

MO 9: Femtosecond Spectroscopy II

Time: Tuesday 10:30–13:00

Location: TOE 317

Invited Talk

MO 9.1 Tue 10:30 TOE 317

Transient generation of carbonic acid in the context of the aqueous chemistry of carbon dioxide — KATRIN ADAMCZYK¹, MIRABELLE PRÉMONT-SCHWARZ¹, DINA PINES², EHUD PINES², and •ERIK T. J. NIBBERING¹ — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — ²Ben Gurion University of the Negev, P.O. Box 653, Beer-sheva 84105, Israel

We have generated carbonic acid, for a long time a species of elusive nature, in aqueous solution by ultrafast protonation of bicarbonate. We follow the reaction dynamics upon photoexcitation of a photoacid by monitoring infrared-active marker modes with femtosecond time resolution. We directly obtain the on-contact proton transfer rate to bicarbonate previously inaccessible when using indirect methods. Our experimental results suggest new approaches for the elucidation of the chemical reaction dynamics of aqueous carbon dioxide under conditions relevant for biophysiology, biogeochemistry, the regulation and evolution of the climate on Earth as well as in the design of large scale carbon sequestration projects.

MO 9.2 Tue 11:00 TOE 317

Transient UV/IR Spectroscopy of Hydrogen Bonded Photoacid Molecules — •MIRABELLE PRÉMONT-SCHWARZ¹, DINA PINES², EHUD PINES², and ERIK T. J. NIBBERING¹ — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie Max Born str 2A 12489 Berlin — ²Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84125, Israel

Photoacids are organic molecules which experience a significant decrease in pKa upon electronic excitation, thereby making them much stronger acids in the excited state than in the ground state. This property has been greatly exploited in the last decades permitting dynamical proton transfer and hydrogen bonding research on femtosecond timescales. While their use is now quite well established, the photo-physics leading to this drastic change in pKa remain unclear. In this study, transient UV pump/ IR probe spectroscopy is used in order to monitor the hydrogen stretching oscillator of 2-Naphthol, a prototype photoacid. The OH stretch provides insight into the nature of the electronic redistribution in the molecule as it is a very sensitive probe for hydrogen bonding and given that it is the local probe of the acidic bond. By looking at a series of solvents with different hydrogen bonding strengths as well as ternary systems, one is able to conclude about the importance of an already existing HB in the ground state as well as the relative contribution of dielectric vs specific interactions.

MO 9.3 Tue 11:15 TOE 317

Vibrational energy flow in artificial amino acids investigated by 2D-IR spectroscopy — •HENRIKE MÜLLER-WERKMEISTER¹, YUN-LIANG LI¹, ELIZA-BETH W. LERCH¹, ANDREAS T. MESSMER¹, DAMIEN BIGOURD^{1,2}, SILVIA EGER³, ANDREAS MARX³, and JENS BREDEBECK¹ — ¹Institute for Biophysics, Goethe-University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt — ²Commissariat à l'énergie atomique, Centre d'études scientifiques et techniques d'Aquitaine, Le Barp, France — ³Institute for Organic Chemistry, University Konstanz, 78457 Konstanz

The unique combination of recent protein engineering methods with ultrafast 2D-IR spectroscopy shows great promise for the investigation of biomolecular dynamics on picosecond timescales. Site-selective, in vivo incorporation of artificial amino acids, absorbing in IR spectral regions well-separated from other protein vibrations will allow for the direct observation of energy flow in real-time. Here, we investigate the spectral properties of azido- and nitrile-labeled amino acids. Two-colour 2D-IR spectroscopy is shown to permit direct determination of energy transfer times between different functional groups in these artificial amino acids. The simultaneous use of two, independently tunable, optical parametric amplifiers for IR-light generation enables us to observe time-dependent cross peaks between vibrations widely separated in the spectrum. A clear correlation between energy transfer time and distance between functional groups is observed. Thus 2C-2D-IR provides information to support the assignment of vibrational absorption bands. Additional DFT-calculations prove the experimental results.

MO 9.4 Tue 11:30 TOE 317

Ultrafast Structural Dynamics in Hydrogen-Bonded Liquids from Coherent Multidimensional Infrared Spectroscopy of Vibrational Excitons — •ALEXANDER PAARMANN^{1,2} and R. J. DWAYNE MILLER^{1,3} — ¹Departments of Chemistry and Physics, University of Toronto, Canada — ²Fritz-Haber Institute of the MPG, Berlin, Germany — ³Max Planck Research Group for Atomically Resolved Dynamics, Department of Physics, University of Hamburg, the Centre for Free Electron Laser Science/DESY, Germany

Coherent two-dimensional infrared (2DIR) spectroscopy is a powerful new method to study temporal as well as spatial correlations in hydrogen-bond networks. We present experimental and theoretical studies of the 2DIR response of two hydrogen-bonded liquids: water and formamide. For liquid water, temperature dependence of the 2DIR spectra revealed strong spatial correlations close to the freezing point, where the OH-stretching vibrations show significant spatial delocalization [1]. The 2DIR response from the more structured formamide exhibits a quite different behavior, being sensitive to time-averaged dipole arrangements and vibrational energy transfer dynamics within the H-bond network. These results are supported by theoretical calculations of the 2DIR spectra [2].

[1] D. Kraemer, M. L. Cowan, A. Paarmann, N. Huse, E. T. J. Nibbering, T. Elsaesser, and R. J. Dwayne Miller, Proc. Natl. Acad. Sci. USA 2008 105: 437-442

[2] A. Paarmann, T. Hayashi, S. Mukamel, R. J. D. Miller, J. Chem. Phys. 2008 128: 191103

MO 9.5 Tue 11:45 TOE 317

Ultrafast Dynamics of N-H Stretching Excitations of Guanosine-Cytidine Base Pairs in Solution — •MING YANG¹, ŁUKASZ SZYC¹, KATHARINA RÖTTGER², HENK FIDDER¹, ERIK T. J. NIBBERING¹, THOMAS ELSAESSER¹, and FRIEDRICH TEMPS² — ¹Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Str. 2A, 12489 Berlin, Germany — ²Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Germany

In DNA hydrogen bonds (h-bonds) between the nucleobases play a key role. We study the N-H stretching vibrations of h-bonded guanosine-cytidine (GC) base pairs in chloroform solution with linear and ultrafast nonlinear infrared (IR) spectroscopy. We assign the IR-active transitions by combining structural information on the h-bonds in the GC pairs with literature on DFT calculations, and empirical relations connecting frequency shifts and intensities of the IR-active vibrations. We adopt a model of local five N-H stretching vibrations, describing motions of free NH groups of G and C, and h-bonded NH groups between G and C, to interpret the femtosecond two-dimensional (2D) photon echo and pump-probe measurements in terms of couplings and relaxation dynamics. The free N-H stretching vibrations of G and C have a population lifetime of 2.4 ps. Besides a vibrational population lifetime shortening to subpicosecond values observed for the h-bonded N-H stretching vibrations, the 2D spectra reveal vibrational excitation transfer from the 3303 cm⁻¹ G(NH₂) to the 3145 cm⁻¹ G(N-H...N) and C(NH₂) modes on a time scale of 1 ps.

MO 9.6 Tue 12:00 TOE 317

Non-statistical molecular dynamics: wavepacket bond cleavage — •NILS KREBS¹, CHRISTIAN F. SAILER¹, BENJAMIN P. FINGERHUT², REGINA DE VIVIE-RIEDLE², and EBERHARD RIEDLE¹ — ¹Lehrstuhl für BioMolekulare Optik, LMU München — ²Department Chemie, LMU München

After 270 nm excitation diphenylmethyl chloride (DPMC) dissociates into a benzhydryl cation and a chlorine anion (heterolysis) or into a radical pair (homolysis). DPMC and the products are spectrally well separated and therefore the dynamics can be recorded with 40 fs resolution in a two-color transient absorption measurement in a liquid jet. We find the appearance of the radical signal at 330 nm to be delayed by about 80 fs with respect to the optical excitation. Ab-initio calculations show that this non-rate behavior is due to wavepacket motion in the Franck-Condon region and its subsequent evolution along the dissociation coordinate through a conical intersection [1]. The transient signal then increases within 300 fs due to the planarization of the DPMC radical, the quasi-exponential signal increase is not due to a statistical behavior of the dissociation process. Measurements at 430 nm show

that the cation appears with a delay of 125 fs. This means that the nascent radical and cation populations evolve from different conical intersections and follow differing bond cleavage pathways. The combination of the time resolved experiment and ab-initio dynamics render a first complete description of the bond cleavage on the atomistic level.

[1] B. P. Fingerhut, D. Geppert, and R. de Vivie-Riedle, *Chem. Phys.* **343**, 329 (2008).

MO 9.7 Tue 12:15 TOE 317

Dependence of the ultrafast initial dynamics of carotenoids on the conjugation length (N) studied by multidimensional spectroscopy — •MARIE S. MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany.

Determination of the detailed energy dissipation pathway in carotenoids following photoexcitation proved to be particularly challenging for optical spectroscopy. Specifically the question whether additional dark states between the well known S_2 and S_1 states participate in the relaxation is highly controversial. Application of pump-degenerate four wave mixing (pump-DFWM) to β -carotene and lycopene in combination with numerical simulations based on the Brownian oscillator model already gave strong evidence for an additional electronic state located energetically below S_2 and playing a role in the deactivation process. Here, we further investigate the interplay between the conjugation length N of carotenoids and the involved electronic states in the very early dynamics by using DFWM and pump-DFWM. We concentrate on carotenoids with $N = 10$ (spheroidene) and 11 (lycopene), for which a crossing of the S_2 state with dark states is proposed. Raman active modes in spheroidene and lycopene differ on the dependence of their amplitude and frequency on the population relaxation. For spheroidene, high-frequency Raman active modes are present directly after the excitation of S_2 and show almost no dependence on the population relaxation. This is in contrast to lycopene, where state specific modes can be identified.

MO 9.8 Tue 12:30 TOE 317

Excited state vibrational coherence dynamics of all-trans retinal protonated Schiff-bases investigated with (Pump-)DFWM — •JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The retinal chromophore performs as a key-element in various biolog-

ical mechanisms such as vision or bacterial photosynthesis. Photon-absorption induces an ultrafast double-bond isomerization, the decisive steps of which still remain to be understood to date. Special attention has recently been attracted by excited state low-frequency vibrational coherences[1]. Particularly, the understanding of their impact on the isomerization and their mechanism of induction are expected to pave the way for a complete understanding of the dynamics. Using Pump Degenerate Four-Wave-Mixing (Pump DFWM)[2], we show that such coherences are activated through coherent internal vibrational energy redistribution. This process requires only low excess photon energy for excitation, contrasting previous assertions[1]. Pump DFWM also reveals that, besides their strongly damped time-evolution, excited state coherences can only be observed in a narrow time window after excitation. The results are discussed in terms of a relaxation model comprising contributions from two close-lying excited electronic states.

[1] G. Zgrablic, S. Haacke, and M. Chergui, *Chemical Physics* **338**, 168 (2007)

[2] J. Hauer, T. Buckup, and M. Motzkus, *Journal of Physical Chemistry A* **111**, 10517 (2007)

MO 9.9 Tue 12:45 TOE 317

Fs time-resolved photoelectron spectroscopy of solvated electrons — •FRANZISKA BUCHNER, ANDREA LÜBCKE, THOMAS SCHULTZ, and INGOLF-VOLKER HERTEL — Max-Born-Institut, Max-Born-Straße 2A, 12489 Berlin

Solvated electrons are potent reagents and have been studied for decades. However, they still ask us riddles.

We combined fs time-resolved photoelectron spectroscopy with a liquid jet of aqueous sodium iodide solution to study energetics and dynamics of solvated electrons. These are generated by ultrafast photodetachment from iodide anions with a 6.20 eV laser pulse. The temporal evolution of these solvated electrons are probed by a delayed 4.65 eV laser pulse. At early delay times, we find two distinct populations of solvated electrons: those that are instantaneously strongly bound ("cold") and a fraction of initially weakly bound ("hot") electrons. We observe thermalization of the "hot" electrons which transform into "cold" electrons on the timescale of about 1 ps and geminate recombination with the iodide radical.

We will further present and discuss concentration-dependent photoelectron spectra and the influence of the counter ion on energetics and dynamics of the species involved. Our results point towards a high surface sensitivity and we will draw conclusions on the existence of surface-bound solvated electrons in aqueous solutions.