

MO 21: Femtosecond Spectroscopy III

Time: Thursday 14:00–15:30

Location: F 102

MO 21.1 Th 14:00 F 102

Influence of the Chemical Environment on Perylene/ZnO and Perylene/TiO₂ Hybrid Systems Varying the Electronic Coupling — ●ANTJE NEUBAUER, ANDREAS BARTELT, JODI SZARKO, RAINER EICHBERGER, OLAF LETTAU, CARLO FASTING, and THOMAS HANNAPPEL — Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin

Heterogeneous electron transfer dynamics are determined by the strength of the electronic couplings, the density of states and the energetics of the reaction. Here, we present a study of molecular dye/semiconductor hybrid systems that vary in electronic coupling due to dye structure and in the density of states due to different semiconductor materials. The dye molecules differed in a C-C single bond vs. a C-C double bond between the perylene skeleton and a carboxylic acid anchor group which bounds the dyes chemically to ZnO or TiO₂ colloidal films. A detailed study of steady-state absorption and fluorescence spectra for these two dye molecules in different solvents as well as for the hybrid systems showed that the ZnO and TiO₂ colloids in the films provide different chemical environments for electron transfer. For the dye with strong electronic coupling this led to a strong broadening of the absorption spectra. This could be explained by a larger dipole moment for the dye with the C-C double bond and a higher intramolecular charge transfer character of the excited state. This has also been shown by excited state spectra measured with femtosecond-resolved transient absorption spectroscopy for the hybrid systems and the dyes in solution.

MO 21.2 Th 14:15 F 102

XUV Pump XUV Probe Experimente an molekularem Sauerstoff — ●OLIVER HERRWERTH¹, MATTHIAS LEZIUS¹, MATTHIAS KLING¹, LUTZ FOURCAR², MORITZ KURKA³, YUHAI JIANG³, KAI-WE KÜHNEL³, CLAUDIUS-SCHRÖTER³, ROBERT MOSHAMMER³, JOACHIM ULLRICH³, STEFAN DÜSTERER⁴, ROLF TREUSCH⁴ and MICHAEL GENSCH⁴ — ¹Max Planck Institut für Quantenoptik, Garching bei München, Deutschland — ²Max-Planck Advanced Study Group at CFEL, 22607 Hamburg, Germany — ³Max Planck Institut für Kernphysik, Heidelberg, Deutschland — ⁴DESY, Hamburg, Deutschland

Die Ionisation von Atomen und Molekülen mit XUV-Licht kann zu hoch angeregten Zuständen des Ions führen, welche daraufhin relaxieren oder zu Autoionisation führen. Insbesondere für Moleküle ist die Autoionisation ein wichtiges Elektronen Vielkörper-Problem. Um dieses zu untersuchen wurde eine Pump-Probe Anordnung für ein Reaktionsmikroskop entwickelt und an den FELs FLASH (DESY, Hamburg) und SCSS (Spring8, Japan) für Experimente an Molekülen eingesetzt. Das Setup erlaubt Verzögerungen zwischen zwei XUV Pulsen von bis zu 1,5 ps mit einer Genauigkeit von ca. 50 as.

Vorgestellt werden Messungen mit Pulslängen von ca. 20-30 fs, in welchen einerseits die Dissoziationsdynamik und andererseits die Autoionisation aus hochangeregten O₂⁺* Zuständen nach XUV Anregung zeitabhängig verfolgt wurde.

MO 21.3 Th 14:30 F 102

Femtosecond Spectroscopy of Alkali Trimers on Helium Nanodroplets — ●CHRISTIAN GIESE¹, BARBARA GRÜNER¹, LUTZ FECHNER¹, MARCEL MUDRICH¹, ANDREAS W. HAUSER², WOLFGANG E. ERNST², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Germany — ²Institut für Experimentalphysik, TU Graz, Graz, Austria

Superfluid helium nanodroplets offer the opportunity to study dopant molecules in the sub-Kelvin range with only weak matrix perturbations. Femtosecond wave packet spectroscopy has been shown to be well suited to obtain high resolution vibrational spectra of cold alkali molecules in weakly bound high-spin states [1]. In a pump-probe scheme a first laser pulse excites a vibrational wave packet that evolves on the molecular potential and is probed by a second ionizing pulse. We present spectroscopic data on Rb₃ and K₃ showing different vibronic progressions. These are assigned with the help of high level *ab-initio* calculations of the electronic structure of the bare trimers [2].

[1] M. Mudrich, Ph. Heister, Th. Hippler, Ch. Giese, O. Dulieu, and F. Stienkemeier, Phys. Rev. A 80, 042512 (2009)

[2] J. Nagl, G. Auböck, A. W. Hauser, O. Allard, C. Callegari, and W. E. Ernst, Phys. Rev. Lett. 100, 063001-1-4 (2008)

MO 21.4 Th 14:45 F 102

One-Dimensional Excitation Migration in Perylene Bisimide Aggregates — ●HENNING MARCINIAK and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock, Germany

Perylene bisimides are excellent dyes and versatile building blocks for supramolecular structures and organic n-type semiconductors. Only recently perylene bisimides became available which show the absorption characteristics of J-aggregates [1]. We apply steady state as well as femtosecond pump-probe absorption spectroscopy to J-aggregates of substituted perylene bisimides to investigate their excitonic properties. For the excitons a delocalization length of two monomers is derived from the narrowing of the absorption line shape due to aggregation. The transient measurements reveal signatures of excited state absorption which are slightly blue shifted from the ground state absorption and which can be assigned to one-exciton to two-exciton transitions. The decay dynamics of the transients shows a strong dependence on the excitation intensity. This points to exciton-exciton-annihilation and indicates that the excitons are mobile. Two models are considered in the analysis of the annihilation dynamics. In one case the exciton motion is described as a diffusive process and in the other case a single step Förster resonance energy transfer (FRET) from an exciton site to another exciton is assumed as rate determining process. Evidence is provided that the relevant motion occurs only along one dimension.

[1] X.-Q. Li, X. Zhang, S. Ghosh, and F. Würthner, Chem. Eur. J. 14 (2008), 8074.

MO 21.5 Th 15:00 F 102

Time-resolved vibrational spectroscopy of externally cold, single molecular ions — ●G. LESCHHORN¹, S. KAHRA¹, T. DOU¹, A. SCHIFFRIN², R. ERNSTORFER², R. KIENBERGER², M. KOWALEWSKI³, R. DE VIVIE-RIEDLE³, and T. SCHAEZT¹ — ¹Max-Planck-Institut für Quantenoptik (MPQ), Garching, Tlamo — ²MPQ, Garching, attosecond-beamlines — ³LMU, München

We report the preparation of externally cold and spacially well ($1\ \mu\text{m}$) localized molecular ions. A selectable amount can be provided by using techniques like RF-trapping and sympathetic cooling. These ions can serve as targets for time resolved diffraction experiments. As a first step towards this goal we are performing vibrational spectroscopy on a single magnesium hydride ion (MgH^+), using a one colour pump-probe scheme in the UV ($1\text{-}5\ \text{GW}/\text{cm}^2$, pulse duration below 4 fs). For this purpose, two time delayed replica of the third gas-harmonic of a few cycle NIR pulse are used. The pump pulse launches a coherent oscillating wave packet in the first excited bound state and the probe pulse maps the intramolecular distance at a given time delay on a dissociative channel. The given UV spectrum favors or suppresses the dissociation probability for a fixed intramolecular distance. The oscillation period of the wave packet (30.9 fs) can thus be measured by observing the variation of the loss rate (dissociation) of molecular ions out of the trap. The dissociation signal of MgH^+ has been observed and first measurements will be discussed. This project is part of the excellence initiative of the DFG (MAP) and financial support of MPG and IMPRS-APS is acknowledged.

MO 21.6 Th 15:15 F 102

Ultrafast vibrational energy redistribution through water-phosphate interactions in hydrated DNA — ●ŁUKASZ SZYC, MING YANG, ERIK T.J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, Berlin, Germany

The interaction of DNA with water plays a key role for its structural conformation and its local hydrogen bond geometries. The role of hydration shells for the ultrafast energy dissipation and the resulting changes of hydrating structures have been studied in real-time by femtosecond vibrational spectroscopy. By direct excitation of antisymmetric (PO_2)⁻ stretching oscillator we were able to measure its $\nu=1$ vibrational lifetime which is around 340 fs and is independent on sample humidity. For the 0% r.h. DNA oligomer, where only a single water molecule interacts with the phosphate group, the recorded time traces show not only an initial fast decay corresponding to $\nu=1$ $\nu_{AS}(\text{PO}_2)^-$

lifetime, but also a slow (≈ 5.5 ps) component, which reflects the time of energy delocalization within the DNA strand. In contrast, in a fully hydrated sample (92% r.h.), the slow relaxation component is completely absent. The excess vibrational energy released by the

$\nu_{AS}(\text{PO}_2)^-$ decay is now mainly transferred to the surrounding water shell. This transfer is faster than the 340 fs decay of $\nu_{AS}(\text{PO}_2)^-$ and suppresses energy accumulation in the phosphate group.