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Direct observation of correlation between electron emission and fragmentation into ions following B 1s excitation of the BF_3 molecule

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An alternative technique of coincidence between energy-selected electrons and mass- and energy-selected photoions, combined with angle-resolved photoion spectroscopy, has been applied to investigate the state-selected dissociation dynamics of the B 1s core-excited BF_3 molecule. Dissociation from the spectator Auger final states both above and below the double-ionization threshold produces energetic B^+ in the secondary processes of stepwise dissociation after the molecular deformation ($D_{3h} \rightarrow C_{3v}$), in marked contrast to dissociation following B 1s ionization in which energetic F^+ is ejected within the D_{3h} plane of the parent BF_3 molecule.

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An extensive study of molecular dissociation following core excitation has been carried out over the past ten years (see, e.g., Refs. [1–4]), stimulated by the continuing development of experimental techniques using synchrotron radiation and its potential applications to the synthesis of new materials. In the present work, we demonstrate that an alternative technique of coincidence between energy-selected electrons and mass- and energy-selected photoions, combined with conventional angle-resolved photoion spectroscopy [5,6], provides unique information about state-selected dissociation dynamics of core-excited molecules. For that purpose we have chosen B 1s core-excited BF_3, but we point out that we expect this method to have general application to any small polyatomic molecules. Furthermore, we emphasize that the information presented in this paper could not be obtained by the well-established (resonance-) Auger-electron–photoion coincidence (RAEPICO and AEPICO) [3] and photoelectron-photoion-photoion coincidence (PEPIPICO).

Figure 1 schematically illustrates B 1s photoexcitation of BF_3 and its subsequent electronic decay. The BF_3 molecule is a planar D_{3h} symmetry molecule in its ground state. The absorption spectrum in the B 1s excitation region (see the equivalent total ion-yield spectrum in Fig. 1) shows two resonance features, $2a_2''$ below the B 1s threshold and $4e'$ above the threshold [8]. The electronic decay following B $1s \rightarrow 2a_2''$ excitation consists of the spectator resonance Auger decay and the participant resonance Auger decay [9,10] (see the electron spectrum in Fig. 1), while the electronic decay following B $1s \rightarrow 4e'$ excitation is the normal Auger decay.

The dissociation pathways from the (resonance-) Auger final states have been investigated [3] using the RAEPICO and AEPICO methods. Even though the energy of the spectator Auger final states probed by the RAEPICO method coincides with the energy of the normal Auger final states probed by the AEPICO method, the RAEPICO spectra were completely different from the AEPICO spectra: B^+ is dominant and BF^+ is negligible in the RAEPICO spectra while F^+ is dominant and BF^+ is as significant as B^+ in the AEPICO spectra. This suggests that, when the B 1s electron is excited to the unoccupied $2a_2''$ orbital, partial dissociation or deformation of the parent molecule occurs before the formation of the doubly charged ion ${BF_3}^{2+}$. Simon *et al.* [7] carried out a PEPIPICO measurement for B 1s core-excited BF_3 and found that the momentum of B^+ is smaller than that of F^+ in the B^+-F^+ ion-pair formation following B 1s ionization and vice versa following B $1s \rightarrow 2a_2''$ excitation: They ascribed this to the difference between the D_{3h} plane geometry for the B $1s^{-1}$ core-ionized state and the C_{3v} pyramidal geometry for the B $1s^{-1}$ $2a_2''$ core-excited state, with the help of *ab initio* self-consistent-field (SCF) calculations (see Fig. 1).

Though the above study showed the importance of the core-excited-state geometry in the dissociation dynamics, the role of the *intermediate* state (the resonance-Auger final state as an initial state of dissociation; see Fig. 1) has not been fully investigated. In the present work, we performed the coincidence experiment between energy-analyzed resonance-Auger electrons and energy-analyzed photoions, and in this way obtained information about intermediate-state-selected dissociation dynamics. Furthermore, we carried out angle-resolved photoion spectroscopy in order to investigate the correlation between the ejection direction of the energetic fragments and the orientation of the molecule created by the photoexcitation or photoionization.

The experiment was carried out using the 24-m spherical grating monochromator [11] on the BL-3B beamline at the Photon Factory. The monochromator bandpass was set to 0.5 eV full width at half maximum (FWHM) at ~200-eV photon

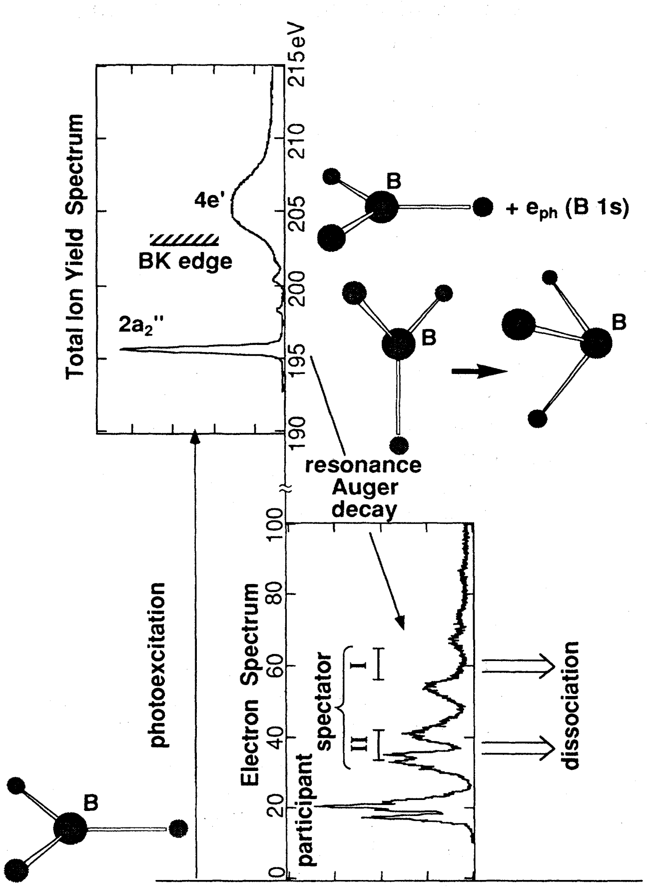

FIG. 1. Schematic illustration of B 1*s* photoexcitation of the BF_3 molecule and subsequent electronic decay. Energy-selected photoions are observed in coincidence with energy-selected spectator Auger electrons at the energies and bandpasses indicated by the two bars I and II.

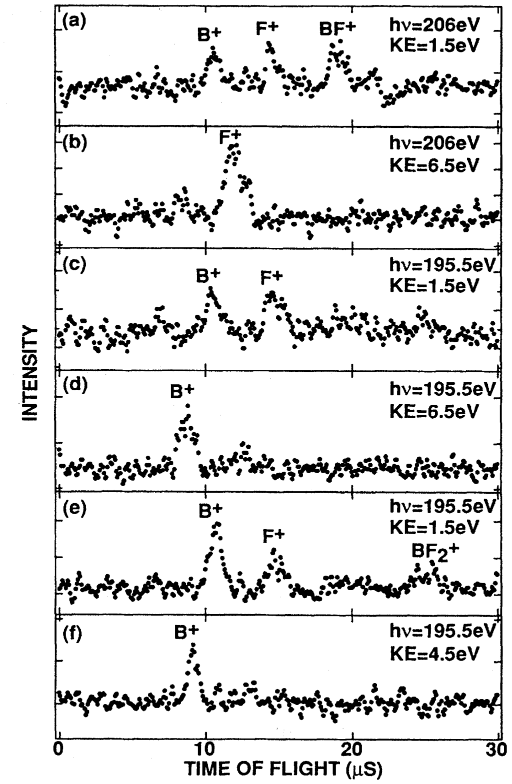

FIG. 2. Energy-selected photoion time-of-flight mass spectra taken in coincidence with energy-selected electrons. (a) and (b) Photoions at kinetic energies (KE) 1.5 and 6.5 eV, respectively, with B 1*s* photoelectrons. (c) and (d) Photoions at KE=1.5 and 6.5 eV, respectively, with spectator Auger electrons at the corresponding state energy 60±5 eV (I in Fig. 1). (e) and (f) Photoions at KE=1.5 and 4.5 eV, respectively, with spectator Auger electrons at the corresponding state energy 37±5 eV (II in Fig. 1). (a) and (b) are recorded at the B $1s \rightarrow 4e'$ excitation at $h\nu = 205$ eV, whereas (c)–(f) are recorded at the B $1s \rightarrow 2a_2''$ excitation at 195.5 eV.

energy. The monochromatized photon beam was brought into the interaction region of an electron-ion coincidence apparatus that comprised a parallel-plate analyzer ($E/\Delta E \sim 20$) for the ions and a 90° spherical sector analyzer ($E/\Delta E \sim 15$) for the electrons. The parallel-plate analyzer was mounted on a turntable whose axis of rotation was aligned to coincide with the incident photon beam direction and operated at 20-eV constant pass energy ($\Delta E \sim 1$ eV FWHM). The ions were detected by tandem microchannel plates. The spherical sector analyzer was aligned along the principal axis of incident light polarization and the deflection voltage was varied to select electrons of the desired energy. The electrons were detected by a channeltron. For the electron-ion coincidence measurement, the ion analyzer was aligned in the direction opposite to the electron analyzer, and signals from the electron and ion detectors were used to start and stop the time-to-amplitude converter. In addition to the coincidence measurement, we measured angular distributions of energetic photoions (6.5-eV kinetic energy). The degree of linear polarization for the incident light was determined by measuring the photoelectron angular distribution of He, using the parallel-plate analyzer.

We first consider the case of the B $1s \rightarrow 4e'$ excitation at 205 eV. When a B 1*s* electron is excited by 205-eV photons, the electron is ejected as a photoelectron and the normal Auger electron emission follows. Then ionic fragmentation results from the Auger final dicationic states. According to the AEPICO [3] and PEPIPICO [7] measurements, the dominant ion-pair formation processes are $BF_3^{2+} \rightarrow B^+ + F^+ + 2F$ and $BF_3^{2+} \rightarrow BF^+ + F^+ + F$. The photoions thus produced would be energetic because of the large kinetic-energy release due to Coulomb repulsion between the two ionic fragments. We have recorded the time-of-flight (TOF) mass spectra of the energetic photoions passing through the analyzer at energies of 1.5, 2.5, 4.5, and 6.5 eV in coincidence with B 1*s* photoelectrons. The TOF spectra thus obtained are given in Figs. 2(a) and 2(b), where the photoion kinetic energies are 1.5 and 6.5 eV, respectively. The photoions at 1.5-eV kinetic energy are B^+, F^+, and BF^+, as in the case of the AEPICO spectra [3], whereas the photoions at 6.5-eV kinetic energy are only F^+. The observation that F^+ is more energetic than B^+ is consistent with the PEPIPICO observation [7]. There seem to be two alternative explanations for the reason why F^+ is more energetic than the lighter ion B^+. If dissociation starts at the D_{3h} plane geometry where the boron atom is at the center of the three F atoms and if the three bonds break simultaneously, then B^+ cannot be energetic because of obstruction by the three F atoms. Alternatively, if charge separation between F^+ and ${BF_2}^+$ occurs and B^+ is ejected subsequently from the fragment ${BF_2}^+$, then B^+ is less energetic than F^+. Thus no decisive conclusion can be drawn.

At 205-eV photon energy, we have measured the angular distribution of the photoions at 6.5-eV kinetic energy, i.e., F^+. If the F^+ fragment is ejected in the plane of the parent molecule in D_{3h} symmetry defined at the time of photoionization (equivalent to the axial-recoil approximation [12,13]), the angular distribution of the F^+ fragment can be expressed as

$$\frac{d\sigma}{d\theta}=\frac{\sigma}{4\pi}\left[1+\frac{\beta}{4}(3P\cos 2\theta+1)\right] , \qquad (1)$$

where P is the degree of linear polarization of incident light, θ is the angle of the photoion ejection direction relative to the principal axis of polarization, and σ and β are the cross section and photoion asymmetry parameter, respectively. The photoion asymmetry parameter β would be -1 for a pure $a_1' \rightarrow a_2''$ transition, which is induced by light polarized perpendicular to the molecular plane, and 0.5 for a pure $a_1' \rightarrow e'$ transition corresponding to in-plane polarization. The angular distribution measured for F^+ at 6.5-eV kinetic energy and at a photon energy of 205 eV results in $\beta=0.3\pm 0.1$. This positive value suggests that the $a_1' \rightarrow e'$ transition is dominant ($\sim$9/10) at 205-eV photon energy and that the F^+ fragment is ejected within the plane of the parent molecule oriented in space due to photoionization by the polarized light.

We now focus our attention on the B $1s \rightarrow 2a_2''$ excitation. When a B $1s$ electron is excited to the $2a_2''$ orbital, both the participant and spectator Auger decay processes occur (see Fig. 1). The branching ratio to these two electronic decay processes is about 1:3 [10]. The final states of the participant Auger decay are outer-valence one-hole states and lead to the molecular dissociation ${BF_2}^+ + F$ [3]. ${BF_2}^+$ thus created will not be energetic and is not our concern. On the other hand, the final states of the spectator Auger decay are one-electron, two-hole states and about a half of these states are above the double-ionization threshold ($\sim$40 eV). These states are expected to produce energetic ions because of their higher internal energy.

We have recorded the TOF spectra of the energy selected photoions in coincidence with the energy selected spectator Auger electrons. The electrons selected with a bandpass of 10 eV FWHM correspond to groups I and II in Fig. 1. The state energy of group I is centered at $\sim$60 eV, whereas that of group II is $\sim$37 eV. Thus the states probed as group I are above the double-ionization threshold and have one hole in the outer-valence orbital and one hole in the inner-valence orbital, whereas the states probed as group II are mostly below the double-ionization threshold and have two holes in the outer-valence orbitals. Note that group II may include contributions from direct photoionization from the inner-valence orbitals whose binding energies are $\sim$40 eV. The resulting TOF spectra are given in Figs. 2(c)–2(f).

Consider the mass spectra taken in coincidence with group I electrons. The photoions at 1.5-eV kinetic energy are B^+ and F^+ [Fig. 2(c)], as in the case of the corresponding RAEPICO spectrum A3′ in Ref. [3], whereas most of the photoions at 6.5-eV kinetic energy are B^+ [Fig. 2(d)]. The states probed by group I electrons are above the double-ionization threshold and would be subject to autoionization to the dicationic states. Thus the two photoions B^+ and F^+ are likely to be produced as a pair. The PEPIPICO measurement [7] revealed that the B^+-F^+ pair formation is dominant at the B $1s \rightarrow 2a_2''$ excitation. The present observation that B^+ is more energetic than F^+ at the B $1s \rightarrow 2a_2''$ excitation is also consistent with the PEPIPICO observation [7] and is in striking contrast with the observation that F^+ is more energetic than B^+ at the B $1s \rightarrow 4e'$ excitation.

We now turn our attention to the mass spectra taken in coincidence with group II electrons. The 1.5-eV spectrum of Fig. 2(e), where B^+ is dominant and F^+ and ${BF_2}^+$ are recognizable, is quite similar to the corresponding RAEPICO spectra A1′ and A2′ in Ref. [3], whereas the 4.5-eV spectrum of Fig. 2(f) shows only B^+, indicating that energetic B^+ formation is common for both group I and II states.

If the dissociation started at the D_{3h} plane geometry and the three bonds broke simultaneously, the central B^+ could not be energetic because of the obstruction by the surrounding three F atoms. The B^+ fragment can be energetic as a result of the momentum recoil without obstruction, if two slow F atoms are released before the ejection of B^+, or, alternatively, if the molecule is deformed so that B is out of plane before B^+ is ejected. According to the *ab initio* SCF calculation [7], the stable geometry is C_{3v} for the B $1s^{-1}$ $2a_2''$ core-excited state (see Fig. 1). Thus energetic B^+ formation seems to be ascribable to molecular deformation to C_{3v} pyramidal geometry, as already discussed in Ref. [7]. Note however that deformation to C_{3v} geometry has not been experimentally proven yet. The possibility that energetic B^+ is produced in the secondary process has also not been excluded.

Hoping to obtain a clue to these unsolved problems, we have measured the angular distribution of the energetic (6.5 eV) B^+ ions at the B $1s \rightarrow 2a_2''$ excitation. The B $1s \rightarrow 2a_2''$ transition is excited by light polarized perpendicular to the molecular plane in D_{3h} symmetry. If the energetic B^+ were ejected within the plane of the parent molecule, the angular distribution would be expressed by Eq. (1) with $\beta=-1$. The measured angular distribution, on the other hand, can be expressed by Eq. (1) with $\beta=-0.2\pm 0.1$. This value indicates that the B^+ ions are ejected almost isotropically and thus out of the plane of the parent molecule. We note that this is rather different from the case of the B $1s \rightarrow 4e'$ excitation, where the energetic F^+ ions are ejected within the plane of the parent molecule, and is consistent with the prediction that the molecule starts to be deformed to C_{3v} pyramidal geometry, pushing the central B atom out of plane just after the B $1s \rightarrow 2a_2''$ excitation [7].

The last question is whether the energetic B^+ is ejected from the C_{3v} pyramidal geometry in the direction of this threefold axis of rotation due to simultaneous bond-breaking. If this were the case, the angular distribution would be expressed by Eq. (1) with $\beta=2$. The measured negative value of β indicates that this is not the case and that the energetic B^+ is produced in a sequential dissociation process where one or two slow F atoms are ejected from the resonance Auger final state, followed by ejection of the energetic B^+ ion.

In conclusion, we have successfully applied the energy-selected-electron–energy-selected-photoion coincidence method and angle-resolved photoion spectroscopy to the complex dissociation dynamics of B 1*s* core-excited BF_3. We have pointed out that our method can be applied to any small polyatomic molecules and that their intermediate-state-specific dissociation dynamics, especially for single-ion formation from the spectator Auger final states below the double ionization threshold, can be probed only by our electron-ion correlation method. It should also be noted that our correlation method could be a powerful tool for obtaining information about the topology of the ion dissociation surface, and we plan such studies in the future.

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