MO 24: Poster: Femtosecond spectroscopy

Time: Thursday 16:00–18:00 Location: P2

MO 24.1 Thu 16:00 P2

Two-dimensional vibronic spectroscopy of coherent wave-packet motion — •Alexander Schubert and Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

We study two-dimensional (2D) spectroscopic signals obtained from femtosecond pulse interactions with diatomic molecules. The vibrational wave-packet dynamics is monitored in the signals. During the motion in the anharmonic potentials the wave packets exhibit vibrational revivals and fractional revivals which are associated with particular quantum phases. The time-dependent phase changes are identified by inspection of the complex valued 2D-spectra [1]. We use the Na$_2$ molecule as a numerical example and discuss various pulse sequences which yield information about vibrational level structure and phase relationships in different electronic states.

[1] Schubert, K. Renziehausen, V. Engel, Phys. Rev. A 82, 013419 (2010).

MO 24.2 Thu 16:00 P2

Interference phenomena in ultrafast spectrally resolved Degenerate Four-Wave-Mixing — •Jan Philip Kraack, Marcus Motzkus, and Tiago Buckup — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Homodyne-detected, spectrally-resolved Degenerate Four-Wave-Mixing (DFWM) with femtosecond pulses is an advantageous spectroscopic technique for the investigation of vibrational coherence dynamics. However, the homodyne detection method results in interferences between contributing response pathways. This has significant impact on the signal dynamics and their interpretation: (i) Interference between vibrational coherence pathways results in combination frequencies (beating) between molecular normal modes. This implies both sum and difference frequencies of the chromophore normal modes. (ii) Interference between non-oscillatory population and vibrational coherence dynamics affects the time-evolution of the wave packet signal intensity. (iii) Interference between response pathways from ground and excited electronic states can dramatically affect the signal dynamics. In this regard, we apply femtosecond DFWM to several molecular systems in solution and demonstrate that interference and normal mode contributions show a different dependence on the delay between excitation pulses and their phase-modulation (chirp). We additionally show that interference contributions provide information about vibrational dephasing time constants and spectrally overlapping ground and excited state absorption bands.

MO 24.3 Thu 16:00 P2

Time-resolved photoelectron spectra from coupled electronic-nuclear motion — •Mirjam Falge[1], Volker Engel[1], and Stefanie Graefe[2] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — [2]Institute for Theoretical Physics, Vienna University of Technology, Wiedner Hauptstr. 8-10, A-1040 Vienna, Austria

We study the effect of electron-nuclei coupling on time-resolved photoelectron spectra resulting from femtosecond pump-probe ionization. Therefore, a model system is employed [1] which allows a straightforward switching from adiabatic to non-adiabatic dynamics. Non-adiabatic effects are identified in comparing Born-Oppenheimer calculations involving a discretization of the ionization continuum with a treatment where electronic and nuclear degrees of freedom are included explicitely.

[1] S. Gräfe, V. Engel, Chem. Phys. 329, 118 (2006).

MO 24.4 Thu 16:00 P2

XUV pump-probe experiments at FLASH — •yuhai jiang[1], artem rudenko[2], oliver herrwerth[3], lutz foucar[2], moritz kurka[1], kai-uwe kühnel[1], matthias Lezius[3], matthias kling[3], fernando martin[4], ali belkacem[5], kiyoshi ueda[6], stefan düsterer[7], rolf treusch[7], claus-dieter schröter[1], robert moshammer[1], and joachim ullrich[1] — [1]MPIK, Heidelberg — [2]ASG at CFEL, Hamburg — [3]MPIQ, Garching — [4]Universidad Autónoma de Madrid, Madrid — [5]LBNL, Berkeley — [6]Tohoku University, Sendai — [7]DESY, Hamburg

The advent of the Free Electron Laser (FEL) delivering unprecedented brilliance and ultra-short pulse duration (a few femtosecond) has opened a door studying the ultra-fast molecular dynamics in the XUV regime employing a Reaction Microscope combined with our novel split-mirror set-up. Using this experimental approach at FLASH we performed a series of XUV pump-probe experiments [1-4] by tracing ultra-fast nuclear wave-packet motion in the D$_2^+$(1sσ_g) state, isomerization and elimination reactions in Acetylene and Ethylene etc., which pave the way to visualize, control and manipulate molecular reactions in the XUV regime in real time.

[1] Y.H. Jiang et al., Phys. Rev. A 81, 051402 (R) (2010)
[2] Y.H. Jiang et al., Phys. Rev. A 82, 041403(R) (2010)
[3] T. Pfeifer et al., Opt. Lett. 35, 3441 (2010)
[4] Y.H. Jiang et al., Phys. Rev. Lett. (accepted)

MO 24.5 Thu 16:00 P2

Molecular dynamics probed via strong-field ionization of oriented molecules — •Sebastian Trippel, Lotte Holmegaard, Stephan Stern, and Jochen Küpper — Center for Free-Electron Laser Science, DESY, Notkestr. 85, 22607 Hamburg, Germany

We are setting up a new experiment to study ultrafast molecular dynamics directly in the molecular frame. Supersonic beams of cold, large and complex molecules will be quantum state selected and, successively, adiabatically oriented by a combination of static electric and strong picosecond laser fields [1, 2]. A second ultrashort laser pulse will initiate a rearrangement of the chemical structure of the molecules. The molecular-frame photoelectron angular distribution of the highest occupied molecular orbitals will be detected to study molecular dynamics during this rearrangement process [2]. The whole experiment will operate at 1 kHz repetition rate, which allows us to investigate weak processes.

[1] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper and G. Meijer, Phys. Rev. Lett., **102**, 023001 (2009)
[2] F. Filsinger *et al.*, J. Chem. Phys. **131**, 064309 (2009)
[3] L. Holmegaard *et al.*, Nature Physics, **6**, 428 (2010)

MO 24.6 Thu 16:00 P2

Interference effects in photo-fragment distributions — •Kilian Hader and Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Pronounced interference effects in the nuclear translational fragment distribution which are caused by the interaction with time-delayed femtosecond laser pulses have been predicted before [1]. Here, we extend the former studies and take the electronic motion explicitely into account. Dissociation, leading to different electronic states results in interesting features of the electron-nuclear wave-packet motion and fragment momentum-space distribution.

[1] M. Lein, M. Erdmann, V. Engel, J. Chem. Phys. 113, 3609 (2000).

MO 24.7 Thu 16:00 P2

Vibrational (De)coherence of I$_2$ in a Krypton Matrix — •Max Buchholz[1], Christoph-Marian Goletz[1], Frank Grossmann[1], Burkhard Schmidt[2], Jan Heyda[3], and Pavel Jungwirth[3] — [1]Technische Universität Dresden, Institut für Theoretische Physik, D-01062 Dresden, Germany — [2]Freie Universität Berlin, Institut für Mathematik, Arnimallee 6, D-14195 Berlin-Dahlem — [3]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague 6, CZ-16610, Czech Republic

In four-wave mixing experiments on iodine in a krypton matrix in the Apkarian group [Segale et al, J. Chem. Phys. 122, 111104 (2005)], quantum coherent vibrations of the matrix phonon modes were observed which were interpreted as a Schrödinger cat-like superposition of macroscopically distinct states. Motivated by this finding, we study the photo-induced dynamics of an I$_2$ molecule in the first microsolvation shell comprising a Kr$_{17}$ double icosahedron using numerical quantum-dynamic models. Quantities of interest are the reduced Wigner distribution and the purity of the I$_2$ vibrations (system) as well as of several Kr (bath) modes. We are investigating signatures of the transfer of coherence from the system to the bath for a hierarchy of reduced dimensionality models comprising bath modes with different coupling to the system mode, thriving a cat-like state through quantum coherent dissipation. This work was partly supported by the DFG under projects GR 1210/4-1,2.

MO 24.8 Thu 16:00 P2

Femtosecond transient absorption with a deep-UV continuum probe — •Michael Foerster, Ulrike Selig, Johannes Buback, Patrick Nuernberger, and Tobias Brixner — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The initial steps of many photochemical reactions evolve on an ultrafast time scale. With fs transient-absorption spectroscopy such dynamics can be investigated directly. The use of a continuum probe in combination with spectrally resolved detection allows for the simultaneous measurement of both sequential and concurrent processes and is well-established in the visible spectral range.

Here we present a setup for transient absorption at much shorter wavelength that combines the femtosecond time resolution of the frequency-doubled output of a commercial noncollinear OPA, tunable between 250 nm and 375 nm, with a broadband deep-UV probe. Focusing the third harmonic of a 1 kHz Titanium Sapphire regenerative amplifier into a moving CaF_2 plate produces a deep-UV continuum covering 235 - 360 nm. Data acquisition on a shot-to-shot basis is achieved by 1 kHz readout of the two-dimensional CCD camera of our spectrometer in combination with chopping the pump beam at 500 Hz.

We discuss constraints and potential of the experimental implementation, spectrally and temporally characterize the deep-UV continuum, and show exemplary time-resolved measurements.

MO 24.9 Thu 16:00 P2

Electron angular distribution of H_2^+-ions in strong laser fields — Matthias Odenweller[1], •Kevin Pahl[1], Maximilian Schütt[1], Norio Takemoto[2], Arno Vredenborg[1], Kyra Cole[1], Lothar Ph. Schmidt[1], Jasmin Titze[1], Till Jahnke[1], Moritz Meckel[1], Tilo Havermeier[1], Robert Wallauer[1], Stefan Voss[1], Hendrik Sann[1], Hong-Keun Kim[1], Jörg Voigtsberger[1], Markus Waitz[1], Florian Trinter[1], Tobias Bauer[1], Nadine Neumann[1], Andreas Becker[2], Horst Schmidt-Böcking[1], and Reinhard Dörner[1] — [1]Institut für Kernphysik, Johann Wolfgang Goethe-Universität, Frankfurt am Main, Germany — [2]JILA, University of Colorado at Boulder, USA

We present the worlds first direct measurement of the electron angular distribution of H_2^+ in strong laser fields. Using circular polarized laserpulses of $I = 6 \cdot 10^{14} W/cm^2$ and $\tau = 40 fs$ we observed an unexpected distribution which exhibits neither a sharp absolute value of radial momentum nor a 90° orientation with respect to the internuclear axis. It emerges that the angular distribution rotates with increasing internuclear separation and shows at least two significant peaks at higher radial momenta.

MO 24.10 Thu 16:00 P2

Experimenteller Aufbau zur Untersuchung von H_2^+ Isotopen in starken Laserfeldern. — •Kevin Pahl, Maximilian Schütt, Matthias Odenweller, Lothar Schmidt, Kyra Cole, Arno Vredenborg, Nadine Neumann, Jasmin Titze, Markus Waitz, Christian Stuck, Daniel Metz, Christoph Goihl, Florian Trinter, Jörg Voigtsberger, Dawiet Haile, Christian Müller, Tilo Havermeier, Hendrik Sann, Deborah Schneider, Horst Schmidt-Böcking und Reinhard Dörner — Goethe-Universität, Frankfurt, Deutschland

H_2^+ ist das einfachste mögliche Molekül. Sein Verhalten in starken Laserfeldern wurde bereits in zahlreichen theoretischen und experimentellen Abhandlungen thematisiert. Nun gelang es erstmals unter der Verwendung eines Ionenstrahls aus H_2^+ Ionen neben den, durch Ionisation oder Dissotiation fragmentierten, Atomkernen auch das bei der Ionisation ausgelöste Elektron zu detektieren. Diese Experimentelle Herausforderung soll hier vorgestellt werden.

MO 24.11 Thu 16:00 P2

Dissoziation von H_2^+, D_2^+ und HD^+ in starken Laserfeldern — •Max Schütt, Kevin Pahl, Matthias Odenweller, Lothar Schmidt, Arno Vredenborg, Kyra Cole, Nadine Neumann, Jasmin Titze, Markus Waitz, Christian Stuck, Daniel Metz, Christoph Goihl, Florian Trinter, Jörg Voigtsberger, Dawiet Haile, Christian Müller, Tilo Havermeier, Hendrik Sann, Deborah Schneider, Horst Schmidt-Böcking und Reinhard Dörner — Institut für Kernphysik Johann Wolfgang Goethe Universität, Max-von-Laue-Str. 1, D-60438 Frankfurt am Main

Untersuchung der Dissoziation von H_2^+, D_2^+ und HD^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser, dessen Leistung $5 \cdot 10^{14} \frac{W}{cm^2}$ im Focus bei einer Wellenlänge von $780nm$ beträgt, zum Überlapp gebracht. Bei der Dissoziation werden die typischen Dissoziationsprozesse Bond Softening und Bond Hardening gezeigt und die Unterschiede bzw. Gemeinsamkeiten zwischen den Isotopen hervorgehoben. Durch eine Messung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 24.12 Thu 16:00 P2

Femtosecond RIXS on liquid jets and first results from LCLS — Philippe Wernet[1], •Kristjan Kunnus[1], Martin Beye[1], Simon Schreck[1], Edlira Suljoti[1], Christian Weniger[1], Christian Kalus[1], Kerstin Kalus[1], Alexander Föhlisch[1], Ivan Rajkovic[2], Sebastian Grübel[2], Wilson Quevedo[2], Mirko Scholz[2], Simone Techert[2], Brian Kennedy[3], Franz Hennies[3], Dennis Nordlund[4], Robert Hartsock[5], Wenkai Zhang[5], Kelly Gaffney[5], Josh Turner[6], Bill Schlotter[6], Ida Josefsson[7], and Michael Odelius[7] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]Max-Planck-Institut für Biophysikalische Chemie — [3]MAX-lab — [4]SSRL, SLAC National Accelerator Laboratory — [5]PULSE, SLAC National Accelerator Laboratory — [6]LCLS, SLAC National Accelerator Laboratory — [7]Stockholm University

We developed a set up for femtosecond time resolved resonant inelastic soft x-ray scattering (RIXS) on liquid jets in vacuum. This allows for complete probing of occupied and unoccupied valence states of molecules in real-time during chemical reactions in solutions. The setup is presented in detail and first results from experiments at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory and the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin are discussed.

MO 24.13 Thu 16:00 P2

Ultrafast Vibrational Dynamics in Ionic Liquids Investigated by Femtosecond Nonlinear Raman Spectroscopy — •Mahesh Namboodiri[1], Mehdi Kazemi[1], Johannes Kiefer[2], and Arnulf Materny[1] — [1]Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — [2]School of Engineering, University of Aberdeen, Kings College, Fraser Noble Bldg, Aberdeen AB24 3UE, Scotland, U.K.

Ionic liquids (ILs) have recently attracted many researchers in the area of chemical physics. ILs are salts consisting of cations and anions, but in contrast to ordinary salts they are liquid at room temperature. ILs are highly useful systems for diverse applications, such as novel electrolytes for energy applications, drug delivery, and as “green" solvents for otherwise insoluble biomolecules like cellulose. In this contribution, we discuss our studies on the structure and vibrational dynamics of room temperature ILs. We mainly focus on imidazolium-based ILs exhibiting [EMIm] and [BMIm] cations investigated by linear and nonlinear Raman spectroscopy. We performed electronically non-resonant nonlinear Raman spectroscopy on ILs where cations and anions were varied systematically in order to probe the interactions between the different ions in the liquid. In addition to experiments in neat ILs, we have studied their mixtures with water. These mixtures showed clearly different dynamics compared to pure ILs. Our results help to better understand the fundamental properties such as structure and interactions with co-solvent molecules of ILs.

MO 24.14 Thu 16:00 P2

CRASY: Correlated Rotational Alignment Spectroscopy Yields Structure Selective Spectroscopic Data — •Christian Schröter, Ingolf-Volker Hertel, and Thomas Schultz — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Mass spectroscopy yields information on the composition of molecules and clusters, but it gives no information about molecular structure or fragmentation occurring in the ionization process. Electron spectroscopy yields information on the electronic structure, but usually with an insufficient resolution to assign molecular structure. To derive structure selective information out of ion masses and emitted electrons, we coupled the mentioned methods to high resolution rotational Raman spectroscopy.

We employ the CRASY method which combines the techniques of rotational alignment with femtosecond-pump-probe spectroscopy. In a two pulse experiment, an IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes molecules and molecular clusters via a resonant electronic state. Every ion and electron signal is modulated with a rotational frequency linked to the ground state geometry, since the transition dipole moments are fixed in the rotating molecular frame. Therefore the CRASY method yields mass-rotational spectra and electron-rotational spectra with unprecedented information content.

We present results obtained with this technique for carbon-disulfide monomer and dimer and the molecule butadiene and its clusters.

MO 24.15 Thu 16:00 P2

Investigating ultrafast molecular dynamics with a femtosecond high-harmonic VUV source — •Torsten Leitner[1], Mateusz Ibek[1], Michael Meyer[2], and Philippe Wernet[1] — [1]Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin — [2]European XFEL, Hamburg

The high-harmonic generation (HHG) setup at HZB provides high peak power femtosecond pulses for ultrafast IR/UV pump and VUV probe spectroscopy for experiments on molecular dynamics.

Two-color multiphoton ionization of atoms and small molecules was investigated by temporally overlapping the VUV pump and IR probe pulses. In the photoelectron spectrum, additional sidebands on both sides of the main line show up in the presence of an intense IR field. The intensity of the sidebands undergoes strong variations as a function of the relative polarization of the two fields. The amplitude of these variations differed for the 4 systems which were investigated (Ar, N_2, O_2, H_2O). This polarization and species dependence provides direct insight into the symmetry of the outgoing electron wave and thus into the symmetry of the outer shell orbitals of the bound system.

Dissociation dynamics of molecules in gas phase is another phenomenon to be investigated with our setup under variation of the relative pump-probe delay. We constructed a high-temperature oven for evaporating solid substances, like for example NaI. First results on the dynamics of dissociating NaI are presented.

MO 24.16 Thu 16:00 P2

The Phycocyanobilin-Derivative AIE as Model System for the Pfr Photoreaction in Phytochromes — •Patrick Singer[1], Sonja Fey[2], Gudrun Hermann[2], and Rolf Diller[1] — [1]Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern — [2]Institut für Biochemie und Biophysik, Friedrich-Schiller-Universität Jena, D-07743 Jena

An insufficiently treated issue in the phototransformation of phytochromes concerns both the bathochromic shift of the ground state absorption as well as the much faster primary photoreaction of the far-red absorbing state Pfr as compared to the red absorbing state Pr. The lactimderivative of phycocyanobilin, phycocyanobilindimethylester-ring-A-monomethylimino-ester (AIE), has been suggested to mimic these static and dynamic properties of the phytochrome Pfr state, i.e. the phytochrome bilin chromophore interacting with specific sites in the protein binding pocket of Pfr [1]. We have used femtosecond transient absorption spectroscopy to investigate the ultrafast light-induced primary processes of AIE in methanol. The results are discussed in the context of previously observed dynamics and absorption shifts of the Pfr state in phytochromes [2,3].

[1] R. Micura and K. Grubmayr *Angew. Chem.* **107**, 1896-2522 (1995)

[2] C. Schumann, R. Groß, M. M. N. Wolf, R. Diller, N. Michael, and T. Lamparter. *Biophys. J.* **94**, 3189-3197 (2008)

[3] Bischoff, M., G. Hermann, S. Rentsch, and D. Strehlow *Biochemistry* **40**, 181-186 (2000)

MO 24.17 Thu 16:00 P2

Ultrafast Energy Transfer and Chromophore Dynamics in Xanthorhodopsin — •Miriam Colindres Rojas[1], Melanie Geier[2], Annik Jakob[1], Ilka Haferkamp[2], Ekkehard Neuhaus[2], and Rolf Diller[1] — [1]Fachbereich Physik, TU Kaiserslautern, Germany — [2]Fachbereich Biologie, TU Kaiserslautern, Germany

Xanthorhodopsin from the extreme halophile eubacterium Salinibacter ruber is one of the simplest bioenergetic systems for collecting light using excited state energy transfer. This member of the retinal protein family is a light driven transmembrane proton pump with two chromophores: a retinal and additionally the carotenoid salinixanthin[1]. Our aim is to investigate the excited state dynamic of both salinixanthin and retinal in xanthorhodopsin applying transient VIS/VIS and VIS/mid-IR femtosecond absorption spectroscopy on a ms resp. subps timescale. The proton pump cycle and the interaction between the two chromophores in xanthorhodopsin are being studied. Experiments include the selective excitation of either salinixanthin or retinal. We will compare xanthorhodopsin with bacteriorhodopsin and sensorrhodopsin[2] to reveal differences and similarities between these retinal proteins[3] as a contribution for a better understanding of the primary reactions of xanthorhodopsin.

MO 24.18 Thu 16:00 P2

Ultrafast dynamics in excited molecules probed by photoelectron spectroscopy: dissociation of NO_2 — •Martin Eckstein[1], Georg Gademann[2], Arjan Gysbertsen[2], Freek Kelkensberg[2], Jesse Klei[2], Christian Neidel[1], Wing-Kiu Siu[2], Chung-Hsin Yang[2], Hans-Jacob Wörner[3], and Marc Vrakking[1,2] — [1]Max-Born-Institut, Berlin, Germany — [2]Amolf, Amsterdam, Netherlands — [3]Steacie Institute for Molecular Sciences, Ottawa, Canada

Femtosecond time-resolved photoionization experiments open up opportunities to look at chemical reactions in real time with element specificity. Here experiments on the simplest chemical process, dissociation, are reported. The dissociation of NO_2 is studied by exciting molecules and recording transient photoelectron angular and energy distributions as the molecule falls apart. First experimental results are reported and compared to the recent study using high-harmonic generation as a probe of the dissociation process. Future extension of the experiments to larger molecules of biological importance and to shorter time-scales are discussed.