

MO 15: Photochemistry II

Time: Wednesday 14:00–15:00

Location: F 142

MO 15.1 We 14:00 F 142

Vibrational dynamics of the OH stretching mode in aqueous hydrates — ●STANISLAV PANDELOV, JASPER WERHAHN, ALFRED LAUBEREAU, and HRISTO IGLEV — Physik-Department E11, Technische Universität München, D-85748 Garching, Germany

Solid hydrates of salts containing a fixed ratio of water molecules in their crystal structures have attracted special interest due to their importance in geology, chemistry, and physics. The quest for deciphering the properties of hydrogen bonds makes those materials ideal candidates for studying the spectral signatures of water in different, well-defined environments with varying bonding partners and distances. We report on the first time-resolved study of the OH stretching vibration in NaCl dihydrate with the use of two-color IR spectroscopy. The water molecules bound in the hydrate show two well separated absorption bands at 3426 cm^{-1} and 3541 cm^{-1} . The transient data display an ultrafast heating of the polycrystalline ice-hydrate samples after excitation of the OH stretching vibration and its transient relaxation. The relaxation time of the low-frequency OH stretching band in the NaCl hydrate is measured to be $6.8 \pm 1\text{ ps}$. The dynamics are significantly slower than those measured in neat water. This fact, together with the reproducible crystalline environment reveals the potential of aqueous hydrates for a systematic investigation of the OH stretching vibration in varying hydrogen bonding environments. An expansion of the investigation to other hydrates will offer new insights into the physics underlying the detection of hydrogen bonded systems via the OH group and should be pursued experimentally and theoretically.

MO 15.2 We 14:15 F 142

A Molecular Movie of Hemithioindigo Z/E-Isomerization — ●ARTUR NENOV, THORBEN CORDES, TEJA HERZOG, WOLFGANG ZINTH, and REGINA DE VIVIE-RIEDLE — Ludwig-Maximilians-Universität, München, Germany

Hemithioindigo (HTI) shows a photochromic behavior due to a photoinduced Z/E-isomerization on a picosecond timescale[1]. The fast switching speed, spectral characteristics and thermal stability makes it a promising candidate for a molecular switch[2]. As both isomers exhibit different spectroscopic properties the question arises how the photochemical behavior is influenced by the molecular structure. We present a quantum chemical study of the isomerization in gas phase at CASSCF level of theory, uncovering a complex excited state (ES) decay mechanism, mediated by a number of conical intersections (CoIns). Furthermore a manifold of energetically low lying CoIns forming a seam was optimized. We could relate the variety of CoIn structures and the characteristics of the reaction to the donating and withdrawing properties of the heteroatoms. MO analysis revealed that the driving force for the ES decay can be rationalized by charge separation and recombination as postulated in the theory of weakly and strongly heterosymmetric biradicaloids[3]. The complete both-way isomerization process could be reconstructed by combining theory and experiment.

[1] T. Cordes et al., Chem. Phys. Lett., 455, 197 (2006) [2] T.

Cordes et al., Chem. Phys. Lett., 428, 167, (2006) [3] J. Michl, V. Bonačić-Koutecký, In Electronic Aspects of Organic Photochemistry 1990, VCH: NY

MO 15.3 We 14:30 F 142

Methoxy benzyl alcohol interferes with its own oxidation: an ultrafast transient absorption study of flavin photocatalysis — ●MATTHIAS WENNINGER¹, UWE MEGERLE¹, ROBERT LECHNER², BURKHARD KÖNIG², and EBERHARD RIEDLE¹ — ¹Lehrstuhl für BioMolekulare Optik, LMU München — ²Institut für Organische Chemie, Universität Regensburg

Flavin is one of the most commonly used cofactors in nature where it acts as redox switch in many metabolic cycles. Flavin shows a strong optical absorption around 450 nm and therefore can be used as a photocatalyst, e.g., for the oxidation of methoxybenzyl alcohol (MBA). Using femtosecond broadband absorption spectroscopy we observe a rapid quenching of the excited singlet state of flavin in MBA via electron transfer (4 ps). By electron back transfer to the MBA (40 ps) the flavin returns to the electronic ground state. The S1 quenching competes with the intersystem crossing to the triplet state, which appears to be the reactive channel for the oxidation of MBA. A fast electron transfer therefore inhibits a high reaction quantum yield.

In acetonitrile solutions with low concentrations of flavine and MBA the quenching is slowed down significantly. The observed kinetics can be well fitted with a diffusion model: it accounts for the higher efficiency of MBA quenchers close to the excited flavin. Now the dynamics proceed on the 100 ps to ns timescale. This leads to a rising triplet formation with decreasing MBA concentration. In this way, understanding the ultrafast dynamics allows to determine the conditions for optimal photocatalysis.

MO 15.4 We 14:45 F 142

Single-molecule studies of photoswitchable chromophore complexes — ●MARTTI PÄRS¹, CHRISTIANE HOFMANN¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Universität Bayreuth, Lehrstuhl für Experimentalphysik IV, 95440 Bayreuth — ²Universität Bayreuth, Angewandte Funktionspolymere, 95440 Bayreuth

We investigate energy transfer dynamics in organic donor-switch-acceptor triad systems consisting of two perylenebisimide (PBI) units that are covalently linked by a dithienylcyclopentene photoswitch (DCP). The DCP behaves as a photoswitchable unit which modulates the energy transfer rate from BPI to DCP unit, because it acts as a fluorescence quencher in the closed form. In order to investigate the kinetics and the quantum yield of the switching process, we use a home-built wide-field imaging setup with multicolor excitations sources. This allows to control the state of the DCP unit and real-time detection of the BPI fluorescence from single triad complexes. Options for deliberate manipulation of the fluorescence intensity from individual molecules will be discussed.