

## MO 18: Biomolecules and Electron Transfer

Time: Friday 11:00–13:00

Location: N 25

MO 18.1 Fri 11:00 N 25

**Ultrafast dynamics of the triazene compound Berenil** — ●LENA GRIMMELSMANN, JOHANNES KNORR, CHRISTIAN SPIES, and PATRICK NUERNBERGER — Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Berenil is a versatile organic compound with a variety of applications, e.g. as the most widely used drug for treating the sleeping sickness in animals. Berenil efficiently binds to DNA, trypsin, and other biomolecules, but in all these cases it is reported to be a “non-fluorescent dye”. This points towards a very short excited-state lifetime and ultrafast nonradiative deactivation channels on which the molecule’s surrounding have a significant impact. Berenil comprises two amidinophenyl moieties linked by a triazene bridge, therefore it is chemically related to azobenzene but exhibits remarkable differences. In femtosecond fluorescence upconversion and transient absorption experiments, we disclose the ultrafast dynamics of berenil in various solvents, as well as berenil bound to trypsin, AT-rich DNA, and G-quadruplex DNA. Our results demonstrate that berenil exhibits an ultrafast deactivation of the  $S_1$  state after photoexcitation, which we ascribe to associated molecular motion which does not require volume significantly beyond that occupied by the ground-state molecule. Studies in solvents with different viscosities substantiate these findings. As a general trend, one finds that the more restriction the binding introduces, the longer the fluorescence lifetimes. The transient absorption experiments provide additional insight into the nonradiative reaction channels and the possibility of photoisomerization.

MO 18.2 Fri 11:15 N 25

**Characterization of Charge Separated States in (6-4)-Photolyase - Mechanistic Implications** — ●MARA OSSWALD and BENJAMIN FINGERHUT — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, D-12498 Berlin

The UV irradiation of DNA causes the formation of cyclobutane pyrimidine dimers and of the (6-4)-photoproduct. The latter can be reverted by the enzyme (6-4)-photolyase. Triggered by light induced electron transfer, (6-4)-photolyase catalyzes the transfer of a hydroxyl group in addition to covalent bond cleavage. We present results on the effect of enzyme-electrostatics on the energetics of charge separated states in the (6-4)-photoproduct repair complex. Excited state calculations in gas phase and with enzyme were conducted using a QM/MM framework and TDDFT methods with modern long-range-corrected functionals as well as local coupled cluster linear response as ab-initio benchmark. By including all relevant molecules in the QM-region (ISO, ADE, (6-4)-lesion, His365, His369), the calculations account for the, up to date, largest QM-region regarding the (6-4)-repair complex. The results show that the electrostatics of the enzyme substantially affect the charge transfer (CT) states of the system. Most notably, the CT states from the isalloxazine ring to the (6-4)-lesion are destabilized and become inaccessible. While the (6-4)-photoproduct acts as electron acceptor in gas phase, a radical cationic state, arising from the reverted electron transfer direction, is favored once the enzyme is taken into account.

MO 18.3 Fri 11:30 N 25

**Time-Resolved Measurement of Photoinduced Electron Transfer Processes in Perylene Diimides** — ●ROBIN C. DÖRING<sup>1</sup>, EDUARD BAAL<sup>2</sup>, MALCOLM A. BARTLETT<sup>2</sup>, CHRISTIAN PRINZISKY<sup>2</sup>, REMCO W. A. HAVENITH<sup>3,4</sup>, JÖRG SUNDERMEYER<sup>2</sup>, and SANGAM CHATTERJEE<sup>1,5</sup> — <sup>1</sup>Faculty of Physics and Materials Sciences Center, Philipps-Universität Marburg, Germany — <sup>2</sup>Faculty of Chemistry and Materials Sciences Center, Philipps-Universität Marburg, Germany — <sup>3</sup>Zernike Institute for Advanced Materials, Stratingh Institute for Chemistry, University of Groningen, The Netherlands — <sup>4</sup>Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Belgium — <sup>5</sup>Institute of Experimental Physics I, Justus-Liebig-Universität Gießen, Germany

Perylene derivatives form an important model system for studies of electron transfer (ET) in (molecular) donor-acceptor dye systems. Here, we introduce highly soluble perylene dihydrazides (PDH). We compare the PDH electron-transfer dynamics with a series of bisalkylperylene diimides. Time-resolved photoluminescence and photoluminescence excitation spectroscopy (PLE) measurements are per-

formed. All samples show non-single-exponential decay dynamics. A rate-equation analysis including a shallow shelving state is able to reproduce the experimental data. Time-dependent density functional theory calculations of the triplet states supported by PLE measurements give evidence of rapid forward and reverse intersystem-crossing between the emissive and the triplet state.

MO 18.4 Fri 11:45 N 25

**Quantum reaction control for quantum-limited biochemical magnetometers** — ●KYRIACOS VITALIS and IANNIS KOMINIS — University of Crete, Department of Physics, Heraklion 71003 Greece

Radical-ion-pair reactions have triggered the study of quantum effects in biological systems. Here we address radical-pair reactions from the perspective of quantum metrology. Since the coherent spin motion of radical-pairs is effected by an external magnetic field, these spin-dependent reactions essentially realize a biochemical magnetometer. Using the quantum Fisher information, we find the fundamental quantum limits to the magnetic sensitivity of radical-pair magnetometers. We then find that the usual measurement scheme of reaction yields approaches the fundamental limits to within an order of magnitude. Finally, we demonstrate that with a realistic quantum reaction control reminding of Ramsey interferometry, here presented as a quantum circuit involving the spin-exchange interaction and a recently proposed molecular switch, we can approach the fundamental quantum limit within a factor of 2. This work opens the application of well-advanced quantum metrology methods to biological systems.

MO 18.5 Fri 12:00 N 25

**Exploring Vibrational Dynamics of Anabaena Sensory Rhodopsin by Pump Impulsive Vibrational Spectroscopy** — ●PARTHA PRATIM ROY<sup>1</sup>, YOSHITAKA KATO<sup>2</sup>, HIDEKI KANDORI<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Physikalisch Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Germany — <sup>2</sup>Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Japan

Anabaena Sensory Rhodopsin is a microbial retinal protein (MRP), which converts the photon energy to chemical energy by a cis-trans isomerization. Like other MRPs, it shows fast isomerization kinetics (<200fs) but surprisingly low quantum yield. Until now, it is not very clear which specific vibrational mode in excited potential energy surface (PES) drives such a fast isomerization kinetics. In this work, pump-impulsive vibrational spectroscopy with time resolution <20fs is utilized to capture the vibrational dynamics in ground and excited state and disentangle them. Excitation pulse (sub-13 fs), resonant with the ground-state absorption of the chromophore, is used for this experiment. The push and probe pulse (15 fs) were made resonant to absorption of K-product of the isomer. This study captures the vibrational signature in low frequency up to 2000  $\text{cm}^{-1}$ . Strong ground state vibrational mode around 812, 1008 and 1539  $\text{cm}^{-1}$  was observed, which matches the spontaneous Raman spectrum of the molecule. Appearance of new vibrational modes around 900 and 1800  $\text{cm}^{-1}$  at certain push delay confirms their activity only in specific region of the excited state PES. This clearly shows the change of vibrational features from the FC-region to photoproduct region through the conical intersection.

MO 18.6 Fri 12:15 N 25

**Laser-induced acoustic desorption of large molecules for FEL experiments** — ●ZHIPENG HUANG<sup>1,2</sup>, DANIEL A. HORKE<sup>1,3</sup>, MATTHIAS SCHUST<sup>1</sup>, TIM OSSENBRÜGGEN<sup>1</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>Department of Physics, University of Hamburg — <sup>3</sup>Center for Ultrafast Imaging, University of Hamburg

Laser-induced acoustic desorption (LIAD) is a promising technique for gentle and efficient preparation of large intact neutral molecules into the gas-phase [1]. Here we demonstrate our newly set-up LIAD source, designed for prolonged measurement time, as required by FEL experiments, through automatic sample replenishment. Using a gas dynamic virtual nozzle we deposit a near-uniform layer of sample on a  $\sim 1$  m long, 10  $\mu\text{m}$  thick tantalum foil band. An acoustic wave was initiated by irradiating the backside of the foil with the third harmonic of a nanosecond Nd:YAG laser. The induced photoacoustic shock wave travels through the foil and desorbs samples into the gas-phase. A

stable neutral phenylalanine plume was prepared and characterized using strong-field ionization by an intense femtosecond laser field with a linear time of flight mass spectrometer. Spatial-temporal profiles, velocity distributions of the LIAD plume as a function of desorption laser intensity were investigated. Its potential for applications in x-ray or electron diffraction imaging will be discussed.

[1] B. Linder and U. Seydel, *Anal. Chem.* **57**, 895 (1985)

MO 18.7 Fri 12:30 N 25

**Momentum imaging of dissociative electron attachment in heterocyclic organic compounds** — •MARVIN WEYLAND<sup>1</sup>, ALEXANDER DORN<sup>1</sup>, XUEGUANG REN<sup>1</sup>, HANS RABUS<sup>2</sup>, and WOON YONG BAEK<sup>2</sup> — <sup>1</sup>Max Planck Institute for Nuclear Physics, Saupfercheckweg 1, 69117 Heidelberg, Germany — <sup>2</sup>Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Dissociative electron attachment (DEA) has been identified as a possible process for radiation damage. In short, DEA is a resonant two-step process in which first a low-energetic electron is captured by a molecule. The created negative ion can subsequently dissociate while the captured electron stays attached to one of the fragments. Detailed understanding of this reaction in biologically relevant molecules is crucial to improve its understanding. We investigated the heterocyclic organic compounds furan and pyridine as prototypes of typical organic molecules. Using a momentum imaging apparatus to detect the negative ions, we investigated the differential cross sections of several fragments after dissociation for each target molecule. From the resonance energy for formation of the fragment, combined with their kinetic energy and angular distributions, we can gain information about the dissociation process.

Our experimental results are compared to recent ab initio calculations with the goal to connect the dissociation process to specific electron scattering resonances in the target molecule.

MO 18.8 Fri 12:45 N 25

**Individual Control of Lifetime and Triplet Yield in Halogen-Substituted Coumarin Derivatives** — •KATRIN OBERHOFER<sup>1</sup>, MARTIN WÖRLE<sup>1</sup>, MIKAYEL MUSHEGHYAN<sup>1</sup>, SEBASTIAN WEGSCHEIDER<sup>1</sup>, ROSITSA NIKOLOVA<sup>2</sup>, REINHARD KIENBERGER<sup>1</sup>, and HRISTO IGLEV<sup>1</sup> — <sup>1</sup>Physik-Department, Technische Universität München, James-Frank-Str., 85748 Garching — <sup>2</sup>Faculty of Chemistry and Pharmacy, Sofia University, 1 J.Bourchier Blvd., 1126 Sofia, Bulgaria

Broadband transient absorption spectroscopy is utilized to examine lifetime and triplet yield in novel medicinally relevant Cl- and Br-substituted coumarin derivatives. Contradictory to the heavy-atom effect (HAE) absorption coefficient and fluorescent quantum yield for Cl-substituted compounds exhibit a strong enhancement. As DFT-calculations confirm several closely lying  $\pi\pi^*$  and  $n\pi^*$  states, we explain this behavior with an increased  $\pi\pi^*$  character of the lowest emitting state, which overcompensates the HAE. Femtosecond pump-probe spectroscopy reveals lifetimes of 100 ps for Cl-, 20 ps for Br- and 40 ps for unsubstituted compounds in acetonitrile. In order to get a quantity for the intersystem-crossing rate we determined the relative triplet yield by the ratio of triplet-triplet and excited singlet absorption after thermalization. While the lifetimes correlate qualitatively with fluorescence quantum yields, attributed to the  $\pi\pi^*$  increase, the triplet yield is significantly increasing with atomic weight of the substituted atom according to the HAE. Hence these two competing effects enable an independent control of lifetime and triplet yield.