

Doppler Effect in Resonant Photoemission from SF₆: Correlation between Doppler Profile and Auger Emission Anisotropy

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Fragmentation of the SF₆ molecule upon F 1s excitation has been studied by resonant photoemission. The F atomiclike Auger line exhibits the characteristic Doppler profile that depends on the direction of the photoelectron momentum relative to the polarization vector of the radiation as well as on the photon energy. The measured Doppler profiles are analyzed by the model simulation that takes account of the anisotropy of the Auger emission in the molecular frame. The Auger anisotropy extracted from the data decreases with an increase in the F-SF₅ internuclear distance.

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If a core electron of an atom in a molecule is promoted to an unoccupied molecular orbital, the core hole decays predominantly with Auger emission. The nuclear motion proceeds in the molecular core-excited state in competition with the Auger decay. The typical time scale of this competition is $<10^{-14}$ s. As a result, molecular Auger-decay features and atomiclike Auger lines can coexist in the resonant photoemission spectra [1–6]. Such electron spectra provide a unique possibility for studying details of the nuclear dynamics as well as Auger dynamics [7–9]. In the present Letter, we discuss a detailed analysis for the Doppler profile of the atomiclike Auger line as a typical example for such studies.

The Doppler effect in resonant photoemission was predicted by Gel'mukhanov and co-workers [10,11]. If the dissociation is highly anisotropic along the polarization vector of the radiation, and if the electron emission is observed along this direction, then the Auger line of the departing atomic fragment can be Doppler split. This Doppler splitting has been observed for O₂ [12], O₃ [13], DF [14], and CF₄ [15]. In the study on CF₄ [15], Ueda *et al.* observed a Doppler split of the F 1s⁻¹ atomiclike Auger line in the resonant photoemission spectra, when the photon energy is tuned to the F 1s → a_{1g}^{*} resonance and electron emission is observed in the direction parallel to the polarization vector. The Doppler splitting disappears when the electron emission is observed in the direction perpendicular to the polarization vector. These observations indicate that one of the C-F bonds is elongated along the direction of the polarization vector and the ultrafast dissociation proceeds in the core-excited state.

In the present work, we extend the observation to the highly symmetric O_h molecule SF₆. The ion yield mea-

surement for SF₆ indicated strong anisotropic fragmentation at the F 1s → a_{1g}^{*} resonance [16], as in the case of CF₄ [15]. The present observation reveals that the Doppler profile of the atomiclike Auger line observed in the direction perpendicular to the polarization vector exhibits a flat peak shape that varies as a function of photon energy. The flat peak shape contrasts to the sharp peak shapes of the corresponding Doppler profiles observed so far [12–15]. We demonstrate that the observed energy-dependent flat peak shape includes the information about the anisotropy of the atomiclike Auger emission in the molecular frame.

Measurements have been carried out on the *c* branch of the soft x-ray photochemistry beam line 27SU at SPring-8 [17]. The radiation source is a figure-8 undulator, whose emitted radiation is linearly polarized either in the plane of the storage ring (1st order) or in the plane perpendicular to it (0.5th order) [18]. Angle-resolved electron emission measurements are performed by changing the undulator gap, without rotating the electron analyzer. The electron spectroscopy apparatus consists of a hemispherical electron analyzer (Gammadata Scienta SES-2002), a gas cell, and a differentially pumped chamber [19]. The overall resolution used in the present measurements is 150 meV.

Figure 1 contains electron spectra measured at seven different photon energies across the F 1s → a_{1g}^{*} resonance at ≈688 eV. The spectra are recorded for electron emission in the directions parallel (0°) and perpendicular (90°) to the polarization vector of the radiation. The kinetic energy of the valence photoelectron bands, labeled X, AB, and C-F, increases with an increase in the photon energy. The nondispersive spectral feature F^{*}, on the other hand, exhibits a splitting, characteristic of the Doppler

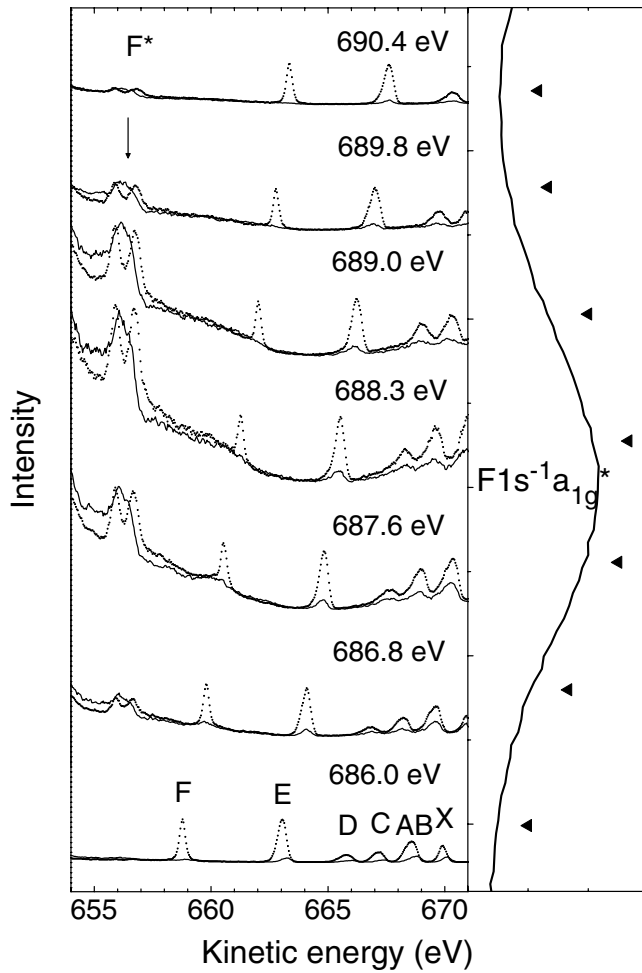


FIG. 1. Electron spectra of SF_6 recorded for parallel (dots) and perpendicular (solid lines) polarizations. The measurements are carried out at seven different photon energies across the $\text{F } 1s \rightarrow a_{1g}^*$ resonance, as indicated by the arrows in the right panel, where the total ion yield spectrum is displayed.

effect, in the 0° spectrum. The Doppler shift of the kinetic energy of electrons emitted from the F^* fragments propagating in opposite directions has the opposite sign and thus the Doppler splitting is observed in the 0° spectrum. (Hereafter F^* indicates the core-excited F atom.) The kinetic energy of this band, ≈ 656.3 eV, is indeed very close to the energy of the Auger line, 656.5 eV, for the $1s2p^6^2S \rightarrow 2p^4^1D$ transition of the F atom [20].

Figure 2 presents the enlarged spectra of the F^* atomiclike Auger line, after subtraction of the baseline. Focus on the 90° spectra where the Doppler splitting is absent. The Doppler broadened profiles exhibit a flat peak shape when the photon energy is tuned to the vicinity of the resonance peak (at 688.28 ± 0.75 eV) and a very shallow dip appears at the center when it is tuned to the low energy side (at 686.8 eV). These peak shapes contrast with the Gaussian-like sharp peak shapes for the corresponding F^* atomiclike Auger lines observed for the 90° spectra of DF [14] and CF_4 [15].

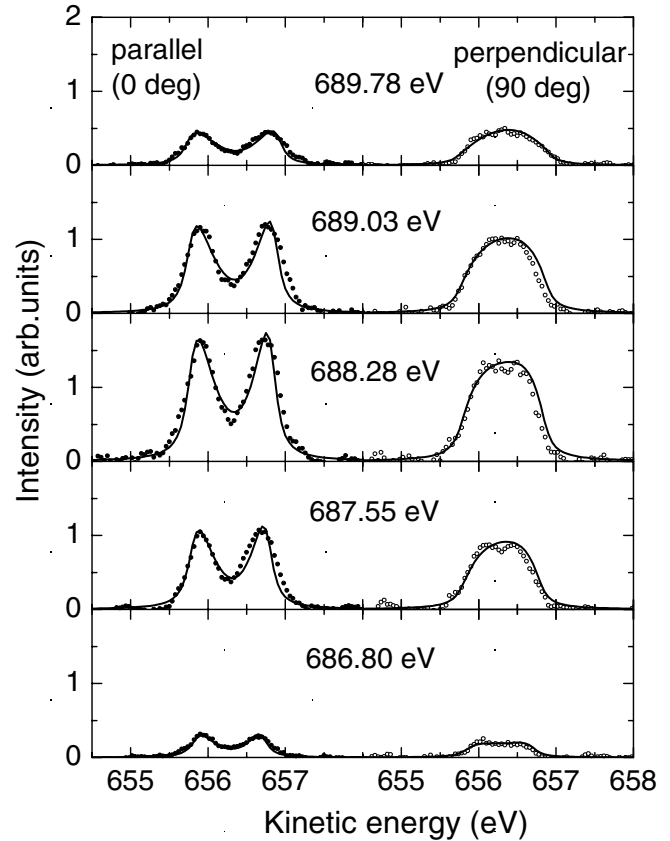
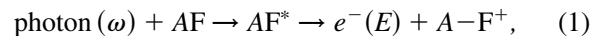


FIG. 2. Doppler profiles of the F^* atomiclike Auger line emitted in the directions parallel and perpendicular to the polarization vector. The spectra are recorded across the $\text{F } 1s \rightarrow a_{1g}^*$ resonance of SF_6 for five different photon energies. Baselines are subtracted.

Let us consider the atomiclike Auger emission in the resonant photoemission. The process consists of photoabsorption and decay:



where $A \equiv \text{SF}_5$, and ω and E are the photon and Auger electron energies, respectively. The photoabsorption takes place at the internuclear distance R_0 between F^* and A , whereas the decay from the core-excited state c takes place at $R = R_0 + \Delta R$ with a displacement ΔR . Then, from the energy conservation law, $\epsilon + E + E_f(R) = \omega + E_0(R_0)$ holds, where ϵ is the kinetic energy release and E_0 and E_f are the energies of the initial ground state 0 and the Auger final state f . As we discuss later, the decay $c \rightarrow f$ may take place before the fragment reaches the dissociation limit ($R \rightarrow \infty$). Then the kinetic energy release ϵ may depend on R .

We define the angle θ between the momentum \mathbf{k} of the Auger electron and the velocity vector \mathbf{v} of the F^* atom. Then $\mathbf{k} \cdot \mathbf{v} = kv \cos\theta$, with $k = \sqrt{2E}$; atomic units are used through the paper unless indicated. The velocity v is related to the kinetic energy release, $\epsilon = m_{\text{F}}^2 v^2 / (2\mu)$,

where m_F is the mass of the F atom and μ is the reduced mass, $\mu = m_F m_A / (m_F + m_A)$, with m_A being the mass of SF₅. The cross section of resonant photoemission near the atomiclike Auger line can then be expressed as

$$\sigma(E, \omega) = \int_0^\pi d\theta \sin\theta \frac{\rho(\cos\theta) Q^2(\cos\theta)}{(\Delta E - kv \cos\theta)^2 + \Gamma^2}, \quad (2)$$

where $\Delta E \equiv E - \omega_{cf}$ is the Auger electron energy relative to the center of the atomiclike Auger line at ω_{cf} ; ω_{cf} also depends on R . Γ is the lifetime width (HWHM) of the core-excited state. The ω dependence of $\sigma(E, \omega)$ is hidden in v and Q (see below). One can see that the spectral shape of the resonant photoemission is influenced by three anisotropic factors. The denominator in Eq. (2) depends on θ due to the Doppler effect. The polarization function ρ of the molecular dissociation also exhibits anisotropy because of the selectivity of the molecular orientation in the core excitation [21]:

$$\rho(\cos\theta) = \frac{1}{3}[1 + \beta P_2(\hat{e} \cdot \hat{k}) P_2(\hat{k} \cdot \hat{v})], \quad (3)$$

where $\hat{k} = \mathbf{k}/k$, $\hat{v} = \mathbf{v}/v$, \hat{e} is the polarization vector, and $P_2(x) = (3x^2 - 1)/2$ is the Legendre second order polynomial. Here we heuristically assumed that the angular distribution of the F* fragment is given by $I \propto [1 + \beta P_2(\hat{e} \cdot \hat{v})]$, with β being the anisotropy parameter of the F* fragment. Third, the squared electronic matrix element, $Q^2(\cos\theta)$, of the Auger transition $c \rightarrow f$ depends on θ due to the anisotropy of molecular orbitals involved in the spectator decay concerned:

$$Q^2 = 1 + \zeta P_2(\cos\theta) + \zeta' P_4(\cos\theta) + \dots \quad (4)$$

One should note that, contrary to this expansion in the molecular frame, the maximum harmonic of the angular distribution in the laboratory frame (2) cannot be greater than $P_2(\hat{e} \cdot \hat{k})$ [22,23]. Let us stress that $\zeta = \zeta' = \dots = 0$ for $R \rightarrow \infty$, because the decay, $1s^1 2s^2 2p^6 \rightarrow 1s^2 2s^2 2p^4 + e^-$, in the isolated F* atom is isotropic. In the real situation, however, R is finite and thus the F* atom is disturbed by the SF₅ fragment. As a result, the anisotropy parameters (ζ, ζ', \dots) can deviate from zero. Since $1 > |\zeta| \gg |\zeta'|$, one can assume $\zeta' = 0$ to the first approximation. Such an assumption agrees nicely with the pump-

probe electron-ion-coincidence measurements for large delay times [24].

To discuss the observed Doppler profiles quantitatively, using the model described above, we have performed a fit of Eqs. (2)–(4) to the experimental spectra. The results of the fit are shown by the solid curves in Fig. 2. Parameters extracted from the fit are the energy for the center of the atomiclike Auger line, ω_{cf} , the velocity v , the anisotropy parameter β of the F* fragment relative to the polarization vector \hat{e} , and the anisotropy parameter ζ for the Auger emission relative to the velocity vector \mathbf{v} , i.e., in the molecular frame. These values are summarized in Table I. Here the kinetic energy release $\epsilon = m_F^2 v^2 / (2\mu)$ is presented instead of the velocity v . The detuning of the photon energy ω from 688.28 eV (the resonance peak), Ω , is also given in the table.

We first focus on ω_{cf} . In principle, ω_{cf} depends on the nuclear distance R where the Auger decay takes place and thus can be dependent on Ω , since R can be dependent on Ω (see below). The extracted ω_{cf} slightly increases with an increase in ω_{cf} but the variation is within the uncertainties. The small variation of ω_{cf} illustrates that the potential energy curves between the core-excited state c and the Auger final state f already become almost parallel in the region of R where the Auger-decay takes place.

The kinetic energy release ϵ is mostly determined by the Doppler splitting in the 0° spectrum in our fitting procedure. It increases by a $\simeq 0.6$ eV step with an increase in the photon energy ω by a $\simeq 0.8$ eV step. This contrasts to the diatomic case of DF [14], where ϵ increases by the same amount as the increase in ω . The ω dependence of ϵ observed for SF₆ implies that only a part of the energy stored in the nuclear motion of the core-excited state is released in dissociation at the point where the Auger decay takes place. The rest may be kept mostly in the SF₅ fragment in the form of vibrational energy (see Ref. [15]). Note also that ϵ depends on the distance R and that R can be dependent on ω . As a result, ϵ can be a nonlinear function of ω .

The extracted values of the anisotropy parameter β for the F* fragment are $\simeq 1.4$ and stay almost constant as a function of Ω . The values of β do not coincide with β_{ion}

TABLE I. Parameters for describing the Doppler profile of the F atomiclike Auger line, obtained via fitting to the experimental data for the resonant Auger emission from SF₆. ω_{cf} , atomiclike Auger line energy; ϵ , kinetic energy release; β , anisotropy of the departing F* fragment with a core hole; and ζ , anisotropy of the atomiclike Auger emission in the molecular frame. The error estimates correspond to statistical uncertainties.

ω (eV)	Ω (eV)	ω_{cf} (eV)	ϵ (eV)	β	ζ
686.80	-1.48	656.31 \pm 0.09	3.0 \pm 1.5	1.21 \pm 0.09	0.8 \pm 0.3
687.55	-0.72	656.32 \pm 0.03	3.8 \pm 0.5	1.39 \pm 0.03	0.3 \pm 0.1
688.28	0.0	656.34 \pm 0.02	4.3 \pm 0.3	1.28 \pm 0.02	0.4 \pm 0.1
689.03	+0.75	656.35 \pm 0.03	4.8 \pm 0.5	1.35 \pm 0.02	0.3 \pm 0.1
690.78	+1.51	656.36 \pm 0.02	5.4 \pm 1.7	1.36 \pm 0.05	0.0 \pm 0.2

determined from the angular distribution of the ion current, $I_{\text{ion}} \propto [1 + \beta_{\text{ion}} P_2(\hat{e} \cdot \hat{v}_{\text{ion}})]$, recorded at $\Omega \simeq 0$ [16]. The ion angular distribution I_{ion} is more isotropic ($\beta_{\text{ion}} \simeq 0.4$) [16] than the angular distribution of the F^* fragment ($\beta \simeq 1.4$). This is because the F^+ ion detected as ion current is not necessarily the one which originally had the $1s$ hole. Note that the deviation of β from 2 implies that the velocity \mathbf{v} of the F^* fragment is not necessarily parallel to the molecular symmetry axis. This situation is different from the diatomic cases such as O_2 [12,21] and DF [14], where $\beta = 2$. In these cases, \mathbf{v} of the atomic fragment lies exactly along the molecular axis, since the rotational motion is much slower than the dissociation. In the case of polyatomic molecules such as SF_6 , however, the velocity component of the F^* fragment perpendicular to the symmetry axis can arise from the perpendicular bending motion within the valley of the dissociation path and result in the deterioration of the anisotropy of the fragment.

We now focus on the Auger anisotropy ζ in the molecular frame. The peak shape of the 90° spectrum becomes flat for positive ζ and a shallow dip appears when ζ approaches 1. One can see such changes of the peak shape when the photon energy decreases across the $F 1s \rightarrow a_{1g}^*$ resonance. Indeed the extracted value of ζ varies from 0 to 0.8 as Ω varies from +1.5 to -1.5 eV, as can be seen in Table I. How can we understand this Ω dependence of ζ ? From Table I, one finds that $v = \sqrt{2\mu\epsilon}/m_F$ increases (decreases) for positive (negative) Ω . To the 0th approximation, the displacement ΔR of the F^* fragment between the points where the photoabsorption and Auger decay take place can be approximated to $\simeq v/\Gamma$, where $\Gamma \simeq 0.1$ eV for the $F 1s$ -hole state. ΔR thus estimated are $\Delta R \simeq 0.4 \text{ \AA}$ for $\Omega = +1.5$ eV, and $\Delta R \simeq 0.2 \text{ \AA}$ for $\Omega = -1.5$ eV. Thus we can conclude that ζ decreases from 0.8 to 0 with an increase in ΔR from 0.2 to 0.4 \AA . Indeed the Auger anisotropy ζ is expected to be zero at the dissociation limit $\Delta R \rightarrow \infty$, since this anisotropic effect is purely a molecular effect due to the anisotropic molecular field.

In conclusion, we have observed the F^* atomiclike Auger line, emitted from the dissociating core-excited SF_6 molecule. This Auger line exhibits a Doppler profile that depends on the direction of observation and the photon energy. We demonstrate that the anisotropy of the Auger emission in the molecular frame can be extracted from the profile analysis of this Auger line. We find that the Auger anisotropy decreases with an increase in the internuclear distance as a natural consequence that the Auger anisotropy is a pure molecular effect.

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