

Photon Tools for Physical Chemistry 2019

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Book of Abstracts

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Welcome

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Ultrafast electronic and molecular dynamics induced by XFEL pulses

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In March 2012, Spring-8 Angstrom Compact free electron LASER (SACLA), started user operation in Japan [1]. We set up a program to investigate ultrafast electronic and nuclear dynamics in atoms, molecules and clusters induced by intense ($\sim 50 \mu\text{J}/\mu\text{m}^2$), ultrashort (~ 10 fs) pulses generated by SACLA. At photon energy of 5.0–5.5 keV, we could identify that Xe^{n+} with n up to 26 is produced, evidencing occurrence of deep inner-shell ionization and sequential electronic decay cycles repeated multiple times in the xenon atom within ~ 10 fs pulse duration [2]. The results for momentum-resolved multiple ion coincidence study on iodine-contained organic molecules (CH_3I , 5-iodouracil, CH_2I_2) illustrate that the charges are produced by the cycles of deep inner-shell ionization of the iodine atom and sequential electronic decay and spread over the entire molecule within 10 fs, leading to Coulomb explosion [3–5]. The measured momentum distributions and correlations are well reproduced by both classical and quantum mechanical MD simulations. The results for electron spectroscopy on argon and xenon clusters, with help of theoretical calculations, illustrate that nanoplasma are formed by the XFEL pulse, in tens of fs, and continuous thermal emission from the plasma occurs in ps [6]. The experiment also confirmed x-ray induced oligomer formation from rare-gas clusters [7]. We have carried out also XFEL pump-NIR probe experiments for xenon atoms and clusters [8], as well as iodine-contained organic molecules [9], at time resolution down to a few tens of femtoseconds, in order to probe the XFEL-induced ultrafast reaction in real time. The latest results will be shown and discussed. I am grateful to coauthors of Refs. [2–9] for their invaluable contributions and to the support by XFEL strategy program by MEXT, five-star alliance and IMRAM program.

- [1] T. Ishikawa et al., *Nature Photon.* 6, 540 (2012); M. Yabashi et al., *JPB* 46, 164001 (2013).
- [2] H. Fukuzawa et al., *PRL* 110, 173005 (2013); K. Motomura et al., *JPB* 46, 164024 (2013).
- [3] K. Motomura et al., *JPCL* 6, 2944 (2015).
- [4] K. Nagaya et al., *PRX* 6, 021035 (2016); K. Nagaya et al., *Faraday Discuss.* 194, 537 (2016).
- [5] T. Takanashi et al., *PCCP* 19, 19707 (2017).
- [6] T. Tachibana et al., *Sci. Rep.* 5, 073002 (2015); H. Fukuzawa et al., *JPB* 49, 034004 (2016).
- [7] Y. Kumagai et al. *PRX* 8, 031034 (2018).
- [8] Y. Kumagai et al., *PRL* 120, 223201 (2018).
- [9] H. Fukuzawa et al., (submitted).

Summary:

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Introduction

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Diffractive imaging of clusters and ultrafast dynamics

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Exciting clusters and nanodroplets with intense laser pulses provides a well-defined scenario to study the correlated dynamics of highly excited matter. We use diffractive imaging of single nanoparticles in free flight with XUV and X-ray free-electron lasers (FELs) to explore the light-induced dynamics with high spatial and temporal resolution. From the measured diffraction patterns the nanoparticles' structure can be determined, allowing to study such fragile and short-lived specimen as superfluid helium nanodroplets (Langbehn et al., accepted at PRL 2018) and the observation of structural changes, like e.g. ultrafast melting in metal clusters. But also the even faster electron dynamics change the scattering response of the irradiated cluster and can therefore in principle be traced by diffractive imaging.

With today's typical pulse duration of FEL pulses of 10-100 femtoseconds, it is not possible to resolve electron dynamics in time. Sub-femtosecond pulses are currently under development at FELs, e.g. at SwissFEL. Already today, isolated attosecond XUV pulses and attosecond pulse trains can be generated with high-harmonic-generation (HHG) sources based on intense femtosecond lasers, but they are typically orders of magnitude weaker than FELs. Thus, an important step towards attosecond diffractive imaging was taken by our demonstration of single-particle single-shot diffractive imaging of individual helium nanodroplets with a high-intensity HHG source (Rupp et al., Nature Communications 8, 493 (2017)).

In my talk I will introduce the method and its applications and discuss recent results from time-resolved diffraction imaging experiments using both FEL and HHG sources.

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The ultrafast soft x-ray and electron diffraction perspective on photophysics in the gas phase

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The conversion of light energy into other energy forms in molecules is the result of a concerted and ultrafast motion of electrons and nuclei, often under breakdown of the Born-Oppenheimer approximation. This talk is about ultrafast experiments aimed at resolving light induced ultrafast molecular dynamics with x-ray probe pulses using free electron lasers as well as relativistic electron pulses.

We present experiments on internal conversion of the nucleobase thymine, which we probe by femtosecond resonant x-ray spectroscopy at the oxygen K-edge. We deduce a less than 100 fs $\pi\pi \rightarrow n\pi$ transition, which plays a crucial role in the photoprotection of this nucleobase [1].

In addition, we present results from femtosecond electron diffraction experiments on electronically excited states of small molecules, that unravel wavepacket dynamics with Angstrom level spatial resolution and femtosecond domain temporal resolution [2,3].

[1] Probing ultrafast $\pi\pi/n\pi$ internal conversion in organic chromophores via K-edge resonant absorption, T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C.

Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch and M. Gühr, *Nature Communications* 8, 29 (2017)

[2] Diffractive Imaging of Coherent Nuclear Motion in Isolated Molecules

J. Yang, M. Guehr, X. Shen, R. Li, T. Vecchione, R. Coffee, J. Corbett, A. Fry, N. Hartmann, C. Hast, K. Hegazy, K. Jobe, I. Makasyuk, J. Robinson, M. S. Robinson, S. Vetter, S. Weathersby, C. Yoneda, X. Wang, M. Centurion, *Phys. Rev. Lett.* 115, 173002 (2016)

[3] Imaging CF₃I conical intersection and photodissociation dynamics with ultrafast electron diffraction, J. Yang, X. Zhu, T.J.A. Wolf, Z. Li, J.P.F. Nunes, R. Coffee, J.P. Cryan, M. Gühr, K. Hegazy, T.F. Heinz, K. Jobe, R. Li, X. Shen, T. Vecchione, S. Weathersby, K.J. Wilkin, C. Yoneda, Q. Zheng, T.J. Martinez, M. Centurion, X. Wang, *Science* 361, 64 (2018)

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Unravelling ultrafast dynamics of polycyclic aromatic hydrocarbons upon photoionization using extreme ultraviolet radiation

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Polycyclic aromatic hydrocarbons (PAHs) are assumed to be key players in interstellar chemistry [1]. Their interaction with energy-rich radiation can trigger the competing processes of ionization, fragmentation and dehydrogenation. Ultra-short pulses of ionizing radiation in a pump-probe experiment present a powerful tool to disentangle the underlying chemical processes that may occur

during these events in the interstellar medium.

In this work, we present results from our study of the ultrafast fragmentation of three medium sized PAHs - fluorene, phenanthrene and pyrene. These molecules were ionized using extreme ultraviolet radiation at 30.3 nm provided by the free-electron laser (FEL) at Hamburg, FLASH [2]. Their reaction dynamics in the femtosecond regime were probed using 800 nm NIR pulses which were temporally delayed relative to the pump FEL pulse. This allowed us to observe the time dependent yield of different ion channels produced during the interaction. The goal of these experiments was to determine the lifetimes of the excited cationic PAHs following extreme ultraviolet excitation, and to identify the preferred reaction pathways of these molecules under such conditions. Here, we will present recent insights from our analysis.

[1] EAS Publications Series, 2011, 46, 3.

[2] J. Phys. B, 2010, 43,194002

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Introduction

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Novel opportunities for physical chemistry: the Low Density Matter beamline at the FERMI Free Electron Laser

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Free-Electron-Lasers (FELs) in the EUV and XUV photon energy range have greatly expanded the feasibility range of experiments at the crossroad between tabletop lasers and synchrotrons, and promise the ultimate achievement of “molecular movies” capturing in particular the early steps of photochemical processes. The FERMI facility in Trieste (Italy) is unique in the FELs landscape because it has been designed as a seeded source, resulting in superior performances in terms of control and reproducibility of its light pulses. Of particular interest for spectroscopic applications are its broad tunability, wavelength purity (approaching the Fourier-transform limit, with sub-linewidth stability), short pulse duration and timing jitter. Transverse and temporal coherence are those expected from a true laser, and have been exploited in a series of pioneering experiments.

The Low Density Matter (LDM) beamline at FERMI has been serving the atomic, molecular and cluster science community since its opening at the end of 2012. Through the use of interchangeable supersonic jet sources, it offers the possibility of studying atoms and molecules (including aligned ones), as well as more exotic systems such as superfluid helium droplets or metallic nanoparticles. Ion and electron spectroscopies (time-of-flight; velocity map imaging) and coherent diffraction imaging are available in one of the few different standard configurations of the endstation. Users' equipment can be accommodated as well, and several experiments have also been performed in non-standard configurations. A synchronized infrared laser (with second- and third-harmonic generation capability) is available for optical+FEL, and a split-and-delay line for FEL-FEL, pump-probe experiments. The LDM beamline has worked in close synergy with the Machine Physics team to help characterize FERMI, and develop new modes of operation.

In this talk I will present the results of a few case studies performed at the LDM beamline as Users' experiments or as internal research and development, and some future perspectives for the physical chemistry community.

The results presented originate from the joint effort of many international laboratories and a large number of researchers, whose work is gratefully acknowledged.

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The FinEstBeAMS beamline at MAX IV laboratory

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The FinEstBeAMS is a materials and atmospheric science beamline located at the 1.5 GeV storage ring of the MAX IV Laboratory, Sweden. FinEstBeAMS received the first light on 24th of November 2017. Currently beamline is under commissioning, we expect to start regular user operation 2018.

The beamline covers a wide photon energy range, 4.3–1000 eV, and gives an opportunity to probe core and valence levels with a focused (0.1 × 0.1 mm) or defocused beam, produced by an elliptically polarizing undulator. The optical layout of the FinEstBeAMS beamline is based on the plane grating monochromator illuminated with collimated light. The beamline delivers 8×10^{13} ph/s – 1×10^{11} ph/s on sample with resolving power up to 10 000.

The FinEstBeAMS has three end stations: (i) gas-phase end station (Photoelectron-Photoion Coincidence Spectroscopy), (ii) FinEstLUMI (Photoluminescence Spectroscopy) and (iii) solid state end station (Ultraviolet and X-ray Photoelectron Spectroscopy).

The FinEstBeAMS allows to investigate atoms, molecules, clusters, nanoparticles, atmospheric solid or liquid particles in gas phase or deposited on substrate, fragmentation pathways of bio- and organic molecules, atmospheric processes, scintillators, surface composition of environmental liquids, steels, and nanomolecular layers on alloy surface.

Main funding for the FinEstBeAMS beamline comes from the Academy of Finland through the Finnish Research Infrastructure funding projects [1-3], from the European Union through the European Regional Development Fund [4] and from the University of Tartu.

[1] The parts of M. Huttula, E. Kukk, and J. Hölsä of the SR-MAXIV project, FIRI2010.

[2] FinEstBeAMS phase II –FIRI2013, University of Turku, University of Oulu and Tampere University of Technology.

[3] MAX IV Infrastructure –FinEstBeAMS Solid State Materials Research, FIRI2014, University of Turku, University of Oulu and Tampere University of Technology.

[4] E. Nömmiste project “Estonian beamline to MAX-IV synchrotron”, University of Tartu.

Summary:

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Development of a sensitive photoionization mass spectrometry apparatus for high-pressure gas-phase reactions**Author:** Leonid Sheps¹¹ Sandia National Lab**Corresponding Author:** lsheps@sandia.gov

Synchrotron-based tunable VUV photoionization mass spectrometry (PIMS) is a powerful analytical technique for nearly universal, sensitive, isomer-selective detection of chemical species. VUV-PIMS is routinely used to probe complex gas-phase and multiphase processes in a variety of sources such as flames, flow reactors, pyrolysis nozzles, and catalytic reactors. However, it has seen limited application to studies of chemistry at elevated pressures. The main reason for this is a fundamental limitation to the sensitivity of VUV-PIMS, associated with sampling from high-pressure environments.

In this talk I will describe a new, highly sensitive PIMS apparatus, coupled to a high-pressure laser photolysis reactor, operating at $P = 0.3 - 100$ bar and $T = 300 - 1000$ K. The mass spectrometer uses ionization in the high-density region of the sampling expansion, followed by custom ion optics that simultaneously achieve high mass resolution and high ion collection efficiency, while avoiding ion-molecule collisions. I will demonstrate the utility of the new approach using several examples of the detection of key products and intermediates in pressure-dependent reactions: $C_2H_5 + O_2$, $OH + CH_3O_2$, and the low-temperature combustion of tetrahydrofuran.

Summary:

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How Synchrotron Measurements Help Advance Attosecond Science**Author:** Fabian Holzmeier¹¹ Politecnico di Milano**Corresponding Author:** fabian.holzmeier@gmail.com

VUV and soft X-ray synchrotron beamlines dedicated to molecular photoionization experiments have recently received strong competitors in the form of new advanced light sources, such as free electron lasers (FELs) and table-top high harmonic generation (HHG) laser systems. While the former provide access to significantly higher light intensities and to a time-resolution of tens of femtosecond, HHG sources offer the prospect to study electronic dynamics on the attosecond time scale. It will be shown, however, that the complementarity of synchrotron experiments, providing a high spectral resolution, and ultrafast time-resolved experiments with HHG sources can be exploited to get a profound understanding of molecular photoionization.

Molecular Frame Photoelectron Angular Distributions (MFPADs) from inner-valence shell ionization of the NO molecule were investigated employing 3D-momentum electron ion coincidence spectroscopy at the Pléiades and Désirs beamlines of Synchrotron SOLEIL as well as at the new 10 kHz HHG beamline of ATTOLab (Paris-Saclay). MFPADs describe the emission direction of the photoelectron in a photoionization reaction with respect to the orientation of the molecule. They encode information on the symmetry of the bound and continuum states, on quantum interferences between ionization channels and the phase and polarization state of the ionizing light. A molecular polarimetry based on reference MFPADs obtained with synchrotron radiation was employed to characterize the complete polarization state of the new HHG attosecond beamline at ATTOLab during commissioning. Ultrafast time-resolved experiments employing an XUV attosecond pulse train pump and a delayed IR probe were then performed to obtain first insights into the angular dependence of time-delay in molecular photoionization encoded in MFPADs.

Nanoscale aggregates / 48**Introduction****Nanoscale aggregates / 26****Low-energy electron transport in water****Author:** Ruth Signorell¹¹ *ETH Zürich***Corresponding Author:** ruth.signorell@phys.chem.ethz.ch

Even though low-energy electron scattering in liquid water is of high relevance for the modelling of radiation damage processes, radiolysis, and the analysis of photoelectron spectra, detailed scattering data have so far neither been accessible by experiment nor by theory. For lack of liquid water data, current descriptions thus use the amorphous ice data and/or rescaled gas phase parameters to describe the scattering of low-energy electrons (LEEs) (< 50eV electron kinetic energy). The important parameters are the multiple differential cross sections (MDCs) with respect to electron kinetic energy, energy loss, and scattering angle, of all relevant scattering processes (elastic; inelastic (electron-phonon, electron-vibron, electron-electron)). Our recent determination of MDCs for liquid water from photoelectron spectroscopy provides a starting point for definite answers to fundamental questions regarding the electron dynamics in water.

Summary:**Nanoscale aggregates / 61****Probing the Electronic Structures and Interfacial Solvation Properties of Aqueous Nanoaerosols via VUV Photoelectron Spectroscopy****Author:** Chia Wang¹¹ *National Sun Yat-sen University***Corresponding Author:** chiawang@mail.nsysu.edu.tw

An in-depth understanding of the fundamental energetic and structural properties at or near the interface of nanoscaled aqueous aerosols is of fundamental and crucial importance in understanding the impacts of organic species, either of biogenic or anthropogenic origins in intervening the cloud formation microphysics and the intrinsic nature of clouds. To address these issues, we applied aerosol VUV photoelectron spectroscopy to investigate the valence electronic structures and interfacial characteristics of pure and several organic-containing aqueous nanoaerosols that are of atmospheric significance. Considering that many organic species emitted from anthropogenic activities may encounter fine water nanodroplets and form aqueous aerosols in the atmosphere, we studied the valence photoelectron spectroscopy of phenol and three dihydroxybenzene isomers including catechol, resorcinol, and hydroquinone aqueous nanoaerosols at varying pH conditions. It reveals that the hydration extents, pH values, deprotonation status, and numbers/relative arrangements of -OH groups are crucial factors affecting the ionization energies of phenolic aqueous nanoaerosols and thus their redox-based activities. The multi-faceted implications of the present study in the aerosol science, atmospheric/marine chemistry, and biological science will be addressed.

Keywords: Aerosols; Aerosol VUV photoelectron spectroscopy; Aqueous nanoaerosols; Valence electronic structures; Interfacial solvation structures.

Summary:

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Single droplet combustion of the flame spray pyrolysis precursor-solvent solutions

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Flame spray pyrolysis (FSP) has been widely used to synthesize nanoparticles. The scale-up of this one-step synthesis technique is able to produce several kilogram nanoparticle per hour, and these synthesized nanoparticles have wide applications including sensor, catalysis, biomaterials, battery, phosphors, and electroceramics. Single droplet combustion experiments have been proved to be very useful in providing fundamental information to FSP. In these experiments droplet micro-explosions were observed during the combustion of the FSP precursor-solvent solutions, which has been verified to promote the production of homogeneous nanoparticles for low volatile nitrate precursors. The high-speed camera recording videos show the continuous explosions of these precursor-solvent droplets. Rainbow refractometry revealed temperature gradient in these precursor-solvent droplets. A theory based on the thermal decomposition of the precursor and subsequent shell formation, heterogeneous vapor nucleation was proposed to explain the droplet micro-explosion. In the near future, we propose to use diffractive imaging with x-ray free-electron lasers to investigate the droplet micro-explosion, especially the crystalline nature of particles during the combustion.

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PEPICO investigation of free transition-metal oxide nanoparticles in a molecular beam through a novel multi-coincidence imaging setup

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Electronic and chemical characterization of isolated nanoparticles produced in the gas phase is fundamental for understanding how peculiar properties of nano-scale matter develop from the atomic and molecular characters towards the macroscopic limit of bulk materials and ordinary interfaces.

In order to perform inner shell spectroscopy on both the free clusters building blocks and, in-situ, on the cluster-assembled nanostructured thin films obtained after particle deposition, a dedicated UHV apparatus is needed. We have been exploiting a setup named CESYRA (Cluster Experiment with Synchrotron Radiation) [1], whose performance we have improved along a decade of experiments at the GasPhase beamline (Elettra, Trieste, I) [2]. The detection scheme adopted ever since is based on PEPICO (Photo-electron Photo-ion coincidence spectroscopy), i.e. on the discrimination and correlation of electrons and ions created during photoionization processes on free clusters.

Despite its great efficiency and diffusion, PEPICO comes with some intrinsic drawbacks, among which the most important when dealing with large clusters is the low sensitivity to heavy ions (at kDa level). Moreover, a much deeper insight in the electronic structure of free cluster through inner-shell PEPICO energy selection of collected electrons is also desirable. For this purpose, the CESYRA set-up has recently been upgraded with a novel VMI-PEPICO spectrometer, equipped with a 3D delay line for electron energy distribution reconstruction and for event discrimination based on both ion velocity and mass-to-charge ratio as well as on hit multiplicity.

Performances of the novel PEPICO spectrometer will be illustrated, along with selected results obtained in the relevant case of transition metal nanoparticles.

[1] P. Piseri, T. Mazza, G. Bongiorno, M. Devetta, M. Coreno, P. Milani; *J. El. Spectr. Rel. Phen.* 166-167 (2008) 28; doi: 10.1016/j.elspec.2008.05.003

[2] <http://www.elettra.eu/elettra-beamlines/gasphase.html>

Summary:

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Size-resolved, angle-dependent photoelectron spectroscopy of neutral alkali metal-doped dimethyl ether clusters: Comparison of Li and Na

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We report the first measurements of electron binding energies and photoelectron anisotropies of size-resolved, angle-dependent photoelectron spectra of lithium-doped dimethyl ether (CH_3OCH_3) clusters. Neutral clusters were studied in the range from the bare lithium atom to an average cluster size of 63 dimethyl ether molecules with a single lithium atom. Using a combination of density functional calculations and experimental spectra we explain trends in electron binding energies and photoemission anisotropies of $\text{Li}(\text{CH}_3\text{OCH}_3)_n$ clusters. The lithium-doping results are compared to a previous study [1,2] performed in our group on sodium-doped dimethyl ether clusters and found to produce similar trends in the evolution of electron binding energies and photoemission anisotropies. We are especially interested in the structural and electronic differences that arise from replacing sodium with the smaller alkali metal, lithium. In highly symmetric clusters, the highest occupied molecular orbital can delocalize over an extended region and form a symmetric charge distribution of mainly s-character, resulting in a pronounced photoemission anisotropy [1]. For $\text{Na}(\text{CH}_3\text{OCH}_3)_n$ clusters, the hexamer ($n = 6$) was shown to produce such a highly symmetric structure and pronounced photoemission anisotropy. In the case of $\text{Li}(\text{CH}_3\text{OCH}_3)_n$ clusters, the tetramer ($n = 4$) exhibits an analogously high symmetry structure with correspondingly high photoemission anisotropy. Calculation results predict highly symmetric geometries and strong s-character for the highest occupied molecular orbitals of both $\text{Na}(\text{CH}_3\text{OCH}_3)_6$ and $\text{Li}(\text{CH}_3\text{OCH}_3)_4$.

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Summary:

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Gas-phase X-ray absorption spectroscopy: clusters and coordination complexes

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The spectroscopy of molecular compounds in the gas-phase delivers valuable information on the intrinsic properties of the molecule or cluster because there is no environment, such as a surface or a solvent, which may disturb the structural and electronic properties of the compound. Moreover, it allows the investigation of highly reactive or unstable species which may have very short lifetimes when deposited or prepared in solution. In the case of x-ray absorption spectroscopy, where monochromatized x-rays of variable energy are required, the available photon flux is limited and thus the study of the highly dilute gas-phase samples is challenging. By using an ion trap, a sufficiently high sample density can be achieved in order to measure the x-ray absorption in ion yield mode. The ion production is independent of the ion trap and thus both sputtering from the solid material or electrospraying of the sample in solution are available as ion sources. With the electrospray ion (ESI) source it is thus possible to investigate chelate or coordination complexes where the element specificity of x-ray absorption spectroscopy is especially valuable as it makes it possible to selectively address the ligand(s) or the metal atom. In this contribution, the NanoclusterTrap end-station at BESSYII at the Helmholtz Zentrum Berlin will be introduced and results from the recently commissioned dedicated electrospray ion (ESI) source will be presented.

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Introduction

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A new electron spectrometer for synchrotron experiments on size-selected cluster ions

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Clusters show a strong size-dependence of their chemical properties. An example is the high catalytic activity of small Au clusters deposited on different substrates. However, any interaction with a substrate alters their properties. To understand the origin of the size dependency, data on free clusters are needed. These could be valence band photoelectron spectra of reacted clusters. In such experiments, a size-selected cluster ion beam intersects a synchrotron beam and the generated photoelectrons are detected. The advantage over laser experiments is the higher photon energy, which is sufficient to study the adsorbate-induced structures at binding energies between 15-20 eV. However, the intensity of the synchrotron radiation is too low for the use of conventional electron spectrometers with typical detection efficiencies of < 1%. Therefore, such experiments normally require laser radiation. In 2018, we developed a new type of magnetic-bottle electron time-of-flight spectrometer. There is no inherent limitation on the collection efficiency. It may be possible to detect virtually all electrons generated at the beam intersection. It can be combined with a continuous light source or a pulsed laser. The maximum energy resolution depends on the length of the instrument. At two meters it is of the order of 1%. The magnetic field serves as a shield against background electrons, making the new instrument suitable for experiments on samples with low target densities.

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Quantum State-Resolved Studies of Gas/Surface Reaction Dynamics by Vibrational Spectroscopies

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Methane dissociation is the rate limiting step in the steam reforming process used by the chemical industry to convert natural gas into a mixture of H₂ and CO known as synthesis gas. To better understand the microscopic mechanism and reaction dynamics of methane chemisorption, we use vibrational spectroscopies and infrared lasers for quantum state-resolved studies of methane dissociation and state-to-state scattering on Ni and Pt surfaces [1]. Our experiments prepare surface incident methane molecules in specific ro-vibrational quantum states by state-selective infrared laser excitation via rapid adiabatic passage in a molecular beam. The state prepared molecules then collide with a clean single crystal transition metal surface in ultrahigh vacuum and both reactive and non-reactive processes are monitored by infrared spectroscopic techniques.

Surface bound methyl species as products of the dissociative chemisorption of methane are detected on the platinum surface by Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS allows for real-time and in-situ monitoring of the uptake of chemisorbed methyl species enabling quantum state-resolved measurements of reactive sticking coefficients. RAIRS is also used to study the vibrationally bond selective dissociation of partially deuterated methanes demonstrating that a single quantum of C-H stretch excitation of the incident methane is sufficient to achieve bond-selective chemisorption. Furthermore, RAIRS allows for site specific detection of reaction products used to measure separately the dissociation probability of methane on steps and terraces sites on Pt(211) [2-3].

Non-reactive, inelastic energy transfer is probed by combining infrared laser tagging of scattered molecules with bolometric detection. These first methane state-to-state scattering experiments yield state-resolved information about rotation and vibrational energy transfer between the incident molecule and the solid surface [4].

Our state-resolved experiments provide clear evidence for mode- and bond-specificity as well as steric effects in chemisorption reactions and show that methane dissociation cannot be described by statistical rate theory but requires a dynamical treatment including all internal vibrational and rotational degrees of freedom of the dissociating molecule. The detailed reactivity and state-to-state

scattering data from our measurements are used as stringent tests in the development of a predictive understanding by first principles theory [5-6] of these industrially important gas/surface reactions.

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Summary:

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Interfacial Energy and Charge Transfer Dynamics studied by Time-Resolved X-ray Photoelectron Spectroscopy

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The success of many emerging molecular electronics concepts hinges on an atomistic understanding of the underlying electronic dynamics. Processes evolving on spatial and temporal scales spanning orders of magnitude have to be connected in order to gain a comprehensive understanding of the fundamental dynamics and scaling laws that enable molecular, interfacial, and macroscopic charge and energy transport. Time-domain X-ray spectroscopy techniques have the potential to provide a deeper understanding of electronic dynamics in complex, heterogeneous systems owing to their elemental site specificity and sensitivity to local valence electron configurations.

We present femtosecond to picosecond time-resolved X-ray photoelectron spectroscopy (TRXPS) studies of photoinduced charge transfer dynamics in nanoporous films of N3 dye-sensitized ZnO and in bilayer heterojunctions consisting of copper phthalocyanine (CuPc) electron donors and C₆₀ acceptors. Differential TRXPS line shifts provide access to transient interfacial dipoles and charge delocalization dynamics in the N3/ZnO system as well as a deeper understanding of exciton transport and charge generation mechanisms in the CuPc/C₆₀ system.

Summary:

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Role of catalyst support in hydrogen spillover

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Catalysis is the workhorse in chemicals production, energy conversion and pollution abatement. There is a continued demand for novel materials and processes and such development is greatly

helped by understanding the fundamental steps in the catalytic process. Catalysts are often nano-sized particle anchored to a support, the role of which in the catalytic process often remains unclear. By designing nano-sized particles on support and performing photo-electron microscopy (in a PEEM) the role of the support on the phenomenon of spillover is investigated. Spillover is an essential process in catalysis, which involves activation of a species on a particular catalyst particle, which then spills over onto the support and displays an action at a distance away from the particle. Such phenomenon is however controversially discussed in the literature, which requires the fundamental understanding of its mechanism and origin.

Karim, W., Spreafico, C., Kleibert, A., Gobrecht, J., VandeVondele, J., Ekinci, Y., van Bokhoven, J. A. *Nature* (2017) 541 68-71

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Surface scattering at extreme ultra-violet (XUV) free electron lasers

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The “Mobile Beamer surface scattering machine” is designed to make use of the advantageous properties of the radiation produced by the XUV free electron laser in Dalian[1] for surface scattering experiments on atoms and molecules. The XUV photolysis of small molecules will be used as a novel source of atomic beams, providing fine control over the electronic state and kinetic energy. In addition, the tunable XUV light source will be used for sensitive, isomer-specific detection of molecular scattering products and reaction intermediates at surfaces, via photoionization mass spectrometry with high time of flight as well as spatial and velocity map imaging resolution.

With this setup we would like to answer following three fundamental questions: Open-shell atoms can interact strongly with the electrons of a metal surface. For example, it has recently been shown that nonadiabatic “electronic friction” is the dominant energy dissipation mechanism that allows hydrogen atoms to stick to metals.[2]

1. To what extent do such forces govern the dynamics of heavier high-electron-affinity atoms (O, C, N) at surfaces? Will current theories for non-Born-Oppenheimer dynamics succeed in describing the scattering process of the atom?
2. Can electronic excitation of atoms lead to an increased reactivity with surface adsorbates or is the electronic energy lost to surface degrees of freedom without enhancing a reaction?

Although elementary kinetic models provide invaluable predictive power for gas-phase reactions, they are practically non-existent in surface chemistry due to the complex structure of interfaces. Recent work has provided the first transferrable kinetic model to treat the elementary site-specific processes in CO oxidation on platinum.[3]

3. By probing surface intermediates, can models based on elementary reaction steps be built for the predictive description of more complex catalytic systems?

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Introduction

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Probing the Dissociation of Interstellar Polyaromatics Using Synchrotron and FEL Radiation

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The presence of interstellar polycyclic aromatic hydrocarbons (PAHs) is inferred from the widespread mid-infrared (IR) emission bands that are observed at 3.3, 6.2, 7.7, 8.6 and 11.2 μm . [1] This IR radiation is emitted as the PAHs cascade down to the ground state after they have been excited by interstellar (vacuum) ultraviolet radiation. [2] PAHs have been observed towards a large number of galactic and extragalactic sources and it has been derived that they constitute up to 15% of the total cosmic carbon budget.

Energetic processing of interstellar polyaromatics may result in ionization and/or dissociation. It has been hypothesized that this chemical evolution is reflected in subtle changes in the interstellar mid-IR emission bands. Observational and laboratory data suggest that dissociation of large interstellar polyaromatics eventually leads to fullerene formation. [3,4] The underlying chemical mechanisms involved in the dissociation of aromatics are not yet understood.

Our group characterizes the dissociation of polyaromatics by means of vacuum ultraviolet synchrotron radiation and mid-infrared free electron laser radiation. By combining these techniques with quantum chemical computations we obtain insight into the isomerization and dissociation at a molecular level of detail. [5-7] I will review our most recent results and will emphasize their importance in light of astronomical observations.

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Summary:

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Titan's atmospheric aerosols as seen by SOLEIL-synchrotron VUV-light

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Titan, the largest moon of Saturn, has a dense atmosphere whose upper layers are mainly composed of methane (CH₄) and molecular nitrogen (N₂). Their photochemistry leads to the formation of aerosols at very high altitudes (>800 km). Once these aerosols are formed and through their descent towards the surface, they will still interact with persistent UV/VUV radiations, at different energies, that can reach lower atmospheric layers. This interaction has some impact, for example on the chemical composition of the aerosols or on the ionization yield of the atmospheric compounds.

So far, nothing is known on the possible photochemical evolution of the organic aerosols composing the haze. Models are a good way to study those processes, but the lack of data on the refractive index or the absolute absorption/ionization cross sections of the aerosols can be an obstacle. Here, we address this interaction process, simulating in the laboratory how solar vacuum ultraviolet irradiation affects the aerosols. In order to shed some light and quantify those processes, we synthesized analogs of Titan's aerosols (tholins) at LATMOS and exposed them under VUV radiation at the DESIRS-beamline (synchrotron SOLEIL). We both studied their photo-ionization efficiency and their chemical evolution.

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Photo-processing of astro-PAHs

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The interaction of polycyclic aromatic hydrocarbons (PAHs) with UV irradiation is a key process in astrochemistry since it governs the heating of the gas by photoelectric effect and can contribute to the catalytic formation of molecules such as H₂ and C₂H₂. The fragmentation rate of these PAH species also determines their survival in astrophysical environments [1]. In this presentation, we show how we can combine the results of different experiments to obtain information on the branching ratios between the different fragments and on dissociation rates as a function of energy. These experiments include: -(i)- fragmentation of trapped PAH cations exposed to multiple photon absorption [2] or to synchrotron VUV light [3] and -(ii)- photoelectron spectroscopy performed on neutral PAHs under synchrotron irradiation [4]. We also report insights into the competition with other relaxation mechanisms, ionization and radiative cooling [5].

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Summary:

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Probing Low Temperature Molecular Mass Growth Processes to Polycyclic Aromatic Hydrocarbons (PAHs) via Vacuum Ultraviolet Photoionization Mass Spectrometry – Saturn’s Moon Titan as a Case Study

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The detection of benzene in Titan’s atmosphere led to the emergence of polycyclic aromatic hydrocarbons as potential nucleation agents triggering the growth of Titan’s orange-brownish haze layers. However, the fundamental mechanisms leading to the formation of PAHs in Titan’s low temperature atmosphere have remained elusive. We provide persuasive evidence through laboratory experiments exploiting tunable vacuum ultraviolet photoionization mass spectrometry and computations that prototype PAHs like anthracene and phenanthrene (C₁₄H₁₀) are synthesized via barrier-less reactions involving naphthyl radicals (C₁₀H₇[•]) with vinylacetylene (CH₂=CHC≡CH) in low-temperature environments. These elementary reactions are rapid, have no entrance barriers, and synthesize anthracene and phenanthrene via van-der-Waals complexes and submerged barriers. This facile route to anthracene and phenanthrene –potential building blocks to complex PAHs and aerosols in Titan – signifies a critical shift in the perception that PAHs can be only formed at high-temperature conditions providing a detailed understanding of the chemistry of Titan’s atmosphere through untangling elementary reactions on the most fundamental level. An outlook is also presented on the synthesis of more complex PAHs containing four rings and potential two dimensional nanostructures via complementary hydrogen abstraction –acetylene addition (HACA), hydrogen abstraction –vinylacetylene addition (HAVA), and phenyl addition –cyclization (PAC) reaction mechanisms.

Summary:

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The prebiotic building blocks of peptides

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Small molecules such as formamide (NH_2CHO), methyl isocyanate (CH_3NCO) and acetamide (CH_3CONH_2) belong to a select group of interstellar molecules considered to be relevant precursors to the formation of peptide structures. On Earth, the peptide bond is the chemical link between amino acids that forms proteins, the engines of life. Recent detections of NH_2CHO , CH_3NCO and $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ with ALMA towards the low-mass, sun-like, protostar IRAS 16293-2422B, make it likely that such building blocks were available in the earliest formational stages of the Solar System. [1,2,3] How these species form and are related to each other is largely unknown, however.

In this presentation, the formation of peptide-like molecules on icy surfaces of interstellar dust grains is discussed. To this end, $\text{CH}_4:\text{HNCO}$ mixtures frozen at 20 K are UV irradiated and analysed with Infrared spectroscopy and temperature programmed desorption - mass spectrometry. The experiments show the simultaneous formation of a variety of peptide-like molecules, including NH_2CHO , CH_3NCO and $\text{CH}_3\text{C}(\text{O})\text{NH}_2$. From the experimental data, a reaction network is constructed which shows that these molecules are related through a series of similar reactions, mainly starting from atomic nitrogen (N), NH and NH_2 . A comparison between laboratory and observational data shows that the formation of peptide-like molecules in the interstellar medium can be explained by reactions taking place on icy dust grains.

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Summary:

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Photoelectron-photoion coincidence spectroscopy for laboratory astrochemistry: VUV Photodynamics of radicals, radical reaction products, PAHs, and more

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The field of astrochemistry is furthered by a synergistic approach between i) telescope-observations, ii) modelling calculations that make use of physical and chemical parameters of relevant molecules and reactions, and iii) laboratory experiments that are designed to inspect and extract the physical characteristics of specific molecules, photon-induced reactions, surface processes, etc., that are relevant to the interstellar medium. This talk will be dedicated to the use of the double imaging photoelectron-photoion coincidence (i2PEPICO) technique to study (dissociative)-ionization processes and the spectroscopy of astrochemically relevant molecules in the VUV range. Experiments are performed at the DESIRS VUV beamline at the Synchrotron SOLEIL (France), on which ~1/3 of projects are carried out annually are relevant to astrophysics and planetary sciences. Recent data obtained on various radical species, radical reaction products, polycyclic aromatic hydrocarbons (PAHs), as well as prebiotically relevant molecules will be presented.

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Desorption of neutrals, cations and anions induced by core-excitation of water ice

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Water ice plays an important role in many different fields of physical sciences. In particular, water ice is ubiquitous in the interstellar medium. Interaction between condensed water and high energy radiation –such as X-ray photons –is a key process in space, that plays an important role in the balance between the gas phase and the solid phase. The core excitation of water ice has been the subject of many investigations. For example, the desorption of the H⁺ ion has brought information on the relaxation processes (Auger decay into various states or ultrafast dissociation) that follow the absorption of a photon. However, desorption of other positive ions or negative ions has to our knowledge not been studied so far, and little is known on the desorption of neutral species.

We studied X-ray induced desorption from water ice in the O 1s range (520–600 eV) using monochromatized synchrotron radiation from the SOLEIL facility. The approach combines neutral and ion quantitative detection as a function of photon energy, and kinetic energy filtering of the ionic species. Neutral species are found to be by far the most abundant species desorbed, and the desorption process is probably dominated by secondary electrons. Cations other than H⁺ have a desorption yield orders of magnitude lower than H⁺, but are nonetheless detected. The spectral signature of fragments such as O⁺ or OH⁺ deviate from the absorption spectrum of the ice and show that they are majorly produced through core excitation of photoproduct molecules in the ice such as H₂O₂. We have detected for the first time desorption of anions, H⁻, O⁻ and OH⁻. Once again, their desorption spectral signatures deviate from the absorption, showing desorption is not dominated by mechanisms associated with secondary electrons (such as DEA), although they do contribute in part to anion production.

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Ice chemistry apparatus with a fast-tuning 7.5 ÷ 11.5 eV vacuum ultraviolet source for processing and detection

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Solid phase processes contribute to the chemical evolution in interstellar and circumstellar media via interactions between icy grains mantles and dissociative and ionizing radiation. Such energetic processing of ices affects the ice composition via non-equilibrium surface desorption processes and chemical reactions throughout the ice. Far ultraviolet radiation is a potentially important source of this processing in many different astrophysical environments. In order to study the detailed kinetics and mechanisms of photon-induced ice desorption and chemistry we have constructed a new astrochemistry laboratory apparatus featuring a laser-based vacuum ultraviolet (VUV) source and a cryo-cooled target in an ultra-high vacuum environment. The tunable VUV source is also used for the selective single-photon ionization coupled with reflectron time-of-flight mass spectroscopy. In parallel, infrared spectroscopic characterization is implemented in both transmission and reflection modes.

The proposed astrochemical studies include tunable wavelength photodesorption, monochromatic processing of ice mixtures, and ionization energy selective mass-spectroscopic detection of complex organics formed in energetically processed ice mixtures of astrophysical relevance. The latter is particularly useful for isomer-specific studies which reveal finer details of chemical processes in the processed ices. Our system's rapid VUV tunability in 7.5 ÷ 11.5 eV range eliminates variations associated with a set of separate experiments at fixed distinct wavelengths, significantly advancing the state of the art in laboratory astrochemistry.

We are presenting the current state of the setup, the laser sub-system's characteristics, as well as

initial experimental results demonstrating its sensitivity and selectivity. We discuss its development and projected research capabilities.

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Introduction

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Combustion-related answers from and questions for photon tools

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Combustion chemistry plays an increasing role in several respects. New combustion regimes are associated with previously unrecognized chemistry, and alternative fuels may have different fuel-dependent reaction pathways. In both contexts, photon tools are of significant importance. They offer the means to probe the reactants directly.

This widely accepted statement might be regarded with a spirit for discussion. Is what we can measure the information that we should know? Several options exist to employ photons for combustion (chemistry) diagnostics. Lasers are indispensable to analyze practical systems, with limited chemical insight, however. Chemiluminescence seems attractive for combustion control, again offering some specific chemical information. Photo-ionization in combination with mass spectrometry techniques is a most powerful current tool to provide experimental information for model development and validation, but with application ranges often quite different from those in applied systems.

With examples from our own experience, collaborative results and recently published work by others, the talk intends to stimulate responses for opportunities where combustion-related questions might be addressed by photon tools.

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Identification of reaction pathways in model flames

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PEPICO spectroscopy was used in flame sampling experiments performed with VUV-photoionization at the Swiss Light Source to identify the fuel radicals and key intermediates in fuel decomposition and in soot formation processes in flames of hydrocarbon fuels.

A key reaction of the fuel decomposition process in pyrolysis as well as in combustion of hydrocarbons is the abstraction of H atoms by small radicals like O, OH and H forming a so-called fuel radical. Because the following reaction steps are highly dependent on the type of radicals formed, the knowledge on H-abstraction pathways is essential for understanding and predicting combustion properties. The flame-sampling PEPICO setup was used to investigate the abstraction of chemically different hydrogen atoms from the hydrocarbon fuels in low-pressure hydrogen flames doped with the different alkanes and alkenes. Ethane, n-butane and i-butane were specifically targeted in a systematic approach to investigate the hydrogen atom abstraction of primary, secondary and tertiary hydrogen atoms. In addition, 1-butene, i-butene and tetramethylethylene were chosen to evaluate the abstraction of allylic and vinylic hydrogen atoms. This set of fuels allows for comparison of different reaction pathways and enables a systematic experimental approach by measuring, identifying and quantifying the fuel radical species in low-pressure flames. Hydrogen was chosen as base fuel to provide sufficient H atoms and to increase the role of hydrogen abstraction or addition in the fuel destruction pathways. Relative H-abstraction ratios for n-butane, i-butane and 1-butene were recorded and give a clear H-abstraction order: tertiary > primary; secondary > primary; allylic > non mesomerically stabilized form. Vinylic radicals were not observed. The comparison of the experimental data to reaction barriers from the literature shows that the mole fraction ratios of the radicals correspond to the ratio of the inverse reaction barriers.

Aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylene are characterized as volatile organic compounds and can be found with up to 20% (w/w) in typical gasoline blends. These compounds contribute significantly to the fuel mix used today in modern engines. For emissions control a detailed knowledge of important reaction steps during combustion of these aromatics is required. Toluene combustion was investigated in laminar, premixed, flat flames with the PEPICO technique. Two reaction routes are of interest for pollutant formation in toluene combustion: the oxidation and the formation of larger polyaromatic hydrocarbons (PAH). Key intermediates of toluene oxidation were observed, e.g. benzyl radicals and C_5H_5CCH . With regard to PAH formation it was observed, that most PAH are not formed from the fuel but from small resonantly stabilized radicals such as propargyl and allyl radicals. Butadiene and acetylene were added to the toluene fuel, to enhance addition of acetylene and butadiene to the aromatic ring in the flame front. Since both fuels also lead to the formation of small resonantly stabilized radicals the influence on species concentration involved in PAH formation was very small and almost negligible.

Summary:

Combustion and flames / 19

Investigation of combustion processes in different reactor setups using i2PEPICO

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Combustion experiments using the i2PEPICO technique have been proven a valuable addition to the existing established synchrotron based methods. High sensitivity towards radicals, especially hard to measure fuel radicals, and a superior identification of isomeric species allow for a more complete experimental investigation of chemical reaction networks. A detailed knowledge of the most important reactions plays a key role for the development of a predictive understanding of combustion

processes and it is particularly important for ignition processes and the mitigation of pollutants. In addition to the successful demonstrated laminar flame experiments, the combination of molecular-beam mass spectrometry (MBMS) and photoelectron-photoion-coincidence spectroscopy (PEPICO) is used to detect the reactive key species experimentally in reactor setups, e.g. plug-flow or jet-stirred configurations. The vast range of operating conditions available in reactors enables access to combustion applications that are typically not achievable by flame experiments. The pressure and the reaction times at a specified temperature can be controlled easier and more systematically in a flow reactor than in a model flame, e.g. enabling the investigation of the peroxy chemistry governing the low temperature oxidation regime.

Expanding the i2PEPICO flame setup with a flow reactor is a future goal to characterize the intermediates formed via low-temperature reaction pathways in a wider parameter range by temperature-dependent concentration profiles. Improvements on the flow reactor setup will be similar to the present DLR flow reactor, which has been modified to be suitable for technical fuels (e.g. multi-component mixtures like Jet A-1) allowing for phenomenological analysis of occurring combustion intermediates like soot precursors or pollutants. Using the superior detection and identification capabilities of the i2PEPICO flame system with such a flow reactor design is a promising addition in combustion diagnostics. Here, initial experiments and design studies of a first flow reactor approach at the Swiss Light Source (SLS) will be shown and discussed.

Summary:

Spectroscopy in action and action spectroscopy / 52

Introduction

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Pyrolysis of Fuels in a Micro-Reactor: Radical/Radical Reactions Make PAHs

Author: Barney Ellison¹

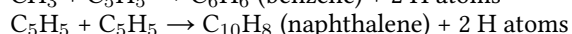
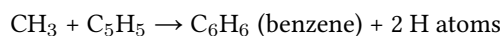
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To understand the thermal decomposition mechanisms of fuels, we are developing a tiny flow tube to study the thermal cracking of complex organic molecules. We use a heated 1 mm × 2 cm SiC microtubular reactor to decompose complex fuels. Thermal decomposition of 0.1 % samples mixed with He or Ar carrier gases takes place at pressures of 75 – 250 Torr and at temperatures up to 1700 K. Residence time of the organics in the reactor is roughly 25 – 150 μsec. The pyrolysis products are identified by several independent techniques: VUV photoionization mass spectroscopy, resonance enhanced multiphoton ionization, microwave spectroscopy, and matrix-isolated, infrared absorption spectroscopy.

Aromatics (toluene, xylenes, alkylbenzenes, etc.) make up roughly ¼ of all aviation fuels. Thermal cracking of these fuels produces a pool of “persistent” radicals. We have observed radical/radical reactions to produce benzene and naphthalene. These are early steps in the formation of “soot”.



Summary:

Spectroscopy in action and action spectroscopy / 35**Probing High Temperature and Pressure Reactions and Gas States with VUV and X-rays**

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Synchrotron light sources offer many opportunities for probing chemical and physical properties. For example, VUV-photoionization mass spectrometry gives detailed insights into the reactions of transient species of importance to atmospheric chemistry and combustion. At much higher photon energies ex-situ and in-situ, X-ray scattering experiments examine particle formation within flames. In recent years, there have been significant advances in the reactors used to perform gas phase experiments at light sources and the diagnostics to probe them. These developments have resulted in gas phase chemical kinetic experiments at simultaneous high temperatures and pressures and in-situ methods of probing conditions in new and traditional reactors such as shock tubes, flow tubes and flames.

X-ray densitometry (Advanced Photon Source, Argonne National Laboratory), to determine post shock gas states, and VUV-PIMS (Advanced Light Source, Lawrence Berkeley National Laboratory), to study chemical reactions, experiments with a miniature shock tube will be presented. Some of the remaining challenges to recovering kinetic as well as mechanistic data from the shock tube experiments will be briefly discussed. X-ray fluorescence and absorption (APS) to determine temperature and density fields in flames and micro-reactors will also be discussed.

Spectroscopy in action and action spectroscopy / 1**Kinetics and isomeric/isobaric product analysis of radical reactions in flow tube investigated by VUV photoionization mass spectrometry**

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Photoionization mass spectrometry (PIMS) as a powerful method has been widely utilized and provided valuable insight in the field of gas-phase reactions. We present here a vacuum ultraviolet (VUV) photoionization orthogonal time-of-flight mass spectrometer (TOFMS) coupled with a microwave discharge generator and a fast flow tube reactor to study radical reactions of atmospheric and combustion interests. The tunable VUV synchrotron radiation at Hefei, China, and a commercial krypton discharge lamp were employed as photoionization light sources and the performances of the experimental setup, like the mass resolution ($M/M \sim 2000$) and the limit of detection (LOD ~ 1 ppb), are described. As representative examples, the self-reaction of the methyl radical, CH_3 , and the reaction of the methyl radical with molecular oxygen were studied and multiple species including radicals and isomeric/isobaric products were detected and identified in the photoionization mass spectra and the photoionization efficiency spectra (PIES) by scanning synchrotron photon energy. In addition, some preliminary results related to the kinetics of the reactions are presented.

Summary:

Spectroscopy in action and action spectroscopy / 60

Gas phase activation and spectroscopy of mass and charge selected ions

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Gas phase spectroscopy offers the unique advantage of accessing intrinsic properties in the absence of solvent, and ultimately provides a mean to test theoretical methods. Biomolecules and large assemblies are fragile and difficult to place in the gas phase intact and studies are usually limited to building blocks and small oligomers.

Modern ionization techniques, such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) have demonstrated their potential to place large, complex and fragile assemblies intact in the gas phase. Direct absorption spectroscopy of ions is not trivial on such dilute matter. Action spectroscopy offers a mean to circumvent the difficulties of measuring the attenuation of photon beams through ion clouds. Hence, mass spectrometry-based action spectroscopy provides unprecedented control over the target, such as the ability to control the isotopic content and elemental composition, the charge, eventually the temperature, or the molecular shape in combination with ion mobility.

Action spectroscopy of polypeptides has been probed using synchrotron radiation in the VUV and soft X-ray ranges. The targets are produced by ESI, stored and irradiated in the photon energy range on interest in an ion trap [1]. The products of the irradiation are monitored by measuring the mass spectrum after photon excitation. This method is sensitive to any changes of the mass to charge ratio of the precursor ion of interest, thereby allowing photoionization, photodetachment and photofragmentation to be detected.

Through some applications to biomolecules we will illustrate the potential of the method for analytical and structural chemistry as well as for gaining information on the electronic structure and the photodynamic of the system.

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Summary:

Photoionization spectroscopy I / 53

Introduction

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Photoionization spectroscopy I / 9

On the ionization and dissociation energies of molecular hydrogen and metastable helium (He₂)

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Few-electron molecules represent attractive systems for precision spectroscopy because their properties can be calculated with extraordinary accuracy by ab initio quantum-chemical methods. [1,2] Comparing experimental and theoretical results thus offers the opportunity to assess the limitations of ab initio calculations, ultimately and ideally at the level where their accuracy is limited by either the uncertainties of the fundamental constants or so far unrecognized physical effects. We present the results of precision measurements in cold samples of hydrogen (H_2) and metastable He_2 molecules. The cold-molecule samples are prepared in supersonic beams using pulsed cryogenic valves and, in the case of metastable He_2 , a multistage Zeeman decelerator.

In the case of the metastable a $^3\Sigma_u^+$ state of He_2 , we exploit multistage Zeeman deceleration to prepare slow beams of cold and fully magnetized molecules in selected spin-rotational components. [3] We use the long transit times of these molecules through microwave and laser fields to carry out highly precise measurements of (i) fine-structure intervals in the metastable a state, (ii) the frequencies of transitions to high Rydberg states of He_2 , and (iii) the spin-rovibrational energy level structure of the $X^+ \ ^2\Sigma_u^+$ ground state He_2^+ by Rydberg-series extrapolation. [4]

In the case of H_2 , we measure transitions from selected rovibrational levels of the GK $^1\Sigma_g^+$ state to high Rydberg states belonging to p and f series converging on different rovibrational levels of $X^+ \ ^2\Sigma_g^+$ ground state of H_2^+ . The transition frequencies are determined with a relative precision ($\Delta\nu/\nu$) of $2 \cdot 10^{-10}$. [5] Extrapolation of these series by multichannel quantum defect theory enables us to determine the spin-rovibrational intervals of H_2^+ and the dissociation energy of H_2^+ at unprecedented accuracy. [6] The relevance of these results in the context of measurements of fundamental constants and elementary-particle properties will be discussed.

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Summary:

Photoionization spectroscopy I / 58

Vibronic Coupling and Photoelectron Angular Distributions: All May Not Be As It Seems

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Improved resolution and flexible polarization control are providing new opportunities to track photoelectron angular distributions over extended photon energy ranges with full vibrational resolution. Such studies provide fresh insight into both well-established vibrational coupling mechanisms and some newer phenomena. The importance of a sound understanding and knowledge of these vibronic coupling effects, whether or not directly observed in an experiment, is emphasised in the context of proposed developments of chiral molecule analytical techniques.

Photoionization spectroscopy I / 27

Advances on the identification of DNA bases specific isomers via high accuracy single photon ionization and ab initio computations

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DNA/RNA bases and amino acids are building blocks of life. The spectroscopy and stability of their ionic forms are relevant to their survival rate under interstellar conditions, and to the field of radiation damage, where ionizing radiation can lead to DNA/RNA strand breaking and production of hazardous by-products through processes involving nucleobases.

Several experimental works at BESSY II, Advanced Light Source and synchrotron SOLEIL were devoted to unveil the structure and the spectroscopy of the cationic species of DNA bases and amino acids and analogues [1]. Since they possess numerous tautomers and isomers that lie close in energy, the experimental characterization of a unique tautomer is challenging.

At present, we apply single photon VUV synchrotron based experiments combined with state-of-the-art ab initio methodology to determine the adiabatic ionization energies (AIE) of specific gas phase DNA bases tautomers produced in a molecular beam. The experiments were performed at the undulator-based DESIRS beamline of the French synchrotron facility SOLEIL in connection with its 6.65 m normal incidence monochromator and the double imaging photoelectron photoion coincidence (i2PEPICO) spectrometer DELICIOUS3. [2] The coincidence scheme allows the photoelectron images to be filtered as a function of mass and ion kinetic energy in a multiplex manner. Treatment of such photoelectron images as a function of the photon energy leads to the threshold / slow photoelectron spectroscopy of the selected masses [3,4].

Theoretically, the structures and the energetics of neutral and cationic DNA bases tautomers were determined using either explicitly correlated methods or density functional theory –explicitly correlated approaches composite schemes, where we consider core-valence (CV), scalar relativistic (SR) and zero point energy (ZPE) corrections. The atoms are described using the aug-cc-pVTZ basis sets. These computations are carried out using Gaussian 09 and MOLPRO suites of programs [5,6].

The experimental spectra of jet cooled DNA bases correspond to well resolved bands that are attributable to the specific contribution of a unique or several neutral tautomers of DNA bases prior to ionization. Their AIEs are experimentally determined for the first time with an accuracy of 0.003 eV. A good agreement with theoretical values is also observed.

Our work can be generalized to other molecular entities presenting a dense pattern of isomeric and tautomeric forms in their spectra that can be investigated to understand the charge redistribution in these species upon ionization. Several examples will be presented [7-10].

Acknowledgments

This work is a long-term collaborative project involving colleagues from Synchrotron SOLEIL, CNRS, CEA, U. Paris Sud, U. Paris Nord, U. Paris-Est Créteil, U. Paris-Est Marne-la-Vallée, U. Tunis Al Manar, City U. Hong Kong and King Saud University.

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Summary:

Photoionization spectroscopy I / 2

Photoionization and Photoelectron Spectroscopy of Biradicals

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Biradicals are molecules with an electronic structure that is characterized by two unpaired electrons in degenerate or near-degenerate molecular orbitals. Their chemical and physical properties differ significantly from those of closed-shell molecules due to the interactions between the energetically close-lying states that result from the degenerate molecular orbitals. Biradicals play an important role in the chemistry of reactive environments like combustion engines, the atmosphere or interstellar clouds. Furthermore electronic states with a biradical character are key intermediates in the formation of light-emitting states in optoelectronic materials. It is therefore of relevance for many areas of chemistry and physics to understand and correctly describe the structure and dynamics of biradicals and molecules with biradicalic electronic states. In my talk I will present recent work on the photoionization of biradicals, including molecules like diborene and ortho-benzynes. The experimental work is accompanied by high-level computations.

Photoionization spectroscopy II / 45

What a (True) Coincidence!

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In Photoelectron Photoion Coincidence Spectroscopy (PEPICO), a gas-phase molecule is ionized by a vacuum-ultraviolet photon and both the photoelectron and the photoion from a single neutral molecule are detected in coincidence. In threshold PEPICO (TPEPICO), photoions are collected in coincidence with only the near-zero kinetic energy electrons and one slice of the TPEPICO data gives the mass-selected threshold photoelectron spectrum.

The continuous nature of the multiple-start-multiple-stop coincidence acquisition, utilized now at most PEPICO research centers, allows rapid data collection, maximizes the duty cycle and, since every coincidence event has an absolute timestamp, makes PEPICO well suited for kinetics experiments, as a selective detection technique.

Recently, the utility of PEPICO has been demonstrated as a universal, isomer-selective and sensitive analytical technique for time-resolved quantitative analysis of bimolecular chemical reactions. Towards this goal, we have built a new PEPICO spectrometer, CRF-PEPICO, utilizing simultaneous

velocity map imaging for both cations and electrons, while also achieving good cation mass resolution through space focusing. With this new instrument, we have also demonstrated a new approach to dramatically increase the dynamic range in PEPICO spectroscopy by combining temporal ion deflection with a position-sensitive ion detector, suppressing the false coincidence background.

A few recent examples to highlight the power of PEPICO spectroscopy are presented here. The simplest alkylperoxy radical, CH_3OO , formed by reacting photolytically generated CH_3 radicals with O_2 , was investigated using the new CRF-PEPICO apparatus at the Swiss Light Source. Modeling the experimental photoion mass-selected threshold photoelectron spectrum using Franck–Condon simulations yielded the most accurate adiabatic ionization energy of this species. Dissociative photoionization of CH_3OO generates the CH_3^+ fragment ion and the appearance energy of this fragment ion, using the methyl cation as the anchor, yields a CH_3OO heat of formation that reduced the uncertainty of the previously determined value by a factor of 5. Statistical simulation of the CH_3OO breakdown diagram provides a molecular thermometer of the free radical's internal temperature, which was confirmed to be slightly over room temperature, indicating quick thermalization.

Small unsaturated resonance-stabilized hydrocarbon radicals play a crucial role in producing PAHs, responsible for molecular weight growth processes that ultimately lead to soot formation. The ability of propargyl radicals to react with themselves makes it key species in molecular weight growth. However, most of these reactions do not produce just a single isomer, rather, a progression through various isomers towards the global energy minimum. The large number of isomers makes unambiguous separation and quantification difficult but the several isomer-specific peaks in mass-selected photoelectron spectra can be much more distinguishable than photoionization spectra. To study the C_6H_6 isomerization pathways, we have performed pyrolytic iPEPICO experiments with continuous flow of a high-energy C_6H_6 isomer, 1,5-hexadiyne, in argon through a temperature-controlled oven (25–500°C) just prior to the iPEPICO ionization region. Analysis of the temperature-evolution of the photoelectron spectra shows clear correlations between decay and formation of various C_6H_6 isomers. Our data shows no evidence for 1,2,4,5-hexatetraene and indicates that fulvene appears at lower temperatures than benzene.

Summary:

Photoionization spectroscopy II / 41

Photodissociation of Acetylacetone: Photoionization and Threshold Photoelectron Spectroscopy Reveal Much More Than OH Radicals

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The absorption of light by an organic molecule, and the subsequent pathways for energy transformation and release, are fundamental processes governing life on earth. Two of the most important electronic chromophores in organic systems are C=O bonds (carbonyl molecules) and C=C bonds (alkenes and polyenes). Carbonyl molecules, such as acetaldehyde (CH_3CHO) also have enol tautomers ($\text{H}_2\text{C}=\text{CHOH}$, vinyl alcohol). This tautomerization converts the weakly absorbing C=O chromophore to a strongly absorbing C=C chromophore. We have studied the photodissociation of acetylacetone (AcAc), which exists at 300 K in the gas phase mostly as the enolone tautomer, rather than

the diketo tautomer. The enolone tautomer is stabilized by both π -conjugation and an internal hydrogen bond. Previous studies have concluded that OH loss is the dominant (or only) channel when AcAc is excited in the ultraviolet at 266 or 248 nm. However, truly universal detection techniques have not been used in these studies. By combining multiplexed photoionization mass spectrometry (MPIMS), threshold photoelectron photoion coincidence spectroscopy (TPEPICO), and time-resolved infrared absorption spectroscopy of OH radicals, we have discovered that photodissociation of AcAc is much richer than previously presumed, and that OH production is not even energetically allowed following one-photon 266 or 248 nm excitation. This work demonstrates the power of multiplexed, universal detection of charged particles in photodissociation studies, and lifts the veil on the photodissociation of a molecule that is both an enol and a ketone.

Summary:

Photoionization spectroscopy II / 20

Dissociation Dynamics of Energy-Selected Ions with Threshold Photoelectron-Photoion Coincidence Velocity Imaging

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During the past ten years, a threshold photoelectron-photoion coincidence (TPEPICO) double imaging setup has been built at the Hefei Light Source (HLS) combining with tunable vacuum ultraviolet (VUV) synchrotron radiation, and applied on the state-of-the-art dissociative photoionization dynamics. The fundamental data, such as ionization energy and appearance potential, and the dissociation dynamics of energy-selected ions have been measured and investigated. The kinetic energy and the angular distributions of fragment ions dissociated from parent ions with definitive internal energy or state have been acquired directly from TPEPICO images. The non-adiabatic quantum effects, like conical intersection and internal conversion, have been revealed to play the significant roles in the dissociation mechanisms of halogenated hydrocarbon in electronically excited state.

Summary:

Photoionization spectroscopy II / 6

Pentadiynylidene, Methylpentadiynylidene and Dimethylpentadiynylidene: Threshold Photoelectron Spectroscopy of R¹-C₅-R² Carbon Chains

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The three unsaturated and carbon-rich pentadiynylidenes of the composition $R^1-C_5-R^2$ are highly reactive biradicals or triplet carbenes in the electronic ground state of the neutral. Nevertheless, they occur as intermediates in harsh chemical environments. Particularly in the chemistry of interstellar medium [1], planetary atmospheres [2] and in combustion processes of fuel-rich hydrocarbon flames [3] these triplet carbenes are key components. They were only briefly studied by matrix isolated technique coupled with IR, EPR and UV/VIS spectroscopy [4]. Threshold Photoelectron Spectra (TPES) of H-C₅-H, Me-C₅-H and Me-C₅-Me with predominant carbene character at C3 didn't exist. To obtain first insights we applied double imaging Photoelectron Photoion Coincidence (*i*²PEPICO) Spectroscopy in this study, which is capable to supply mass selective TPES.

1-Diazo-penta-2,4-diyne, 1-diazo-hexa-2,4-diyne and 2-diazo-hexa-3,5-diyne, synthesized by the procedure of Bowling et al. [4], were selected as precursors generating triplet pentadiynylidene, methylpentadiynylidene and dimethylpentadiynylidene. Afterwards, the corresponding carbenes were produced by flash pyrolysis, stabilized in the gas phase and photoionized by tunable vacuum ultraviolet synchrotron radiation.

This presentation will offer first results in the photoelectron spectroscopy of pentadiynylidenes, executed at the Swiss Light Source (SLS) for synchrotron radiation (Villigen, Switzerland).

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Summary:

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Introduction

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Reaction kinetics and mechanisms I / 22

Reaction product determination using photoionization/mass spectrometry techniques down to very low temperatures: applications to combustion and molecular astrophysics

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Understanding the mechanism of elementary gas phase reactions leading to the formation of molecules and clusters in various conditions, especially at very low temperatures (i.e. low collision energies), is of fundamental interest and yields crucial information for modelling gaseous environments encountered in the fields of atmospheric chemistry (of the Earth and other planets) and astrophysics. We present a new instrument, CRESUSOL, developed by the Laboratory Astrophysics group at the Institute of Physics of Rennes in collaboration with the DESIRS beamline group at SOLEIL. The main

scientific aim of this project is to identify the product of reactions at substantially lower temperatures than has been attempted before (< 100 K) and estimate their branching ratios. Associated aims include the measurement of rate coefficients for a selection of reactions, including dimerization, down to low temperatures.

To achieve this feat, a CRESU (Cinétique de Réaction en Écoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) reactor is associated with a photoelectron-photoion coincidence (PEPICO) mass spectrometer to probe reactants and products of reaction after threshold photoionisation by the VUV beamline of the SOLEIL synchrotron. The original experimental set up will be presented and preliminary results will be shown for (i) the kinetics of dimerization of formic acid HCOOH observed at 50 and 70 K, (ii) the detection of C_4H_2 resulting from the reaction of C_2H with C_2H_2 at 50 K.

Summary:

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Automated exploration of reactive potential energy surfaces

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The determination of accurate rate coefficients remains a key challenge for a wide variety of chemical research areas, such as heterogeneous catalysis, liquid-phase chemistry and gas-phase processes. While research in the past decades has focused intensively on how to accurately calculate rate coefficients, the developed methods often incorporate several manual actions and need expert user knowledge. This is a particularly severe hinderance for finding reaction pathways, which forms the basis of rate coefficient calculations. Therefore, it is desirable to create tools that automatically search for reaction pathways, largely reducing the need for manual interventions. KinBot, our open-source code is one such tool, currently aiming at complex gas-phase chemical systems. It can uncover reaction pathways computationally in a way that is convenient for automated reaction mechanism generator and ab initio rate coefficient calculator codes, and can take advantage of high-performance computing facilities. KinBot aims to characterize all chemically significant stationary points on multidimensional potential energy surfaces as will be shown through various examples. A key step in finding reactions pathways is the ability to efficiently and robustly optimize to saddle points. Sella, our other open-source code achieves this goal via a series of algorithmic innovations demonstrated on literature benchmarks. Current research directions, such as the adaptation of our toolset to heterogeneous catalytic systems, will be also discussed.

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Isomerisation studies in ion traps

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The benzylium/ tropylium ion ($C_7H_7^+$) dichotomy is well known in mass spectrometry and could be of interest for larger species such as the 1-methylpyrene fragment ($C_{17}H_{11}^+$) [1].

Common ways of distinguishing isomers are spectroscopy and chemical reactivity. In ion traps, the density of species is too low for conventional absorption spectroscopy and action schemes have to be applied. However, one would like to avoid schemes that introduce considerable internal energy in order not to affect the initial populations.

In this work we present the application of the FELion cryogenic rf ion trap to the spectroscopy of $C_7H_7^+$ and $C_{17}H_{11}^+$. Using tagging spectroscopy and the wavelength coverage of the free electron laser FELIX, we were able to record the mid-IR spectra of tropylium and benzylium ion, and confirm these are the only two stable isomers produced upon electron bombardment of toluene [2]. Using the same electron bombardment for 1-methylpyrene, we found only one isomer, the $PyrCH_2^+$ (pyrene with a methylene group, analogous to benzylium ion)[3]. This result is consistent with recent calculations on the unimolecular dissociation of 1-methylpyrene ion to $PyrC_7^+$ ion, which is predicted to be extremely unlikely [5].

Using the cryogenic FTICR setup PIRENEA, we are now investigating the possibility to overcome the barrier between the two isomers. In this experiment, we apply chemical reactivity to probe and isolate isomers. We hope to generalize the benzylium/ tropylium ion dichotomy.

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Summary:

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Specific Peptide-Bond Dissociation and Effects of a Phenyl Group of Some Peptide Model Molecules

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Near-edge X-ray absorption fine structure (NEXAFS) spectra at carbon, nitrogen, and oxygen K-edges of some peptide model molecules were measured utilizing an orthogonal acceleration time of flight mass spectrometer and were calculated with time-dependent density functional theory. Excitation source such as soft X-ray photons were from synchrotron radiation at Taiwan Light Source. The intensity and branching ratio (as per cent) as functions of photon energy were obtained for all

ionic products. Based on our theoretical calculation, the absorption peaks were assigned as core excitations to various destination virtual orbitals. From the profiles of intensity ratios, the enhancement phenomena resulted from specific dissociation were recognized. To verify what the dissociation paths are, isotopic molecules were utilized to reveal the identities of the enhanced ionic fragments. It is interesting to note that most of the enhanced products were produced via breaking the peptide bond (including hydrogen atom(s) elimination) no matter the initial excited atom was carbon, nitrogen or oxygen. The branching ratios of breaking peptide bonds could be as high as 71% following a specific excitation. Adding a phenyl group on the peptide model, the branching ratios decrease dramatically to about 35%. It is very possible attributed to that the destination molecular orbital is mixed on the amide and phenyl groups.

Summary:

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Angry Aromatics: Substituted phenyl radical reactions probed with VUV synchrotron photoionization MS

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This presentation will describe our recent results probing the gas-phase radical reaction of various phenyl-radicals using synchrotron VUV photoionization mass spectrometry at the Advanced Light Source synchrotron.

Functionalized aromatic molecules are prevalent in gas-phase reactive environments including combustion, atmospheric chemistry, and extra-terrestrial atmospheres but the precise pathways that initiate PAH and PANH are not well formalized. Using synchrotron VUV photoionization mass spectrometry, the fates of highly-reactive phenyl radicals are probed in the presence of a neutral, closed-shell co-reactant. These phenyl radicals, including substituted variants, are synthesized using laser photolysis and the ensuing chemical reactions are followed. This provides kinetic detail while the VUV photoionization can be tuned to probe reaction products (and transients).

Using this method, our group has been targeting substituted phenyl radicals (ortho, meta) to determine how these additional groups perturb, or indeed dictate, the ensuing chemistry. Recent results with methyl-phenyl radicals reacting with small hydrocarbons (allene, propene, propyne) will be shown and compared to calculations that rationalize the mechanistic pathways and support the product assignments. Several ring-growth pathways are elucidated. These studies also draw on previous results of reactions with O₂.

As might be expected, ortho-substituted phenyl radicals have unique bimolecular reaction pathways (compared to meta variants) due to interactions between the radical adduct site and the adjacent ring-substitute but it is not a simple story...

Summary:

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Kinetics of the C₃H₅ + O₂ reaction investigated by photoionization using synchrotron radiation

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The kinetics of the ubiquitous allyl radical, C₃H₅, with molecular oxygen has been studied at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source. The new CRF-PEPICO (Combustion Reactions Followed by Photoelectron Photoion Coincidence Spectroscopy) setup uses a slow flow tube reactor and enables the recording of threshold photoelectron spectra necessary for a background free, isomer selective analysis of the reaction. We compared the rate constants of direct and indirect sources of allyl radicals. Photolysis of allyl iodide at 266 nm and 213 nm was used as a direct source, and H-atom abstraction of propene by Cl atoms, generated from photolysis of oxalyl chloride, as an indirect one. All experiments used Ar as bath gas and were performed at room temperature with an excess of oxygen to maintain pseudo-first order conditions and at various pressures from 0.8 to 3 mbar. Although the allyl radical could be observed and identified, the main reaction product the allyl peroxy was not observed. This can be attributed to the very weakly bound allyl peroxy cation leading to dissociative photoionization. From the concentration-time profiles of the allyl radical second order rate constants between $1.35 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.75 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 3 mbar were determined. While the rates for the direct and indirect generation of allyl radicals agree well with each other, the found rate constants are about a factor 2 higher than reported values in the literature. In part the reason for this may be the use of He as bath gas, resulting a lower collision efficiency causing a different fall-off behavior. Using the photolysis of oxalylchloride to generate allyl radicals an interesting product is observed at $m/z = 68$, which could be identified as 1,3-butadienal by its threshold photoelectron spectrum. A possible formation mechanism involves the reaction between allyl the intermediately generated COCl radical from the 266 nm photolysis of oxalyl chloride.

Summary:

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From grains to fragments: the study of polycyclic aromatic hydrocarbons in multiple radiation environments

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Polycyclic aromatic hydrocarbons (PAHs) are thought to play important roles in interstellar chemistry, from ice grain formation to catalyzing reactions; however, much about their photophysics and photochemistry is not yet known. Therefore, a multi-spectroscopic approach has been employed to study PAH fragmentation upon interaction with high radiation fields, PAH homo-clustering and

clustering with water, and the products from discharges of PAHs with organic molecules. The former has been done at the free electron laser facility FLASH in which the fragmentation products of PAHs are studied after interaction with XUV-IR radiation. The latter experiments have been undertaken at the free electron laser, FELIX. Here, IR-UV ion dip experiments revealed the mass-selective mid- and far-IR spectra of the PAH, acenaphthene, clustered with itself and up to three water molecules. We have also investigated the discharge products of several small PAHs with acetonitrile (CH_3CN), in which we observed the formation of larger cyano group containing PAHs.

Summary:

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Design of the CRF-PEPICO

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The CRF-PEPICO is a new double-velocity map imaging photoelectron photoion coincidence spectrometer that is currently being designed and built at Sandia. The purpose of this new instrument is to study fundamental gas phase reactions with transient species pertinent to combustion and atmospheric chemistry. This instrument will be used at the Advanced Light Source in Berkeley and at Sandia. PEPICO spectroscopy yields multidimensional data sets consisting of ion mass spectra, photoionization spectra, mass-selected photoelectron spectra and kinetic time profile of all species. Mass-selected photoelectron spectra are powerful molecular fingerprints to enable studies of isomers that cannot be distinguished by conventional photoionization mass spectrometry.

Summary: