

MO 3: Electronic Spectroscopy 1

Time: Monday 14:30–16:30

Location: f102

MO 3.1 Mon 14:30 f102

Theoretical soft X-ray spectroscopy from time correlation functions — ●SVEN KARSTEN, SERGEY BOKAREV, SERGEI IVANOV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock

Soft X-ray spectroscopy can reveal element-specific information about the electronic structure of an absorbing atom and its interactions with the local environment. The interpretation of experimental X-ray spectra requires a detailed theoretical consideration of the core-excited electronic states. Conventionally, the electronic spectra are obtained via single point calculations combined with phenomenological broadening. A more realistic account of vibrational and environmental effects is commonly provided by an incoherent sampling of molecular dynamics (MD) trajectories. However, this completely neglects nuclear dynamical correlations. In the present contribution such correlations are included via a rigorous reformulation of X-ray absorption spectra (XAS) and resonant inelastic X-ray scattering spectra (RIXS) in terms of transition dipole correlation functions. The time evolution is provided by ground state (*ab initio*) MD simulations. Performing DFT or RASSCF static point calculations for each MD snapshot yields, upon tracing the entire manifold of relevant electronic levels, all necessary ingredients. The success of the proposed methodology is exemplified for oxygen K-edge XAS and RIXS of bulk water which provides insight into H-bond dynamics.

MO 3.2 Mon 14:45 f102

Electronic Spectra of 2- and 3-Tolunitrile in the Gas Phase — ●FELIX GMEREK, JOSEFIN WILKE, MARTIN WILKE, BENJAMIN STUHLMANN, and MICHAEL SCHMITT — Heinrich-Heine-Universität, Düsseldorf, Germany

The electronic structures of tolunitriles find considerable interest, because they are prototypes for small aromatic push-pull systems containing an electron pushing methyl-group and an electron pulling nitrile-group.

Therefore, we investigated the structure of 2- and 3-tolunitrile by combining the results of single vibronic level fluorescence (SVLF) spectroscopy^[1] and rotationally resolved laser induced fluorescence (HRLIF) spectroscopy^[2], which allows us to determine the structural changes upon electronic excitation, *via* a combined Franck-Condon/rotational constants fit with unique accuracy.

Additionally, the torsional barriers of the methyl groups, determined *via* SVLF and HRLIF spectroscopy, respectively, have been used as a probe for the structural changes upon electronic excitation for both molecules.

[1] J. A. Ruiz-Santoyo, J. Wilke, M. Wilke, J. T. Yi, D.W. Pratt, M. Schmitt, L. Álvarez-Valtierra, JCP, 2015, submitted

[2] F. Gmerek, B. Stuhlmann, L. Álvarez-Valtierra, D. W. Pratt, M. Schmitt, JCP, 2015, submitted

MO 3.3 Mon 15:00 f102

Electronic Stark measurements with rotationally resolved laser induced fluorescence spectroscopy — ●JOSEFIN WILKE, MARTIN WILKE, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of electronically excited singlet states to be 1L_a and 1L_b states in the nomenclature of Platt. 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. Also the permanent electric dipole moment of the ground and the first excited states can be used for the assignment, because the 1L_a state has a larger permanent dipole moment than the unpolar 1L_b state. Therefore, a homogeneous electric field is needed, which lifts up the M degeneracy by the Stark effect. By changing the polarization of the excitation light from parallel to perpendicular related to the orientation of the electric field different field configurations which are linked to the selection rules $\Delta M=0$ and $\Delta M=\pm 1$ can be measured. In this talk recent results for the permanent dipole moments of planar substituted indoles will be presented.

MO 3.4 Mon 15:15 f102

Experimental study of the conformational space of a neurotransmitter: Serotonin — ●MARTIN WILKE¹, JOSEFIN WILKE¹, CHRISTIAN BRAND², and MICHAEL SCHMITT¹ — ¹Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf — ²Faculty of Physics, University of Vienna, Austria

The conformational space of the neurotransmitter serotonin (5-hydroxytryptamine) has been studied in the ground and the first electronically excited state, using a combination of rotationally resolved electronic spectroscopy and *ab initio* theory. On the basis of the rotational constants, the excited state life times and the orientations of the transition dipole moments four conformers can be assigned. Furthermore a characteristic change of 230 cm^{-1} was observed experimentally between the excitation energies of the Gpy(out)/*anti* and Gpy(out)/*syn* conformer. Changing the orientation of the ethyl amine side chain towards the Phenyl moiety leads to an increase of the excitation energy. Several reasons for this behaviour are discussed and an incremental system for the prediction of excitation energies of doubly substituted indoles is presented.

MO 3.5 Mon 15:30 f102

Observation of 3-methoxyphenol rotational isomers via high resolution laser induced fluorescence spectroscopy — ●MICHAEL SCHNEIDER, JOSEFIN WILKE, MARTIN WILKE, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

Three of four possible 3-methoxyphenol isomers have been studied via high resolution laser induced fluorescence spectroscopy. By means of evolutionary algorithms the molecular parameters of the measured spectra of different isomers were determined. With the aid of CC2/cc-pVTZ *ab initio* calculated structures the measured isomers were matched to one of the possible rotational isomers. The assignments agree with the results of microwave spectroscopy of other research groups. Furthermore, the transition dipole moment orientation were determined and the electronic origins of the isomers of 3-methoxyphenol and its parent molecules anisole and phenol were compared.

MO 3.6 Mon 15:45 f102

Fluorescence measurements from x-ray irradiated liquid water — ANDREAS HANS¹, ANDRÉ KNIE¹, ●CHRISTIAN OZGA¹, ROBERT SEIDEL², PHILIPP SCHMIDT¹, XAVER HOLZAPFEL¹, MARVIN POHL², PETR SLAVÍČEK³, BERND WINTER², and ARNO EHRESMANN¹ — ¹Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — ²Helmholtz-Zentrum für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin, Germany — ³Department of Physical Chemistry, University of Chemistry and Technology, Technická 5, 16628 Prague, Czech Republic

The investigation of the decay dynamics of liquids and solutions after x-ray irradiation became accessible in recent years owing to the tremendous progress in liquid microjet techniques. This method meets the high vacuum conditions required for experiments using x-ray excitation at synchrotron radiation facilities. Mainly via electron spectroscopy, several non-local de-excitation processes and intermolecular interaction mechanisms were identified. Their role in radiation biology is currently lively discussed. However, the detection of charged particles as a probe for decay mechanisms is constrained due to their short escape length in dense media. We present a complementary experimental method in which fluorescence detection is used to investigate reaction products after excitation of liquid microjets with synchrotron radiation. This approach is especially beneficial to track neutral and long-living species.

MO 3.7 Mon 16:00 f102

TD-DFTB analysis of time- and geometry-dependent excitonic couplings in PTCDI crystals — ●PER-ARNO PLÖTZ¹, JÖRG MEGOW², THOMAS NIEHAUS³, and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, Germany — ²Institut für Chemie, Universität Potsdam, Germany — ³Institut Lumière Matière, Université Claude Bernard Lyon 1, France

Polarisation effects on chromophores and their influence to the excitonic coupling are simulated for a PTCDI (perylene-tetracarboxylic-diimide) crystal [1], whose thin films are possible building blocks for

optoelectronics. Starting from a classical MD trajectory Frenkel excitation parameters are calculated, i.e. the monomeric transition energies as well as the Coulomb couplings between the on-site transitions. The efficient TBFE [2] method making use of tight-binding-based density functional theory in the linear response formulation (TD-DFTB) [3] is capable not only to follow the specific inter- but also the intramolecular structural changes in a thermal environment, distinguishing it from other methods computing the Coulomb coupling with fixed transition charges. Thus the calculation of the spectral density from a classical trajectory is possible. Its analysis provides the key to assign optical properties to specific vibrational modes.

[1] J. Megow et al., *J. Phys. Chem. C*, 2015, 119, 5747-5751.

[2] P.-A. Plötz et al., *J. Chem. Phys.*, 2014, 140, 174101.

[3] T. A. Niehaus et al., *Phys. Rev. B*, 2001, 63, 085108.

MO 3.8 Mon 16:15 f102

IR/UV Ion Dip Spectroscopy of the Phenyl Radical and Propargyl Radical Self-Reaction — ●PHILIPP CONSTANTINIDIS¹, HANS-CHRISTIAN SCHMITT¹, FLORIAN HIRSCH¹, INGO FISCHER¹, BIN YAN², ARGHYA DEY², and ANOUK M. RIJS² — ¹University of

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It is a major concern of combustion research to elucidate the growth mechanisms of polycyclic aromatic hydrocarbons (PAHs), which occur as products of incomplete combustion. Due to their carcinogenic and pollutant nature, efforts are directed towards their prevention.

Our group applies IR/UV ion dip spectroscopy combined with free jet technique to investigate the intermediates and reaction products formed by pyrolytically generated hydrocarbon radicals in a high-temperature flow reactor. The mass-selected IR spectra contain both mass and structural information of the observed species, which allow identification of isomers. As intense tunable IR radiation is needed for this type of experiment, the measurements are performed with the free electron laser FELIX in Nijmegen.

Subject of our study is the self-reaction of propargyl and phenyl radicals, which are assumed to be important components of PAH formation.