

MO 11: X-ray Spectroscopy

Time: Wednesday 11:00–12:45

Location: HS 3044

MO 11.1 Wed 11:00 HS 3044

Photon-recoil imaging: Nonlinear X-ray physics in molecules — ●L. GERMEROOTH¹, M. AGÅKER², T. BAUMANN³, R. BOLL³, A. DE FANIS³, S. EISEBITT⁴, M. GÉNÉVRIEZ⁵, V. KIMBERG⁶, H. LEE¹, E. MARIN-BUJEDO⁵, T. MAZZA³, M. MEYER³, J. MIKOSCH¹, Y. OVCHARENKO³, S. PATCHKOVSKII⁴, D. REISER³, J.-E. RUBENSSON², J. SÖDERSTRÖM², P. SCHMIDT³, B. SENFTLEBEN³, A. SENFTLEBEN¹, S. USENKO³, and U. EICHMANN⁴ — ¹Universität Kassel — ²Uppsala University — ³XFEL Hamburg — ⁴MBI Berlin — ⁵UCLouvain — ⁶KTH Stockholm

Non-linear Raman spectroscopy was originally developed for narrow-band lasers. It has since become important in the spectroscopy and microscopy of technological and biological processes. Stimulated Raman scattering with optical femtosecond lasers is routinely used to excite coherent vibrational and rotational wavepackets. The advance of ultrabright FELs enabled the extension of non-linear physics to the X-ray domain. Some of us have recently established photon-recoil imaging as a background-free technique to detect stimulated X-ray Raman scattering (SXRS) [1]. This process is similar to STIRAP, a form of state-to-state coherent control well known in the optical domain. Here we extend the pioneering experiments on Neon atoms to molecules. Near and far-off resonance SXRS in CO molecules populates efficiently an electronically excited long-lived metastable final state. Demonstration of far-off resonance SXRS in molecules opens new possibilities to study site-selective non-linear processes avoiding spontaneous decays. [1] Eichmann et al., *Science* 369, 1630 (2020)

MO 11.2 Wed 11:15 HS 3044

Testing the potential energy curves of the H₂ B-X system using its Condon diffraction bands — ●ADRIAN PETER KRONE¹, PHILIPP SCHMIDT², JOHANNES VIEHMANN¹, NIKLAS GOLCHERT¹, LUTZ MARDER¹, DANA BLOSS¹, CATMARNA KÜSTNER-WETEKAM¹, PETER BAUMGÄRTEL³, ANDREAS HANS¹, and ARNO EHRESMANN¹ — ¹Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Deutschland — ²European XFEL, Holzkoppel 4, 22869 Schenefeld, Deutschland — ³Helmholtz-Zentrum Berlin, BESSY II, Abteilung Optik und Strahlrohre, Albert-Einstein-Str. 15, 12489 Berlin, Deutschland

The H₂ B-X system is investigated using its Condon diffraction bands in order to test for a shift between the independently calculated electronic potential energy curves of the B and X electronic states. The Condon diffraction bands for the rovibronic states B (v' = 8, 9, ..., 13, J' = 0) are calculated from literature potentials, to which internuclear distance shifts are applied. Data from a first measurement of the H₂ photon-excitation photon-emission map is analyzed and compatible with the unmodified literature potentials. Planned future measurements will significantly improve the accuracy and uncertainty.

MO 11.3 Wed 11:30 HS 3044

X-ray absorption of CF₄ driven by x-ray free-electron laser — ●RUI JIN¹, ADAM FOUADA², ALEXANDER MAGUNIA¹, MARC REBHOLZ¹, ALBERTO DE FANIS³, KAI LI², GILLES DOUMY², JAN-ERIK RUBENSSON⁴, MARIA NOVELLA PIANCASTELLI⁵, MARC SIMON⁵, THOMAS BAUMANN³, MICHAEL STRAUB¹, SERGEY USENKO³, YEVHENIY OVCHARENKO³, TOMMASSO MAZZA³, NINA ROHRINGER^{6,7}, MICHAEL MEYER³, LINDA YOUNG^{2,8}, CHRISTIAN OTT¹, and THOMAS PFEIFER¹ — ¹MPIK, Heidelberg — ²Argonne National Laboratory, USA — ³European XFEL, Schenefeld — ⁴Uppsala University, Sweden — ⁵Sorbonne Universités, Paris — ⁶DESY, Hamburg — ⁷Universität Hamburg — ⁸University of Chicago, USA

X-ray absorption spectroscopy (XAS) is widely used to study atomic and molecular structure and dynamics, especially at the core level. X-ray free electron lasers (XFEL) have introduced coherent, high-brilliance, and ultrashort laser pulses with tunable energies, thereby enabling the study of multiphoton x-ray matter interactions. In this work, the EuXFEL is combined with a grating spectrometer for a single-pulse transient absorption study of the intermediate electronic states arising from multiphoton-induced molecular dynamics in CF₄. The central photon energy is tuned to initiate dynamics with and without producing fluorine K-holes. The spectra are measured at different FEL intensities to study multiphoton effects. Two main findings are:

(1) neutral fluorine atoms are observed within the pulse duration (40 fs), and (2) short-lived molecular fragments with fluorine 1s-core hole state are observed for high intensities. Precise atomic and molecular structure calculations as well as semi-classical molecular dynamics are used to interpret the results. Overall, this study demonstrates the potential of XFEL-driven transient-absorption spectroscopy to study ultrafast multiphoton dynamics of molecular systems.

MO 11.4 Wed 11:45 HS 3044

Simulation of X-ray photoelectron spectroscopy in atoms, molecules, and clusters: Core-electron excitation from ab initio many-body approach — ●ISKANDER MUKATAYEV¹, GABRIELE D'AVINO^{2,3}, FLORIENT MOEVUS¹, BENOÎT SKLÉNARD^{1,4}, VALERIO OLEVANO^{2,3,4}, and JING LI^{1,4} — ¹Université Grenoble Alpes, CEA, Leti, F-38000, Grenoble, France — ²Université Grenoble Alpes, F-38000 Grenoble, France — ³CNRS, Institut Néel, F-38042 Grenoble, France — ⁴European Theoretical Spectroscopy Facility (ETSF)

X-ray photoelectron spectroscopy (XPS) technique, measuring directly core-electrons binding energies (BEs), provides information about electronic structure, chemical bonding, and stoichiometry for molecules/solids. This work presents the benchmark study of core electrons BEs in noble gas atoms between theories, including density functional theory (DFT), Hartree-Fock (HF) and many-body theory perturbation theory (GW approach) against experiments first, pointing out significant improvement of computed BEs from HF/DFT to GW. Furthermore, XPS of noble gas clusters with 3000 atoms were studied with embedded many-body theory to estimate the environmental polarization effect on relative BEs (chemical shifts). An analytical formula derived from classical electrostatics accurately describes these polarization effects, aligning well with experimental XPS for noble gas clusters. Finally, by investigating the core-electron excitation in carbon 1s among various molecules, we found that the main contribution to chemical shift comes from classical electrostatic interaction and is one order of magnitude larger than the correlation effects.

MO 11.5 Wed 12:00 HS 3044

Soft X-Ray-induced Dimerization of Methane — ●SIMON REINWARDT¹, IVAN BAEV¹, PATRICK CIESLIK¹, KAROLIN BAEV², TICIA BUHR³, ALEXANDER PERRY-SASSMANNSHAUSEN³, STEFAN SCHIPPERS³, ALFRED MÜLLER³, FLORIAN TRINTER⁴, JENS VIEFHAUS⁵, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Deutschland — ²Deutsches Elektronen-Synchrotron, Hamburg, Deutschland — ³Justus-Liebig-Universität Gießen, Gießen, Deutschland — ⁴Fritz-Haber-Institut, Berlin, Deutschland — ⁵Helmholtz-Zentrum Berlin für Material und Energie, Berlin, Deutschland

Carbon 1s photo excitation of methane, CH₄ and subsequent multimerization in CH₄ gas has been studied using the PIPE ion-trap setup [1] at PETRA III of DESY. Photoions resulting from the decay of the 1s vacancy are stored within the ion trap so that they can undergo reactions with the surrounding neutral methane molecules. The experimental results clearly show that the initial photoionization event leads to the formation of reaction products with up to three carbon atoms [2]. Accordingly, such addition reactions can play an important role in the formation of larger molecular ions in planetary ionospheres. A better understanding of photoinduced reactions forming larger molecules is essential for understanding the chemistry and chemical composition of atmospheres such as those of exoplanets, whose investigation is planned with celestial observatories like the James Webb Space Telescope.

[1] S. Reinwardt et al., *Rev. Sci. Instrum.* **94**, 023201 (2023).[2] S. Reinwardt et al., *Astrophys. J.* **952**, 39 (2023).

MO 11.6 Wed 12:15 HS 3044

Multi-electron emission from irradiated iodide anion in solution — ●YUSAKU TERAO, DANA BLOSS, GABRIEL KLASSEN, JOHANNES VIEHMANN, ADRIAN KRONE, NIKLAS GOLCHERT, ARNO EHRESMANN, and ANDREAS HANS — Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel

Radiation effects in solvated matter is of great interests, since many aspects of them are still poorly understood and better knowledge can be beneficial for radiation protection and radiation therapy. Recently, interatomic/intermolecular processes, that transfer deposited

excess energy or charge from the initially ionized size to so surrounding water molecules, were newly discovered. Some of these mechanisms have been experimentally observed in our group for the decay of the ionized Mg dication in aqueous solution by multi-electron coincidence spectroscopy. Here, we focused on iodide anion in solution, which has a large photoionization cross-section at its 3d ionization region and decays by multiple Auger steps, competitors to interatomic/intermolecular processes. For a better understanding of complex decay processes of irradiated atoms and molecules in solution, multi-electron emission from iodide anion in aqueous solution by ionizing 3d iodide electrons was studied by combining the liquid micro jet technique and multi-electron coincidence spectroscopy.

MO 11.7 Wed 12:30 HS 3044

Solvated pyrimidine molecules as donor or acceptor of X-ray induced intermolecular energy transfer — •DANA BLOSS¹, FLORIAN TRINTER^{2,3}, NIKOLAI V. KRZYHEVOI⁴, ALEXANDER KULEFF⁴, LORENZ S. CEDERBAUM⁴, ARNO EHRESMANN¹, and ANDREAS HANS¹ — ¹Institute of Physics and Center for Interdisciplinary Nanostruc-

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We investigated the effect of the presence of an aqueous environment for small bio-relevant organic molecules after their exposure to X-ray irradiation in a photoelectron-ion-ion coincidence experiment performed at the P04 beamline of PETRA III. In the decay of electronic inner-shell vacancies located in the solvated pyrimidine itself or in the water environment of the molecule we found evidence for intermolecular energy transfer in both directions. These processes can protect the molecule from reaching dicationic states via Auger decay and their inevitable fragmentation. The observations are compared with the results of theoretical calculations for a deeper understanding of the occurring effects.