

MO 23: Ultrafast Dynamics III (joint session MO/A)

Time: Friday 14:30–16:30

Location: F102

MO 23.1 Fri 14:30 F102

Photodissociation dynamics of CH₂Br — •LILITH WOHLFART, CHRISTIAN MATTHAEI, and INGO FISCHER — Julius-Maximilians-Universität Würzburg, 97074 Würzburg, Germany

Bromomethyl belongs to the class of organic halogen radicals. Therefore, it can potentially influence the atmosphere by reacting with the ozone layer and causing its depletion similar to HCFCs. The photoionization of bromomethyl was already investigated by several groups, including Steinbauer and coworkers. They determined the ionization energy and structure with VUV synchrotron radiation and investigated the dissociative photoionization. To obtain further insights into the dissociation of bromomethyl, we analyzed the fragments of the radical using velocity map imaging (VMI).

CH₂Br-NO₂ was used as a precursor for the halogenated methyl radical, because the weaker C-NO₂ bond can be cleaved through pyrolysis. Subsequently, laser light with 235 nm was deployed to dissociate the formed CH₂Br radical. The major dissociation pathway gave the methylene and bromine fragments which were detected with SPI at 118 nm and [1+1]-REMPI at 356 nm respectively. With velocity map ion imaging, the translational kinetic energy distribution of the photofragments was determined. The recorded images of the bromine and methylene photofragments showed an anisotropic distribution, implying a direct dissociation.

MO 23.2 Fri 14:45 F102

Fragmentation of fulminic acid, HCNO, following core excitation and ionization — •DOROTHEE SCHAFFNER¹, MARIUS GERLACH¹, TOBIAS PREITSCHOPF¹, EMIL KARAEV¹, FABIAN HOLZMEIER², JOHN BOZEK³, and INGO FISCHER¹ — ¹Universität Würzburg, 97074 Würzburg — ²imec, 3001 Leuven, Belgium — ³Synchrotron SOLEIL, 91190 Saint-Aubin, France

In 2008 fulminic acid, HCNO, was first detected in space in the starless cores B1, L1544 and L183.^[1] Its isomer HNCO is also ubiquitous in interstellar systems.^[2] Due to their composition of biogenic elements, the CHNO isomers have been proposed to play a prebiotic role as intermediates for organic life. Investigating the molecules' interaction with X-ray radiation is critical to understand their fate in space.

Here we report a study of the fragmentation of fulminic acid in the gas phase after resonant core excitation and core ionization on the K-edge of carbon, oxygen and nitrogen. The ionic fragmentation products formed after the auger decay were investigated at the PLEIADES beamline at the synchrotron SOLEIL using Auger-electron/photoion coincidence spectroscopy. Branching ratios were determined which show a site-selective fragmentation upon ionization and excitation. Different fragmentation tendencies could be related to differences in the occupation of the auger final states.

[1] N. Marcelino, J. Cernicharo, B. Tercero, E. Roueff, *Astrophys. J.* **2008**, 690, L27-L30.

[2] Nguyen-Q-Rieu, C. Henkel, J. M. Jackson, R. Mauersberger, *Astron. Astrophys.* **1991**, 241, L33-L36.

MO 23.3 Fri 15:00 F102

Ultrafast dynamics of OCS — •WUWEI JIN¹, SEBASTIAN TRIPPEL^{1,3}, HUBERTUS BROMBERGER^{1,3}, TOBIAS RÖHLING¹, KAROL DLUGOLECKI¹, SERGEY RYABCHUK¹, ERIK MÅNSSON¹, ANDREA TRABATTONI¹, VINCENT WANIE¹, IVO VINKLÁREK⁴, FRANCESCA CALEGARI¹, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Center for Ultrafast Imaging, Universität Hamburg — ⁴Department of Chemical Physics and Optics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Imaging ultrafast photochemical reactions with atomic-spatial and femtosecond-temporal resolution is one of the ultimate goals of physical chemistry and the molecular sciences [1]. We will discuss our ultrafast (sub 10 fs) time-resolved study of the photodissociation dynamics of carbonyl sulfide (OCS) after UV-photoexcitation at $\lambda = 267$ nm. OCS was purified and separated from the helium seed gas using the electrostatic deflector [2]. The UV-induced dynamics was studied through strong field ionization using a velocity map imaging spectrometer in combination with a Timepix3 camera [3].

[1] J Onvlee, S Trippel, and J Küpper, *doi:10.1038/s41467-022-33901-w*, arXiv:2103.07171 [physics]

[2] YP Chang, D Horke, S Trippel, and J Küpper, *Int. Rev. Phys. Chem.* **34**, 557 (2015), arXiv:1505.05632 [physics]

[3] H Bromberger, *et al.*, *J. Phys. B Atomic Mol. Opt. Phys.* **55**, 144001 (2022), arXiv:2111.14407 [physics]

MO 23.4 Fri 15:15 F102

Ultrafast dynamics in iodomethane induced by few-fs ultraviolet pulses — •SERGEY RYABCHUK^{1,2}, LORENZO COLAIZZI^{2,3}, ERIK P. MÅNSSON³, KRISHNA SARASWATHULA³, JESÚS GONZÁLEZ-VÁZQUEZ⁴, VINCENT WANIE³, ANDREA TRABATTONI^{3,5}, FERNANDO MARTÍN^{4,6,7}, and FRANCESCA CALEGARI^{1,2,3} — ¹The Hamburg Centre for Ultrafast Imaging, Hamburg, Germany — ²Universität Hamburg, Hamburg, Germany — ³DESY, Hamburg, Germany — ⁴Universidad Autonoma de Madrid, Madrid, Spain — ⁵Leibniz Universität Hannover, Hannover, Germany — ⁶IMDEA-Nanoscience, Madrid, Spain — ⁷IFIMAC, Madrid, Spain

Iodomethane has been extensively used as a model system to study photodissociation dynamics by ultraviolet (UV) light excitation. The molecule is prompted to rapid fragmentation along the C-I bond due to the repulsive character of the neutral states accessed by single UV photon absorption in the energy range of 4.1-5.4 eV. In this work, we used 4 fs UV pulses with central energy of 4.9 eV as a pump with delayed few-cycle infrared pulses, probing the dynamics via multi-photon ionization. The dynamics of methyl and iodine fragments allow us to track the field-free wavepacket evolution on the neutral states with unprecedented time resolution. Moreover, the experimental observations combined with a theoretical study revealed that the implementation of such ultrashort pulses allows for the production of an intact parent ion with a 5-fs lifetime, preventing molecular cleavage. This becomes possible only in a narrow time window close to the Frank-Condon regime before the dissociation takes place.

MO 23.5 Fri 15:30 F102

Photoemission chronoscopy of the Iodoalkanes — •CHRISTIAN SCHRÖDER, MAXIMILIAN POLLANKA, PASCAL SCIGALLA, ANDREAS DUENSING, MICHAEL MITTERMAIR, MAXIMILIAN FORSTER, MATTHIAS OSTNER, and REINHARD KIENBERGER — Physik Department, Technische Universität München, James-Frank-Str. 1, 85748 Garching, Germany

Photoemission timing measurements on primary and secondary iodoalkanes up to 2-iodobutane are performed in the gas phase and reveal an unexpected and yet unexplained dependency of the 14d photoemission time delay τ_{14d} on the molecular species.

The experiment is carried out at photon energies around the giant resonance in the 14d $\rightarrow \epsilon f$ channel, which is expected to be largely indifferent to its chemical environment. If true, observable differences in the 14d photoemission time between molecules should be a direct consequence of differences experienced by the leaving photoelectron during its propagation alone, and not due to a distortion of its initial bound state.

We find a strong variation of τ_{14d} between different molecules, but no clear correlation with the attached functional group's size as it has been suggested by previous theoretical studies (S. Biswas et al., *Nature Physics* **16** (2020)).

MO 23.6 Fri 15:45 F102

X-ray diffractive imaging of UV-induced ultrafast dynamics in CF₂I₂ — •NIDIN VADASSERY^{1,3}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Department of Physics, Universität Hamburg — ³Department of Chemistry, Universität Hamburg

Disentangling chemical dynamics, including the traversal of transition states, provides important insight into (bio)chemical processes. Roaming for example, a proposed ultrafast mechanism occurring in unimolecular photodissociation, follows an unusual reorientation motion after the excitation near bond dissociation energies [1]. Difluorodiodomethane (CF₂I₂), has shown roaming mechanism following excitation with 350 nm light.

X-ray pulses generated at XFELs provide the opportunity to study

such ultrafast rearrangements on the atomic scale with femtosecond resolution by diffractive imaging. Here, we present a computational proposal of the time-resolved coherent x-ray diffractive imaging of the photodissociation of CF_2I_2 using CMI-diffract, an in-house python software to predict and analyze molecular-ensemble diffraction patterns[2]. We also detail efforts to produce a pure sample of CF_2I_2 using the electric deflector in the eCOMO end-station, in preparation for UV-pump x-ray-probe studies at EuXFEL.

[1] D. Townsend, *et al.*, *Science* **306**, 1158, (2004)

[2] J. Küpper, *et al.*, *Phys. Rev. Lett.* **112**, 083002, (2014), arXiv:1307.4577

MO 23.7 Fri 16:00 F102

Dynamics of H_2 -roaming processes, H_3^+ formation, and cationic fragmentation in ethanol and aminoethanol initiated above and below the double-ionization threshold —

•AARON NGAI¹, JAKOB ASMUSSEN², BJÖRN BASTIAN², MATTEO BONANOMI^{3,4}, CARLO CALLEGARI⁵, MICHELE DI FRAIA⁵, KATRIN DULITZ^{1,6}, RAIMUND FEIFEL⁷, SARANG GANESHAMANDIRAM¹, SEBASTIAN HARTWEG¹, SIVARAMA KRISHNAN⁸, AARON LAForge⁹, FRIEDEMANN LANDMESSER¹, BEN LTAIEF LTAIEF², MORITZ MICHELBACH¹, NITISH PAL⁵, OKSANA PLEKAN⁵, NICOLAS RENDLER¹, FABIAN RICHTER¹, AUDREY SCOGNAMIGLIO¹, TOBIAS SIXT¹, RICHARD SQUIBB⁷, AKGASH SUNDARALINGAM², FRANK STIENKEMEIER¹, and MARCEL MUDRICH² — ¹Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Germany — ²Department of Physics and Astronomy, Aarhus University, Denmark — ³Dipartimento di Fisica and CIMaNa, Università degli Studi di Milano, Italy — ⁴Istituto di Fotonica e Nanotecnologie, CNR-IFN, Milano, Italy — ⁵Elettra - Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy — ⁶Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria — ⁷Department of Physics, University of Gothenburg, Sweden — ⁸Department of Physics, Indian Institute of Technology Madras, Chennai, India — ⁹Department of Physics, University of Connecticut, US

The trihydrogen cation (H_3^+) is the simplest and one of the most abundant triatomic cation in the universe. It plays a crucial role in interstellar gas-phase chemistry as it facilitates molecule-forming chemical reactions. Building upon the work of Ekanayake [1], we further investigated the competition between pathways leading to H_3^+ formation in

doubly ionized ethanol and 2-aminoethanol molecules and their respective clusters using time-resolved XUV-UV pump-probe spectroscopy. While formation of H_3^+ in doubly-ionized alcohol molecules is due to intramolecular H_2 -roaming, H_3^+ formation in clusters likely occurs via more complicated intermolecular pathways involving fragmentation and recombination of excited ionic fragments e.g. in nanoplasmas [2]. We compare results between XUV-photoionization below and above the double-ionization threshold, including the lifetimes of intermediate states. Notably, we report the absence of H_3^+ -formation in aminoethanol, and the suppression of H_2 -roaming in ethanol clusters.

[1] Ekanayake, N. *et al.* *Nature Comm.* **9**, 5186 (2018).

[2] Michiels, R. *et al.* *Phys. Chem. Chem. Phys.* **22**, 7828 (2020).

MO 23.8 Fri 16:15 F102

Probing well aligned molecular environments on surfaces in the time-domain — •PASCAL SCIGALLA¹, CHRISTIAN SCHRÖDER¹, SVEN PAUL¹, PETER FEULNER², and REINHARD KIENBERGER¹ — ¹Chair for laser and x-ray physics, E11, Technische Universität München, Germany — ²Surface and Interface Physics, E20, Technische Universität München, Germany

We report on the photoemission timing measurements of well-aligned iodomethane and -ethane molecules on a Pt111 surface. In this set of experiments we clock the $I4d$ photoemission of iodine against the Platinum valence photoemission using the attosecond streak camera technique, allowing the extraction of a relative photoemission delay. As the $I4d$ photoemission in the selected energy range is dominated by a giant resonance in the $I4d \rightarrow ef$ channel its photoemission time is mostly unaffected by its chemical environment. Thus any observed change in the photoemission delay can be attributed to the traversed potential landscape of the molecule. By carefully selecting the detection angle and crystal surface coverage we can reliably choose whether only parts of the molecule or its entirety was traversed by the detected photoelectron wavepackets. It is furthermore possible to investigate the influence of slight coverage variations onto the observed photoemission delay. Planned, complementary scattering simulations will be used to gain deeper insight into the observations with the goal to establish photoemission timing experiments as an efficient and accurate means to study molecular environments on surfaces.