

MO 20: Electronic Spectroscopy 2

Time: Thursday 16:30–18:30

Location: BEBEL SR144

MO 20.1 Thu 16:30 BEBEL SR144

Electronic Spectroscopy of 1-Phenylethynyl-Naphthalene — ●PHILIPP CONSTANTINIDIS¹, MELANIE LANG¹, JÖRG HERTERICH¹, INGO FISCHER¹, JOHANNES AUERSWALD², and ANKE KRUEGER² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

A recent IR/UV double resonance study identified 1-phenylethynyl-naphthalene (1-PEN) as the major dimerization product of phenyl-propargyl radicals. Considering the importance of C₃ hydrocarbons in the initial phase of the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion processes, both the phenylpropargyl radical as C₉ unit and its stable dimer 1-PEN could also play a conceivable role in PAH growth [1].

We investigated the S₁ excited state of 1-PEN by means of [1+1]-REMPI spectroscopy. A rich structure of low wavenumber bands was observed, which could be assigned to the torsional motion. Vibrational frequencies of 6 cm⁻¹ and 17 cm⁻¹ respectively were derived for the torsional mode in the ground and excited state. Spectra of the 1-PEN/Ar cluster exhibit a red shift of the origin of 22 cm⁻¹, comparable to argon clusters of other aromatic molecules.

[1] K. H. Fischer, J. Herterich, I. Fischer, S. Jaecx and A. M. Rijs, *J. Phys. Chem. A* **116**, 8515 (2012)

MO 20.2 Thu 16:45 BEBEL SR144

The Hydrogen Bond of Water in Mixtures with Organic Solvents and in Aqueous Ion Solutions — ●KATHRIN MARIA LANGE, TRISTAN PETIT, GERRIT CONRAD, KENJI YAMAMOTO, CHRISTOPH SCHWANKE, KAI HODECK, MARKUS DANTZ, TIM BRANDENBURG, EDLIRA SULJOTI, and EMAD FLEAR AZIZ — Helmholtz-Zentrum Berlin, Germany

Knowledge about the hydrogen bond network of water is essential for understanding its anomalies as well as its special role for several biochemical systems. Soft X-ray absorption (XAS) and emission spectroscopy (XES) as well as resonant inelastic X-ray scattering (RIXS) at the oxygen K-edge of water allow investigating its local electronic structure by probing the occupied- and unoccupied-valence molecular orbitals. The recent combination of these methods with the liquid microjet technique opened the door to studies of the hydrogen bond nature in a membrane-free spectrometer.[1-4] The effect of confining water in organic solvents free from oxygen[2], replacing hydrogen by deuterium [3] as well as of dissolving monovalent cations (Li⁺, K⁺, NH₄⁺, Na⁺) [4] on the hydrogen bond structure of water was characterized. For the ionic solutions cation ordering with respect to their impact on hydrogen bond network was revealed and the effect of the counterion was investigated. [1] Lange et al., *Chemical Physics* **377**, 1-5 (2010) [2] Lange et al., *Angewandte Chemie* **123**, 45, 10809 (2011) [3] Lange et al., *Phys. Rev. B* **85**, 155104 (2012) [4] Petit, Lange, Conrad, Yamamoto, Schwanke, Hodeck, Dantz, Brandenburg, Suljoti, Aziz, Submitted 2013

MO 20.3 Thu 17:00 BEBEL SR144

Determination of Excited State Dipole Moments from Electronic Stark Measurements — ●MICHAEL SCHMITT¹, JOSEFIN ROLF¹, MARTIN WILKE¹, and W. LEO MEERTS² — ¹Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie, Düsseldorf, Deutschland — ²Radboud University, Molecular and Biophysics group, Nijmegen, The Netherlands

The dipole moments of electronically excited states may differ considerably from those of the ground state, as a consequence of the altered electron distribution upon excitation. This change of the dipole moment upon electronic excitation has a large influence on solvation dynamics, which is largely governed by the interactions of solute and solvent dipole moments.

We modified the existing setup for rotationally resolved electronic spectroscopy by inserting a pair of Stark plates in the laser-molecular beam interaction region. They consist of a parallel pair of electroformed nickel wire mesh (70 mesh per inch) with a transmission of 95% in the UV. The polarization plane of the incoming laser beam can be rotated by 90° inside the vacuum chamber by means of an

achromatic $\lambda/2$ plate. For the polarization being parallel to the electric field of the Stark plates $\Delta M = 0$ and for the polarization being perpendicular to the electric field $\Delta M = \pm 1$ selection rules apply.

The spectra of several indole derivatives have been fit automatically using an evolutionary strategy. The nature of the excited states is discussed, using the informations from the excited state dipole moments.

MO 20.4 Thu 17:15 BEBEL SR144

Ultrafast dynamics of solvated electrons in NaI aqueous solution — ●ALEXANDER KOTHE, NICHOLAS ENGEL, ALEXANDRE MOGULEVSKI, MARTIN WILKE, IGOR YU. KIYAN, and EMAD F. AZIZ — Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq), Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Albert-Einstein-Str. 15, 12489 Berlin, and Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin, Germany

Due to the importance of water in physics, chemistry and biology the solvated electron has drawn a lot of scientific interest since its discovery [1]. In our pump-probe experiment we generated solvated electrons in a liquid microjet with 20 mM NaI aqueous solution using laser pulses with a wavelength of 266 nm. The system was probed via photoemission spectroscopy with pulses of 350 nm wavelength. We observed the so called "hot" solvated electrons [2] and an additional excited state with a binding energy of 1.6 eV and a lifetime of approximately 4 ps.

Furthermore, rotating the pump beam and thus orienting the excited state with respect to the probe beam and the spectrometer axis revealed polarization dependence of the "hot" solvated electrons. In contrast to this finding, the excited state with the binding energy of 1.6 eV did not depend on its orientation.

[1] E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.* **84**, 4090 (1962).

[2] A. Lübcke, F. Buchner, N. Heine, I. V. Hertel and T. Schultz, *Phys. Chem. Chem. Phys.* **12**, 14629 (2010).

MO 20.5 Thu 17:30 BEBEL SR144

Chemical Bonding in Aqueous Ferrocyanide: Experimental and Theoretical X-ray Spectroscopic Study — ●NICHOLAS ENGEL¹, SERGEY I. BOKAREV², EDLIRA SULJOTI¹, RAUL GARCIA-DIEZ¹, KATHIN M. LANGE¹, KAAAN ATAK¹, RONNY GOLNAK¹, ALEXANDER KOTHE¹, MARCUS DANTZ¹, OLIVER KÜHN², and EMAD F. AZIZ¹ — ¹Joint Ultrafast Dynamics Lab in Solutions and at Interfaces at Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 14, 12489 Berlin and Freie Universität Berlin, Department of Physics, Arnimallee 14, 14195 Berlin — ²Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

Exploiting the recently developed micro-jet technique enables to investigate liquid phase samples with the use of soft X-ray spectroscopy. Here, resonant inelastic X-ray scattering (RIXS) and X-ray absorption (XA) experiments at the iron L- and nitrogen K-edge are combined with high-level first principles restricted active space self-consistent field (RASSCF) calculations for a systematic investigation of the nature of the chemical bond in potassium ferrocyanide in aqueous solution. The atom- and site-specific RIXS excitations and the high resolution of the beamline and spectrometer <0.5 eV allow for direct observation of ligand-to-metal (Fe L-edge) and metal-to-ligand (N K-edge) charge transfer bands and thereby evidence for strong σ -donation and π -back-donation. The effects are identified by comparing experimental and simulated spectra related to both the unoccupied and occupied molecular orbitals in solution.

MO 20.6 Thu 17:45 BEBEL SR144

Triplet-triplet exciton dynamics in single-wall carbon nanotubes — ●FLORIAN SPÄTH¹, DOMINIK STICH¹, HANNES KRAUS², ANDREAS SPERLICH², VLADIMIR DYAKONOV^{2,3}, and TOBIAS HERTEL¹ — ¹Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany — ²Institute of Physics, Julius-Maximilian University Würzburg, Germany — ³Bavarian Center for Applied Energy Research e.V., Würzburg, Germany

Understanding triplet excitons dynamics is crucial for the optimization of optoelectronic devices, since triplet excitons can either increase the efficiency of devices such as OLEDs and organic solar cells or can act as a loss channel. For the first time, triplet-triplet exciton interactions in (6,5)-single-wall carbon nanotubes (SWNTs) were studied by optically detected magnetic resonance (ODMR) spectroscopy[1]. By

using a master equation ansatz and taking into account the excitation intensity and frequency dependence of the ODMR signal, we were able to determine the quantum yield of triplet exciton formation of $(5 \pm 2)\%$ and the triplet exciton lifetime of $(30 \pm 10) \mu\text{s}$.

[1] D. Stich, F. Späth, H. Kraus, A. Sperlich, V. Dyakonov and T. Hertel, *Nature Photonics*, in press (doi: 10.1038/nphoton.2013.316)

MO 20.7 Thu 18:00 BEBEL SR144

From 5 to 6: High resolution laser induced fluorescence spectroscopy of differently substituted indole derivatives. — ●MARTIN WILKE, JOSEFIN ROLF, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

The assignment of the electronic nature of several 6-substituted indole derivatives with high resolution laser induced fluorescence spectroscopy will be presented. Its characterization to an La or an Lb state based on the nomenclature of Platt results of some molecular parameters like the orientation of the transition dipole moment, the changes of the bond lengths or the frontier orbital contribution upon excitation. Comparing the experimental results with state-of-the-art ab initio calculations shows a strong discrepancy in the orientation of the transition dipole moment from the results for the 5-substituted indoles. The surprising behavior of the 6-substituted derivatives compared to the 5-substituted

derivatives will be discussed.

MO 20.8 Thu 18:15 BEBEL SR144

A new experimental set-up for electronic Stark measurements with rotationally resolved laser induced fluorescence spectroscopy — ●JOSEFIN ROLF, MARTIN WILKE, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Institut für Physikalische Chemie I, Düsseldorf

High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of excited singlet states. Therefore, several molecular parameters like the orientation of the transition dipole moment, the changes of the bond lengths or the frontier orbital contribution upon excitation are needed to determine the electronic nature. It is also possible to get the permanent electric dipole moment of the ground and the excited state by changing the experimental set-up. These realized technical changes to generate a homogeneous electric field and to modify the polarisation of the laser beam will be presented. The electric field lifts the M degeneracy by the Stark effect and results in a band splitting depending on the intensity of the electric field and on the order of the dipole moment in the ground and in the excited state. By switching the polarization of the laser between horizontal and vertical different selection rules will be applied.