Breakup of the SF_6^{3+} photoion revealed by momentum correlation between fragments

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Fragmentation of SF_6^{3+}, formed from SF_6 by absorption of soft x-ray photons, has been investigated using a momentum imaging time-of-flight spectrometer. We observe triple ion coincidences between two F^+ ions and SF_m^+ where $m=0,\ldots,3$. Strong correlation between the momentum distributions of the two F^+ ions is observed across all dissociation channels involving triple ion coincidences. We present a method of estimating the contribution of the neutral fragments to the kinematics of ion ejection based on the scalar triple product of the ion momentum vectors. The noncoplanarity of the three ion ejecta inferred in this manner allows us to discern the fragmentation sequence of SF_6^{3+}. The proposed sequence is loss of a neutral F followed by violent ejection of two F^+ ions and gentle removal of remaining F atoms from SF_3^+.

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I. INTRODUCTION

Molecular ions may often lose an atom in a bid to attain stability. A fine example is provided by SF_6—there have been no reports of observation of SF_6^+, but SF_5^+ is routinely seen in mass spectra under a variety of ionizing perturbations. The stability of molecular ions stemming from SF_6 shows a pattern that can be explained on the basis of the number of electrons in it and the valence-bond model [1,2]. There exist exceptions in which even multiply charged parent ions show stability. For instance, UF^{3+} has been reported to be stable by Schröder *et al.* [3], while SF_4^{2+} [4] and CO_2^{2+} [5] exhibit metastability.

Photoionization of SF_6 has been studied over a wide energy range [1,2,6–9]. Issues such as electron correlations, resonance effects from S *L* shell (2*p* levels), and electronic decay processes following the resonance have been studied extensively [9,10]. While fragmentation dynamics of singly ionized SF_6 has been well established and that of doubly ionized SF_6 has been studied by many groups in detail [11,12], there are very few attempts to unravel the sequence of breakups stemming from the instability of triply or higher charged SF_6.

In this paper, we focus on the chain of breakups of the SF_6^{3+} photoion that lead to the formation of smaller molecular ions and atomic ions, and suggest a method of determining the sequence of fragmentation, based on the analysis of the correlated momentum vectors of the fragment ions. The experiment is performed at photon energies of 170 eV and 231 eV, which are chosen to be well below and well above the 2*p* shell energy of S in SF_6 ($2p_{3/2}$ and $2p_{1/2}$ ionization edges are 180.27 eV and 181.48 eV, respectively [13]). There are significant differences in the intensities of various ions in the mass spectra at two energies, attributable to the inner shell hole creation at the higher photon energy, in agreement with past reports [1]. However, fragmentation sequences for the triple breakup at these two energies are found to be largely similar.

II. EXPERIMENT

The experiment was performed at the Indus-1 synchrotron, which is a second generation 450 MeV electron storage ring. The photon beam was monochromatized by a toroidal grating monochromator. The beam cross section was 1×3 mm^2, and the photon flux was approximately 10^{10} s^{-1}, with energy resolution $E/\Delta E=300$. A polyamide filter was used to prevent the second-order diffracted beam from reaching the target, even though the second-order contamination in a 450 MeV synchrotron is very small.

The fragment ion momentum spectrometer is based on the principle of simultaneous measurement of ion flight time and spatial spread transverse to the flight direction, under the action of a uniform electric field (130 V/cm). Its construction is similar to the one described in [14]. The electric field is generated by a set of parallel rings in a potential divider arrangement. The rings at the ends have wire meshes on them to ensure field uniformity. The field is applied over a length of 99 mm. Ions travel through this field, followed by a field free drift region of length 198 mm, before hitting the detector. Electrons are guided in the opposite direction to another detector by the same field. Complete collection (irrespective of the direction of emission) is ensured for electrons with energies $\leq$35 eV and for F^+ ions with energies $\leq$13 eV. The resolving power of the instrument ($M/\Delta M$) is 230. The photon beam crossed the effusive molecular beam at a right angle to the axis of the spectrometer in a volume of about 3 mm^3. The spectrometer axis was oriented approximately along the polarization vector of the photon beam. The vacuum in the chamber was 5×10^{-8} mbar without the target gas and around 1×10^{-6} mbar with the target gas. The target beam number density is approximately 10^{12} cm^{-3}, ensuring single collision conditions. We obtain an ion count rate of

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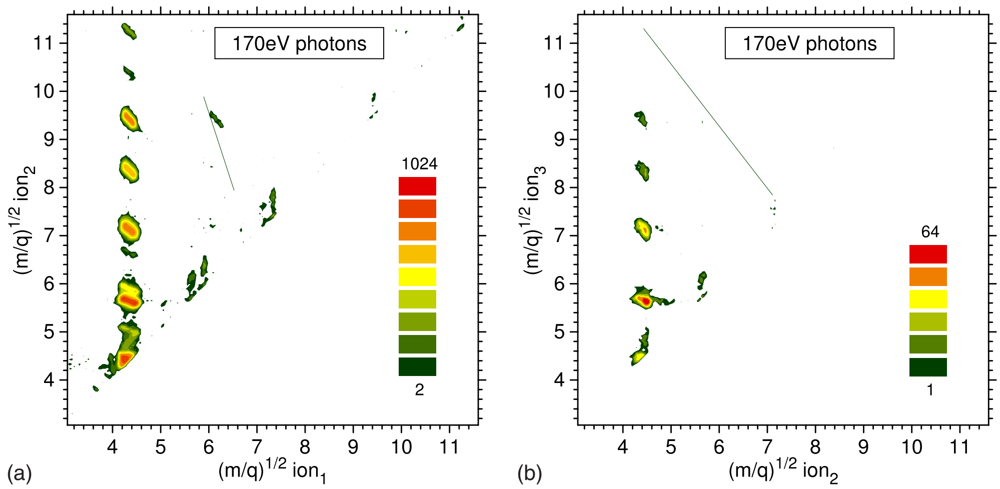

FIG. 1. (Color online) Correlation maps for the first and second hits (upper map) and for the second and third hits (lower map) from ionization of SF_6 by 170 eV photons. Note that the spectra are presented in terms of the square root of the mass-to-charge ratios (in atomic units) rather than the time of flight.

approximately 500 Hz under these conditions.

Ion time-of-flight (TOF) measurement was performed via electron-ion coincidence. The electron detector was a dual microchannel plate (MCP) of 40 mm diameter, placed 60 mm away from the ionization volume, and provided the start pulses for the TOF measurement. Ions were detected using a dual MCP of diameter 80 mm in conjunction with a delay-line anode. MCP signals provided the stop pulses for the TOF measurement, while the delay-line signals provided position encoding with a resolution of 0.25 mm. A multichannel time-to-digital converter (TDC) was used to process the TOF and position signals. The detector and TDC combination permits successive detection of four ion hits for the same start pulse with a deadtime of 10 ns, enabling us to measure the momentum of up to four ions from the same ionization event and thence extract many details of the fragmentation. Events were recorded in list mode and the acquired data were analyzed off line. The number of fully determined events at each energy was $>10^6$.

III. DATA ANALYSIS

Multiple ions arising from the dissociation of a highly charged precursor are labeled Hit1, Hit2,… in the order of their arrival at the detector. Correlation maps of the first and second hits as well as the second and third hits are shown in Fig. 1. No fourfold coincidence event has been recorded in the entire experiment. The shapes of the islands in the map and the slopes of the best-fit line to the correlated (t_1,t_2) values in an island provide significant information about the dissociation of doubly ionized precursors. A detailed analysis of the ion-pair distributions in the case of double ionization of SF_6 by electron impact can be found in [12]. The features of the (t_1,t_2) pair distributions in the present case are largely similar to those in [12], apart from significant differences in relative intensities of the pair coincidences. In the case of triple fragmentation, however, correlation maps alone are insufficient for understanding the *dynamics*. For that purpose we propose a method that exploits the full vector correlation between the momenta.

A. Triple coincidences

Five triple ion coincidences can be identified from the (t_2,t_3) correlation map. All triple coincidences have an F^+ ion as the first as well as the second hit. Furthermore, neither the triple ion coincidence $F^+:F^+:SF_4^+$ nor the pair coincidences $F^{2+}:SF_5^+$ or $F^+:SF_5^{2+}$ have been observed, ruling out the possibility of a concerted breakup of SF_6^{3+}. No SF_5^{3+} signal is seen in the mass spectrum either.

These observations lead us to the conclusion that SF_6^{3+} dissociates not via a simultaneous three-body or two-body breakup, but via a sequential breakup. The first step in the fragmentation of SF_6^{3+} is the loss of a neutral F and formation of SF_5^{3+}, which subsequently dissociates. A three-body breakup of SF_5^{3+} with equal charge sharing gives fragments $F^++F^++SF_3^+$. The kinematics of this reaction are determined from the correlated ion momenta. The sum of the momentum vectors of the three ions is determined, and is found to be nonzero. This residual momentum must be due to the recoil in the first stage of the dissociation, in which the F atom separates from SF_6^{3+}. The residual momentum peaks at 70 a.u. and has a tail extending up to 300 a.u.

Three other ion triple coincidences, in which the third partner is of the type SF_m^+ $(m=0,\ldots,2)$, are observed. The intensities of the coincidences $F^+:F^+:SF_m^+$ $(m=0,\ldots,3)$ increases with decreasing m, indicating higher stability of ions with fewer F atoms. To discern the complete fragmentation sequence, we investigate the vector correlation between the momenta of the two F^+ ions in each dissociation channel.

Figure 2 shows the distribution of the momentum of the second arriving F^+ ion with reference to the momentum of the first arriving F^+ ion. The latter momentum is taken to be directed along the x axis. The magnitude of the momentum of the reference F^+ ion is also shown. We notice from the figure that the distribution of the direction of emission of the

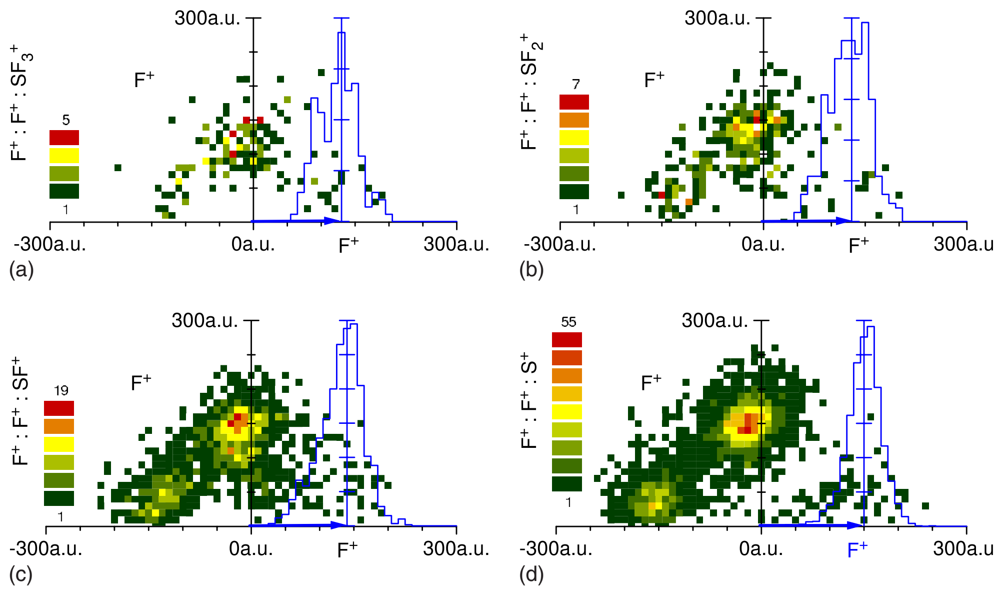

FIG. 2. (Color online) Momentum correlation maps between the two F^+ ions in the triple ion coincidences F^+:F^+:SF_m^+ (m=0, … ,3). The momentum of the first detected F^+ ion is taken as the reference (blue arrow). The components of the momentum of the second F^+ ion parallel and perpendicular to the reference vector are plotted. The color scale shows the number of events. The histogram accompanying the arrow shows the distribution of the magnitude of the momentum of the first ion.

two F^+ ions is preserved across *all* dissociation channels. They are ejected either (nearly) opposite or perpendicular to each other. Furthermore, the magnitude of the momenta are also nearly the same in *all* dissociation channels. The correlation between the emission of F^+ ions will be maintained across all channels only if they are ejected simultaneously.

B. Estimation of the role of the neutral fragments

The role of the neutral fragments in a breakup is usually very difficult to ascertain. In the present situation, due to the fact that we have correlated momentum information about the ions, we can obtain an estimate of their role in determining the kinematics in the following manner. A three-body breakup will always be coplanar, but the presence of a fourth fragment (which is undetected in the present case) will alter the coplanarity of the three momentum vectors. The quantity α, defined by

$$\alpha = \hat{p}_3 \cdot (\hat{p}_2 \times \hat{p}_1), \tag{1}$$

is a measure of the coplanarity, where $\hat{p}_i$ is the unit vector along the momentum of the ith ion. The distribution of this variable will have a narrow peak at zero in the case of coplanar emission. We have exploited this point to discern the behavior of the neutral fragments in the channels leading to the coincidences F^+:F^+:SF_m^+ (m=0, … ,3). The distributions are shown in Fig. 3. The significance of the width of the distributions $\Delta\alpha$ is ascertained by a comparison with the instrumental width. The value of $\Delta\alpha$ for the pure three-body breakup C^+:O^+:O^+ arising from photo-triple-ionization of CO_2, under conditions similar to the present experiment, is found to be 0.29, and is taken to be the instrumental width. In comparison, the values of $\Delta\alpha$ for the dissociation channels F^+:F^+:SF_m^+ (m=0, … ,3) are 0.55, 0.98, 0.65, and 0.62, respectively. The large values of $\Delta\alpha$ give an intuitive picture of the manner in which the neutrals are lost: they are released from a cage which has the S atom at the center. If there is only one F-bond break, the recoil suffered by the residue (SF_2^+) will be large, whereas if there are two or three F-bond

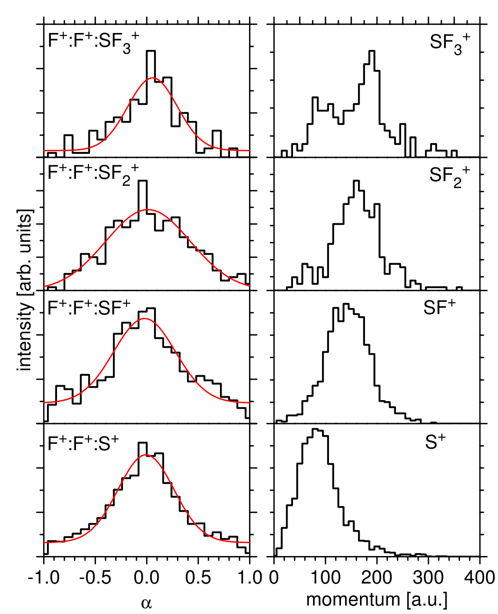

FIG. 3. (Color online) (Left) Distribution of α [see Eq. (1)], which is a measure of the noncoplanarity of momenta of the three ions ejected in the fragmentation of SF_6^{3+}. The smooth curves are Gaussian fits, with widths 0.55, 0.98, 0.65, and 0.62, respectively. The instrumental limit of the width of α is determined to be 0.29 (see text). (Right) Momentum distribution of SF_m^+ ions in the four dissociation channels. There are 163, 310, 1200, and 2507 events in the four channels, respectively.

breaks, the momentum balance is very likely to be maintained between the light F fragments and the residual ion (SF^+ and S^+) will have small net momentum.

Further corroboration of the proposed mechanism is found from the (scalar) momentum distribution of the third ion, which is shown in right panel of Fig. 3. The momentum distribution of the $SF_3{}^+$ ion is expected to be bimodal: one mode at a small value corresponding to antiparallel ejection of F^+ ions and another at a larger value, corresponding to perpendicular ejection of F^+ ions. A double peak structure is clearly seen in the momentum distribution of $SF_3{}^+$. By setting appropriate conditions on the events, we have verified that the $SF_3{}^+$ peak at lower momentum corresponds to antiparallel ejection of the F^+ ions, and the peak at higher momentum corresponds to perpendicular ejection. As we progress to more bond breaks, the momentum of the third ion ($SF_m{}^+$) is seen to reduce, which is consistent with the picture that the F atoms ejected in various directions carry away much of the momentum, leaving the heavier, central sulfur with little momentum.

C. Complete fragmentation sequence

The above observations lead us to the conclusion that there are at least two steps in the dissociation of $SF_6{}^{3+}$. The first of these is the loss of an F atom, forming $SF_5{}^{3+}$. The breakup of $SF_5{}^{3+}$ occurs via violent ejection of two F^+ ions and slow separation of F atoms from the core sulfur, leading to the triple ion coincidences $F^+:F^+:SF_m^+$ ($m=0,\ldots,3$).

The tendency of the emission of the F^+ ions in either (nearly) antiparallel or perpendicular directions gives hints about the geometry of $SF_5{}^{3+}$. Notice that the most probable angles between the emitted F^+ ions are not exactly 90 or 180 degrees, which suggests that the S-F bonds are no longer perpendicular to each other, as is the case in the neutral geometry. Also, the relative intensities in the two lobes of the second F^+ ion momentum distribution show that the F^+ ions are more likely to be ejected in perpendicular directions than in opposite directions.

IV. CONCLUSIONS

We have studied the complete dissociation sequence of $SF_6{}^{3+}$ formed by photoionization of SF_6. $SF_6{}^{3+}$ is shown to fragment in a sequential manner, the first step being the loss of an F atom and formation of $SF_5{}^{3+}$, followed by violent ejection of two F^+ ions. Slow separation of F atoms brings the residual $SF_3{}^+$ to the stable S^+ ionic state, and at each F loss there is an increasing likelihood of the $SF_m{}^+$ ($m=0,\ldots,2$) ion being stable. We believe that these observations throw light on the dissociative states of $SF_6{}^{3+}$ and make the theoretical problem of determining its states more tractable.

We have observed no photon energy-dependent differences in the kinematics of the various dissociation channels discussed in the paper. This observation is counterintuitive to our understanding of the formation of the intermediate states (such as $SF_6{}^{3+}$ or $SF_5{}^{3+}$). When a sulfur $2p$ shell electron is ejected, the cascade of vacancy filling transitions is different from the case where a $3p$ or higher electron is ejected. One would then expect the rearranged orbitals to be different at the two photon energies. Consequently the fragmentation mechanisms cannot be expected to be similar. The observed insensitivity of the fragment momentum distributions to the photon energies suggests that the fragmentation is governed mainly by Coulomb repulsion between the nuclei, rather than by electron correlations.

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