

Doppler effect in fluorine K-Auger line produced in electron-induced core ionization of SF₆

S. Mondal

Atomic Physics Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

R. K. Singh

Centre for Advanced Technology, Indore 452 013, India

R. Shanker^{a)}

Atomic Physics Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

(Received 21 October 2005; accepted 28 November 2005; published online 17 January 2006)

An experimental evidence is reported on the observation of the Doppler effect in fluorine K-Auger line emitted from a core-ionized SF₆ molecule under an impact of 16 keV electrons. The emitting source of the Auger line is found to acquire a kinetic energy of 4.7 ± 0.3 keV. We propose that such large energy is released from the Coulomb repulsion taking place between F⁺ and SF₅⁺ fragment ions under influence of an intense focusing field of the incident electrons. In the presence of the Coulomb field of these ions, the Auger line obtains a polarization $P = 76\% \pm 7\%$. © 2006 American Institute of Physics. [DOI: [10.1063/1.2158995](https://doi.org/10.1063/1.2158995)]

I. INTRODUCTION

Ionic fragmentation of molecules induced by energetic charged particles has been the subject of basic research in collision physics for a long time. This field of research is motivated by its various applications in adjacent fields, such as in atmospheric physics, accelerator physics, and biology.¹ Within this field of study, a molecule having suffered an ionization via ejection of its core electrons provides a suitable test bed to explore the interplay between the dynamics of atomiclike Auger decay and the nuclear motion of the molecule. During the molecular dissociative ionization, if a core electron of an atom in the molecule is promoted to an unbound molecular state, then the produced core hole may decay by an autoionization.^{2–6} In contrary, if a core electron of the molecule is directly ionized, then the unbalance created in the molecular charges induces the Coulomb explosion which in turn breaks the molecular bonds and results into ionic fragmentations in a time scale of femtosecond. The fragmented ions may acquire the relative kinetic energies of large values^{7,8} and finally decay through the Auger emission in the time scale less than 10^{-14} s. As a consequence, the atomiclike Auger decay feature can coexist in molecular Coulomb explosion with its core ionization. Hence, the nuclear motion of the core-ionized atom may influence the characteristics of the emitted Auger electrons. The obvious influence is due to the Doppler effect on Auger electrons emitted from the core-excited or the core-ionized moving particles. The study of such Doppler effect in the electron spectra of a core-ionized molecule may prove to be a unique tool in studying the details of dynamics of nuclear motion as well as Auger emission in a given collision reaction.

Energy shift, line broadening, and change in intensity of the characteristic Auger line under Doppler effect were first

studied by Rudd *et al.* in Ar⁺–Ar collisions.^{9,10} It is known that the relative strength of Doppler effect depends on the direction of observation of ejected electrons with respect to the direction of motion of the emitting source particle. In this context, these workers determined the energy shift due to the Doppler effect by studying the angular distributions of the ejected electrons from the moving particles. In their studies, it was noted that the electrons ejected from Ar⁺–Ar collisions lost their memory to distinguish between the projectile and the target from which they were emitted. Thus, in such type of completely symmetric collision systems, a number of characteristic peaks which shift with projectile velocity and a number of others which do not were observed under an influence of the Doppler effect.

When a molecule is core-ionized by an impact of a charged particle, it usually dissociates following a Coulomb explosion. If the electron emission is observed in different directions with respect to the motion of the fragmented atomic ion, then the emitted Auger line shows up different intensities due to the alignment effect and shifts in energy at different emission angles due to the Doppler effect. It may be pointed out here that the splitting of resonant phototransition due to Doppler effect in ejected electrons from diatomic and triatomic molecules has been observed for O₂,¹¹ O₃,¹² and DF.¹³ Doppler effect and splitting of resonant F1s photoexcited transition line have been studied for a polyatomic molecule CF₄ by Ueda *et al.*¹⁴ and for SF₆ by Kitajima *et al.*¹⁵ The Doppler effect in these studies has been suggested to arise from the nuclear motion of the dissociated “excited F atoms.” The above-mentioned splitting was observed when the emitted electrons were detected from an excited fluorine atom moving in both forward and backward directions with respect to the polarization vector of the incident photons.

^{a)}Electronic mail: rshanker@bhu.ac.in

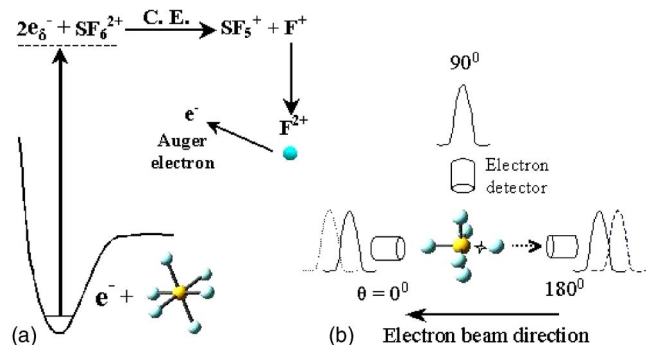


FIG. 1. (Color online) Schematics of the reaction flow for fast e^- - SF_6 collisions. (a) Ionization, fragmentation of SF_6 , and Auger electron emission. Directly ionized electron (e_s^-) and Coulomb explosion (CE). (b) Detection scheme for electrons ejected from the collision reaction, wherein the dotted and the dashed curves refer to the shifted positions of the Auger peaks corresponding to the detection in forward and backward directions with respect to an unshifted position (solid line curve).

II. ORIGIN OF DOPPLER EFFECT

In this paper, we present the first evidence of Doppler effect causing energy shift, intensity variation, and polarization of the atomiclike fluorine K -Auger line emitted from a core-ionized fluorine atom of a highly symmetric polyatomic molecule, viz., SF_6 under an impact of 16 keV electrons. The Doppler effect is shown to arise due to the motion of core-ionized F^+ ions which are formed by Coulomb explosion of the parent molecule. How does the Doppler effect come into play in atomiclike F K -Auger transition can be understood with the help of Fig. 1. It shows a schematic reaction flow diagram for the occurrence of Doppler effect in an atomiclike F K -Auger line when it is emitted from a core-ionized SF_6 molecule under an impact of energetic electrons. Here, as suggested in earlier work,¹⁶ the initial core ionizations of SF_6 take place in an extremely short period (in about femto-second); this reaction yields a doubly charged SF_6^{2+} molecule, as shown in Fig. 1(a). The two ejected electrons out of which, one comes from K shell of the fluorine atom and the other from L shell of the sulfur atom of the molecule. The simultaneous ejection of these electrons produces interference effect and leads to the formation of F^+ and SF_5^+ ions after Coulomb explosion. Due to the short lifetime of the core holes of these ions, they preferentially decay via emission of respective F K - and S L -Auger electrons.¹⁷ Here, we concentrate on the studies of Auger electrons which are emitted from a core-ionized F^+ ions [see Fig. 1(a)]. As the Coulomb explosion and the Auger decay are two parallel and competing processes, they proceed almost simultaneously. Because of the nuclear motion of F^+ ions, the F K -Auger electrons observed at different angles with respect to the direction of ion motion are found to possess different characteristic energies by virtue of Doppler effect. If the velocity vector of F^+ ions is set opposite to the electron-beam direction, then the characteristic Auger electrons ejected in the forward direction, i.e., $\theta < 90^\circ$, will lose their kinetic energy and those ejected in the backward direction, i.e., $\theta > 90^\circ$, will gain a kinetic energy due to Doppler effect, here θ is the detection angle subtended between the electron detector and the direction of electron beam. Hence, the detection of F

K -Auger electrons in the forward and backward directions with respect to the incident electron beam is expected to yield a redshifted and a blueshifted Auger lines, respectively, due to this effect, while an unshifted line is detected at $\theta = 90^\circ$ [see Fig. 1(b)].

The Doppler shift can be determined from a basic relation $v = u_0 + u$, where v is the velocity of ejected electrons in the laboratory frame of reference, u_0 is the velocity of the electrons in the source frame, and u is the velocity of the source particle. The corresponding kinetic energies of electrons in the laboratory frame and in source frame are $E = mv^2/2$ and $E_0 = mu_0^2/2$, respectively, where m is the mass of the electron. The kinetic energy of source particle is $T = Mu^2/2$, where M is the mass of the source particle. If ϕ is the emission angle of Auger electrons with respect to the direction of motion of the source particle, then a calculation yields the energy relation for the Doppler effect as $E_0 = E - 2(mTE/M)^{1/2} \cos \phi + (m/M)T$. Hence, the Doppler shift ΔE of a characteristic Auger line emitted at an angle ϕ is given by

$$\Delta E = E - E_0 = 2 \sqrt{\frac{m}{M} TE} \cos \phi - \frac{m}{M} T. \quad (1)$$

Since the energy T of source particle (F^+ ion) is not known in the collision events of the present studies, we have, therefore, determined T from the slope of a graph plotted between $\sqrt{E} \cos \phi$ and ΔE [see Eq. (1)]. Further, it is evident from Eq. (1) that the Doppler shift at $\phi = 90^\circ$ is minimum, negative for $90^\circ < \phi < 270^\circ$ and positive for $90^\circ > \phi > 270^\circ$ with respect to the movement of the source particle. Hence, such observations establish the existence of a preferential direction of motion of the F^+ ions after fragmentation in the considered collisions.

III. EXPERIMENT

The present measurements were carried out on an experimental facility developed for studying the energetic electron-atom/molecule collisions in our laboratory.¹⁸ Since a detailed description of the scattering chamber and that of the electron spectrometer has been given elsewhere,¹⁹ we present here only the major features of the involved components of the setup in the present experiments. A monoenergetic electron beam was obtained from a custom-built electron gun (STAIB Instruments, GmbH, Germany). A beam of 16 keV electrons with a current of 300 nA was used and monitored by a biased Faraday cup after it transmitted through the target gas. The target gas of SF_6 (99.80% purity) was made to effuse from a multicapillary tube at 90° to the incident electron beam at a thermal velocity. The collisionally induced continuum and characteristic electrons emitted from SF_6 were recorded in the energy range of 0–1000 eV and energetically analyzed by a 45° parallel-plate electrostatic analyzer and were detected by a channel electron multiplier. Angle-resolved energy spectra of continuum and characteristic electrons were measured by positioning the electrostatic analyzer at a desired angle around the collision center. The energy spectra of the ejected electrons as a function of their energy for different detection angles θ with respect to

incident-beam direction were recorded in a multichannel scaling (MCS) mode of a Pentium-based 4 K multichannel analyzer (MCA). The relative double differential cross sections (DDCSs) for emission of the fluorine *K*-Auger electrons were determined after subtracting the continuum background underneath the Auger peak and normalizing them with the corresponding integrated beam currents collected in the Faraday cup. The experimental uncertainty in measurements of the DDCS is estimated to be about 20%.

IV. RESULTS AND DISCUSSION

Figure 2 shows the fluorine *K*-Auger yields at different angle θ which ranges between 60° and 135°. The fluorine *K*-Auger peak is found to lie at 626 eV when it is detected at 90°. It shifts towards lower-energy side when it is viewed in the forward direction and towards higher-energy side when detected in the backward direction. Such a shift in the F *K*-Auger line with respect to $\theta=90^\circ$ takes place due to an energy gain or loss by the Auger electrons by virtue of Doppler effect which is basically caused due to the motion of the F⁺ ions. The motion of source ion is set as a result of energy gain from the Coulomb explosion of the core-ionized doubly charged SF₆ radical ions that are transiently formed in the collisions. The dynamics of the nuclear motion of the fragmented ions with regard to their kinetic-energy release from Coulomb explosions and the correlated Doppler shift in Auger electrons are presented in the following paragraphs.

If the motion of the source F⁺ ion is taken in the direction opposite to the direction of the incident electron beam, then Doppler effect and hence the energy shift occurring in the Auger line at $\theta=\phi=90^\circ$ are expected to be minimum; however, it should increase at emission angles $\phi<90^\circ$ or $\theta>90^\circ$ and decrease at $\phi>90^\circ$ or $\theta<90^\circ$ [see Eq. (1)]. Also, from the present results, it is found that the Doppler shift is positive for $\theta>90^\circ$ and negative for $\theta<90^\circ$. This observation suggests that the core-ionized F⁺ ions preferentially fly and orient themselves in the direction opposite to the electron beam and decay via Auger transitions resulting into F²⁺ ions.

The value of kinetic energy of F⁺ ions determined from the measured Doppler shifts using Eq. (1) is found to be 4.7 ± 0.3 keV. It is to be pointed out that due to the heavier mass of the counterfragment partner SF₅⁺ radical ion, the energy share for it is comparatively small. Therefore, the total value of the kinetic-energy release (KER) in F⁺-SF₅⁺ fragmentation should be greater than the KER of F⁺ ions. We propose for the first time the existence of such a large KER in the case of electron-impact core ionization of SF₆ molecule as follows: During the energetic *e*⁻-SF₆ collisions, it is noted that an extremely unstable SF₆²⁺ radical ion is formed via ejection of two electrons simultaneously from the molecule in a very small time (of the order of femtosecond) (see, e.g., Ref. 16). In the present case, it occurs due to the accessibility of incident electrons (with a plane wave) to a small impact parameter (0.07 Å) close to the radii of F *K* (0.06 Å) and S *L* (0.15 Å) atomic shells. Because of the symmetry of the molecule, the incident beam faces F atom first, then the S atom next in the collision. In this configuration, two elec-

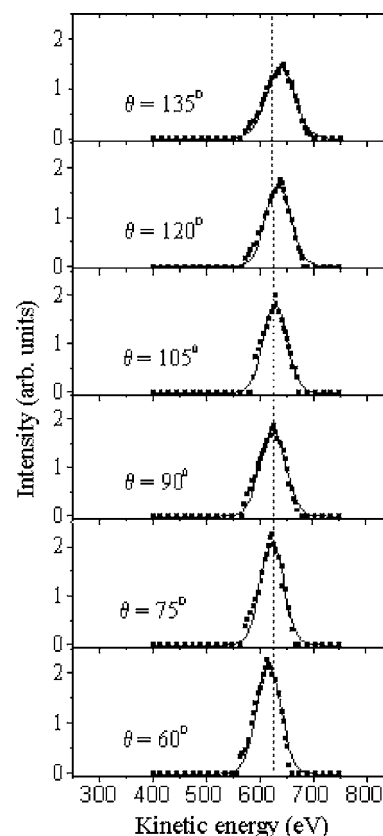


FIG. 2. Intensity and energy shift of the F *K*-Auger peak as a function of detection angle θ in 16 keV *e*⁻-SF₆ collisions. The vertical dotted line shows the relative shift of different peaks with respect to the peak at $\theta=90^\circ$.

trons of the molecule, one from F atom facing the beam and the other from S atom, are ejected;¹⁷ ejection of further electrons in the same collision has an extremely low probability. The corresponding F-S bond (1.54 Å) associated with the interaction requires that it initially be aligned with the incident beam. Immediately after the formation of SF₆²⁺, it gets dissociated into F⁺ and SF₅⁺ ions due to Coulomb explosion with about 9.4 eV energy; then in the second step, in the presence of these ion's plasma, the plane wave of incident electron beam (300 nA) gets electromagnetically focused²⁰ in the premises of collision zone. The focused beam makes the two fragment ions move radially towards the center of the collision zone. While doing so, the ions approach each other to a critical separation. As a result of this, the two ions repel each other with a large amount of Coulomb energy (a few keV) and fly apart with a high velocity collinear to the beam direction. The core-ionized F⁺ ions while flying apart in the opposite direction to the incident beam due to Coulomb repulsion emit Auger electrons which suffer the Doppler effect. In the present observation the origin of a large KER associated with F⁺ suggests that the F⁺ and SF₅⁺ radical ions approach to a critical distance of the order of 10⁻¹¹ cm. However, the exact estimation of this critical distance is not feasible at present without the knowledge of dynamic parameters involved in the collision. A similar type of phenomenon of high keV KER in Coulomb explosion of H₂O and NH₃ clusters was observed in the work of Wisniewski *et al.*⁷ and Snuder *et al.*,⁸ respectively; the detailed reason of such high

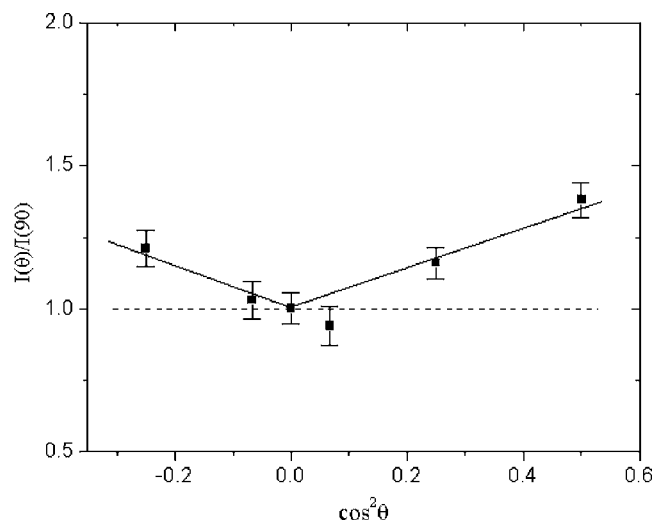


FIG. 3. Angular dependence of the intensity ratio $I(\theta)/I(90)$ for F K -Auger electrons emitted from 16 keV e^- -SF₆ collisions; $I(\theta)$ and $I(90)$ are the intensities of the Auger peak at angle θ and at 90°, respectively.

KER is, however, not given in their paper. From the present analysis and from our previous observations,¹⁷ it is noted that SF₅⁺ ion finally decays into S²⁺ via Auger transition yielding S L -Auger line. As a matter of fact, we have observed the sulfur L -Auger peak at about 120 eV in the energy spectrum as well as the presence of stable S²⁺ ions in the time-of-flight (TOF) spectra (see Refs. 17 and 21).

The polarization P of F K -Auger electrons is obtained by determining their emission cross sections from the spectra of angular distributions using the relation²²

$$I(\theta)/I(90) = 1 - P \cos^2 \theta, \quad (2)$$

where $I(\theta)$ and $I(90)$ are the intensities of Auger electrons ejected at an angle θ and at 90°, respectively, with respect to the incident-beam direction. The intensity of Auger line at a given angle is obtained by integrating the area under the peak. The ratios of intensities at different angles $I(\theta)/I(90)$ are determined and are plotted in Fig. 3 as a function of $\cos^2 \theta$ [see Eq. (2)]. In the plot, all data points are found to lie on the fitted curve except one datum at $\theta = 105^\circ$, the deviation of which from the curve is presently not understood. The slope of the line gives the polarization P of F K -Auger electrons. P is found to be $76\% \pm 7\%$. Occurrence of the polarization can be qualitatively understood by the fact that owing to the short lifetime of F K vacancy, the Auger electrons during their emission due to decay of the core vacancy still lie in the vicinity of parent source and the fragmented SF₅⁺ ion. Coulomb fields associated with these species tend to polarize the ejected electrons along their respective directions of motion.

V. CONCLUSIONS

The present work provides an experimental evidence which has shown that F K -Auger line produced from a core-ionized polyatomic SF₆ molecule suffers Doppler effect under an impact of energetic (keV) electrons. This effect comes

into play due to the motion of F⁺ ions which gain a large kinetic energy from the reaction of Coulomb explosion of a transiently formed SF₆²⁺ ion followed by a Coulomb repulsion produced in response to the electric field of a focused incident beam, which has been generated by the associated ion plasma. Results on intensity variation and energy shift of the Auger line have been presented and discussed. A strong anisotropy or polarization P of F K -Auger electrons $P = 76\% \pm 7\%$ is found to arise due to the presence of Coulomb fields of aligned ions during their flight times. The observation reported here is, indeed, a scientific curiosity which may find a practical application in Auger and Doppler spectroscopies and in production of the low-energy ion sources.

ACKNOWLEDGMENTS

The authors are thankful to the Department of Science and Technology (DST), New Delhi for providing the financial support under a research Project No. SP/S2/L-08/2001. The authors are also grateful to Professor Dr. R. Hippler for his keen interest in this work. One of the authors (S.M.) would like to thank the DST and the Council of Scientific and Industrial Research (CSIR), New Delhi for providing research fellowships during the execution of the work.

- ¹S. H. Lee, J. M. Reeves, J. C. Wilson, D. E. Hunton, A. A. Viggiano, T. M. Miller, J. O. Ballenthin, and L. R. Lait, *Science* **301**, 1886 (2003); B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, *ibid.* **287**, 1658 (2000).
- ²E. Kukk, H. Aksela, S. Aksela, F. Gel'mukhanov, H. Ågren, and S. Svensson, *Phys. Rev. Lett.* **76**, 3100 (1996).
- ³O. Björneholm, S. Sundin, S. Svensson, R. R. T. Marinho, A. Naves de Brito, F. Gel'mukhanov, and H. Ågren, *Phys. Rev. Lett.* **79**, 3150 (1997).
- ⁴S. Tanaka, Y. Kayanuma, and K. Ueda, *Phys. Rev. A* **57**, 3437 (1998).
- ⁵Z. W. Gortel and D. Menzel, *Phys. Rev. A* **58**, 3699 (1998).
- ⁶M. N. Piancastelli, R. Sankari, S. Sorensen, A. De Fanis, H. Yoshida, M. Kitajima, H. Tanaka, and K. Ueda, *Phys. Rev. A* **71**, 010703(R) (2005).
- ⁷E. S. Wisniewski, J. R. Stairs, and A. W. Castleman, Jr., *Int. J. Mass. Spectrom.* **212**, 273 (2001).
- ⁸E. M. Snuder, S. Wei, J. Purnell, S. A. Buzza, and A. W. Castleman, Jr., *Chem. Phys. Lett.* **248**, 1 (1996).
- ⁹M. E. Rudd, T. Jorgensen, and D. J. Volz, *Phys. Rev. Lett.* **16**, 929 (1966).
- ¹⁰M. E. Rudd, T. Jorgensen, and D. J. Volz, *Phys. Rev.* **151**, 28 (1966).
- ¹¹O. Björneholm, M. Bassler, A. Ausmees, I. Hjelte, R. Feifel, H. Wang, C. Miron, M. N. Piancastelli, and S. Svensson, *Phys. Rev. Lett.* **84**, 2826 (2000).
- ¹²L. Rosenqvist, K. Wiesner, A. Naves de Brito *et al.*, *J. Chem. Phys.* **115**, 3614 (2001).
- ¹³K. Wiesner, A. Naves de Brito, S. L. Sorensen, F. Burmeister, M. Gisselbrecht, S. Svensson, and O. Björneholm, *Chem. Phys. Lett.* **354**, 382 (2002).
- ¹⁴K. Ueda, M. Kitajima, A. De Fanis *et al.*, *Phys. Rev. Lett.* **90**, 233006 (2003).
- ¹⁵M. Kitajima, K. Ueda, A. De Fanis *et al.*, *Phys. Rev. Lett.* **91**, 213003 (2003).
- ¹⁶J. H. Sanderson, R. V. Thomas, W. A. Bryan, W. R. Newell, P. F. Taday, and A. J. Langley, *J. Phys. B* **30**, 4499 (1997).
- ¹⁷S. Mondal and R. Shanker, *Phys. Rev. A* **69**, 060701(R) (2004).
- ¹⁸R. K. Singh, S. Mondal, and R. Shanker, *J. Phys. B* **36**, 489 (2003).
- ¹⁹S. Mondal, R. K. Singh, and R. Shanker, *Pramana, Pramana, J. Phys.* **60**, 1203 (2003).
- ²⁰J. L. Cox, Jr., *Phys. Rev. Lett.* **35**, 944 (1975).
- ²¹R. K. Singh, R. Hippler, and R. Shanker, *Phys. Rev. A* **67**, 022704 (2003).
- ²²R. Hippler, *Nucl. Instrum. Methods Phys. Res. A* **255**, 17 (1987).