

## MO 9: Femtosekundenspektroskopie 3

Zeit: Dienstag 16:30–18:00

Raum: VMP 6 HS-F

MO 9.1 Di 16:30 VMP 6 HS-F

**Observation of vibrational wave packet dynamics in a single isolated molecular ion** — ●STEFFEN KAHRA, GÜNTHER LESCHHORN, HSIANG-TAI DOU, WOLFRAM SCHMID, WERNER FUSS, and TOBIAS SCHAETZ — Max-Planck-Institut für Quantenoptik, Garching

Encouraged by the present and still improving excellent temporal resolution of short laser pulses in the UV (< 4 fs) [1] our TlAMo-project focuses on the combination of temporal control in the optical domain with precise methodology of molecular ions in a Paul trap. Our set-up has been layed out for various pump-probe experiments ranging from X-ray diffraction to spectroscopy in the visible.

We present the current experiment that should allow us to observe vibrating molecular ions. The present scheme bases on  $\text{MgH}^+$  ions albeit other molecular ions of interest and suitable size could be loaded, too. A pulse around 270 nm creates an oscillating wave packet. By absorption of another time delayed UV photon a dissociative channel becomes accessible depending on the position of the wave packet [2]. Thus the dissociation probability is expected to be modulated by the pump-probe delay and is proposed to reflect the molecular vibrational period of 31 fs. The speciality of our concept lies in the target consisting of only one or few isolated molecular ions embedded in a laser cooled fluorescing  $\text{Mg}^+$  ion crystal. Our detection method exploits the non-fluorescence of  $\text{MgH}^+$  occupying crystal lattice sites and enables us to count the modulated number of dissociated dark molecular ions.

[1] U. Graf et al., *Opt. Express*, 2008, 16, 18956-18963

[2] S. Jørgensen et al., *J. Chem. Phys.*, 2005, 123, 094302-9

MO 9.2 Di 16:45 VMP 6 HS-F

**Spektral- und zeitaufgelöste Untersuchung der Relaxationsdynamik organischer Moleküle mit Hilfe der Fluoreszenz-Aufkonversion** — ●HUBERT ROSSMADL, STEFANIE BENSMANN und HRISTO IGLEV — Physik-Departement E11, Technische Universität München, 85748 Garching, Germany

Die zeitaufgelöste Anrege-Abfrage-Spektroskopie wird erfolgreich zur Untersuchung von schnellen Relaxationsprozessen in organischen Molekülen angewandt. Dabei ist es aber oftmals schwierig zwischen heißen Grundzuständen und höher angeregten Niveaus zu unterscheiden. Weiterhin kann der Abfrage-Impuls auch störenden Einfluss auf die vorhandenen Zustände haben. Die zeitaufgelöste Detektion der bei der Relaxation emittierten Fluoreszenz selbst umgeht diese Probleme. Bei der Anregung können sehr kurzlebige intermediäre Zustände auftreten. Möglich ist eine chemische Veränderung des Moleküls mit eigener Relaxationsdynamik. Zur Messung der Lebensdauern dieser Zustände wurde ein sub-100fs-Ti:Saphir-Lasersystem aufgebaut. Die zu untersuchenden Moleküle werden mit der dritten Harmonischen im UV-Bereich bei 266nm angeregt. Die genaue Zeitauflösung ist durch die Summenfrequenzerzeugung des Fluoreszenzlichts mit einem kurzen 800nm-Puls realisiert. Mit Hilfe eines Monochromators und eines Einzel-Photon-Detektors können noch sehr geringe Intensitäten spektral analysiert werden. Der genaue Aufbau sowie erste Ergebnisse der Messungen an Coumarin-Derivaten in unterschiedlichen Solvaten sollen präsentiert und diskutiert werden.

MO 9.3 Di 17:00 VMP 6 HS-F

**Inherently phase-stable coherent 2D spectroscopy** — ●ULRIKE SELIG, FLORIAN LANGHOJER, FRANK DIMLER, TATJANA LÖHRIG, CHRISTOPH SCHWARZ, BJÖRN GIESEKING, and TOBIAS BRIXNER — Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

In recent years, coherent two-dimensional spectroscopy was introduced to the optical regime. As a nonlinear technique that determines the third-order response function of a quantum mechanical system, 2D spectroscopy in the visible spectral range has been able to unravel the excitation migration process in photosynthetic light harvesting complexes and coherence transfers in electronically coupled multichromophore systems [1].

We introduce an inherently phase-stable setup for coherent two-dimensional femtosecond spectroscopy in non-collinear box geometry using only conventional beam splitters, mirrors, and delay stages [2] Avoiding diffractive optics, pulse shapers and active phase-locking loops, our spectroscopy setup is simple, robust, and works for ultra-broad bandwidths in all spectral regimes (IR/VIS/UV). First results

on a model system, the laser dye Nile Blue in acetonitrile, recorded with roughly twice the bandwidth reported in earlier experiments, will be shown.

[1] M. Cho, *Chem. Rev.* 108, 1331 (2008)

[2] U. Selig, F. Langhojer, F. Dimler, T. Löhrig, C. Schwarz, B. Gieseeking, and T. Brixner, *Opt. Lett.* 33, 2851-2853 (2008)

MO 9.4 Di 17:15 VMP 6 HS-F

**Pulse train excitation- dynamics and spectroscopy** — ●JUDITH VOLL and REGINA DE VIVIE-RIEDLE — LMU Department Chemie, Butenandt-Str. 11, 81377 München, Germany

Optical control of molecular and biological systems aims at steering reactions by special shaped laser pulses as well as at spectroscopic informations about the participating pathways. In several control experiments sequences of pulses, separated in time, were obtained as best results to control the outcome of a light induced reaction. Comparable pulse sequences can be obtained by parameterisation, using a sinusoidal modulator mask,  $\Phi(\omega) = a \sin(b\omega + c)$ , leading to a train of pulses with defined phase relation [1]. Successful control application of pulse trains have been demonstrated for energy transfer in  $\text{LH}_2$  [2], a light-harvesting complex, and for enhancement of ground state modes of  $\beta$ -carotene [3].

Based on quantum dynamical calculations on a model of  $\beta$ -carotene, we present systematic studies on the electronic excitation mechanisms due to pulse trains in the low energy regime. We follow the induced wave packet dynamics on the excited states including the process of internal conversion. We discuss and explain the effect of the individual pulse parameters  $b$  and  $c$ . Relating the pulse parameters to the system response, we outline a strategy for the use of pulse trains in spectroscopy and signal processing.

[1] T. Hornung et al., *Chem. Phys. Lett.*, **326**, (2000) 445.

[2] J. L. Herek et al., *Nature* **417**, (2002) 533.

[3] J. Hauer et al., *Chem. Phys. Lett.*, **421**, (2006) 523.

MO 9.5 Di 17:30 VMP 6 HS-F

**Dissociation and bond formation dynamics in the laser induced  $\text{S}_{\text{N}}1$  reaction of diarylmethane derivatives** — ●BENJAMIN FINGERHUT and REGINA DE VIVIE-RIEDLE — Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, 81377 München, Germany

The primary processes in the formation of electrophilic precursor ions, key intermediates in organic synthesis, are studied on a microscopic scale by quantum chemical and quantum dynamical methods. We investigate ultrafast dissociation processes of diphenylmethyl chloride in gas phase. For the competing reaction channels of ion pair and radical pair formation, induced by a femtosecond laser pulse, the interaction of different electronic states leads to ultrafast bond cleavage.

Based on ab initio data we derived a system Hamiltonian which is suitable to describe the multidimensional dissociation process in a reduced reactive coordinate space [1]. Quantum dynamical calculations suggest that dissociation induced by a Fourier limited femtosecond laser pulse provides the ion pair as the main product in gas phase despite its higher potential energy.

Subsequent bimolecular recombination leading to bond formation, which constitutes the second part of the  $\text{S}_{\text{N}}1$  reaction, is investigated by on-the fly molecular dynamics simulations. The direct reaction with solvent molecules restricts the lifetime of generated carbo cations to several picoseconds.

[1] B. Fingerhut, D. Geppert and R. de Vivie-Riedle, *Chem. Phys.* **343**, 329 (2008).

MO 9.6 Di 17:45 VMP 6 HS-F

**Three-Pulse Photon Echo beyond the Impulsive Limit - For Example Nile-Blue** — INES MYNTTINEN<sup>1</sup>, ●WICHARD J.D. BEENKEN<sup>1</sup>, TÖNU PULLERITS<sup>2</sup>, and ERICH RUNGE<sup>1</sup> — <sup>1</sup>Technische Universität Ilmenau, Germany — <sup>2</sup>Lund University, Sweden

We performed computational study of the three pulse photon echo experiments with Nile-blue as a reference molecule. Our aim is to go beyond the impulsive limit and simulate the effect of spectral properties of the incoming laser pulses. We calculated the time-integrated intensity of the third-order polarization generated by three laser pulses. The signal was analysed in terms of the photon-echo peak-shift and the

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frequency-resolved echo signal. Both, finite pulse duration and chirp of the incoming pulses lead to a faster decay of the integrated intensity in dependency on the second delay time. This influences the photon-echo peak-shift considerably. However, only the chirp affects the time-scales of the peak-shift decay. This means that one has to be extra careful in interpreting the photon echo peak shift as the time-correlation function

of the system-bath interaction. The presence of chirp can be checked via the frequency-resolved third-order polarization. The advantage of this method is that in frequency-resolved plots one can easily distinguish the characteristics occurring due to the chirp of the incoming pulses from effects resulting from the molecular system and its interaction with the surrounding bath.