

## MO 27 Poster: Femtosecond Spectroscopy

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 27.1 Di 16:30 Labsaal

**Shaping of CARS spectra using optimal control theory** — ●S. PEZESHKI, J. LIEBERS, M. SCHREIBER, and U. KLEINEKATHÖFER — 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 [1,2]. Here we use the theoretical tool of optimal control [3,4] to influence femtosecond time-resolved coherent anti-Stokes Raman scattering (CARS) signals and spectra. The calculations are done by using time-dependent wave packet calculations together with perturbation theory in the laser field strength. The CARS signals can then be determined using those wave packets of different order in the field strength.

- [1] J. Konradi, A. K. Singh, and A. Materny, PCCP. **7** 3574 (2005)
- [2] N. Dudovich, D. Oron, and Y. Silberberg, Nature **418**, 512 (2002).
- [3] A. Kaiser and V. May, Chem. Phys. Lett. **405** 339 (2005)
- [4] J. Werschnik and E. K. U. Gross, J.Opt. B **7** S300 (2005)

MO 27.2 Di 16:30 Labsaal

**Molecular Decoherence in Solid Environments: Br<sub>2</sub> in solid Ar** — ●MARKUS GÜHR<sup>1,2</sup>, HEIDE IBRAHIM<sup>1</sup>, and NIKOLAUS SCHWENTER<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin — <sup>2</sup>Stanford Synchrotron Radiation Laboratory, Menlo Park, California 94025-7015

The intramolecular wave packet dynamics on the electronic B (<sup>3</sup>Π<sub>0</sub>) potential of Br<sub>2</sub> in solid argon is induced and interrogated by femtosecond pump-probe spectroscopy. An effective potential of the chromophore in the solid is derived from the wave packet period for different excitation photon energies. Deep in the potential well, it is consistent with vibrational energies from wavelength resolved spectra. At higher energies, the vibrational progression merges to a continuum and no potential can be derived from the high resolution spectra. In contrast, the time resolved spectra display pronounced wave packet dynamics which allow to construct an effective potential of the molecule in the matrix, even above the gas phase dissociation limit. This advantage of pump-probe spectroscopy is related to a reduced contribution of homogeneous and inhomogeneous linebroadening. A very large energy loss in the first collision of the molecule with the Ar crystal is observed. This strong interaction with the matrix is directly displayed in an experimental trajectory. Despite the strong energy loss, coherent wave packet oscillations can be observed after the collision. This is attributed to the special symmetry of the molecule-host system.

MO 27.3 Di 16:30 Labsaal

**Ultraschnelle Dynamik eines molekularen Schalters: Fulgide** — ●THOMAS BRUST<sup>1</sup>, STEPHAN MALKMUS<sup>1</sup>, SIMONE DRAXLER<sup>1</sup>, CHRISTINE SCHULZ<sup>2</sup>, STEFFEN DIETRICH<sup>2</sup>, KAROLA RÜCK-BRAUN<sup>2</sup>, WOLFGANG ZINTH<sup>1</sup> and MARKUS BRAUN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, 80538 München — <sup>2</sup>Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin

Reversible molekulare Photo-Schalter, deren Konformationsänderungen durch unterschiedliche Photonenenergien induziert werden, sind interessante Kandidaten für mögliche Anwendungen (optische Speicher, licht-induzierte Konformationsänderungen). Unter diesen photochromen Substanzen zeichnet sich insbesondere die Klasse der Indolylfulgide durch thermodynamische Stabilität ihrer Konformere aus.

Wir untersuchen mittels Femtosekundenpektroskopie die Dynamik dieser Schaltvorgänge, in diesem Fall eine perizyklische Ringschluss- bzw. Ringöffnungsreaktion [1]. Die benötigten Femtosekunden-Lichtimpulse für die beiden Reaktionsrichtungen werden mittels eines selbstgebauten Ti:Sa-basierten Lasersystems und eines nicht-kollinearen optisch parametrischen Verstärkungsprozesses (NOPA) bereitgestellt. Die Reaktionsdynamik wird durch Abtastimpulse im UV/VIS Bereich in einem Anreg-Abtast-Experiment untersucht. Sowohl für die Ringöffnungs- als auch die Ringschlussreaktion werden Zeitkonstanten von unter 10 ps beobachtet. Die Abhängigkeit der Quantenausbeuten von der Temperatur und Anregungswellenlänge wird diskutiert.

- [1] S. Malkmus et al., Chem. Phys. Lett. **417** (2005) 266

MO 27.4 Di 16:30 Labsaal

**Molecular tomography: test of accuracy and improvements using time-dependent calculations** — ●ELMAR VAN DER ZWAN and MANFRED LEIN — Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg

Recently a method to perform tomographic imaging of molecular orbitals using High Harmonic Generation (HHG) has been proposed [1]. The method is based on the simplification that the returning electron in the three-step model can be modeled as a plane wave. We investigate the effect of this assumption in a time-dependent calculation by numerically comparing results for the final reconstructed orbital using two different methods which, without the plane-wave assumption, should lead to identical results; namely the reconstruction based on dipole matrix elements or on momentum matrix elements. From this we try to improve on the method. The 3D orbital of a diatomic molecule can be recovered from the 2D projection that results from the tomographic reconstruction. We investigate molecules with anti-symmetric valence orbitals, since these are expected to cause problems in the original scheme.

- [1] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J.C. Kieffer, P.B. Corkum and D.M. Villeneuve. *Tomographic imaging of molecular orbitals*. Nature **432**, 867-871 (2004)

MO 27.5 Di 16:30 Labsaal

**Sub-Picosecond Time-Resolved Infrared Spectroscopy of Phytochrome** — ●CHRISTIAN SCHUMANN<sup>1</sup>, RUTH JAKOBER<sup>1</sup>, ROLF DILLER<sup>1</sup>, NORBERT MICHAEL<sup>2</sup>, and TILMAN LAMPARTER<sup>2</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — <sup>2</sup>Institut für Pflanzenphysiologie, Freie Universität Berlin, D-14195 Berlin

The properties of phytochrome have been subject to numerous investigations, including stationary and low-temperature FTIR, resonance Raman and femtosecond transient absorption spectroscopy in the visible[1].

Here we present the first results of sub-picosecond time-resolved IR vibrational spectroscopy of the primary photoinduced processes of the phytochromes Cph1-PCB and Agp1-BV, which can help elucidate the ultrafast structural dynamics of such systems. The time constant of ca. 16 ps as observed in the band shift dynamics of the chromophore carbonyl stretch vibration indicates a fast chromophore  $P_r$  to  $P_{fr}$  isomerization in Cph1-PCB and is in good agreement with previous results[1].

- [1] K. Heyne, J. Herbst, D. Stehlik, B. Esteban, T. Lamparter, J. Hughes and R. Diller; Biophysical Journal **82** (2002), 1004-1016

MO 27.6 Di 16:30 Labsaal

**FS-Study on Bacterial LH1 Complexes: Carotenoid Energy Relaxation Channels** — ●PETER GAERTNER<sup>1</sup>, HELMUT PORT<sup>1</sup>, MARCUS BRANSCHADEL<sup>2</sup>, and ROBIN GHOSH<sup>2</sup> — <sup>1</sup>3. Physikalisches Institut, Uni Stuttgart — <sup>2</sup>Abteilung Biophysik, Biologisches Institut, Uni Stuttgart

Comparative fs-spectroscopic investigations on light-harvesting 1 (LH1) complexes from mutants of *Rhodospirillum rubrum* (*R.r.*) are reported. The carotenoid chain length effects in LH1 environment are different from carotenoids in solution. The competitive energy relaxation pathways are distinguished upon state-selective photoexcitation.

MO 27.7 Di 16:30 Labsaal

**Trans-cis reaction dynamics in sensory rhodopsin II by femtosecond time-resolved IR spectroscopy: protein and chromophore dynamics** — ●RUTH JAKOBER<sup>1</sup>, CHRISTIAN SCHUMANN<sup>1</sup>, ROLF DILLER<sup>1</sup>, JOHANN P. KLARE<sup>2</sup>, and MARTIN ENGELHARD<sup>2</sup> — <sup>1</sup>Fachbereich Physik, Technische Universität Kaiserslautern, 67663 Kaiserslautern — <sup>2</sup>Max-Planck-Institut f. Molekulare Physiologie, 44227 Dortmund

Transient vibrational spectroscopy, which provides insights into processes associated with protein-based photoreactions such as structural changes of the chromophore, its vibrational relaxation and the dynamics of the protein environment, has been performed on sensory rhodopsin II from *Natronomonas pharaonis* at sub-picosecond time resolution.

We present new data on the dynamics of the chromophore and the surrounding protein due to the primary all-trans to 13-cis retinal photoisomerization. Three time constants (0.5 ps, 4 ps and 11 ps) were obtained [1]. It was found that the isomerization takes place within 0.5 ps, fol-

lowed by an electronic ground state relaxation (4 ps) which corresponds to experiments in the visible spectral region. The 11 ps time constant is discussed as an indication of protein dynamics or a vibrational cooling process.

[1] Rolf Diller, Ruth Jakober, Christian Schumann, Frank Peters, Johann P. Klare, Martin Engelhard; Biopolymers: Biophysics, submitted 2005.

MO 27.8 Di 16:30 Labsaal

**External Electric Field Effects on Ultrafast Electron Transfer Dynamics** — ●A.K. SINGH, J. KONRADI, A.V. SCARIA, and A. MATERNY — International University Bremen, Bremen

The ubiquitous nature of electron transfer (ET) reactions has made them a subject of extensive theoretical and experimental research for many decades. However, the number of studies concerning the effect of a static electric field on intramolecular and intermolecular ET processes is limited. An external electric field is expected to influence the rate of the charge separation process considerably in a photo-excited donor-acceptor system through a significant modification of the free energy change ( $\Delta G$ ). Additionally, changes of the electronic coupling between the initial and final states of the ET process have an important influence. Due to a large dipole moment associated with the radical ion pairs produced in the charge separation process,  $\Delta G$  changes in the presence of the external field. As the electron transfer rate is a function of  $\Delta G$ , the reaction dynamics for the production of radical ion pairs is influenced by the introduced perturbation of the system. Depending on the magnitude of the dipole moment and its orientation relative to the electric field, the forward ET rate depends on the applied field. In our contribution, we present results of investigations of the ultrafast ET dynamics under the influence of an external electric field by means of femtosecond time-resolved spectroscopy.

MO 27.9 Di 16:30 Labsaal

**Ultrafast Energy Transfer Between Pigment Molecules Embedded in Mesoporous Cages** — ●S. TORK, R.M. RICHARDS, and A. MATERNY — International University Bremen, Bremen

Chlorophylls, along with Carotenoids are crucial pigment molecules involved in light-harvesting processes in photosynthetic organisms. Mimicking the highly efficient energy transfer (ET) systems is a subject of intense investigation to attain the ultimate goal of highly efficient solar energy conversion systems. Considerable efforts have been directed towards the preparation of donor-acceptor (D-A) systems immobilized in various media (*e.g.* films, surfactant micelles, and lipid vesicles). Mesoporous silicas are attractive because of their high surface area, uniform mesopores, and high adsorption capacities. We have synthesized and characterized various mesoporous materials such as MCM (mobile crystalline material) and FSM (folded-sheet mesoporous material) having honeycomb (hexagonal) structures with ordered cylindrical channels of 2–10 nm in diameter. They are potential hosts for the inclusion of bulky organometallic and inorganic complexes and offer nano-scale spaces for the desired arrangement of functional molecules such as chlorophyll. In this contribution, we will present our results on synthesis of mesoporous-chlorophyll-carotenoid compounds and the investigation of the energy transfer process from carotenoids to chlorophylls using femtosecond transient absorption spectroscopy in order to get insight into the energy transfer mechanism.

MO 27.10 Di 16:30 Labsaal

**Considerations for the measurement of the ultrafast heterogeneous electron transfer at metal oxide surfaces using two-photon photoelectron spectroscopy** — ●JODI SZARKO, CHARAF CHERKOUK, LARS GUNDLACH, LIANA SOCACIU-SIEBERT, ANTJE NEUBAUER, RALPH ERNSTORFER, RAINER EICHBERGER, GUIDO MORBACH, and FRANK WILLIG — Hahn-Meitner-Institute, Dept. SE4, Glienicke Str. 100, 14109 Berlin, Germany

The photoinduced electron transfer from organic chromophores into metal oxide surfaces was investigated in our group using time-resolved two-photon photoelectron spectroscopy (2-PPE). A two-color pump-probe technique was made possible by utilizing two nonlinear optical parametric amplifiers (NOPAs) operating at 150 kHz. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were also used to characterize the systems. The bare surfaces of the metal oxide crystals were first investigated to determine the best preparation procedure for the optimal surface cleanliness, stoichiometry, and work function for each crystal. The chromophores were then chemically anchored to the surfaces using a wet chemistry technique under inert gas conditions. Finally, the electron injection and transport were

determined for the chromophore/metal oxide interfaces.

MO 27.11 Di 16:30 Labsaal

**Dynamics of electron transfer through a chromophore/semiconductor interface** — ●LIANA SOCACIU-SIEBERT, ANTJE NEUBAUER, LARS GUNDLACH, JODI SZARKO, RALPH ERNSTORFER, CHARAF CHERKOUK, GUIDO MORBACH, RAINER EICHBERGER, and FRANK WILLIG — Hahn-Meitner Institut, Abteilung Dynamik von Grenzflächenreaktionen SE4, Glienicke Str. 100, 14109 Berlin, Germany

The ultrafast heterogeneous electron transfer through a chromophore/semiconductor interface was investigated by means of time-resolved two-photon photoemission spectroscopy (TR-2PPE). This pump-probe technique allowed for monitoring simultaneously the time evolution as well as the energy distribution of the injected electrons. The chromophore/semiconductor systems were chosen so that the first excited state of the molecule (donor state) was energetically positioned above the conduction band minimum of the semiconductor. The organic chromophores (perylene derivatives) were chemically anchored on the rutile TiO<sub>2</sub>(110) surface. Different molecular groups, which acts as a bridge, were also inserted between the chromophore and the anchor. The electron transfer rate is strongly influenced by the length and structure of the molecular bridge and, subsequently, the injection times vary over a few orders of magnitude. A systematic study of the dynamics of electron transfer for chromophores with different molecular bridges is presented in this contribution.

MO 27.12 Di 16:30 Labsaal

**Optimal Control of Metal Cluster Reactions by Modulated Ultra-broadband Laser Pulses** — ●BRUNO E. SCHMIDT<sup>1</sup>, DENISIA POPOLAN<sup>1,2</sup>, SANDRA LANG<sup>1,2</sup>, THORSTEN M. BERNHARDT<sup>1,2</sup>, and LUDGER WÖSTE<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Abteilung Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm

During the last years the NeNePo technique was applied to study catalytic reaction properties of noble metal cluster-adsorbate complexes in a temperature controlled rf-ion trap. To further innovate this work, we not only aim to analyze the reaction dynamics, but also to steer the reactive system along one desired reaction coordinate and thus to optimize, *e.g.*, the products of a catalytic reaction. To realize this goal, ultra-broadband laser pulses are generated by means of self phase modulation during filamentation process in noble gas atmosphere. Subsequently the broadband pulses are modulated by a liquid crystal mask and irradiated onto the cluster system. The concentration of desired reaction products is optimized in a active feedback loop employing a genetic algorithm. The experimental task is the realization of a broad spectrum which is stable enough to send it to a pulse shaper and to optimize the algorithm for this type of reaction. First results on the spectral properties of the continuum generation relying on self-guiding in noble gas will be presented and its application to the reaction control will be discussed.