

MO 15: Environment Controlled Processes

Time: Thursday 14:30–16:30

Location: N 6

Invited Talk

Tracking electronic processes inside dense matter by luminescence — ●ANDRÉ KNIE — Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT)

Typically electronic processes are investigated by charged particle detection - very often by electron spectroscopy. The step from small ideal systems, e.g. atoms, molecules, or clusters, to dense (real life) systems is obstructed for those techniques due to the very short penetration depth (few nm) of the charged particles. Another approach is the detection of photons, with orders of magnitude larger mean free paths.

Here, it will be shown how we employ high-resolution luminescence spectroscopy to observe ultra-fast energy transfers, namely the interatomic Coulombic decay (ICD), in noble gas clusters and electronic processes of photo excited liquid water within a liquid microjet.

In noble gas clusters as prototypes for dense systems, the photon emission following the electronic process can be investigated from small to large clusters. The fingerprint of the ultra-fast ICD feature, which can be identified by excitation energy and decay times, shows dramatic trends upon transition from small (dilute) to large (dense) clusters. Another very dense sample with a major impact on our daily life is liquid water and the electronic processes occurring upon XUV irradiation. Due to their luminescence fingerprint, those processes and thereby liquid water itself could be tracked over vast distances, e.g. astronomical distances.

MO 15.2 Thu 15:00 N 6

Interatomic coulombic decay in macroscopic environments — ●JOSHUA LEO HEMMERICH, ROBERT BENNETT, and STEFAN YOSHI BUHMANN — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Interatomic coulombic decay (ICD) [1] has been a subject of study for the last two decades. The process takes place when a subunit of a cluster is ionized by removal of an inner valence electron. If the energy of the resulting state lies beneath the double ionization threshold a second subunit can be ionized by exchange of a virtual photon. Using the framework of macroscopic quantum electrodynamics [2] and time-dependent perturbation theory we study this process in arbitrary material environments, e.g. near a conducting plate. We compare our results in free space with the asymptotic quantum chemistry results based on the non-retarded Coulomb interaction to elucidate the impact of retardation. Finally, we briefly comment on the influence of macroscopic dielectric bodies on the ICD process.

[1] L.S. Cederbaum, *et. al.* Phys. Ref. Lett. **79** (24) 1997

[2] S. Scheel and S. Y. Buhmann, *Acta Physica Slovaca* **58** (5) 2008

MO 15.3 Thu 15:15 N 6

Femtosecond spectroscopy of the solvated electron in liquid ammonia over a wide range of excitation energies — ●TIM VOGLER, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

We recently reported on the vertical and below-band-gap ionization of liquid-to-supercritical ammonia employing photolytical excitation energies E_g of 9.3 eV [1] and 6.2 eV [2], respectively. In these studies the so called escape probability, i.e. the fraction of solvated electrons that are able to escape from their parent molecule, was around 70% in the first case and only 5% in the latter one (at room temperature and a pressure of 300 bar). This dramatic change in dependence on E_g opens up a very attractive window for further investigations: While the previous work puts special emphasis on the quantification of the escape probability under varying thermodynamic conditions, we now determined its behavior as a function of the excitation energy E_g .

To do so we extended our femtosecond pump-probe-spectrometer with a tunable UV light source providing a wide and gapless range of excitation energies E_g from 6 eV to 12 eV, implying a two-photon dependence of the ionization mechanism as found in [1]. Finally, the experimental results can be interpreted with a model regarding the optical band gap of liquid ammonia, which is around 8.2 eV [2].

[1] J. Urbanek *et al.*, *J. Phys. Chem. B* **116.7** (2012),

[2] J. Urbanek and P. Vöhringer, *J. Phys. Chem. B* **118.1** (2013)

MO 15.4 Thu 15:30 N 6

Mean free path of slow electrons retrieved from velocity map imaging of aerosol particles — ●MAXIMILIAN GOLDMANN¹, BRUCE L. YODER¹, STAVROS AMANATIDIS¹, EGOR CHASOVSKIKH¹, LUKAS LANG¹, ANDRAS BODI², DAVID LUCKHAUS¹, and RUTH SIGNORELL¹ — ¹Laboratorium für physikalische Chemie, ETH Zürich, 8093 Zürich — ²Swiss Light Source, Paul Scherrer Institut, 5232 Villigen

Electron mean free paths are important quantities for a number of physico-chemical phenomena ranging from aerosol physics and chemistry to radiation damage of biological tissues. We introduce and apply a novel method to determine the electron mean free path of low energy electrons in solid and liquid materials by velocity map imaging photoelectron spectroscopy of neutral aerosol particles using vacuum ultraviolet light. We extract the electron mean free path by comparing experimental with simulated photoelectron velocity map images of aerosol particles. For the simulation, we use a detailed scattering model [1].

Experimental photoelectron spectra of potassium chloride nanoparticles [2], liquid water droplets [1], and liquid-coated nanoparticles are presented. These photoelectron images were recorded at the VUV beamline at Paul Scherrer Institute and by means of a home-built table-top laser system.

[1] R. Signorell *et al.*, *Chem. Phys. Lett.* **658**, 1 (2016).

[2] M. Goldmann *et al.*, *J. Chem. Phys.* **142**, 224304 (2015).

MO 15.5 Thu 15:45 N 6

Monitoring the proton-transfer dynamics of a super-photoacid in acetone — ●JOHANNES KNORR¹, BASTIAN GEISSLER¹, CHRISTIAN SPIES^{1,2}, BJÖRN FINKLER², GREGOR JUNG² and PATRICK NUERNBERGER¹ — ¹Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum — ²Biophysikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken

Photoacidity, i.e., a molecule's higher tendency to release a proton after electronic excitation, caused by changes in the molecule's electronic distribution that in turn affect corresponding hydrogen bonds, is frequently encountered in aromatic alcohols capable of transferring a proton to a suitable acceptor [1]. In this study, we investigate an extraordinarily strong super-photoacid, namely tris(1,1,1,3,3,3-hexafluoropropan-2-yl)8-hydroxypyrene-1,3,6-trisulfonate [2,3] in the aprotic solvent acetone—an environment which has not been addressed in previous time-resolved studies with other photoacids due to their weaker proton-transfer capabilities. In-depth analysis of time-correlated single-photon counting and femtosecond transient absorption experiments allows us to disclose solvation dynamics and radiative relaxation processes, as well as to derive a reaction scheme comprising the relevant steps of proton transfer along with the characteristic time scales.

[1] T. Förster, *Naturwissenschaften* **36**, 186 (1949)

[2] C. Spies *et al.*, *Phys. Chem. Chem. Phys.* **15**, 19893 (2013)

[3] B. Finkler *et al.*, *Photochem. Photobiol. Sci.* **13**, 548 (2014)

MO 15.6 Thu 16:00 N 6

An Experimental Test of Fermi's Golden Rule using Femtosecond IR Pump-Probe Spectroscopy — ●JEANNINE GLEIM, TOBIAS UNRUH, DENIS CZURLOK, JÖRG LINDNER, and PETER VÖHRINGER — Institut für Physikalische und Theoretische Chemie, Universität Bonn

Fermi's Golden Rule describes the coupling of an eigenstate of a quantum system with a resonant continuum of "background" states. In the context of vibrational energy relaxation in liquid solutions Fermi's Golden Rule (FGR) has never been tested rigorously through experimental studies. In the recent past, aqueous solutions of pseudohalide anions were used to study dynamical solute-solvent interactions and vibrational energy relaxation in hydrogen-bonded networks. Here, the cyanide stretching vibration of SC14N-, SC15N-, SeCN- and OCN- anions dissolved in water were studied with FTIR-spectroscopy as well as femtosecond IR-pump-probe spectroscopy. This solute vibration can couple resonantly to the continuum of bending-librational combination states of the liquid. All experiments were carried out under isobaric conditions at a pressure of 500 bar over a wide temperature range. T-dependent relaxation rates ($k(\text{VER})$) were determined from the decay of the $v = 1$ excited state absorption. Furthermore, the T-dependent

spectral overlap $S(T)$ between the solute and solvent absorption bands were determined independently and were used as a measure of the density of "background" states that enters Fermi's Golden Rule. According to FGR, a linear relationship between $S(T)$ and $k(\text{VER})$ exists which provides insight into the coupling strength of the solute and solvent.

MO 15.7 Thu 16:15 N 6

Photophysics and electrodynamics of indole and indole-water clusters — THOMAS KEIRSPPEL^{1,2}, MELBY JOHNY¹, JOSS WIESE^{1,2}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free Electron Laser Science (CFEL), Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

The properties of atoms and molecules are strongly dependent on their

environment and hydrogen bonds are of universal importance in chemistry and biochemistry [1]. Therefore, it is highly desirable to bridge the gap between single, isolated molecules and molecules in solvation.

Here, we investigate the photophysics of a spatially separated pure sample of indole-water clusters, an amino-acid chromophore (indole) solvated by single water molecule [2]. The photofragmentation owing to 1s core hole ionization of indole's nitrogen were analysed with (photoelectron) photoion-photoion coincidence (PIPICO) maps. Indications for electron and proton or hydrogen atom transfer to the hydrogen bonded water molecule, as well as different Coulomb explosion channels, due to further emission of electrons on the indole-side of the cluster, were observed.

[1] A. L. McClellan, *J. Chem. Educ.*, 44 (9), 547 (1967)

[2] Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* 34(4), 557-590 (2015)