

MO 6: Electronic Spectroscopy II

Time: Tuesday 14:00–16:30

Location: f102

MO 6.1 Tue 14:00 f102

Determination of excited state dipole moments in solution via thermochromic methods - an overview — ●MIRKO LINDIC, MATTHIAS ZAJONZ, and MICHAEL SCHMITT — Heinrich-Heine-University, Düsseldorf

In the last years considerable effort has been invested to develop and optimize excited state dipole determinations in solution with thermochromic methods. The aim was to obtain a complete method, which incorporates the measurement and evaluation of all necessary parameters, which are the cavity volume which is occupied by the solute, the refractive index and permittivity of the solution, and the temperature dependence of the absorption and fluorescence spectra.

Additionally, all results are compared with results from quantum chemical calculations at the SCS-CC2/cc-pVTZ (COSMO) level of theory, and, if obtainable, to the results of Stark measurements from the gas phase.

An overview of all used techniques and evaluation steps will be given, including published results from the past as well as an outlook to future plans with this project.

MO 6.2 Tue 14:15 f102

Determination of dipole moments in the electronically excited state of different constitutional isomers of cyanoin-dole via thermochromic methods — ●MATTHIAS ZAJONZ, MIRKO LINDIC, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

In this contribution we present the determination of dipole moments in the electronically excited state of different cyanoin-doles via thermochromic methods. These methods were introduced by Gryczynski and Kawski due to their advantages over solvatochromic methods [1]. Their basic advantage is that the combination of solvent and solute is kept constant and the required variation of the permittivity ϵ and index of refraction n to generate spectroscopic shifts of the absorption and emission spectra is mediated through temperature changes. Our goal is to improve the methods of dipole moment determination in solution via thermochromic methods, since the superior Stark spectroscopy in the gas phase is not feasible for all molecules. In addition, investigations are carried out to better understand the temperature dependence of the variables ϵ , n and the cavity volume, which replaces the inaccurate Onsager-Radius in thermochromic equations [2]. Cyanoin-doles were selected because they can be measured in gas phase using Stark spectroscopy within the research group [3], so values can be compared with gas phase values and *ab initio* calculations as well.

[1] Gryczynski *et al*, *Zeit. f. Nat.*, 1975, **30**

[2] Lindic *et al*, *Spec. Acta Part A*, 2019, **in press**

[3] Schneider *et al*, *Phys. Chem. Chem. Phys.*, 2018, **20**

MO 6.3 Tue 14:30 f102

Photoelectron spectroscopy of Boron containing reactive intermediates using synchrotron radiation and photoelectron/photoion coincidence (i2PEPICO) spectroscopy — ●DEB PRATIM MUKHOPADHYAY¹, DOMENIK SCHLEIER¹, INGO FISCHER¹, JEAN-CHRISTOPHE LOISON², CHRISTIAN ALCARAZ³, and GUSTAVO GARCIA⁴ — ¹Institute for Physical and Theoretical Chemistry, University of Würzburg, Würzburg, Germany — ²Université de Bordeaux, Talence, France. — ³Univ. Paris-Sud and Paris Saclay, Orsay, France. — ⁴Synchrotron SOLEIL, Gif sur Yvette, France

Determination of accurate ionization and appearance energies, as well as recording photoelectron spectra (PES), are always crucial for any reactive intermediate as it permits to derive accurate binding energies, standard heats of formation and nature of bonding. BH₂, a simple hydride and a free radical with only seven electrons but the IE, as well as PES, was not measured yet. As the photoionization leads to a linear cation from a bent neutral molecule, recording of vibrationally resolved PES, as well as spectral simulation, are both challenging. In this study, we report the first recorded slow photoelectron spectrum (SPES) of BH₂ and precisely determined its IE as about 8.12 eV. Recorded SPES portrayed a long progression of bending vibration indicating a large change of bond angle upon ionization. Spectral simulation is also done by calculating Franck-Condon (FC) factors between neutral and cationic states. Apart from that we also record SPES of BH from both ground singlet and triplet states which allow us to first

experimentally determined the singlet/triplet gap of BH.

MO 6.4 Tue 14:45 f102

Ultrafast non-local decay of core vacancies: from noble gas clusters to the suppression of radiation damage — ●ANDREAS HANS¹, CATMARN KÜSTNER-WETEKAM¹, PHILIPP SCHMIDT¹, SASCHA DEINERT², FLORIAN TRINTER², GREGOR HARTMANN¹, ARNO EHRESMANN¹, LORENZ CEDERBAUM³, NIKOLAI KRZYZHOVOI³, and ANDRÉ KNIE¹ — ¹Institut für Physik und CINSA, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany — ²Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22607 Hamburg, Germany — ³Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

We discuss the influence of an environment on the decay of core vacancies. In isolated atoms or molecules, core ionization is typically followed by Auger decay into doubly ionized states. In molecules, the severe consequence is the irreparable fragmentation. In an environment, charge and energy dissipation to the surrounding may protect the dicationic molecule from fragmentation. Here, we present experimental evidence that the protective effect of the environment sets in even earlier, namely by direct intermolecular decay of the initial core vacancy.

MO 6.5 Tue 15:00 f102

Investigation of the fragmentation of Isocyanic acid HNCO after inner-shell excitation by soft x-ray radiation — ●MARIUS GERLACH¹, FABIAN HOLZMEIER², MARKUS GÜHR³, JOHN BOZEK⁴, CHRISTOPHE NICOLAS⁴, ENGELBERT REUSCH¹, LILITH WOHLFART¹, DENNIS MAYER³, KARINA KOPP¹, and INGO FISCHER¹ — ¹Würzburg/De — ²Milan/It — ³Potsdam/De — ⁴St. Aubin/Fr

Hydrogen, oxygen, nitrogen, and carbon are the basic building blocks of all organic life. Isocyanic acid, HNCO, is the smallest molecule that consists of those elements. Isocyanic acid is also ubiquitous in interstellar systems[1] and has been linked to the formation of formamide, a potentially prebiotic molecule.[2]

Our group previously investigated the normal and resonant auger electron spectra of isocyanic acid.[3] In order to further elucidate the interaction of HNCO with cosmic x-ray radiation we investigated the fragmentation after these auger processes. These experiments were carried out at the PLÉIADES Beamline at the SOLEIL Synchrotron in St. Aubin, France. The fragmentation was examined with the EPICEA detector. With this setup we simultaneously recorded the auger electrons and the time of flight of the created ions. This information reveals detailed insights into the various fragmentation pathways.

Literature: [1] Nguyen-Q-Rieu *et al.*, *Astron. Astrophys.* 1991, 241, L33.

[2] M. Ferus *et al.*, *Astron. Astrophys.* 2018, 616, A150.

[3] F. Holzmeier *et al.*, *J. Chem. Phys.* 2018, 149, 034308.

MO 6.6 Tue 15:15 f102

Studying the dynamics and decay channels of C₄O⁻ in the electrostatic Cryogenic Storage Ring — ●V.C. SCHMIDT¹, K. BLAUM¹, P. FISCHER², S. GEORGE², M. GRIESER¹, F. GRUSSIE¹, J. GÖCK¹, R. VON HAHN¹, Á. KÁLOSI¹, H. KRECKEL¹, P.M. MISHRA¹, D. MÜLL¹, O. NOVOTNÝ¹, F. NUSSLIN¹, D. PAUL¹, S. SAURABH¹, C. SCHUMACHER¹, L. SCHWEIKHARD², P. WILHELM¹, and A. WOLF¹ — ¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany — ²Institut für Physik, Universität Greifswald, 17489 Greifswald, Germany

The electrostatic Cryogenic Storage Ring (CSR) at the Max Planck Institute for Nuclear Physics in Heidelberg offers a variety of experimental methods for the study of charged molecules. By cooling the experimental vacuum chambers down to 6K, a unique environment with nearly negligible blackbody radiation is created, allowing even infrared-active systems to lower their internal energies down to a few Kelvin through radiative cooling [1].

Photo-induced electron detachment and fragmentation of the astrophysically relevant C₄O⁻ anion were studied as a benchmark system. To this end, a tunable, pulsed OPO laser was used to induce resonant fragmentation into the neutral CO and the charged C₃⁻ fragments. The fragmentation process in dependence of photon energy as well as

its evolution with storage time in the CSR were studied. Preliminary results will be presented and discussed.

[1] C. Meyer et al., Phys. Rev. Lett. 119, 023202 (2017)

MO 6.7 Tue 15:30 f102

Structural Properties of Small Silicon Oxide Cations — ●KAI POLLOW, KARIM SAROUKH, ROBERT RADLOFF, LARS DAHLÖF, MARKO FÖRSTEL, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany

Interstellar dust is an important ingredient in the formation of solar systems like our own. Some properties of interstellar dust are known, many questions, however, are still unanswered. Molecular SiO can form in the atmospheres of oxygen-rich stars and interstellar dust contains particles made of macroscopic silicates of various compositions. Intermediates have been elusive to observations.

We present fragmentation pathways, geometric structure and optical properties of several possible intermediate species obtained via photodissociation spectroscopy and quantum chemical calculations. Knowledge of these parameters may help to model the complex formation processes and enable an observational search for these intermediate species.

MO 6.8 Tue 15:45 f102

Probing the Valence Electronic Structure of Aqueous Diazines Using Resonant X-ray Photoelectron Spectroscopy — ●MD SABBIR AHSAN^{1,2} and IAIN WILKINSON¹ — ¹Methods for Material Development, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ²Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Aqueous diazines play important roles in the photophysicochemical properties of bio-molecules such as DNA and RNA. We present liquid microjet based soft x-ray resonant photoelectron spectroscopy (RPES) measurements that probed the valence electronic structure of aqueous diazines. A number of core-valence resonances were identified by RPES scans over the diazine N K-edges and photoelectron spectra were subsequently recorded at different resonances. The solute signal was selectively enhanced in the RPES spectra with respect to solvent contributions. Moreover, by comparing the resonant Auger contributions with the non-resonant Auger signals, participator and spectator features were identified in the photoelectron spectra. Identification of participator peaks allowed us to determine aqueous-phase binding energies (BEs) associated with valence orbitals which are more generally hidden in non-resonant experiments. The associated BE information allowed us to map the valence electronic structure of the aqueous diazines and yielded valuable information for the interpretation of ongoing valence excited state time-resolved liquid-jet photoelectron spectroscopy experiment.

MO 6.9 Tue 16:00 f102

Time-resolved soft x-ray photoelectron spectroscopy on 2-thiouracil at FLASH2 — ●DENNIS MAYER¹, JAN METJE¹, FABIANO LEVER¹, AXEL HEUER¹, MARIO NIEBUHR¹, MATTHEW S. ROBINSON¹, SKIRMANTAS ALISAUSKAS², FRANCESCA CALEGARI², STEFAN DUESTERER², BASTIAN MANSCHWETUS², ANDREA TRABATTONI², TOMMASO MAZZA³, RAIMUND FEIFEL⁴, RICHARD SQUIBB⁴, MÅNS WALLNER⁴, THOMAS J. A. WOLF⁵, and MARKUS GÜHR¹ — ¹University of Potsdam, Germany — ²Deutsches Elektronen-Synchrotron, Hamburg, Germany — ³European XFEL GmbH, Hamburg, Germany — ⁴University of Gothenburg, Sweden — ⁵Stanford PULSE Institute, Menlo Park, USA

Sulfur-substituted nucleobases show an interesting photophysical and photochemical behavior attributed to their efficient relaxation to long living triplet states [1,2].

We performed ultrafast UV pump - x-ray probe spectroscopy at the FLASH 2 free electron laser in Hamburg to monitor the ultrafast relaxation processes of 2-thiouracil into the triplet states. In this talk, we present delay-dependent core level photoelectron and Auger electron spectra taken at and close to the sulfur L-edges. We use the spectra to elucidate the dynamics from an element specific point of view.

We used the newly built URSA-PQ instrument, which is now open for users and compatible with beamlines at FLASH1 and FLASH2 in Hamburg.

[1] Arslançan et al. Molecules 22, 998 (2017)

[2] Ashwood et al. Photochem. Photobiol. 95, 33-58 (2019)

MO 6.10 Tue 16:15 f102

Development of a software-based lock-in amplifier for non-linear spectroscopy — ●DANIEL UHL, ULRICH BANGERT, MARCEL BINZ, LUKAS BRUDER, FRIEDEMANN LANDMESSER, ANDREAS WITUSCHEK, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Lock-in amplification of modulated signals is widely used to improve detection sensitivity. We use this technique in phase-modulated wave packet interferometry and two-dimensional spectroscopy, which drastically improves the sensitivity [1,2].

To further improve our detection scheme, we've developed a software-based lock-in amplifier that provides additional flexibility in the data analysis and readily enables up-scaling of demodulation channels. With this approach, multiple signals can be demodulated simultaneously and custom demodulators and filters can be implemented. As an application example, we have used this technique to improve the phase noise characteristics in wave packet interferometry experiments performed in the XUV spectral range.

[1] L. Bruder et al., Phys. Chem. Chem. Phys. 17, 23877 (2015).

[2] L. Bruder et al., Nat Commun 9, 4823 (2018).