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Ultrafast High Harmonic, Soft X-Ray Probing of Molecular Dynamics

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14. ABSTRACT

A three-year experimental investigation of the photochemistry and molecular dynamics of ionic liquids in vapor phase and aerosol is completed. The photochemistry and thermodynamics of ionic liquids are studied using the quasi-continuous vacuum ultraviolet light of the Advanced Light Source at Lawrence Berkeley National Laboratory. The molecular dynamics is also studied using short soft x-ray pulses that were produced by the method of pulsed laser high order harmonic generation. A collaboration with Steven Chambreau and Ghanshyam Vaghjiani produced results on the thermodynamic, kinetic, ultrafast, and photochemical properties of ionic liquid molecules, especially those of interest for propulsion. Also a new experimental setup has been constructed for the investigation of ultrafast photoinduced processes of charge localization at the surface of photocatalytic materials. Understanding ultrafast photoinduced processes at surfaces is a defining principle that will guide advances in the next generation of catalysts to produce storable fuels from sustainable inputs as desired by the Air Force.

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Final Report
Ultrafast High Harmonic, Soft X-ray Laser Probing of Molecular Dynamics
Stephen R. Leone - Principal Investigator
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1 Introduction

With AFOSR support (FA9550-10-1-0163, entitled "Ultrafast High Harmonic, Soft X-ray Laser Probing of Molecular Dynamics"), the method of high order harmonic generation of ultrashort vacuum ultraviolet pulses was used to investigate molecular photodissociation, ultrafast photodynamics, thermodynamics, and reactivity of small molecules and ionic liquid vapors and aerosols. High order harmonics of a femtosecond Ti:sapphire laser are produced in the vacuum ultraviolet or soft x-ray spectral regions by focusing the intense laser output into a rare gas jet.[1] By combining these outputs with visible and ultraviolet pump pulses in a pump-probe configuration, ultrafast photoelectron and photoion spectroscopic measurements were performed.

Earlier AFOSR research in the Leone laboratory pioneered the use of high order harmonic radiation and femtosecond soft x-ray pulses for several new experiments: time-resolved photoelectron spectroscopy of molecular fragmentation processes;[2-6] phase shaping of the harmonic pulses themselves;[7] the preparation and observation of Rydberg wave packets;[8] and imaging of time-resolved photoelectron angular distributions during Rydberg wave packet motion.[9,10] Experiments also combined synchrotron radiation in the vacuum ultraviolet or soft x-ray regime with pulsed optical laser excitation for two-color[11] and high resolution core level spectroscopy.[12] Novel work on superexcited states prepared by high order harmonics demonstrated a new way to make time-resolved measurements using the harmonics for the pump excitation.[13] In recent work, high order harmonic radiation was applied for the first time to the investigation of ionic liquid vapors,[14,15] and synchrotron studies augmented these investigations, pioneering ionic liquid aerosols and aerosol reactivity, as well as thermodynamic and threshold energetics.[16-22]

Recent developments in the generation of high-order harmonics with femtosecond laser pulses in rare gases offer excellent opportunities for the experimental investigation of time-resolved valence- and core-level spectroscopy of dynamical processes in atoms and molecules. Until recently, these laser sources were primarily investigated by groups working on the

harmonic generation process itself. Now the high harmonic process can be used to address a number of intriguing chemical and materials problems of interest. Here, harmonics up to 100 eV photon energy are used; these wavelengths are referred to as extreme ultraviolet (EUV and XUV), and in this report the terminology "soft x-ray" will be used as a simplified descriptor for the high harmonic radiation. This final report provides a brief description of the apparatus, followed by highlights of the completed ionic liquids work. Furthermore, the new experimental setup constructed to investigate the electron dynamics at the surface of photocatalytic materials via femtosecond core-level photoemission is described.

2 Results of Soft X-Ray Probing of Ionic Liquids

2.1 Methods for Ultrafast and Synchrotron Soft X-Rays

The apparatuses used for ultrafast soft x-ray research consist of a 1000 Hz Ti:sapphire laser that produces 2.5 mJ per pulse at 800 nm with pulses of 40-70 fs duration, a cell containing a high density rare gas that is used for the harmonic generation source, a vacuum chamber to introduce gaseous samples, a beam or solid surface sample, and a time-of-flight or velocity map imaging photoelectron spectrometer. The apparatus incorporates frequency doubling, tripling, and quadrupling of the Ti:sapphire fundamental pulses in nonlinear crystals to generate a separate pump (or probe) pulse, and the high harmonic pulses are used for the probe (or pump pulse). The timing is achieved by a high-precision optical delay line on the visible/ultraviolet pulse. A grazing incidence grating is used to select individual harmonics, for energy-selected probing in either photoelectron or mass spectrometry (ionization) experiments.

For the process of high order harmonics in rare gases, the laser is focused to 10^{14} -10^{15} W cm^{-2} in a high density of a rare gas (≈10^{18} cm^{-3}) in a cell. Semiclassically, the mechanism involves driving an electron away from the ionic core of the rare gas and then, on the opposite cycle of the light, driving the electron back into the core, whereupon the harmonic light is generated by the recombination of the returning electron with the core.[3,23] The light is produced with good efficiency over a large number of odd harmonics up to a cutoff energy. The odd harmonics are typical, resulting from symmetry in an isotropic medium. With this apparatus, harmonics of 800 nm light are produced up to the 65th (≈100 eV) in Ne and excellent static photoelectron spectra are obtained with good signal-to-noise (100:1 in minutes).

In some experiments, photoelectron spectra are acquired over a series of pump-probe time delays. For pump-probe experiments, the signal-to-noise ratio needs to be 10,000 or higher to obtain the desired differential changes in the photoelectron spectra. This is accomplished by subtracting signals of the pump only and the probe only from the pump + probe measurements. In some experiments on beams of ionic liquid molecules, the method of soft ionization of atomic and molecular fragments is employed. In this case the time-of-flight mass spectrometer and velocity map ion imaging is configured to detect ions and their kinetic energies, which are techniques introduced especially for the ionic liquid pump-probe experiments.

With the close proximity of the Advanced Light Source to the femtosecond high harmonic laboratory and successful methods developed at the Chemical Dynamics Beamline, it became possible to perform synchrotron experiments on ionic liquids. Together with Air Force Research Laboratory scientists Steven Chambreau and Ghanshyam Vaghjiani, experiments were performed to study the thermodynamic properties and the hypergolic reaction dynamics of ionic liquids.

Selected results of experiments on ionic liquids performed in the grant period are described below. Experiments utilize ultrafast dynamics measurements, time-of-flight velocity map imaging, and tunable synchrotron ionization for product branching and threshold energy measurements.

2.2 Vacuum Ultraviolet Excited Ionic Liquid (IL)

Ionic liquids are room temperature molten salts that have unique properties such as negligible vapor pressure, thermal stability, high conductivity, and high energy density. Ionic liquids are usually composed of an asymmetric organic cation and a halogenated anion or an organic anion. A broad range of applications is possible because of their tunability based on the cation−anion (C^+-A^-) combinations, with a vast number (10^{18}) of possible pairings.[24] Ionic liquids have found remarkable applications as catalysts, in batteries, and as rocket propellants. The synthesis of hypergolic ionic liquids (spontaneous ignition when combined with another reagent) has stimulated interest in novel ways to store chemical energy for propulsion in ionic liquids.[5] Moreover, researchers have recently developed a less corrosive and toxic rocket fuel system using a hydrogen-rich ionic liquid that is hypergolic with hydrogen peroxide as the oxidizer.[25]

These low-volatility, safe and hypergolic materials are of substantial importance to the Air Force.

Calculations and measurements reveal much information about the fundamental properties of ionic liquids, but methods were lacking to investigate the isolated ion pairs in the vapor phase until the demonstration that intact ion pairs could be produced upon thermal vaporization without decomposition, as evidenced in previous work in our laboratory.[15] Studying the ion pairs provides understanding of the interaction between the isolated cation and anion, which primarily determines the electronic and nuclear structure. The electronically excited states of the IL ion-pairs is a subject for which little is known. Photoelectron spectra[15] and photoionization efficiency curves[20] in the near threshold ionization region of those isolated ion pairs have shown convincing evidence of dissociative photoionization ($C^+A^- + h\nu \rightarrow C^+ + A + e^-$). However, the ionization and dissociation mechanisms have not been studied in greater depth, even for this previously observed dissociative ionization channel.

New velocity map ion imaging experiments were initiated to study the dissociative pathways upon photoexcitation.[14] Dissociative ionization and photodissociation of an isolated ion-pair of an ionic liquid, 1-ethy-3-methyl-imidazolium ($[Emim]^+$) bis(trifluoromethyl-sulfonyl)imide ($[Tf_2N]^-$), were investigated using mass-selected, time-sliced velocity map ion imaging initiated by laser produced high harmonic extreme ultraviolet excitation. The time-sliced velocity map ion imaging method provides velocity and angular distributions of the selected ions such as the intact cation and anion and can separate different dissociative pathways by their kinetic energies.

Ion images of the intact cation, $Emim^+$, show that photoexcitation of the ion-pair produces the intact cation with near zero kinetic energy (See Fig. 1). The kinetic energy distribution of this slow intact cation is compared to the kinetic energy distribution formed by ionizing thermal argon gas to produce argon ions that have essentially zero kinetic energy, also shown in Fig. 1. The available energy (14.5 ± 0.2 eV), which is the difference between the photon energy

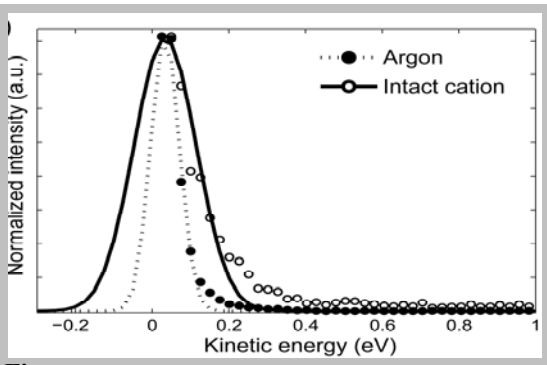

Fig. 1 Kinetic energy distribution of the intact cation (○) with its fitted gaussian function (—) compared to the distribution of argon (●) with its fitted Gaussian function (---).

(23.4 eV) and the dissociative ionization energy of 8.9 ± 0.2 eV that is obtained by previous investigations, is primarily distributed to the kinetic energy of the light electron, 14.5 ± 0.2 eV, which was measured by photoelectron spectroscopy. This intact cation with zero kinetic energy shows that the intact cation is produced from the dissociative ionization, resulting in the cation and neutral anion with little or no kinetic energy and agrees well with the previously suggested mechanism. The isotropic angular distribution in the ion image, not shown here, also indicates the intact cation arises from a slow post-ionization fragmentation of a larger rotating cation.

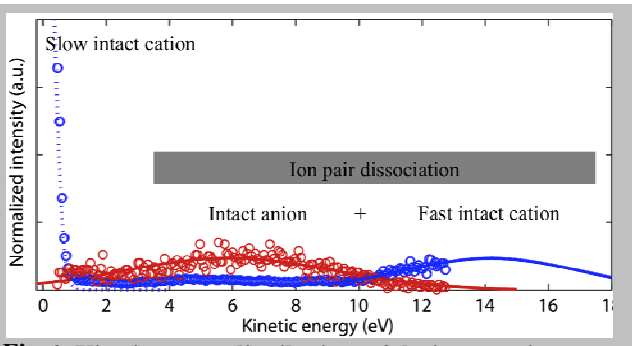

Fig. 2 Kinetic energy distributions of the intact cation (blue) with its fitted gaussian function (—) and the intact anion (red) with its fitted Gaussian function (—).

Fast intact cations upon photoexcitation of the ionic liquid vapor, shown in Fig. 2, are also observed, indicating that the isolated ion pairs undergo two-body photodissociation with no photoelectron ejection. Anions were investigated to find the counter fragment of the intact cation, and the intact anion is directly observed. The intact anion with a kinetic energy centered at 5.9 ± 0.5 eV, shown in Fig. 2, complements the observed momentum of the fast intact cation with a kinetic energy centered around 14.6 ± 0.7 eV, as the final momentum of the photodissociation products (cation + anion) should correlate with each other. Therefore, the kinetic energies of the two ions suggest that the intact cation and the intact anion are a result of ion-pair dissociation, $Emim^+ + Tf_2N^-$, of the isolated neutral ion-pair. Observation of this ion-pair dissociation shows a previously unobserved photodissociation pathway and provides direct evidence for isolated ion-pairs in the effusive beam, specifically neutral cation−anion 1:1 pairs.

2.3 Pump-Probe Dissociative Chemistry of Ionic Liquids

Ultrafast investigations were performed to study the excited state dynamics of isolated ion pairs of ionic liquids in the vapor phase.[21] The ionic liquid, 1-ethyl-3-methylimidazolium ($[Emim]^+$) bromide ($[Br]^-$), was chosen for the first system because the bromide anion is small and compact and is able to form a relatively tight local binding to the cation. The ionic liquid with the bromide $[Br]^-$ anion has much richer fragmentation patterns compared to ionic liquids with the larger $[Tf_2N]^-$ anion, possibly because there are many fewer degrees of freedom in

$[Emim]^+[Br]^-$, but also possibly because the $[Br]^-$ anion interacts in a much more site-specific way with the $[Emim]^+$ cation and can undergo reactive chemistry. This shows that the interaction strength and location specificity of different anions affects specific fragmentation patterns. Some of the possible photodissociation pathways of $[Emim]^+[Br]^-$ are illustrated in Fig. 3.

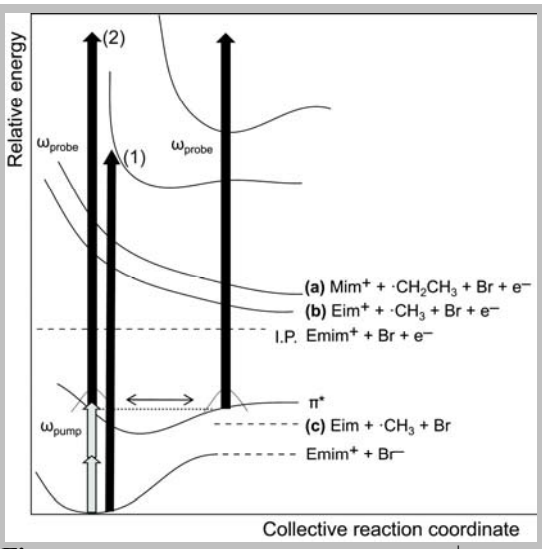

Fig. 3 Schematic potential curves of $[Emim]^+[Br]^-$, showing 400 nm excitation (grey) and single photon high harmonic ionization (black). It shows the probe ionization of (1) ground and (2) excited state.

To explore the excited state dynamics, an excited state is prepared by multiple photons of 400 nm light and is detected using time-delayed single photon ionization with 54 nm light from the high harmonic source. The first time-resolved results for the intact cation and some of the other photofragments are illustrated in Fig. 4. In all the experiments, the mass spectra are derived by subtraction of the signal of pump + probe minus the probe only, thus eliminating the process due to the probe alone. Time-resolved signals of the (a) intact cation that arises from the isolated ion pair shows a momentary depletion around time zero. Also appearance of the (b) methyl imidazolium cation ($[Mim]^+$) and (c) ethyl imidazolium cation ($[Eim]^+$) are observed at delay times of 50 ± 50 fs and 150 ± 50 fs, respectively. The simultaneous depletion of the intact cation that represents the isolated ion pairs and appearance of alkyl-loss fragments suggests several possibilities, involvement of the π* excited state or reaction dynamics induced by vibrationally excited molecules.

The imidazole ring π cloud of the cation can absorb two photons of visible or one photon of ultraviolet light via its electronic excitations. The short lifetime of the π* excited state can explain a temporary depletion of the intact cation and a transient appearance of alkyl-loss fragments, but previous studies[26,27] provide evidence for a long lifetime (> 100 ns) of the π* excited state. However, if there is an additional $[Emim]^+$ emerging channel, shown by the blue dotted line in Fig. 4(a), on top of the long depletion signal, shown by the black dashed line in Fig. 4(a), this can explain the momentary depletion signal of the intact cation. Alkyl-loss fragments should have a similar or long lasting depletion feature as they are dissociative ionization products of the isolated ion-pair as well, but the signal of Eim^+ and Mim^+ is

temporally positive indicating that alkyl-loss fragments are produced more when probing the π* excited state near time zero.

A short-lived internally excited state, upon 53.8 nm ionization, can yield more alkyl-loss fragments of Eim^+ and Mim^+. In general, the higher internal energy acts like raising the temperature, so greater fragmentation occurs. Not only can the internally "hot" ion pair undergo more fragmentation by dissociative ionization to produce Eim^+ and Mim^+, but also there can be more neutral Eim^0 and Mim^0 fragments produced by decomposition of highly vibrationally excited $[Emim]^+[Br]^-$.

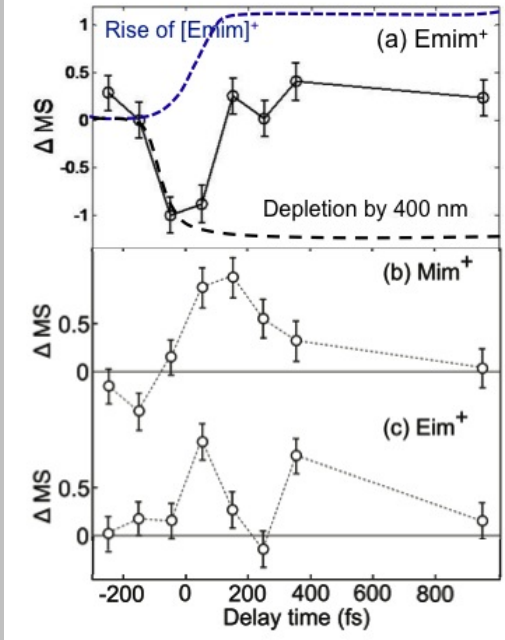

Fig. 4 Time dependence of photodissociation products of (a) intact cation, $Emim^+$, (b) methyl imidazolium, Mim^+, and (c) ethyl imidazolium, Eim^+.

2.4 Ionic Liquids Thermal Vaporization and Decomposition

New experiments were initiated at the Advanced Light Source in collaboration with Steven Chambreau and Ghanshyam (Gammy) Vaghjiani of Edwards Air Force Research Laboratory to study the thermal vaporization and decomposition of ionic liquids. The heats of vaporization of the room temperature ionic liquids (RTILs) were determined using a heated effusive vapor source in conjunction with the tunable vacuum ultraviolet light from advanced Light Source (Beamline 9.0.2.3).[18] The observed heats of vaporization of 1-butyl-3-methylimidazolium dicyanamide (ΔH_{vap} at 298.15 K = 174 ± 12 kJ/mol) and N-butyl-N-methylpyrrolidinium dicyanamide (ΔH_{vap} at 298.15 K = 171 ± 12 kJ/mol) are in good agreement with previously reported experimental values using electron impact ionization. To our knowledge, this study is the first reported measurement of the heat of vaporization of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ((ΔH_{vap} at 298.15 K = 195 ± 19 kJ/mol).

The intact ion pair photoionization efficiency curve (PIE) for a vaporized ionic liquid, 1-butyl-3-methylimidazolium ($[Bmim]^+$) tricyanomethanide ($[Tcm]^-$),[17] shown in Fig. 5, was directly measured for the first time using tunable vacuum ultraviolet photoionization time-of-flight mass spectrometry. The ionization potential for the ion-pair is experimentally determined to be 6.6 ± 0.5 eV, which matches reasonably well with the theoretically calculated value of 7.3

± 0.2 eV. The calculated lifetime to dissociation of the cation−radical complex formed upon ionization of the ion pair shows a high dependence on entropic contributions. A large barrier on the free energy coordinate that leads to dissociation might keep the cation−radical complex intact long enough to follow the ionization of the ionic liquid, $[Bmim]^+[Tcm]^-$, unlike other aprotic ionic liquid systems. The enthalpy of vaporization, measured as in our previous studies, is substantially lower (ΔH_{vap} at 298.15 K = 143.5 ± 6.2 kJ/mol) than the enthalpy of activation for thermal decomposition (ΔH = 183 ± 4.3 kJ/mol), providing further evidence that the vaporization is the dominant mechanism.

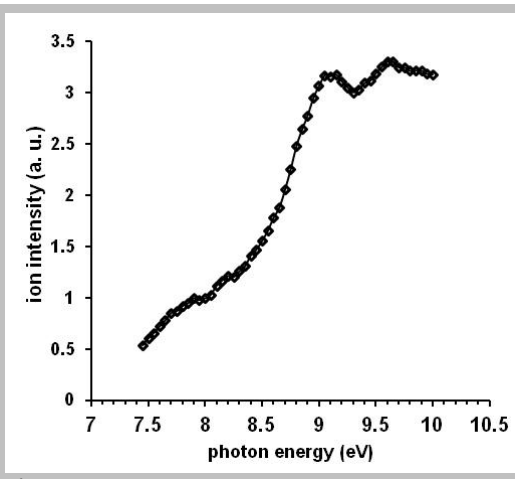

Fig. 5 Photoionization efficiency curve of the ion pair, $[Bmim]^+[Tcm]^-$.

However, in one ionic liquid, the 1-alkyl-3-methylimidazolium bromide, system, we found thermal decomposition competing with the vaporization process.[16] The intact cation ($[Emim]^+$) was absent or negligible, precluding the possibility of vaporization of the ionic liquid, $[Emim]^+[Br]^-$, and instead alkyl bromides (ethyl and methyl bromide) were produced, presumably through alkyl abstraction via an S_N2 type mechanism. This showed how the thermal decomposition mechanism, which is important for rocket fuel applications, can be studied and how the vaporization and thermal decomposition processes can be controlled by changing the combination of ion pairs.

2.5 Hypergolic reaction dynamics of ionic liquid

An aerosol flow tube apparatus at the ALS Beamline 9.0.2.1 was developed in order to study the reaction mechanisms and kinetics of hypergolic reactions between ionic liquids and an oxidizer. Among several hypergolic reactions of ionic liquids, we chose the ionic liquid 1-butyl-3-methylimidazolium ($[Bmim]^+$) dicyanamide ($[Dca]^-$), which was shown to be hypergolic with nitric acid, for our first system to study.

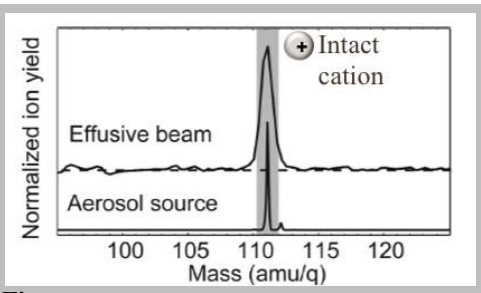

Fig. 6 Mass spectra of isolated ions pairs of ionic liquid, $[Emim]^+[Tf_2N]^-$, prepared from aerosol (bottom) and effusive source (top).

Before we actually investigated the hypergolic

reaction dynamics, as a proof of concept, we generated isolated ion pairs from ionic liquid aerosols and compared the aerosols to the effusive source.[19] In this preliminary investigation with the synchrotron, the non-hypergolic ionic liquid, 1-ethyl-3-methylimidazolium ($[Emim]^+$) bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$), as well as the hypergolic ionic liquid, $[Bmim]^+[Dca]^-$, were studied. Photoionization of vaporized ionic liquids, $[Emim]^+[Tf_2N]^-$ and $[Bmim]^+[Dca]^-$, from aerosol particles with diameters of 187 nm and 184 nm, respectively, showed intact cations, similar to when IL vapor from the effusive source is photoionized. These intact cations, shown in Fig. 6, indicate that isolated ion-pairs are produced upon vaporization of IL aerosol particles as in the effusive source. The photoionization efficiency curve of these intact cations from $[Emim]^+[Tf_2N]^-$ shows the internal energy of the isolated ion pairs prepared from the aerosol source or the effusive source. The higher appearance energy of intact cation from the aerosol source in Fig. 7 indicates lower internal energy in the isolated ion pairs when prepared from the aerosol source compared to the effusive source. Here we showed that the ionic liquid aerosol particles are successfully generated and can be monitored by single photon ionization after vaporization of the particles. Using these ionic liquid aerosol particles as an effective micro-reactor, hypergolic reaction dynamics were investigated.[22] As shown in the schematic of the experimental apparatus in Fig. 8, reaction dynamics are studied by sampling the reaction intermediates after the ionic liquid, $[Bmim]^+[Dca]^-$, aerosol particles are reacted with an oxidizer (fuming nitric acid) during a well defined reaction time in the flow tube. First the mass spectrum of the reaction intermediates were obtained and then the photoionization efficiency curves of the selected masses were studied in depth. Several intermediates with masses 42 amu, 44 amu, 85 amu, 126 amu were identified as important reaction intermediates or products from the hypergolic

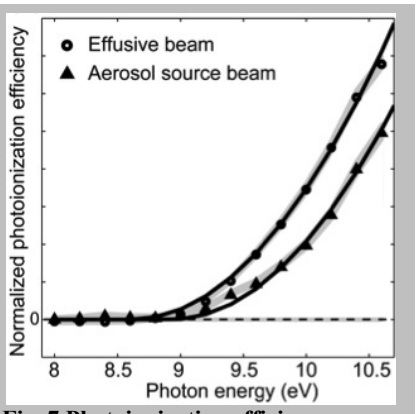

Fig. 7 Photoionization efficiency curve of isolated ion pairs of $[Emim]^+[Tf_2N]^-$, from aerosol source (triangle) and effusive beam (circle).

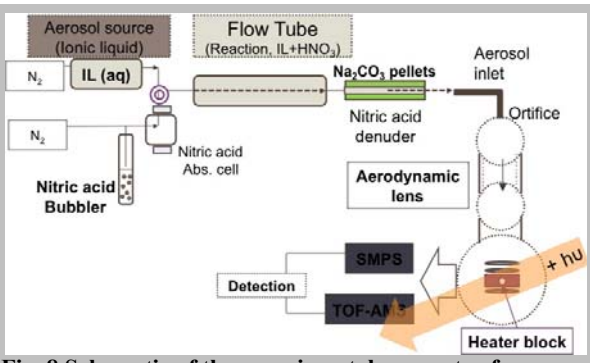

Fig. 8 Schematic of the experimental apparatus for hypergolic reaction dynamics studies using aerosol flow tube method.

reaction (42, 44, and 85 amu) or a byproduct from a side reaction (126 amu). Fig. 9 shows the photoionization efficiency curves of the intermediates with mass 42 amu (IP=10.3 ± 0.1 eV), which is cyanoamide, and 85 amu (IP=10.2 ± 0.2 eV), which is isocyanourea. A most probable mechanism to form the intermediate of cyanoamide and isocyanourea is through the nitro-substituted intermediate ($C_2N_4O_3H_2$) where the cyanoamide can be made by decomposition of the nitro-substituted intermediate or by decomposition of isocyanourea formed from proton addition to the nitro-substituted intermediate.

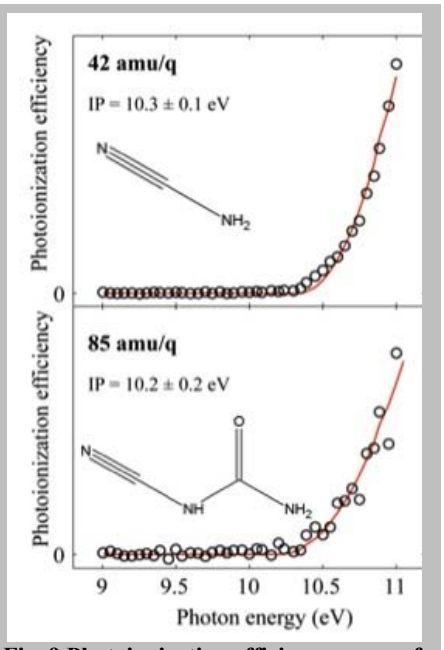

Fig. 9 Photoionization efficiency curve of reaction intermediate with mass 42 amu/q and 85 amu/q.

Also, the reaction kinetics measurements were performed to find the reaction rates of each reaction step. Kinetics was measured by changing the nitric acid concentration in the flow tube with fixed reaction time. As a result, we have found that the cyanoamide is formed faster (t_{42amu}=0.15 ± 0.02 conc./s) than the isocyanourea (t_{85amu}=0.09 ± 0.03 conc./s). This indicates that the cyanoamide cannot be formed by decomposition of isocyanourea and that the cyanoamide is more likely formed by decomposition of the nitro-substituted intermediate. The counter products of N_2O and CO_2 to the cyanoamide have been detected in the gas phase and N_2O was confirmed to be resulting from the nitric acid addition by isotope labeling the nitric acid to $H^{15}NO_3$. This determination of the nitro-substituted intermediate that is very likely to be responsible for the spontaneous ignition helps to understand the complex reaction and will eventually facilitate in designing new hypergolic ionic liquids.

3 Construction of a New Experimental Setup to Study Electron Dynamics at Photocatalytic Material Surfaces

A new experimental setup has been designed and constructed to study the ultrafast electron dynamics at photocatalytic material surfaces by means of femtosecond core-level photoemission spectroscopy. It consists of two main parts (i) the femtosecond laser system in conjunction with the pump-probe setup as well as the high order harmonics generation (HHG) system, and (ii) an

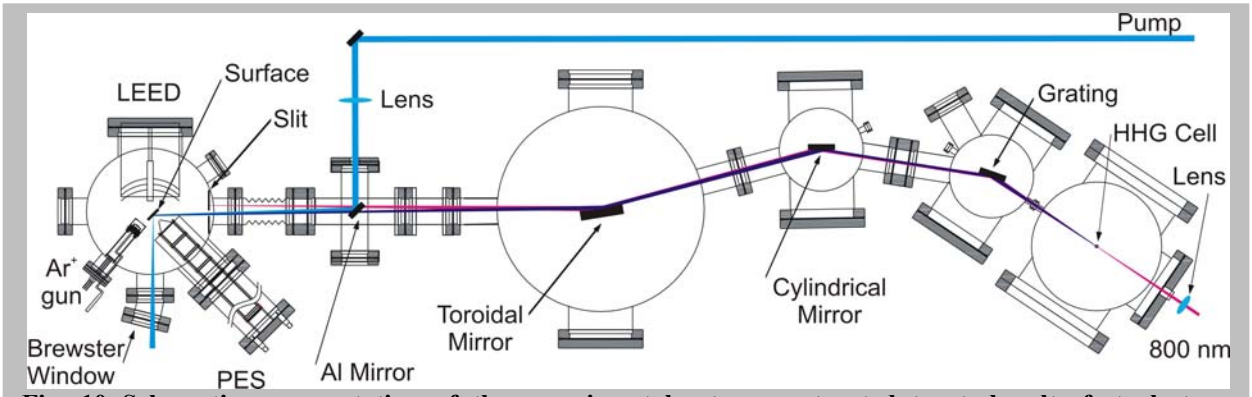

Fig. 10 Schematic representation of the experimental setup constructed to study ultrafast electron dynamics at photocatalytic material surfaces by means of femtosecond core-level photoemission spectroscopy.

ultra-high vacuum (UHV) surface science chamber. Fig. 10 shows a schematic representation of the HHG setup together with the UHV chamber.

In order to produce femtosecond soft x-rays with photon energies up to 100 eV a commercial amplified femtosecond laser system that delivers pulses as short as 30 fs and energies up to 3 mJ has been implemented. Briefly, the femtosecond laser light is produced with a Ti:sapphire oscillator (KMLabs) continuously pumped by a 6 W Spectra Physics Millennia Nd:YVO4 laser. The laser pulses are amplified with a Nd:YLF laser pumped Ti:sapphire amplifier (Dragon, KMLabs) to yield 30 fs pulses with a typical power of 3 W at a repetition rate of 1 kHz. The pump laser pulses at 400 or 266 nm are generated by frequency doubling or tripling of the fundamental wavelength in a homebuilt third harmonic generator using BBO crystals. Femtosecond soft x-ray pulses produced via HHG are used to probe the electron dynamics at the surface. For the process of HHG in rare gases, the laser beam at the central wavelength of 800 nm is focused to 10^{14}-10^{15} Wcm^{-2} in a high density of a rare gas in a small gas cell (about 3 mm long) for the efficient production of low energy harmonics up to 42 eV or in a semi-infinite gas cell (300 mm long) for the efficient production of higher energy harmonics up to 100 eV. The present experimental setup permits a quick exchange of the gas cells. In order to get monochromatic femtosecond soft-x ray pulses, the HH beam is dispersed by a plane grating in first order diffraction at grazing incidence. Subsequently the HH beam is focused on the sample surface inside of the UHV chamber by cylindrical and toroidal mirrors to a spot size of about 0.2 mm. A slit mounted at the entrance in the UHV chamber allows a single harmonic to enter the UHV chamber and stops all the other wavelengths. This slit also allows an efficient differential pumping of the vacuum apparatus. An aluminum mirror installed inside of the

vacuum apparatus a few millimeters above the HH (cf. Fig. 10) beam is used to steer the pump into the UHV chamber and to ensure the overlap between the pump and the probe beams onto the sample surface.

The UHV surface science chamber contains specific tools for surface preparation and characterization arranged on two levels. The upper level of the surface science chamber is equipped with a homebuilt time-of-flight photoelectron spectrometer (TOF-PES) to investigate the electron dynamics at the surface of photocatalytic materials, a commercial low energy electron diffraction (LEED) instrument to study the surface crystallinity, and an Ar ion gun for surface cleaning. The upper level of the surface science chamber is schematically represented in Fig. 10.

On the lowest level, an Auger electron spectrometer to investigate the surface composition and cleanliness is located. Also on this level an ion gauge used to measure the vacuum pressure, two gas inlets as well as two evaporators are positioned. An electron beam evaporator will be used to evaporate high melting point metals, such as Ni. The second evaporator will be used for the deposition of low melting point metals, i.e. Zn, onto the surface and consists of a coil of 0.4 mm thick tantalum filament in which is placed the material to be evaporated.

The surface sample is attached to a liquid nitrogen cryostat and it is mounted in the center of the UHV chamber. The surface sample-cryostat assembly can be vertically translated to both vacuum chamber levels and horizontally rotated by 360° by a mechanical manipulator. Furthermore, a xy-horizontal translation stage allows a movement of the assembly by ±12 mm from the midpoint. The crystal position can be reproduced with better than 0.02 mm and 0.5° accuracy.

The sample surface can be cooled down to 100 K and resistively heated up to 1200 K. A base pressure of about 2×10^{-10} mbar in the surface science chamber is achieved with a 1000 L/s turbo molecular pump backed by a 590 L/s scroll pump and a titanium sublimation pump.

A TOF-PES has been designed and constructed to analyze the energy of the photoelectrons. In Fig. 11 a schematic representation of the time-of-flight photoelectron spectrometer is presented. The sample surface is positioned 10 mm from the TOF-PES entrance with the surface normal parallel to the spectrometer axis. The entrance electrode of the

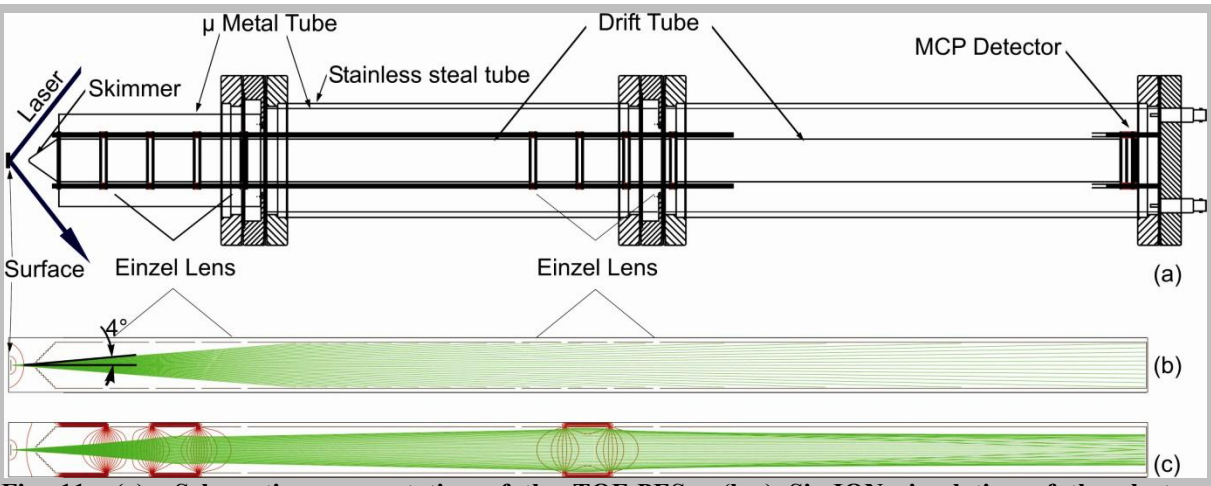

Fig. 11 (a) Schematic representation of the TOF-PES. (b-c) SimION simulation of the electron trajectories (green curves) in the TOF-PES. (b) No potentials are applied on the TOF-MS elements. (c) Potentials are applied on both electrostatic lenses. See text for more details.

spectrometer has a conical form with a center hole of 2.5 mm diameter. In this way, most of the electrons emitted parallel to the spectrometer axis are analyzed. In order to collimate the electrons to be analyzed and at the same time to improve the transmission of the electrons, two electrostatic lens systems are mounted inside the spectrometer. The first lens is placed at 65 mm from the spectrometer entrance, while the second lens is positioned close to the middle of the spectrometer. The total length of the spectrometer is 1000 mm.

The electrostatic lens systems are also used to slow down the photoelectrons and hence to increase the energy resolution of the spectrometer for high kinetic energy electrons. In the proposed experiment, a transient shift of the core level electrons between 10 meV and 250 meV is expected to be induced by the pump pulse. By choosing the appropriate potentials on these lenses, a zoom in the photoelectron spectrum can be performed, and consequently small shifts in energy of the photoemission peaks can be monitored.

Figs. 11(b) and (c) present a longitudinal cross-section image of SimION simulations of the electron trajectories in the TOF-PES when no potential is applied on the spectrometer elements [Fig. 11(b)] and when potentials are applied on both electrostatic lenses [Fig. 11(c)]. The electrons in all simulations are starting from the same point situated at the center of the surface (on the TOF-PES symmetry axis), within a ±4 deg angle with respect to the spectrometer axis. A small potential of -2 V is applied on the surface to repel the slow photoelectrons.

The photoelectron signal is amplified by a factor of 10^6 - 10^7 via a micro channel plate arrangement at the end of the field free double-wall μ-metal drift tube. Subsequently, the electron signal is collected on a metal anode and analyzed by a multichannel scaler with a

resolution of 100 ps (FAST P7889). In order to avoid the alteration of the photoelectron measurements by external magnetic fields, additionally, the inner part of the whole UHV chamber is covered with a μ-metal wall.

Preliminary results in our laboratory, taken with an older apparatus, have been obtained using high harmonics to perform photoemission spectroscopy on semiconductor surfaces, highlighting the elemental specificity of this technique. Fig. 12a shows the photoelectron spectrum of a GaAs(100) single crystal surface. The peaks at 19 eV and 41 eV binding energies correspond to the photoemission from the 3d core levels of Ga and As, respectively. Fig. 12b shows the photoelectron spectrum of a CdTe polycrystalline surface. The photoemission below 6 eV is due to the valence electrons, while the peak at 11 eV is due to the Cd 4d electrons.

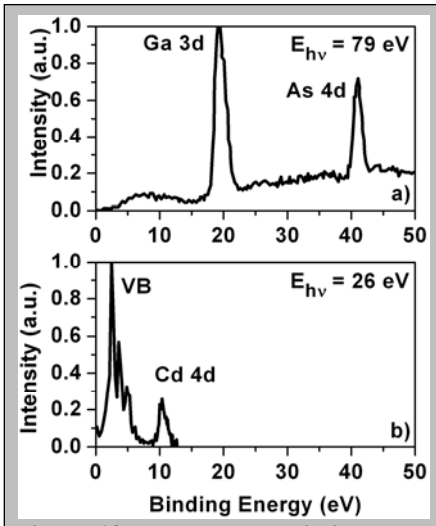

Figure 12: XUV photoemission spectra recorded from A) GaAs (100) surface and B) CdTe poly-crystalline surface.

4. Publications Sponsored by AFOSR 2010-2012:

1 D. Strasser, F. Goulay, L. Belau, O. Kostko, C. Koh, S. D. Chambreau, G. Vaghjiani, M. Ahmed, and S. R. Leone, *Tunable wavelength soft photoionization of ionic liquid vapors*," J. Phys. Chem. A **114**, 879 (2010).

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4 S. D. Chambreau, J. A. Boatz, G. L. Vaghjiani, C. Koh, O. Kostko, A. Golan, and S. R. Leone *Thermal decomposition mechanism of 1-ethyl-3-methylimidazolium bromide ionic liquid*, J. Phys. Chem. (A: A. R. Ravishankara Festschrift) **116**, 5867 (2012).

5 C. J. Koh, and S. R. Leone *Simultaneous ion-pair photodissociation and dissociative ionization of an ionic liquid: velocity map imaging of vacuum-ultraviolet-excited 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide*, Mol. Phys. **110**, 1705 (2012).

6 S. D. Chambreau, G. L. Vaghjiani, C. J. Koh, A. Golan, S. R. Leone, *Ultraviolet Photoionization Efficiency of the Vaporized Ionic Liquid 1-Butyl-3-methylimidazolium Tricyanomethanide: Direct Detection of the Intact Ion Pair*, Journal of Physical Chemistry Letters **3**, 2910 (2012).

7 C. J. Koh and S. R. Leone, *Ultrafast excited state dynamics of an imidazolium based ionic liquid*, (to be submitted).

8 C. J. Koh, D. Popolan, A. Golan, S. D. Chambreau, G. Vaghjiani, S. R. Leone, *Identification of reaction intermediates: hypergolic reaction of an ionic liquid with nitric acid*, (to be submitted).

Personnel:

Christine Koh (graduate student, now postdoctoral associate at Northwestern University), Jordy Bouwman (postdoctoral associate), Mihai Vaida (postdoctoral associate), Nare Janvelyan (undergraduate student).

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20. D. Strasser, F. Goulay, L. Belau, O. Kostko, C. Koh, S. D. Chambreau, G. L. Vaghjiani, M. Ahmed, and S. R. Leone, J. Phys. Chem. A **114**, 879 (2010).
21. C. J. Koh and S. R. Leone, (To be submitted).
22. C. J. Koh, D. Popolan, A. Golan, S. D. Chambreau, G. Vaghjiani, and S. R. Leone, (To be submitted).
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Abstract

A three-year experimental investigation of the photochemistry and molecular dynamics of ionic liquids in vapor phase and aerosol is completed. The photochemistry and thermodynamics of ionic liquids are studied using the quasi-continuous vacuum ultraviolet light of the Advanced Light Source at Lawrence Berkeley National Laboratory. The molecular dynamics is also studied using short soft x-ray pulses that were produced by the method of pulsed laser high order harmonic generation. A collaboration with Steven Chambreau and Ghanshyam Vaghjiani produced results on the thermodynamic, kinetic, ultrafast, and photochemical properties of ionic liquid molecules, especially those of interest for propulsion. Also a new experimental setup has been constructed for the investigation of ultrafast photoinduced processes of charge localization at the surface of photocatalytic materials. Understanding ultrafast photoinduced processes at surfaces is a defining principle that will guide advances in the next generation of catalysts to produce storable fuels from sustainable inputs as desired by the Air Force.

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