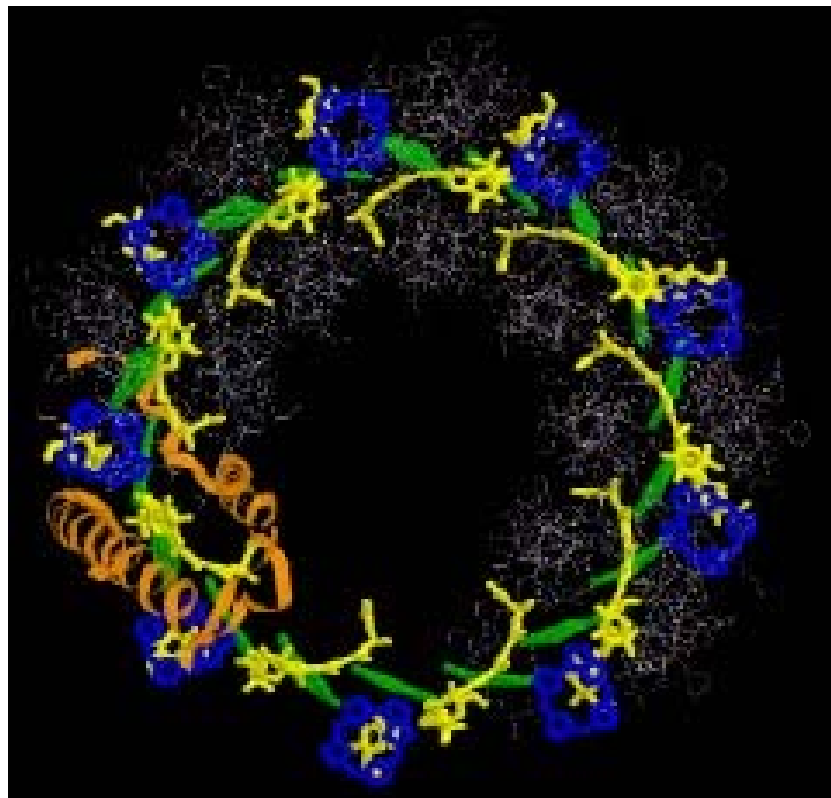


Sfb 450
Symposium ACU IV

October 8-10, 2009

*Analysis and control of ultrafast
photoinduced reactions*



2nd Ed.

Program and Abstracts of the Workshop ACU IV

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Welcome to ACU IV!

After 12 years of successful operation, the Sfb 450 “*Analysis and Control of Ultrafast photo induced reactions*” will come to an end on June 30 of the coming year. Its fourth status seminar ACU IV intends to demonstrate what has been accomplished so far, what is new and what needs still to be done. In order to allow for a comparison with related activities elsewhere, we have invited experts from Germany and from abroad next to our friends and colleges from Berlin. All participants, and especially those, who came from far away are most welcome. We are curious and look forward to hearing their opinions and ideas!

Among them there are also those colleagues, who have accompanied the Sfb 450 over its four funding periods as referees. We owe them many thanks for their competence and trust. Guided by their recommendations, the DFG was willing to generously finance our research program over twelve years. We are very grateful for this continued support. We would also like to thank our participating institutions: The Freie Universität, the Humboldt Universität, the University of Potsdam, the Max-Born-Institut, the Fritz-Haber-Institut and the Helmholtz research center, who constantly stood behind us in support.

The scientific activities of our Sfb 450 successfully brought together physicists and chemists as well as theoreticians and experimentalists. This has allowed for a very active and interdisciplinary research network to establish itself, guided by the fascinating topic: “*Analysis and Control of Ultrafast photo induced reactions.*” As a result, a large number of prominent and frequently cited publications have emerged from this fruitful mixture of subjects and participants. Furthermore, the Sfb 450 has allowed for many young scientists to obtain their masters, diploma, doctoral degree or even habilitation, providing the opportunities for future carriers. The numerous professorial positions taken by former members of the Sfb 450 are an excellent example.

But this is not yet the end, and nine thrilling months are still ahead of us to reach out for final goals. From the perspective gained, new horizons for future endeavors will hopefully come forth! ACU IV is also intended to ring the bell for a great finish, until the final curtain falls:

“It ain't over ‘til the fat lady sings”

Berlin. October 2009

Ludger Wöste



Analysis and Control of Ultrafast Chemical Processes in Molecules and Aggregates

Lindinger, T. Siebert, L. Wöste

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With the advent of ultrafast laser sources, the utilization of pump & probe spectroscopy in the fs-regime has allowed for detailed insights to elementary dynamical molecular processes such as vibrations, fragmentation, isomerization, internal vibrational relaxation (IVR), neutralization, ionization, charge reversal and even photo-association. These phenomena were first investigated in great detail on simple molecular systems in the controlled environment of the gas phase. However, these fundamental studies soon lead to the realization that the observed photo-induced processes could not only be monitored, but also guided along a desired path in real time by the applied light fields. As a consequence, the employed laser pulses rapidly evolved from simple pump&probe sequences to highly structured light fields, optimally shaped in phase, amplitude and polarization. Exciting features could be extracted from the optimized pulse shapes, promoting a fruitful convergence with theory. These achievements demand for new challenges and applications: examples are the control of binary reactions and photo-catalytic processes together with a significantly increased spectral range and sub fs-time resolution for addressing the respective electron dynamics, exploiting the nonlinear response regime and reaching out for the atmosphere.

Towards molecular computing.

- New directions in laser chemistry -

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It has been said that the next new development in computer science may be molecular computers, based on ultrafast molecular switching on a fs time scale („frozen nuclei“) and in a nanoscopic regime, making use of the two-dimensional vibrational spectroscopy of even small molecules.

A necessary ingredient of the operation is pulse shaping to optimize switching and to control switching (cross-coupling) that would otherwise not occur. The concept will benefit from strong-field excitation. Ladder climbing among vibrational modes is important and will be experimentally demonstrated for carbonyl compounds.

A small attempt will also be made to connect to existing technology.

Analysis and control of the dynamics of molecules and nanoparticles

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The dynamics of molecules and nanoparticles in intense laser fields is of great scientific interest. Ionization is the most fundamental of the processes induced by intense femtosecond laser pulses. Molecules and nanoparticles are suitable model systems to investigate the ionization dynamics due to their unique properties. The nuclear degrees of freedom in a molecule enable to study the rotational and vibrational excitation of molecular cations and dissociative ionization. Nanoparticles show a strong nonlinear behavior in intense laser fields leading to interesting phenomena, such as the ejection of fast electrons. We will report on the control of the ultrafast ionization and dissociation dynamics of molecules as well as on the electron emission dynamics of isolated nanoparticles. The following issues will be discussed:

- Control of the internal degrees of freedom of N_2^{+} following chirped pulse multiphoton ionization of molecular nitrogen is investigated, where we find a strong influence of the chirp of the laser pulse on the rotational state distribution of N_2^+ ($B^2\Sigma_u^+, v=0$).
- Ultrafast ionization dynamics of C_2H_5BrCl and C_3H_7BrCl is studied with respect to control the dissociative ionization of bromochloroalkanes using shaped laser pulses ($\lambda = 804$ nm).
- Electron emission dynamics of isolated NaCl nanoparticles has been investigated using femtosecond dual-pulse laser excitation ($\tau = 85$ fs, $\lambda = 804$ nm). An enhanced electron emission and an increase in the electron kinetic energy are observed for characteristic time delays indicating an enhanced coupling of the laser pulses to the nanoparticle.
- The waveform control of the electron emission from isolated SiO_2 nanoparticles is investigated using intense, few-cycle ($\tau < 5$ fs) laser fields. A significant increase in the cut-off in the electron energy spectra of SiO_2 nanoparticles as compared to Xe for the same laser conditions is observed.

Optically driven adiabatic transfer processes: Historical perspective and new developments

Prof. Dr. Dr. h.c. Klaas Bergmann, Technische Universität Kaiserslautern, Fachbereich Physik, Erwin-Schroedinger-Str. , 67653 Kaiserslautern - Germany

First, comments about how the method of stimulated Raman adiabatic passage came about will be offered and key steps along the line will be mentioned. Second, new developments and applications of STIRAP, mainly from labs outside of Kaiserslautern, will be presented. These new developments include optically driven adiabatic transfer processes in a solid state environment, progress towards making ultracold molecules from degenerate atomic quantum gases, as well as new insight into how to optimize the transfer efficiency and attempts to apply the STIRAP concept in classical systems. Obviously, a detailed discussion of all those aspects is not possible, rather some key aspects will be mentioned and commented on.

FROM MOLECULES TO CRYSTALS: COHERENT ROTATIONAL, PHONON AND VIBRONIC DYNAMICS

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The coupling of coherent quantum systems to the environment and the correlation of decoherence with the number of degrees of freedom is an important topic. We pick up and trace coherences in free molecules, matrix-isolated molecules and molecular crystals with delocalized excitations up to a mesoscopic scale. We demonstrate, that collinear pump-probe type measurements of birefringence (Optical Kerr Effect) allow a very sensitive detection of induced anisotropies. An alignment $\langle \cos^2\theta \rangle$ of the molecular axis to the pump-field's linear polarization of the order of 10^{-5} can still be resolved. We derived detailed information for the J-dependence of dephasing, depopulation and thermalization cross-sections for N_2 -molecules at ambient conditions. Specific rotational wavepackets from selected J sub-ensembles can be prepared by tuning the pulselength for a nonresonant pump between adiabatic and nonadiabatic with respect to the Jstate transition energies and by adding appropriately timed second pulses (C5). Scaling to a molecular quantum-crystal with cryogenic pH_2 , kept at a temperature below the rotational energies, yields to coherent oscillations in the 94fs range, which last for about 1000 periods. They originate from delocalized rotons with subtle 0.5fs splitting into three |M| sub-states, which can be resolved and is also visible in a beat pattern of 17ps in time frame. These rotons interact with a single, delocalized lattice phonon with 900fs period, which follows

the Raman-selection rule. With phase-stabilized pulse trains from a pulse shaper unit we imprint frequency combs into isolated Br₂-molecules embedded in a classical Ar-matrix. In this rational control scheme the combs are derived from the spectroscopic information on vibronic zero-phonon line and phonon-sideband progressions. The combs become active in the molecules only if the pulse sequence is absorbed coherently. We demonstrate by the phonon-sideband response, that a coherent, coupled vibron-phonon wavepacket is prepared in a volume containing the chromophore and of the order of 1000 matrix-atoms. Coherent control of predissociation via selective excitation of relevant phonon-modes according to the theoretical prediction (C1) is pursued.

Singlet-Triplet Coupling in Organic Chromophores

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Inter-system crossing (ISC) plays a central role in photochemistry, photobiology, and photodynamic therapy since many photo-induced chemical reactions proceed on the first excited triplet hypersurface. While a high triplet quantum yield is desirable for photosensitizers, rapid quenching of the T₁ state is preferable for photoprotectors. A prerequisite for the understanding of the underlying mechanisms is the knowledge of the excited states and their interactions. State-of-the-art quantum chemical methods can help to shine light on the cascade of relaxation processes following the primary photo excitation.

The combined density functional and configuration interaction method (DFT/MRCI)^[1] has proven to yield high-quality electronic excitation spectra. Electronic spin-orbit matrix elements are calculated using the SPOCK^[2-5] program package while vibrational contributions to ISC rates are determined using the SNF^[5] and VIBES^[6] programs. By means of the above mentioned methods, we have investigated the electronic spectra and spin-orbit coupling of a variety of organic chromophores. In this contribution I would like to present our results on a few model cases: (1) flavone where the ISC mechanism follows the well-known El-Sayed rules,^[7] (2) porphyrin where vibronic spin-orbit coupling between S₁ and T₁ states is responsible for the high triplet quantum yield,^[8,9] and (3) flavin where different mechanisms have to be invoked in the gas phase and in solution^[10,11]

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Photochemistry of DNA bases and base clusters

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The photochemistry of large molecules may be due to inherent properties of the light-absorbing chromophores, but can also be dominated by intermolecular interactions. The latter play a very important role in biological systems, where well defined macromolecular structure determines molecular properties and function.

We investigate the photochemistry of DNA building blocks in vacuo and reproduce the relevant intermolecular interactions of base pairing, base stacking and solvation in small molecular clusters. The combination of gas-phase spectroscopy and high-level theory allow a detailed description of excited state processes and we present examples for intra- and intermolecular reaction and relaxation pathways. From an evolutionary point of view, we expect that all DNA constituents must be highly resistant to photochemical damage, but we show that photostability is sensitively connected to tautomeric structure and intermolecular conformation.

ATTOSECOND STEERING OF ELECTRONIC MOTION

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Using a reaction-microscope, three-dimensional electron and ion momentum (\vec{P}) spectra have been recorded for carrier-envelope-phase (CEP) stabilized few-cycle (~ 5 -6 fs), intense ($4 \cdot 10^{14}$ W/cm²) laser pulses (740 nm) interacting with atoms and molecules. In a collaborative effort experiments on He atoms have been performed at the MPQ whereas the fragmentation of H₂ molecules was investigated at the new CEP stabilized pump-probe facility at the MPIK. For He atoms preferential emission of low-energy electrons ($E_e < 15$ eV) to either hemisphere is observed as a function of the CEP¹. Clear interference patterns emerge in \vec{P} -space at CEPs with maximum asymmetry, interpreted as attosecond holographic “self”-images of rescattered electron wave-packets by means of a simple model and in line with previous theoretical

predictions². For H_2^+ molecules we do observe, for the first time and different from earlier measurements³, electron localisation in the 1ω and effective 2ω fragmentation channels depending on the kinetic energy release (KER)⁴ in general agreement with but at better significantly better contrast than predicted by theory⁵. Moreover, we find the asymmetry varying as a function of the orientation of the molecules and inspect CEP dependent coincident electron emission from the first step, i.e. ionizing the H_2 molecule and starting the bound-state dynamics in H_2^+ . Finally, we present results of wave-packet dynamic calculations, show data for more complicated molecules and envision future directions.

¹ R. Gopal et al., Phys. Rev. Lett. (accepted)

² D.G. Arbó et al. Phys. Rev. A **74**, 063407 (2006).

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⁴ M. Kremer et al., Phys. Rev. Lett. (submitted)

⁵ V. Roudnev and B. D. Esry, PRA **76**, 023403 (2007)

Orientation-dependent ionization in intense laser pulses: A tool for time-resolved imaging?

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The possibility of performing time-resolved imaging studies of molecules using ultrashort intense light pulses is currently steering a lot of interest. Many schemes are based on the so-called three-step model in which a strong linear polarized laser pulse distorts the Coulombic potential of a molecule in such a way that close to the electric-field maxima of a laser cycle an electron can tunnel out. This electron is subsequently accelerated by the electric field until the direction of the field vector reverts and the released electron may be driven back to the ion it originated from. This encounter may induce processes like elastic scattering, inelastic scattering (including excitation or fragmentation), or high-harmonic generation. In the latter case the electron recombines radiatively with its ion. All the three processes should reveal structural information while the laser-cycle dependence of the ionisation step provides time resolution.

In this talk the first step of the three-step model, strong-field ionisation of molecules, is investigated in more detail. This should shed more light on the question how the created and thus also the rescattering electron wavepacket looks like for different molecules and what consequences this has for imaging schemes based on the three-step model. Furthermore it is discussed whether the ionisation step itself and thus the so-called direct electrons that form

the vast majority may reveal (time-resolved) structural information. For this purpose, two theoretical approaches have been developed recently. In one case the time-dependent Schrödinger equation (TDSE) describing both electrons of an H₂ molecule (in full dimensionality) has been developed. An alternative approach is based on the single-active-electron (SAE) approximation, but allows for treating in principle arbitrary molecules. After a discussion of the validity of the SAE for H₂ its orientation-dependent ionisation is discussed. Then the results obtained within SAE for N₂, O₂, and CO₂ are compared to experiment. An explanation is provided for the surprising experimental result for CO₂. Finally, results for H₂O are presented. The effect of the dipole-moment on the ionisation in extremely short (1- to 2- cycle) laser pulses is demonstrated.

Molecular vibrational response of ice layers after ultrashort-laser excitation of metal surfaces

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Electrons as excess charges in polar solvents result in molecular motion within the solvent to stabilize the new charge distribution known as electron solvation. We employ time-resolved broadband-IR-VIS SFG (sum frequency generation) spectroscopy as a powerful technique to study the changes in the vibrational spectra of D₂O water layers upon electron injection from a Ru(001) surface. Unlike in time-resolved photoemission experiments where the electron binding energy is traced and the solvent response is inferred subsequently, SFG vibrational spectroscopy *directly* monitors the molecular reorientation induced by the excess charge. If the Ru surface is excited with 266-nm (4.65 eV) photons, excess electrons injected into the adsorbate layer induce –dependent on layer morphology and layer thickness– drastic changes in the vibrational spectra of the OD stretch vibration. While in amorphous ice layers only weak changes are observed, a SFG signal increase by several orders of magnitude is found in crystalline D₂O layers (enhancement factor of 10³ up to 10⁴). The physical and chemical processes involved will be discussed.

Radical reactions in combustion

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Reactive, short-lived intermediate species play a crucial role in combustion. Small radicals are involved at all stages of the combustion reaction network which determines important factors of the process, including the available energy, the amount of greenhouse gases emitted, and the formation of undesired air toxics and aerosols. It is a considerable challenge to quantitatively detect such reactive intermediates which are typically formed in small concentrations, and in-situ techniques are necessary for this analysis.

To investigate the species composition in flames suited to unravel details of the combustion chemistry, we typically combine laser diagnostic and molecular beam mass spectrometry. Especially valuable methods include cavity ring-down spectroscopy (CRDS) and laser-induced fluorescence (LIF) which were used to detect some key di- and triatomic radicals. Collisional energy transfer, investigated using picosecond time resolution, has been studied as a prerequisite for quantitative LIF measurements. From the several variants of *in situ* molecular beam mass spectrometry, which can provide a complete analysis of the reactive mixture, photoionization techniques using synchrotron radiation are especially useful to distinguish isomeric species. This combination of techniques has been invaluable in studying important reaction pathways for a variety of fuel families, including hydrocarbons, ethers, alcohols, aldehydes, ketones, esters and amines, as well as fuel mixtures. Many of these investigations have been performed in collaborations, including teams from the USA and China. As a general conclusion, the structure of the fuel molecule is of significance for the formation of some undesired combustion emissions – a fact which must be considered in the discussion of alternative, bio-derived fuels.

Radicals are also at the origin of some of the characteristic luminous emissions of flames. The chemiluminescent signature of a flame depends on the combustion conditions and is proposed as an intrinsic sensor for active control of practical combustion devices. While flame luminescence has been described in the literature for more than hundred years, its spectral structure is not easily predicted since radiative and energy transfer processes are involved. These will depend on the reaction channels producing nascent energy level distributions that may not be known and on the specific collisional environment. Some recent results will be presented to discuss this approach of using chemiluminescence as a flame sensor.

Tracking stilbene excited state evolution with femtosecond stimulated raman spectroscopy

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Stilbene (1,2-diphenylethylene) exists at room temperature in cis and trans isomeric forms. The molecule has attracted attention in the past as a photoswitch because UV excitation enables the interconversion of the isomers.

Here femtosecond transient Raman spectroscopy has been applied to track the path of the excited stilbene molecules to the ground state. As a key device an optical parametric amplifier for the generation of tunable narrowband pulses was developed. Starting from the output of a Ti:Sa oscillator, 10 cm^{-1} pulses were achieved and applied in a three-beam experiment. The stimulated Raman spectra were acquired with a peak accuracy of 1 cm^{-1} and a temporal resolution of 120 fs, limited by the 290 nm pump pulses. Resonance enhancement due to the cis and trans excited state absorption was utilized by tuning the Raman beam to 580 and 620 nm respectively.

The S_1 excited state Raman spectrum of cis-stilbene is dominated by a 228 cm^{-1} low frequency mode. During the risetime of the signal a significant bandshape change occurs. In contrast to previous impulsive Raman measurements in time domain^[1] however, neither in n-hexane nor in acetonitrile a proceeding frequency shift of the corresponding band was observed. The deviant position of trans-stilbene on the excited state potential manifests in a clearly structured transient Raman spectrum. In n-hexane, intramolecular vibrational redistribution leads within 500 fs to an intensity decay of the Raman excited state spectra accompanied by an up-shift of the high-frequency bands, most prominently observed in the C=C stretching band around 1540 cm^{-1} . On the 10 ps timescale vibrational cooling induces further up-shifts. In acetonitrile, on the other hand, solvation causes a downshift of the 1540 cm^{-1} band.

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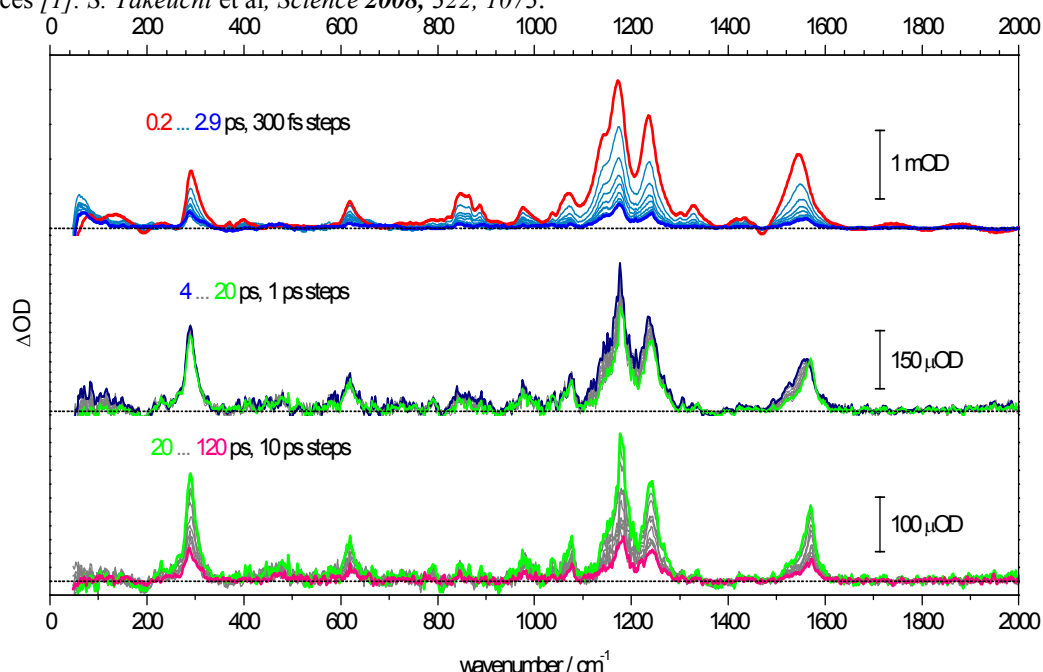


Figure 1: Time-resolved resonance Raman spectra of excited state trans-stilbene in n-hexane.

Ultrafast vibrational dynamics of hydrated DNA

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The interaction with water plays a key role for the structure and function of deoxyribonucleic acid (DNA). While the time-averaged equilibrium structure of hydrated DNA has been studied in detail by x-ray diffraction and nuclear magnetic resonance, there is very limited information on vibrational dynamics^{1,2} and the couplings governing the interaction of water molecules with base pairs and with ionic phosphate groups in the DNA backbone. In this paper, we present new insight into the interaction of DNA oligomers with their hydration shell, originating from femtosecond nonlinear infrared spectroscopy. Both pump-probe data and two-dimensional infrared spectra will be presented for a wide range of DNA hydration levels. The ultrafast dynamics and the transient spectra of NH and (PO₂)⁻ stretching vibrations of DNA and of the water OH stretching mode are determined in DNA oligomers containing 23 alternating adenine (A) – thymine (T) base pairs in Watson-Crick geometry.

Measurements with DNA-surfactant complex films allow for discerning the NH stretching bands of the A-T base pairs and the OH stretching band of water^{3,4}. The NH stretching mode of T and the symmetric NH₂ stretching mode of A, both occurring around 3200 cm⁻¹, display a pronounced coupling. At 0% relative humidity (r.h.), corresponding to N_≈2 H₂O molecules per base pair, the OH stretching band of water at 3500 cm⁻¹ shows a negligible spectral diffusion and a constant anisotropy of 0.4, due to a direct interaction of individual H₂O molecules with the phosphate groups of the DNA backbone. At 92% r.h. (N>20), the DNA hydration shell displays transient properties closer to bulk water^{5,6,7}.

The antisymmetric (PO₂)⁻ stretching vibration around 1250 cm⁻¹, a sensitive probe of DNA hydration, allows for mapping energy dissipation processes and changes of hydrating structures in real-time. The water shells around the phosphate groups accept excess energy from DNA on a femtosecond time scale, much faster than the picosecond energy transport within DNA. Transient heating of the water shells reduces the number of hydrogen bonds between water and DNA.

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Linear and non-linear spectroscopy of quantum aggregates

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We present time-dependent quantum calculations describing the spectroscopy of molecular aggregates. In a first example, we compare absorption and circular dichroism (CD) spectra of merocyanine dimers and show which information can be gained from a time-dependent approach to CD spectroscopy ^[1]. We then discuss 2d-vibronic spectra of dimers of perylenebisimide dyes and in particular their dependence on the dimer geometry ^[2]. As an outlook, the vibronic dynamics in larger molecular oligomers is discussed ^[3].

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Manipulation of large molecules

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Large molecules have complex potential-energy surfaces with many local minima. They exhibit multiple stereo-isomers, even at the low temperatures of ~1 K in a molecular beam. We have developed methods to manipulate the motion of large, complex molecules and to select their quantum states. We have exploited this state-selectivity, for example, to spatially separate individual conformers (structural isomers) of complex molecules and to demonstrate unprecedented degrees of laser alignment and mixed-field orientation of these molecules.

Such clean, well-defined samples would strongly benefit or simply allow novel experiments with complex molecules, for instance, femto-second pump-probe measurements, X-ray or electron diffraction in the gas-phase, high-harmonic generation, or tomographic reconstructions of molecular orbitals. These samples would also be very advantageous for metrology applications, such as, for example, matter-wave interferometry or the search for electroweak interactions in chiral molecules. Moreover, they provide an extreme level of control for stereo-dynamically controlled reaction dynamics of complex molecules.

In this presentation, I will describe and compare the manipulation methods employed and our respective results. In addition, I will discuss the prospects of imaging experiments on gas-phase molecules and their dynamics using the upcoming X-ray free-electron lasers.

DNA getting sunburned

Wolfgang Zinth, Wolfgang J. Schreier, Julia Kubon, Nadja Regner, Karin Haiser, Tobias E. Schrader, Pascale Clivio, and Peter Gilch

Ultraviolet (UV) radiation induces various photo-damages in DNA. Among them the CPD (cyclobutane pyrimidine dimer) photo-damage caused by 2+2 photo-addition of adjacent thymine basis is the most abundant lesion. The formation of this photo-damage is discussed since the 1960ies: Dimerization of monomeric thymine in solution requires diffusion to bring thymine molecules in close contact. At reasonable concentrations contact formation is much slower than the 1 ps lifetime of the excited singlet state. Thus CPD-formation in solutions with monomeric bases can only occur via the long-lived triplet state. For thymine in DNA strands, where the thymine molecules are in close proximity, diffusion is not necessary and the singlet as well as the triplet channel may be involved. In this contribution we will present investigations on different dimerizable model systems using time-resolved IR techniques combined with quantum yield measurements and show, that the singlet channel dominates CPD-formation^{1,2}.

The experiments show that in all stranded systems (different thymine dinucleotides as well as single stranded dT₁₈) the IR marker-bands of the CPD photo-damage appear within 1ps after UV irradiation (at 266 nm), i. e. with the decay of the originally excited singlet state of the thymine molecule. Thereafter the amplitudes of the marker-bands do not change on the 10 ps to ns timescale. This finding rules out the possibility of delayed CPD formation on this time scale. In addition we show that the quantum efficiency recorded from the IR absorption change on the 10 ps time scale matches the stationary values, indicating that the major fraction of CPD-damage is formed ultrafast and is directly related to the decay of the excited singlet state.

The observation of rapid CPD photo-damage formation within 1 ps yields interesting information regarding the evolutionary optimization of DNA stability. The time scale of 1 ps is too short to allow large scale structural changes of a DNA strand. Therefore CPD formation only takes place for thymine pairs prearranged in reactive conformations. Thus CPD photo-damage probability may be minimized by suitably designed DNA structures.

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REACTION DYNAMICS OF ANTHRACENE-9,10-ENDOPEROXIDE

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Femtosecond electronic and vibrational spectroscopic studies, steady-state absorption and emission investigations, ¹H NMR spectroscopy, and theoretical *ab initio* calculations were combined to obtain a comprehensive picture of the photochemistry of anthracene-9,10-endoperoxide (APO).^{1,2} Femtosecond UV pump excitation at 282 nm triggers the two primary reaction channels: cycloreversion, and homolytic cleavage of the peroxide bridge. The transient evolution of the product absorptions is followed with a white light continuum probe. Control measurements were also performed on two reaction products of APO, i.e., anthracene and anthraquinone. Polarization-resolved femtosecond UV pump/ IR probe, emission excitation studies, and *ab initio* calculations were combined to obtain a consistent assignment of APO electronic states to spectral features. Steady-state absorption spectroscopy and ¹H NMR spectroscopy were used to map out both primary and secondary reaction pathways in APO photochemistry. Moreover, the absolute reaction quantum yields for the different photoproducts were extracted for excitation varying from 240 to 450 nm.

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Quantum Control of Biomolecules using UV Pulse Shaping Techniques

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The identification and discrimination of molecules that exhibit almost identical structures and spectra using fluorescence spectroscopy is considered quite difficult. In order to evaluate the capability of optimal control for discriminating between the optical emissions of nearly identical molecules, we developed a new approach called “optimal dynamic discrimination (ODD). A proof of principle ODD experiment has been performed using Riboflavin (RBF) and Flavin Mononucleotide (FMN) as model system. We used a complex multipulse control field made of a pair of pulses (shaped UV and ultrashort IR). Clear discrimination was observed for optimally shaped pulses, although the linear spectra from both molecules are virtually identical. A further experiment showed that, by using the optimal pulse shapes that maximize the fluorescence depletion in FMN and RBF in a differential manner, the concentration of both molecules could be retrieved while they were mixed in the same solution. Another application of shaped UV-pulse that is currently investigated is the control of the quantum paths in DNA basis in order to prevent quenching and increase the fluorescence yield.

Excitation and ionization of C₆₀ by intense, elliptically polarized short laser pulses

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Multiphoton processes in complex molecules and clusters are of great scientific interest. The aim of such research is to understand the excitation process and the subsequent relaxation processes. The C₆₀ fullerene is an ideal model system for such studies. It is, on one hand, a quite complex system having 60 delocalized π electrons and more than 100 vibrational modes, but on the other hand, C₆₀ is highly symmetric making it attractive for theoretical studies. In this presentation recent results on the effect of the laser radiation ellipticity on the ionization and fragmentation of C₆₀ will be shown [1]. Information about the photo induced processes can be extracted from these experiments such as the properties of the intermediate states and whether or not the recolliding electron transfers additional energy into the excited C₆₀. A qualitative theory description of such polarization studies has been derived [2]. It turns out, that polarization dependence can very sensitively distinguish single (SAE) and multi-electron dynamics (MAE).

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Adsorbing proteins, sticking bacteria and climbing geckos: Van der Waals-forces revisited

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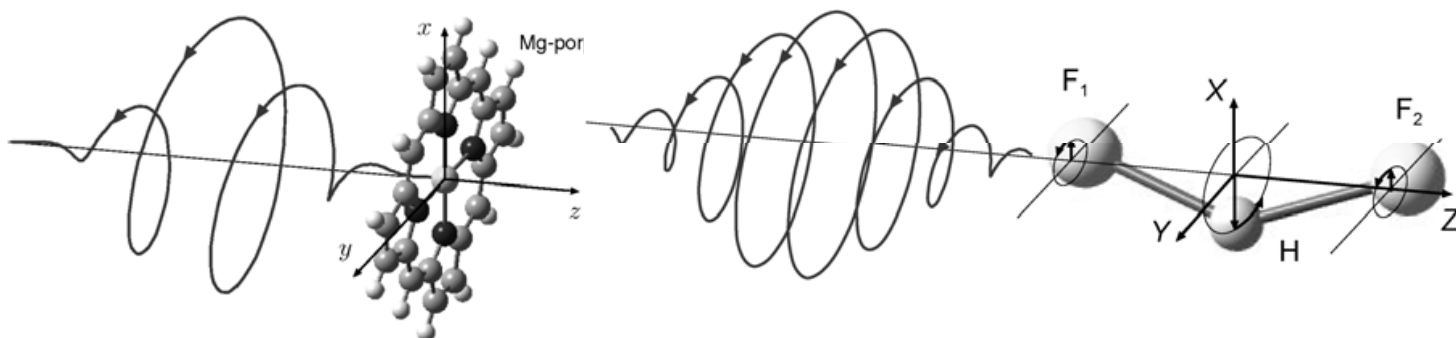
Intermolecular forces embrace all forms of matter and are also present in our every-day life as they e.g. determine the strength of a glue or the wetting properties of water on textiles. In my talk I will describe our way to access these forces by studying thin liquid films in the nanometer range. The examples demonstrate that long-ranged van der Waals-forces have to be taken into account, which is especially important for composite substrates. The lessons learned can then be applied to more complex situations like the adsorption of proteins to surfaces like dental implant materials or the adhesion of bacteria or the adhesion of geckos.

QUANTUM CONTROL BY LASER PULSES: FROM NUCLEAR TO ELECTRON DYNAMICS, AND BACK

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Important concepts of quantum control by laser pulses, e.g. by "pump-dump" type series of laser pulses, by coherent control, or by means of series of π - or $\pi/2$ laser pulses, have been developed during the last two decades, first for control of nuclear dynamics. Typical applications are in the femto-to-pico-second time domain. Recent generations of laser pulses in the femto-to-atto-second time domain suggest extensions to quantum control of electron dynamics. We shall present a brief survey of pioneering progresses in this field of quantum control, before focusing on our contributions to quantum control of electronic and nuclear ring currents and circulations, by means of circularly polarized laser pulses. The ring currents in turn induce magnetic fields. Applications range from pre-oriented medium size organometallic molecules via triatomic and diatomic molecules to atoms or atomic ions, see Refs. [1-8]. The corresponding effects which are induced by laser pulse control are much more efficient than traditional generations of ring currents by means of magnetic field.



We should like to express our gratitude to all co-authors for their important contributions to Refs. [2,4-6], and also to Deutsche Forschungsgemeinschaft (DFG) for financial support.

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Hiking Over Quantum Control Landscapes and Beyond

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Seeking the best control over a posed quantum dynamic objective entails climbing over the associated control landscape, which is defined as the quantum mechanical observable as a function of the controls. The topology and general structure of quantum control landscapes as input \rightarrow output maps dictate the final attainable yield, the efficiency of the search for an effective control, the possible existence of multiple dynamically equivalent controls, and the robustness of any viable control solution. Normal optimization problems in virtually any area of engineering and science typically have landscape topologies that remain a mystery. Quantum mechanics appears to be quite special in that the topology of quantum control landscapes can be established generically based on minimal physical assumptions. Various features of these landscapes will be discussed and illustrated for circumstances where the controls are either an external field or the time independent portions of the Hamiltonian; the latter circumstance corresponds to subjecting the material or molecules to systematic variation and hence viewed in the context of being controls. Both theoretical and experimental findings on control landscapes and their consequences will be discussed, including issues of robustness to noise, search algorithm efficiency, existence of multiple control solutions, simultaneous control of multiple quantum systems (optimal dynamic discrimination (ODD)), and mechanism analysis. The implications of this analysis for various application domains will be discussed.

Development of strategies for the optimal control in complex systems

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We present a newly developed „Field induced surface hopping“ method (FISH) which combines quantum electronic state population dynamics with classical nuclear dynamics carried out „on the fly“. This method can be combined with optimal control in order to steer molecular processes by optimizing laser fields using evolutionary algorithms. For the propagation of classical trajectories the whole spectrum of methods ranging from empirical force fields, semiempirical to ab initio quantum chemical methods can be employed, opening the possibility of broad application in complex systems. Furthermore our approach allows to gain a fundamental insight into the mechanisms underlying the control of molecular processes by direct application of experimentally optimized laser pulses. We illustrate our approach on the optimal control of multiphoton ionization, trans-cis isomerization and control of photodynamics in biochromophores such as flavins and adenine.

Controlling molecular orientation and alignment: From gas phase to condensed phases

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In recent years, the non-resonant interaction of intense laser fields with molecules through their anisotropic polarizability has been successfully employed to orient and/or align molecular axes. In our theoretical work, we characterize the quantum dynamics of pendular states using a semi-analytical approach. In particular, we study pendular analogues to coherent and squeezed states and derive closed expressions for wave functions and expectation values in certain cases. If the duration of the light pulses used to align molecules exceeds the time scale of molecular rotation, free rotor states adiabatically transform into pendular states. In the contrasting, non-adiabatic limit, shorter pulses create wave packet states exhibiting revival phenomena thus giving rise to post-pulse alignment. Recently, we have shown how suitable combinations of adiabatic and non-adiabatic scenarios can be used to achieve spectral selection for non-resonant alignment. In other work, we consider the alignment of molecules in gaseous mixtures. We show how the timescales of dissipation and decoherence can be separately determined from the post-pulse alignment signals thereby allowing to characterize underlying collision processes. Finally, also the orientation/alignment of molecules embedded in rare gas matrices is studied. Depending on the relative strength of molecular interaction with the internal (crystal) field and the external (laser) field, possibilities and limitations for molecular alignment in host crystals are discussed.

(Joint work with TP A3: N. Schwentner)

Quantum Control of Femtochemistry in the Gas Phase, Liquid Phase and on Surfaces

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Ever since their invention lasers were considered as the ideal tool for microscopic control of cleavage and formation of chemical bonds. In femtosecond quantum control, selectivity over photoinduced reactions is achieved by exploiting the ultrashort time scales and the coherence properties of fs - laser radiation. In combination with a learning algorithm which processes experimental feedback to adaptively find optimized electric field shapes best suited for solving the control task, chemical reactions can even be steered into a desired direction without a priori knowledge about the reaction mechanism.

The experiments represent a first step and a new reaction path towards laser-induced catalysis of molecular systems, further improved by the benefits of femtosecond laser pulses tailored especially for a desired outcome.

Theory of Higher Order Nonlinear Optical Spectra: Application to Dissolved Chromophores and Biological Chromophore Complexes

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Starting from the simulation of an third order pump-probe spectrum we want to pave the way for higher order spectroscopy. In general, calculating nonlinear spectra is a three step process. First the model Hamiltonian has to be created, identifying a few important degrees of freedom e. g. by quantum-chemical calculations. In a second step the coupling to the other degrees of freedom has to be considered, defining if a density matrix description including dissipation is necessary. As a last step particular spectra - as measured in the experiment - are calculated either by a perturbation expansion with respect to the electric field, or by multiple propagations using a field dependent Hamiltonian.

We begin with the simulation of the third order transient absorption spectra of a chromophore [1]. Then we focus on higher order spectra and address what specific information about dynamics in the excited

states can be gained. A few examples from recent work will be given:

Exciton-exciton annihilation probes the mobility of excitons and their relaxation pathways in chromophore complexes [2]. Transient stimulated Raman tests the wavepacket motion in the excited state and the excited state Raman profile. Finally, using the optimal control algorithm in a pump - shaped dump - probe scheme one directly receives a picture of the multidimensional wavepacket motion in the excited state.

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How to keep coherent control under control

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Pulse shaping has been and still is one essential ingredient in coherent control experiments. It is long known that standard 4f pulse shapers introduce space-time coupling but it has never been analyzed in detail as to what extent space-time coupling does influence the outcome of coherent control experiments. Moreover, most theoretical work in coherent control assumes a perfectly modulated pulse, whose electric field depends on time or frequency only. Some experimental demonstrations seem to agree well with those theoretical predictions, suggesting that the influence of space-time coupling is not overwhelmingly important. Here, we try to answer the question why the effects of space-time coupling are hardly seen in certain types of quantum control experiments while having a considerable influence in others. We begin with a summary of the Fourier optical description of pulse shaping and present experimental results. After that, we proceed with investigating the influence of space-time coupling on three different nonlinear effects. For a relatively simple nonlinear interaction, namely, second harmonic generation, we compare experimental results with simulations. Based on simulations only, we then evaluate the effects of space-time coupling on the interaction of laser pulses with a resonant atomic three-level system and a resonant diatomic molecule. We conclude the talk with new experiments on coherent control of the population distribution in a multiplet of Stark levels of rare earth ions embedded in a crystalline matrix and show that feedback-controlled optimization can be well understood if the effects of space-time coupling are minimized.

Correlated many electron dynamics from different perspectives

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In this talk various approaches to the correlated quantum dynamics of electrons in atoms and molecules are discussed. We do so by solving the Time-Dependent Schrödinger Equation with first principle methods for several systems. The emphasis is on wave function based methods, especially Multi-Configuration Time-Dependent Hartree-Fock (MCTDHF). Selected applications, like the controlled manipulation of the electronic state of LiH, and the onset of thermalization of electrons in Na₈ clusters, serve to illustrate the opportunities and challenges of first principles electron dynamics. Also, the relation to Configuration Interaction based methods, and approaches to go beyond the fixed nuclei approximation are presented.

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Fast pulses and slow atoms: synthesizing molecules and controlling decoherence

Ian A. Walmsley, Hooke Professor of Experimental Physics, Pro-Vice-Chancellor for Research, University of Oxford

Methods of coherent control have wide application in the manipulation of simple molecules: two very different such applications will be outlined.

First, I shall describe progress on a general approach to the formation of ultracold ground state molecules by synthesis from pairs of cold atoms using shaped ultrashort optical pulses. This method combines an effective and widely applicable control technology to the problem of preparing molecules in the ground state of all their degrees of freedom.

Second, I shall discuss the application of closed loop control to the mitigation of decoherence in vibrational wavepackets excited in such molecules. This provides a number of challenges, but gives evidence that closed loop methods are effective in locating regions of phase space that are less susceptible to dephasing than others, without any prior knowledge of the system-bath interactions. Further, it is possible to completely characterize the quantum map describing the quantum state evolution in a simple and "cheap" manner.

Two-photon coherent control of femtosecond photoassociation

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Photoassociation (PA) has emerged as a technique to create ultracold ground state molecules.

The difficulty lies in the unfavorable Frank Condon overlap between the wavefunctions of the colliding atom pair and the molecular ground state. Therefore such a scheme requires a series of excitation and deexcitation steps. A broad band excitation containing all these transitions seems a natural choice [1]. In order to discriminate between the desired goal of reaching the ground state and all other possible outcomes, coherent control schemes have to be adopted to PA. However, one of the main obstacles is to eliminate the atomic excitation which hampered first attempts at femtosecond PA [2]. Indeed, the broad bandwidth of femtosecond lasers appears to be an obstacle for PA rather than a tool for control. A possible remedy is to reduce the bandwidth from femtosecond to picosecond pulses [3]. But picosecond pulse shaping has yet to be developed and to date the reduced bandwidth limits the possibilities of control.

To overcome the ostensible conflict of driving a narrow transition by a broad-bandwidth laser, we explore a two-photon photoassociation scheme. An antisymmetric phase pattern [4] can be employed to eliminate the atomic line. This is based on the fact that excitations carried out by more than one photon can take advantage of constructive and destructive interferences which lead to different pathways of the field. In addition further control of molecular pathways can be achieved. While two-photon absorption may pave the way toward coherent control of PA, the success of two-photon coherent PA will ultimately depend on the pair density of atoms at short enough internuclear distances where PA is efficient. The possibility to enhance the pair density via control of scattering resonances will be discussed.

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Photostability of the Building Blocks of Life

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Stability with respect to photochemical destruction by ultraviolet light is a decisive property of biological molecules. Recent excited-state electronic-structure calculations and time-dependent quantum wave-packet calculations of the nuclear motion have revealed the role of conical intersections of electronic potential-energy surfaces in the highly efficient excited-state deactivation in biological molecules such as aromatic amino acids and DNA bases. Evidence is provided that specific electron-driven proton-transfer processes play a universal role in the photochemistry of biomolecules and biopolymers (DNA and proteins). These processes may be the origin of the exceptional photostability of these compounds which has led to their selection at the very beginning of the biological evolution.

Correlated Vibrational Dynamics of DNA Base Pairs

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Hybrid QM/MM molecular dynamics simulations have been carried out for the Watson-Crick base pair of 9-ethyl-8-phenyladenine and 1-cyclohexyluracil in deuteriochloroform solution at room temperature [1]. Trajectories are analyzed putting special attention to the geometric correlations of the N-H...N and N-H...O hydrogen bonds in the base pair. Even though the two hydrogen bonds are only approximately linear and the heterocycles are tilted with respect to each other, hydrogen bond and N-H lengths follow a simple empirical correlation based on Pauling's valence bond order model. In order to describe the IR line shape of the two NH stretching vibrations, the correlation between their fundamental transition frequencies and the hydrogen bond lengths is exploited. This facilitates efficient determination of the fluctuating transition frequencies along the QM/MM trajectory. Using IR line shape theory, the fundamental NH stretching transitions are obtained in reasonable agreement with experiment [2]. Analysis of the frequency correlation functions is shown to provide insight into anharmonic couplings to low-frequency modes that are responsible for the line broadening. Finally, the line shape function is used to explore the dynamics of the two hydrogen bonds on the basis of the two-dimensional IR spectrum. The shape of the off-diagonal peaks in the spectrum reveals clear signatures of positive correlation between the two stretching vibrations.

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Abstracts of Posters

1 VSCF in Internal Coordinates and the Calculation of Anharmonic Torsional Mode Transitions

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The Vibrational Self-Consistent Field (VSCF) method employing normal modes is often used to calculate the anharmonic vibrational spectra of polyatomic molecules. However, the method fails in certain cases, such as the calculation of soft torsional mode transitions. In this work, the VSCF equations and algorithm are developed in internal coordinates, which can adequately describe torsional modes.

The VSCF method with internal coordinates is applied to several test systems: *trans*-HONO, *cis*-HONO, H₂S₂, and H₂O₂. Our code uses directly points from *ab initio* calculations, and the method proves to be accurate in all types of transitions. In typical torsional modes, the improvement in the frequency is of factor three compared to the VSCF in normal coordinates. In the other types of modes, some results are better than those of the VSCF in normal coordinates and some are worse; the geometry of the described motion determines the efficiency of using internal coordinates in the non-torsional modes in comparison to the normal ones. The single wave function for the ground and for the first excited state of the torsional mode is compared with the corresponding harmonic wave functions. The differences are large, showing the failure of the harmonic and the anharmonic normal mode approximations for this mode.

2 Mixed Quantum Classical Computation of Excitation Energy Transfer in Pheophorbide-a Complexes

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The excitation energy transfer in a chromophore complex dissolved in ethanol is computed utilizing a mixed quantum classical methodology. The complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model. We address two issues:

1. A new approach is introduced to directly include intramolecular vibrations from the MD-simulations into the former mixed quantum classical methodology. This approach shall be used to further improve the existing calculations of excitation energy transfer, linear absorbance and time- and frequency resolved emission spectra. Therefore the intramolecular vibrations are separated from the translation, rotation and low frequency chromophore oscillations for the full MD-trajectory by a complete analysis of all single atom trajectories. Thus translation, rotation and low frequency chromophore oscillations together define the so called reference structure. Making a harmonic approximation to the single atom positions in respect of the related reference structure atom positions using the Cartesian Hessian matrix elements given by HF-/CIS-calculations a highly fluctuating energy was calculated and added to the chromophore complex Hamiltonian.

2. The full quantum formula for the emission spectrum is translated into the mixed quantum classical case and time-resolved spectra up to 2 ns are computed. The chromophore complex excited state dynamics are described by the density matrix theory to account for both radiative and non-radiative decays. While the full emission spectrum only reflects excited state decay, the analysis of partial spectra reveals details of the excitation energy redistribution among the chromophores.

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3 From Synchronous to Sequential Double Proton Transfer: Quantum Dynamics Simulations for the Model Porphine

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Double Proton Transfer (DPT) was a widely studied topic in the last decades. Porphyrins and metalloporphyrins are one of the most common subjects of research. These “pigments of life” play a crucial role in biologically relevant processes, such as photosynthesis, oxygen transport and activations and therefore they drove to the development of theoretical models for systematic studies. Questions of interest in this field concern the nature of the DPT: concerted (called 1-step or synchronous, as well) or sequential (called 2-step or asynchronous, as well) reaction mechanism [1,2,3], influences of quantum effects on reaction rates, and possibility to control the DPT are just few examples [4].

We present a quantum-mechanical reaction dynamics approach to DPT in porphine, using the symmetric model of Smedarchina et al. [5]. Such approach has the advantage to give information about the quantum dynamics of the wave packets far away from the minimum energy path in a multidimensional space. In order to carry out the quantum dynamics, the MCTDH method [6] was applied. The propagated nuclear wavefunctions discover a surprising phenomenon in DPT, i.e. the mechanism may switch from concerted to sequential. We conclude that, in general, it is not sufficient to consider just the potential energy surface (PES) in order to predict the mechanism of DPT. The same PES may support different reaction mechanisms depending on the initial preparation of the system. The discrimination of the mechanism calls for quantum dynamics simulations, beyond quantum chemistry calculations of the PES.

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4 Relating vibrational spectra and conformational structures of small model peptides: From gas phase to microclusters

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Biopolymers such as peptides and proteins are known to exist in a huge number of conformational structures for a given sequence of amino acid residues. In addition to our insufficient knowledge of molecular interaction, a microscopic understanding for the driving force of biomolecular conformations is further hampered by the coexistence of intra- and intermolecular forces: In particular, we often do not know whether a certain spatial structure is an intrinsic property of the biopolymer itself or whether it is mainly stabilized by the presence of solvents.

In recent years, the advent of gas phase experiments of small peptides with a controllable number of attached solvent molecules opens the way to separate inter- from intramolecular effects on biomolecular conformations. Under favorable circumstances, UV/IR double resonance techniques can be used to measure vibrational spectra for individual conformations of a peptide with fixed number of solvent molecules. By comparison with simulated spectra, molecular conformers can be assigned to the experimental spectra. Repeating this procedure for an increasing number of solvent molecules, the evolution of molecular conformation from the gas phase toward the gaseous solution can be monitored.

In our present work, the tripeptide Z-Aib-Pro-NHMe is chosen as a model system. In a first step, quantum-chemical DFT and MP2 methods have been used to locate a large number of minimum energy structures exhibiting different H-bonding patterns. Alternatively, trajectories based on empirical force fields are used to extract information on molecular conformations. Second, vibrational spectra are calculated for all conformers to set up a structure-spectrum relation by carefully analyzing the effects of all possible Hbonding sites on various parts of the infrared spectrum. Comparison with experiments carried out in project B7 reveals competing β and γ turn structures, depending on the details of microsolvation environment.

(Joint work with TP B7: G. v. Helden, G. Meijer)

5 Electronic deactivation of keto- and enol-cytosine: A theoretical approach using mixed quantum-classical dynamics

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It is well known that in DNA bases there are several ways to relax after light irradiation. The presence of singlet excited states of different character (basically $\pi\pi^*$ and $n\pi^*$ states) allows for different relaxation pathways to the ground state. Additionally, triplet states can have an important role, being responsible for deactivation events in a much longer time scale. The disentangling of the different relaxation mechanisms is subject of several experimental and theoretical studies, often without clear consensus.

In this contribution, we present dynamical simulations to describe the different relaxation pathways in the canonical form of cytosine (the keto form) and the most stable isomer in gas phase (the enol form). Due to the time scales investigated (fs), pathways involving triplet states can be neglected. In order to account for all the degrees of freedom of the system, we have performed classical trajectories for the nuclei, in combination with *ab initio* quantum calculations for the electrons. This combination is widely applied to describe dynamics in the electronic ground state, but it is still a challenge to employ it to describe non-adiabatic dynamics in the excited state. Here, the quantization of the electronic states in the classical dynamics is considered using the surface hopping method.

Our dynamical studies show different relaxation times for the keto and enol isomers of cytosine and how the presence of two different excited states $n\pi^*$ and $\pi\pi^*$ modifies the deactivation mechanism.

6 Ultrafast electron dynamics at alkali-ice interfaces probed with two-photon photoemission

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An excess charge in a polar environment, i.e. an electron or an ion, is known to form a charge-solvent complex [1]. This process involves a re-orientation of the molecules surrounding the charge, resulting in the screening of the extra charge and in the increase of its binding energy [2]. Electron and ion solvation is very common in nature and well studied. However, the microscopic steps involved are not fully understood, yet. Deeper insight into the dynamics of the process is of fundamental interest, as the ion solvation in condensed polar molecules is highly relevant in numerous fields such as, atmospheric heterogeneous chemistry [3]. Solvated electrons can also be very reactive species depending on their binding site and lifetime, as has been shown before [4]. The ability to control both of these properties is therefore highly interesting.

In this study we investigated the electron dynamics in ice water layers adsorbed on a Cu(111) single crystal with co-adsorbed sodium ions by means of time-resolved two-photon photoelectron spectroscopy. In amorphous ice multilayers these electrons are located in the bulk of the ice film [5] and the lifetime and the energetic stabilization rate of the excited electrons are known. After adsorption of sub-monolayer coverages of sodium the 3s electron of the parent Na atom is transferred into the water ice and decays back to the metal before spectroscopy is performed. The accumulation of positively charged sodium ions on top of the D₂O film can be monitored by a decrease in the system workfunction, which is depending on the Na coverage. A new species of solvated electrons is observed in the presence of the alkali ions. By titration experiments with either Xenon atoms or by adsorption of an additional water overlayer, we can demonstrate that the binding site of these electrons is located at the ice/vacuum-interface. Furthermore the lifetime of the excited electrons in this state is in the order of several picoseconds, so more than one order of magnitude longer compared to solvated electrons in amorphous water ice. The energetic stabilization rate is with ~800 meV/ps almost three times higher than in the case without sodium. Possible scenarios for the origin of the alkali-induced state will be discussed.

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7 Control of the fragmentation dynamics of bromochloroalkanes

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We report on the coherent control of the ultrafast ionization and fragmentation dynamics of bromochloroalkanes ($C_nH_{2n}BrCl$, $n = 2, 3$) using shaped ultrafast laser pulses ($\lambda = 804$ nm) and femtosecond pump-probe experiments. Evolutionary algorithms are applied in a feedback loop in order to optimize the intensity of selected fragment ions. The time structure of the optimal pulses that result in an enhancement of the fragment ions and at the same time in a depletion of the parent ion shows a characteristic sequence of pulses. Typically, a less intense probe pulse follows an intense pump pulse where optimal time delays of 300 – 500 fs in the control experiments on C_2H_4BrCl and C_3H_6BrCl are observed. The interpretation of the underlying control mechanism is achieved with the results from one-color 804 nm pump-probe experiments. The ion yields of the parent molecule and several fragments show broad dynamic resonances with a maximum at 300 – 500 fs. The experimental findings are explained in terms of an enhanced fragmentation during the dissociative ionization of $C_nH_{2n}BrCl$ ($n = 2, 3$). The importance of dynamic resonances on the fragmentation dynamics of $C_2H_4BrCl^+$ and $C_3H_6BrCl^+$ are discussed.



Analysis and control of the electron dynamics of isolated nanoparticles

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We report on experiments on the interaction of isolated NaCl and SiO₂ nanoparticles with strong femtosecond laser fields employing dual pulse laser excitation and waveform-control of few-cycle laser fields, respectively. The emitted electrons are detected by velocity map imaging allowing the simultaneous measurement of their kinetic energy and angular distribution. A beam of isolated nanoparticles is formed using state-of-the-art aerosol preparation techniques and aerodynamic lens focusing. The electron emission dynamics of isolated NaCl nanoparticles is investigated using femtosecond dual-pulse laser excitation ($\tau = 85$ fs, $\lambda = 804$ nm). An enhanced electron emission and an increase in the electron kinetic energy are observed for characteristic time delays indicating an enhanced coupling of the laser pulses to the nanoparticle.

The waveform control of the electron emission from isolated SiO₂ nanoparticles is investigated using intense ($4 \cdot 10^{14}$ W/cm²), few-cycle ($\tau < 5$ fs) laser fields. In the experiments a significant increase in the cut-off in the electron energy spectra of SiO₂ nanoparticles as compared to Xe for the same laser conditions is observed. The asymmetry of the electron emission along the laser polarization axis shows a pronounced dependence on the carrier-envelope phase (CEP) of the few-cycle waveform-controlled light field. The role of field enhancement near the nanoparticle surface for the extended cut-off and the observed CEP dependence is discussed.

9 Dynamics of Conformational Transitions in Biological Molecules

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Many biological processes are based on conformational changes of biomolecules. Therefore detailed studies of conformational equilibria and dynamics of conformational changes in relevant systems can contribute to understanding the principles of many processes in nature. For our study we chose some simple molecules for which experimental spectra are available. The first system of interest is 3-aminophenol. There are at least two conformers of this molecule (*cis* and *trans*) which can be separated with using an ac quadrupole m/μ selector because they significantly differ in the dipole moment.¹ This enables measurement of both rotational and vibrational spectra for each conformer in gas phase. The energies, geometries and harmonic IR spectra of both conformers were calculated at MP2/6-311++G** level and compared to the data found in literature.^{2, 3} The spectroscopic data were used as a tool of identification of the conformers.

The transition state geometry and the barrier were calculated to receive information about the *cistrans* isomerization and the reaction pathway was investigated. It was found that the isomerization occurs by torsion. In future, the reaction dynamics will be investigated. On this project we cooperate with Prof. J. Manz, Dr. J. Küpper, Prof. G. Meijer and Dr. G. von Helden.

Another system convenient for the studies of simple conformation changes is the protonated dimer of glycine which is an example of a proton pump. There are several conformers of such systems which were described in the literature.^{4, 5} We investigated the equilibrium geometries and energies of these conformers at both DFT and MP2 level, while each of these method identified a different structure to be energetically favored. In future we will investigate which of these structures corresponds to real systems by the means of vibrational spectroscopy and describe the dynamics of the proton exchange.

The results obtained for the two mentioned systems will be used in future studies of conformational changes in more complicated systems, such as saccharides.

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10 Ultrafast dynamics in sodium-doped water clusters

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Even after more than four decades of research the behaviour of loosely bound electrons in a polar environment is still a challenging topic. Gas phase clusters of polar solvent molecules doped with an alkali metal atom are a well suited model system, since the number of molecules interaction with the bound electron can be varied.

In the past years our group has investigated some spectroscopic properties of size-selected $(\text{H}_2\text{O})_n \cdots \text{Na}$ and $(\text{NH}_3)_n \cdots \text{Na}$ clusters, such as ionization potential [1] and energy of the first electronically excited state [2,3]. In addition femtosecond-pump-probe experiments allow studying the dynamics of electronically excited states [4]. Previous work on $(\text{NH}_3)_n \cdots \text{Na}$ clusters has shown the lifetime of the lowest electronically excited states to decrease strongly with cluster size. For $n \geq 4$ it is on the order of picoseconds and lower. The situation resembles that of pure water cluster anions [5].

In the present work we are dealing with two colour femtosecond pump probe spectroscopy on $(\text{H}_2\text{O})_n \cdots \text{Na}$ clusters. The clusters were created by expanding water vapour through a 50 μm nozzle into vacuum, creating a continuous beam of water clusters. The clusters traverse a pickup oven, where they are doped with a sodium atom. The cluster is excited using a 800 nm photon and the population of the excited state is probed with a 400 nm pulse, using laser pulses of 35 fs duration. Finally the ions created are detected in a linear time of flight mass spectrometer. Due to Franck-Condon principle only the excited state can be ionized, in contrast to a highly vibrationally excited ground state. Hence the decay of the ion signal is a measure for lifetime of the excited state.

The lifetime of clusters up to $n = 40$ has been measured. Since binding of the electron in $(\text{H}_2\text{O})_n \cdots \text{Na}$ clusters is similar to water cluster anions, it is not astonishing to find their lifetimes to be in the same range. The measured values around 100 fs for $(\text{H}_2\text{O})_n \cdots \text{Na}$ with $n \geq 14$ is even smaller than the lifetimes for $(\text{H}_2\text{O})_n^-$ clusters.

A process explaining this fast decay of this state is a fast internal conversion to intra molecular vibrations [4]. To back up this assumption the lifetimes of $(\text{D}_2\text{O})_n \cdots \text{Na}$ clusters have been measured, which exhibit larger lifetimes of the excited state.

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11 Coherent control of selective bond breaking in model peptides

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The control of photo physical processes with judiciously tailored intense femtosecond laser pulses is a cutting edge topic in modern laser science and might pave the way to optically controlled organic chemistry. In this contribution we report on pulse-shaping experiments using closed-loop, optimal control feedback for selective bond breaking in amino acid complexes, such as Ac-Phe-NHMe. This molecule contains a -CO-NH-CHR-CO- moiety, the key structural element of peptides and may be regarded as a “model peptide”.

We show that strong-field control strategies making use of coherent properties of the electromagnetic wave allow one to cleave the strong acyl-N (“peptide”) bond in the molecular system preferentially, while keeping other more labile bonds intact [1]. A detailed analysis of the spectral content of the optimal pulse sequence indicates that the S1 state acts as an isomer selective “doorway” in the highly non-linear excitation and fragmentation process.

Studies on different chromophores, such as Phenylalanine and Alanine, while keeping the backbone structure unchanged elucidates the effect of the excitation dynamics on the relaxation pathways [2]. The observation of protonated species in the corresponding mass spectra indicates that optimal control of ultrafast laser pulses may even be useful to study intramolecular reactions such as hydrogen- or proton-transfer in particular cases. This opens new perspectives for biophysical and biochemical research, since these photochemical reactions are suggested to explain e.g. photo stability of DNA.

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12 Conformations and Vibrational Spectra of Cyclosporine A in Solutions: Molecular Dynamics Simulation and DFT Study

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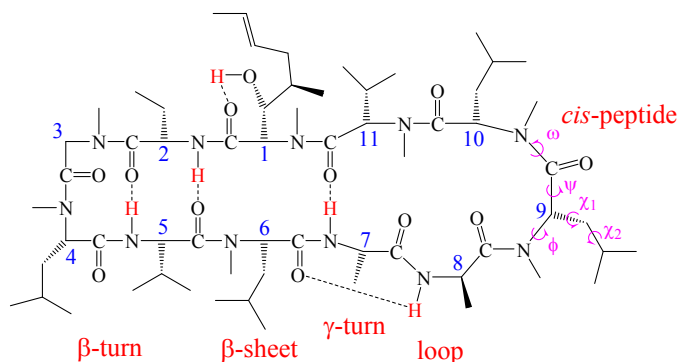
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Cyclosporine A is an important immunosuppressive undecapeptide drug, which shows interesting secondary structures and various conformations under different environmental conditions. A combined MD simulation and DFT study is performed to understand the main conformations and vibrational spectra of cyclosporine A in gas-phase and in chloroform and acetonitrile solutions. It is shown that in nonpolar environments the backbone β -sheet and loop structures as well as the side-chain ${}^1\text{OH}\dots\text{OC}^1$ H-bond of the residue MeBmt¹ are mostly maintained during long-time MD simulations, with two main conformations observed dependent on the orientations of bulky side-chains. The “starting” conformation with the MeBmt¹ and MeLeu⁶ side-chains staying close to the respective Abu² and Ala⁷ residues shows a type II' β -turn and an inverse γ -turn, with considerable inverse H-bonding bifurcations for both turn structures. The “final” conformation with the MeBmt¹ and MeLeu⁶ side-chains staying close to the respective MeVal¹¹ and Val⁵ residues instead shows a looser β -sheet structure and a β -turn interconvertible between type II' and type I with less inverse H-bonding bifurcation. The “intermediate” conformation containing a tight ${}^1\text{OH}\dots\text{OC}^3$ H-bond is observed only during simulations in acetonitrile solution. DFT calculations are used to refine important CsA conformers and to predict their infrared and vibrational circular dichroism spectra. The characteristic absorption bands in the amide II, I and A regions are discussed for important secondary structures including the β -turn, β -sheet, γ -turn, side-chain H-bonds, and N-methyl substitution to peptide bonds. A detailed comparison with available experimental data suggests that in nonpolar solutions CsA mainly assumes the “starting” conformation.

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Schematic structure of cyclosporine A (CsA, 196 atoms)



13 Study of the first excited $B^1\Sigma_u^+$ state of H_2 exposed to intense laser fields

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Ionization, excitation, and deexcitation to the ground state is studied theoretically for the first excited state $B^1\Sigma_u^+$ of H_2 exposed to intense laser fields assuming a parallel orientation of a linear polarized laser and the molecular axis. Within the dipole and fixed-nuclei approximations the time-dependent Schrödinger equation describing the electronic motion is solved in full dimensionality for different laser parameters. The validity of different single-active-electron approximations in the single-photon ionization regime is investigated. The results for a large range of laser wavelengths (400nm to 3000 nm) will be shown. It is shown that due to the close spacing of the $B^1\Sigma_u^+$ state to other excited states it is difficult to find even in this large range of laser parameters the typical signatures of tunneling ionization.

The time-dependent Schrödinger equation is solved by expanding the time-dependent electronic wavefunction in terms of a superposition of field-free eigenstates. The field-free eigenstates are calculated in two ways. In the first approach, which is applicable to two electron systems like H_2 , fully correlated field-free eigenstates are obtained in complete dimensionality using a configuration-interaction calculation where the one-electron basis functions are built from B splines [1]. In the second approach, which is even applicable to larger molecules, the field-free eigenstates are calculated within the single-active-electron (SAE) approximation using density functional theory [2]. Another single-active-electron approach is developed by using a restricted basis in the configuration-interaction method. In this approach only those configurations are taken where one electron is fixed in the ground state of the ion (H_2^+). Using these three approaches results for various laser parameters are obtained and the validity of these single-active-electron approximation is investigated.

Another single-active-electron approach for the $B^1\Sigma_u^+$ state of H_2 was recently proposed in [3]. This approach is based on time-dependent extension of Koopmans' picture for the ionization in a laser pulse. The validity of this approach is also tested. It is shown that the single-active-electron approximation is not suitable for the description of single-photon ionization from the $B^1\Sigma_u^+$ state of H_2 .

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14 **Highly accurate solution for inhomogeneous and homogeneous Schrödinger equations**

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A great effort has been devoted in quantum dynamics to finding efficient and accurate numerical methods to solve the time-dependent Schrödinger equation. Inhomogeneous time-dependent Schrödinger equations arise for example in reactive scattering and in optimal control theory with time-dependent targets or state-dependent constraints.

First, we present a propagation scheme for time-dependent inhomogeneous Schrödinger equations [1]. A formal solution of the inhomogeneous Schrödinger equation is derived based on a polynomial expansion of the inhomogeneous term. This formal solution is adapted to a Chebychev propagation scheme. Different variants for the inhomogeneous propagator are demonstrated and applied to two examples from optimal control theory. Convergence behavior and numerical efficiency are analyzed.

Second, we introduce a novel algorithm to solve the homogeneous Schrödinger equation for explicitly time-dependent Hamiltonians based on iterative time-ordering. The basic idea consists in rewriting the time-dependence as an inhomogeneous term. In order to demonstrate the accuracy of the iterative time-ordering algorithm, analytically solvable examples are considered. The numerical efficiency is analyzed by comparison with the (t; t₀) [2] method.

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15 **Photochemistry of Cytosine Tautomers**

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The building blocks of DNA must be photostable to prevent the loss of genetic information on the sunlit surface of our planet. We investigate the molecular mechanisms responsible for this photostability in the corresponding DNA base chromophores. The DNA base cytosine presents a particular challenge, because the isolated base exists in 3 tautomers with different spectroscopic properties. We resolved the excited state processes in two of the tautomers and assign an excited state tautomerization reaction from the biologically relevant keto tautomer to the keto-imino tautomer. In the condensed phase, we may expect fast, hydrogen-bond catalyzed reverse tautomerization and this process could offer a pathway for rapid excited state relaxation and enhanced photostability.

16 **Spectroscopy in the Fourier Domain: Correlated Measurement of Rotational and Electronic Structure**

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Femtosecond spectroscopy is used extensively to resolve ultrafast reaction mechanisms. Due to Heisenberg's uncertainty principle, the spectroscopic resolution of such experiments is low and rarely contains enough information to resolve molecular structure. As a result, femtosecond experiments are limited to clean samples with established molecular structure. In a novel experimental scheme, we combine short-pulse experiments with high-resolution rotational spectroscopy and obtain correlated structural and dynamic information, thereby breaking the limitations discussed above. We demonstrate the power of our approach with first experimental results for CS₂.

17 A Rational coherent control scheme applied to the solvent induced

Predissociation of Br₂ in solid Ar

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In order to manipulate the predissociation dynamics of a chromophore-bath system (here Br₂ embedded in a crystalline Ar environment) we excite and probe it with appropriately shaped femtosecond pulses. A sequence of five phase-stabilized ultrashort pulses allows in a first step to prepare out the coherent population in the inflow channel (here the covalent B state) from a dominant incoherent contribution (A state) strongly coupled to the motion of the solvent atoms [1]. The driving process for this excitation cleaning is constructive interference between subsequently excited wave packets by subpulses building up the pulse train [2]. Only those parts of the excited population preserving vibronic phase memory contribute to the interference term. We observe coherence times of about 1.2 ps, which is surprisingly long concerning condensed phase systems. In a second step we open the predissociation channel by steering the phases of the pulses and selecting this way the solvent phonon contributions. These are responsible for the efficient predissociation as predicted by recent results of quantum calculations [3]. Our rational control scheme is based on the available spectroscopic information on the system [4]. We directly write it into the spectrum of an ultrashort excitation pulse using a typical pulse shaper unit with a liquid crystal display as an active device. This way we generate in the chromophore spectral combs matching either the spectral positions of the chromophore's vibrational levels or those originating from phonon excitation. In the time domain that corresponds to the generation of excitation pulse trains where the spectral selection is stored in the temporal phases of the subpulses.

Frequency resolved spectra show that the reaction dynamics is restricted to a sharp spectral region [4]. Therefore, the duration of excitation and probe pulses has to be optimized in order to provide the required spectral resolution of the process without destroying the dynamical character of the excitation. We show experimentally and in combination with gas phase simulations how the pulsewidth affects the quality of monitoring the reaction's fast time evolution.

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18 Time resolved alignment: From para-Hydrogen crystals to ambient Nitrogen

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Strong, linearly polarized laser pulses are widely used to induce alignment in molecules possessing an anisotropic polarizability. A short nonresonant pulse prepares a coherent superposition of rotational eigenstates, as a result of which $\langle \cos^2\theta \rangle$ for the angle θ between polarization vector and molecular axis becomes time-dependent. The alignment induces birefringence and recording it between crossed polarizers (Optical Kerr Effect) provides a sensitive and convenient tool to detect the alignment dynamics. We demonstrate this in a collinear detection scheme using the fundamental of a Ti:sapphire laser for alignment and its second harmonic for probing [1].

At a field strength of about 10 TW/cm² very large phase shifts between ordinary and extraordinary beam can be achieved due to the large interaction length. In a sample of nitrogen gas under ambient conditions they lead to ellipticity angles α of the order of 10 degrees. Good polarizers allow to resolve α down to 10^{-5} , thus a huge range is available to study quantitatively and in detail the dynamics. The revival period of N₂ of about 8 ps provides an optimal clock to follow collisions, which occur for ambient pressure on a 100 ps time scale. We demonstrate that the phase dependent and the phase independent parts in θ enable to record the dephasing and the depopulation cross sections independently and we compare them with theoretical predictions and results from alternative experimental methods.

For pH₂-crystals at a temperature below the rotational energies the same technique reveals coherent oscillations as stimulated Raman-sidebands in the 94 fs range, which last for about 1000 periods. They originate from delocalized rotons and the subtle splitting into the three $|M|$ sub-states leading in time frame to three components at 93.7, 94.2 and 94.8 fs, which can be resolved and are also visible in a beat pattern of 17 ps. These rotons appear together with a single-frequency oscillation with 900fs period, originating from a delocalized lattice phonon. It strictly follows the Raman-selection rule and is long lived, lasting for several ten ps.

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19 Spin, Charge and Structural Dynamics:

Elements for the Control of Cluster-Mediated Chemical Reactions

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The optical control of a bimolecular reaction mediated in the environment of a metal site cluster is investigated [1,2]. Generally, the strategy of utilizing the distinct character of a series of different electronic states available to the metal center for guiding the reaction pathway is pursued. By sequential excitation through a set of electronic states in the reaction complex, the unique charge distribution and characteristic structural dynamics on the individual potentials can be utilized for dynamic control of the system. The experiment is carried out within the instrumentation of a tandem mass spectrometer and a radio frequency ion trap. The general strategy can hereby be expanded to include not only the neutral but also the electronic states of the anionic and cationic species. By optically driving a charge reversal process with a sequential electron photo-detachment from the anionic state and a multi-photon ionization process to the cationic state via the neutral system, changes in charge and spin are included to the degrees of freedom that control the reaction pathway. Specifically, an ultrafast photo-induced charge reversal in the $[\text{Au}_2\text{O}_2\text{CH}_4]^-$ complex allows for the activation of oxygen in the negative doublet state, structural evolution in a variable ultrafast time window on the neutral state potentials and specific methane activation in the cationic doublet state of the gold cluster adsorbate system. A controlled, cold oxidation of methane is the objective of the optical manipulation of the system. This approach of an ultrafast sequential charge and spin modification allows for specifically addressing the significantly different nature of the reactants. Additionally, an optimization in the yield of a specific dissociation product from the cationic complex can be achieved with the structural rearrangements to a critical geometry in a neutral intermediate state. With the molecular scale analysis that can be gained from this approach, insight to the decisive electronic and geometric structures can be obtained for the rational design of heterogeneous catalytic systems. The application of a newly developed supercontinuum source will enhance these efforts [3].

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20 Towards Supercontinuum Spectroscopy and Control of Ultrafast Molecular Processes

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Elementary to the endeavor of manipulating the state of a molecular systems through the interaction with light is the capability to address the time scales as well as resonance conditions involved in driving a particular molecular process [1-5]. In view of this, the precision with which a molecular system can be controlled in its interference to a desired final state is largely determined by the bandwidth of the field driving the manipulation. The possibility of employing the octave-spanning radiation obtained from the filamentation of standard amplified femtosecond pulses in gaseous media is explored in this context [6]. The generation of white-light pulses and their compression to sub 7 femtosecond pulses in a single filamentation process in air is presented. The control over the full spectral bandwidth via a liquid crystal based modulation technique is demonstrated by the transcription of parametric phase functions in the construction of a desired pulse form. The spectroscopic application of this capability is further exemplified by an optimization of the spectral phase over the white-light envelope in a genetic algorithm controlled feedback loop. This was applied to driving the sequential electron photo-detachment and multi-photon ionization processes within the $\text{Ag}_3^{-/0/+}$ system under the conditions of space-charge limited densities in a radio frequency ion trap. For this case, pulses composed of ultrashort substructures with a variable time sequence of different spectral components and a total duration spanning into the picosecond domain are obtained from the optimization. Accompanying this, the versatility of analyzing the synthesized pulse forms via a transient grating based four-wave mixing FROG is shown, with the capability to indiscriminately characterize octave spanning pulses with substructures ranging the lower femto- to picosecond domain in intuitive traces. The technique described above presents a general instrumentation for precision control of ultrafast molecular processes.

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21 **Matrix-Assisted Laser Desorption/Ionization with ultrashort laser pulses**

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Matrix-Assisted Laser Desorption/Ionization (MALDI) is one of the most important tools to transfer non-volatile large molecules into the gas-phase. In combination with mass spectrometry, it is a powerful technique in the field of biochemical or physiological research. Nevertheless, the MALDI process itself is still controversial, especially the charge transfer from the matrix to the analyte [1].

Several theoretical and experimental investigations have been performed in order to examine the charge transfer. Common matrix substances have got absorption bands in the UV and a weak bounded proton, which is transferred to the analyte molecule. Due to its wavelength (337 nm) and its pulse duration in the nanosecond regime, N₂-lasers are widely used in commercial MALDI apparatuses.

In our group, we perform successfully MALDI by using femtosecond laser techniques in order to examine the ionization process. One recent result is MALDI with ultrashort laser pulses in the near IR (central wavelength of $\lambda=800$ nm) [2]. In this wavelength regime, used matrix substances have no absorption bands. Experiments with different laser pulse durations suggest that multi photon ionization is a relevant factor. Charge transfer reactions have also been examined by using cations like K⁺ instead of protons. Employing ultrashort laser pulses in the near IR regime, it was possible to apply coherent control techniques on MALDI. First results will be presented.

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Femtosecond pulse shaping is a very powerful technique and was successfully applied to a variety of different systems - especially in the field of coherent control. Extending the common parameters phase and amplitude by including the parameter polarization became an emerging topic in the past few years. Since physical systems are mostly three dimensional, adding the polarization increases significantly their controllability.

We present new setups for pulse shaping which enable us to simultaneously and independently modulate the parameter phase, amplitude, and polarization [1,2,3]. We demonstrate the capabilities of these setups using systematic scans of the relevant pulse parameters and parametric example pulses [4]. Furthermore, we present the implementation in a feedback loop optimization of multi photon ionization of NaK in a molecular beam. The resulting pulse increases the ionization yield compared to a pulse without polarization modulation. The pulse form reveals the ionization dynamics including the orientation of the transition dipole moment of the participating electronic states [5].

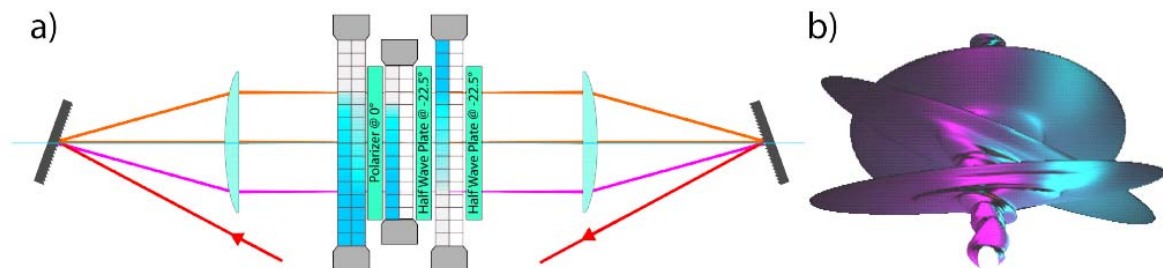


Figure (a) depicts a schematic of our latest setup [3]. It utilizes a sequence of four liquid crystal arrays for control of phase, amplitude and polarization. It is the first non-interferometric setup which is capable of unrestricted manipulation of the polarization ellipse of the electric field. In figure (b) a parametrically shaped triple pulse sequence is shown. Two linear pulses at 0° and 30° separated by 300 fs are followed by a circular one. The three dimensional picture is retrieved from measured crosscorrelation data.

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Control of ultracold rubidium photoassociation with shaped femtosecond laser pulses

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We investigate the interaction of femtosecond laser pulses with an ensemble of ultracold rubidium atoms in a magneto optical trap. Particularly the process of photoassociation is time resolved studied in a pump probe scheme. Thereto, the pump pulse is shaped with a frequency filter to suppress trap loss due to resonant atomic excitation. Via off resonant excitation by the strong field a pair of free atoms is transferred to a bound molecule. The transient of the molecular formation reveals an oscillatory behavior. We study the dependence of the molecular coherent transients on different pump pulse shapes. Moreover, the process is simulated by quantum dynamical calculations which show a good agreement with the experimental data. Together with further experiments the analysis provides a detailed picture of the underlying processes.

In a second experiment we applied a closed loop optimization on the multi-photon ionization of Rb_2 using a parametric evolutionary algorithm. The result is approved by a systematic investigation of the relevant frequency components and allows to assign the transitions to certain electronic states.

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24 Public Scientific Relation and Education

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In the subproject „Public Scientific Relation and Education“ of the Sfb 450 we are preparing new didactical material with contents from modern molecular science and laser physics for schools, science centers, museum exhibitions. A special highlight last year was our second exhibition in the science museum „Palais de la découverte“ in Paris with the new topic „Captured in a trap, tools of the nanoworld“. Starting with the demonstration of different methods to capture small charged and uncharged particles, the museum visitors had the opportunities to discuss with scientists about recent topics and results from their research laboratories. In order to access a large interested public we are parallel developing a multimedia learning environment, a so called „Virtual Research Lab“. This new environment, based on video representations of laboratory situations, interactive screen experiments, commented photo series, etc. allows not only information about the current research topics, but also supports the learn effect by the individual control of the situation or experiment by the user.

Additionally we are developing educational computer games for school children containing learning objects related to the research topic of Molecular Dynamics (MD). We offer workshops to school classes to train students and teachers to become designers and creators of “Educational Computer Games of MD”. Due to the game development process, students will internalize topics of molecular science.

During the conference we present first examples of our new experiments, interactive software und computer games.

25 Photoinduced reactions and ultrafast dynamics of anthracene-9,10-endoperoxide

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Anthracene-9,10-endoperoxide (APO) undergoes two different photoinduced reactions depending on the excitation wavelength: Cycloreversion, resulting in anthracene and singlet oxygen ($^1\text{O}_2$), and homolytic cleavage of the peroxide bridge, initially generating a biradical. Eventually this intermediate produces a diepoxide and other rearrangement products like anthraquinone. Room-temperature thermolysis of APO only produces AQ.

The wavelength dependence of the photochemistry of APO was quantitatively investigated by absorption and ^1H NMR spectroscopy. The absolute photoreaction quantum yields of the primary and secondary products were determined for excitation wavelengths from 240 to 450 nm.

The ultrafast dynamics of the photoinduced reactions were investigated using femtosecond UV pump / white light continuum probe spectroscopy. Excitation at 282 nm activates both reaction channels, but signals of different product contributions were separated in the analysis. Anthraquinone and anthracene were measured for comparison. The results on anthracene are supportive in the analysis and interpretation of vibrational cooling processes. Finally the time constants for the photoreaction processes upon APO excitation were deduced from the transient absorption data.

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