MO 56: Poster: Femtosecond Spectroscopy

Zeit: Donnerstag 16:30–18:30 Raum: Poster A

MO 56.1 Do 16:30 Poster A

High Harmonic Imaging of Conical Intersections — •Markus Gühr[1,2], Brian McFarland[1,2], Joseph Farrell[1,2], and Philip Bucksbaum[1,2] — [1]Stanford PULSE Center, SLAC, Menlo Park CA 94025, USA — [2]Physics Department, Stanford University, Stanford CA 94305,USA

Conical intersections (CI) are crucially involved in light harvesting, primary visual processes, DNA UV stabilization and atmospheric chemistry. A wave packet typically moves through the intersection on a femtosecond time scale, demonstrating the need for ultrafast tools that are sensitive to the electronic state change occurring in passing the CI. We theoretically propose a novel femtosecond pump-probe scheme for CIs based on high harmonic generation (HHG). A first pulse (pump) creates a molecular wave packet on excited electronic surfaces, and the time delayed, high intensity probe pulse produces HHG on the excited molecule as it moves through the CI region. We use the symmetry of the electronic wave functions [1] to detect the electronic state change in the CI via HHG. Furthermore, we can use two center interference effects in the HHG [2,3] to determine the nuclear dynamics that is accompanied by the CI passage. To demonstrate our scheme, we perform simple model calculations on the triatomic molecule SO_2, which will be ideally suited for future experiments because of its high UV excitation cross sections for pumping the wave packet to the CI region.

[1] J. Itatani et al, Phys. Rev. Lett., 94, 123902 (2005)
[2] M. Lein et al, Phys. Rev. A, 66, 023805 (2002)
[3] T. Kanai et al, Nature, 435, 470 (2005)

MO 56.2 Do 16:30 Poster A

Schwingungsrelaxation und Prädissoziation, Dephasierung und Dispersion : Br_2 in festem Argon — •Mónika Héjjas[1], Heide Ibrahim[1], Markus Gühr[2] und Nikolaus Schwentner[1] — [1]FU Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — [2]Stanford PULSE Center, Varian Physics Bldg., 382 Via Pueblo Mall, Stanford CA 94305-4060, USA

Wir untersuchen an einem modellartigen System die Dynamik von molekularen Wellenpaketen für den Fall, dass die Schwingungsfreiheitsgrade des Moleküls an eine Vielzahl von Schwingungsmoden eines umgebenden Bades ankoppeln können. Damit enthält diese Dynamik mehrere Effekte, die eine Amplituden- und Phasenmodulation der Pakete bewirken:(1.) Die reversible Dispersion, die von der Anharmonizität der elektronischen Potentiale des Moleküls herrührt und zu Revival-Effekten führt; (2.) Den irreversiblen Verlust von Phaseninformation an das Bad durch Schwingungsdephasierung; (3.) Energiedissipation in Form von Schwingungsrelaxation; (4.) Amplitudenverlust infolge umgebungsinduzierter Prädissoziation. Auf der Zeitskala von mehreren Femto- bis einigen Pikosekunden zeigt die Dynamik der Wellenpakete die Auswirkungen dieser Prozesse in korrelierter Form. Wir beobachten die Schwingungswellenpaketdynamik mittels Femtosekunden-Pump-Probe-Spektroskopie an Brom in einer Argon-Matrix. Wir zeigen wie sich mithilfe von Simulationen und durch Variation der Pump- und Probe-Wellenlänge, Polarisation und Dauer der Pulse, diese verschiedenen Prozesse entkoppeln lassen, sodass eine Ableitung der charakteristischen Zeiten möglich wird.

MO 56.3 Do 16:30 Poster A

Collision-induced decay of rotational coherence of N_2-molecules — •Philipp Giese, Nina Owschimikow, and Nikolaus Schwentner — FU Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin

Interaction of the anisotropy polarizability $\Delta\alpha$ of a molecule with a short and intense linearily polarized laser pulse induces a transient recurrent alignment of the molecular axis along the field dirction. The revivals of the rotational wave packet are probed via the optically induced Kerr effect. In gases at atmospheric pressure, the rotational coherence persists for several hundred ps. Populations and phases are modified only by bimolecular collisions, which makes gases an ideal model system to study the dynamics of alignment. We non-adiabatically create a rotational wavepacket using IR laser pulses (785 nm) of 150 fs duration with a power density of 10^{12} W/cm^2, and subsequently monitor the collision-induced decay of the rotational revivals in pure N_2 as well as mixtures of N_2/O_2 and N_2/Ar at pressures up to 3 atm. The experimental results are compared with models [1] and [2] for the influence of the environment. The investigations are extended to higher densities up to molecular dopants in crystalline matrices.

[1] S.Ramakrishna, T. Seideman *J. Chem. Phys.* **124**, 244503 (2006)
[2] B. Lavorel et al. *J. Raman Spectr.* **31**, 77 (2000)

MO 56.4 Do 16:30 Poster A

Calculation and shaping of CARS spectra including rotations — •Jörg Liebers[1,2], Soroosh Pezeshki[1], Michael Schreiber[2], and Ulrich Kleinekathöfer[1] — [1]International University Bremen (Jacobs University Bremen as of spring 2007), Campus Ring 1, 28759 Bremen — [2]Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz

In experiments it is possible to mode-selectively excite molecules using feedback-controlled shaping of femtosecond laser pulses [1]. Here we use the theoretical tool of optimal control [2] to influence resonant and non-resonant femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) signals and spectra. The calculations are done by using time-dependent rotational and vibrational wave packet calculations together with perturbation theory in the laser field strength. For the non-resonant transitions an effective Schrödinger equation [3] is used to include the off-resonant states. The CARS signals can then be determined using the wave packets of different order in the field strength.

[1] J. Konradi, A. K. Singh, and A. Materny, PCCP. **7** 3574 (2005)
[2] A. Kaiser and V. May, Chem. Phys. Lett. **405** 339 (2005)
[3] D. Ambrosek, M. Oppel, L. Gonzalez, and V. May, Opt. Commun. **264** 2 (2006)

MO 56.5 Do 16:30 Poster A

Molecular Dynamics of Pigment Molecules in Mesoporous Materials: Femtosecond Studies — •Khadga Karki, Juncheng Hu, Ryan Richards, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

Silica-based mesoporous materials like SBA, FSM, MCM, *etc.* are interesting hosts for larger pigment molecules. These materials have pore sizes ranging from 2 nm to 50 nm. The organized nano-channels, nanocages and the unique solvent nature of these materials have profound influence on the photochemistry and photophysics of the guest pigment molecules. The molecules, like chlorophyll, show remarkable photostability in these cages. Moreover, the chemical environment of the molecules can also be tuned by changing the groups on the inner surface of the cages. These interesting properties of the mesoporous materials have led to the research in organization of molecular assemblies in the cages aiming for artificial photosynthesis. In this respect, it is of interest to study how the molecular dynamics and charge transfer processes occur in the molecules caged in the functionalized nano-channels. Femtosecond studies have been performed to gain a better understanding of the molecular dynamics of the natural pigment molecules and their assemblies in the channels and cages of the mesoporous materials. In our contribution we discuss our newest results.

MO 56.6 Do 16:30 Poster A

Investigation of Molecular Dynamics in all-*trans*-β-Carotene Using Femtosecond *Pump*-FWM Spectroscopy — •Abraham Scaria, Vinu Namboodiri, Jakow Konradi, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

The many degrees of freedom offered by four wave mixing (FWM) spectroscopy makes it a versatile tool for the investigation of complex molecular dynamics. Here, we have used *pump*-FWM spectroscopy on a femtosecond time scale to follow the molecular dynamics occurring in all-*trans*-β-carotene. The transients show clear signatures of the different spectroscopic pathways that the molecules follow after the excitation. This provides a deeper understanding of the excited state dynamics of carotenoids, which is important due to their active participation in light harvesting process. The initial pump pulse excites the molecules into the first optically accessible state (S_2). From there it undergoes a fast internal conversion (IC) in to the electronic dark state (S_1). The FWM process is chosen to be resonant with S_1 and a higher lying excited state (S_n). The results of the dependence of the initial pump power as well as the pump wavelength on the transients will be presented. Possible contributions of other electronic states are discussed.

MO 56.7 Do 16:30 Poster A

Optimal Control of CARS Spectra with Tailored Femtosecond Laser Pulses: Theory and Experiment — •Jakow Konradi, Soroosh Pezeshki, Jörg Liebers, Abraham Scaria, Vinu Namboodiri, Ulrich Kleinekathöfer, and Arnulf Materny — International University Bremen (Jacobs University Bremen as of spring 2007), Germany

The goal of coherent control in femtosecond spectroscopy is the preparation of desired quantum states of a molecule. Here, the most versatile approach is the use of suitably shaped excitation fields. In order to provide the correct pulse shapes, an exact knowledge of the molecular Hamiltonian is required, which in most cases is not available. An experimental way to solve this problem is the use of feedback-controlled learning-loop techniques. Recently, we have demonstrated the application of such an optimal control scheme for the selective excitation of vibrational modes in femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS). Here, the femtosecond laser pulses were shaped in a 4f-arrangement by means of phase and amplitude modulation guided by an evolutionary algorithm. The ratio of the mode intensities in the nonlinear spectrum served as feedback for the optimization. In our contribution we are presenting the optimal control of the femtosecond CARS spectrum of iodine. The experimental results are compared with theoretical calculations. For a simulation of the anti-Stokes spectra, the experimentally found pulse shapes were employed.

MO 56.8 Do 16:30 Poster A

Pump – Degenerate Four Wave Mixing (Pump – DFWM) as a technique for time resolving and controlling molecular excited state dynamics — •Jürgen Hauer, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Time resolving structural dynamics on short lived molecular excited states presents a challenging yet wide ranging field of ultrafast spectroscopy. We present a technique which delivers highly resolved vibrational modes as well as information on the concerned electronic states. The potential for coherent control of the observed dynamics is outlined and demonstrated on first results.

The presented method is based upon Degenerate Four Wave Mixing (DFWM). By adding an additional pump pulse preceding the DFWM – sequence (Pump – DFWM), resolving excited state dynamics becomes feasible. By chopping the pump – pulse, the observed vibrational modes can be unambiguously discerned from ground state dynamics. The time resolution achieved is only limited by the duration of the employed ultrashort laser pulses (sub 20 fs in the presented set up). Since Pump - DFWM is a pure time domain method, the spectral resolution is typically only limited by the vibrational life time. Under experimental conditions, resolution better than 20 cm^{-1} can be achieved.

Coherent control of excited state behaviour is achieved by phase modulating the pump pulse, whereas the DFWM – sequence serves as a heterodyne detection method. The effects of intuitive pulse shapes on the early excited dynamics of β carotene are discussed.

MO 56.9 Do 16:30 Poster A

Molecular Dynamics Investigation with Time-Resolved Optical Kerr Effect on CS2 - C6H6 and CS2 - PS Mixtures — •Ismael A. Heisler[1], Tiago Buckup[2], Silvio L.S. Cunha[1], and Ricardo R.B. Correia[1] — [1]Instituto de Física, UFRGS, 91501-970 Porto Alegre, Brazil — [2]Physikalische Chemie, Philipps Universität Marburg, D-35032 Marburg, Germany

The low frequency domain of the spectral density associated to the liquid state is a peculiar region where the discrimination among different relaxation processes is not so far clearly defined. To obtain information about this region, we applied time resolved heterodyne detected optical Kerr effect technique (HD-OKE) to a series of carbon disulfide - benzene (CS2-C6H6) and carbon disulfide - polystyrene (CS2-PS) mixtures. CS2-C6H6 mixtures simulate the interactions between the CS2 molecules with phenyl rings, which are the principal interacting structures present in the PS molecules. The results show that the diffusive times for pure liquids and the mixtures follow the Debye-Stokes-Einstein equation. The fast time constants were analyzed in terms of the non-diffusive component of the spectral response, which is directly associated with the molecular dynamics. The variations of the spectra were quantified and explained in terms of structural interaction configurations which produced changes in the intermolecular potential.

MO 56.10 Do 16:30 Poster A

Optimierung der Singulett-Sauerstoff-Erzeugung für die photodynamische Therapie — •Johannes Schneider, Jutta Mildner, Matthias Wollenhaupt und Thomas Baumert — Universität Kassel, Institut für Physik, Heinrich-Plett-Str.40, D-34132 Kassel

Eine effiziente Methode zum Ausschalten von kranken Zellen in der Medizin, die sogenannte photodynamische Therapie, beruht auf der lokalen Erzeugung von Singulett-Sauerstoff ($^1O_2(^1\Delta_g)$). Dabei wird ein zuvor applizierter Photosensibilisator durch Laserlicht elektronisch angeregt, gefolgt von einem Energietransfer vom Photosensibilisator zu molekularem Sauerstoff der Umgebung. Ziel der Untersuchungen ist es, die Effizienz der $^1O_2$-Produktion zu steigern und somit den Einsatzbereich der Methode in der Medizin zu erweitern.

Dazu werden neben prominenten Vertretern neu entwickelte Photosensibilisatoren (z.B. Quinoxalinoporphyrazine) in einem optisch stabilen freifließenden Flüssigkeitsfilm (Jet) präpariert und mit fs-Laserpulsen (High-Energy Oscillator, 50 fs @ 400/800 nm) angeregt. Erfolgter Energietransfer wird über die charakteristische Phosphoreszenz von $^1O_2$ bei 1270 nm per Lock-In-Detektion im fW-Bereich direkt nachgewiesen.

Ansatzpunkte für die Effizienzsteigerung der photodynamischen Therapie sind die langwellige (TiSa) Anregung der Photosensibilisatoren bei maximaler Gewebetransmission, sowie die kohärente Kontrolle des im Farbstoff stattfindenden Interkombinations-Prozesses (ISC) per Polarisations-Pulsformung im Starkfeldregime. Erste Ergebnisse der Untersuchungen werden vorgestellt.

MO 56.11 Do 16:30 Poster A

Ultrafast IR-Spectroscopy on Flavin Systems — •Matthias Wolf[1], Ruth Gross[1], Christian Schumann[1], Rolf Diller[1], Britta Person[2], and Joachim Heberle[2] — [1]Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — [2]Fakultät für Chemie, Universität Bielefeld, D-33615 Bielefeld

The function of biological blue light receptors is based on the photochemistry of the diverse flavin chromophores in the respective protein environment.

Riboflavin and flavin-adenine-dinucleotide (FAD) in solution (DMSO) were studied by sub-picosecond time resolved infrared spectroscopy. The decay of the excited electronic state on the nanosecond timescale is preceeded by vibrational cooling within a few picoseconds. These dynamics allow the identification of S_1 vibrational states as well as their spectral position.

In addition we present and discuss first measurements on the flavin mononucleotide binding LOV1 domain of the Phot1 protein from the green algae *Chlamydomonas reinhardtii*.

MO 56.12 Do 16:30 Poster A

Schwingungsspektroskopie im Femtosekundenbereich kleiner Moleküle — •Gerome Weiland, Dagmar Jones, Martin Linke, Henk Fidder und Karsten Heyne — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

Nichtlineare schwingungsspektroskopische Untersuchungen nach elektronischer Anregung oder Schwingungsanregung wurden mit einem dreistufigen OPA an Corroles und Chloroform durchgeführt. Mehrere μJ im infraroten und nahen infraroten Spektralbereich ermöglichten die Untersuchung höherer Schwingungszustände und Mehrphotonenabsorptionsprozesse. Erste Ergebnisse dieser Untersuchungen werden präsentiert.

MO 56.13 Do 16:30 Poster A

Effects of different bridge/anchor groups on the mechanisms of ultrafast heterogeneous electron transfer in a dye/semiconductor system — •Antje Neubauer, Jodi Szarko, Carlo Dinkel, Guido Morbach, Liana Socaciu-Siebert, Rainer Eichberger, and Frank Willig — Hahn-Meitner-Institut, Glienicker Str. 100, D - 14109 Berlin

Two mechanisms for ultrafast heterogeneous electron transfer are known. For molecules bound to a TiO2 surface via a carboxylic anchor group the standard mechanism for photoinduced electron injection is widely accepted, where the chromophore of the organic dye is excited by light in a first step and the electron is injected from the excited state of the molecule in a second step. For dihydroxy compounds, where the two hydroxy groups bind to one Ti atom an alternative mechanism is known, the direct optical charge transfer.

We investigated new perylene derivatives at nano-porous colloidal TiO2 films in order to clarify the mechanisms for those heterogeneous electron transfer reactions. In these systems the perylene molecule functions as electron donor, and the wide-band gap semiconductor TiO2 functions as electron acceptor. The perylene chromophores are bound via a hydroxyl group, catechol and two hydroxy groups as bridge/anchor groups. The spectral features of the linear absorption spectra in solution and attached to TiO2 give information concerning the dynamics and therefore the mechanisms for the electron transfer, which are supported by the short time constants for the electron injection of less than 30 fs measured with transient absorption spectroscopy.

MO 56.14 Do 16:30 Poster A

Analysis and Control of Metal Cluster Reactions by Modulated Ultra-broadband Laser Pulses — •Bruno Schmidt, Shaohui Li, Xin Zhang, Aldo Mirabal, Waldemar Unrau, Juri Demuth, Torsten Siebert, and Ludger Wöste — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

The aim of the presented work lies in further developing femtosecond time-resolved NeNePo (negative, neutral, positive) spectroscopy within the study of catalytic reaction properties of noble metal cluster-adsorbate complexes. We seek to expand from the original analysis of the cluster dynamics to an active steering of a reactive system along a desired coordinate through coherent control strategies. To realize this goal, ultra-broadband laser pulses are generated by means of self phase modulation through filamentation in noble gas atmosphere. Subsequently, the obtained pulses can be modulated by a liquid crystal mask within a pulse shaper setup especially designed for manipulating broadband spectra. Within these efforts, emphasis is made on characterizing the spectral phase and amplitude of the broadband, tailored pulses. This instrumentation allows for optimizing a desired reaction pathway in an active feedback loop employing genetic algorithms that control the structure of the excitation pulse. First results on the spectral properties of the continuum generation and capability of four-wave-mixing for analyzing the pulse structure will be presented.

MO 56.15 Do 16:30 Poster A

Kohärenz und Doppelspaltinterferenz bei der Doppelionisation von H2 — •Dominique Akoury[1], Katharina Kreidi[1], Thorsten Weber[2], Till Jahnke[1], Markus Schöffler[1], Lothar Schmidt[1], Ottmar Jagutzki[1], Lutz Foucar[1], Tilo Havermeier[1], Nadine Neumann[1], Horst Schmidt-Böcking[1], Reinhard Dörner[1], Tim Osipov[2], Ali Belkacem[2], Mike Prior[2], Allen Landers[3], Predrag Ranitovic[4] und Lewis Cocke[4] — [1]Institut für Kernphysik Frankfurt, Universität Frankfurt, Deutschland — [2]LBNL, 1 Cyclotron Road, Berkeley, CA 94720, USA — [3]Department of Physics, Auburn University, Auburn, Alabama 36849, USA — [4]Dept, of Physics, Kansas State University, Manhattan, KS 66506, USA

Die Emission von Photoelektronen aus einem diatomaren homonuklearen Molekül bildet ein dem klassischen Doppelspalt ähnliches System. In einer Reihe von Doppelionisationsexperimenten an H2 haben wir Interferenzstrukturen in der Elektronenwinkelverteilung relativ zur Molekülachse gefunden, die denen des klassischen Doppelspaltes ähneln. In diesen Experimenten wurden mit Hilfe der COLTRIMS Technik die Impulse beider Elektronen und Protonen in Koinzidenz gemessen. Diese Art der Messung erlaubt es, die komplexe Wechselwirkung zwischen Elektronenkorrelation und Interferenz zu untersuchen und zu verstehen.