

MO 3: Ultrafast Processes in Solution

Time: Monday 10:30–12:30

Location: S HS 001 Biologie

Invited Talk

MO 3.1 Mon 10:30 S HS 001 Biologie
Solvent-Specific Facets in the Ultrafast Photochemistry of Reactive Intermediates — JOHANNES KNORR¹, PANDIAN SOKKAR², SVENJA WORTMANN¹, PAOLO COSTA³, NIKLAS GESSNER¹, JULIEN ROWEN³, WOLFRAM SANDER³, ELSA SANCHEZ-GARCIA², and •PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Computational Biochemistry, Universität Duisburg-Essen, 45141 Essen — ³Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum

Organic diazo compounds can release a nitrogen molecule upon photoexcitation, yielding very reactive species that will further pursue different reaction pathways on an ultrafast time scale. Among those pathways are rearrangement, intersystem crossing, intermolecular proton uptake, or complexation with a solvent molecule, giving rise to variable product distributions. The underlying processes strongly depend on the solvent environment and are accompanied by processes like solvation, vibrational cooling, and ion separation.

We will present an overview of recent femtosecond studies on diazo precursors excited in protic and aprotic solvents as well as in binary solvent mixtures. In combination with multiscale molecular dynamics simulations, we elucidate the reactivity of nascent intermediate carbenes and carbocations and the remarkable sensitivity to hydrogen-bonding among adjacent solvent molecules which take the role of key abettors rather than bystanders for the fate of the reactive intermediate. Variation of solvent mixing ratios thus provides a means to control the time scales and also the pursued pathways of the reaction.

MO 3.2 Mon 11:00 S HS 001 Biologie
Spectroscopic signatures of the dynamical hydration shell formation — •HENNING KIRCHBERG¹, PETER NALBACH², and MICHAEL THORWART¹ — ¹Universität Hamburg, I. Institut für Theoretische Physik, Jungiusstr. 9, 20355 Hamburg — ²Westfälische Hochschule, Münsterstr. 265, 46397 Bocholt

The hydration shell, a specific formed water molecule network with hydrogen bonds near a solute, strongly influences the energetic and electronic properties of the solute and its (non-) solubility in a polar environment. The dynamical formation of a hydration shell is a process of central interest in many physical and chemical systems. We generalize the Onsager model of a static spherical cavity with a point dipole placed in a dielectric continuum solvent towards a dynamically varying Onsager sphere. In particular, we assume a dynamical growing layer of water around the central sphere. We calculate the response of the central molecular dipole to an external electric field in the presence of the dynamically growing layer. By this, we determine the energy cost for the solvation shell formation, which is responsible for the low solubility of hydrophobic agents in water. We find a frequency upshift in the absorptive part of the response. Moreover, we are able to connect time-dependent spectroscopy signatures, i.e. the line width of the absorption spectrum, to dynamical time scales of the hydration shell formation and to the characteristic fluctuations of the structured water within the hydration shell.

MO 3.3 Mon 11:15 S HS 001 Biologie
Broadband Ultrafast Transient Absorption Spectroscopy of Triplet Phenylpentadienylidene and Diphenylpropynylidene — •LEA RESS, ENGELBERT REUSCH, HANS-CHRISTIAN SCHMITT, INGO FISCHER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The chemical and physical properties of unsaturated carbon-rich chain molecules like phenylpentadienylidene (PhC₅H) and diphenylpropynylidene (PhC₃Ph) are of significance in research areas such as astrochemistry and combustion processes, wherein biradical or rather carbenic structures and their electronic characteristics play an important role. Those molecules were previously generated by photolysis and characterized by matrix isolated EPR, IR and UV/Vis spectroscopy [1],[2]. Their precursors (5-diazopenta-1,3-dien-1-yl)benzene (PhC₅N₂H) and (3-diazoprop-1-yn-1,3-diyl)dibenzene (PhC₃N₂Ph) have not been characterized via ultrafast transient absorption spectroscopy in liquid phase at room temperature. In this contribution, we investigate the photolysis of the diazo group with ultrashort laser pulses by excitation at 260 nm to generate triplet PhC₅H and PhC₃Ph.

We study the ultrafast photochemistry of these triplet species in dichloromethane and ethanol as aprotic and protic solvents, respectively, and further discuss reaction pathways and ultrafast dynamics up to three nanoseconds within these solvents.

- [1] S. N. Knezz et al., *J. Am. Chem. Soc.*, **138**, 12596-12604 (2016)
 [2] P. S. Thomas et al., *J. Org. Chem.*, **75**, 6372-6381 (2010)

MO 3.4 Mon 11:30 S HS 001 Biologie
Microsolvation vs. Acid Dissociation at 0.4 K: Sequence Matters — •DEVENDRA MANI¹, RICARDO PÉREZ DE TUDELA², RAFAEL SCHWAN¹, NITISH PAL¹, SASKIA KÖRNING², HARALD FORBERT², BRITTA REDLICH³, LEX VAN DER MEER³, GERHARD SCHWAAB¹, DOMINIK MARX², and MARTINA HAVENITH¹ — ¹Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, 44801 Bochum, Germany. — ²Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany. — ³FELIX laboratory, Institute for Molecules and Materials, Radboud University, 6325 ED Nijmegen, The Netherlands.

Acid dissociation in the aqueous medium is of fundamental importance. In order to understand the fundamental steps of this reaction, many experimental and theoretical studies have been carried out on small HCl-H₂O clusters, in the past.[1-3]

We have studied the dissociation of HCl on stepwise addition of H₂O molecules, in helium droplets. Ultrabright pulsed-free electron lasers, at FELIX laboratory in Nijmegen, were used to measure the umbrella motion of the H₃O⁺ moiety of the dissociated H₃O⁺(H₂O)₃Cl⁻ cluster, in the frequency range of 1000-1700 cm⁻¹. Our experiments along with high-level ab initio MD simulations show that the dissociation of HCl is highly specific of the sequence in which molecular aggregation takes place. Details will be presented in the talk.

References: 1. H. Forbert, et al. *J. Am. Chem. Soc.*, 2011, **133**, 4062-4072. 2. A. Gutberlet et al., 2009, **324**, 1545-1548. 3. J. S. Mancini and J. M. Bowman, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6222-6226.

MO 3.5 Mon 11:45 S HS 001 Biologie
Solvent-dependent time-resolved photoelectron spectroscopy study of relaxation dynamics in Quinoline Yellow — •EVGENII IKONNIKOV, JOHAN HUMMERT, and OLEG KORNILOV — Max-Born-Institute, Max-Born-Strasse 2A, Berlin, Germany

Relaxation dynamics of molecules often depends on their environment. In water, next to intramolecular relaxation processes, additional processes like solvent rearrangement and proton transfer upon photon absorption are possible. Recently we demonstrated pump-probe photoelectron spectroscopy in solution, which is a powerful tool for obtaining binding energies and lifetimes of molecular excited states of solvated molecules [1]. In our experiments we use a short XUV pulse as a probe pulse and 800/400 nm pulse as a pump pulse with pulse duration of 30 fs. In this contribution we will present measurements of relaxation dynamics of Quinoline Yellow (QY) in different solvents. In Ref. [1] we studied QY in water and observed three relaxation times: 250 ± 70 fs, 1.3 ± 0.4 ps and 90 ± 20 ps. We proposed that the two latter timescales may represent intramolecular proton transfer, while the fast timescale corresponds to solvent rearrangement. To clarify the nature of these processes we measure relaxation dynamics of QY in water with pH=9 and in heavy water to investigate the role of intermolecular proton transfer processes, which are expected to be slower for D₂O. [1] J. Hummert, G. Reitsma, N. Mayer, E. Ikonnikov, M. Eckstein and O. Kornilov, *J. Phys. Chem. Lett.*, 6649-6655, 9 (22), 2018.

MO 3.6 Mon 12:00 S HS 001 Biologie
(Time-resolved) Photoelectron circular dichroism in solution — JANINA LEBENDIG-KUHLA, PASCAL ENGL, HANS-HERMANN RITZE, and •ANDREA LÜBCKE — Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born Strasse 2A, 12489 Berlin

Chiral systems play a very important role in nature, in particular in biology. Among the most widely spread chiral systems are DNA, amino acids, sugars, and peptides. We will investigate the role of chirality for the function of those molecules by the newly developed technique of (time-resolved) photoelectron circular dichroism in solution and provide new insights into the excited state dynamics of chiral systems. First results are presented for the model system fenchone, for trypto-

phan and a DNA nucleotide.

MO 3.7 Mon 12:15 S HS 001 Biologie

Experimental traces for ultrafast halogen-bond breaking in solution — •BASTIAN GEISSLER¹, CHRISTIN PFLIEGER¹, CLAUDIO BEAKOVIC¹, ELMERIC ENGELAGE², STEFAN HUBER², and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Organische Chemie I, Ruhr-Universität Bochum, 44780 Bochum

Non-covalent halogen bonds between an iodine substituted organic compound and a Lewis base can play key roles in various chemical and biological processes. For instance, halogen bonds are already commonly used for crystal engineering. In the liquid phase, deciphering

and exploiting the complex behavior of halogen bonds between solutes is an emerging area of research, still mostly focused on organic synthesis, catalysis, supramolecular self-assembly or molecular recognition processes.

In this study, we address the photophysical properties of compounds capable of halogen bonding by employing ultrafast time-resolved fluorescence upconversion and transient absorption techniques. Benzoimidazole derivatives serve as halogen bond donors and pyridine derivatives as Lewis base acceptors. Absorption studies suggest the existence of iodine halogen bonds in acetonitrile solution, indicative of a modified charge distribution along the halogen bond which is only observable in the presence of the donor-acceptor pair. Upon excitation, signals assigned to the halogen bond rapidly disappear, suggesting that the halogen bond breaks reversibly within a few picoseconds.