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Anisotropic Ultrafast Dissociation Probed by the Doppler Effect in Resonant Photoemission from CF_4

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The resonant Auger spectrum from the decay of F $1s$-excited CF_4 is measured. Several lines exhibit a nondispersive kinetic energy as the exciting photon energy is tuned through the resonance region. The F $1s^{-1}$ atomiclike Auger line is split into two components due to the emission of Auger electrons by a fragment in motion, when electron emission is observed along the polarization vector of the light. This Doppler splitting is direct evidence that the core excitation leads to $T_d \rightarrow C_{3v}$ symmetry lowering, by elongation of a specific C—F bond preferentially aligned along the polarization vector of the incident photon.

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Resonant excitation of core electrons in molecules provides a unique opportunity to study the interplay between Auger decay and nuclear motion of the molecule. The core hole relaxes via Auger electron emission within the core-hole lifetime of the order of 10^{-15} sec. Within this time scale, the nuclear motion of the molecule can proceed. Some 15 years ago, Morin and Nenner observed electron emission from the core-excited Br atom in the resonant Auger electron spectrum of the HBr molecule following Br $3d \rightarrow \sigma^*$ excitation [1]. Since this pioneering work, ultrafast dissociation followed by the Auger decay of the fragment has been observed for various molecules (see, for example, Refs. [2–6] and references therein for earlier publications). This body of work confirms that molecular Auger features coexist with atomiclike Auger lines, and that such electron spectra provide a unique possibility to study the details of nuclear dynamics in core-excited molecular states [7–9]. One particularly interesting aspect is the observation of the Doppler effects in the fragment spectra. The existence of the energy split of the atomiclike Auger line due to the Doppler effect depends upon a well-defined angular dependence of the dissociation on the polarization vector of the incident light. If electron emission is observed along this direction, then the Auger line of the departing atomic fragment can be energy split according to the forward-backward velocity components of the fragment at the instant of Auger emission [10]. This Doppler splitting was first observed for O_2 [11] and more recently for O_3 [12] and DF [13].

For polyatomic molecules, this tool is of great interest as a way to monitor the development of the fragmentation process. The geometry of the core-excited state is often different from that of the ground state, and thus core excitation effectively initiates nuclear motion. This nuclear motion breaks the symmetry of the molecule, affecting subsequent electronic decay and ionic fragmentation processes [14–17]. A particularly interesting case is core excitation of equivalent atoms in a symmetric molecule. In this case, a coupling between the electron and the asymmetric nuclear motion causes pseudo—Jahn-Teller mixing between the nearly degenerate core-excited states, and thus the molecular symmetry is lowered. A well-documented example is the O $1s$ ionization of the CO_2 molecule [18–20]. When one O $1s$ electron is ionized, the potentials at the oxygen atoms are no longer identical, and the molecule relaxes to a new geometry where the C—O bond lengths differ. This mechanism excites the antisymmetric stretching vibrational mode.

In the present Letter, we discuss symmetry lowering of the highly symmetric spherical top molecule CF_4 that belongs to the T_d point group, to the C_{3v} symmetrical top, caused by the F $1s$ excitation. Previously, anisotropic angular distributions of F^+ fragment ions were measured for the F $1s$ excitation of CF_4, as well as of SiF_4 and SF_6, and interpreted as due to preferential bond rupture at the F $1s$ core-hole site [21–23]. Although these cases are convincing, fragmentation cannot be connected unequivocally with nuclear motion of the intermediate core-excited state, since the fragmentation can very likely arise from the Auger-final electronic state. In the present work, we have observed the Doppler splitting of the F $1s^{-1}$ atomiclike Auger line. Since the shift arises from nuclear motion before Auger decay takes place and fragmentation is initiated on the excited-state potential energy surface, this phenomenon constitutes direct proof that the asymmetric nuclear motion proceeds in the F $1s$-excited state, along the direction of the polarization vector of the incident light, leading to symmetry lowering from T_d to C_{3v}.

Measurements have been carried out on the *c* branch of the soft x-ray photochemistry beam line 27SU at SPring-8 [24,25]. The radiation source is a figure-8 undulator, whose emitted radiation is linearly polarized either in the plane of the storage ring (first order) or in the plane perpendicular to it (0.5th order) [26]. Angle-resolved electron-emission measurements are performed by changing the undulator gap without rotating the electron analyzer. The electron spectroscopy apparatus (Gammadata Scienta AB) consists of a hemispherical electron analyzer (SES-2002) fitted to a gas cell (GC-50) via a multielement lens in a differentially pumped chamber [27]. The overall resolution used in these measurements is 150 meV. The yield spectra $I(0°)$ and $I(90°)$ of the fragment ions ejected with kinetic energies ≥ 6 eV in the directions 0° and 90° relative to the axis of polarization vector of the incident light are measured using two identical retarding-potential ion detectors [28]. The total ion yield spectrum is simultaneously measured using another ion detector [28]. The degree of linear polarization for the incident light is $P_{\text{lin}} > 0.97$. The incident photon energy bandwidth is <0.1 eV at 700 eV.

In Fig. 1, we present the angle-resolved energetic-ion yield spectra $I(0°)$ and $I(90°)$ of CF_4 (middle panel), as well as the total ion yield spectrum (top panel) near the F $1s$ ionization threshold. Values of the photo-ion anisotropy parameter β obtained from $I(0°)$ and $I(90°)$ are also plotted in Fig. 1 (bottom panel). The results are in agreement with earlier measurements [22], although the resolution and statistics are superior. The largest anisotropy of $\beta \sim 0.36$ is around the weak shoulder structure A at $\sim$690 eV. We measure the Auger decay spectra after excitation in the energy region close to this feature.

Figure 2 contains a series of electron-emission spectra from the decay of core-excited states with energies close to 690 eV. The measurements were made at eight different photon energies indicated by arrows in Fig. 1, at angles both parallel and perpendicular to the polarization vector of the incident light. The spectral feature P disperses linearly in kinetic energy according to the Stokes-Raman dispersion law as the photon energy is tuned through the state; this feature corresponds to the D $^2A_1$ photoelectron band. The broader features S1 and S2 corresponding to the spectator Auger decay appear at fixed kinetic energies of about 654 and 658 eV. This nondispersive behavior stems from transitions between potential energy surfaces which are locally parallel. The spectral feature F at 656.2 ± 0.2 eV also remains at the same kinetic energy in all spectra. The kinetic energy of this peak is very close to that of the F atomic Auger line, 656.5 eV for the $1s2p^6\,{}^2S \rightarrow 2p^4\,{}^1D$ transition [29]. Looking more closely at peak F, we find that the spectra measured around 690 eV show a double peak structure at 0°. This behavior is indicative of the Doppler splitting measured previously in O_2 [11], O_3 [12], and DF [13]. If the dissociation of the molecule occurs on a time scale comparable to the Auger decay and takes place preferentially along the polarization vector of the light [10], then electron emission can be observed with Doppler shifts due to the motion of the fragment that emits the electron. The Doppler shift of the electron kinetic energy for the fragments propagating in opposite directions has the opposite sign. The double peak structure in the 0° spectrum corresponds to this Doppler splitting. When dissociation takes place preferentially in the axis perpendicular to the observer, the direction of the dissociation is symmetric with respect to the measurement direction. Thus, the Auger electron emitted from the departing fragment results in a single peak structure as seen in the 90° spectrum.

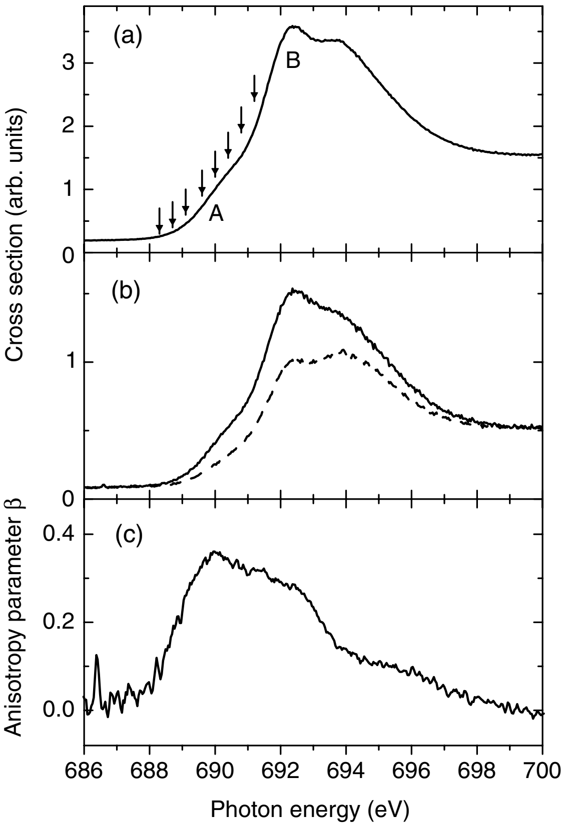

FIG. 1. (a) Total ion yield spectrum in the F $1s$ excitation region of the CF_4 molecule. (b) Yield spectra of energetic ions measured in the directions parallel and perpendicular to the polarization vector of the light (solid and dashed line, respectively). (c) Photo-ion anisotropy parameter β extracted from the angle-resolved spectra. The photon energies used in the Auger decay study are indicated by arrows on the total ion yield spectrum.

We now discuss the origin of the preferential dissociation along the polarization vector. To do it, we start with the symmetry-adapted molecular orbital picture [18,21].

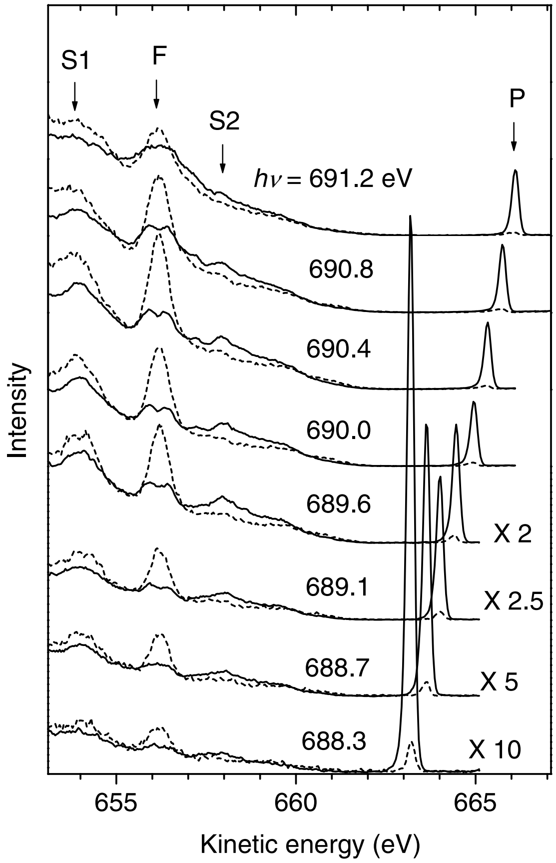

FIG. 2. Angle-resolved electron spectra recorded across the F $1s \rightarrow a_1^*$ resonance for eight different photon energies indicated by arrows in Fig. 1. The dotted line is the measurement with the electron spectrometer lens mounted perpendicular to the polarization vector of the incident light, and the solid line is the in-plane measurement.

Then the F $1s$ shell forms symmetry-adapted t_2 and a_1 molecular orbitals in CF_4. The dipole-allowed transitions from F $1sa_1$ lead to t_2^*, whereas those from F $1st_2$ lead to both a_1^* and t_2^*. In analogy with the case of SiF_4 [23], the main peak B in Fig. 1 may correspond primarily to the F $1sa_1, t_2 \rightarrow t_2^*$ excitation, whereas the weak feature A is assigned to the F $1st_2 \rightarrow a_1^*$ excitation. Introducing the molecular frame axis z that coincides with one of the four F-C axes and the x axis in such a way that one of the other three F atoms lies in the x-z plane, we can label the F atom on the z axis $F^{(1)}$, one on the x-z plane $F^{(2)}$, and the other two $F^{(3)}$ and $F^{(4)}$. Using the localized-hole wave functions $\Phi_i \equiv F^{(i)} 1s^{-1} a_1^*$ as a basis set, we can express symmetry-adapted wave functions of the core-excited states F $1sa_1^{-1}a_1^*A_1^*$ and F $1st_2^{-1}a_1^*T_2^*$ in the following manner:

$$A_1^* = \tfrac{1}{2}(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4), \tag{1}$$

$$T_2^*(x) = \frac{1}{\sqrt{6}}(2\Phi_2 - \Phi_3 - \Phi_4), \tag{2}$$

$$T_2^*(y) = \frac{1}{\sqrt{2}}(\Phi_3 - \Phi_4), \tag{3}$$

$$T_2^*(z) = \frac{1}{\sqrt{12}}(3\Phi_1 - \Phi_2 - \Phi_3 - \Phi_4). \tag{4}$$

Photoabsorption from the A_1 ground state to the three degenerate T_2^* states is allowed, while the transition to A_1^* is dipole forbidden.

We can take the axis of the F^+ ion ejection to be the $F^{(1)}$-C axis (i.e., z axis) without loss of generalization. The ion detectors in the angle-resolved ion yield measurement are mounted parallel (0°) and perpendicular (90°) to the polarization vector of the light. The F^+ detection at 0° corresponds to the events in which the $F^{(1)}$-C axis (z axis) coincides with the polarization vector of the incident light. In this case, referring to Eq. (4), we find that there is a large possibility that the $F^{(1)}$ has a F $1s$ hole. On the other hand, the F^+ detection at 90° corresponds to the events in which the $F^{(1)}$-C axis (z axis) is perpendicular to the polarization vector. Then, referring to Eqs. (2) and (3), we find that there is no possibility that $F^{(1)}$ has a F $1s$ hole. Thus, the positive value of $\beta \simeq 0.36$ at the feature A in Fig. 1 is attributed to the preferential rupture of the F—C bond along the axis where the F core hole is situated [21–23]. It should, however, be noted that, even if asymmetric nuclear motion does not occur in the core-excited state, Auger decay can transfer the alignment to the Auger-final state (see, for example, [30]), where asymmetric nuclear motion in the Auger-final state may result in anisotropic ionic fragmentation. The ion yield measurement cannot distinguish symmetry breaking in the core-excited state from that in the Auger-final state. The observation of the Auger emission of the atomiclike F^* fragment and its Doppler splitting in the 0° spectrum is, on the other hand, direct evidence that the asymmetric nuclear motion proceeds in the F $1s$-excited state, preferentially along the direction of the polarization vector, leading to the symmetry lowering from T_d to C_{3v}.

We now discuss how this asymmetric nuclear motion is caused. The F $1s^{-1}a_1^*$ core-excited states consist of nearly degenerate A_1^* and T_2^* states. A coupling between the electron motion and the asymmetric nuclear motion causes pseudo–Jahn-Teller mixing between these A_1^* and T_2^* core-excited states, in addition to the Jahn-Teller mixing within T_2^*. When one C—F bond is elongated, the molecule belongs to the C_{3v} point group. The T_2^* state splits into the A_1^* and E^* components. The A_1^* couples with the other A_1^* which originates from A_1^* in the symmetric CF_4 geometry. As a result of these couplings, one of the A_1^* potential energy curves is expected to be strongly repulsive along the asymmetric stretching coordinate. We suggest that this mechanism leads to fast fragmentation along one C—F axis and results in Auger electron emission from the departing fragment. Note the similarity of these multistate vibronic couplings and the resulting diabatic potential energy surfaces to those for the C 1s core-excited states of CF_4 discussed in Ref. [14], although the core-excited states are different.

Following the discussion by Wiesner *et al.* on the HF molecule [13], we can estimate the kinetic energy release, using a so-called Born-Haber cycle, where the energies involved in the process are added up according to energy conservation. The asymptotic kinetic energy of the F fragment in the $1s^1 2p^6\,{}^2S$ core-excited state thus estimated is ~8 eV. On the basis of the Doppler splitting, the average kinetic energy of the F fragments is estimated to be only ~5 eV. Thus, the fragments are not fully accelerated when the Auger decay takes place. This is in contrast to what is seen in HF, where it appears that the fragments are fully accelerated, and suggests that the residual energy is kept in the fragment CF_3 in the form of the vibrational energy.

In conclusion, a split of the F $1s^{-1}$ atomiclike Auger line due to Doppler effects was observed in the resonant Auger electron spectra of highly symmetric CF_4 molecules, when the photon energy was tuned to the F $1s \rightarrow a_1^*$ resonance and electron emission was observed along the polarization vector of the light. Strongly anisotropic dissociation thus probed is direct evidence that the asymmetric nuclear motion proceeds in the F 1s-excited state, preferentially along the direction of the polarization vector, leading to the symmetry lowering from T_d to C_{3v}. Detailed discussion about the anisotropy of the Auger emission and analysis of the Doppler profile will be given in a separate paper.

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