

## MO 7: Femtosecond Spectroscopy 2

Time: Tuesday 11:00–13:00

Location: f102

## Invited Talk

MO 7.1 Tue 11:00 f102

**Monitoring ultrafast excited-state intramolecular proton transfer by ultrafast electronic and fluorescence spectroscopy**

— ●ANDREAS STEINBACHER<sup>1</sup>, PRAMOD KUMAR VERMA<sup>2</sup>, FREDERICO KOCH<sup>1</sup>, ALEXANDER SCHMIEDEL<sup>3</sup>, PATRICK NUERNBERGER<sup>4</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Korea University, Seoul 136-701, Republic of Korea — <sup>3</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>4</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Excited-state intramolecular proton transfer (ESIPT) is one of the most successful models for understanding complex proton transfer dynamics. In general, ESIPT is an ultrafast process occurring on a subpicosecond time scale. Hence, we employ transient absorption from the deep-UV to the visible spectral region and fluorescence upconversion to investigate the photoinduced ESIPT dynamics in  $\beta$ -diketones. Electronic excitation in the UV is followed by ultrafast proton transfer to form a vibrationally hot tautomeric species. Further relaxation steps are determined by the actual symmetry of the investigated  $\beta$ -diketone and also by the solvent environment. Here, we address both issues by comparing the results for symmetric and unsymmetric  $\beta$ -diketones in various solvents. Depending on the actual molecular system, photoisomerization reactions and even ground-state intramolecular proton transfer could be observed.

MO 7.2 Tue 11:30 f102

**Pursuing Primary Processes of Diphenylcarbene in Binary Solvent Mixtures**

— ●JOHANNES KNORR<sup>1</sup>, PANDIAN SOKKAR<sup>2</sup>, SEBASTIAN SCHOTT<sup>3</sup>, PAOLO COSTA<sup>4</sup>, WOLFRAM SANDER<sup>4</sup>, ELSA SÁNCHEZ-GARCÍA<sup>2</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — <sup>2</sup>Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr — <sup>3</sup>Institut für Physikalische und Theoretische Chemie, Am Hubland, Universität Würzburg, 97074 Würzburg — <sup>4</sup>Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

The ultrafast reaction dynamics of carbenes in solution are governed by intersystem crossings, intermolecular proton uptake, or concerted reactions with the solvent. In this study, we combine quantum mechanics/molecular mechanics calculations and broadband femtosecond transient absorption spectroscopy applied to diphenylcarbene, and unravel the underlying dynamics and reaction mechanisms that take place in binary solvent mixtures at room temperature. The results show that a competition between the reaction pathways occurs that not only depends on the solvent molecule near-by but also on its interaction with other solvent molecules. In-depth analysis of the solvation dynamics and the amount of nascent intermediates corroborates the importance of a hydrogen-bonded complex with a protic solvent molecule, in striking analogy to complexes found at cryogenic temperatures [1].

[1] P. Costa and W. Sander, *Angew. Chem.* 2014, 53, 5122-5125

MO 7.3 Tue 11:45 f102

**A ps time-resolved study of NI, Me-NI and NDCA**

— ●HANS-CHRISTIAN SCHMITT, THIEMO GERBICH, INGO FISCHER, JENS PETERSEN, and ROLAND MITRIC — Institute for Physical and Theoretical Chemistry, University of Würzburg, Germany

In a molecular beam experiment we investigated the excited state dynamics of isolated Naphthalimide (NI), N-Methyl-Naphthalimide (Me-NI) and 1,8-Naphthalic anhydride (NDCA).

Our ps-laser system allowed us to probe different vibronic states with a resolution of 20 cm<sup>-1</sup>. Hereby we found an interesting dependence of the decay time from the excitation energy. In NDCA the lifetime drops from 1.2 ns at the origin of the S<sub>1</sub> to 30 ps at an excess energy of 800 cm<sup>-1</sup>. In NI and Me-NI the lifetimes are nearly constant at around 10-17 ps. The experiments were accompanied by surface hopping dynamics simulations that give detailed insights into the occurring photochemical processes. These are a fast internal conversion via a conical intersection and intersystem crossing which compete as deactivation processes.

MO 7.4 Tue 12:00 f102

**Two-Dimensional Electronic Spectroscopy Can Fully Characterize the Population Transfer in Molecular Systems**

— ●JAKUB DOSTÁL<sup>1</sup>, BARBORA BENEŠOVÁ<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — <sup>2</sup>Department of Mathematics, University of Würzburg, Emil-Fischer-Straße 40, 97074 Würzburg

Excitation energy transfer (EET) in complex systems often proceeds through series of intermediate states. One of the goals of time-resolved spectroscopy is to identify the spectral signatures of all of them in the acquired experimental data and to characterize the energy transfer scheme between them. It is well known that in the case of transient absorption (TA) spectra such a decomposition can be ambiguous even if many simplifying considerations (such as described below) are taken. The systematic decomposition of coherent 2D spectra has not been investigated to date.

Here we show that the unique retrieval of the complete set of rate constants and TA spectra of all states is possible by simultaneously fitting the 2D spectrum and absorption spectrum. An efficient implementation of the fitting routine is proposed. We focus on the ideal case of a system with well separated spectral bands, with no dark states present and with EET strictly governed by a set of linear rate equations of the first order. We also assume that the spectra of the intermediate states are not linearly dependent. This represents a theoretical basis for quantitative analysis of EET in experimental 2D spectra.

MO 7.5 Tue 12:15 f102

**Quantum chemical studies of pyrene: long known molecule, new insights**

— ●MATTHIAS K. ROOS, TERESA KÜBLBÖCK, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Pyrene, an intensively studied molecule especially known for its excimers, is used today as a fluorescence marker. Yet, the microscopic mechanism accounting for its photophysics is still rather unclear. It is experimentally known that after excitation to the S<sub>2</sub> (L<sub>a</sub>) ultrafast relaxation to the S<sub>1</sub> (L<sub>b</sub>) occurs followed by fluorescence or excimer formation.

We studied pyrene with quantum chemical methods including TD-DFT and CASSCF in the gas phase and in solution (PCM). With this, we optimized minima for the L<sub>a</sub> and L<sub>b</sub> state and simulated absorption spectra that are in excellent agreement with the experimental ones. We also located a conical intersection between the S<sub>2</sub> and S<sub>1</sub> near the excited states minima enabling the ultrafast relaxation. In addition, an explanation is presented for the difference in oscillator strength between L<sub>a</sub> and L<sub>b</sub> without considering the symmetry of the molecule.

Furthermore, we investigated possible structures for the pyrene excimer. Minima are located on the S<sub>1</sub> and S<sub>2</sub> surface that differ in the rotation angle between the pyrene moieties. Hirayama's rule is confirmed that excimers for bridged pyrenes should exist especially for a propyl bridge. For the first time, we can present optimized structures for such bridged excimers already suggested in the literature.

MO 7.6 Tue 12:30 f102

**Detection of multiple-quantum coherences in dilute samples**

— ●LUKAS BRUDER, MARCEL BINZ, ULRICH BANGERT, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, 79104 Freiburg

Multidimensional spectroscopy allows efficient isolation and detection of multiple-quantum coherences (MQCs). MQC signals have been used to explore higher-lying molecular states and many-body phenomena in various systems. Detecting such higher order effects usually requires particularly sensitive methods. We present a simple approach based on quasi-continuous phase modulation which allows efficient isolation of MQC signals in a collinear two-pulse experiment [1]. We demonstrate the detection of multiphoton quantum beats in atomic vapors and supersonic doped helium droplet beams. Furthermore, collective resonances up to the 5th order are observed, which is surprising considering the low density in our samples. The origin of these features is currently investigated. Our approach can readily be extended to higher dimensional spectroscopy. Moreover, it may facilitate coherent time-resolved spectroscopy in the XUV spectral range.

[1] L. Bruder, M. Binz, and F. Stienkemeier, Phys. Rev. A 92, 053412 (2015).

MO 7.7 Tue 12:45 f102

**Ultrafast Dynamics of Vibrational Relaxation of Pseudohalides in Liquid-to-Supercritical Water. A Critical Test of Fermi's Golden Rule** — •JEANNINE GLEIM, DENIS CZURLOK, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

In recent years, the vibrational spectroscopy of pseudohalide anions in condensed media has attracted much attention. They were studied in the context of dynamical solute-solvent interactions and vibrational energy relaxation (VER) in hydrogen-bonded liquids like water.

Here, the stretching vibration of  $^{15}\text{N}$ -labelled thiocyanate, seleno-

cyanate and azide anions in aqueous solution were studied with Fourier-Transform IR-spectroscopy (FTIR) as well as femtosecond IR-pump-probe spectroscopy (fs-IR-PP). All experiments were carried out under isobaric conditions at a pressure of 500 bar over a wide temperature range covering the liquid and supercritical phases of water.

Relaxation rate constants were determined from the decay of the  $v = 1$  excited state absorption. In all studied cases, the temperature dependencies of the relaxation rate constants are similar. However, the relaxation pathways differ. While the relaxation of thiocyanate and selenocyanate follow the VET pathway, that of azide follows a combination of both, the IVR and VET pathways. The results are interpreted in terms of Fermi's Golden Rule and a resonant VET from the solute's stretching mode to the combination tone of the bending and librational modes of water.