

MO 19: Femtosecond Spectroscopy 2

Time: Thursday 16:30–18:15

Location: BEBEL HS213

MO 19.1 Thu 16:30 BEBEL HS213

Ultrafast emission quenching in perylene diimides by structure rearrangement induced electron transfer — ●PATRICK KÖLLE¹, IGOR PUGLIESI², ARTUR NENOV¹, HEINZ LANGHALS¹, EBERHARD RIEDLE², and REGINA DE VIVIE-RIEDLE¹ — ¹LMU München, Department Chemie, München, Germany — ²LMU München, LS BioMolekulare Optik, München, Germany

Perylene dyes have attracted great interest for the design of intramolecular energy and charge transfer systems. The influence of substitution of two fluorescent perylene diimides on the ultrafast intramolecular dynamics leading to efficient fluorescence quenching are investigated by transient spectroscopy and quantum chemical calculations. The fluorescent systems show no dynamics in the sub-nanosecond time region. For the first, the amino-functionalized molecule the stimulated emission signal decays rapidly on a sub-picosecond timescale, while the excited state absorption decreases with a time constant of several picoseconds. The theoretical analysis assigns the fast decay of the emission to a charge transfer from the amino substituent to the perylene diimide chromophore. Experiments and theoretical PCM calculations in different solvents demonstrate that the dynamics of this fluorescence quenching correlate with the solvation time. For the second, the phenyl-functionalized perylene diimide a similar charge transfer emission quenching mechanism is observed. An efficient and fast fluorescence quenching still occurs but in comparison with the amino-functionalized molecule the lifetime of the charge separation is increased by more than a factor of ten.

MO 19.2 Thu 16:45 BEBEL HS213

Quantum dynamical studies of diphenylmethylchloride including geometry relaxation and a three-state conical intersection seam — ●MATTHIAS K. ROOS, SEBASTIAN THALLMAIR, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

Reactive species like carbocations and -radicals are ubiquitous in organic synthesis. A convenient precursor for such intermediates is diphenylmethylchloride that is undergoing a carbon-chlorine bond cleavage after laser irradiation. We are using quantum chemical and quantum dynamical methods to evaluate the branching ratio between product pathways through consecutive conical intersections for this sub-picosecond ultrafast dissociation reaction. We present a new reduced coordinate space to describe the reaction using the Wilson G matrix approach for the kinetic Hamiltonian. With this method we can use combined internal coordinates that particularly account for all relaxation in the molecule during the dissociation process.

Resulting 1D and 2D potential energy surfaces on the ONIOM(CASSCF(12,10)/B3LYP) level of theory are presented and compared with respect to the approximation applied. Especially the influence of the chlorine lone pairs is discussed that have a significant impact on the dissociation dynamics through a prominent three-state conical intersection seam in the Franck-Condon region. The shape of the G matrix elements can be traced back to the relaxation included in the chosen coordinates. Dynamical results taking into account all relevant conical intersections are presented.

MO 19.3 Thu 17:00 BEBEL HS213

H-bond analysis of acetic acid by spontaneous and coherent Raman spectroscopy — ●MATTHIAS LÜTGENS, FRANK FRIEDRISZIK, SUSANA CHATZIPAPADOPOULOS, and STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, 18055 Rostock

The formation of hydrogen bonds leads in many liquids to the appearance of molecular complexes and greatly affects their macroscopic properties. The structural motives of acetic acid (AA) are still under intense investigation, since AA has multiple H-bond donor and acceptor sites allowing for several configurations. The H-bonded complexes are investigated by comparing spontaneous Raman and coherent anti-Stokes Raman scattering (CARS) spectra of the C=O vibration. The spontaneous Raman spectrum shows three distinct features but cannot clearly decide if a fourth mode is contributing or not. CARS measurements with coherent excitation of the C=O band via a femtosecond Stokes and a narrowband Raman pump pulse followed by a narrowband probe pulse in the ps range can discriminate slow dephasing modes from faster dephasing vibrational contributions.[1] They reveal

an additional mode hidden under the dominating broad Raman band proving the coexistence of more than one H-bonded configuration in liquid AA.

[1] M. Lütgens, S. Chatzipapadopoulos, and S. Lochbrunner, *Opt. Express* 20, 6478-6487 (2012)

MO 19.4 Thu 17:15 BEBEL HS213

Excited-State Dynamics of the 2-Methylallyl Radical — ●JÖRG HERTERICH, THIEMO GERBICH, and INGO FISCHER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg

The excited-state dynamics of hydrocarbon radicals is not well understood and only a few species have been studied. In many radicals, the electronically excited states are short-lived due to rapid internal conversion (IC). This fast deactivation can be used to prepare internally hot radicals for further studies of their unimolecular reactions. The excited-state dynamics of the 2-methylallyl radical are studied by time-resolved photoionization. The radical, which is relevant for combustion processes, is generated by pyrolysis from the corresponding bromide. The lifetime of the electronically excited B state was measured to be 14 ps and shorter.

MO 19.5 Thu 17:30 BEBEL HS213

Photodynamics and structure of a 1-methylthymine self-pair mediated by a silver trimer — ●YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, GEREON NIEDNER-SCHATTEBURG¹, and WIM KLOPPER² — ¹TU Kaiserslautern, FB Chemie und Forschungszentrum OPTIMAS, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern — ²Karlsruher Institut für Technologie (KIT), Institut für Physikalische Chemie, Fritz-Haber-Weg 2, 76131 Karlsruhe

A cationic self-pair of deprotonated 1-methylthymine (1MT-H) mediated by a unique linear arrangement of three silver ions, [(Ag)₃(1MT-H)₂]⁺, was obtained by electrospray ionization from a methanolic solution and investigated in an ion trap at ca. 305 K by laser spectroscopy. Structure and photodynamics of the MBP was explored using IR multiple photon dissociation, femtosecond transient photo-fragmentation (PF) and ab initio calculations at the CC2 level of theory. Two time constants, 0.16(12) ps and 1.0(3) ps, are obtained from fitting of the 283 nm pump - 700 nm probe transient PF spectrum. The picosecond component is several times faster than in the thymine monomer, indicating an acceleration of the electronic relaxation induced by the metal coordination. Electronic relaxation pathways via LMCT or metal centered singlet excited states are discussed.

MO 19.6 Thu 17:45 BEBEL HS213

Pyrene: A textbook paradigm for excimer formation with some surprises — ●BASTIAN BAUDISCH, MARIO MASETTO, IGOR PUGLIESI, and EBERHARD RIEDLE — LS für BioMolekulare Optik, LMU München

Pyrene is the textbook example for excimers and their formation. It relies largely on nanosecond fluorescence measurements by Birks in the 60s [1]. After excitation 370-425 nm fluorescence occurs out of the S₁ state. Due to the long S₁ life time the excited pyrene molecules diffusively encounter ground state pyrenes and form excimers which give rise to red shifted fluorescence around 475 nm. We have investigated pyrene with extended pump-probe capabilities [2]. After 334 nm excitation into the S₂ state, we observe 85 fs relaxation to the S₁ state. In the subsequent dynamics an approximate doubling of the GSB in 6.6 ps occurs. In the ps and ns regime we observe clear signatures of anionic and cationic pyrene. Contrary to the commonly accepted mechanism our results indicate the presence of pre-associated dimers: After the optical excitation of one of the monomers a charge separation/transfer happens and leads to the bleaching of a second monomer. The resulting excited dimer then fluoresces and finally crosses into the triplet manifold. Observation of the dynamics is obscured by an intrinsic impurity identified by excitation wavelength dependent ns fluorescence decay dynamics. The impurity is found even for highly purified samples and seems to originate from a photochemical process.

[1] J. B. Birks et al., *Proc. Roy. Soc. A* **1963**, 275, 575.

[2] E. Riedle et al., *Faraday Discuss.* **2013**, 163, 139.

MO 19.7 Thu 18:00 BEBEL HS213

Impact of Different Hydrogen Bond Sites on the Molecu-

lar Network of Ionic Liquids from Ultrafast CARS Spectroscopy — •SUSANA CHATZIPAPADOPOULOS¹, MATTHIAS LÜTGENS¹, FRANK FRIEDRISZIK¹, TOBIAS ZENTEL¹, DANIELA KERLÉ², OLIVER KÜHN¹, RALF LUDWIG², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Institut für Chemie, Universität Rostock, Germany

Ionic liquids (ILs) have unique properties which depend critically on the interaction between the ions. Understanding the intermolecular forces might enable an application-oriented tuning of their macroscopic properties. Here we study different imidazolium based ILs of the type [TeMIM][NTf₂] with femtosecond multiplex CARS. Dephasing times and vibrational resonance frequencies are extracted by quantitative

modeling of the complete CARS response. In previous investigations on a similar system of the type [C_nMIM][NTf₂] we found a hydrogen bond network formed by the three hydrogen atoms of the imidazolium ring [1]. In the present study we modified the ILs and replaced two hydrogens by methyl groups. In this way a simplified network with only one hydrogen bond per cation results and the bond position can be varied. From the frequencies of the isolated resonances an unambiguous assignment of the hydrogen bonds in the complete network with three hydrogen donors per cation is established. Spectral shifts and changes in dephasing times are discussed with respect to differences between the complete and the simplified hydrogen bond network.

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