

Ultrafast Dissociation of Molecular Core-excited States by High-Resolution Auger Electron Spectroscopy

Soft X-ray absorption spectra of many kinds of molecules show rich structure in the pre-edge region, due to excitation of core electrons to unoccupied molecular orbitals. The core hole decays predominantly with Auger emission. Recent studies of high-resolution resonant Auger electron spectroscopy have shown that the nuclear motion of the molecular core-excited states is promoted in competition with the Auger decay [1]. The typical time scale of this competition is $< 10^{-14}$ s. Gel'mukhanov and coworkers predicted that the Doppler effect in resonant photoemission may occur, when the resonant Auger spectrum from the decay of repulsive core-excited states reflects both the molecular decay and that from excited dissociation fragments [2]. Doppler-type line shift is the energy-split atomic fragment emission lines arising from dissociation on a time scale comparable to the core-hole lifetime, which is of the order of 3 fs, i.e., ultrafast dissociation. The existence of Doppler-type line shift due to the ultrafast dissociation of core-excited molecules has been reported for small molecules such as DF, O₂, O₃, and CF₄ [3]. Here, we report on an extensive study of the Doppler-type line shift observed in the F 1s resonant Auger spectra from SF₆ molecules [4].

Figure 1 shows a schematic diagram of the Doppler effect observed in the resonant Auger emission. If the dissociation is highly anisotropic and occurs along the polarization vector of the light, and if the electron emission is observed along this direction, then the Auger line of the departing atomic fragment can Doppler split. The Doppler splitting disappears when the electron emission is observed in the direction perpendicular to the polarization vector. Precise analysis of Doppler-type line shift can provide information on anisotropy of the dissociation (β), dissociation energy (DE), Auger electron energy (KE), and anisotropy of the atomic-like Auger emission in the molecular frame (ζ).

Measurements have been carried out on the c-branch of beamline BL27SU. The figure-8 undulator at BL27SU provides linearly polarized radiation either in the plane of the storage ring or in the plane perpendicular to it. 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

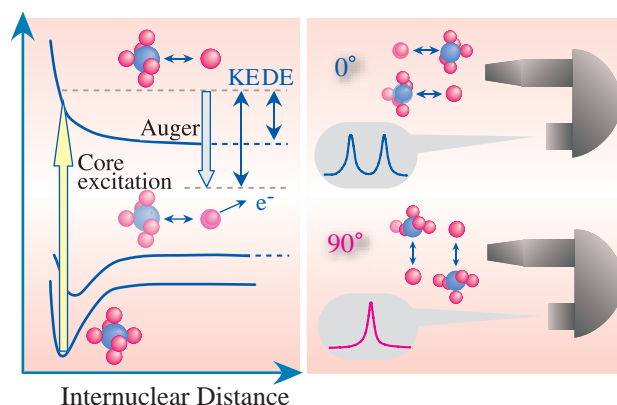


Fig. 1. Schematic representation of the formation of “atomic” contributions to the Auger spectrum and Doppler-type line shift of the “atomic” Auger lines following the dissociation of core-excited molecules. Doppler-type line shift results in a splitting of the peak when the electron emission is observed in the direction perpendicular to the dissociation, i.e. $\theta = 0^\circ$. The Doppler splitting disappears when the electron emission is observed in the direction perpendicular to the dissociation, i.e. $\theta = 90^\circ$.

SES-2002), a gas cell, and a differentially pumped chamber. The overall resolution used in the present measurements is 150 meV.

Figure 2 shows electron-emission spectra of SF₆ at 14 different photon energies across the F 1s \rightarrow a_{1g} resonance at ≈ 688 eV and F 1s \rightarrow t_{1u} resonance at ≈ 694 eV, as indicated by arrows in the right panel, where the total ion yield spectrum is displayed. The spectra are recorded for electron emission in the direction parallel and perpendicular to the polarization vector of the incident light. The kinetic energy of the valence photoelectron bands, labeled by X, A, B, C to F, increases with an increase in the photon energy. The non-dispersive spectral feature indicated by the dotted circle, on the other hand, exhibits a splitting, characteristic of the Doppler effect, in the 0° spectrum. The kinetic energy of this band, 656.3 eV, is very close to the energy of the Auger line, 656.5 eV, of the atomic fluorine fragment. This shows the existence of ultrafast dissociation of the F 1s \rightarrow a_{1g} core-excited state of SF₆.

In order to analyze Doppler-type line shift, a fitting based on the model of Gel'mukhanov *et al.* [2] has been employed. The results of the fit are shown in Fig. 3 by solid curves together with the experimental results. Parameters extracted from the fit are the energy for the center of the atomic-like Auger line, KE,

dissociation energy, DE, the anisotropy parameter β of the F fragment relative to the polarization vector, and the anisotropy parameter ζ for the Auger emission in the molecular frame. Fitting results show that dissociation energy of the core-excited F fragment (DE) increases with increasing the excitation photon energy ($h\nu$). However, the increase in DE is only about half of that of $h\nu$. Therefore, dissociation counterpart, SF₅, is considered to be highly vibrational excited after the ultrafast dissociation. The most interesting finding is that Auger anisotropy ζ decreases with increasing photon energy. The displacement of the F*, $\Delta R \equiv v/\Gamma$, with v and Γ being the velocity of the F* and the decay width of the F*, increases with increasing in $h\nu$. Thus ζ decreases with increasing in ΔR . This shows that the anisotropic effect is a purely molecular effect due to the anisotropic molecular field.

We have shown that ultra-high-resolution measurement of the resonant Auger spectra provides a unique possibility for studying details of the nuclear dynamics as well as Auger dynamics. Further systematic studies are now in progress.

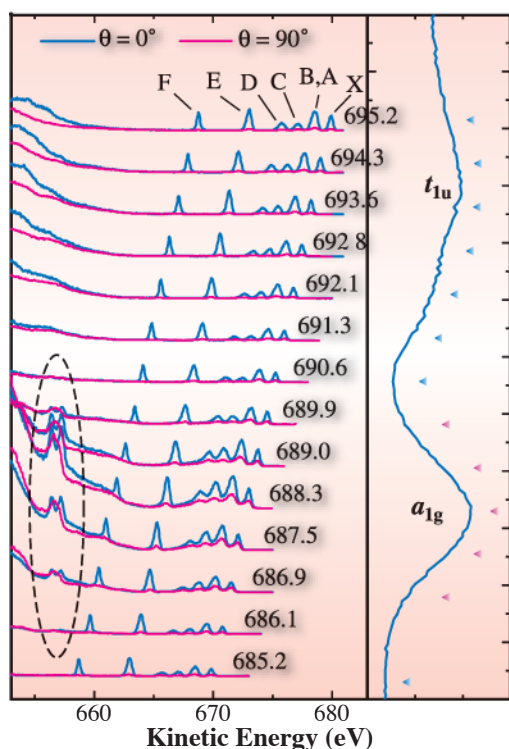


Fig. 2. Electron spectra of SF₆ recorded for parallel and perpendicular polarizations. The measurements are carried out at 14 different photon energies across the F 1s → a_{1g} and F 1s → t_{1u} resonances, as indicated by the arrows in the right panel, where the total ion yield spectrum is displayed.

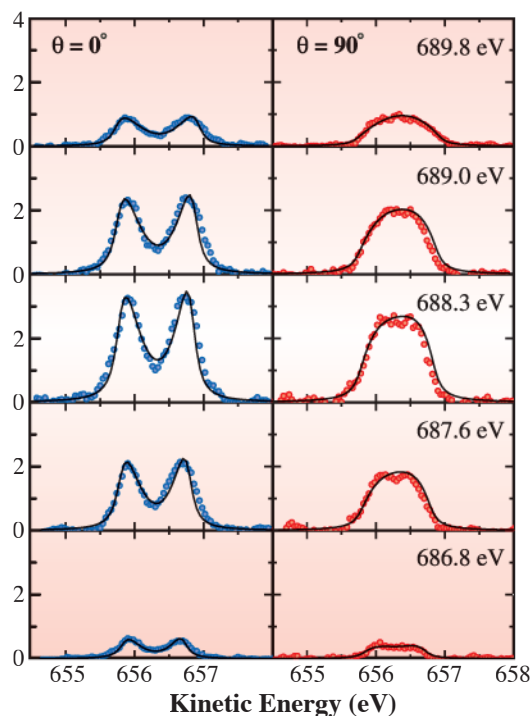


Fig. 3. Experimental and fitted curves for Doppler split peak observed in the Auger spectra obtained at SF₆ → F 1s⁻¹ a_{1g} resonance. Baselines are subtracted.

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References

- [1] K. Ueda: J. Phys. B **36** (2003) R1, and references cited therein.
- [2] F. Gel'mukhanov *et al.*: Phys. Rev. A **57** (1998) 2511.
- [3] O. Björneholm *et al.*: Phys. Rev. Lett. **84** (2000) 2826; L. Rosenqvist *et al.*: J. Chem. Phys. **115** (2001) 3614; K. Wiesner *et al.*: Chem. Phys. Lett. **354** (2002) 382; K. Ueda *et al.*: Phys. Rev. Lett. **90** (2003) 233006.
- [4] M. Kitajima *et al.*: Phys. Rev. Lett. **91** (2003) 213003.