

## MO 14: Poster 1: Cluster, Femtosecond Spectroscopy

Time: Tuesday 16:00–18:30

Location: Empore Lichthof

MO 14.1 Tue 16:00 Empore Lichthof

**Ultrafast photochemistry of a CO-releasing molecule under two-photon excitation** — PHILIPP RUDOLF<sup>1</sup>, FLORIAN KANAL<sup>1</sup>, JOHANNES KNORR<sup>1</sup>, CHRISTOPH NAGEL<sup>2</sup>, ULRICH SCHATZSCHNEIDER<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

There is steadily increasing interest in CO-releasing molecules (CORMs) as a promising in-situ source of carbon monoxide, which is an important endogenous gasotransmitter in higher organisms, including humans [1,2]. In previous UV-pump/MIR-probe studies on  $[\text{Mn}(\text{CO})_3(\text{tpm})]\text{Cl}$  in aqueous solution, we could show that several electronic transitions in the UV will lead to CO release and that only one CO ligand is released within the first few picoseconds after UV excitation. With regard to biological applications, we currently aim at the elucidation of the primary reaction steps of the above-mentioned CORM under two-photon excitation. Using pump wavelengths from the therapeutic window, the employment of tissue-damaging UV light can be avoided. Moreover, this approach benefits from the capability to selectively excite well-defined volumes owing to the non-linear interaction step.

[1] C. C. Romão et al., Chem. Soc. Rev. 2012, 41, 3571-3583

[2] R. Alberto and R. Motterlini, Dalton Trans. 2007, 17, 1651-1660

MO 14.2 Tue 16:00 Empore Lichthof

**Vibronic energy localization in weakly coupled small molecular aggregates** — JOHANNES WEHNER, ALEXANDER SCHUBERT, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany

Within a one-exciton picture, molecular dimers ( $M_1$ - $M_2$ ) possess excited states of even and odd parity which correspond to linear combinations of locally excited configurations ( $M_1^*$ - $M_2$ ,  $M_1$ - $M_2^*$ ). If this symmetry is broken, the excitation energy localizes in one or the other monomer. We perform time-dependent quantum calculations on dimer and trimer aggregates which are subject to time-dependent perturbations. The latter induce exciton localizations which are influenced by the monomer vibrational degrees-of-freedom. This influence is characterized by comparison with purely electronic models.

MO 14.3 Tue 16:00 Empore Lichthof

**Two-dimensional vibronic spectroscopy of molecular predissociation** — JULIAN ALBERT, ALEXANDER SCHUBERT, and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany

We calculate two-dimensional (2D) spectra reflecting the time-dependent electronic predissociation of a diatomic molecule. The laser-excited electronic state is coupled non-adiabatically to a fragment channel, leading to the decay of the prepared quasi-bound states. This decay can be monitored by the three-pulse configuration employed in optical 2D-spectroscopy. It is shown that in this way it is possible to state-selectively characterize the time-dependent population of resonance states with different lifetimes. A model of the NaI molecule serves as a numerical example.

MO 14.4 Tue 16:00 Empore Lichthof

**A simple model for the relaxation dynamics in perylene-bisimide dimers excited by femtosecond laser pulses** — MARTIN KESS<sup>1</sup>, ALEXANDER SCHUBERT<sup>1</sup>, VOLKER SETTELS<sup>1</sup>, BERND ENGELS<sup>1</sup>, FRANK WÜRTHNER<sup>2</sup>, STEFAN LOCHBRUNNER<sup>3</sup>, CHRISTOPH MEIER<sup>4</sup>, and VOLKER ENGEL<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>3</sup>Institut für Physik, Universität Rostock, Universitätsplatz 3, Germany — <sup>4</sup>Laboratoire Collisions, Agrégats et Réactivité, IRSAMC, Université Paul Sabatier, 31062 Toulouse, France

We evaluate a model for the self-trapping dynamics in perylene-bisimide dimers. Adiabatic potential energy curves and charge-transfer characters determined from ab-initio electronic structure computations

are employed to establish a diabatic model for the quantum dynamics along an effective deformational mode. It is then possible to characterize the fast de-population of the state, accessed in the femtosecond preparation process. The influence of the laser parameters and the dissipation rate on the decay dynamics is studied in detail. The results are in excellent agreement with transient absorption measurements.

MO 14.5 Tue 16:00 Empore Lichthof

**Fingerprints of adiabatic versus diabatic vibronic dynamics in the asymmetry of photoelectron momentum distributions** — MIRJAM FALGE<sup>1</sup>, VOLKER ENGEL<sup>1</sup>, and STEFANIE GRÄFE<sup>2</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Institut für Theoretische Physik Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

When the Born-Oppenheimer approximation is valid, electrons follow adiabatically the nuclear motion in molecules. For strong non-adiabatic coupling between electronic states, one encounters a diabatic motion where the electrons remain local and do not adapt to molecular geometry changes. We show that the mentioned limiting cases are reflected differently in the asymmetry of time-resolved photoelectron momentum distributions. Whereas for adiabatic dynamics, the asymmetry directly maps the time-dependent average nuclear momentum, in the diabatic case the asymmetry is determined by a non-classical interference effect arising from the mixing of wave function components in different electronic states which is present at times non-adiabatic transitions take place.

MO 14.6 Tue 16:00 Empore Lichthof

**Attosecond electronic coherence in molecular dissociation** — LUKAS MEDIŠAUSKAS<sup>1,2</sup> and MISHA IVANOV<sup>1,2</sup> — <sup>1</sup>Imperial College London, UK — <sup>2</sup>Max-Born-Institute Berlin, Germany

We show that electronic coherence can significantly influence nuclear dynamics when interference of paths associated with vibrational motion along different potential energy surfaces becomes important.

We consider attosecond XUV pump - IR probe setup. A  $N_2$  molecule is first ionized by an XUV pump pulse. Ionization creates a coherent superposition of two excited electronic states in  $N_2^+$  ion. The dissociation of the molecular ion then takes place over two different potential energy surfaces. Interaction with IR field ensures that both of them lead to the same dissociation limit. The fragment spectrum obtained depends significantly on how the two paths interfere.

Interference is observed if the continuum electron wavepackets correlated with each of the paths have an overlap. This condition is set during ionization, which happens in a fraction of a femtosecond and is given by the length of the XUV pump pulse. However, it determines the appearance of molecular dissociation spectrum hundreds of femtoseconds later.

When one of the pathways involves a direct and the other a sequential transition to a dissociative state, the phase acquired along the propagation on sequential path creates a chirp in the interference pattern. This chirp encodes information on the initial wavepacket and the potential energy surface.

MO 14.7 Tue 16:00 Empore Lichthof

**Tensorial approach to anisotropy effects in third-order response spectroscopy with arbitrarily polarized laser pulses** — SEBASTIAN SCHOTT, ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We present a theoretical study in which an arbitrary tensor of rank four is used to describe the properties of a molecular sample. Since most studies focus on the investigation of isotropic samples, we apply as only assumption rotational averaging over randomly oriented molecules to the response function tensor. By also choosing the most general polarization state and an arbitrary propagation direction for each laser pulse the simulation of various experimental scenarios is possible.

We specifically calculate the magic angle condition for transient absorption spectroscopy and expand the well-known condition for linearly polarized pump and probe pulses to arbitrarily polarized pulses. Im-

plications for experiments with polarization shaped laser pulses as e.g. used in quantum control are addressed. We further explore which role contributions due to anisotropy may play in coherent two-dimensional spectroscopy and how to circumvent them by variation of the polarization of the laser pulses.

MO 14.8 Tue 16:00 Empore Lichthof

**Ultrafast mid-infrared spectroscopy of sensory rhodopsin II from *Natronomonas pharaonis*** — ●CHRISTIAN KIJATKIN, KRISTIN SPRINGFELD, JOHANN KLARE, HEINZ-JÜRGEN STEINHOFF, and MIRCO IMLAU — School of Physics, Osnabrück University, Germany

A multitude of several rhodopsins offer functional properties, which are necessary for the use as pumps, sensors or even molecular phototaxis [1]. Transient mid-infrared vibrational spectroscopy is performed to obtain more information of the light-induced trans-cis isomerization process of sensory rhodopsin II from *Natronomonas pharaonis* (NpSRII). We use femtosecond laser pulses with wavenumbers in the fingerprint region of the chromophore NpSRII between  $1180\text{ cm}^{-1}$  and  $1206\text{ cm}^{-1}$  and of the ethylenic stretch vibrations between  $1530\text{ cm}^{-1}$  and  $1572\text{ cm}^{-1}$ .

The transmission of mid-infrared  $\tau \approx 150\text{ fs}$  pulses is detected by a multichannel MCT detector as a function of time delay to an intense VIS pump pulse of  $\tau \approx 100\text{ fs}$  pulse duration. We present our results on the studies of the light-induced changes of such vibrational modes on the  $100\text{ fs}$  time scale compared to FTIR difference spectra.

Financial support by the DFG (IM 37/5, INST 190/137-1) is gratefully acknowledged.

[1] J. P. Klare et al., *Bioenergetics*, **45**, 73-122 (2008)

MO 14.9 Tue 16:00 Empore Lichthof

**Transient coupling spectroscopy and control of electronic states in the liquid phase** — ●KRISTINA MEYER<sup>1</sup>, RIMA SCHÜSSLER<sup>1</sup>, CHRISTIAN OTT<sup>1</sup>, PHILIPP RAI<sup>1</sup>, ANDREAS KALDUN<sup>1</sup>, MARTIN LAUX<sup>1</sup>, THOMAS DING<sup>1</sup>, ZUOYE LIU<sup>1</sup>, YIZHU ZHANG<sup>2</sup>, and THOMAS PFEIFER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — <sup>2</sup>Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

Recently, pump-probe experiments on helium atoms using infrared (IR) and attosecond pulses were performed [1]. There, the presence of a laser field shifts the phase of the metastable excited states and modifies the natural Fano absorption line shapes. Here, we study this phenomenon for larger molecules in the liquid phase, in particular a solution of the dye IR144 in methanol, using a compact transient-absorption setup. Modifications of absorption line shapes at delay times where the probe pulse precedes the pump pulse are observed, which are a first indication of excited-state dressing effects as observed before with attosecond pulses in helium. The same experimental setup has recently been proven to work also for 2D spectroscopy measurements [2]. A combination with a pulse shaper will soon allow the control of electronic states in complex molecules. The pulse shaper can also be used to increase the temporal resolution [3] and/or improve the system's excitation transfer response [4] in the future.

[1] C. Ott et al., arXiv: 1205.0519v1, [2] Y. Zhang et al., submitted, [3] K. Meyer et al., *PRL* **108**, 098302 (2012), [4] A. W. Chin et al., *NJP* **12**, 065002 (2010),

MO 14.10 Tue 16:00 Empore Lichthof

**Photoelectron Circular Dichroism in the Above-Threshold-Ionization of Bicyclic Ketones observed via Femtosecond Laser Ionization** — CHRISTIAN LUX, VANESSA BRANDENSTEIN, ●TOM RING, JENS KÖHLER, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) so far investigated using synchrotron radiation on chiral molecules shows asymmetries in forward/backward direction with respect to the light propagation. The effects observed are several orders of magnitude larger than in conventionally CD [1]. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass spectrometry of chiral molecules using laser pulses results in strong asymmetries in the absorption of circularly polarized light [2,3]. We demonstrated that PECD is also accessible via REMPI on chiral molecules using femtosecond laser pulses, containing highly structured asymmetries up to  $\pm 15\%$  [4]. In this poster we show that PECD also appears in the Above-Threshold-Ionization on the bicyclic ketones Camphor, Norcamphor and Fenchone. We observe contributions of higher order Legendre polynomials in the angular distributions as compared to the threshold ionization.

[1] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* **138**, 267-329 (2008)

[2] C. Logé, U. Boesl, *Chem. Phys. Chem.* **12**, 1940-1947 (2011)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, *Chirality* **24**, 684-690 (2012)

[4] C. Lux et al., *Angew. Chem. Int. Ed.* **51**, 5001-5005 (2012)

MO 14.11 Tue 16:00 Empore Lichthof

**Femtosekundenröntgenbeugung an Halbleitern und organischen Kristallen** — ●STEFAN M. HOFMANN, FLORIAN J. LEDERER, JULIAN SCHAUSEIL, FLORIAN TROMMER und WOLFGANG ZINTH — LMU München, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München

Schon seit langem werden zeitaufgelöste Informationen aus Molekülen über spektroskopische Analysen gewonnen. Die Struktur von Kristallen wurde mit Röntgenbeugungsexperimenten bestimmt. Durch das Verwenden von Röntgenimpulsen, die eine Dauer im Femtosekundenbereich haben, ist es möglich diese zwei Methoden miteinander zu kombinieren. Mit dem bekannten Aufbau aus der Anrege-Abtast Spektroskopie kann man die Strukturauflösung mit einer zeitlichen Auflösung im Femtosekundenbereich realisieren.

Die Röntgenimpulse entstehen durch Fokussieren eines intensiven fs-Lichtimpulses auf ein Kupferband, in dem durch Elektronenbeschleunigung charakteristische  $K_{\alpha}$ -Strahlung hervorgerufen wird. Diese ca. hundert Femtosekunden dauernden Röntgenimpulse werden als Abtastimpulse verwendet. Es wurden Galliumarsenid und 4-(Diisopropylamino)benzonnitril (DIABN) Kristalle untersucht. Mit dem Galliumarsenid wird der zeitliche und räumliche Überlapp des Anrege- und Abtastimpulses verifiziert. In DIABN wird ein Ladungstransfer beobachtet, der eine Änderung der Kristallbasis und damit der reflektierten Intensität bewirkt [1].

[1] M. Braun et al., *Applied Physics A*, **96**(1) 107 (2009)

MO 14.12 Tue 16:00 Empore Lichthof

**Circular dichroism in the photoelectron distribution from multiphoton ionization of chiral molecules** — ●INGO DREISSIGACKER and MANFRED LEIN — Institut für Theoretische Physik und Centre for Quantum Engineering and Space-Time Research (QUEST), Leibniz Universität Hannover, Appelstr. 2, 30167 Hannover, Germany

Circular dichroism in the photoelectron angular distribution from chiral molecules illuminated with XUV radiation has been predicted [1] and measured [2] long ago. For application in chemical analytics, however, methods based on table-top laser systems and thus longer wavelengths would be preferable, since XUV sources are rarely available. In contrast to the dichroism effect in the photoelectron distribution from single-photon ionization, dichroism in multiphoton ionization has been proven experimentally only recently [3].

Motivated by this progress, we investigate the asymmetry in the electron distribution from chiral molecules theoretically with the help of the strong-field approximation. We calculate photoelectron spectra for randomly oriented camphor and fenchone molecules. The initial bound states required for the integration are obtained from quantum chemistry calculations. We compare our results to the experimental findings of [3] and investigate the dependence of the dichroism on various laser parameters.

[1] N. A. Cherepkov, *Chem. Phys. Lett.* **87**, 344 (1982)

[2] N. Böwering et al., *Phys. Rev. Lett.* **86**, 1187 (2001)

[3] C. Lux et al, *Angew. Chem. Int. Ed.*, **51**, 5001 (2012)

MO 14.13 Tue 16:00 Empore Lichthof

**Wave Packet Interferometry at Potassium Atoms Applying a Band-pass Filtering Technique** — ●LUKAS BRUDER, SABRINA LIPPS, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

The achievements in generating ultra-short laser pulses have opened opportunities for studying wave packet dynamics in quantum systems. However, experiments for demonstrating coherent dynamics of electronic states are often very sensitive to laboratory noise. Especially controlling the relative phase of the temporal envelopes in a coherent fs-pulse train remains a difficult task. In our collinear pump-probe setup we investigate electronic wave packet interference of atomic potassium. On the basis of [1], we greatly reduce the influence of laboratory noise applying a band-pass filtering technique: Acousto-optical phase modulation imparts a characteristic signature on the fluorescence signal that is demodulated using a lock-in amplifier. Simultaneous acquisition of in-phase and in-quadrature components yields the full phase information. This technique leads to a strongly undersampled quantum beating of the coherences and greatly reduces the scaling of laboratory

noise. These characteristics are great advantages in view of a setup for 2D-spectroscopy. [1] P. F. Tekavec, T. R. Dyke, and A. H. Marcus, *J. Chem. Phys.* 125, 194303 (2006).

MO 14.14 Tue 16:00 Empore Lichthof

**Fs-pump-probe spectroscopy and strong field ionization of doped He-nanodroplets** — ●HARALD SCHMIDT<sup>1</sup>, JOHANNES VON VANGEROW<sup>1</sup>, BARBARA GRÜNER<sup>1</sup>, MANUEL ROMETSCH<sup>1</sup>, ALEXANDR BOGOMOLOV<sup>2</sup>, ALEXEY BAKLANOV<sup>2</sup>, FRANK STIENKEMEIER<sup>1</sup>, and MARCEL MUDRICH<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — <sup>2</sup>Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Institutskaya 3, Novosibirsk, 630090, Russia

The low temperature and weak interaction with dopants makes He-nanodroplet isolation a widely used technique for high resolution spectroscopy. We combine two-colour fs-pump-probe spectroscopy and velocity-map-imaging - of both ions and electrons - to investigate vibrational wave-packet dynamics and photodissociation of alkali halides. By comparing molecules in the gas phase to those embedded in He-nanodroplets, we study the effect of the surrounding He on the photo-dynamics.

When illuminated by intense NIR laser pulses, the doped He nanodroplets can turn into a highly reactive nanoplasma environment, in which both the He and the rare gas dopants are multiply ionized to high charge states. Surprisingly, the formation of a nanoplasma is strongly suppressed when doping the droplets with surface-bound alkali and earth-alkali metals. This points at pronounced geometrical effects in the dopant-induced ignition process.

MO 14.15 Tue 16:00 Empore Lichthof

**The ultrafast dynamics of electron-transporting analogs of pentacene** — ●JULIA HERZ<sup>1</sup>, JENS ENGELHART<sup>2</sup>, TIAGO BUCKUP<sup>1</sup>, UWE BUNZ<sup>2</sup>, and MARCUS MOTZKUS<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — <sup>2</sup>Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Pentacene derivatives are attractive targets to construct electron transporting materials in organic electronic devices. While pentacene is utilized in organic field effect transistors, the modified aza-pentacenes could find application as acceptor molecules in organic solar cells. The presence of electronegative nitrogen atoms in the systems changes the ground state as well as the excited state behaviour considerably. Transient-absorption spectroscopy allows the observation of the population flow after photo excitation. The evolution of the exciton and furthermore the formation of states and the charge generation process can be followed. We demonstrate preliminary studies of Diaza-TIPS-pentacene and Tetraaza-TIPS-pentacene in two different solvents. The ground state properties of these two molecules are presented as well as time-resolved absorption and fluorescence measurements. The influence of the nitrogen substitution and the symmetrical charge distribution on the excited state lifetimes are presented. The revealed oscillations of 270 cm<sup>-1</sup> from the excited state are more distinctive in an unpolar solvent like toluene compared to THF. We find a pronounced concentration dependence on the excited state absorption signal, thus the aggregation of molecules in solution has to be considered.

MO 14.16 Tue 16:00 Empore Lichthof

**Control of the Photoinduced Dynamics of DCM and Coumarin 307 in the Ultraviolet Regime** — ●INA HALFPAP, JÜRGEN PLENGE, and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

The control of molecular dynamics with femtosecond laser pulses has been intensively studied in recent years and has improved the understanding of molecular photochemical processes [1]. Often, dye molecules have been used as model systems to explore control mechanisms. In particular, the optimization of the two-photon induced fluorescence of different dyes has been investigated using infrared shaped laser pulses [2]. In contrast, the control of photoprocesses in the linear absorption regime has been far less studied. We present recent results on the control of the relative fluorescence yield following excitation of DCM and Coumarin 307, respectively, in the linear absorption regime using shaped ultraviolet laser pulses ( $\lambda = 400$  nm). In one-parameter control experiments a strong influence of the linear chirp on the radiative relaxation of the S<sub>1</sub> state has been found. The enhancement of the relative fluorescence yield with increasing chirp can be explained by a resonance-mediated (1+2) photoionization process which competes with the radiative relaxation. Complementary results have been

obtained from feedback controlled optimization experiments. The possibility to control the fluorescence yields of dyes can contribute to an improvement of various techniques, such as fluorescence microscopy.

[1] M. Dantus et. al, *Chem. Rev.* 104, 1813 (2004).

[2] S. Zhang et. al., *Chem. Phys. Lett.* 415, 346 (2005).

MO 14.17 Tue 16:00 Empore Lichthof

**Similarities and Differences in the Optical Response of Perylene-based Hetero-bichromophores and Their Monomeric Units** — ●PATRICK NUERNBERGER<sup>1</sup>, ULRIKE SELIG<sup>1</sup>, VOLKER DEHM<sup>2</sup>, VOLKER SETTELS<sup>1</sup>, MARCEL GSÄNGER<sup>2</sup>, BERND ENGELS<sup>1</sup>, FRANK WÜRTHNER<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The linear and nonlinear optical response of molecular hetero-dimers and the composing perylene units is explored with fluorometry, steady-state and transient absorption, and coherent two-dimensional electronic spectroscopy. Supported by a Förster theory approach and ab-initio calculations, we disclose the photoinduced dynamics comprising excitonic coupling, conformational changes, charge transfer, and relaxation dynamics. The influence of the actual orientation of the two chromophore units on these processes is investigated by employing two bichromophores built of the same monomeric units but linked differently.

MO 14.18 Tue 16:00 Empore Lichthof

**SVD analysis for the time-resolved study of the electron transfer in photosynthetic reaction center of Rhodobacter Sphaeroides** — ●JEFF MICHELMANN, PABLO NAHUEL DOMINGUEZ, MATTHIAS HIMMELSTOSS, and WOLFGANG ZINTH — Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Deutschland

The purple bacteria, *Rhodobacter Sphaeroides*, contains a very simple and well studied reaction center. Upon light absorption it can convert the incoming energy into chemical energy with high efficiency via electron transfer and charge separation. Ultrafast spectroscopy gives insight into its electron transfer dynamics in the picoseconds regime. Current methods to analyze time-resolved absorption data of this process involve different approaches, e.g. a direct multiexponential fit of the original data and a fit of the basis vectors of the Single Value Decomposition (SVD) matrix. SVD is a powerful filtering mechanism capable of creating a smooth output signal by removing smaller SVD components. If not applied correctly, however, small signal amplitudes may be rejected and corresponding physical processes are lost. With new developments in subpicosecond pump-probe experiments we recorded data on reaction centers which can be analyzed without any smoothing algorithm. A multiexponential fit based on a sequential rate model has been applied directly. The results confirm the existence of an intermediate radical pair state P+B- with a decay time of 0.9ps. Based on different data evaluation procedures we discuss the significance of the 0.9ps kinetic component.

MO 14.19 Tue 16:00 Empore Lichthof

**Open chain carotenoids with N=9-13 conjugated double bonds studied by multidimensional spectroscopy** — ●TAKESHI MIKI, MARIE S.MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

All-trans carotenoids are ubiquitous biomolecules with a central function in photobiology. Detailed investigation of the initial energy dissipation pathway following photo-excitation in carotenoids proved to be challenging for ultrafast optical spectroscopy. In this work, we apply pump-degenerate four wave mixing (pump-DFWM) to a series of carotenoids with the conjugated double bond lengths from N = 9 (neurosporene), 10 (spheroidene), 11 (lycopene) and 13 (spirilloxanthin). We concentrate on the initial ultrafast dynamics (< 1 ps) and how high-frequency modes evolve in this time window. Raman active modes differ on the dependence of their amplitude and frequency on the population relaxation. For shorter chain carotenoids, high-frequency Raman active modes are present directly after the excitation of S<sub>2</sub> and showed less pronounced dependences on the population relaxation than the modes in the longer chain carotenoids, where state specific modes can be clearly identified.

MO 14.20 Tue 16:00 Empore Lichthof

**Shot-to-shot data acquisition at 100 kHz for high-repetition pump-probe experiments** — ●FLORIAN KANAL, SABINE KEIBER, REINER ECK, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

For laser systems with low repetition rates near 1 kHz it is easily possible to record transient absorption data via shot-to-shot techniques. State-of-the-art CCD cameras allow for broadband acquisition of every single probe pulse in the ultraviolet and visible spectral regime. By blocking every second pump pulse transient absorption changes can be monitored with good signal-to-noise ratios. In order to decrease the total measurement time high repetition rates are desirable. However, shot-to-shot techniques near 100 kHz are challenging due to limitations in CCD readout and mechanical shutter speed.

Here we present 100 kHz broadband shot-to-shot pump-probe spectroscopy. Using an ultrafast line camera in combination with a home-built high-speed mechanical chopper, we achieve single-pulse detection. This method combines the advantage of a broadband spectral detection with reduced measurement time.

MO 14.21 Tue 16:00 Empore Lichthof

**Attosecond molecular dynamics** — ●JESSE KLEI, CHRISTIAN NEIDEL, CHUNG-HSIN YANG, LUKAS MEDISAUSKAS, MARTIN GALBRAITH, MISHA IVANOV, and MARC VRAKING — Max-Born-Institut, Berlin

Ultrafast molecular dynamics have been investigated by employing an XUV-IR pump-probe scheme. We probe the electron-electron or electron-nuclear correlations on their natural attosecond timescale by varying the time delay between the pump and probe pulses with attosecond precision. The XUV radiation consists of a train of attosecond pulses (APT) that are generated by the process of high harmonic generation (HHG). Using a velocity map imaging spectrometer (VMIS), angular resolved photoion and photoelectron measurements are performed.

We report experiments, where the time-dependent polarization of neutral molecules ( $N_2$ ,  $CO_2$  and  $C_2H_4$ ) under the influence of a moderately strong near-infrared laser field is monitored with attosecond time resolution, showing pronounced oscillations with a half IR cycle period in the parent molecular ion yield as a function of the pump-probe delay. Furthermore, investigations into the dissociative ionization of  $N_2$  are discussed. We show that the kinetic energy spectra of the  $N^+$  fragment have a structure at low energies corresponding to the vibrational levels of the ionic  $C^2\Sigma_u^+$  state of  $N_2$ . Clear half IR cycle period oscillation of the  $N_+$  yield can be seen in this energy range due to the effect of attosecond electronic coherence in femtosecond molecular dynamics.

MO 14.22 Tue 16:00 Empore Lichthof

**Scanning Near-Field Femtosecond CARS Microscopy** — ●MAHESH NAMBOODIRI, TAHIR ZEB KHAN, GÜNTER FLACHENECKER, SIDHANT BOM, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Recently, organic semiconductors have attracted increasing attention, *e.g.* for the fabrication of cheap solar cells. In these devices nanostructures play an important role. The small size of these semiconductor materials results in different electronic and vibrational properties when compared to bulk samples. Also the light induced dynamics depends on size, shape and environment of the nanostructures. In order to study these processes, femtosecond time-resolved optical spectroscopy in resonance with electronic transitions is required. We have used nonlinear femtosecond time-resolved Raman techniques to obtain highly spatially resolved images in combination with near-field microscopy. We present our first results of femtosecond coherent anti-Stokes Raman scattering (fs-CARS) detected with sub-diffraction limited resolution. For this, a scanning near-field microscope with fiber tips having apertures down to 200 nm were employed. SNOM-CARS images of poly(3-hexylthiophene) (P3HT) nanostructures have been obtained. A comparison between thin films (145 nm) and thick films (1.5  $\mu\text{m}$ ) of this organic semiconductor shows that especially the depth resolution obtained with SNOM-CARS clearly surpasses the resolution that can be obtained with high NA ( $\approx 1.2$ ) objectives.

MO 14.23 Tue 16:00 Empore Lichthof

**Fs-Photoelectron spectroscopy of adenine and adenosine in aqueous solution** — ●FRANZISKA BUCHNER and ANDREA LÜBCKE — Max-Born-Institut Berlin

Interaction of ultraviolet light with DNA molecules may lead to photodamage and consequently may cause development of cancer. Upon excitation, natural DNA bases reveal ultrafast relaxation mechanisms that prevent photodamage.

We report on the photoelectron spectra of adenine and adenosine in aqueous solution including both the pump probe spectra and spectra due to one-colour multi-photon ionization (pump-only and probe-only). Sub-100 fs pulses of 266 nm are used to excite a 1 mmolar buffered solution of adenine and adenosine. Delayed pulses in the range of 238-248 nm (sub-100 fs) probe the excited state by photoionization. The kinetic energy distribution of the electrons contains information on the time-dependent binding energy of the excited state.

We will describe and interpret in detail the photoelectron spectra in terms of the excited state dynamics of adenine and adenosine.

MO 14.24 Tue 16:00 Empore Lichthof

**Charge oscillation controlled molecular excitation** — ●HENDRIKE BRAUN<sup>1</sup>, TIM BAYER<sup>1</sup>, CRISTIAN SARPE<sup>1</sup>, ROBERT SIEMERING<sup>2</sup>, PHILIPP VON DEN HOFF<sup>2</sup>, REGINA DE VIVIE-RIEDLE<sup>2</sup>, THOMAS BAUMERT<sup>1</sup>, and MATTHIAS WOLLENHAUPT<sup>1</sup> — <sup>1</sup>University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany — <sup>2</sup>Ludwig-Maximilians-Universität München, Departement Chemie, D-81377 München, Germany

Direct manipulation of charge oscillations has emerged as a new perspective in chemical reaction control. Here we demonstrate in a joint experimental and theoretical study, that the electron dynamics of a molecule is efficiently steered by controlling the interplay of a driving femtosecond laser pulse with the photo-induced charge oscillation on the sub-cycle time scale. Specifically, we show how precision pulse shaping is used to manipulate the coupled electron and nuclear dynamics in order to address different bound electronic target states in a molecule. We present a strong field coherent control mechanism which is understood in terms of a simple classical picture and at the same time verified by solving the time-dependent Schrödinger Equation [1]. This mechanism is universally applicable and opens a wide spectrum of applications in reaction control of complex systems [2].

[1] M. Wollenhaupt *et al.*, JPPA **180**, 248 (2006)

[2] M. Wollenhaupt, T. Baumert, *Faraday Discuss.* **153**, 9-26 (2011)

MO 14.25 Tue 16:00 Empore Lichthof

**Optimizing High Harmonic Generation - A Challenge for Optimal Control Theory** — ●MARKUS KOWALEWSKI, EMIL KIERI, and KATHARINA KORMANN — Division of Scientific Computing, Uppsala University, Sweden

We theoretically investigate the possibility to optimize the yield of extreme ultra violet radiation generated by ultra-short and intense infrared laser pulses in an atomic gas. Optimal control theory is employed to find an electric field which increases the intensity of the emitted field in specific frequency range.

MO 14.26 Tue 16:00 Empore Lichthof

**Hints at Glass Transitions in Free Water Clusters** — ●ADAM PIECHACZEK<sup>1</sup>, MARTIN SCHMIDT<sup>2</sup>, and BERND VON ISSENDORFF<sup>1</sup> — <sup>1</sup>Fakultät für Physik, Universität Freiburg, Germany — <sup>2</sup>Laboratoire Aimé Cotton, Université Paris Sud, France

We studied caloric curves of free water clusters with different charge centers by nanocalorimetry. We observed transitions, indicated by pronounced excess heat capacities that vary with cluster size and the type of impurity. The transition temperatures as well as their extrapolations towards the bulk are close to glass transitions known for bulk-water and water in nanopores, but they are far below any melting and freezing points known for water under various conditions like crystalline structure, pressure and different types of confinements or impurities.

For most of the investigated impurities, we observed an increase of the transition temperatures with cluster size, which fits well to the concentration dependence of glass transitions in various dilute aqueous solutions. An exception is the *aniline*<sup>+</sup>-water system. Here, the size dependence is less pronounced. The location of the charge center, which is in this case on the aniline molecule outside of the water cluster, might be responsible for observed difference.

We applied two different techniques of nanocalorimetry. We use photo-excitation calorimetry for water clusters with excess electron and for those with the charging impurities  $O_2^-$  and *aniline*<sup>+</sup>. We excited protonated water clusters that do not provide sufficient photo-absorption cross-sections by multi-collisions with rare gas atoms.

MO 14.27 Tue 16:00 Empore Lichthof

**Linear and nonlinear spectroscopy of size selected silver clusters on surfaces** — ●MARTIN TSCHURL, PHILIPP HEISTER, TOBIAS LÜNSKENS, and UELI HEIZ — Technische Universität München, Lehrstuhl für physikalische Chemie

It has been shown that the catalytic activity of small metal clusters vary by orders of magnitude upon addition of a single metal atom. Through a precise knowledge of the electronic structure and geometry from spectroscopic studies a better understanding of the interplay between the electronic and geometrical structure and the catalytic activity of the clusters may be gained. Therefore we use different spectroscopic methods to investigate size selected metal clusters on surfaces under UHV conditions. Highly sensitive techniques such as surface Cavity Ring-Down spectroscopy (s-CRD) and surface Second-Harmonic-Generation spectroscopy (s-SHG) are applied for obtaining the optical properties of the clusters. This study mainly focuses on the size and shape dependent electronic structures and plasmon-like transitions of small deposited Ag-clusters. By monitoring these plasmon oscillations further information about oxidation and reduction of the supported size selected clusters can be obtained. In addition, cluster-plasmon size effects are studied and a behavior of their optical properties with their geometric structure is observed.

MO 14.28 Tue 16:00 Empore Lichthof

**Benzene activation and H/D isotope effects in reactions of size selected iron, cobalt and nickel cluster ions** — CHRISTINE MERKERT, ●JENNIFER MOHRBACH, MATTHIAS TOMBERS, LARS BARZEN, MAXIMILIAN GAFFGA, and GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

A Penning ion trap served to investigate the reaction of size selected transition metal cluster ions in the size range  $3 < n < 30$  with benzene and benzene-d<sub>6</sub> under single collision conditions. We performed kinetic studies by Fourier-Transform Ion-Cyclotron-Resonance (FT-ICR) mass spectrometry on anionic and cationic iron, cobalt and nickel clusters. Kinetic Isotope Effects KIE(n) in total reaction rates are inverse, Dehydrogenation Isotope Effects DIE(n) are predominantly normal. A multistep model of adsorption and stepwise dehydrogenation from the precursor adsorbate proves suitable to rationalize the found KIEs and DIEs in principle<sup>[1]</sup>.

[1] M. Tombers, L. Barzen, G. Niedner-Schatteburg, Inverse H/D isotope effects in benzene activation by cationic and anionic cobalt clusters, accepted at Journal of Physical Chemistry

MO 14.29 Tue 16:00 Empore Lichthof

**Investigation of the helium dimer and trimer in strong laser-fields** — JÖRG VOIGTSBERGER<sup>1</sup>, JASPER BECHT<sup>1</sup>, NADINE NEUMANN<sup>1</sup>, FELIX STURM<sup>1,2</sup>, MAKSIM KUNITSKI<sup>1</sup>, ANTON KALININ<sup>1</sup>, JIAN WU<sup>3</sup>, STEFAN ZELLER<sup>1</sup>, MARKUS SCHÖFFLER<sup>1</sup>, WIELAND SCHÖLLKOPF<sup>4</sup>, DARIO BRESSANINI<sup>5</sup>, ACHIM CZASCH<sup>1</sup>, LOTHAR SCHMIDT<sup>1</sup>, ●MAXIMILIAN SCHÜTT<sup>1</sup>, ROBERT GRISENTI<sup>1</sup>, TILL JAHNKE<sup>1</sup>, and REINHARD DÖRNER<sup>1</sup> — <sup>1</sup>Goethe Universität Frankfurt a. M., Institut für Kernphysik, Frankfurt, Germany — <sup>2</sup>Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — <sup>3</sup>East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — <sup>4</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Molecular Physics Atom and molecule optics, Berlin, Germany — <sup>5</sup>University of Insubria, Department of Chemical and Environmental Sciences, Como, Italy

In a free gas expansion small helium clusters were produced at low temperatures. Passing a transmission diffraction grating they are separated into pure dimer respectively trimer jets. After ionization with a Ti:Sa Laser, the Coulomb exploding fragments were measured with the COLTRIMS technique, giving direct access to the vibrational wavefunction and structure of the small clusters.

MO 14.30 Tue 16:00 Empore Lichthof

**Isomer-Selective Double Resonance Spectroscopy: Isolating the Spectral Signatures of  $H^+ \cdot (H_2O)_7$  Isomers** — NADJA HEINE, ●MATIAS R. FAGIANI, TORSTEN WENDE, and KNUT R. ASMIS — Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen,  $H_3O^+(aq)$ , and Zundel,  $H_2O \cdot H^+ \cdot OH_2(aq)$ , binding motifs, even though the detailed mechanism is more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer  $H^+(H_2O)_6$ . For the heptamer,  $H^+(H_2O)_7$ , the presence of at least three isomers has been suggested but, due to spectral congestion, these could not be unambiguously assigned. Here, we present results on isomer-selective infrared/infrared (IR/IR) double resonance experiments on  $H^+(H_2O)_7$ . Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures and messenger-tagged ( $H_2$ ) in a buffer gas filled ion trap. Isomer-selective IR photodissociation spectra are measured from 2880–3850  $cm^{-1}$  by population-labeling IR/IR double resonance spectroscopy. Aided by electronic structure calculations four isomers, three Eigen and one Zundel-type isomers, are identified.

MO 14.31 Tue 16:00 Empore Lichthof

**Cluster Mass Spectroscopy at PIPE** — IVAN BAEV, STEFFEN PALUTKE, KAROLIN MERTENS, ●STEPHAN KLUMPP, and MICHAEL MARTINS — Institut für Experimentalphysik, Universität Hamburg

Metal clusters of various type have great variations of their properties, like their geometric structure, their magnetism or their catalytic behavior. Especially, not looking on different members of the periodic table, but on clusters of the same elements but different number of atoms (each atom counts). Using the ICARUS cluster source we produced a beam of small metal clusters of kinetic energy between 500eV and 2000eV of different atom species, like Fe, Co, FeRh, etc., and mixed these clusters at two different points, within the source itself, and right after the source, with reactive gases, like O<sub>2</sub>, CO or N<sub>2</sub>O. The resulting reactants were mass-to-charged analyzed with the 1.5T ion preparation dipole magnet of PIPE (Photo-Ion-Spectrometer at PETRA III) at P04, DESY. In first commissioning measurements with Xe<sup>+</sup> ions it could be shown the mass resolution of this magnet varies between  $m/\Delta m \approx 170 - 920$  only depending on the width of the exit slits. We will present mass spectra of the reaction between the produced clusters and the used reactive gases depending on different parameters, like ion beam kinetic energy, reactive gas pressure and interaction volume in the cluster source.

MO 14.32 Tue 16:00 Empore Lichthof

**Excitation Energy and Temperature Dependent Photoluminescence of Diamondoids** — ●ANDRE KNECHT<sup>1</sup>, ROBERT RICHTER<sup>1</sup>, TORBJÖRN RANDER<sup>1</sup>, TOBIAS ZIMMERMANN<sup>1</sup>, ANDREA MERLI<sup>1</sup>, DAVID WOLTER<sup>1</sup>, PHILIPP REISS<sup>2</sup>, ARNO EHRESMANN<sup>2</sup>, PETER SCHREINER<sup>3</sup>, and THOMAS MÖLLER<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin — <sup>2</sup>Institut für Physik, Fachbereich Universität Kassel — <sup>3</sup>Institut für Organische Chemie der Justus-Liebig-Universität Giessen

Diamondoids are perfectly mass and size selected, hydrogen passivated, sp<sup>3</sup>-hybridized nano-carbon-cages. Through chemical functionalization their optical luminescence and absorption properties can be influenced. Diamondoids have negative electron affinity and are of interest for electronic applications like self-assembled monolayer as field emitters. We used synchrotron radiation to measure the fluorescence yield, absorption and luminescence spectra of samples like adamantane, 1-methyladamantane and (2,2\*)-biadamantanyl. The compounds were brought into the gas phase using a heatable target cell. The luminescence spectra show vibronic transitions. To study the thermally inhomogeneous broadening of the features and spectral congestion due to intramolecular vibrational redistribution, excitation energy and temperature-dependent measurements were performed. In addition, calculations on the density functional theory level were performed. We conclude that the excess energy provided by an absorbed photon is redistributed entirely before luminescence takes place. This technique allows us to probe caloric properties at a nanoscopic level.