-atom translocation along an H-bonded cluster

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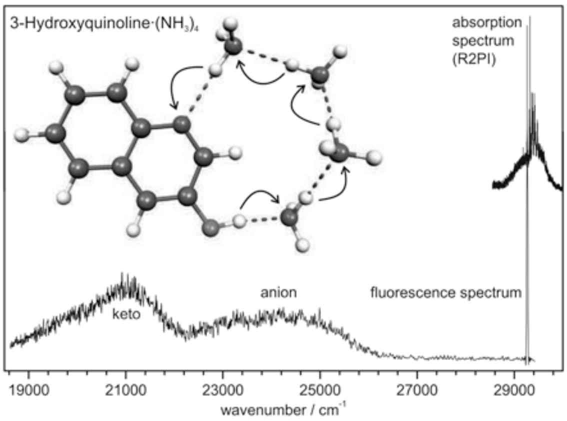
We have employed supersonic-jet cooled 3-hydroxyquinoline·$(NH_3)_n$ clusters for the study of proton and H-atom translocation reactions along hydrogen-bonded wires. 3-hydroxyquinoline (3HQ) has an -O-H donor and a quinolinic H-acceptor site and can act as an H-bonding scaffold for solvent wires. The acid/base properties of 3HQ increase strongly upon photoexcitation, leading to proton or H-atom transfer [1] along the H-bonded solvent wire. The $S_1 \leftarrow S_0$ resonant two-photon ionization (R2PI) spectrum is characteristic of the *enol* 3HQ $\pi\pi^*$ excited state. In contrast, the fluorescence spectra exhibit broad bands in the blue and green spectral region. The former is characteristic for the $3HQ^{*-}$ anion, the latter for the 3-ketoquinoline ($3KQ^*$) tautomer. We propose that photoexcitation triggers formation of a protonated solvent cluster and the $3HQ^{*-}$ anion. Further H-atom translocations along the ammonia wire lead to $3KQ^*$ which in turn exhibits green fluorescence.



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Physical Chemistry **413**

Rebinding Molecular Dynamics Simulations of Nitric Oxide to the V68FMyoglobin Mutant

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The study of reactive processes in chemically and biologically relevant systems is a topic of much current interest. Here, an atomistically detailed picture of NO rebinding from myoglobin V68F is presented. Using reactive molecular dynamics [1] the rebinding probability as a function of time after dissociation is calculated. Reactive molecular dynamics considers two intersecting potential energy manifolds which dissociate to different adiabatic states. During the simulations, crossings are detected by monitoring an energy criterion and the surfaces are mixed over a finite number of time steps. The unbound surface (Fe...NO) is a standard force field, whereas the bound surface (Fe-NO) is based on ab initio calculations. The rebinding is nonexponential in time, in agreement with experimental studies [2] and can be described using two time constants. Particular emphasis is paid to the asymptotic separation Δ between the two potential energy manifolds. An extension of the original reactive molecular dynamics approach with a conformationally varying Δ is discussed.

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Physical Chemistry **414**

In Situ EXAFS/XRD Study on a Pd/ZrO$_2$ Catalyst Applied in Methane Combustion

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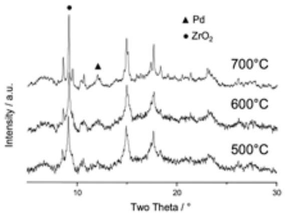
Catalytic combustion has received much attention amongst catalysis researchers due to its importance in various technical applications. Potential applications in energy generation, such as in lean-burn natural gas vehicles and gas-turbines, or pollution control have stimulated research in this area, resulting in a plethora of catalysts [1]. Among these, palladium based catalysts have been regarded as the most active for catalytic methane combustion. The nature of the active species in these catalysts is still subject to debate. While PdO seems to be more active than Pd, catalysts containing both metallic and oxidized palladium are reported to outperform even PdO. Relevant data on these systems can almost only be obtained by *in situ* methods [2]. In this contribution an *in situ* EXAFS/XRD investigation of a Pd/ZrO$_2$ catalyst will be discussed. The effect of temperature and atmosphere (H$_2$/He, O$_2$/He, CH$_4$/O$_2$/He) on the Pd oxidation state and crystallite size will be shown and correlated to the activity of the catalyst during catalytic methane combustion.



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Physical Chemistry **415**

Stark Effect in Rydberg States of Neon

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The Stark spectra of Rydberg states of neon with effective principal quantum number n^*=25 belonging to the $^2P_{3/2}$ and $^2P_{1/2}$ ionisation thresholds, respectively, have been measured at electric fields between 0 and 180 V/cm following two-photon excitation from the Ne ($^1S_0$) ground state via the 3s$[3/2]_1$ and 3s$'[1/2]_1$ intermediate states. Spectra of $M_J = 1$ and $M_J = 0$ Stark states are recorded separately using linearly polarised lasers with polarisation vectors either parallel or perpendicular to the static electric field. These spectra are very different in appearance reflecting the very strong dependence of the cross sections to the accessible channels on the polarisation vectors already observed in zero field measurements [1]. The spectra provide information on the quantum defects of the s, p and d Rydberg levels of neon and are analysed using multichannel quantum defect theory (MQDT).

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Polymer Science **416**

Bulk Heterojunction Polymer Solar Cells

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Nanostructured phase-separated blends, or bulk heterojunctions, of conjugated polymers and acceptor materials (e.g. fullerenes, inorganic nanocrystals, or a second polymer) form an attractive approach to large-area, solid-state organic solar cells. The key feature of these cells is that they combine easy processing from solution on a variety of substrates with promising performance. Efficiencies up to 4-5% in solar light have been achieved. Further improvements can be expected when the energy lost in the initial electron transfer step can be reduced. This increases the open circuit voltage and power conversion efficiency. Another important parameter that currently limits the performance of polymer solar cells is the mismatch between the absorption spectrum of the photoactive layer and the solar emission. Typically, the best polymer solar cells absorb light with wavelengths below 650 nm, while the solar photon flux maximizes around 700 nm and extends into the near infrared. Low band gap materials can alleviate this problem. We will present new low band gap polymers that are able to convert solar light up to 1000 nm in bulk heterojunction devices.