Circularly Polarized X Rays: Another Probe of Ultrafast Molecular Decay Dynamics

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Dissociative nuclear motion in core-excited molecular states leads to a splitting of the fragment Auger lines: the Auger-Doppler effect. We present here for the first time experimental evidence for an Auger-Doppler effect following F1$s \rightarrow a_{1g}^*$ inner-shell excitation by circularly polarized x rays in SF_6. In spite of a uniform distribution of the dissociating S-F bonds near the polarization plane of the light, the intersection between the subpopulation of molecules selected by the core excitation with the cone of dissociation induces a strong anisotropy in the distribution of the S-F bonds that contributes to the scattering profile measured in the polarization plane.

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The origin of the enantiomeric homogeneity of nature has fascinated researchers over decades [1,2]. Considerable effort has been made to explore different types of external factors (e.g., magnetic, electric, and gravitational fields and polarized light) as a source of asymmetric induction [1]. In addition, it has also been demonstrated that site-selective bond cleavage can be achieved by using soft x rays of specific wavelengths [3]. One of the crucial steps to take when addressing the problem of asymmetric photochemistry is understanding the fundamental mechanisms involved in the interaction of matter with circularly polarized light (CPL). While conventional circular dichroism (CD), recorded as the difference in sample absorbance for left and right CPL, is widely used in structural biology [4], photoelectron circular dichroism has recently been applied to the study of a number of smaller organic chiral molecules [5]. Recent work demonstrates that in chiral species photoelectron circular dichroism is very sensitive to molecular conformation and to the chemical nature of the ligands [6,7]. However, this technique cannot be applied to achiral species because of their inherent symmetry.

Resonant photoemission or resonant Auger scattering (RAS) has been recognized as a powerful investigation tool in atomic, molecular, and chemical sciences. It is often used as a fine probe of nuclear motion in molecules [8–13]. In particular, the anisotropy caused by the dissociative nuclear motion [14] in the emission of Auger electrons from core-excited molecules leads to a splitting of the Auger lines of the ejected neutral fragments and is called, by analogy with the acoustical Doppler effect, the Auger-Doppler (AD) effect [8,15,16]. This effect has been revealed by using linearly polarized light, first in experiments performed with angular selectivity [17–19] or, more recently, with full angular resolution [20]. The experimental Doppler profiles of the fragment lines may serve as a fingerprint of nuclear dynamics [8,14] and are widely used in investigations of ultrafast dissociation processes in core-excited states [8,9,15,17–25].

In gas phase experiments, the observation of the Doppler splitting of Auger lines of atomic fragments requires preferential alignment of the dissociating chemical bond. In previous work, such an axial alignment has been obtained by using linearly polarized x rays [18,19,23–25]. These studies, performed on fluorine-containing molecules (CF_4, CH_3F, SF_6, and CF_3SF_5), have shown that, following the excitation of a F1s electron to an unoccupied antibonding molecular orbital, a bond elongation occurs preferentially along the light polarization vector **e**. This leads to the ultrafast dissociation of the molecule during the F1s core-hole lifetime [$(2\Gamma)^{-1} \approx 3.3$ fs] and the subsequent emission of an Auger electron from the core-excited fragment:

$$\omega + [A - \mathrm{F}] \underset{\text{excitation}}{\overset{\text{core}}{\rightarrow}} [A - \mathrm{F}^*(1s^{-1}\sigma^*)] \underset{\sim 3.3\ \text{fs}}{\overset{\text{dissociation}}{\rightarrow}} A + \mathrm{F}^*(1s^{-1}2p^6) \underset{\text{decay}}{\overset{\text{Auger}}{\rightarrow}} A + \mathrm{F}^+ + e^-_{\text{Auger}}. \quad (1)$$

Core excitation allows selecting the alignment of the molecular axis but not the specific orientation of the gas phase molecules. Consequently, the core-excited fragment can be ejected in two opposite directions along the polarization vector **e**, and the Doppler-split Auger lines can be observed in the direction parallel to **e**. The situation is qualitatively different in the case of CPL, because, in contrast to the axial alignment arising for linearly polarized light, the dissociating chemical bonds are then aligned in the polarization plane. The first expectation would be that AD splitting is absent in this case owing to the isotropic alignment of the dissociating bonds. In this Letter, we demonstrate that this expectation is erroneous, and we present the first observation of the Doppler splitting of Auger lines using circularly polarized x rays by detecting the Auger electrons in the light polarization plane.

The measurements have been performed on the soft x-ray beam line PLEIADES [26] at the SOLEIL synchrotron in France. The radiation source is an elliptical undulator delivering linearly or elliptically polarized light in the range 35–1000 eV. The beam line is equipped with an in-house designed high-resolution plane grating monochromator with varied line spacing and varied groove depth gratings. The resonant Auger spectra were recorded with a high-resolution VG Scienta R4000 spectrometer. The total instrumental broadening was about 73 meV, resulting from the electron spectrometer resolution of ~50 meV at 100 eV pass energy and a photon bandwidth of ~53 meV. For the normalization of the electron spectra, the acquisition time, gas pressure, and photon flux were taken into account. Spectra were recorded at the F1$s \rightarrow a^*_{1g}$ resonance ($\omega =$ 688.3 eV [18]) in SF_6 for linear horizontal (LH), linear vertical (LV), and right-handed CPL. The 99.999% pure sample was commercially obtained from Air Liquide.

When photon energy ω is tuned to the F1$s \rightarrow a^*_{1g}$ resonance, the system is promoted into a dissociative state along the S-F coordinate (σ^*). The subsequent neutral fragmentation is fast, owing to the large kinetic energy ϵ released in the dissociation process. Hence, the Auger decay may occur in the already dissociated F* atom, and narrow atomic Auger peaks can be observed at $\omega_{\rm at}$ in the RAS spectrum [see Eq. (1)] [14].

As predicted earlier [15], the "atomic" Auger line experiences the Doppler shift $\mathbf{p} \cdot \mathbf{v} = pv\cos\theta$. Here $\mathbf{p} = p\hat{\mathbf{p}}$ is the Auger electron momentum, $\mathbf{v}$ is the speed of the dissociating atom, and $\theta = \angle(\mathbf{p}, \mathbf{v})$. Both $\mathbf{v}$ and the transition dipole moment $\mathbf{d}_{1s\rightarrow\sigma^*}$ are oriented along the direction of the S-F* bond $\mathbf{n}$ ($|\mathbf{n}| = 1$). In the region of the atomic peak, the RAS cross section for fixed-in-space molecules is proportional to the absorption probability and to the probability of the Auger decay

$$\sigma(E, \omega, \mathbf{n}) = \Lambda(\mathbf{n})|Q(\theta)|^2 \frac{\Gamma}{\pi[(\Delta E - pv\cos\theta)^2 + \Gamma^2]}, \tag{2}$$

where the excitation function $\Lambda(\mathbf{n}) = |\mathbf{e} \cdot \mathbf{n}|^2$ contains the anisotropy of the core-excitation process and $\Delta E = E - \omega_{\rm at}$ is the energy of the Auger electron E relative to the atomic resonance $\omega_{\rm at}$. The probability of the Auger decay $|Q(\theta)|^2 \approx 1 + \chi P_2(\hat{\mathbf{p}} \cdot \mathbf{n})$, where χ is the Auger electron anisotropy parameter in the molecular frame and $P_2(x)$ is the 2nd-order Legendre polynomial, depends on the angle θ due to the anisotropy of the molecular orbitals involved in the Auger process. When light is linearly polarized, the atomic peak is split in two components [17] $\Delta E = \pm pv$ [see Eq. (2)] due to the preferential alignment of the core-excited molecules along the polarization vector ($\mathbf{n} \parallel \mathbf{e}$; $\cos\theta = \pm 1$).

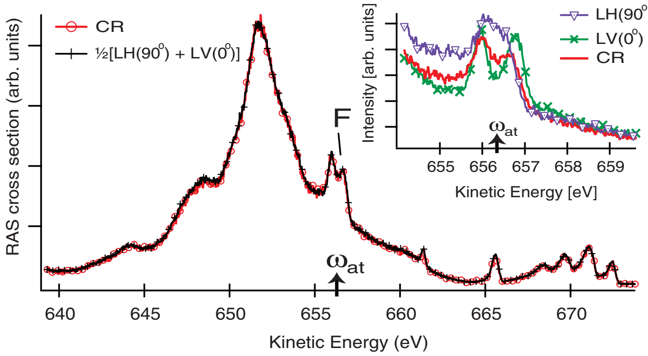

FIG. 1 (color). Comparison of the resonant Auger decay spectra recorded at the F1$s \rightarrow a^*_{1g}$ resonance in SF_6 molecule with right-handed CPL (CR, red curve), and the average of the RAS spectra recorded with linear vertical [LV (0°), $\mathbf{e} \parallel \mathbf{p}$] and horizontal [LH (90°), $\mathbf{e} \perp \mathbf{p}$] polarizations (black curve). The inset shows a blowup of the kinetic energy region of the F-atomic peak for independent measurements with LV (green), LH (purple), and CR (red) polarizations.

Let us focus now on Fig. 1 illustrating our RAS measurements. The inset in Fig. 1 displays a blowup of the kinetic energy region containing the atomic fluorine peak for the three polarization types of the x rays. Two important observations can be made: (i) In contrast to the initial expectation based on the isotropic bond alignment considerations, an AD splitting can be clearly identified when using circularly polarized x rays (Fig. 1, inset); (ii) the kinetic energy distribution of the Auger electrons produced when using CPL is identical to the average of the Auger kinetic energy distributions recorded by using two perpendicular linear polarizations (horizontal and vertical). The latter is a direct consequence of the polarization dependence of the excitation function $\Lambda(\mathbf{n})$ in Eq. (2). Indeed, when averaging $\Lambda(\mathbf{n})$ for all possible orientations of the molecular axis $\mathbf{n}$ with a fixed angle θ with respect to $\mathbf{p}$, it can be shown that the excitation function $\Lambda(\mathbf{n})$ can be written as a function of θ as follows:

$$\Lambda(\theta) = \overline{\Lambda(\mathbf{n})} = \frac{1}{3}[1 + \beta P_2(\hat{\mathbf{p}} \cdot \mathbf{n}) P_2(|\hat{\mathbf{p}} \cdot \mathbf{e}|)]$$
$$= \frac{1}{3}\begin{cases} 1 + \beta P_2(\cos\theta), & \mathbf{p} \parallel \mathbf{e}, \\ 1 - \frac{\beta}{2} P_2(\cos\theta), & \mathbf{p} \perp \mathbf{e}, \\ 1 + \frac{\beta}{4} P_2(\cos\theta), & \mathrm{circ}(\mathbf{p} \subset \mathbf{e}), \end{cases} \tag{3}$$

where β is the fragment asymmetry parameter. This equation clearly explains the fact that the two curves in Fig. 1 may be superimposed.

The reason for the initially unexpected observation of the AD splitting (Fig. 1, inset), when using CPL characterized by a polarization vector $\mathbf{e} = (\mathbf{e}_\parallel + \imath\mathbf{e}_\perp)/\sqrt{2}$, is the following. In our experiment, the electrons are detected at 90° with respect to the light propagation axis; i.e., $\mathbf{p}$ is lying in the polarization plane. Let us chose $\mathbf{e}_\parallel$ along $\mathbf{p}$ [Fig. 2(a)]. In contrast to the linear polarization case, core excitation by CPL does not induce an axial selection of the molecular orientations. Indeed, the spatial distribution of the S-F* bond's directions $\mathbf{n}$, characterized by the excitation function $\Lambda(\mathbf{n})$, is uniform near the polarization plane, and

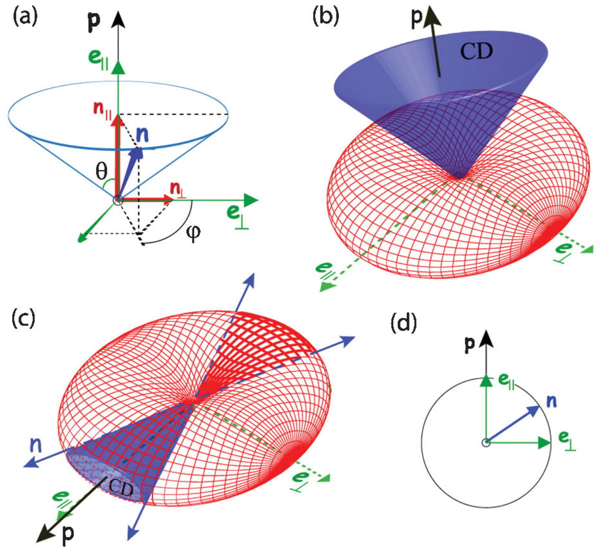

FIG. 2 (color). Schematics of the experiment showing possible orientations of the Auger electron momentum $\mathbf{p}$ and dissociation direction $\mathbf{n}$ with respect to the polarization plane $(\mathbf{e}_\parallel, \mathbf{e}_\perp)$. (a) Auger electron ejection in the polarization plane. Here $\mathbf{n}_\parallel, \mathbf{n}_\perp$ are the projections of the dissociation direction $\mathbf{n}$ on the plane of polarization. (b) Auger electron ejection perpendicular to the polarization plane. (c) The intersection of the excitation torus with the cone of dissociation selects the molecules active in the RAS process. (d) The excitation function is isotropic when $\mathbf{n}$ is lying in the $(\mathbf{e}_\parallel, \mathbf{e}_\perp)$ plane ($\varphi = 0°$).

it describes a torus as shown in Figs. 2(b) and 2(c). Such a uniform distribution suggests the absence of AD splitting in the case of CPL excitation. This naïve expectation is true only when the Auger electrons are ejected perpendicular to the polarization plane [Fig. 2(b)] or when the dissociation axis is lying exactly in the polarization plane [Fig. 2(d)], but it is not true in other cases.

According to Eq. (2) the RAS profile is formed by the dissociating fluorine atoms moving mainly along the unit vector $\mathbf{n}$ on the cone of dissociation [15] [see Fig. 2(c)]:

$$\cos\theta = \frac{\Delta E}{pv}, \qquad \mathbf{v} \parallel \mathbf{n}. \tag{4}$$

This anomalous "final state" anisotropy selects from the core-excited molecules only those that have a S-F* bond lying on the cone of dissociation and breaks the uniformity of the $\mathbf{n}$ distribution of the molecules participating in the RAS process. Therefore, when the opening angle of the cone of dissociation is tight enough, Doppler splitting can be expected as a consequence of the detection of the electrons with their momentum $\mathbf{p}$ along the dissociation axis. At first glance, it may seem that the AD splitting should be strongest when the S-F* bonds are lying exactly in the polarization plane of the CPL [Fig. 2(d)]. However, as demonstrated below, no AD splitting can be observed in this case. Moreover, the deviation of the dissociation direction $\mathbf{n}$ from the plane of polarization is shown to play a crucial role for the formation of the AD-split profile.

To quantitatively describe the AD effect for $\mathbf{p} \subset (\mathbf{e}_\parallel, \mathbf{e}_\perp)$, let us point out that the excitation function $\Lambda(\mathbf{n})$ [Eq. (3)] is the half sum of the excitation functions for parallel and orthogonal linearly polarized x rays with respect to $\mathbf{p}$: $\Lambda(\mathbf{n}) = \frac{1}{2}[(\mathbf{e}_\parallel \cdot \mathbf{n})^2 + (\mathbf{e}_\perp \cdot \mathbf{n})^2] = \frac{1}{2} \times (n_\parallel^2 + n_\perp^2)$. The parallel and perpendicular components of the CPL give qualitatively different contributions to the RAS process: The excitation function for the parallel polarization ($n_\parallel^2 = \cos^2\theta$) has a minimum at $\theta = \pi/2$ and hence causes the observation of AD splitting, contrary to the orthogonal case ($n_\perp^2 = \sin^2\theta\cos^2\varphi$). Surprisingly, the sum of these two contributions is anisotropic, in general:

$$\Lambda(\mathbf{n}) = \tfrac{1}{2}[\cos^2\theta + \sin^2\theta\cos^2\varphi] = \tfrac{1}{2}[1 - \sin^2\theta\sin^2\varphi]. \tag{5}$$

This function is isotropic (no AD splitting) only when the dissociating S-F* bond is lying in the polarization plane [Fig. 2(d)]: $\Lambda(\mathbf{n}) = 1/2$, $\varphi = 0$. However, when the dissociation direction lies in the orthogonal plane ($\varphi = \pi/2$), the orthogonal component contribution vanishes, and the excitation function becomes anisotropic: $\Lambda(\mathbf{n}) = (1/2)\cos^2\theta$ [Fig. 2(a)]. Averaging over φ leads to an intermediate result $[\Lambda(\theta) = \overline{\Lambda(\mathbf{n})} = [1 + \cos^2\theta]/4]$ between the two cases above ($\varphi = 0$ and $\varphi = \pi/2$), where the minimum near $\theta = \pi/2$, responsible for the observed AD splitting, is preserved. Therefore, the physical reason of the observed AD splitting, in the case of CPL, is the contribution from molecules with the dissociating bonds tilted with respect to the CPL polarization plane ($\varphi \neq 0$).

The RAS cross section (Fig. 3) for randomly oriented molecules $\sigma(E, \omega) = \frac{1}{2}\int_0^\pi \overline{\sigma(E, \omega, \mathbf{n})} \sin\theta d\theta$ has been calculated by using the following parameters [18]: $\beta = 1.4$, $\chi \approx 0.4$, and $\epsilon = 3.8$ eV for $\omega = 688.3$ eV. Here $\overline{\sigma(E, \omega, \mathbf{n})}$ is given by Eq. (2), where $\Lambda(\mathbf{n}) \rightarrow \Lambda(\theta)$. The simulations confirm the experiment and show that contrary to intuition the interaction with CPL results in AD splitting of the atomic peak (Figs. 1, 3). Moreover, the RAS profile for CPL can be reconstructed as the average of the RAS profiles (normalized per incident photon flux) for orthogonal linear polarizations with $\mathbf{p} \parallel \mathbf{e}$ and $\mathbf{p} \perp \mathbf{e}$:

$$\sigma(E, \omega) = \tfrac{1}{2}[\sigma_\parallel(E, \omega) + \sigma_\perp(E, \omega)] \tag{6}$$

in agreement with Eq. (3).

Let us discuss below the potential implications of this work starting from the apparent question of whether CD can be observed or not in the AD profiles. The current experiment would give the same result for left- and right-handed CPL. In order to observe CD, the present experimental scheme of the AD measurements has to be modified. The theory of CD in the Auger-Doppler effect, described in detail elsewhere [27], allows us to propose the following experimental arrangements where the measured AD profiles display CD even for achiral molecules. (i) The first scheme is the measurement of the AD

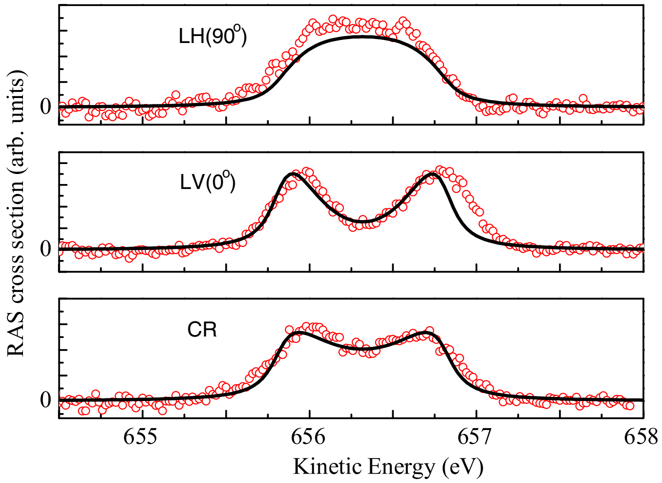

FIG. 3 (color online). Doppler splitting of the atomic Auger peak following core excitation of the SF_6 molecule. The theoretical cross sections (black curves) are shifted in energy to match the experimental spectra; linear polarization LH ($\mathbf{e} \perp \mathbf{p}$), linear polarization LV ($\mathbf{e} \parallel \mathbf{p}$), right-handed circular polarization CR. Baselines are subtracted.

splitting for a class of dissociative core-excited states (e.g., $2p_{1/2} \rightarrow \sigma^*$) in fixed-in-space molecules [16] by a coincidence technique used recently to probe the AD effect in CH_3Cl molecules excited by linearly polarized light [20]. In this scheme the AD profile depends on the chiral contribution $\mathbf{s}_{\mathrm{ph}} \cdot [\mathbf{p} \times \mathbf{n}]$, which changes its sign when the photon's spin $\mathbf{s}_{\mathrm{ph}} = [\mathbf{e}_{\parallel} \times \mathbf{e}_{\perp}]$ is inverted. (ii) Detection of the spin $\mathbf{s}$ of the Auger electrons [28] for the same type of dissociative core-excited states displays sensitivity to the handedness of the CPL even for randomly oriented molecules. Because of contributions such as $(\mathbf{s}_{\mathrm{ph}} \cdot \mathbf{p})(\mathbf{s} \cdot \mathbf{n})$ and $(\mathbf{s}_{\mathrm{ph}} \cdot \mathbf{s})(\mathbf{p} \cdot \mathbf{n})$, the relative intensity of the two components of the AD-split profile is inverted for left- and right-handed CPL. (iii) The third scheme is based on core excitation above the ionization threshold near a shape resonance. The coincident detection of the photoelectron of momentum $\mathbf{k}$ and of the corresponding Auger electron [29] will also allow us to display CD in the RAS profile due to the $(\mathbf{k} \cdot \mathbf{n})(\mathbf{k} \cdot [\mathbf{s}_{\mathrm{ph}} \times \mathbf{n}])$ term in the cross section that is sensitive to the handedness of the CPL. In this latter scheme, the magnitude of the CD gives insight into the photoionization dynamics itself, since it is related to the scattering phase difference of the σ and π photoelectron waves near the shape resonance [27].

In conclusion, we have observed for the first time by using circularly polarized x rays the Doppler splitting of the atomic Auger lines in core-excited SF_6. This effect is explained by the orientational selectivity of the excitation process in the polarization plane of the CPL. The required anisotropy in the distribution of the S-F* bonds is due to the intersection between the uniform excitation probability and the strongly anisotropic cone of dissociation associated to the Doppler effect. Theoretical modeling indicates that the deviation of the dissociation direction from the plane of polarization of the CPL plays a fundamental role in the formation of the Doppler-split profile of the atomic fragment Auger lines. We suggest several experimental arrangements allowing us to detect CD in the AD profiles observed for achiral species. The magnitude of this CD effect is expected to be about 2 orders of magnitude larger than the one of natural CD for chiral species. It will be a challenge for future experiments to demonstrate the use of CD in AD profiles as an efficient probe of the photoionization dynamics, as well as of the molecular structure and chemical environment in achiral species.

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