

MO 6: Molecular Spectroscopy of Liquid Jets II

Time: Tuesday 11:00–13:00

Location: HS XV

MO 6.1 Tue 11:00 HS XV

Determination of chemical kinetics from diffusion limited chemical reactions in free-flowing liquid flat-jets — ●HANNS CHRISTIAN SCHEWE¹, NICOLAS VELASQUEZ², BRUNO CREDIDIO², AARON GHRIST², ANDREAS OSTERWALDER³, GERARD MEIJER², BERND WINTER², and CHRISTOPHE NICOLAS⁴ — ¹J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ³Institute for Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland — ⁴Synchrotron SOLEIL, Gif-sur-Yvette Cedex, France

We present a methodology for conducting chemical kinetics studies at the interface between two (aqueous) solutions. When two streams from two microchannels impinge under laminar flow conditions, a flat-leaf structure forms, thereby creating an inherent liquid-liquid interface between the two solutions flowing along each other. Initially, the chemiluminescence from a luminol oxidation reaction is employed to demonstrate that the fluids do not exhibit turbulent mixing in the first leaf of a flat-jet, thus providing a clean interface between the liquids from the impinging jets [1]. Next, we examine the (de-)protonation dynamics of amine or carboxylic groups, which can be studied using either X-ray absorption spectroscopy to characterize electronic structure changes or Raman microscopy to quantify vibrational changes. We illustrate how kinetic data is obtained wherein diffusion represents the sole transport process responsible for mixing across the liquid-liquid interface. [1] H.C.Schewe et. al. J. Am. Chem. Soc. 2022, 144, 17

MO 6.2 Tue 11:15 HS XV

Electronic dynamics created at conical intersections and its dephasing in aqueous solution — ●YI-PING CHANG¹, TADAS BALCIUNAS^{1,2}, ZHONG YIN², MARIN SAPUNAR³, BRUNO TENORIO⁴, ALEXANDER PAUL⁵, SHOTA TSURU⁶, HENRIK KOCH⁵, JEAN-PIERRE WOLF¹, SONIA CORIANI⁴, and HANS JAKOB WÖRNER² — ¹Université de Genève, Switzerland — ²ETH Zürich, Switzerland — ³Ruder Boskovic Institute, Croatia — ⁴DTU, Denmark — ⁵NTNU, Norway — ⁶Ruhr University Bochum, Germany

Understanding the electronic dynamics of molecular systems is important for many fields in photophysics and photochemistry. This is especially challenging in the vicinity of a conical intersection, where the Born-Oppenheimer approximation breaks down. In this work [1], we present two experimental breakthroughs: (1) the observation of electronic and vibrational dynamics corresponding to a circular rearrangement of the electronic structure created by conical intersection dynamics and (2) the sub-40 fs dephasing induced by aqueous solvation. Using a state-of-the-art table-top HHG source covering the entire water window, we performed time-resolved X-ray absorption spectroscopy (XAS) of single-UV-photon-excited liquid and gaseous pyrazine samples. At the carbon and nitrogen K-edges, we observed different non-adiabatic dynamics between gas and liquid phases, showing large-amplitude rearrangement of the electronic structure caused by the conical intersection and dephasing of electronic dynamics due to solvation. [1] Y.-P. Chang*, T. Balciunas*, Z. Yin*, M. Sapunar*, B.N.C. Tenorio*, A. Paul* et al. Nat. Phys. (2024).

MO 6.3 Tue 11:30 HS XV

Impact of solvation on the ultrafast ring-opening dynamics of furfural — ●JOEL TRESTER^{1,2}, PENGJU ZHANG^{1,3}, ROBIN SANTRA^{2,4,5}, LUDGER INHETER^{2,5}, and HANS JAKOB WÖRNER¹ — ¹Laboratory of Physical Chemistry, ETH Zürich, Zurich, Switzerland — ²Center for Free-Electron Laser Science CFEL, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ³Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China — ⁴Department of Physics, Universität Hamburg, Hamburg, Germany — ⁵Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

We investigated the photoinduced ring-opening dynamics of furfural in both the gas phase and pure liquid phase using a table-top monochromatized high-harmonic source combined with heatable in-vacuum sample delivery and liquid micro-jet technology. By leveraging a UV-pump XUV-probe scheme we have performed time-resolved photoelectron spectroscopy (TRPES) to access all outer-valence molecular orbitals. By achieving excellent agreement with hybrid QM/MM surface-

hopping molecular dynamics simulations, this study provides the first comprehensive comparison of such dynamics between the gas and liquid phases under identical experimental conditions. Notably, we reveal that the underlying mechanism of ring opening changes significantly from the gas to the liquid phase, both in timescale and pathways. This work opens new perspectives in the field of ultrafast photochemical dynamics, by enabling a detailed exploration of solvent effects on nuclear dynamics triggered by electronic relaxation on ultrafast timescales.

MO 6.4 Tue 11:45 HS XV

Multielectron coincidence spectroscopy of solvated iodide ion — ●YUSAKU TERAO, DANA BLOSS, GABRIEL KLASSEN, JOHANNES VIEHMANN, ADRIAN KRONE, NIKLAS GOLCHERT, ARNO EHRESMANN, and ANDREAS HANS — Universität Kassel, Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSA), Heinrich-Plett-Strße 40, 34132 Kassel

Radiation effects in solvated matter are of great interest, since many aspects of them are still poorly understood and better knowledge can be beneficial for radiation protection and radiation therapy. Especially, relaxation processes between core-shell ionized solvated samples and surrounding water molecules are worth investigating. They are called interatomic/intermolecular processes that dissipate deposited energy and charge to neighboring atoms and molecules. Here, the final states of initially ionized targets can be less charged compared to the case that the target is an isolated system where Auger decay most likely occurs. For a better understanding of complex decay processes of irradiated atoms and molecules in solution, Auger cascade processes, that create highly charged final states, and its suppression via competitive interatomic/intermolecular decay processes, of core ionized iodide anion in aqueous solution was investigated. Results are obtained by a combination of liquid microjet technique and multielectron coincidence spectroscopy.

MO 6.5 Tue 12:00 HS XV

Photoelectron spectroscopy from microjets and flatjets — ●BRUNO CREDIDIO¹, DOMINIK STEMER¹, HANNS CHRISTIAN SCHEWE², SEBASTIAN MALERZ¹, MICHELE PUGINI¹, FLORIAN TRINTER¹, HENRIK HAAK¹, UWE HERGENHAHN¹, GERARD MEIJER¹, SREPHAN THÜRMER³, and BERND WINTER¹ — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²Czech Academy of Sciences, Prague, Czech Republic — ³Kyoto University, Kyoto, Japan

Among its various successful applications, LJ-PES (Liquid Jet Photoelectron Spectroscopy) enables the study of biological molecules in their environment of relevance, i.e., aqueous phase. Despite that, the curved geometry of a LJ had hampered, e.g., soft X-ray absorption studies. This has prompted the development of planar flatjets (FJs) which has now evolved into a well-matured technique. Several experimental approaches have been realized, and their applicability to PES will be evaluated. Furthermore, the larger surface area of FJs is well suited for exploring angular-resolved scattering of a molecular beam from a planar liquid, including aqueous solution. The FJ geometry is also superior when detecting Photoelectron Angular Distributions (PADs). Our other focus here is on the unique ability to generate a flowing well-defined liquid-liquid interface in vacuum, acting as a steady-state chemical reactor and defined reaction time, accessible by IR, optical and X-ray photon detection. I will finally discuss the generation of an electric potential across the FJ that may be used to modify solution-vacuum structural and electric properties.

MO 6.6 Tue 12:15 HS XV

Time-resolved photoelectron spectroscopy of a biomimetic photoswitch NHIP — ●OLEG KORNILOV¹, XINGJIE FU², MATTHEW MGBUKWU², ALINA KHODKO¹, JEREMIE LEONARD², and STEFAN HAACKE² — ¹Max Born Institute, Berlin, Germany — ²Institute of Physics and Chemistry of Materials, Strasbourg, France

Time-resolved photoelectron spectroscopy (TRPES) using XUV pulses from high-order harmonic generation is the state-of-the-art powerful experimental technique, which can probe transient electronic states of relaxing molecules down to their electronic ground states, follow dynamics through optically *dark* states and conical intersections. In this contribution we will report on the recent progress in studies of ultrafast isomerization of N-protonated indanylidene pyrroline Schiff

bases (NHIP) using TRPES. This chromophore mimics photoisomerization properties of retinal Schiff bases in rhodopsin. We record ultrafast relaxation of the electronically excited molecule solvated in water, which appears to be nearly ballistic, and discuss the observations in comparison with the transient absorption spectroscopy results published previously. Measurements presented here open route to direct observation of ultrafast relaxation via conical intersections, which are typically not visible in all-optical time-resolved measurements.

MO 6.7 Tue 12:30 HS XV

Field Resolved Spectroscopy of flat liquid sheets — ●KILIAN SCHEFFTER^{1,2}, ANCHIT SRIVASTAVA^{1,2}, ANDREAS HERBST^{1,2}, SOYEON JUN^{1,2}, and HANIEH FATTAHI^{1,2} — ¹Max Planck Institute for the Science of Light, Erlangen, Germany — ²Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany

We present femtosecond fieldoscopy at near-petahertz frequencies in flat liquid sheets. The interaction between femtosecond optical pulses and molecules in a sample results in the imprint of a molecular response on the electric field of the excitation pulses. By resolving the electric field of the transmitted pulses with attosecond precision, we achieve broadband background-free spectroscopic detection of molecules with high dynamic range and sensitivity. In liquid-phase measurements, the container's material often introduces absorption, dispersion, birefringence and nonlinearity, which limits the detection sensitivity. To overcome these challenges, we developed a 3D printed nozzle capable of producing micrometer thick liquid sheets, enabling direct spectroscopic measurements of liquids. This talk will present the integration of the liquid jet into field-resolved spectroscopy, allowing for the measurement of Raman, overtone, and combination bands of liquid samples

across the entire fingerprint region.

MO 6.8 Tue 12:45 HS XV

Liquid sample delivery at EuXFEL — ●JOANA VALERIO, MARCO KLOOS, KATERINA DÖRNER, HUIJONG HAN, ELISA DELMAS, AGNIESZKA WRONA, GISEL PEÑA, ALEXANDER GIERKE, ELIZABETH GALTRY, and JOACHIM SCHULZ — European XFEL, Schenefeld, Germany

One of the most distinctive characteristics of the European XFEL is the high repetition rate of the X-ray pulses. The intra-train repetition rate of up to 4.5 MHz represents a significant challenge for the sample injection systems. The Sample Environment & Characterisation (SEC) group of the EuXFEL is developing sample delivery systems for all scientific instruments, in addition to providing user support in sample preparation, characterization, and delivery.

Cylindrical microjet injection systems remain the most prevalent type of sample injection system employed in the fields of soft and hard X-ray science. Nevertheless, this methodology is subject to several intrinsic constraints. For example, the curved surface of the nozzle presents a challenge in determining the path length of the X-rays within the sample. The sample must have a well-defined and controllable thickness of just a few tens of microns or less, and the efficiency of sample usage requires the use of micron-sized liquid sheet jets. In light of these limitations, various 3D-printed nozzle designs have been developed to produce micron-thick and highly stable microscopic flat sheet jets. These designs are based on colliding and impingement nozzle designs, to make this technology more widely available to users, especially for spectroscopy.