

## MO 18: Femtosekundenspektroskopie

Zeit: Dienstag 14:00–19:00

Raum: Poster C1

MO 18.1 Di 14:00 Poster C1

**Femtosecond Optical and Vibrational Spectroscopy of Flavins and Flavoproteins** — ●ALEXANDER WEIGEL and LUIS PEREZ LUSTRES — Institute for Chemistry, Brook-Taylor-Str. 2, 12489 Berlin

Flavin photoreceptors form a newly discovered class of blue-light sensing proteins which bind flavin chromophores as cofactors. Excitation of the chromophore leads to long living conformational changes in the protein, which trigger multiple biological responses. Contrary to the other known photoreceptor families, photactivation of flavoproteins does not occur by E/Z isomerization but displays unusual activation mechanisms which remain largely unknown. We apply femtosecond broadband transient absorption and report here on riboflavin and the phototropin mutant LOV1C57S. In the latter a critical cysteine residue was substituted by serine to hinder signalling state formation. Ultrafast loss of oscillator strength in riboflavin on a  $\sim 10$  fs timescale is assigned to vibronic coupling between the optically active  $\pi\pi^*$  state and the dark  $n\pi^*$  state. In the LOV1 mutant we were able to resolve spectral hole-burning at early time and its development on a 100 fs time scale. Weak spectral evolution with 1 ps time constant reflects structural reorganisation of the cofactor in the protein pocket. Vibrational wavepackets give rise to strong oscillations with frequencies ranging from 40 to 500  $\text{cm}^{-1}$ . Remarkably, a 190 ps time constant and a series of oscillations with zero phase over the 20,000  $\text{cm}^{-1}$  spectral window exhibit similar spectral amplitudes, which may reflect coherent oscillations from vibronic coupling in the mutant. We present first results from broadband femtosecond stimulated Raman spectroscopy.

MO 18.2 Di 14:00 Poster C1

**Controlling the photodissociation dynamics of methyl iodide** — A. KLUMPP<sup>1</sup>, M. KRUG<sup>1</sup>, ●C. LUX<sup>1</sup>, M. WOLLENHAUPT<sup>1</sup>, J. DURA<sup>2</sup>, J.G. IZQUIERDO<sup>2</sup>, R. DE NALDA<sup>2</sup>, L. BANARES<sup>2</sup>, and T. BAUMERT<sup>1</sup> — <sup>1</sup>Universität Kassel, Institut für Physik und — <sup>2</sup>Universidad de Complutense Facultad de Ciencias Químicas

Due to its simple structure but nevertheless complex and interesting dissociation dynamics methyl iodide is a well investigated molecule in femtochemistry (e.g.[1, 2]). In previous fs experiments (e.g. [2]) the methyl iodide bond was broken and the methyl was probed with REMPI radiation. In our experiment, we used a shaped femtosecond 800 nm pulse [3] in addition to exert control during the pump probe sequence. Pulse shaping was performed in the frequency domain applying polynomial spectral phases. The methyl states ( $^3Q_0, ^1Q_1 \nu = 0, ^1Q_1 \nu = 1$ ) [4] were detected using a velocity-map-imaging method [5]. Using the pulse shaper in combination with an evolutionary algorithm the ratio of the ion yield corresponding to molecular states was optimized. The yields of the above photo-products were studied as a function of the relative pulse delay and chirp parameter in a two dimensional map.

- [1] D. Zhong and A.H. Zewail, J.Phys.Chem.A 102, 4031 (1998)
- [2] R. de Nalda, et al., J.Chem.Phys. 126, 021101 (2007)
- [3] A. Präkelt et al., Rev.Sci.Instr., 74, 11, 4950 (2003)
- [4] Y. Amatatsu, et al., J. Chem. Phys. 104, 9783 (1996)
- [5] A.T.J.B. Eppink et al., Rev.Sci.Instrum. 68, 3477 (1997)

MO 18.3 Di 14:00 Poster C1

**Influence of environment on rotational wave packets in gases** — ●JOCHEN MAURER, NINA OWSCHIMIKOW, FALK KÖNIGSMANN, and NIKOLAUS SCHWENTNER — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

A linearly polarized short laser pulse interacts with a molecule with anisotropic polarizability via non-resonant Raman transitions and induces recurrent transient alignment of the molecular axis along its electric field direction. This rotational wave packet leads to a time-dependent change in birefringence of the sample which we detect using optical Kerr effect spectroscopy (OKE). We use a Ti:Sa laser (wavelength 780 nm, pulse length 150 fs) that is focused to an intensity of up to  $10^{14}$   $\text{W}/\text{cm}^2$  to create alignment of  $\text{N}_2$  molecules in the gas phase. Our experiments cover pressures ranging from few mbar to 5 bar and temperatures from 80 K to 300 K. We find a quadratic increase in signal intensity with density characteristic for coherent superpositions. In addition to this effect the signal amplitude grows in accordance with theoretical predictions on the susceptibility  $\chi^{(2)}$ , as with decreasing temperature the thermal occupation of rotational levels is narrowed.

The homodyne detected signal is proportional to the square of the degree of alignment  $\langle \cos(\theta)^2 \rangle^2$  and decays with time as the wave packet dephases due to bimolecular collisions. We study the temporal evolution of the degree of alignment depending on pressure in pure  $\text{N}_2$  and mixtures of  $\text{N}_2$  with the noble gases He, Ar and Kr. From the rate of decay of revivals we extract interaction radii for dephasing and find that dephasing is mainly due to inelastic collisions.

MO 18.4 Di 14:00 Poster C1

**Zur kohärenten Kontrolle matrixinduzierter Prädissoziation von Brommolekülen in einer festen Argon Umgebung** —

●LISA-MARIE KROCKER<sup>1</sup>, MÓNIKA HÉJJAS<sup>1</sup>, HEIDE IBRAHIM<sup>1</sup>, MARKUS GÜHR<sup>2</sup> und NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin — <sup>2</sup>Stanford PULSE Center, Varian Physics Bldg., 382 Via Pueblo Mall, Stanford CA 94305-4060, USA

Neue Resultate frequenz aufgelöster Spektroskopie an Brom in einer Argon-Matrix zeigen eine effiziente Prädissoziation auf einer Pikosekunden-Zeitskala [1]. Die schnelle Zeitentwicklung dieser chemischen Reaktion wird von uns mittels Femtosekunden-Pump-Probe-Spektroskopie verfolgt. Dies geschieht durch simultane Beobachtung der molekularen Schwingungswellenpaketdynamik auf den verschiedenen elektronischen Potentialen zwischen denen der Populationstransfer stattfindet. Durch Vergleich mit der Dynamik auf den einzelnen Potentialen und durch Polarisationsanalyse lassen sich die prädissoziativen Wellenpaketanteile im ursprünglich angeregten B-Zustand in Form eines Signalabfalls (etwa 10% pro Umlauf) identifizieren. Nach der Dissoziation über den repulsiven Zustand werden diese Anteile durch den Käfigeffekt der Matrix wieder in einen gebundenen Bereich des A-Zustandes überführt und dort als entsprechender Signalanstieg nachgewiesen. Weiterhin zeigen wir, wie sich mithilfe geeignet geformter Anregungspulse die Effizienz der Prädissoziation modifizieren lässt. [1] H. Ibrahim, M. Gühr und N. Schwentner, J. Chem.Phys. 2007, akzeptiert

MO 18.5 Di 14:00 Poster C1

**Anisotropy in ultrafast experiments** — ●ANDREAS-NEIL UNTERREINER and OLIVER SCHALK — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe

A new ansatz for anisotropy in ultrafast experiments is presented. It is capable of describing systems with non-degenerate, degenerate and quasi-degenerate excited states (the latter concerning systems which are excited near a conical intersection) for one- or multiphoton pump-probe experiments. This contribution focuses on degeneracy and quasi-degeneracy. The degenerate case exhibits a high time zero anisotropy that decays due to coherence and population decay. This decay can be described with an Ornstein-Uhlenbeck process. Discrepancies to former models are discussed. In this model, quasi-degeneration in anisotropy experiments can be explained as a mixture of non-degenerate and twofold degenerate excited states and represents the first quantitative description of such processes.

MO 18.6 Di 14:00 Poster C1

**Long living, coherent phonons in quantum-crystals: cryogenic normal- and para-hydrogen** — ●FALK KÖNIGSMANN<sup>1</sup>, DAVID T. ANDERSON<sup>2</sup>, and NIKOLAUS SCHWENTNER<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, D-14195 Berlin — <sup>2</sup>Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA

Coherent optical phonons are a hot topic in metals and insulators, but did not show up in previous ultrashort pulsed excitations of quantum crystals. We grow 3 cm long, transparent para- and normal-hydrogen crystals in an enclosed cell at 8 K, which are then cooled down to 4 K. The crystals are pumped with 150 fs pulses at 780 nm of a Ti:Sa amplified laser system and the induced birefringence is detected with the second harmonic in a colinear way. We observe long lasting ( $> 20$  ps) sinusoidal birefringence modulation with a period of 900 fs in para-hydrogen. While the phonon density of states would cover a broad range from 0-180 wavenumbers, the observed coherent phonon has a sharp frequency centered at 36,8 wavenumbers. It coincides with the transverse, optical phonon at the center of the Brillouin-zone, which is observed exclusively in Raman scattering. The phonon wave packet

is anisotropic and the amplitude lies perpendicular to the *c* axis. In normal-hydrogen the same class of phonon, slightly shifted to higher frequencies and more strongly damped, is observed.

MO 18.7 Di 14:00 Poster C1

**High Harmonic Generation on Molecular Excited Electronic States** — ●MARKUS GÜHR, BRIAN K. MCFARLAND, JOE P. FARRELL, and PHILIP H. BUCKSBAUM — Stanford PULSE Center, Stanford University and SLAC, California, USA

We discuss schemes for the generation of high harmonics on excited electronic states of molecules. The high harmonic generating pulse is used to probe the dynamics initiated with a first pump pulse. This opens the chance to observe dynamics on those states without involving other electronic states in a probe process.

The main difficulty arising is the low ionization potential and thus the inherent high ionization rate for molecules in the excited state. We present a method to overcome this problem using the symmetry of the molecular wave function.

A further complication is given by the fact that a small harmonic signal from the excited state is sitting on a big background from molecules in their electronic ground state. Four-wave-mixing techniques can be applied to generate a background-free signal. We present prototypical four-wave-mixing measurements, using the third harmonic generated in air.

MO 18.8 Di 14:00 Poster C1

**Quantum dynamical simulations of femtosecond Pump-DFWM spectroscopy of higher excited states** — ●JÖRG LIEBERS, ABRAHAM SCARIA, VINU NAMBOODIRI, JAKOW KONRADI, ARNULF MATERNY, and ULRICH KLEINEKATHÖFER — Jacobs University Bremen, Germany

Nonlinear time- and frequency-resolved four-wave mixing (FWM) spectroscopy is one of the major tools to investigate dynamic properties of molecules. Until now the dynamics of the ground state and lower lying excited states were accurately investigated in numerous experiments. Recently it was demonstrated that dynamics of higher lying excited states in molecular iodine can be accessed and probed by a time-resolved DFWM process as well by combining the DFWM process with an initial pump pulse [1]. In this contribution we present the results of quantum dynamical simulations of rovibrational wavepackets which reproduce the results of these experiments. The wavepacket dynamics on the potential energy surfaces of the ion pair states of iodine were calculated for different pulse sequences and compared to the dynamics monitored in the experiments. The experiments are detailed in a separate contribution.

[1] A. Scaria, V. Namboodiri, J. Konradi, and A. Materny, *J. Chem. Phys.* **127**, 144305 (2007)

MO 18.9 Di 14:00 Poster C1

**Detection of C-Deuterium compounds by CARS microscopy** — ●GERO BERGNER<sup>1,3</sup>, DENIS AKIMOV<sup>1</sup>, MICHAEL SCHMITT<sup>1,2</sup>, SEBASTIAN SCHLÜCKER<sup>3</sup>, and JÜRGEN POPP<sup>1,2</sup> — <sup>1</sup>Institut für Photonische Technologien, Albert-Einstein-Straße 9, 07745 Jena — <sup>2</sup>Institut für Physikalische Chemie, Lessingstraße 10, 07743 Jena — <sup>3</sup>Institut für Physikalische Chemie, Am Hubland, 97074 Würzburg

Coherent anti-Stokes Raman scattering (CARS) microscopy is a powerful imaging technique with chemical specificity. In particular, it provides vibrational contrast without need of external labelling. Here, we present first steps to establish CARS as a new method for drug localization in living cells. Chemical contrast in the images is obtained by probing the C-D stretch vibration of internally labelled (Deuterium-substituted) compounds. For determining the ratio of Raman-resonant signal to non-Raman-resonant background, both C-D and C-H species of the same compound are investigated. First results for systematically determining the detection limit of this methodology are presented.

MO 18.10 Di 14:00 Poster C1

**A Comparison of the Selective Excitation of Molecular Modes in Gas and Liquid Phase Using Femtosecond Pulse Shaping** — ●ABRAHAM SCARIA, VINU NAMBOODIRI, JAKOW KONRADI, and ARNULF MATERNY — Jacobs University Bremen, Germany

In our previous publications we have demonstrated that a selective excitation of specific vibrational modes in a molecule is possible by using a feedback-controlled optimization in a coherent-anti Stokes Raman scattering (CARS) process [1,2]. The mechanism behind the selective enhancement and suppression of vibrational modes is not clearly understood. The experiments suggest an important contribution by intermolecular dynamical processes. Here, it would be of importance to determine, what influence the interaction with surrounding molecules plays on the control result. In our contribution, we present results from optimal control experiments performed on CS<sub>2</sub> molecules in the gas phase as well as in its liquid form. The CARS excitation was chosen to be not in resonance with an electronic transition in the molecule but to excite different vibrational modes coherently. A pure phase modulation of the Stokes pulse resulted in changes of the ratio of the Raman lines observed in the nonlinear scattering spectrum. This could also be achieved when no temporal shift between pump and Stokes laser resulted in a simple change of the Raman resonances. The differences between gas and liquid phase measurements will be discussed.

[1] J. Konradi, A.K. Singh, and A. Materny, *PCCP* **7**, 3574 (2005).

[2] J. Konradi, A. Scaria, V. Namboodiri, and A. Materny. *J. Raman Spectrosc.* **38**, 1006 (2007).

MO 18.11 Di 14:00 Poster C1

**Ultrakurze Laserimpulse zur Anregung von Photosensibilisatoren** — ●JOHANNES SCHNEIDER, JUTTA MILDNER, MATTHIAS WOLLENHAUPT und THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, Heinrich-Plett-Str. 40, D-34132 Kassel

Photosensibilisatoren werden typischer Weise mit kontinuierlichem Licht angeregt. Nach dem Übergang aus einem angeregten Singulett-Zustand ins Triplett-System (ISC) wird die Anregungsenergie dieser Systeme mittels Energietransfer effizient an Moleküle der Umgebung abgegeben.

Bei Anregung mit Femtosekunden-Laserimpulsen kann die Dynamik der Anregung mit hoher Zeitaufösung untersucht werden. Zudem erhält man mittels Impulsformung die Möglichkeit den Anregungsprozess des Moleküls zu beeinflussen.

Als Beobachtungsgrößen für unsere Experimente dienen Absorption, Fluoreszenz und Phosphoreszenz der Photosensibilisatoren in der flüssigen Phase. Besonderes Augenmerk gilt dem ISC-Prozess, welcher die Effizienz der Photosensibilisierung einschränkt. Der direkte Nachweis dieses Übergangs gelingt über die Phosphoreszenz von gelöstem Sauerstoff nach erfolgtem Energietransfer vom Photosensibilisator. Dieses Signal steht am Ende der Reaktion und eignet sich damit für eine rückkopplungsgesteuerte Optimierung.

Der Aufbau zur Messung der Lumineszenzen und zur Aufnahme von Absorptionstransienten wird präsentiert. Erste Untersuchungen an Zink-Porphyrin und Porphyrinen werden vorgestellt.

MO 18.12 Di 14:00 Poster C1

**Phase modulation of ultrashort laser pulses by rotational wave packets** — ●RAPHAEL KÜHNEN and BERND V. ISSENDORFF — Universität Freiburg, physikalisches Institut, Stefan-Meier-Strasse 19, D-79104 Freiburg

Molecular rotational wave packets introduce a time dependent phase modulation to ultrashort optical pulses. This phase modulation can be imaged by observing the spectrum of a probe laser pulse sent with a tunable delay to an alignment pulse.

The processes affecting the probe laser pulse depend on the polarisation of the pump pulse. This influence as well as the temporal evolution of the rotational wave packets can be observed by recording the transmitted spectrum of a 400nm, linear polarized, laser pulse depending on the pump-probe delay as well as the rotation angle of a quarter-wave-plate in the pump-beam.

It is possible to tune the phase in a way that the spectrum of the laser pulse is broadened and shifted by raman scattering. As a result it is possible to introduce a negative chirp to the probe laser pulse and to reduce the pulse duration below 25 fs.

(1) M. Wittmann et al., *Appl. Phys. B*, **70**, 261 (2000)

(2) R.A. Bartels et al., *Phys. Rev. Lett.*, **88**, 1 (2002)

(3) V.P. Kalosha and J. Herrmann, *Phys. Rev. A*, **68** (2003)

(4) R. Torres et al., *Phys. Rev. A*, **72**, 023420 (2005)