

MO 21: Femtosecond Spectroscopy V

Time: Thursday 11:00–12:30

Location: F 102

MO 21.1 Thu 11:00 F 102

Just arrived and already gone: Tracking the ultrafast reaction of carbocations with femtosecond spectroscopy — ●ROLAND WILCKEN¹, JULIA BENEDIKTER¹, CHRISTIAN SAILER¹, HERBERT MAYR², and EBERHARD RIEDLE¹ — ¹LS für BioMolekulare Optik, LMU München — ²Department Chemie, LMU München

Biomolecular chemical reactions in solution are generally believed to be limited in their speed by the diffusive approach. We perform ultrafast measurements where a highly reactive carbocation is immersed in a solution of the nucleophilic reaction partner. In this way the diffusion limit can readily be surpassed. The carbocations are generated from selected benzhydryl chlorides by 30 fs UV pulses. The heterolytic bond cleavage takes 125 fs and is followed by a sp^3 to sp^2 hybridization within hundreds of fs. The signals of the intermediates are recorded by broadband femtosecond spectroscopy up to 2 ns with a 100 fs time resolution. In the reactive solvents the cation signal decreases rapidly on the sub-ps to 100 ps time scale. This is the direct signature of the chemical reaction.

We measure the reaction of carbocations with alcohols and amines to drive reaction times to the extreme. The reaction times decrease with the increasing reactivity of the carbocation and the nucleophile. In the alcohols times approximately down to the rotational diffusion time are found, still varying with the partners. For the amines the selectivity decreases and the times are well below the rotational time, as low as 250 fs. These are the fastest bimolecular reactions of reactive ground state species ever reported.

MO 21.2 Thu 11:15 F 102

Molecular wave packets decelerated by solvent environment: The dynamic continuum ansatz — ●SEBASTIAN THALLMAIR^{1,2}, MARKUS KOWALEWSKI¹, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

Most reactions in organic as well as biochemistry take place in solution. Electrostatic solvent effects are known to change the reactivity of the solute dramatically. The same holds for photochemical reactions where often dissociative processes are included. Here not only the electrostatic influence but also the dynamic impact of the solvent becomes important. For bulky leaving groups, like in phosphonium salts, the solvent cage substantially decelerates the photogenerated fragments depending on the viscosity of the solvent. Subsequent distance dependent processes like electron or energy transfer between the photofragments become feasible as the fragments are kept at a reasonable distance.

Also on the shorter time scale below 200 fs frictional deceleration is essential. The molecular system gets the chance to deposit energy into motions additional to the primary dissociation coordinate. Thereby regions decisive for the branching into competing product channels can be reached.

We present a new dynamic continuum ansatz to describe the frictional force exerted on moving wave packets in a solvent cage. The frictional deceleration is treated in the quantum mechanical formalism including the dynamic viscosity and Stokes' law. The solvent interferes on the fs time scale, but decides the reaction outcome.

MO 21.3 Thu 11:30 F 102

Dephasing Dynamics of Hydrogen Bonded CH-Modes in Ionic Liquids from Ultrafast CARS Spectroscopy — ●SUSANA CHATZIPAPADOPOULOS¹, MATTHIAS LÜTGENS¹, FRANK FRIEDRISZIK¹, CHRISTIAN ROTH², DANIELA KERLÉ², RALF LUDWIG², OLIVER KÜHN¹, and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, 18051 Rostock — ²Institut für Chemie, Universität Rostock, 18051 Rostock

Currently ionic liquids (ILs) receive increasing attention as new types of solvents. To understand their unique physico-chemical properties the intermolecular forces and especially hydrogen bonds have to be investigated. Therefore we applied multiplex ultrafast coherent anti-Stokes Raman scattering (CARS) to reveal hydrogen bonds formed by CH groups of the cations with anions and to study the dynamics of the system. Multiplex CARS combines broadband excitation with narrowband probing resulting in simultaneous high spectral and temporal resolution. Recently, we approached the question of the contro-

versially discussed existence of hydrogen bonds in ILs by Raman, IR, and CARS spectroscopy and showed that hydrogen bonding appears in imidazolium based ILs [1].

Here, we present new studies on vibrational dephasing processes of the ring CH modes, which are involved in hydrogen bonding. From the decay of the CARS signatures and the simulation of the full CARS response the dephasing times are extracted providing information about the fluctuations of the hydrogen bond network.

[1] C. Roth et al., *New J. Physics* **14** (2012), 105026.

MO 21.4 Thu 11:45 F 102

Ultrafast reversible switching dynamics and solvation shell rearrangements of a photo-switchable catalyst tracked from femto to nanoseconds. — ●MANUEL PESCHER¹, LUUK VAN WILDEREN¹, SUSANNE GRUETZNER², STEFAN HECHT², and JENS BREDENBECK¹ — ¹Johann Wolfgang Goethe-Universität, Institut für Biophysik, Frankfurt am Main — ²Humboldt-Universität zu Berlin, Institut für Chemie, Berlin

Photoswitchable catalysts offer means for ultrafast temporal and microscopic control of chemical processes. Here we characterize the behaviour of an azobenzene-based ultrafast photo-switchable catalyst ("Azokat") in an environment of substrate molecules potentially forming H-bonds to the catalytically active site. After optical activation of the catalyst (developed by Stoll et al. [1]) by a 700 fs laser pulse in the visible, the reversible isomerisation of Azokat to its on/off states can be tracked by infrared probe pulses spectrally spanning 200/cm. We measure characteristic eigenvibrations of the system in a regime from 1500/cm up to 3700/cm. This approach resolves the isomerisation and concomitant state-selective binding of hydrogen bond partners and their dynamics, leading to a kinetic model from the femtosecond to nanosecond regime: We observe ultrafast isomerisation of Azokat, leading to chemical activity on a sub-picosecond time scale, subsequent breaking and formation of hydrogen bonds between substrate molecules and the catalyst and finally exchange between species of free and clustered substrate molecules forming hydrogen bonds with each other. [1] Stoll et al, *JACS*, 131(1):357-67, January 2009.

MO 21.5 Thu 12:00 F 102

Combined Marcus-Smoluchowski model for electron transfer from photo-generated benzhydryl to chlorine radical — ●SEBASTIAN THALLMAIR^{1,2}, CHRISTIAN F. SAILER², BENJAMIN P. FINGERHUT¹, EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, LMU München — ²LS für BioMolekulare Optik, LMU München

The precise mechanism and dynamics of the photo-generation of carbocations and carbon radicals is a fundamental issue in organic chemistry. The role and importance of electron transfer (ET) subsequent to homolytic bond cleavage of benzhydryl chloride that leads to the formation of carbocations is discussed. We combine a distance dependent ET model given by Marcus theory with the Smoluchowski diffusion model. It is based on a hard sphere model starting at contact distance. We consider time dependent population distributions for the radical pairs and the ion pairs and include the radial distribution function of the solvent as well as the Coulomb interaction for the ion pairs in the inter pair potentials. Geminate recombination, ET, diffusion and full solvent stabilization due to the formation of a complete solvent shell are included in terms of distant dependent rates. A close accord with the experiment can only be reached if a broad distance distribution of the nascent radical pairs is assumed. The fast depletion of the radical pair distribution at small distances leads to the observed non-single exponential ET dynamics. Our results demonstrate that traditional descriptions of reaction mechanisms based on the concept of contact and solvent-separated pairs have to be reassessed.

MO 21.6 Thu 12:15 F 102

Transient spin states in the ultrafast relaxation of met-Myoglobin — ●CRISTINA CONSANI^{1,2}, OLIVIER BRÄM¹, GERARD AUBÖCK¹, FRANK VAN MOURIK¹, and MAJED CHERGUI¹ — ¹Laboratory of Ultrafast Spectroscopy, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland — ²currently at: LS Physikalische Chemie I, IPTC Universität Würzburg, Germany

Myoglobin (Mb) is a small protein consisting of a single polypeptide

chain and an iron porphyrin (haem), which is its active site. The central Fe can be found in ferrous (Fe(II)) or ferric (Fe(III)) redox states and bind a variety of small molecules, among them water (met Mb). Despite being one of the most studied proteins, the early haem relaxation pathways following photo-excitation are still subject to controversies. During the last decade, similarities among the ultrafast (UF) transients of different ligated forms of Mb lead to the idea that the haem relaxation is dominated by cooling and is independent of the Fe redox state, of the axial ligand, and of its eventual photo-induced

detachment.

Here we present the successful combination of broadband UF fluorescence and transient absorption experiments with a target analysis, which revealed a branching in the ultrafast relaxation of the haem. A significant fraction of the excited state population (about 40%) is found to relax through a cascade pathway involving two transient states, which we assign to electronically excited configurations of the iron characterized by different spin states. The potential of this approach for the study of porphyrin based systems will also be discussed.