

MO 14: Femtosecond Spectroscopy II

Time: Wednesday 14:00–16:00

Location: F 102

Invited Talk

MO 14.1 We 14:00 F 102

Ultrafast Conformational Dynamics of Azopeptides — ●JOSEF WACHTVEITL¹, LISA LORENZ¹, KARSTEN NEUMANN¹, HEIKE STAUDT¹, ULRIKE KUSEBAUCH², and LUIS MORODER² — ¹Institute of Physical and Theoretical Chemistry, Institute of Biophysics, Johann Wolfgang Goethe-University, 60438 Frankfurt/Main — ²Max-Planck-Institute of Biochemistry, 82152 Martinsried, Germany

Azobenzene derivatives have been used as backbone constituents or side-chain clamps to photocontrol in reversible manner conformational states of model peptides [1]. Because of the ultrafast isomerization (within picoseconds), this chromophore allows spectroscopic monitoring of the fast kinetics of folding/unfolding of model peptides with ordered secondary structure motifs such as β -turns, α -helices and most recently even of β -hairpins. Aim of the present work is to gain new insights into the kinetics of assembly of tertiary structure motifs such as the collagen triple helix. For this purpose model peptides were conformationally restricted with a suitable azobenzene clamp in the trans-isomeric state, which upon photoisomerization provokes unfolding of the triple helix [2]. Upon excitation of the $\pi\pi^*$ -transition, *trans-cis* isomerisation of a specially designed collagen-sample and its azobenzene clamp is examined by time resolved spectroscopy in the visible and infrared spectral region. The functionality of the azobenzene clamp is conserved upon binding, making it a promising tool for the investigation of tertiary structure formation.

[1] Wachtveitl, J., Spörlein, S., Satzger, H., Fonrobert, B., Renner, C., Behrendt, R., Oesterhelt, D., Moroder, L. and Zinth, W., *Ultrafast Conformational Dynamics in Cyclic Azobenzene Peptides of Increased Flexibility*, *Biophys. J.*, **86**, 2350 (2004)

[2] Kusebauch, U., Cadamuro, S.A., Musiol, H.-J., Lenz, M. U., Wachtveitl, J., Moroder, L. and Renner, C., *Photocontrolled Folding and Unfolding of a Collagen Triple Helix*, *Angew. Chem. Int. Ed.*, **45** 7015-7018 (2006)

MO 14.2 We 14:30 F 102

Investigation of the hot-S₀ model with an excitation energy dependence experiment — ●TIAGO BUCKUP^{1,2}, MARIE MAREK^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

The ultrafast relaxation dynamics of carotenoids have been challenging spectroscopists for a long time. Energy level models of increasing complexity, containing additional electronic states or vibrationally excited species, have been used to describe the deactivation network of carotenoids. One of such models involves a vibrationally hot ground-state populated via impulsively Raman scattering (IRS). In such a process, the initial excitation pulse must interact two times with the molecule, suggesting the presence of a two-photon excitation scheme. Here we investigate this model by varying the excitation energy in a pump-degenerate four-wave mixing (Pump-DFWM) setup [1-2] applied to lycopene. The experiment shows two distinct excitation dependence regimes obtained for two initial pump delays. In order to clarify this observation, we implemented several deactivation models and simulated the variation of excitation energy on a Pump-DFWM experiment for each model. We found out that a model involving the three well-known electronic states of carotenoids (S₂, S₁, and S₀) and the respective vibrational manifolds is the most suitable scheme to describe the observed energy dependence. Our findings confirm that IRS is an important interaction in carotenoids.

MO 14.3 We 14:45 F 102

New insights into the excited state relaxation network by simulation of Pump-DFWM in carotenoids — ●MARIE MAREK^{1,2}, TIAGO BUCKUP^{1,2}, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

Carotenoids are together with chlorophylls the most abundant natural pigments and play a key role in photosynthetic light-harvesting complexes. However, the exact relaxation following excitation with visible light is still not clear, despite extensive spectroscopic investigations. For the exploration of the excited states dynamics of these complex

molecules we used pump-degenerate four wave mixing (pump-DFWM). Pump-DFWM is a two-dimensional technique where the system is promoted to the excited state by an initial pump pulse and the subsequent dynamics is probed by a DFWM sequence. By simulating the pump-DFWM signal of several carotenoids, namely β -carotene and lycopene, and comparing the results with the experimental data we gain detailed knowledge about the internal conversion between the S₂ and S₁ state. We observe an additional very fast component directly after excitation of S₂ in both carotenoids. For lycopene, this component is populated from the S₂ state in an ultrashort time scale with a time constant of about 20 fs and which decays to S₁ with the 140 fs generally ascribed to the S₂ lifetime. We discuss the nature of this component with respect to new theoretical and experimental investigations.[1]

[1] E. Ostroumov et al., *PRL* 103 (2009) 108302.

MO 14.4 We 15:00 F 102

Discrimination between low-frequency structural dynamics and beating using pathway-selective Four-Wave-Mixing Spectroscopy — ●JAN PHILIP KRAACK^{1,2}, TIAGO BUCKUP¹, and MARCUS MOTZKUS^{1,2} — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany — ²Physikalische Chemie, Philipps-Universität, D-35043 Marburg, Germany

The coherent preparation of vibrational states and determination of their femtosecond time-evolution is a powerful method for investigating ultrafast dynamics in the condensed phase. In the context of nonlinear spectroscopy, it is challenging to discriminate between contributions of molecular low frequency modes and beating between high-frequency modes. In order to investigate molecular low-frequency modes and to elucidate the time-evolution of wave-packets on the sub-20 fs timescale we applied Degenerate Four-Wave-Mixing (DFWM) to bio-physically relevant samples (Bacteriorhodopsin, Retinal Protonated Schiff-Bases, β -carotene). DFWM is an ideal spectroscopic technique combining advantages of high time-resolution, homodyne signal detection and allowing additionally investigations of electronic coherence dynamics. The signal modulations are interpreted regarding ground- and excited-state dynamics as well as environmental effects. We present a method for discrimination between beating contributions and normal modes and clarify the origin of low-frequency modes in carotenoids. It is shown that electronic coherence dynamics allow the induction of wave-packets after up to more than 100 fs of pulse separation.

MO 14.5 We 15:15 F 102

Electron Localization in Fragmentation of H₂ with CEP Stabilized Laser Pulses — ●MANUEL KREMER¹, BETTINA FISCHER¹, BERNOLD FEUERSTEIN¹, VITOR L. B. DE JESUS², VANDANA SHARMA¹, CHRISTIAN HOFRICHTER¹, ARTEM RUDENKO³, UWE THUMM⁴, CLAUDIUS DIETER SCHRÖTER¹, and ROBERT MOSHAMMER¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (IFRJ), Nilópolis, RJ, Brazil — ³Max-Planck Advanced Study Group at CFEL, D-22607 Hamburg, Germany — ⁴James R. Macdonald Laboratory, Kansas State University, Manhattan, Kansas 66506-2606, USA

Fully differential data for H₂ dissociation in ultrashort (6 fs, 760 nm), linearly polarized, intense (0.44 PW/cm²) laser pulses with a stabilized carrier-envelope phase (CEP) were recorded with a reaction microscope. Depending on the CEP, the molecular orientation, and the kinetic energy release (KER), we see a clear asymmetry in the proton emission for kinetic energy releases between 0 – 3 eV as basically predicted by Roudnev and Esry [1] and much stronger than in earlier measurements by Kling et al. [2]. Wave packet propagation simulations were carried out, which reproduce the salient features and together with the KER-independent electron asymmetry observed in the experiment, rule out the first ionization step to be the reason for the asymmetric proton emission.

[1] V. Roudnev and B.D. Esry, *Phys. Rev. A* 76, 0234033 (2007).

[2] M. F. Kling et al., *Science* 312, 246 (2006).

MO 14.6 We 15:30 F 102

Energy Transport by Exciton Diffusion in Thin Organic Films — ●FRANZISKA HELLMUTH and STEFAN LOCHBRUNNER — Universität-splatz 3, 18055 Rostock

Thin organic films are central components of organic light emitting diodes, solar cells and plastic electronics. Energy transport via exciton migration is a crucial element for their functional capabilities. However, in most organic films trapping limits the transfer to short distances. To circumvent this limitation we incorporate in polymer films dye molecules as active sites. Perylene Red is used as dye due to its high quantum yield and little interaction with the environment. To characterize the energy transport properties an additional energy acceptor is added at low concentration to the film (0.1 M Perylene Red, 1.4 mM acceptor). We find that the excitation is transferred from the optically excited Perylene Red molecules to the acceptor with an efficiency of 90%. To model the energy transfer and calculate the exciton diffusion length a diffusion approach is applied. A diffusion length of about 30 nm is estimated for the studied system. The results are in good agreement with Förster theory. However, femtosecond pump probe measurements indicate a red shift of the transient spectra within the first picoseconds. The evaluation of the excitation induced anisotropy and its picosecond decay leads to distinctly shorter transfer times than predicted by Förster theory. Those two facts might be ex-

plained by dispersive energy transport, i.e. the primary transfer steps lead from more energetic donors to less energetic acceptor states.

MO 14.7 We 15:45 F 102

Vibrational-state and isotope dependence of high-harmonic generation in water molecules — ●MIRJAM FALGE¹, VOLKER ENGEL¹, and MANFRED LEIN² — ¹Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Centre for Quantum Engineering and Space-Time Research (QUEST) and Institut für Theoretische Physik, Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover

We report calculations on high-harmonic generation in water molecules. Spectra are determined for various initial vibrational states of H₂O and its isotope D₂O. It is demonstrated that the ratio of the spectra for D₂O and H₂O is close to unity when the initial state is the vibronic ground state, indicating that nuclear dynamics is of minor importance. For vibrationally excited initial states, the high-harmonic intensities show a clear dependence on both, the initial state quantum number and the isotopic species.