

MO 21: Molecular Physics with X-rays

Time: Friday 11:00–13:00

Location: F102

MO 21.1 Fri 11:00 F102

X-ray induced luminescence for DNA molecules in aqueous solution via nitrogen core ionization — ●YUSAKU TERAO¹, YOSHIKI KUMAGAI¹, ISSEI SUZUKI¹, TAKAHIRO TSUCHIYA¹, MASATOSHI UKAI¹, AKINARI YOKOYA², KENTARO FUJII², YOSHIHIRO FUKUDA³, and YUJI SAITOH⁴ — ¹Dept. of Applied Physics, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan — ²Institute for Quantum Life Science, Naka-gun, 319-1195, Ibaraki, Japan — ³SPRING-8 Service Co. Ltd., Tatsuno-shi, Hyogo 679-5165, Japan — ⁴Synchrotron Radiation Research Center, Hyogo 679-5148, Japan

Radiation effect to biological matter can lead to various kinds of damages on a molecular level. However, a protective environmental effect of surrounding water is expected to play an important role to suppress damage inductions. To get to know about the protective environmental effect, we studied intermediate species along the reaction pathway of core ionized DNA molecules in aqueous solution. We conducted X-ray induced luminescence spectroscopy for nucleotides in aqueous solution using monochromatic soft X-rays in the nitrogen K-shell region at SPRING-8 BL23SU. We obtained the excitation spectra of total luminescence yields for four nucleotides samples and the filtered luminescence spectra as well. Those results indicated the luminescence from parent base species which are maintained even after the Auger ionization of core-hole state, implying significant emission processes of their excess charge and energy can take place in the relaxation pathway.

MO 21.2 Fri 11:15 F102

Experimental investigation of solvated metal ions after X-ray-induced ionization — ●DANA BLOSS¹, FLORIAN TRINTER^{2,3}, UWE HERGENHAHN², ARNO EHRESMANN¹, and ANDREAS HANS¹ — ¹Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Universität Kassel, Heinrich-Platt-Straße 40, 34132 Kassel — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ³Institut für Kernphysik, Goethe-Universität, Max-von-Laue-Str.1, 60438 Frankfurt am Main

Exploration of the microscopic response of biological systems to ionizing radiation is a key to understanding radiation damage on a molecular level. Of special interest in this context are low-energy electrons (LEEs) with energies below 30 eV, which are known to be genotoxic. One source of these LEEs upon X-ray irradiation are secondary processes like the interatomic Coulombic decay (ICD) - an energy-transfer process - or the electron-transfer-mediated decay (ETMD) - a charge-transfer process. Both have attracted attention as a source of efficient localized emission of LEEs close to the site of ionization and been studied intensely throughout the last decades in clusters and solutions. A multi-step cascade of ICD and ETMD processes upon X-ray ionization of microsolvated metal ions, e.g., Mg²⁺, was predicted. We experimentally investigate this theoretically predicted LEE emission for Mg²⁺, Ca²⁺ and Al³⁺ solutions at different synchrotron facilities with a combination of liquid microjets and coincident electron detection.

MO 21.3 Fri 11:30 F102

Tracking the birth of the solvated electron with x-rays — ●ARTURO SOPENA MOROS¹, LUDGER INHESTER¹, and ROBIN SANTRA^{1,2} — ¹Center for Free-Electron Laser Science, DESY — ²Department of Physics, Universität Hamburg

The attention that the solvated electron, e⁻(aq), has received over the past half century, both from theory and experiment, is well justified due to its fundamental role in the chemistry of water. Its high reactivity and its role in radiation damage of DNA [1] have important implications in physics, chemistry, and biology. Albeit the apparent simplicity of this system, a unified picture of the solvation process remains elusive. In this theoretical study, we explore the capabilities of time-resolved x-ray absorption spectroscopy (XAS) as a new tool to investigate the ultrafast dynamics of the formation of the solvated electron.

We used classical and ring-polymer molecular dynamics together with a recently published neural network-based force field trained on MP2 electronic structure calculations [2] to simulate the evolution of an excess electron placed in bulk water. The simulations reveal that

e⁻(aq) localizes in a cavity with a radius of 2.4 Å within 1.6 ps. For snapshots of the simulations, we have calculated the XAS using the ab-initio electronic structure toolkit XMOLECULE [3]. The calculations reveal that it is possible to trace the solvation dynamics of the electron in liquid water by inspecting distinct features in the time-resolved XAS.

[1] Chem. Rev. 112, 5553 (2012). [2] Nat. Commun. 12, 766 (2021). [3] Struct. Dyn. 2, 041707 (2015)

MO 21.4 Fri 11:45 F102

Chemical effects on the dynamics of organic molecules irradiated with high intensity x rays — ●SOURAV BANERJEE^{1,2}, ZOLTAN JUREK^{1,2,3}, MALIK MUHAMMAD ABDULLAH², and ROBIN SANTRA^{1,2,3,4} — ¹Center for Free-Electron Laser Science (CFEL), Notkestr. 85, 22607 Hamburg, Germany — ²Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany — ³The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany — ⁴Department of Physics, Universität Hamburg, Notkestr. 9-11, 22607 Hamburg, Germany

High intensity ultra-short x-ray pulses, produced by X-ray free-electron lasers (XFEL), induce complex dynamics in matter. Over the past several years, numerical simulations for various molecular systems and clusters have successfully been performed with the classical molecular dynamics (MD) based hybrid code XMDYN.

The present study [1] extends the XMDYN toolkit to capture the effect of charge transfer and chemical bonds. The chemical bonds are approximated by the reactive force field (ReaxFF) description. The system under examination is a small organic molecule, glycine, which, being an amino acid, has relevance to general biological systems. Effects on key quantities, e.g., time dependent charge states, etc. are analyzed. The present study suggests that the chemical effects are of importance for realistically achievable fluences, whereas bondless simulation is accurate for high fluence.

[1] S. Banerjee et al., Struct. Dyn. 9, 054101 (2022) and references therein.

MO 21.5 Fri 12:00 F102

Probing the UV-induced ultrafast dynamics of thionucleobases with time-resolved x-ray absorption at the Free Electron Laser FLASH — ●F LEVER^{1,2}, D MAYER^{1,2}, D PICCONI⁶, S ALISAUSKAS², F CALEGARI², S DUESTERER², C EHLERT⁴, R FEIFEL³, M KUHLMANN², T MAZZA⁷, J METJE¹, M ROBINSON^{1,2}, R SQUIBB³, A TRABATTONI^{2,8}, M WARE⁵, P SAALFRANK¹, T WOLF⁵, and M GHUER^{1,2} — ¹Universität Potsdam, Germany — ²DESY, Germany — ³University of Gothenburg, Sweden — ⁴Heidelberg Institute for Theoretical Studies, Germany — ⁵SLAC, USA — ⁶University of Groningen, Netherlands — ⁷XFEL, Germany — ⁸IQO, Germany

Light-induced ultrafast reactions play a fundamental role in the photochemistry of DNA, as they can lead to the formation of lesions in the genetic code. Thionucleobases are sulfur-substituted nucleobases that show an increased rate of UV-induced lesion formation. In a previous work by this group, we have investigated the photoinduced dynamics of 2-thiouracil (2-tUra) via time resolved x-ray photoemission [1,2]. In this work, we study the ultrafast dynamic 2-thiouracil in a UV-pump, x-ray probe experiment at the Free Electron Laser FLASH. The molecule is excited by the pump pulse in the S2 state ($\pi\pi^*$ character), and its dynamic is probed by a delayed x-ray pulse that is resonant with 2p and 2s excitations of the sulfur atom. The localized probe on the sulfur allows us to image the excitation of the dark S1 ($n\pi$) state within a 100fs time scale, and to follow oscillations in its population fraction with a period of 200fs. [1] Mayer et al. Nat Comm 13, 198 (2022) [2] Lever et al. J. Phys. B 54 014002 (2021)

MO 21.6 Fri 12:15 F102

Creating Electronic Molecular Movies Using Time-Resolved X-Ray Photoelectron Spectroscopy at Free-Electron Lasers — ●DENNIS MAYER¹, FABIANO LEVER¹, DAVID PICCONI², SKIRMANTAS ALISAUSKAS¹, AGATA AZZOLINI³, FRANCESCA CALEGARI^{3,4,5}, GIOVANNI CIRMI^{1,4}, STEFAN DÜSTERER¹, ULRIKE FRÜHLING¹, ALICE GREEN^{6,7}, INGMAR HARTL¹, MARION KUHLMANN¹, TOMMASO MAZZA⁶, STEFFEN PALUTKE¹, SEBASTIAN SCHULZ¹, ANDREA TRABATTONI^{3,8}, ATIA TUL NOOR¹, and MARKUS GÜHR¹ — ¹DESY, Hamburg, Germany — ²University of Groningen, The Netherlands —

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Recently, we were able to extend the chemical shift concept to excited state molecular dynamics [1]. Here, we present a follow-up experiment performed at FLASH, showing C 1s time-resolved photoelectron spectra of 2-thiouracil after UV excitation. The photoelectron spectra show a strong shift towards lower binding energies suggesting a charge movement towards the pyrimidine ring. These measurements verify the concept of the excited-state chemical shift [1] and pave the way to create electronic molecular movies for the UV-induced relaxation using time-resolved x-ray photoelectron spectroscopy.

[1] Mayer et al., Nature Communications 13, 198 (2022)

MO 21.7 Fri 12:30 F102

Tracking Conical Intersections with Nonlinear X-ray Raman Spectroscopy — ●DEEPENDRA JADOUN and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Albanova University Centre, SE-106 91 Stockholm, Sweden

Conical intersections (CIs) play a vital role in processes such as the event of vision, and DNA damage from sunlight. A CI appears in a molecule when electronic and nuclear motions are strongly coupled, and it acts as a funnel that guides a molecule from one electronic state to another. Substantial efforts have been made toward understanding such non-adiabatic phenomena. X-ray Raman techniques have been proposed in the past to investigate the presence of a CI in molecules.

We propose a two-dimensional Raman probe scheme that uses a visible/infrared pulse and an ultra-short X-ray Raman probe pulse. The visible/infrared pulse interaction creates a coherent superposition of electronic states in the molecule. Probing the coherent superposi-

tion using ultra-short X-ray pulses allows to visualize the dynamic energy separation between electronic states throughout the photochemical process. The lifetime of the coherent superposition created using the infrared pulse can be read directly from two-dimensional Raman spectra. Therefore, the method aids to the observation of multiple indicators of a conical intersection and may allow for a more detailed study of non-adiabatic dynamics in molecules.

MO 21.8 Fri 12:45 F102

X-FEL induced Coulomb explosion: Advanced analysis of coincident ion momenta — ●BENOÎT RICHARD^{1,2,3}, ROBIN SANTRA^{1,2,3}, and LUDGER INHETER^{1,2,3} — ¹CFEL, DESY, Hamburg, Germany — ²CUI, Hamburg, Germany — ³Universität Hamburg, Hamburg, Germany

Intense x-ray pulses from x-ray free-electron lasers (X-FEL) ionize small molecular systems leading to their violent dissociation into several atomic fragments on a femtosecond time scale. Recent experiments with the 2-iodopyridine molecule have demonstrated that measuring the momenta of only 3 fragments in coincidence is sufficient to distinguish individual ion contributions. [1] However, combining all the different n-particle coincidence data, where in each a different subset of ion fragments is detected, into a joint distribution is not trivial.

We present a general method to perform such analysis. We demonstrate its application using simulation data of the X-FEL-induced Coulomb explosion of 2-iodopyridine and use it to extract correlations between ion momenta. We show that such correlations contain fingerprints of collisions during the explosion. [2] Moreover, we demonstrate that this data is related to the structure of the molecule just before being hit by the x-ray pulse that destroyed it.

[1] R. Boll, J. Schäfer, B. Richard et al. 2022. Nat. Phys. 18, 423-428

[2] B. Richard et al. 2021. J. Phys. B: At. Mol. Opt. Phys. 54 194001