

MO 21: Electronic Spectroscopy I

Time: Thursday 10:30–13:00

Location: MER 02

MO 21.1 Thu 10:30 MER 02

Soft x-ray absorption spectroscopy on liquids, solutions and solvated molecules using ultrathin liquid films — ●SIMON SCHRECK, CHRISTIAN WENIGER, and PHILIPPE WERNET — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

Soft x-ray absorption spectroscopy is a powerful technique for investigating the electronic structure of atoms and molecules. Here we present its application to bulk liquids, liquid solutions and solvated molecules to study the interplay of electronic and geometric structures.

Soft x-ray absorption spectra were recorded in transmission mode using a recently developed setup for preparing ultrathin liquid films separated from vacuum or He atmosphere. The thickness of these films can be controlled from the nanometer range to some micrometers.

We present spectra of the near edge x-ray absorption fine structure (NEXAFS) of the Oxygen (O) K-edge of H₂O, D₂O and aqueous solutions of 3d metal chlorides. For the 3d metal chlorides additional measurements were performed at the corresponding metal L-edges. The combined O K-edge and metal L-edge measurements on aqueous solutions allow for new interpretations in terms of the hydration of metal ions and their interaction with the solvent. Furthermore, spectra of the extended x-ray absorption fine structure (EXAFS) of H₂O and D₂O are presented. For D₂O, these are the first NEXAFS spectra recorded with soft x-rays and the first EXAFS studies at all. The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 21.2 Thu 10:45 MER 02

Charge Transfer between Co(II) and H₂O vs D₂O quantified by Dark Channel Fluorescence Yield XAS. — SAMIRA GHADIMI¹, SEBASTIEN BONHOMMEAU², ●MIKHAIL SOLDATOV^{1,3}, KATHRIN M LANGE¹, TOM STALINSKI¹, ALEXANDER KOTHE¹, KAI F HODECK¹, ALEXANDER SOLDATOV³, and EMAD F AZIZ^{1,4} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — ²Institut des Sciences, Moléculaires, Université Bordeaux 1, Talence Cedex, France — ³Southern Federal University, Research Center for Nanoscale Structure of Matter, Rostov-on-Don, Russia — ⁴Freie Universität Berlin, FB Physik, Berlin, Germany

The electronic structure of Co(II) ions in water vs D₂O solution was characterized by soft X-ray absorption spectroscopy. The X-ray absorption of the Co(II) L_{2,3}-edges was obtained experimentally in both, transmission and fluorescence mode. The spectra measured in fluorescence mode show significant deviations in shape and intensity of the L₃ and L₂ edge features as compared to the transmission spectra. This can be explained by the dark-channel fluorescence yield (DCFY) mechanism found recently by us [1,2]. Ligand-field multiplet simulations of the spectra were performed, to model the charge transfer of the Co(II) ions in the different solvents, and analyzed in terms of the Co-O-H₂ bonding strength. The intensity of the L_{2,3}-edges fluorescence from the Co(II) ions was reduced due to the DCFY mechanism but shows no sub background dip as it was observed for Fe(III) ions in water [1,2].

[1] Emad F. Aziz et al., Nature Chemistry 2010, 768, 853-857

[2] News and Views Nature Chemistry 2 2010, 800-802

MO 21.3 Thu 11:00 MER 02

Sub-Femtosecond Electron Delocalization between Fe³⁺ and H₂O versus D₂O Solvents — ●TOM STALINSKI¹, SEBASTIEN BONHOMMEAU², SAMIRA GHADIMI¹, KATHRIN LANGE¹, ALEXANDER KOTHE¹, RENÉ KÖNNECKE¹, KAI HODECK¹, MAJED CHERGUI³, and EMAD AZIZ^{1,4} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, c/o BESSY GmbH, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany — ²Institut des Sciences Moléculaires, UMR 5255 CNRS, Université Bordeaux 1, 351 cours de la Libération, F-33405 Talence Cedex, France — ³Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Spectroscopie Ultrarapide, Faculté des Sciences de Base, ISIC, Station 6, CH-1015 Lausanne, Switzerland — ⁴Freie Universität Berlin, FB Physik, Arnimallee 14, D-14195 Berlin, Germany

Charge transfer processes from aqueous Fe³⁺ ions to solvent molecules have been reported by using dark channel fluorescence-yield (DCFY) spectroscopy at the L-Edge. It was found that the interaction with the water solvent molecule around this ion leads to an appearance of a dip feature in the L₃-edge of the fluorescence yield[1]. Here we report

on the difference between Fe³⁺ ions dissolved in water (H₂O) versus heavy water (D₂O) as revealed by fluorescence yield L-edge X-ray absorption spectroscopy of these two systems. Comparison with the corresponding transmission absorption spectra and Multiplet Calculations are used to quantify the DCFY mechanism. Furthermore core-hole lifetimes of the involved states are estimated in a sub-femtosecond timescale. [1]: E. F. Aziz et al., Nature Chemistry 2, 853 (2010).

MO 21.4 Thu 11:15 MER 02

Absolute cross section of ionization, dissociation and fluorescence of H₂ superexcited states — MICHELE GLASS-MAUJEAN¹, CHRISTIAN JUNGEN², HANS SCHMORANZER³, ●IRINA TULIN-HAAR⁴, ANDRÉ KNIE⁴, PHILIPP REISS⁴, RAINER HENTGES⁴, WITOSLAW KIELICH⁴, KARI JÄNKÄLÄ⁴, and ARNO EHRESMANN⁴ — ¹Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France — ²Laboratoire Aimé Cotton du CNRS, Batiment 505, Université de Paris-Sud, F-91405 Orsay, France — ³Fachbereich Physik, Technische Universität Kaiserslautern, D-67653 Kaiserslautern — ⁴Institut für Physik, Universität Kassel, D-34132 Kassel, Germany

Absolute cross sections of three competing decay channels, namely ionization, dissociation and fluorescence, were determined after excitation of superexcited states of the hydrogen molecule. The experimental data was recorded by irradiating H₂ with VUV photons (14.8 eV - 16 eV) at the U125/2-10m-NIM beamline (BESSY II, Berlin).

In addition to the absolute cross section of the decay processes: autoionization σ_{ion} , predissociation σ_{dis} and molecular fluorescence σ_{fluo} the absolute absorption cross section σ_{abs} was determined. Measuring the complete cross section data set of absorption and all decay channels, this experiment allows a cross validation of the individual decay channels. The measured data has been compared to MQDT calculation and allows the identification of the intermediate superexcited molecular states.

MO 21.5 Thu 11:30 MER 02

IR-UV double resonance spectroscopy of radicals using a free electron laser — ●KATHRIN FISCHER¹, PATRICK HEMBERGER¹, INGO FISCHER¹, and ANOUK RIJS² — ¹Institut für Physikalische und Theoretische Chemie, Würzburg, Germany — ²FOM Intitute for Plasma Physics, Rijnhuizen, Netherlands

A suitable technique to distinguish between isomers is IR spectroscopy, if they have different or characteristic absorption bands. When the isomer of interest is a carbene or radical, normal IR spectroscopy is not possible, because of low number density. Hence, the solution for this challenge is a free electron laser experiment, which combines IR spectroscopy with mass spectrometry. Initial experiments on the allyl radical showed that pyrolytically generated radicals can be investigated. During our measurements of trifluoromethylphenyl carbene (TFPC) we noticed that a third isomer exists in the free jet beside the singlet and triplet isomers. This isomer could be identified as trifluorostyrene and shows the greatest percentage. This result was confirmed by calculations, which revealed that the trifluorostyrene is 185 kJ mol⁻¹ lower in energy than the carbene. [1]

MO 21.6 Thu 11:45 MER 02

Gas-Festkörper-Verschiebung der C 1s → π*-Anregung in Benzol — ●ROMAN FLESCH¹, PETER FEULNER², FLORIAN BLOBNER², ERTUGRUL SERDAROGLU¹ und ECKART RÜHL¹ — ¹Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — ²Physik-Department E20, TU München, James-Franck-Str., D-85748 Garching

Im Bereich der Rumpfniveauanregung liegen bisher nur wenige Untersuchungen zu spektralen Verschiebungen beim Übergang von der Gasphase zum Festkörper vor. Dies betrifft insbesondere die Anregung von Rumpfniveaus in unbesetzte Valenzzustände. Am Berliner Elektronenspeicherring BESSY-II wurden hochaufgelöste Messungen zur spektralen Verschiebung des C 1s → π*-Überganges vom isolierten Molekül zum Festkörper mit hoher Genauigkeit vorgenommen.

Diese Experimente wurden simultan in zwei hintereinander montierten Kammern unter Nutzung von Synchrotronstrahlung im weichen Röntgenbereich durchgeführt, so dass auch geringfügige spektrale Verschiebungen von <5 meV nachgewiesen werden können. Es wird eine

Rotverschiebung des C 1s \rightarrow π^* -Überganges von $\Delta E = 60 \pm 5$ meV im Festkörper relativ zum isolierten Molekül gefunden, die sogar geringfügig geringer als in kleinen Benzol-Clustern ist [1]. Diese Beobachtungen werden im Zusammenhang mit der Veränderung der Struktur des festen Benzols im Festkörper im Vergleich zu Mikroclustern diskutiert.

[1] I.L. Bradeanu, R. Flesch, N. Kosugi, A.A. Pavlychev und E. Rühl, Phys. Chem. Chem. Phys. 8, 1906-1913 (2006).

MO 21.7 Thu 12:00 MER 02

Mono-hydroxy[2.2]paracyclophane: a model compound for strongly interacting π -systems — ●CHRISTOF SCHON, WOLFGANG ROTH, INGO FISCHER, JOHANNES PFISTER, REINHOLD F. FINK, and BERND ENGELS — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Paracyclophane-based materials have been suggested for applications in organic solar cells, organic thin film transistors and organic light emitting diodes due to their photophysical properties and their high electric conductivity. Paracyclophane molecules have conjugated ring systems and the rings are rigidly connected by bridges. Therefore, they are suitable model systems for studying the interaction between cofacially oriented π -moieties. In recent years, paracyclophanes with two identical π -moieties (e.g. two benzene or two phenol moieties) have been investigated in detail. Now, we have investigated an isomer with different π -moieties (one benzene and one phenol moiety): monohydroxy[2.2]paracyclophane (MHPC). In the REMPI spectrum the electronic origin of MHPC is at 30772 cm^{-1} . We observe rich vibronic progressions. The experimental results were interpreted on the basis of *ab initio* calculations of the electronic ground state (SCS-MP2) and the lowest excited state (SCS-CC2). The ground state potential curve of MHPC shows a single minimum. In the first excited state a double minimum potential along the twist coordinate was calculated. This is an indication of an experimentally observed progression with inverse anharmonicity. Overall an excellent agreement between experiment and theory is observed.

MO 21.8 Thu 12:15 MER 02

Theoretical study of charge transfer complexes using hybrid functional the vdW correction. — ●SHAHAB NAGHAVI¹, THOMAS GRUHN¹, CLAUDIA FELSER¹, KATERINA MEDJANIK², GERD SCHÖNHENSE², RALPH RIEGER³, MARTIN BAUMGARTEN³, and KLAUS MÜLLEN³ — ¹Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg - Universität Mainz, Germany — ²Institut für Physik, Johannes Gutenberg - Universität Mainz, Germany — ³Max-Planck-Institut für Polymerforschung, Mainz, Germany

The electronic structure of the PAHs has been studied with the help of B3LYP hybrid density functionals. Using the Δ SCF method, electron binding energies have been determined which affirm, specify and complement the experiment measured by UPS. The calculated electron affinity (EA) provides a quantitative classification of the donor/acceptor properties of the studied molecules. Some of the strong donor/acceptor molecules are chosen for the further investigation were they formed the $\pi - \pi$ complexes as a dimer. Density functional theory (DFT) calculations were carried out to determine the geometric structure of these complexes. For the coronene dimers, the attraction is based on vdW interaction while all other interactions are repulsive. Therefore, the pure DFT calculations provide a purely repulsive inter-

action. For the charge transfer complexes, DFT calculations provide a minimum on the PES. This attraction caused by Coulomb interactions. However, the attraction based on Coulomb interaction is not the strongest interaction in CTCs.

MO 21.9 Thu 12:30 MER 02

Efficiency of energy transfer in the FMO complex under the influence of a Non-Markovian environment — ●CHRISTOPH KREISBECK¹, MIRTA RODRIGUEZ PINILLA², BIRGIT HEIN¹, and TOBIAS KRAMER¹ — ¹Institute for Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany — ²Instituto de Estructura de la Materia, Madrid, Spain

Laser spectroscopy experiments by Engel *et al.* (Nature 2007) and also by Collini *et al.* (Nature 2010) suggest that quantum coherent effects may be essential in the energy transfer in light-harvesting complexes despite their high operating temperatures. The interplay between coherent and environment assisted energy transfer leads to highly efficient transport to the reaction center. Strong coupling to the environment requires a non-Markovian approach and we use the hierarchical equations (HE) proposed by Ishizaki and Fleming in 2009, which includes properly the reorganization process. We compare the HE with the Markovian dynamics for different temperatures and a wide range of reorganization energies. For both cases the Markov limit overestimates thermalization, yielding higher efficiencies than the HE. Our results demonstrate that initial quantum beatings are important for the energy distribution but of limited influence to the efficiency. To overcome the long computation times of the numerically demanding HE we use the high-performance of graphics processing units (GPU) resulting in tremendous speedups (400 fold) compared to standard CPUs. Our efficient GPU implementation allows us to calculate nonlinear spectra of the FMO complex (see Birgit Hein).

MO 21.10 Thu 12:45 MER 02

Simulation of 2D-echo spectra of excitonic transfer in systems with large reorganisation energy on a GPU — ●BIRGIT HEIN¹, CHRISTOPH KREISBECK¹, TOBIAS KRAMER¹, and MIRTA RODRIGUEZ PINILLA² — ¹Institute for Theoretical Physics, University of Regensburg, Germany — ²Instituto de Estructura de la Materia, Madrid, Spain.

We analyse the Fenna-Matthews-Olson (FMO) complex of photosynthetic bacteria. Experimentally long lived quantum beatings have been observed at 77K (Engel, *et al.* (2007), Nature, 446, 782) and 294 K (Collini, *et al.* (2010). Nature, 463 644) which cannot be reproduced with a Markovian approach.

We calculate two dimensional echo spectra of the multi-site system, using an hierarchical propagation scheme suggested by Ishizaki and Fleming in 2009. This propagation scheme reproduces the long lived quantum beatings and works for systems with large coupling between excitonic and vibrational degrees of freedom. It also takes a back-action of the phonon-bath on the system into account. We tackle the computational demanding problem by implementing it on a graphic processing units (GPU) and using the enormous speed-up provided thus. This efficient implementation obliterates the need for approximate methods frequently used and facilitates the interpretation and comparison of theory and experiments for systems with large reorganisation energy.