

## MO 8: Electronic Spectroscopy 1

Time: Tuesday 14:00–16:00

Location: BEBEL HS213

**Invited Talk**

MO 8.1 Tue 14:00 BEBEL HS213

**Selected Personal Highlights of Electron Collision Work** — ●MICHAEL ALLAN — Department of Chemistry, University of Fribourg, Switzerland

The research in Fribourg is a continuation of the ingenious experiment of Franck and Hertz, the 100th anniversary of which we celebrate this year, as well as a continuation of later classical work of researchers like George Schulz or Helmut Ehrhardt. The talk will present a personal retrospective of few Fribourg experiments, performed in part in collaboration with the Kaiserslautern group of Hartmut Hotop, experiments which I believe the early pioneers would have appreciated. They will include older experiments where instrumental progress permitted insight into phenomena such as dipole-bound resonances, electron-driven proton transfer, or excitation of vibrational Fermi-resonances. More recent experiments where detailed information on the nuclear and autodetachment dynamics of temporary molecular negative ions is gained from 2-dimensional electron energy loss spectra will also be mentioned. Finally, some of the current trends of the electron collision field will be indicated.

MO 8.2 Tue 14:30 BEBEL HS213

**Laser-assisted electron scattering in strong-field ionization of dense water vapor by few-cycle laser pulses** — ●MARTIN WILKE, RUBA AL-OBAYDI, ALEXANDRE MOGUILJEVSKI, ALEXANDER KOTHE, JAN METJE, IGOR YUREVICH KIYAN, and EMAD FLEAR AZIZ — Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq) Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin and Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin, Germany

Strong-field ionization of dense water gas was studied by means of angle-resolved time-of-flight electron spectroscopy. In contrast to diluted gases where above-threshold ionization (ATI) and high-order ATI (HATI) of single molecules dominate electron emission a collective effect of radiation absorption by neighboring particles known as laser-assisted electron scattering (LAES) was observed. This study was realized irradiating the vicinity of a liquid-microjet in a high vacuum chamber by 8-cycle near-infrared (1450 nm) laser pulses. Due to this combination strong-field photoelectron spectroscopy at liquid interfaces under high vacuum condition was facilitated.

MO 8.3 Tue 14:45 BEBEL HS213

**Molecular Electronic Imaging via Laser Tunnelling** — ●CHRISTOPHER T L SMEENK<sup>1</sup>, LADAN ARISSIAN<sup>2</sup>, ALEXEI V SOKOLOV<sup>3</sup>, KEVIN F LEE<sup>1,3</sup>, MICHAEL SPANNER<sup>1</sup>, ANDRE STAUDTE<sup>1</sup>, DAVID M VILLENEUVE<sup>1</sup>, and PAUL B CORKUM<sup>1</sup> — <sup>1</sup>Joint Lab for Attosecond Science, Ottawa, Canada — <sup>2</sup>University of New Mexico, Albuquerque, USA — <sup>3</sup>Texas A & M University, College Station, USA

Photoionization by intense, infrared laser pulses occurs via a tunnelling process. The photo-electrons emitted in laser tunnelling provide insight into atomic and molecular orbitals, much in the same way that the tunnelling current in a scanning tunnelling microscope (STM) gives information about surfaces. Laser STM therefore provides an avenue to unite the Ångström scale spatial resolution of tunnelling with femtosecond temporal resolution of optical pulses, allowing for new kinds of microscopy on the sub-atomic length and time scales.

We use circularly polarized femtosecond laser pulses at 800 nm to control and image N<sub>2</sub>, O<sub>2</sub>, and benzene. A non-resonant pump laser pulse prepares a rotational wavepacket allowing us to align the molecular axis in the lab frame. A precisely timed probe pulse singly ionizes the aligned molecules. By recording the emitted photo-electron spectrum in the molecular frame of reference, we show how laser tunnelling probes the symmetry and local electron density in the highest-occupied-molecular-orbital. Our results on these prototypical  $\Sigma$  and  $\Pi$  bonded molecules suggest how a laser STM could be applied to image dynamics on the sub-atomic scale.

MO 8.4 Tue 15:00 BEBEL HS213

**Orbital mixing and charge transfer in aqueous ferric and ferrous aqueous solutions** — ●JIE XIAO, ISAAK UNGER, RONNY GOLNAK, BERND WINTER, NÚRIA LLOBERA VILA, MARVIN POHL, EDLIRA SULJOTI, and EMAD F. AZIZ — Department of Functional Materials in Solution, BESSY II, Helmholtz Zentrum Berlin, Berlin, Germany

Charge transfer processes in Fe<sup>3+</sup> and Fe<sup>2+</sup> aqueous solutions were

analyzed based on combined energy-resolved photon and electron detections following soft X-ray excitation and ionization of a liquid microjet in vacuum. From the Auger-electron spectra and X-ray emission spectra, we access the ultrafast electron delocalization between ionic solute and water solvent. Experimentally, iron-water interactions are unequivocally identified through strong and orbital-specific intensity variations of the resonant photoelectron (RPE) spectra, and we also discuss how RPE spectra correlate with the respective X-ray emission spectra. Different Auger-decay channels, involving valence electrons versus deeper bound electrons, and X-ray emissions were investigated to reveal the state-dependent charge delocalization in iron ionic aqueous solution. Fe<sup>3+</sup>(aq) is found to exhibit larger charge transfer than Fe<sup>2+</sup>(aq). Our experimental results will be discussed with the help of DFT calculations.

MO 8.5 Tue 15:15 BEBEL HS213

**The effect of ligand field symmetry on charge transfer process: x-ray absorption and emission investigation on Fe L edge of iron porphyrins** — ●MARVIN POHL, JIE XIAO, RONNY GOLNAK, KAAAN ATAK, CHRISTOPH SCHWANKE, EDLIRA SULJOTI, and EMAD AZIZ — Department of Functional Materials in Solution, BESSY II, Helmholtz Zentrum Berlin, Germany

Iron porphyrin is the central and functional part existing in many vital proteins in biological system. The iron ion is the actual active site catalyzing a variety of complicated chemical reactions in which the iron 3d orbitals are strongly involved. Soft X-ray spectroscopy is an ideal tool to probe local electronic structure, which has recently been implemented by our team for the investigation of applied materials in liquid phase. Two iron porphyrin complexes with different side groups, iron octaethylporphyrin chloride (FeOEPCL) and iron tetraphenylporphyrin chloride (FeTPPCL), dissolved in solvent dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) have been investigated in flow cell by x-ray absorption and emission spectroscopy on Fe L edge. Their liquid phase resembles the real situation in biological system. The different delocalization extents of the certain Fe 3d orbital over the ligand N atoms under the x-ray excitation were revealed in the XAS and XES spectra of the two porphyrin molecules. The respective ligand field symmetry was found responsible for the various Fe 3d orbital overlapping with the ligand N 2p orbital in these two molecules which plays a significant role in the charge transfer process.

MO 8.6 Tue 15:30 BEBEL HS213

**Dissociative photoionization of 1,4-di-tert-butyl-1,4-azaborine** — ●FABIAN HOLZMEIER<sup>1</sup>, MELANIE LANG<sup>1</sup>, PATRICK HEMBERGER<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland Süd, 97074 Würzburg, Deutschland — <sup>2</sup>Swiss Light Source, Paul-Scherrer-Institut, 5232 Villigen PSI, Schweiz

Boron containing organic molecules play an important role for applications in optoelectronics and biomedicine. By synthesizing a 1,4-azaborine derivative, 1,4-di-tert-butyl-1,4-azaborine, inorganic chemists have found a synthetic route for an interesting, novel class of molecules. In an iPEPICO-experiment (imaging Photoelectron Photoion Coincidence) at the Swiss Light Source the photoionization of 1,4-di-tert-butyl-1,4-azaborine was investigated using VUV synchrotron radiation. The ionization energy of this molecule could be determined by threshold photoelectron spectroscopy, as well as the energetics of excited states in the cation. In addition, dissociative photoionization (DPI) was observed at higher photon energies. Several parallel and sequential dissociation channels were identified. The appearance energies of the fragment ions yield information on the chemical bonding. Using a RRKM rate theory approach the experimental data on the DPI to the three most important channels was modeled and accurate appearance energies were determined.

MO 8.7 Tue 15:45 BEBEL HS213

**Threshold Photoionization of the 2-methylallyl radical** — ●MELANIE LANG<sup>1</sup>, FABIAN HOLZMEIER<sup>1</sup>, INGO FISCHER<sup>1</sup>, and PATRICK HEMBERGER<sup>2</sup> — <sup>1</sup>Institut of Physical and Theoretical Chemistry, Am Hubland Süd, D-97074 Würzburg, Germany — <sup>2</sup>Molecular Dynamics Goup, Paul Scherrer Institut (PSI), CH-5232 Villigen PSI, Switzerland

Small radicals like 2-methylallyl are supposed to be reactive interme-

diates in combustion processes. Combustion-relevant molecules can be detected by photoionization in flames on-line. To assign a structure requires the knowledge of the ionization energy (IE) of the investigated reactive species. For this purpose we created 2-methylallyl by vacuum flash pyrolysis from 2-bromo-3-propene.

We obtained a gas phase TPES (threshold photoelectron spectrum) with an adiabatic IE of 7.88 eV for the singlet cationic state with several vibrational bands. Furthermore we detected the triplet cation at 9.55 eV, 1.67 eV above the adiabatic ionization energy.