Photon Tools for Physical Chemistry 2014

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Book of Abstracts

Contents

0

Welcome

Session 1 Flames and reactors (Taatjes/Tranter) / 35

A brief history of TPEPICO –and the critical features that make it so powerful

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Threshold photoelectron photoion coincidence has evolved during the past four decades into a uniquely powerful tool that is ideally carried out at synchrotron radiation facilities. This talk will combine a bit of history with key experimental features that permit the simultaneous optimization of electron resolution, and electron and ion collection efficiencies. A critical aspect for extracting metastable ion dissociation rates and translational energy release information is an extended and constant electric field in the first acceleration region. The talk will be illustrated with examples such as the H loss from the formic acid ion, which proceeds by passing over a surprisingly large barrier.

Session 1 Flames and reactors (Taatjes/Tranter) / 38

Physical chemistry with free electron Lasers (FEL) sources: A prospective view on some experiments and concepts

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The development of elaborate sustainable and regenerative energy concepts has reached a point at which scientist necessarily have to move beyond macroscopic descriptions and take the steps that enable the ability to probe and decode the microscopic quantum world. Chemical processes, involved in combustion, in atmospheric and in surface science have to be understood on a molecular level, at which energy transfers and rearrangements of nuclei dictate the chemistry. Excited molecules tend to rapidly distribute their energy on sub-ps timescales and monitoring of energy transfer requires ultrafast spectroscopy. Pump-probe techniques with temporal resolution of a few 10 fs are state of the art. Optical spectroscopy typically involves transitions of valence electrons within a molecular system, while X-ray spectroscopy is concerned with transitions of core electrons. New concepts of X-ray coherent nonlinear spectroscopic techniques have to be developed. I will give a short overview of the new SwissFEL free electron laser facility and discuss some prospective concepts of spectroscopic methods in physical chemistry in matters of their feasibility and practicability at advanced FEL light sources.

Session 1 Flames and reactors (Taatjes/Tranter) / 3

A Chemical Kinetics Shock Tube for Synchrotron Studies

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In recent years many impressive studies have been conducted at synchrotron light sources using X-rays and VUV photons to probe combustion phenomena from chemical mechanisms in low pressure flames and flow reactors to particle formation in flames. Recent developments promise to bring more synchrotron based diagnostics to bear on combustion studies. However, most practical combustion devices operate in temperature and pressure spaces that are not accessible to the reactors that are most frequently used at synchrotrons. In laboratory studies shock tubes have provided much of the high temperature experimental kinetic data and also have been used to probe reactions at pressures up to 1000 bar and as a class encompass the conditions found in most combustors. Consequently, shock tube experiments at synchrotrons have the potential to complement existing synchrotron based kinetic experiments. However, due to their large size and very low firing rates traditional shock tubes are not compatible with synchrotron based diagnostics.
A miniature (0.25”bore, ˜24”long) shock tube has been designed that can be fired at repetition rates up to 4Hz and generate reaction conditions in the range 700-3000 K and P < 100 bar. The shock tube has been designed in a modular manner to facilitate use with a variety of diagnostic devices. The apparatus has been installed at both the Advanced Photon Source (Argonne National Laboratory) and the Advanced Light Source (Lawrence Berkeley National Laboratory). At the APS X-ray densitometry has been used to measure gas properties behind shock waves and at the ALS VUV-photoionization mass spectrometry studies were performed, both of which will be discussed.

Session 1 Flames and reactors (Taatjes/Tranter) / 13

Multiplexed Synchrotron Photoionization Mass Spectrometric Characterization of Fuel Oxidation Reactions

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Multiplexed Synchrotron Photoionization Mass Spectrometry has been demonstrated to be a powerful experimental technique for the observation and characterization of important reaction intermediates, such as peroxy radicals in combustion and Criegee intermediates in atmospheric chemistry, and fuels reaction pathways. In this talk the oxidation reactions, carried out at the Chemical Dynamics Beamline of the Advanced Light Source of Lawrence Berkeley National Laboratory, of a naphthenic and an aromatic fuel will be presented showing how different information, such as reaction mechanism steps, reaction species identification, and branching fractions can be gained.

Session 1 Flames and reactors (Taatjes/Tranter) / 36

Advances and Challenges in Experimental Research of Combustion

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Over the last decade the Chemical Dynamics Beamline at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory has been used extensively to provide unprecedentedly detailed insights into the chemical structure of flames. The isomer-resolved, quantitative data has been used world-wide to update and improve chemical kinetic models for the combustion of hydrocarbon fuels and for prototypical biofuels, i.e. alcohols, ethers, and esters. This presentation summarizes some of the recent findings, for which synchrotron radiation and its properties had been essential.
In the second part of the talk, I will highlight the new combustion experiments at the ALS, which are targeted towards gaining a deeper understanding of the formation of aromatic species and their growth to soot particles in combustion environments and towards unravelling details of the low-temperature combustion chemistry. To this end, we have installed diffusion flames and jet-stirred reactors and also utilize flame-sampling aerosol mass spectrometry. Some early highlights, e.g. limitations of the so-called HACA growth mechanism and the detection of ketohydroperoxides, will be presented.
The experimental work which will be presented is done in collaboration with the groups of Kohse-Höinghaus (Bielefeld), Kasper (Duisburg-Essen), Sarathy (KAUST), Yang (Tsinghua), Michelsen (Sandia), Dagaut (Orleans), Taatjes (Sandia), Leone (Berkeley), and Yu (Princeton).

Session 1 Flames and reactors (Taatjes/Tranter) / 48

Disentangling reactive isomers in flames using PEPICO

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One key aspect to the improvement of combustion devices is the knowledge of how a fuel burns. Flame-sampling molecular-beam mass spectrometry (MBMS) has become a standard technique for chemical analysis of reacting gas flows in premixed laminar low-pressure flames. The MBMS measurements typically result in speciation data that contribute as validation data base to the construction and refinement of chemical kinetic reaction mechanisms [1].
The talk discusses measurements performed with the iPEPICO spectrometer at the VUV-beamline of the Paul Scherrer Institute in Villigen, Switzerland coupled to a newly developed molecular-beam interface and flat-flame burner [2] and focuses on its strengths in the detection of reactive radicals. In particular, fuel radicals formed by hydrogen abstraction from the fuel molecule are the starting points for branching in the fuel destruction pathways. Consequently, the measurement of their (relative) concentrations is of particular importance for reaction mechanism development and validation. The spectral information in the mass-resolved threshold-photoelectron spectra adds a new dimension to isomer detection that allows more precise species identification than other isomer detection strategies in combustion research and provides for the first time evidence that vibrationally excited molecules can be sampled by MBMS from flames.
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Session 1 Flames and reactors (Taatjes/Tranter) / 58

International (Photo)-Ionization Cross-section Database

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Molecular Beam mass spectrometry has developed into a staple technique for the investigation of gas phase reactive systems including for instance kinetics (Sandia: Kinetics Machine, Univ. Colorado: Reactor, Argonne: Shock tubes), Flow and jet stirred reactors (Princeton, Bielefeld University, NSRL, DLR, Sandia, LBL) and flames (Université catholique de Louvain, Bielefeld University, Princeton, Sandia, University of Duisburg-Essen, Siberian Branch of the Russian Academy of Sciences). The quantitative and even qualitative results of all these experiments and many more rely heavily on the knowledge of ionizations properties of the investigated molecules (Thresholds, cross-sections, electronic structure of the ground and ion states, maybe even interaction between different components). The NIST Chemistry Webbook (http://webbook.nist.gov/chemistry/) only lists ionization thresholds and fragment appearance energies stating all the measurements known to them and sometimes an evaluated value. Even this database is maintained only in long cycles and does not keep pace with the measurements and needs of this Community or other communities which also rely on such data and measure them as byproducts of their work. Most recently Fei Qi et al at NSRL gathered all the published cross-sections in a database which was made available online. (http://flame.nsrl.ustc.edu.cn/database/) This list is likely not comprehensive as new cross-sections are generated frequently and are inefficiently stored in closed loops that could be easily accessible to all researchers. Furthermore an evaluation of the cross-sections in respect to their accuracy would be most useful. Accurate and reliable data is scarcely available in the literature. E.g. a given photoionization efficiency curve measured on different machines at the same beamline has led to different results. Obtaining cross-sections by computational methods is a route employed recently. The calculations can yield cross-sections with reasonable trustworthiness. The usual problem is that this work either needs some serious time commitment by the experimentalists who need the cross-section, or relies on computational chemists/physicists who usually does not have funding on which this type of work can be performed on. The Physikalisch Technische Bundesanstalt PTB as the German Metrology institute has the scope of improving the accuracy and precision of measurements. Therefore we would like to outline a concept to establish a network of institutions to coordinate the individual efforts and to acquire funding from the metrology community to establish, maintain and expand this crucial reference database.

Session 2 Chemical kinetics (Osborn/Ahmed) / 44

Hot Nozzles & Cold Beams: Revealing Ion Chemistry, Solvation, & Combustion

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Tunable vacuum ultraviolet radiation generated at a synchrotron provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry. Used in conjunction with theory, this provides profound insight into proton transfer mechanisms, solvation and electronic structure in organic molecules and clusters. New results from in-source molecular beam ionization of water and methanol leading to nucleation and ion induced chemistry mediated via proton transfer will be presented. I will also discuss the use of a novel microtubular reactor (The Chen Source) to follow model mechanisms relevant to the formation mechanisms of polycyclic aromatic hydrocarbons (PAHs), and PANHs (Nitrogenated Hydrocarbons) and oxidation in hydrocarbon-based combustion processes. These studies are being extended to probe the energy transfer processes that occur in these heated reactors using velocity map imaging in conjunction with synchrotron radiation.

Session 2 Chemical kinetics (Osborn/Ahmed) / 14

Pyrolysis Mechanism of Cyclopentadienone Revealed by Synchrotron Radiation

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The study of the pyrolysis of complex fuels is carried out in a heated, CW micro-reactor. Reactions are studied in a resistively-heated SiC microtubular (0.66 mm i.d. x 2.5 cm) flash pyrolysis flow reactor from 1000 –1800 K. The standard reactor operating conditions of 280 sccm He flow have been studied by computational fluid dynamics. [International J. Phys. Chem. 2014, (submitted)]. The gas flow has been found to be laminar and the residence time in the reactor is of the order 25 —150 μsec. The reaction mechanism for the pyrolysis of cyclopentadienone, C5H4=O, has been studied. Cyclopentadienone is an intermediate in the high temperature oxidation of aromatic fuels and in the thermal cracking of biomass. The molecular structure of C5H4=O is known by microwave spectroscopy (J. Phys. Chem. Letts. 2014, 5, 2201-2207); polarized IR spectroscopy has established the vibrational force field (J. Phys. Chem A 2014, 118, 708-718). We have studied the pyrolysis of C5H4=O over a 1000 K —1600 K range. We find two channels: Reaction (1) C5H4=O (+ M) → CO + 2 HC≡CH and Reaction (2) C5H4=O (+ M) → CO + HC≡C-CH=CH2. The decomposition of C5H4=O is shown to be unimolecular and the products, HC≡CH from (1) and HC≡C-CH=CH2 from (2), were detected in situ by means of tunable synchrotron photoionization mass spectroscopy at LBNL's ALS. The temperature-dependent branching ratio of [HC≡CH]/[HC≡C-CH=CH2] was established and the ratio of k1/k2 was measured. Separate iPEPICO measurements at the PSI's SLS were used to measure IE(C5H4=O) = 9.408 ± 0.011 eV.

Session 2 Chemical kinetics (Osborn/Ahmed) / 4

Experimental Investigation of the Low Temperature Oxidation of the Five Isomers of Hexane

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The low-temperature oxidation of the five hexane isomers (n-hexane, 2-methyl-pentane, 3 methyl-pentane, 2,2-dimethyl-butane and 2,3-dimethyl-butane) was studied in a jet-stirred reactor (JSR) at atmospheric pressure under stoichiometric conditions between 550 and 1000 K. The evolution of reactant and product mole fraction profiles were recorded as a function of the temperature using two analytical methods: gas chromatography and synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Experimental data obtained with both methods were in good agreement for the five fuels. These data were used to compare the reactivity, the nature of the reaction products and their distribution. At low temperature (below 800 K), n-hexane was the most reactive isomer. The two methyl-pentane isomers have about the same reactivity, which was lower than that of n-hexane. 2,2 dimethyl-butane was less reactive than the two methyl-pentane isomers, and 2,3-dimethyl-butane was the least reactive isomer. These observations are in good agreement with research octane numbers given in literature. Cyclic ethers with ring including 3, 4, 5 and 6 atoms have been identified and quantified for the five fuels. While the cyclic ether distribution was notably more detailed than in other literature JSR studies of branched alkane oxidation, some expected oxiranes were missing amongst the cyclic ethers expected from methyl-pentanes. Using SVUV-PIMS, the formation of C2-C3 monocarboxylic acids, ketohydroperoxides, and species with two carbonyl groups has also been observed, supporting their potential formation from branched reactants in line with what was previously demonstrated from linear fuels. Possible structures and ways of decomposition of the most probable ketohydroperoxides were discussed.

Acknowledgment
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Session 2 Chemical kinetics (Osborn/Ahmed) / 5

Experimental study of the low- and high-temperature oxidation of dimethyl ether in a jet-stirred reactor

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Due to the current issue concerning the growing primary energy demand, not to mention a general interest in sustainable development, bio-fuels became very fashionable in recent years. They are subject to a lot of research on combustion with the characterization of the reactivity and pollutant emissions. The molecule of dimethyl ether (DME) has led to a strong interest in the field of combustion. Corresponding to the simplest linear ether (CH3-O-CH3), it has a high cetane value (55-60) and a low toxicity. Promising studies have highlighted key-strengths of this molecule as an additive agent or even an alternative diesel fuel. Among these advantages, we find a particularly significant decrease in the formation of soot and NOx particles.

Due to its simplicity, DME is a good choice for understanding the mechanisms of ether oxidation. It exhibits typical "two-stages"ignition characteristics common to many hydrocarbons: low temperature, negative temperature coefficient, and hot ignition phenomena. Several experimental and theoretical studies have investigated on DME combustion, using various equipments (jet-stirred reactor, shock-tube, counterflow diffusion flame, variable-pressure flow reactor…) and at different operational conditions. Even if they bring essential information, they are unable to predict a single valid model for all circumstances. The objective of this study is to investigate DME oxidation with a different approach in order to complete existing experimental data, and subsequently better understand its reaction mechanism.

This was done with several experiments carried out in a jet-stirred reactor operating at 800 Torr, 500-1100 K, and at different equivalence ratios: 0.25, 1 and 2. The products obtained have been analyzed using two complementary methods: gas chromatography (GC) and cavity ring-down spectroscopy (CRDS). GC is efficient in separating compounds and allows us to analyse a wide range of products like CO, CO2, hydrocarbons, CH3CHO and CH3OCHO ; while CRDS is an absorption spectroscopic technique and allows us to analyze species such as CH2O, H2O and H2O2 (undetectable by GC).

Profiles of DME conversion and products were compared with expected theoretical profiles (cf. Zhao et al., J. of Chem. Kin. 2008,401-18). While they are quite similar at high temperatures, a significant difference appears at low temperature (from 500 to 750K). Whatever equivalence ratio studied, the model overestimates the conversion of the reactant over this range of temperature. Pre-established mechanisms are then not yet optimal and should be improved to better predict the oxidation of DME.

Session 2 Chemical kinetics (Osborn/Ahmed) / 22

The N + CH3, N + H2CN and N + CH2 reactions: kinetics and products.

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The N(4S) + CH3 reaction is an important reaction for Titan's atmosphere as well as in evolved dense molecular clouds and in protoplanetary disks, leading to HCN through various reactions involving H2CN and CH2 radicals. We have studied the kinetics of the N + CH3 reaction between 147 K and 440 K using a fast flow reactor (300 K –440 K) and the CRESU technique (147 K). The reactants and various products (CH3, H2CN, CH2 radicals and H atoms) were detected either through mass spectroscopy after ionization at 10.54 eV or by VUV-LIF, the photons being produced through tripling in rare gas. By modelling the kinetics of CH3, H2CN and CH2 radicals for various conditions, we were able to determine the rate constant and the branching ratio of the N + H2CN reaction showing that the main products were CH2 + N2. We have performed DFT and ab-initio calculations on the N + H2CN reaction to elucidate the mechanisms involved. We have also measured the absolute ionization cross section of H2CN at 10.54 eV (using CH3 as reference) through the N + C2H5 reaction which lead to the same amount of CH3 and H2CN radicals.

Session 2 Chemical kinetics (Osborn/Ahmed) / 32

Femtosecond Time-Resolved X-ray Absorption Spectroscopy of Liquids using SACLA

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We present time-resolved X-ray absorption spectroscopy (TRXAS) of aqueous solutions using a hard X-ray free electron laser (SACLA: SPring-8 Angstrom Compact Free Electron Laser). An aqueous solution of [Fe(III)(C2O4)3]3- is photoexcited by a femtosecond 266 nm pulse, and transient X-ray absorption spectra were measured as a function of pump-probe delay time. The Fe K-edge exhibited an instantaneous red-shift upon 266 nm photoexcitation followed by a slight blue shift within 2 ps and remained unchanged over 100 ps. The X-ray fluorescence method offers higher sensitivity than a direct absorption method [Obara et al. Optics Express, 22, 1105 (2014)] and enables TRXAS at one order of magnitude lower sample concentration. Comparison with TDDFT calculations of the K-edges of the product candidates reveals that the most likely products within 100 ps are [Fe(II)(C2O4)2]- or [Fe(III)(C2O4)2]2-.

Session 2 Chemical kinetics (Osborn/Ahmed) / 23

Investigation of reactions of CnH (n = 1 –6) radicals with propyne using synchrotron VUV ionization

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Carbon is the fourth most abundant element in our solar system and in the universe. Hydrocarbon chemistry plays an important role in planetary atmospheres, interstellar environments, and fuel combustions. Thus, the study of dynamics of hydrocarbon reactions can facilitate the understanding of stellar evolution, air pollution, etc. A crossed molecular-beam apparatus combined with synchrotron vacuum-ultraviolet ionization has been demonstrated to be a powerful tool in the investigation of dynamics of elementary chemical reactions. Recently, we have explored the dynamics of C/H and C/X exchanges in the reactions of 3P carbon atoms with ethene (C2H4), vinyl fluoride (C2H3F), vinyl chloride (C2H3Cl), and propene (C3H6) using the crossed molecular-beam apparatus established at NSRRC; X = F, Cl or CH3. The success encourages us to investigate the reactions of hydrocarbon radicals (e.g., CH, C2H, C3H, C4H, C5H, and C6H) with unsaturated hydrocarbons (e.g. C3H4). Those free radicals were produced from a mixture of 1% ethyne (C2H2) seeded in He by pulsed high-voltage discharge. We will present some of the experimental results of the reactions of CnH (n = 1 –6) radicals with propyne (C3H4) leading to product Cn+3H4 + H. The mechanisms of production of methylpolyynes were investigated by interrogating translational-energy distributions, angular distributions, and photoionization spectra of products Cn+3H4. Furthermore, the potential-energy surfaces of reactions CnH + C3H4 -> Cn+3H4 + H were established with ab-initio methods. The combination of crossed-beam experiments and quantum-chemical calculations gives an outline for the mechanisms of reactions of CnH radicals with propyne.

Session 2 Chemical kinetics (Osborn/Ahmed) / 34

Product Detection and Kinetic Studies of Combustion Intermediates: Substituted-Phenyl Oxidation Reactions

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Using a combination of experimental and computational techniques, we are examining ortho-substituted phenyl + O2 reactions to provide a useful framework for understanding aryl radical oxidation in combustion environments. Our results show that ortho-substituted phenyl radicals have access to unique chemical pathways, compared to the meta and para counterparts, due to the proximity of nearby functional groups. The links between the molecular details, such as this ortho effect, and the combustion properties of these molecules are not well understood despite aromatic molecules comprising a large fraction of conventional gasoline (40-45%).

Our experimental investigation utilizes two strategies: (i) ion trap mass spectrometry, with the distonic ion approach [1], and (ii) VUV synchrotron photoionisation spectroscopy conducted at the Advanced Light Source, LBNL, in collaboration with scientists at Sandia National Laboratories. Quantum chemical calculations and RRKM/Master Equation modelling are also preformed to rationalise the experimental results.

In the example case of 2-hydroxyphenyl + O2, after O2 addition, proximity of the OH group to the peroxyl radical allows for peroxyl ⟶ phenoxyl isomerization and subsequent OH elimination to produce 1,2-benzoquinone (oBQ, m/z 108). Cyclopentadienone (CPO, m/z 80) is also detected. Isomers are identified by examining VUV photoionization spectra. The CPO product has also been identified in the decomposition of biofuel surrogates [2], however its formation in this case is difficult to reconcile as a primary product. Utilising ion trap mass spectrometry, and charge-tagged analogues (distonic radical ions), allows for the isolation and collisional activation of the charge-tagged oBQ. Upon collisional activation, this oBQ is found to yield the corresponding CPO (by CO elimination). This important result, along with computational reaction energies, supports the notion that neutral CPO is a secondary reaction product, formed via decomposition of the nascent oBQ primary product. Quantum chemical calculations are in accord with this mechanism. This system and several other substituted phenyl radical systems will be described in this presentation.

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Session 2 Chemical kinetics (Osborn/Ahmed) / 31

Investigation on Combustion Chemistry of Aromatic Hydrocarbons Using Synchrotron and Kinetic Modeling Tools

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Aromatic hydrocarbons are a major component family in petroleum-based transportation fuels and their surrogate fuels, and are also key precursors of soot. The benzene ring structures of aromatic hydrocarbons result in complex intermediate pools in their combustion, especially the great amount of large free radicals and isomers, making aromatics combustion one of the most complicated targets for combustion diagnostics. In recent years, synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) has been introduced to investigate pyrolysis and flame chemistry of aromatic hydrocarbons. The unique simultaneous detectability of SVUV-PIMS for free radicals and isomers help detect a variety of free radicals and distinguish a great deal of isomers. The mole fraction profiles of combustion species were measured as the function of heating temperature in the flow reactor pyrolysis and the function of distance from burner surface in the premixed flames, providing useful validation data for kinetic models of aromatics combustion. Based on recent theoretical progresses in combustion kinetics of aromatic hydrocarbons, kinetic models of benzene, toluene, styrene, ethylbenzene, o-xylene, n-propylbenzene and tetralin combustion have been developed and validated against both our SVUV-PIMS data and previous experimental data. For example, the vast amount of validation data of the toluene model include species profiles in flow reactor pyrolysis and oxidation, shock tube pyrolysis and oxidation, jet stirred reactor oxidation and premixed flames, and global combustion parameters such as ignition delay times and laminar flame speeds, covering a wide range of conditions from low to high temperatures, subatmospheric to high pressures and very lean to pyrolysis conditions. The decomposition kinetics of aromatic hydrocarbons investigated and the formation kinetics of PAHs were investigated using modeling tools such as the rate of production analysis and sensitivity analysis.

Session 3 Spray and particulate matter (Ossler) / 15

Developments of in-situ X-ray scattering diagnostic tools for studies of combustion and reactive systems

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Emerging high brilliance X-ray radiation at different accelerator facilities around the world will give access to many types of new studies in-situ under complex experimentally challenging dynamic conditions: High temperatures, pressures, and densities, which also can present strong gradients.
During the last decade our group has been performing experiments at MAX-lab, the APS, and the ESRF. During this time it has been possible to develop detection systems and diagnostics tools for the study of combustion related phenomena, such as particles formation dynamics in flames, aggregation and phase transitions of particles under combustion like condition. It has also been possible

to do introductory studies on levitated drops and study evaporation and structural properties. One of the achievements is a combined small-angle and wide-angle X-ray scattering (SAXS+WAXS) detection system that has been built and operated at different beamlines.
In this presentation an overview of our tools, activities, results and future perspective will be given.

Session 3 Spray and particulate matter (Ossler) / 11

X-Ray Diagnostics of Cavitation and Sprays

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Scientists at Argonne National Laboratory have been developing synchrotron-based diagnostics for fuel injection, cavitation, and sprays. This presentation will outline the capabilities of several diagnostics, including time-resolved radiography, small-angle scattering, x-ray flourescence, and phase contrast imaging. Applications of these techniques to measurements of droplet size, cavitating flows, and fuel/air mixing will be presented.

Session 3 Spray and particulate matter (Ossler) / 42

Barrierless proton transfer across weak CH•••O hydrogen bonds in dimethyl ether dimer

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Proton transfer is of general interest due to the important role it plays in biological, chemical and atmospheric sciences. Hydrogen bonds are known to facilitate inter- and intra-molecular proton transfer, defining a coordinate for the transfer to proceed. The observation of protonated cluster fragments upon photoionization is typically explained by a fast intermolecular proton transfer occurring across hydrogen bonds. Hydrogen atom and proton transfer are common gas phase ion-molecule reactions of both polar and non-polar species. Therefore, clusters bound by weak van der Waals interactions, filling the gap between strongly hydrogen bonded systems and molecules interacting upon collision, are of particular interest for studying gas phase ionization-induced chemistry.
Dimethyl ether dimer is an example of a system that exhibits extremely weak, or arguably no hydrogen bonding. We present threshold photoelectron-photoion coincidence spectra of fully deuterated dimethyl ether monomer, dimer and their major ion fragments in the photon energy range of 9 to 14 eV. The lowest energy fragment ion arising from dissociation of the dimer is CD3ODCD3+ with an appearance energy at 0 K of 9.730 ± 0.030 eV, which points to efficient ionization-induced intramolecular proton transfer. Results from electronic structure calculations confirm barrierless proton transfer in the ionized state of the dimer. The calculations suggest that at least five dimer isomers may have significant population in the molecular expansion. All neutral dimethyl ether dimer isomers studied exhibited only weak, unconventional hydrogen bonding, but were nevertheless found to undergo barrierless proton transfer upon photoionization producing the same isomer of the radical cation.

Session 3 Spray and particulate matter (Ossler) / 16

In-situ Soft X-Ray Absorption Spectroscopy of Flames

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The feasibility of in-situ soft x-ray absorption spectroscopy for imaging carbonaceous species in hydrocarbon flames is demonstrated using synchrotron radiation. Soft x-rays are absorbed by core level electrons in all carbon atoms regardless of their molecular structure. Core electron spectroscopy affords distinct advantages over valence spectroscopy, which forms the basis of traditional laser diagnostic techniques for combustion. In core level spectroscopy, the transition linewidths are predominantly determined by the instrument response function and the decay time of the core-hole, which is on the order of a femtosecond. As a result, soft x-ray absorption measurements can be performed in flames with negligible Doppler and collisional broadening. Core level spectroscopy has the further advantage of measuring all carbonaceous species regardless of molecular structure in the far edge region, whereas near-edge features are molecule specific. Interferences from non-carbon flame species are unstructured and can be subtracted. In the present study, absorption measurements in the carbon K-edge region are demonstrated in low-pressure methane jet flames. Two-dimensional imaging of the major carbonaceous species, CH4, CO2, and CO, is accomplished by tuning the synchrotron radiation to the respective carbon K-edge near-edge x-ray absorption fine structure (NEXAFS) transitions and scanning the burner. We also investigate the feasibility of soft x-ray absorption measurements in flames with larger hydrocarbon fuels.

Session 3 Spray and particulate matter (Ossler) / 26

VUV Photoelectron Spectroscopy of Aqueous Aerosols

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The crucial roles of aerosols have been increasingly recognized in a variety of important research fields, encompassing the atmospheric chemistry, the environmental science and the planetary science. Recently, the implications of aerosols in the biomedical science, pharmaceutical administration and micro-fabrications of nano-structured novel materials have also been actively explored. To probe the valence electronic structure of aerosols, which decisively determines their chemical activities, an aerosol VUV photoelectron spectroscopy apparatus equipped with a high resolution hemispherical energy analyzer has been recently built, using the VUV radiation generated from the undulator beamline (U9) at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan as the ionization photon source. Preliminary efforts have been focused on studying the aqueous aerosols. By introducing the aqueous samples of interest into the aerosol droplet phase with an average droplet size of ˜ 100 nm and collimating them to a focused nanoparticle beam in vacuo via the aerodynamic lens system, this new aerosol apparatus readily creates a microscopic aqueous environment, which allows ones to study the hydrated structure of biologically important materials and extract valuable information that can only be accessed under relevant aqueous conditions, such as the solvent effect, pH effect and the solvent-solute interaction. Recently, we applied this newly constructed aerosol VUV photoelectron spectroscopy apparatus to investigate the valence electronic structure of glycine and cysteine aqueous aerosols for the first time. The effect of pH value on the electronic properties of the chosen aqueous aerosols has been interrogated. Ultimately, due to the significance of aerosols in numerous fields and the crucial role of their electronic structure in determining their chemical activities, this new aerosol VUV photoelectron spectroscopy instrument sheds new lights in advancing our understanding on the fundamental electronic characteristics of aerosols and in unraveling the physical chemistry underlying their significance in various fields.

Keywords: aerosols, aerosol VUV photoelectron spectroscopy, undulator,
glycine aqueous aerosols, cysteine aqueous aerosols, pH effect

Session 3 Spray and particulate matter (Ossler) / 27

Studies of combustion engine exhaust: An in-situ laser induced fluorescence oil consumption method and simulations of Diesel particulate matter via laser desorption time of flight mass spectrometry.

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Combustion engines are still largely the most commonly used in the automobile industry. Higher efficiency and a better knowledge of internal processes are constantly pursued by engineers. Optimization and improvements can be made by monitoring the exhaust stream. Oil consumption method is one of the most interesting techniques to reach that goal. In-situ and on-line techniques based in SO2 laser induced fluorescence constitute the best approach. Our department has built and designed an apparatus consisting on such a methodology1. The robust mobile prototype delivers reliable data within a very short acquisition time, and with a limit of detection down to 25 ppb. The incorporation of a steady and easy to handle optical parametric oscillator has been essential to perform a commercial system. Oil consumption data acquired in different engine regimens (load and r.p.m.) represents the final step of the long engine development. Another component in the engine exhaust such soot and aerosols, are related to the efficiency as well. These compounds are produced during combustion processes, especially in diesel engines. The number of them and the size are regulated by law and the incoming Euro 6 will become more restrictive. However, one key aspect is still being the composition of such particles. Composition and formation process are critical to minimize their generation as well as for understanding the internal engine processes. Therefore, structural studies need to be performed. Laser desorption (LD) sources can be used since thermally labile molecules can be introduced into an adiabatic regime. The created clusters can be investigated by time of flight mass spectrometry (TOF-MS). A new LD source based on a channel-type desorption source2-3 was set up. Mass spectra of the steadier aggregates formed in a relatively low effective temperature regime, might be recorded. Carbonaceous substances will be investigated as a model of soot particles. The aggregation of those with sulphur containing aromatic compounds (existing in oil and fuel) might be used as a model of exhaust aerosols. Comparison with desorbed soot under same conditions could reveal critical information about the nucleation and growing processes.

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Session 3 Spray and particulate matter (Ossler) / 8

SIMULTANEOUS X-RAY RADIOGRAPHY AND X-RAY FLUORESCENCE MEASUREMENTS FOR AERATED-LIQUID SPRAYS

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The aerated-liquid (or effervescent, or barbotage) jet is a promising fuel injection scheme for efficient combustion in high-speed air-breathing propulsion systems. By preparing a two-phase mixture inside the injector with a small amount of gas to mix with the liquid fuel, the resulting aerated-liquid jet is capable of generating a well-dispersed plume for effective mixing with the ambient air and therefore for efficient combustion. In the past, structures of aerated-liquid jets were characterized by liquid-only measurements, using conventional and X-ray diagnostics, resulting in an incomplete understanding of the two-phase flows within the near field of spray plumes. In the present study, near-field structures of aerated-liquid jets discharged into a quiescent environment were explored, using simultaneous X-ray radiography for liquid phase measurement and X-ray fluorescence for gas phase measurement. Water and argon were used as the injectant and aerating gas, respectively. The experiment was carried out at the 7-BM beamline at the Argonne National Laboratory. This beamline is dedicated to time-resolved X-ray radiography, tomography, and fluorescence experiments for fuel sprays and associated phenomena. The X-ray source for the beamline is a synchrotron bending magnet, which produces nearly collimated, broadband X-ray emission. The X-ray photon energy was kept at 8 keV to provide a good compromise between absorption of the beam by the spray and excessive absorption by X-ray windows and ambient air. Raster scanning with a beam focus of 5 (V) ⊠ 6 (H) µm FWHM was used to interrogate a wide field of view of the spray. Two areas of interest will be presented. First, methodologies to derive quantitative liquid and gas mass concentrations and averaged plume properties within the aerated-liquid jets from the simultaneous radiography and fluorescent measurements were discussed. It was concluded that the present diagnostic approaches can give fairly good mass concentration profiles at locations beyond the first few mm of the flow field. The strong signal-trapping of the argon fluorescence signal by the surrounding liquid, however, was a significant limitation to quantitative measurements in the flow field immediately adjacent to the exit orifice. Ideas to mitigate this uncertainty were proposed for future efforts. Second, mass distribution profiles and averaged plume properties for representative aerated-liquid jets were explored. It was found that liquid and aerating gas exhibit different plume characteristics, even for the injection condition with vigorous mixing schemes to generate a uniform two-phase mixture inside the injector prior to the final injection. The gas plume stays along the injector axis and is narrower than the liquid plume, especially at the downstream locations for well-dispersed sprays. The potential mechanisms for the separation of liquid and gas plumes were proposed in this study.

Session 3 Spray and particulate matter (Ossler) / 33

Probing Molecular Weight Growth and Decomposition of Organic Particles in Planetary Atmospheres Using Vacuum Ultraviolet Photoionization Mass Spectrometry

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The heterogeneous chemical transformations of organic aerosols in planetary atmospheres is governed by complex free radical chemistry. Free radical reaction pathways lead to both molecular weight growth and decomposition of the aerosol. In Earth's atmosphere, developing a molecular level understanding of aerosol oxidation chemistry requires deeper insight into the role of peroxy and alkoxy radicals and their subsequent termination and chain cycling pathways. We employ synchrotron-based vacuum ultraviolet photoionization mass spectrometry, two dimensional gas chromatography and stochastic simulations to better elucidate how molecular structure and thermodynamic phase control these free radical oxidation pathways. These studies are aimed at providing better molecule-based parameterizations of aerosol formation and decomposition pathways in models of planetary atmospheres.

Session 4 Coincidence Spectrometry (Gerber) / 20

Photoelectron spectroscopy of radicals using double imaging coincidence techniques

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Radicals are key intermediate species whose detection and study lead to invaluable knowledge on the mechanism of the reactions where they participate. However, their reactivity makes their stable production a challenge, and often clean production is not possible as they are detected alongside many other byproducts, including an excess of precursor.
Here, we will show how double imaging coincidence techniques help to extract the photoelectron spectroscopy of pure radicals out of a complex mixture, which can then be used as a footprint for isomer differentiation. Two recent examples will be given: the NO3 radical produced by flash pyrolysis of N2O5, and the OH/OD radicals, produced in the newly commissioned flow tube reactor by the reaction H2O/D2O + F ⟶ HF + OH/OD. Perspectives on the application of the flow tube reactor to gas kinetics will be mentioned.

Session 4 Coincidence Spectrometry (Gerber) / 30

Diagnostic issues for clean(er) combustion

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The transition towards renewable and sustainable energy is thought to phase out combustion. With growing population, industrial production and transportation especially in emerging economies, and with substantial life spans of current technology, this transition will, however, take decades. Cleaner combustion with higher efficiency and reduced emissions must thus be addressed with urgency.
Understanding the reaction pathways that lead to undesired combustion emissions is therefore an important issue. Reliable and predictive combustion models for conventional and alternative fuels are being be developed that can be reduced for application in practical combustion systems; they must be validated with information from defined laboratory combustion conditions, using e.g. shock tubes, flow and jet-stirred reactors and flames of different configurations.
To analyze the combustion chemistry in flames and reactors in collaboration with international partners, we have relied on a unique combination of sensitive laser-based diagnostics and advanced

molecular-beam mass spectrometry. Mass spectrometric instruments using electron ionization and isomer-selective photoionization with radiation from the synchrotron sources in Berkeley, USA, and Hefei, China, have been used, as well as gas chromatography, to highlight reaction pathways for selected fuels, including hydrocarbons, alcohols, esters, furanic compounds and small amines. Most of these experimental investigations have been accompanied by detailed kinetic modeling. Recently, photoelectron photoion coincidence spectroscopy (PEPICO) performed at SOLEIL, France, has been added to this pool of methods. Examples from this collaborative research will be given with a focus on open questions and research opportunities.

Session 4 Coincidence Spectrometry (Gerber) / 24

Multiplexed Photo-Ionization Mass Spectrometry Studies of Atmospheric Peroxy Radical Reactions

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Peroxy radicals are important intermediates in the oxidation of Volatile Organic Compounds(VOCs) in the troposphere, and play a crucial role in air pollution, the formation of photochemical smog and organic aerosols. The reactions of peroxy radicals with the hydroperoxyl radical are important loss processes in atmospheres with low nitrogen oxide concentrations. Laboratory studies of the kinetics of peroxy radical reactions are complicated by the many competing self- and cross-reactions that typically occur. The large number of possible products, especially chain-propagating radical channels, further complicates the chemistry.

Time-resolved photoionization mass spectrometry (PIMS) using VUV synchrotron radiation provides a powerful approach for studying the product branching ratios and reaction rates, by selective time-resolved detection of most of the reactants, intermediates, and primary products. We report our studies of this reaction in a laser-photolysis low-pressure flow cell experiment which utilizes tunable VUV radiation generated at the Advanced Light Source synchrotron at the Lawrence Berkeley Laboratory, coupled to the Sandia multiplexed PIMS apparatus. Here we describe experiments on the self-reaction of the ethyl peroxy radical, as well as the reaction of the acetyl peroxy radical with the hydroperoxyl radical. We are able to determine relative product yields based on measurements of absolute radical concentrations, coupled with kinetic modeling of the time-dependence of the observed species.

Session 4 Coincidence Spectrometry (Gerber) / 9

Application of Coincidence Spectroscopy to Inorganic Chemistry

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Threshold photoelectron-photoion coincidence spectroscopy (TPEPICO, iPEPICO) is an excellent method to obtain structural and thermochemical information on molecules. The enhanced properties of new synchrotron radiation (SR) sources now permit to study molecules that are only available in small quantities, among them reactive open-shell molecules or inorganic species. In this presentation I will summarize recent work performed at the SLS and SOLEIL storage rings focussing at species that contain N- (nitrogen) and/or B- (boron) atoms. Among them are small radicals like NH2 and H2CN, but also more complex species like BN-heterocycles and metal complexes with B-ligands. The data permit an isomer-selective identification of the species and allow to extract ionization- and appearance energies that serve to derive binding energies through thermochemical cycles.

Session 4 Coincidence Spectrometry (Gerber) / 25

Dissociative photoionization and pyrolysis of Diazomeldrum's acid: A threshold photoelectron spectroscopy study

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Diazomeldrum's acid (DMA) is a molecule used in the investigation of the photoinduced and thermal induced Wolff rearrangement reaction and therefore of importance in photolithography.
We investigated DMA in an imaging photoelectron photoion coincidence study with the (iPEPICO) setup at X04DB VUV Beamline at the Swiss Light Source.
The threshold photoelectron spectrum (TPES) of DMA will be shown and the vibrational structure of the DMA cation will be presented. The dissociative photoionization and the fragmentation upon pyrolysis will be analyzed in detail. We identified the major fragmentation pathways in the DMA cation. Furthermore several reactive intermediates were thermally produced from DMA. Here we present the threshold photoelectron spectra of two particularly interesting pyrolysis products 2-diazoethenone N=N=C=C=O and E-formylketene O=C=(CH)-(CH)=O.

Session 4 Coincidence Spectrometry (Gerber) / 21

Threshold Photoelectron Spectra of HNCO and the NCO radical

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Isocyanic acid HNCO, a small molecule of great importance for the chemistry in the interstellar space, was investigated in a threshold photoelectron photoion coincidence (TPEPICO) experiment at the DESIRS vacuum ultraviolet (VUV) beamline at the SOLEIL synchrotron. Due to the high resolution of the DELICIOUS III experiment, the ionization energies of the first electronic states of HNCO were assigned accurately. A detailed analysis of the corresponding vibrational structures in the threshold photoelectron spectrum (TPES) is also presented.

In addition, preliminary data on the mass-selected TPES of the isocyanate radical NCO are shown. The radical, which is relevant in combustion processes, was generated by flash pyrolysis of chloroisocyanate and investigated using the iPEPICO setup at the X04DB VUV Beamline at the Swiss Light Source.

Session 4 Coincidence Spectrometry (Gerber) / 50

Photoelectron Photoion Coincidence Spectroscopy for High-Accuracy Thermochemistry (···and More!)

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Photoelectron photoion coincidence (PEPICO) spectroscopy is a marriage of photoelectron spectroscopy and mass spectrometry. Electron / ion pairs are created by single photon ionization and the two charged species are measured in delayed coincidence with each other. Ions are selected in narrow range of internal energy by collecting only ions created in delayed coincidence with the photoelectrons. The use of the PEPICO technique is demonstrated on two systems. A) Methanol isotopologues were measured using iPEPICO and, from the four independent appearance energies from the isotopologue ions, very accurate heat of formation was determined for CH2OH+. This value then yields the heat of formation of an important species in combustion processes, the CH2OH radical. B) Protonation is arguably the most important basic chemical process and the proton affinity (PA) of water is a fundamental quantity in many areas. Yet, it is notoriously difficult to determine this number accurately. Using only very accurate literature spectroscopic data and two iPEPICO measurements, one on water and one on the water dimer leads directly to PA(H2O) with an accuracy that is an order of magnitude better than the current literature value.

Photoionization mass spectrometry is a powerful detection method in gas-phase chemical kinetics. Tunable synchrotron light enables isomer separation based on unique photoionization (PI) spectra; however, mixtures of three or more isomers can be difficult to resolve by this method. By measuring the photoelectron spectrum corresponding to each cation m/z ratio, PEPICO spectroscopy provides a more detailed spectral fingerprint and higher isomer selectivity than PI spectra. Compared to PI spectra, the higher information content of mass-selected TPES spectra has been demonstrated for static mixtures and reacting systems and we believe this advance will be critical in achieving the next generation of highly multiplexed, isomer-resolved methods for time- or space-resolved chemical analysis.

Session 4 Coincidence Spectrometry (Gerber) / 56

Lignin Fast Pyrolysis –Mechanistic Studies of Model Compounds

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Catalytic fast pyrolysis is an effective method for polymerization and stabilization of reactive intermediates.1 Understanding the depolymerization mechanism during pyrolysis is evidently critical for establishing the parameters that influence the selectivity and yield of the products. During fast pyrolysis many different reaction mechanisms compete2, but also radical formation by homolytic fission of ether bonds is dominant.3 We performed fast pyrolysis of diphenylether and guaiacol under collision reduced conditions using the iPEPICO at the X04DB VUV Beamline at the Swiss Light Source and under ambient pressure (pyrolysis-GC/MS) in order identify the formed primary radicals and the stabilized end products in situ.4 Our primary objective was to determine the relationship between depolymerization initiation and the final product distribution. We found three reaction pathways depending on the conditions and the nature of the formed radicals. The formed intermediates either decomposed further, as the phenoxy radical into cyclopentadienyl radical by decarbonylation2 or the radicals recombined steadily. Radical initiated rearrangement reactions dominated the selectivity in ambient conditions. New radicals were formed and then rearranged internally, like 1-hydroxy-benzaldehyde from guaiacol.5 Importantly the temperature dependent selectivities of guaiacol resemble that of lignin.

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Session 4 Coincidence Spectrometry (Gerber) / 29

The strange spectroscopy and fragmentation dynamics of the X 2B2 ground state of CH2F2+

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At low resolution, the first photoelectron band of CH2F2, first recorded in the 1970s at a resolution of ca. 800 cm-1 (or 0.1 eV), shows an apparently simple progression in the HCH bending mode. This is consistent with the large reduction in HCH bond angle, from ca. 113o to 85o, predicted by ab initio calculations. As new technologies and photon sources have evolved over the last 40 years and the resolution has improved to better than 1 cm-1, this apparently simple spectrum has ‘changed’to reveal a complex structure of overlapping symmetric and non-symmetric vibrational modes. Interpretation is only possible allowing for coupling between anharmonic vibrations.1 In part, the complexity of the spectrum arises due to the very low dissociation limit of CH2F2+ 2B2 by H-atom loss to CHF2+ + H (D0 = 2650 cm-1). Experiments performed at the X04DB vacuum-ultraviolet beamline of the Swiss Light Source have re-recorded both the photoelectron spectrum and the coincidence fragmentation spectrum by imaging threshold photoelectron photoion coincidence spectroscopy at a resolution of ca. 15 cm-1 (or 0.002 eV).2,3 They shed new light both on the spectroscopy and fragmentation of the ground state of CH2F2+. These results will be presented and discussed at PTPC 2014.

see attached Word file

Session 4 Coincidence Spectrometry (Gerber) / 18

Dissociative photoionization dynamics of vinyl chloride in an excitation energy range of 11.0 –14.5 eV

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Photoionization and dissociative photoionization of vinyl chloride (C2H3Cl) in the excitation energy range of 11.0˜14.5 eV were investigated with the method of threshold photoelectron-photoion coincidence (TPEPICO) velocity imaging. Only C2H335Cl+ and C2H337Cl+ molecular ions with a ratio of their natural abundances were detected in the TPEPICO time-of-flight (TOF) mass spectrum at 11.67 eV, indicating that the C2H3Cl+(A2A') excited state is stable and not dissociative. C2H3+ was the unique fragment ion in the dissociation of C2H3Cl+ ion at B2A" and C2A' states below 14.2 eV. Through the TPEPICO 3D time-sliced images of C2H3+ fragment ion, kinetic energy released distribution (KERD) and anisotropic parameters in dissociation of energy-selected C2H3Cl+ ion were obtained. It is shown that the KERD at 13.14 eV is exhibited with an apparent bimodal distribution, and the KERD at 13.65 eV involves an additional shoulder at lower kinetic energy. With the aid of the re-calculated potential energy curves, the detailed dissociative photoionization mechanisms of C2H3Cl+ ion at B2A" and C2A' states have been proposed.

Session 4 Coincidence Spectrometry (Gerber) / 17

Dissociation of energy-selected CH3F+ ions studied with double imaging photoelectron-photon coincidence

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The dissociation of halogenated methane ions in different electronic states is interesting since it usually undergoes specific reactions to different products. Presently we are focusing on methyl fluoride ion CH3F+, the lightest halogenated methane, which should exhibit specific dissociation dynamics too.

We will present a detailed study of the photoionization and dissociative photoionization of methyl fluoride obtained with the double imaging photoelectron photoion coincidence (PEPICO) spectrometer, DELICIOUS III, [1] permanently installed on the DESIRS vacuum ultraviolet (VUV) beamline [2] at SOLEIL Synchrotron, France. For example, threshold photoelectron spectrum (TPES) in the energy range of 12.2-19.8 eV has been recorded and is presented in Figure 1. The X2E, A2A1 and B2E electronic states are covered, with the A2A1 and B2E excited sates overlapping and lacking structure.

The mass-selected threshold PEPICO spectra of CH3F+, CH2F+, CHF+, CH3+ and CH2+ ions are also presented in Figure 1. It is shown that the dissociation of CH3F+ ions in different electronic states can be specific, even outside the Franck-Condon region. Based on the obtained electron and ion kinetic energy correlation diagram, such as the one shown in Figure 2, the detailed dissociation mechanism of energy-selected CH3F+ ions will be revealed.

Figure 1. (a) TPES and (b) mass-selected threshold PEPICO spectra in the energy range of 12.2-19.8 eV.

Figure 2. Electron and ion kinetic energy correlation of CH3+ fragments at photon energy of 19.8 eV.

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Session 4 Coincidence Spectrometry (Gerber) / 53

Gas phase structures of small alkanes by femtosecond rotational Raman coherence spectroscopy and ab initio calculations

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The gas phase rotational motion of the all trans alkanes butane to octane has been measured in real time using femtosecond (fs) time resolved rotational Raman rotational coherence spectroscopy (RR-RCS) at two temperatures T=160 and 295 K. Four-wave mixing transients are recorded over times up to 5 ns. The method probes the rotation of non-polar (and polar) gas phase molecules with fs time resolution. In addition to the dominant RCS signals of the lowest-energy all-trans form, for n-pentane to n-octane the rotational recurrences of several low energy gauche rotamers are also observed in the room temperature T=295 K gas-cell experiments, Due to large differences in structure, the contributions of the different gauche and trans rotamers to the RCS signal are clearly separated. At room temperature the low-energy thermally excited vibrational bending levels contribute up to 50% of the population for each given rotamer. Upon cooling the alkanes to 80 K in a supersonic jet, almost all the gauche rotamers and the thermally excited low frequency bending vibrations relax to the all trans v'=0 levels.
The supersonic jet measurements yield accurate B0 rotational constants. Combining these B0 with the results of all-electron coupled-cluster CCSD(T) calculations, the intermolecular distances can be predicted.

Session 4 Coincidence Spectrometry (Gerber) / 54

Investigation of 2-Methylfurane pyrolysis at VUV beam line of Swiss Light Source

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2-Methylfurane, which can be produced from uneatable biomass, has the potential to be used as alternative fuel in engines. Its combustion chemistry was investigated within the last few years by

several groups. But much less knowledge is available about its thermal pyrolysis behaviour, especially the formation of intermediates and pollutants, which can be produced at fuel rich combustion conditions, too.

Therefore the thermal pyrolysis of 2-methylfurane was investigated at the VUV beam line of Swiss Light Source.
Temperature dependent mass spectra of intermediates and products were obtained during thermal pyrolysis, as well as threshold photoelectron spectra. They were used, in addition to the ionisation energies, to identify pyrolysis intermediates and products through comparison with our predicted spectra. The necessary Franck-Condon factors were calculated in the harmonic approximation using quantum chemical calculations results for involved molecules in ground and excited states, as well as ions.
Additionally some reaction pathways describing the formation of identified pyrolysis products were verified through quantum chemical calculations.

Also the dissociative threshold photoionization process of 2-methylfurane ion was investigated. The intermediates and products, as well as reaction pathways were identified. Quantum chemical calculations and RRKM/Master Equation modelling were also preformed to rationalise the experimental results.

Session 5 Astrochemistry (Nahon) / 7

Chiral photons as trigger of life's asymmetry?

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All life on Earth is defined by its asymmetry –both our genetic material and our proteins have a "twist"inherent within their structure. Understanding how this asymmetry initially arose is a key question related to intimate processes at the origin of life. Given the detection of circularly polarized light in star-forming regions and the identification of amino acids from meteoritic samples which possess measurable enantiomeric excesses of the naturally occurring left-handed form, it is reasonable to postulate that interstellar/circumstellar asymmetric photochemistry could have introduced the initial chiral biases into key biomolecular building blocks. From cometary ice simulations, advanced carbonaceous meteorite analyses and chiroptical properties in the vacuum-UV of target molecules to the use of circularly polarized synchrotron light, we will present our current research investigating the generation of chirality and asymmetry. We will specifically focus on our recent work on the asymmetric photolysis and photosynthesis of amino acids in pre-cometary ice analogues and discuss its important implication for understanding the origins of homochirality in living matter.

Figure 1. (Click: abstract files on the right). Energy-tunable asymmetric photolysis. (a) Anisotropy spectra g (λ) of isotropic amorphous D alanine (red) and L-alanine (blue) in the vacuum UV and UV spectral region. (b) Photolytic induction of ee values into amino acids in the amorphous solid state as function of circularly polarized light (CPL) energy and helicity.

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Session 5 Astrochemistry (Nahon) / 2

Photon Induced Desorption of interstellar relevant ices in the VUV

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During the cold and dense phase of star- and planet-formation, ices frozen out on microscopic interstellar dust particles are the dominant reservoir of molecules other than H2. When exposed to UV radiation from protostars, background stars or through secondary H2 emission induced by cosmic rays, the mantle molecules non-thermally desorb into the gas phase. Because of negligible thermal evaporation in these cold regions, this process is crucial to explain the abundance of gas phase species below their accretion temperatures. In the past, most of laboratory experiments have been focused on the solid phase irradiated by broad-band discharge sources, delivering radiation peaking at Ly-α (10.2 eV). We present a novel approach which focuses on the detection of species into the gas phase, and by using tunable monochromatic synchrotron radiation is the soft UV (DESIRS beamline, SOLEIL, France). Amorphous ice films of various composition (pure, binary) and various structure (mixed, layered) have been systematically between 7-14 eV (SOLEIL facility, France). The Photon Induced Desorption spectra (PSD) from simples ices (CO, N2, O2) and isotopologues reveal an indirect desorption mechanism induced by electronic transition and occurring within the upper layers of the ice film. This indirect mechanism is clearly observed for mixed N2:CO ices, in which excited CO molecule transfers its energy to neighboring molecules. The role of CO as a promoter of the photodesorption of other species has been also observed in the case of the pure CO2 photodesorption, where CO is produced in situ by CO2 photolysis. The importance of this mechanism in the context of the interstellar medium is discussed together with future complementary investigations that need to be performed.

Session 5 Astrochemistry (Nahon) / 28

Structure and energetics of PAH clusters of interstellar relevance

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Polycyclic aromatic hydrocarbons (PAHs) are key species in the physics and chemistry of UV-irradiated astronomical environments [1]. Still, our understanding of the formation and evolution of these species remains very partial and is a challenge for astronomers, physicists and chemists. From the analysis of the mid-infrared spectra, Rapacioli et al. [2] have proposed an evolutionary scenario in which gas-phase PAHs are produced by photo-evaporation of nanograins, which could be PAH clusters.
In the collaborative frame of the ANR project GASPARIM, we are studying the electronic properties and stability of ionized PAH clusters. Charge delocalization in these large systems is described using a density functional tight-binding method combined with an additional valence-bond configuration interaction scheme [3]. Theoretical studies predict that there should be an ionized core of 2-4 units and that larger ionized clusters have evaporation rates for the loss of one monomer that are close to the neutral ones [4].
We have used a molecular beam coupled to the photoelectron-photoion coincidence spectrometer DELICIOUS II/ III [5] at the VUV beamline DESIRS of the synchrotron SOLEIL to characterize the electronic properties of cationic coronene (C24H12) and pyrene (C16H10) clusters up to the pentamer and heptamer, respectively. The obtained experimental results are compared with theoretical predictions. We will show that the good match between measured and calculated values for the ionization potential, gives us strong confidence into the predicted structures for these PAH clusters. We will also present first results on the dissociation of the clusters, in particular their appearance energies.

Acknowledgment
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Session 5 Astrochemistry (Nahon) / 19

Electronic Spectra of Organic Radicals and Ions of Relevance to Combustion and Interstellar Space

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A number of modern approaches of chemical physics and spectroscopy are used to identify for the first time the electronic spectra of reactive intermediates of organic molecules. The reactive species selected are intermediates in terrestrial processes such as combustion of hydrocarbons leading to formation of aromatics, as well as in interstellar environments of diffuse and dark clouds and planetary nebula. The species are produced in situ within supersonic expansions using discharges and laser vaporization and detected in small concentration by laser approaches. The electronic spectra of mass-selected cations at 15 K are measured in a radiofrequency trap following collisional cooling with helium. The gas phase studies are supported by measurements of the electronic absorptions in 6 K neon matrices of mass-selected radicals and ions. The spectroscopic information of the electronic spectra, supported by theoretical calculations, enables the structure of the species to be identified. The knowledge of the electronic transitions provides the means of in situ monitoring of these reactive intermediates in inaccessible environments.

Session 5 Astrochemistry (Nahon) / 10

Exploring the Ion Chemistry of Small Polycyclic Aromatic Hydrocarbons with Coincidence Spectroscopy

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Polycyclic aromatic hydrocarbon (PAH) molecules have been postulated to be key species in astrochemistry. This proposal has motivated numerous laboratory studies to advance our understanding of the formation and evolution of these species in space and their impact on the physics and chemistry of interstellar and circumstellar environments. In particular, PAHs absorb UV photons from stars, which can lead to their photoionization and dissociation and therefore limit their survival in astrophysical environments. Molecular H2 is the most prolific molecular species found in the interstellar medium (ISM). Whereas it has been long recognized that H2 is formed on dust grains, investigation of the involved mechanisms is still a very active subject of research. One popular theory is that polycyclic aromatic hydrocarbons (PAH) may play a role in the formation of H2 by acting as catalysts. Atomic hydrogen would adsorb onto the surface of the molecules, thus hydrogenating the PAHs, prior to the desorption of H2. This reaction channel demonstrates the importance of investigating the energetics of not only PAHs but modified PAHs as well, such as hydrogenated species.

In this presentation, we have explored the photoionization and subsequent unimolecular dissociation of small PAH molecules ranging from naphthalene, anthracene and pyrene as well as two dihydrogenated species 1,2-dihydronaphthalene and 9,10-dihydrophenanthrene using the imaging photoelectron photoion coincidence apparatus at the Swiss Light Source. RRKM modeling of the competitive dissociation pathways provides reliable reactions energetics and entropics that agree with reactions mechanisms derived from calculations and tandem mass spectrometry.

Not only does the derived data from the above experiments allow speculation on the stability and chemical role of PAHs in the interstellar environment, they have also been used as standard systems to probe the reliability of modeling the dissociation of these systems by collision-induced dissociation mass spectrometry. A brief summary of these results will also be presented in this presentation.

Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 47

X-ray absorption spectroscopy on catalysts, a photon tool to determine structure –performance relationsX-ray absorption spectroscopy on catalysts, a photon tool to determine structure –performance relations

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Catalysts are the enabling technology for conversion and synthesis of energy and chemicals. To increase the sustainability of chemicals and fuels production, new and better processes must be developed, which requires the development of new and better catalysts. Their design is greatly helped by the fundamental understanding of why one catalyst is a better one than another. To this end, in situ or operando (under working conditions) characterization is an indispensable tool. X-ray absorption and more recently, X-ray emission spectroscopy are versatile tools to determine the structure of a catalyst. Because of the large penetration depth of X-rays, notably in the hard X-ray regime, in situ and operando measurements are generally applied.

Heterogeneous catalysts often consist of nano-sized catalyst particles supported on a carrier. Often, dopants are added to increase activity, selectivity and / or stability. In a methane steam-reforming catalyst, rhodium supported on ceria-doped alumina, we elucidated the roles of the different catalyst components. The rhodium nano-particles are responsible for C-H activation of methane, which is the rate-limiting step; the role of dopant ceria is two-fold: the first is stabilization of the rhodium particles and the second water activation to generate oxygen that reacts to carbon atoms on the catalyst to prevent its further reaction to coke. In situ XAS measurements at the Rh K and Ce L3 edge combined with classical characterization tools and transient measurements enabled drawing a molecular level mechanism, which lead to the suggestion of improvement of the catalyst.

Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 49

Photoelectron spectroscopy of size-selected cluster ions using synchrotron radiation

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Catalytic properties of metal clusters exhibit a pronounced size dependence. In general, catalytic properties depend on the chemisorption bond between the molecule (e.g., CO) and the catalyst. One well studied case is the chemisorption of CO to metal surfaces. Depending on the metal, the 4 sigma, 1 pi and 5 sigma orbitals which form the bond show strong variations in binding energy. For clusters, similar variations are expected to occur depending on the size of the particles. So far, such experiments could not be performed because of low intensities. For photoelectron spectroscopy on size selected clusters, high intensity light sources (lasers) had to be used to compensate for the low target densities. The photon energies of lasers are too low for the spectroscopy of adsorbate orbitals. We present a new setup combining a high intensity cluster ion source and a velocity map imaging electron spectrometer /1/. The new setup employs synchrotron radiation for the photoelectron spectroscopy of size selected cluster ions.

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Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 39

Application of Strong VUV Light Sources in Chemical Dynamics Research

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Abstract

Strong VUV light sources are essential in the study of chemical reaction dynamics because of it potential for highly sensitive and high resolution detection of atomic, molecular and radical species through VUV ionization detection. In this work, I will provide a brief overview in the applications of various VUV light sources in the study of chemical reactions research in our laboratory during the last decade or so. State-to-state molecular beam scattering is a powerful probe to the dynamics of elementary chemical reactions. During the last few years in our laboratory, we have employed the high resolution H atom Rydberg tagging technique through VUV excitation to investigate elementary chemical reactions at the full quantum state resolved scattering level. We will present the results obtained in our laboratory in the last few year on a few benchmark elementary chemical reactions using this powerful method. Results on several important chemical systems will be reviewed here,
 Photodissociation of H2O: Direct and conical intersection dynamics ,
 The O(1D) + H2 reaction: State-to-state picture of insertion chemistry
 The H+H2 reaction system: Dynamics of quantized transition states ,
 The F+H2 reaction system: Dynamics of reaction resonances ,
The discussion of the experimental results will be made in combination with theoretical results on these bench mark systems. In addition, I will discuss new developments of VUV light sources for chemistry and chemical dynamics research.

Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 41

Catalysis and Electrocatalysis by Clusters: Size, Composition and Support Effects

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The elucidation of the size, composition, shape, structure and function relationship, of the effect of support along with the determination and control of the nature of the catalytic particles under reaction conditions are instrumental for addressing fundamental aspects of catalysis on the way to the design and understanding the function of existing and new classes of cluster-based catalytic materials. Highly uniform particles on technologically relevant supports are prerequisites for such studies, hand-in-hand with the characterization of the working particles under realistic reaction conditions of pressure and temperature.

Our experimental studies are based on 1) the use of technologically relevant oxide and carbon based supports, 2) size- selected cluster deposition with atomic precision control of cluster size as well as composition and 3) in situ and ex situ synchrotron X-ray characterization of cluster size, shape and oxidation state under realistic working conditions, combined with mass spectroscopy analysis of the reaction products. The synchrotron-based studies are complemented with in situ and ex situ microscopies and DFT calculations.

The first part of the lecture will focus on the size-and support dependent catalytic properties of clusters and their assemblies in selective oxidative reactions such as the dehydrogenation of propane and cyclohexene, or in the selective partial oxidation of propylene.

In the second part of the presentation the strongly size-dependent performance of sub-nanometer clusters in water splitting and batteries will be discussed.

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Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 55

Identifying the transient phase in CO oxidation by XAS spectroscopy

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Supported platinum catalysts for the oxidation of carbon monoxide adopt different structures depending on temperature and reactant concentrations. These structures, which show vastly different activity, can be identified by X-ray absorption spectroscopy (XAS). While the low-temperature, low-activity state and the high-temperature, high-activity state are each well characterized, there is evidence of an additional transient phase, the nature of which is subject of strong debate[1].
Identifying a transient state poses a particular challenge, as both the transient phases'spectrum and its concentration are unknown, essentially turning the analysis into an optimization problem.
In this work, we investigate the nature of the transient state on platinum catalysts in CO oxidation through transient X-ray absorption spectroscopy. By switching the gas feed from pure CO to a CO oxygen mix at high temperature, light-off is induced and the change in the catalyst structure is followed by time resolved XAS. The intermediate state is shown to contain a significant amount of bare platinum surface.
Through linear combination fitting, time dependent concentrations of all involved species could be obtained. A reaction mechanism is proposed and it is shown that it offers a significant improvement in the fit of the concentrations compared to a simple two-step mechanism.

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Session 6 Catalysis, Surfaces and Reacted Clusters (Jeroen van Bokhoven) / 57

In situ XAS of ceria redox materials under relevant conditions for solar thermochemical fuel generation

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The conversion and storage of solar energy by generating fuels from H2O and CO2 using thermochemical redox cycles driven by concentrated solar radiation present a viable pathway towards a sustainable and environmentally benign energy future.
A two-step cycle based on non-stoichiometric ceria that requires challenging operation conditions - typically 1773 K for the reduction and 1073 K for the oxidation step - has recently been demonstrated.
Both thermodynamic properties and the kinetic performance are crucial for the design of advanced materials for enhancing process efficiency. The introduction of dopants into the fluorite-type
ceria lattice strongly affects the non-stoichiometry, which is pivotal for the efficiency of the process.
In order to establish relationships between structure, oxygen storage capacity, reaction kinetics and stability, a high temperature flow cell for in situ XAS under relevant conditions has been built. In the same setup, the kinetics of the H2O splitting reaction with doped ceria materials and Pt/ceria have been determined. XAS at the Ce K edge allows determining the Ce(III)/Ce(IV)-ratio at temperatures up to 1773K.
In the light of these extreme conditions, the opportunities and limitations of in situ XAS are discussed.