

# Dissociative Ionization by Ion Imaging with Undulator Radiation: Dissociation Dynamics of SF<sub>6</sub>

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Interaction of molecules with VUV radiation dominates over all other regions, and dissociative ionization is the principle decay mechanism from excitation of molecules in the VUV. Dissociative ionization (D.I.) is thus arguably one of the most important photophysical processes. This is especially true for the stratosphere, in interstellar regions, plasmas, and any environment where VUV radiation is abundant. Despite this importance much that is known is based on experiments that are, in some ways, incomplete. For many of these processes, accurate angular distributions, for example, have not previously been obtained. Sophisticated approaches have been employed in recent years using coincidence methods[1,2], for example, to study dissociative ionization from energy selected ions. In general, these methods rely on analysis of the ion time-of-flight peak shape to characterize both the kinetic energy released as well as the angular distributions for the process. These approaches achieve a precise definition of the initial state of the ion, but because of possible couplings between the energy and angular distributions generally do not yield the complete kinetic energy or angular distributions for the process of interest. We have recently adapted the ion imaging technique [3,4] for use on the Chemical Dynamics Beamline, an undulator beamline at the Advanced Light Source [5]. The beamline provides intense ( $10^{16}$  photons/sec at 2% bandwidth, 5-30 eV), continuously tunable horizontally polarized VUV radiation for a range of studies of chemical reaction dynamics and photoionization processes. Ion imaging has the advantage that complete energy and angular distributions are recorded simultaneously, and the data analysis may be accomplished by direct inversion of the raw data. This approach is ideally suited for detailed characterization of dissociative ionization dynamics, in that the complete double differential cross sections (energy and angle) for the process are obtained directly.

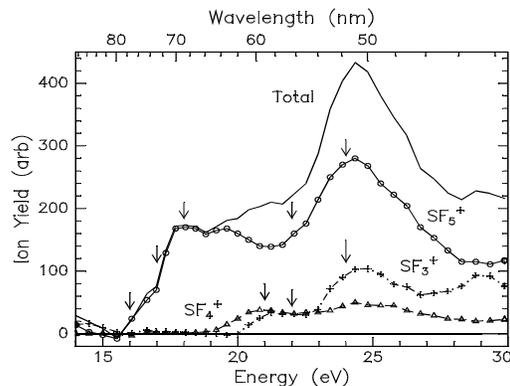
Here we present a preliminary imaging-based study of the dissociative ionization dynamics of SF<sub>6</sub> in a pulsed molecular beam, excited at energies from 15 to 30 eV, with particular attention paid to the anisotropy in the angular distributions and the dynamics of the channels leading to SF<sub>4</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup>. The experiments were performed in a recently commissioned ion imaging-based endstation on the Chemical Dynamics Beamline. Briefly, it features a molecular beam source pumped by a 2000 l/s magnetic bearing turbomolecular pump (Seiko-Seiki). The molecular beam is skimmed once before entering the ionization chamber, which has two 400 l/s magnetic bearing turbomolecular pumps. Dissociative ionization studies were performed using the tunable VUV undulator radiation, looking solely at the ionic products. Product ions are electrostatically accelerated into a 0.5 meter flight tube perpendicular to the plane of the beams. They then strike a position sensitive dual microchannel plate coupled to a phosphor screen viewed by an integrating fast-scan video camera system employing thresholding in conjunction with a linear video look-up table. Typical accumulation times were 10 minutes for each image.

The Photoion efficiency (PIE) curves were obtained by collecting the integrated ion signal for each of the fragments in 0.5 eV intervals from 15 to 30 eV. Mass-selected images were obtained by gating the microchannel plate with 300 nanosecond duration “on” pulse. The detector is viewed by an integrating fast-scan video camera system (Data Design AC101/I) employing

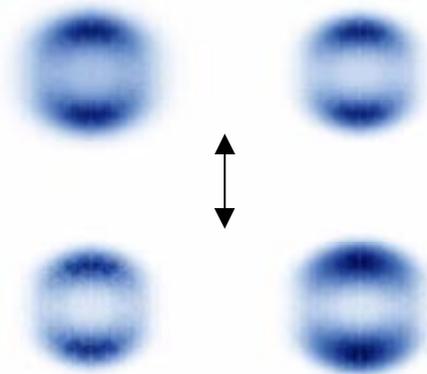
thresholding in conjunction with a linear video look-up table. Images of  $SF_5^+$ ,  $SF_4^+$  and  $SF_3^+$  were recorded (when observed) at photon energies from 15.0 to 30 eV. To isolate contributions from particular electronic states, difference images were created during analysis. These difference images show the ion contribution from newly accessed electronic states. Analysis of the images was performed using the conventional inverse Abel transform to reconstruct the product-flux contour maps from the images, which are 2-dimensional projections of the 3-dimensional fragment distributions [4]. These were then integrated radially and about the polar angle to yield the velocity and angular distributions, respectively.

The PIE curves we see are consistent with the literature. The onset of  $SF_5^+$  formation is  $\sim 15.5$  eV, with  $SF_4^+$  and  $SF_3^+$  being seen at  $\sim 19$  eV and 20 eV respectively (Figure 1). A dominant feature in the PIE curves of  $SF_5^+$  and  $SF_3^+$  is the large peak at  $\sim 25$  eV. This is ascribed to a shape resonance in the  $SF_6$  parent potential surface[6]. Because this is not an energy selected experiment for the electron, difference images were generated to isolate the contributions from newly accessed excited. On the rising edge of a feature in the PIE curve, two images were taken, and then subtracted. The resulting images contains only the contribution of the higher energy. The arrows on Fig. 1 indicate where these images were taken.

Immediately apparent from the  $SF_5^+$  images (Figure 2) is that any analysis method which can not quantitatively determine the anisotropy and use it as a parameter for TOF kinetic energy fits will necessarily be missing information to accurately determine translational energy release. Using the familiar equation  $I(\Theta) = 1 + \beta P_2(\cos(\Theta))$  to obtain the  $\beta$  parameters [7] we find  $\beta$ 's of about 1 for the  $SF_6 \rightarrow SF_5^+ + F + e$  process. This is indicative of a transition moment relatively parallel to both the recoil axis of the (non-electron) fragments and the polarization of the VUV light. Such behavior in a molecule of such high symmetry means that



**Fig 1** Photoion Efficiency curve of the Dissociative Ionization of  $SF_6$ . Arrows indicate energies where images were collected. Curves are labeled as to their fragment channel.



**Fig 2**  $SF_5^+$  Images (clockwise from top left)  $SF_5^+$  at 16 eV,  $SF_5^+$  at 17-16 eV,  $SF_5^+$  at 24-22 eV, and  $SF_5^+$  at 18-17 eV. The images show marked anisotropy in the dissociative ionization event. VUV polarization is indicated by arrow. The  $\beta$  parameters for these processes are  $\sim 1$  indicating a parallel transition.

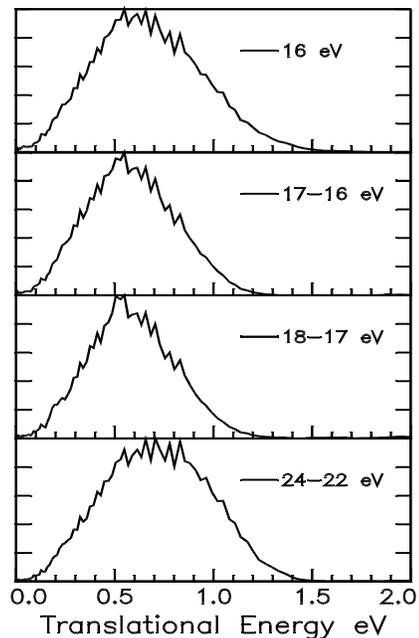
the transition moment is localized on a particular bond axis; in fact, the first 3 electronic states of  $\text{SF}_6^+$  arise from the removal of an electron from a lone pair on one of the fluorine atoms[8].

Examining the translational energy release (Figure 3), there is not much change despite a large increase in excitation energy. This excess energy can be realized as internal energy in the  $\text{SF}_5^+$  fragment. From photoion efficiency data taken on this endstation, we see the  $\text{SF}_4^+$  fragment formed precisely when the excess energy available to the  $\text{SF}_5^+$  is equal to the thermodynamic threshold for the decomposition of  $\text{SF}_5^+$  to  $\text{SF}_4^+ + \text{F}$ . The actual translational energy releases are likely to be governed by the barrier arising from the extensive electronic and nuclear rearrangement that  $\text{SF}_5^+$  must undergo after initial formation from  $\text{SF}_6^+$ . (The newly formed  $\text{SF}_5^+$  is square pyramidal, while the ground state structure is trigonal bipyramidal [9]).

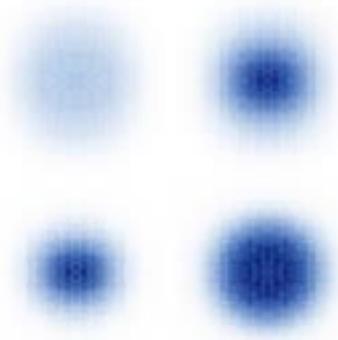
Also interesting to note is the large increase in  $\text{SF}_5^+$  production in the region of the shaped resonance. Excitation of  $\text{SF}_6$  with a 24 eV photon produces an excited bound state of  $\text{SF}_6$  with over 8 eV excess energy as compared to the  $\text{SF}_5^+ + \text{F} + \text{e}$  process. This is well above the threshold for subsequent fragmentation to  $\text{SF}_4^+ + \text{F} + \text{F} + \text{e}$ , yet the  $\text{SF}_4^+$  production does not increase. There must be efficient conversion from this excited state of  $\text{SF}_6$  to the lower lying states of  $\text{SF}_6^+$ . As this would not be a zero energy electron process, PEPICO studies are blind to this interesting phenomenon. Further work on this endstation is underway; imaging the photo-electrons from this process. The photoelectron spectra of this process pinpoint the final states and energies of the resulting  $\text{SF}_5^+$  fragment.

The  $\text{SF}_4^+$  and  $\text{SF}_3^+$  fragments have a nearly isotropic angular distribution (Figure 4). This is consistent with  $\text{SF}_4^+$  being formed via statistical decomposition of  $\text{SF}_5^+$  with large levels of internal excitation. The lack of anisotropy is likely due to a combination of long lived  $\text{SF}_5^+$  parent relative to its rotational period, and statistical symmetry of different F atoms in the  $\text{SF}_5^+$  ion.  $\text{SF}_3^+$  displays

$\text{SF}_5^+$  Total Translational Energy



**Fig 3**  $\text{SF}_5^+$  Total translational energy distributions for the process  $\text{SF}_6 + h\nu \rightarrow \text{SF}_5^+ + \text{F} + \text{e}$ . The translational energy release is essentially constant with an 8 eV increase in photon energy implying that the  $\text{SF}_5^+$  fragment must contain significant amounts of internal energy after high energy excitation.



**Fig 4**  $\text{SF}_n^+$  Images (clockwise from top left)  $\text{SF}_3^+$  at 24-22 eV,  $\text{SF}_3^+$  at 24 eV,  $\text{SF}_4^+$  at 22 eV, and  $\text{SF}_3^+$  at 22 eV. The images are nearly isotropic indicating a long lived parent ion and a statistical dissociation.

similar behavior in its angular distribution, consistent with a stepwise decay of  $\text{SF}_5^+$  into daughter fragments, which then decompose yielding  $\text{SF}_3^+$ .

## Conclusion

We have adapted the technique of photofragment imaging, widely used in the study of neutral photochemistry, to use on a VUV undulator beamline at the Advanced Light Source. The technique allows direct inversion of the raw data to yield the full angular and translational energy distributions for the product ions. The method was applied to study the dissociative ionization of  $\text{SF}_6$  at photon energies from 16 to 24 eV. The experiment allows for detailed characterization of the angular and translational energy distributions of the fragments, yielding clear insight into the decay mechanisms of these excited ionic states even in the absence of energy selection of the initial ion.

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