

Winter School of Experimental Molecular Dynamics & Kinetics

22 | February
23 |
24 | 2021

<https://winterschool.cc/experimental-molecular-dynamics-and-kinetics>

Artwork by: Greg Stewart/SLAC National Accelerator Laboratory

Program Overview

Monday, 22 January 2021

- 3:00 pm – 3:15 pm CET **Opening**
- 3:15 pm – 4:45 pm CET **Patrick Hemberger** (PSI): *How can we capture reactive and elusive intermediates to unveil reaction mechanisms in catalysis?*
- 5:00 pm – 6:30 pm CET **Thomas Bierkandt** (DLR): *Photoionization molecular-beam mass spectrometry to study combustion chemistry in flames*
- 6:45 pm – 8:15 pm CET **Gabriela Schlau-Cohen** (MIT): *Ultrafast non-adiabatic dynamics in biomolecular systems*
- 8:15 pm – 9:15 pm CET **Posterblitz Session I**

Tuesday, 23 February 2021

- 12:00 pm – 1:30 pm CET **Jie Yang** (SLAC): *Ultrafast electron diffraction as a tool for the study of structural dynamics in gas phase molecules*
- 1:45 pm – 3:00 pm CET **Posterblitz Session II**
- 3:15 pm – 4:45 pm CET **Chris Milne** (EuXFEL): *Probing Ultrafast chemical dynamics using X-rays*
- 5:00 pm – 6:30 pm CET **Michael Meyer** (EuXFEL): *Small Quantum Systems (SQS) instrument at the European X-ray Free Electron Laser*
- 6:45 pm – 8:15 pm CET **Matteo Lucchini** (Politecnico Milano): *Attosecond optical techniques for the study of ultrafast dynamics in solids*

Wednesday, 24 February 2021

- 3:15 pm – 4:45 pm CET **Helen Fielding** (UCL): *Liquid-microjet photoelectron spectroscopy of organic molecules*
- 5:00 pm – 6:30 pm CET **Jan Verlet** (Durham): *Photoelectron spectroscopy as a window into electron driven chemistry*
- 6:45 pm – 8:15 pm CET **Robert Seidel** (BESSY): *Electrolyte-to-metal transition of electrons dissolved in ammonia and water*
- 8:15 pm – 8:30 pm CET **Closing Remarks**

Each talk is 60 min and at least 20 min for questions and discussions.

How can we capture reactive and elusive intermediates to unveil reaction mechanisms in catalysis?

Patrick Hemberger – Beamline scientist Swiss Light Source

Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institute, Villigen, Switzerland

Catalytic processes are all abundant in our daily life. From exhaust gas aftertreatment to production of chemicals, fuels and pharmaceuticals, catalysis is a key technology of the 21st century. Catalysts increase reaction rates and are responsible for making a chemical process more efficient and selective to yield only the desired products. To optimize this process chemists and chemical engineers vary the process conditions, like temperature, pressure or the catalyst, and observe the outcome. If this cook-and-look approach however fails, only a detailed description of the chemical reaction mechanism provides the necessary insight to control a catalytic reaction. Reactive intermediates, such as radicals, carbenes or ketenes, hold the key to unveiling the mechanism. If we understand the reaction pathways, we may be able to manipulate them in a targeted way.

The detection of radicals is however not trivial as standard chemical analysis tools like NMR and GC/MS fail. In this lecture I will introduce three analytical dimensions (AD) to unveil reactive species in catalytic processes utilizing photoionization techniques with vacuum ultraviolet (VUV) synchrotron radiation.

Mass spectrometry (MS, 1st AD) is universal, as ionization is always allowed, and exhibits a very high sensitivity, due to charged particle detection. *Photoelectron spectroscopy* (PES, 2nd AD), on the other hand, sheds light on vibrationally resolved transitions, which can be compared to reference spectra or simulated using Franck Condon spectral modeling, to enable even isomer-selective assignment. Furthermore, *Ion velocity map imaging* (VMI, 3rd AD) overcomes sampling effects and helps to distinguish fragmentation from direct ionization. These three analytical dimensions are united in imagining photoelectron photoion coincidence (iPEPICO) spectroscopy. We will discuss several recent examples, where these techniques helped to extract deep mechanistic insights from catalytic processes:

Lignin is an abundant material in biomass, full of valuable phenols and aromatics, which are accessible utilizing catalytic fast pyrolysis. By detection of fulvenone, a highly reactive ketene species, we could unveil the reaction mechanism and identified important reaction pathways towards prototypical fuels (benzene) and fine chemicals (phenols).

Photoionization molecular-beam mass spectrometry to study combustion chemistry in flames

Thomas Bierkandt – Researcher German Aerospace Center

Institute of Combustion Technology, German Aerospace Center (DLR), Stuttgart, Germany

Understanding the chemistry of novel fuels is essential for reducing pollutants and predicting relevant technical properties. One of the standard environments to investigate combustion processes in flames is the laminar premixed low-pressure flame. In this kind of flame, the flame front is stretched by the low pressure to enable a good spatial resolution and reaction pathways can be described one-dimensional. The molecular-beam mass spectrometry (MBMS) is an established technique to identify and quantify combustion species in such a reactive flow. A gas sample is directly withdrawn by a quartz nozzle from the flame and due to the two-stage expansion a molecular beam is formed and all reactions are instantly “frozen”. This invasive sampling method allows even the detection of radicals, which play an important role in combustion. For example, fuel consumption is mostly initiated by H and OH radicals. Besides the detection of radicals, there is a special interest to disentangle isomeric combustion species. Isomers have exactly the same mass, but different chemical structures, and may follow different reaction pathways in flames. In combination with tunable vacuum ultraviolet (VUV) synchrotron radiation and time-of-flight mass spectrometry, isomer-selective identification of many combustion species can be achieved by measuring photoionization efficiency (PIE) curves. The first MBMS experiment using the advantages of single-photon ionization with synchrotron radiation was put into operation at the Advanced Light Source (ALS) in Berkeley, USA. However, isomers can only be distinguished if their ionization energies differ more than the energy resolution of the photons used in the ionization process and their PIE curves have characteristic, non-overlapping features with a good signal-to-noise ratio. Difficulties in identification can arise with more than two isomers present. Here, the imaging photoelectron photoion coincidence (iPEPICO) spectroscopy can improve the species identification of isomers. Each electron can be assigned to a single photoionization event, which enables the measurement of mass-selected threshold photoelectron (ms-TPE) spectra. The data can be filtered to consider only electrons with nearly zero kinetic energy to improve selectivity and get information about the internal energy of the ion. The ms-TPE spectrum obtained in this way shows vibrational transitions from the neutral to a specific ionic state. Such a spectrum is like a spectroscopic fingerprint of a species and adds a new analytical dimension in species identification. The first flame experiment with the benefits of iPEPICO spectroscopy was demonstrated in 2013 at the Swiss Light Source (SLS) in Villigen, Switzerland.

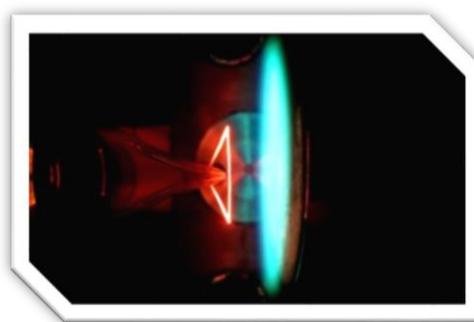


Figure 1. Temperature measurement by a thermocouple in a nozzle-perturbed flame.

Ultrafast non-adiabatic dynamics in biomolecular systems

Gabriela Schlau-Cohen – Professor of Chemistry, MIT

Massachusetts Institute of Technology, Cambridge, USA

Electronic excited states control energy for applications such as light harvesting and molecular electronics. Coherent transfer via non-adiabatic transitions allows extremely rapid and directed energetic relaxation. We introduce ultrabroadband multidimensional spectroscopy to map out the spectral and temporal dynamics of these transitions [1]. First, in the primary antenna protein in green plants, LHCII, we identified a debated dark state (S_x) that mediates energetic relaxation. Absorbed energy in higher lying states (S_2) undergoes a non-adiabatic transition in <20 fs into S_x , which can then rapidly transfer energy to the S_1 states that drive biochemical reactions. These non-adiabatic dynamics enable rapid and efficient collection of sunlight from across the visible region of the solar spectrum [2]. Second, in the widely used fluorescent marker, Cy3, we identify a nonradiative decay pathway via a previously unknown dark state formed within ~ 1 ps of photoexcitation. Our experiments, in combination with electronic structure calculations, suggest that the generation of the dark state is mediated by picosecond vibrational mode coupling, likely via a conical intersection. Identification of the structural elements responsible provides a blueprint for efforts to improve the fluorescence properties [3]. Collectively, these experiments reveal the ability of non-adiabatic transitions to control photophysical pathways in molecular systems.

[1] M. Son et al., *Opt. Exp.* 2017 **25**, 18950. <https://doi.org/10.1364/OE.25.018950>

[2] M. Son et al., *Chem* 2019 **5**, 575. <https://doi.org/10.1016/j.chempr.2018.12.016>

[3] S. M. Hart et al., *J. Phys. Chem. Lett.* 2020 **11**, 5000. <https://doi.org/10.1021/acs.jpcllett.0c01201>

Ultrafast electron diffraction as a tool for the study of structural dynamics in gas phase molecules

Jie Yang – Staff scientist SLAC

SLAC National Accelerator Laboratory, Menlo Park, USA

Excited state molecular dynamics often involve complex interplay between nuclei and electrons on femtosecond timescales. Since the birth of ultrafast lasers, time-resolved spectroscopy has been serving as the workhorse for experimental studies. In time-resolved spectroscopy, electronic dynamics are directly probed, while nuclear structural dynamics are often indirectly inferred. Time-resolved diffraction (TRD), including both ultrafast electron diffraction (UED) and time-resolved X-ray diffraction, is a complementary experimental tool that is selectively sensitive to the nuclear structural dynamics. With recent breakthroughs in temporal resolution, a series of high quality “molecular movies” are made using TRD experiments, where atomic motions are directly captured in photoexcited molecules.

In this presentation, I will give a comprehensive overview on the experimental methodology of UED, with the focus on its applications to small molecules in the gas phase. I will introduce the fundamental concept of UED, review the early stage and recent development in experimental techniques, and discuss the scientific applications with several concrete examples. In addition, I will introduce the recent progress where nuclear and electronic dynamics are simultaneously captured in a single UED dataset and, finally, give a brief outlook on the future development of gas phase UED methodology.

Probing Ultrafast Chemical Dynamics using X-rays

Chris Milne – Group leader FXE, EuXFEL

FXE group, European X-ray Free Electron Laser, Hamburg, Germany

TBA

Small Quantum Systems (SQS) Instrument at the European X-ray Free Electron Laser

Michael Meyer – Group leader SQS, EuXFEL

SQS group, European X-ray Free Electron Laser, Hamburg, Germany

The Small Quantum Systems (SQS) instrument is one of the six end-stations currently available at the European XFEL. This instrument is dedicated to investigations of non-linear phenomena and time-resolved studies of photo-induced dynamics in atoms, molecules, clusters, nanoparticles and bio-molecules upon irradiation with ultra-short and ultra-intense soft X-rays pulses. There are currently three experimental chambers available, which are dedicated to different approaches to interrogate small, atomic-like and large, nano-sized systems. In this lecture, I will first give a general overview of the SQS instrument, then describe the experimental capabilities of SQS including available spectrometers and detectors and highlight some of the experimental results from experiments performed at SQS during the first two years of operation. Additionally, I will present some recent instrumental upgrades for dynamical studies using a pump-probe excitation scheme based on the combination of x-rays and synchronized optical laser pulses or two X-ray pulses of different photon energies. Finally, I will outline the process of submitting proposals in order to perform experiments at SQS.

Attosecond optical techniques for the study of ultrafast dynamics in solids

Matteo Lucchini – Assistant Professor in Physical Engineering

Physics Department, Politecnico di Milano, Milan, Italy

TBA

Liquid-microjet photoelectron spectroscopy of organic molecules

Helen Fielding – Professor of Chemical Physics, UCL

Department of Chemistry, University College London, London, United Kingdom

In nature, light drives many important processes such as photosynthesis and vision. Light-driven processes are also important in technology, such as in nanoscale electronic devices. At the heart of all these processes are small chromophores that absorb light and, subsequently, undergo small-scale structural changes. Understanding the fundamental photophysics and photochemistry of the chromophores that determine the efficiency of light-driven processes in nature and technology is crucial for the rational design of new photomaterials for a range of applications such as photovoltaics and bioimaging. In addition to a detailed knowledge of the intrinsic electronic structures of these chromophores, it is important to have an understanding of the roles of their environments. Experimentally, the most direct way of probing electronic structure is through the measurement of electron binding energies using photoelectron spectroscopy (PES). Liquid-microjet UV PES is emerging as a valuable probe of the electronic structure of chromophores in solution. This tutorial-style lecture will include a brief review of the history of liquid-microjet photoelectron spectroscopy and an explanation of the challenges facing UV PES of liquids. It will include a description of the design and operation of the recirculating liquid-microjet PES instrument we have built at UCL for studying samples that are available in relatively small quantities and illustrative liquid-microjet PES measurements of fluorescent protein chromophores and their building blocks.

Photoelectron spectroscopy as a window into electron driven chemistry

Jan Verlet – Professor in Chemistry, Durham University

Department of Chemistry, Durham University, Durham, United Kingdom

I will discuss the chemical physics of electron-molecule reactions. Electrons are initially captured by electronic states of the anion that lie in the detachment continuum. The dynamics of these resonances determine the fate of the reaction. Electron spectroscopy has been used to probe the dynamics of resonances for many years. Here, I will show how anion photoelectron spectroscopy provides a complementary method to probe such reaction with some very important advantages, such as: mass-selection, angular distributions of the electrons and time-resolution. I will support the discussion with some recent examples.

Electrolyte-to-metal transition of electrons dissolved in ammonia and water

Robert Seidel – Young Investigator Group Leader, BESSY

Helmholtz Zentrum Berlin / BESSY, Berlin, Germany

What does it mean to be a metal and how is a metal formed? These seem like textbook questions with a simple answer – a metal is characterized by (quasi)free electrons which give rise to its high electric conductivity. In contrast to metals, ions in electrolytes are disordered and electrical conductivity even decreases with increasing ion concentration. So how does metallic behaviour arise from the many individual metal atoms dissolved in an electrolyte? At what concentration and exactly how does a conduction band form, and how do the electron orbitals behave during this process?

Together with colleagues from FHI Berlin, USC Los Angeles, IOCB Prague, Charles University Prague, University of Kyoto, Humboldt-University Berlin and from the Helmholtz-Center Berlin we investigated the electrolyte-to-metal transition spectroscopically for the first time.

We studied alkali metals dissolved in liquid ammonia representing archetypal systems to explore the transition from localized and dilute (blue) electrolytes at low concentrations to bronze colored metallic solutions with higher concentrations of excess electrons. Photoelectron spectroscopy (PES) represents an ideal tool for establishing the electronic structure pertinent to this transition. PES as an ultra-high vacuum technique has long been thought to be incompatible with volatile liquids, until the technique of liquid microjets was developed for water and aqueous solutions. Our very recent development of a cryostat-controlled liquid ammonia microjet [1,2] opened the door to PES studies of alkali metal – liquid ammonia systems using soft X-ray synchrotron radiation.

In this way, we have captured for the first time the photoelectron signal of excess electrons in liquid ammonia.[3] They are characterized by a peak at ~ 2 eV pertinent to ammoniated electrons and di-electrons. This peak then broadens asymmetrically toward higher binding energies upon increasing the alkali metal concentration, gradually forming a band with a sharp Fermi edge in the spectrum, as is characteristic of metals, accompanied as well by signals associated with collective excitations (plasmons) – characteristic of free metallic electrons.

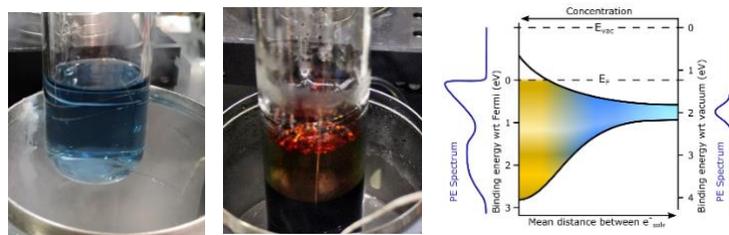


Figure 1: With increasing alkali concentration in liquid ammonia (blue – low concentration to bronze/golden – high concentration), gradually a conduction band is forming in the photoelectron spectrum.

[1] Buttersack et al., *J. Am. Chem. Soc.* 2019, **141**, 1838-1841. <https://doi.org/10.1021/jacs.8b10942>

[2] Buttersack et al., *Rev. Sci. Instrum.* 2020, **91**, 043101. <https://doi.org/10.1063/1.5141359>

[3] Buttersack et al., *Science* 2020, **368**, 1086-1091. <https://doi.org/10.1126/science.aaz7607>

Contact: winterschool.exp.mol.dyn.kin@gmail.com

Organizing Committee

- Anja Röder
Max Born Institute, Berlin, Germany
anja.roeder@mbi-berlin.de
- Camila Bacellar
Paul Scherrer Institute, Villigen, Switzerland
camila.bacellar@psi.ch
- Fabian Holzmeier
IMEC, Leuven, Belgium
fabian.holzmeier@imec.be
- João Pedro Figueira Nunes
University of Nebraska-Lincoln, Lincoln, USA
joao-pedro.figueira-nunes@unl.edu
- Rico Mayro Tanyag
Technical University Berlin, Berlin, Germany
tanyag@tu-berlin.de

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