Dynamical model of nuclear motion in the Auger emission spectrum of the core-excited BF$_3$ molecule

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Nuclear motion of a plane polyatomic molecule BF$_3$ is theoretically investigated under the core excitation of the B 1s electron to the antibonding 2a$_2^*$ unoccupied molecular orbital. The B atom starts to move in the direction out of plane immediately after the core excitation. Owing to the finite core-hole lifetime comparable to a vibrational period, the B atom can move around the new equilibrium position of the core-excited state and the Auger decay occurs while this nuclear motion is going on. The x-ray absorption spectra and the resonant Auger emission spectra are calculated quantum mechanically. The calculated results are in reasonable agreement with the recent experimental results, illustrating that the dynamical aspect in the nuclear motion in the core-excited state is directly reflected in the resonant Auger emission spectrum.

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I. INTRODUCTION

When a core electron in a molecule is excited, the core-excited state decays through the Auger transition and the molecular dissociation is usually observed. It has long been considered that the lifetime of the core-excited state is so short that a molecular dissociation follows after the Auger decay process [1,2]. In 1986, however, Morin and Nenner [3] reported electron emission from the core-excited Br atom following the Br 3d$\rightarrow$$\sigma^*$ excitation of HBr as clear evidence of fast dissociation followed by electron emission of the core-excited fragment. Since this pioneering work, some groups have extensively investigated the competition between the molecular dissociation and the electronic decay of core-excited molecules [4,5].

From the theoretical viewpoint, the dynamics of the core-excited state is to be directly reflected in the spectrum of the second-order quantum processes, such as the resonant x-ray-emission spectrum (RXES) or the resonant Auger electron-emission spectrum (RAES). Gel’vukhanov and Ågren developed a general theory of RXES and RAES for molecules involving the dissociative state [6,7]. Pahl et al. extensively discussed the competition between excitation and electronic decay [8], partly stimulated by some high-resolution RAES data [9,10]. Tanaka and Kayanuma [11], in contrast, analyzed the experimental data of the RXES for the 1s core-exciton state of diamond [12], within the formalism of the second-order optical process by a simple cluster-vibronic model. These theoretical studies clearly demonstrate how the nuclear motion is reflected in the RXES and/or RAES.

The main difference of polyatomic molecules, such as BF$_3$ to be discussed here, from diatomic molecules, extensively investigated so far [3–10], is that the relevant potential-energy surfaces are multidimensional and thus the molecular shape or the symmetry can be changed for each excited state. Indeed, the molecular-orbital calculation based upon the Z + 1 equivalent-core approximation has shown that the BF$_3$ molecule with $D_{3h}$ symmetry in its ground state deforms its shape into the $C_{3v}$ symmetry when the B 1s electron is excited to the lowest unoccupied molecular orbital 2a$_2^*$ [13].

The molecular deformation from $D_{3h}$ to $C_{3v}$ in the core-excited state of BF$_3$ has been confirmed experimentally by Simon et al. [13] and Ueda et al. [14,15]. According to their observations, the most energetic ion is F$^+$ for the excitation above the ionization threshold and is ejected within the plane of BF$_3$, whereas the most energetic fragment ion B$^+$ is ejected to the out-of-plane direction for the B 1s$\rightarrow$2a$_2^*$ excitation. The energetic B ion ejections in the out-of-plane direction clearly indicate the displacement toward the out-of-plane direction of the B atom in the core-excited state.

In the B 1s x-ray absorption spectrum (XAS) of BF$_3$ [16,17], the dipole-forbidden transition to the (3s)3a$_1^*$ symmetry unoccupied state appears at about 2.5 eV above the B 1s$\rightarrow$2a$_2^*$ resonance. The reason for this is because the B 1s$\rightarrow$3a$_1^*$ transition borrows the intensity from the B 1s$\rightarrow$2a$_2^*$ transition by coupling of the 3a$_1^*$ state with the 2a$_2^*$ state through the a$_2^*$ symmetry vibrational mode. Thus the appearance of this dipole-forbidden transition also implies the displacement of the B atom in the B 1s$^{-1}$2a$_2^*$ core-excited state toward the out-of-plane direction.

In general, there are two channels in the resonant Auger emission process: One is called a participator Auger emission (PAE) and the other a spectator Auger emission (SAE). In the former, the excited core electron participates in the Auger decay, while in the latter it remains in the excited state and the other valence electrons participate in the Auger decay. Therefore, though the core-excited (or intermediate) state is identical for both processes, the final states become different: The final state has one hole in the valence orbital for the PAE process, while the final state of the SAE process...
is a two-hole–one-electron state. It should be noted that the final state in the PAE process is identical to that of the direct photoemission process.

Ueda et al. [18] and Simon et al. [19] found that the PAE spectrum (PAES) of BF$_3$ for the $1s ightarrow 2a''_2$ resonance has a long tail toward the lower-kinetic-energy side, although such a tail does not appear in the corresponding photoemission peak. In the SAE spectra (SAES), on the other hand, such a long tail does not appear toward the lower kinetic-energy (higher-binding-energy) side, but a short tail appears toward the higher-kinetic-energy (lower-binding-energy) side, showing a striking contrast to the case of the PAES.

In addition to the spectral features described above, Simon et al. found also that the behaviors of the excitation energy dependence of PAES and SAES are characteristically different from each other [19]. In the PAES, there is a linear dispersion of kinetic energy of the Auger electrons as a function of photon energy, which is known as the Auger resonant Raman effect [6,20,21], while in the SAES any correlation between the Auger electron kinetic energy and the incident photon energy was not observed.

The aim of the present paper is to explain the above-described experimental data on the RAES of BF$_3$, as well as the XAS, from a unified point of view and to elucidate the dynamical aspect of the nuclear motion in the B $1s^{-1}2a''_2$ core-excited state. For that purpose, we calculate the B $1s$ XAS and RAES quantum mechanically using a vibronic model, where the former and the latter processes are treated as first-order and coherent second-order quantum processes, respectively.

We consider the displacement of the B atom to the out-of-plane direction in the $1s^{-1}2a''_2$ core-excited state to be caused by the quasi–Jahn-Teller coupling between the $1s^{-1}2a''_2$ and $1s^{-1}3a'_1$ core-excited states through the $a''_2$ symmetry vibration. Such a spontaneous symmetry breaking induced by a light excitation is often seen in polyatomic molecules [22,23] and clear evidence of such a symmetry breaking due to the Jahn-Teller coupling has been observed in the resonant x-ray Raman scatterings [24,25].

The model and the formulation are presented in Sec. II. The calculated results for the B $1s$ XAS and RAES are presented in Sec. III together with some discussion. Section IV is devoted to a conclusion.

II. MODEL AND FORMULATION

In this paper we consider the B $1s ightarrow 2a''_2$ resonance excitation, where only the $a''_2$ symmetry vibrational mode is taken into account, which is important for the displacement of the B atom to the out-of-plane direction. The coordinate of this mode is denoted by $Q$. We propose here a simple vibronic model that describes the instability of the core-excited BF$_3$ along $Q$ [19].

The Hamiltonian for the initial state is written as

$$H_g = \frac{1}{2}(P^2 + \omega^2 Q^2),$$

where $P$ is the conjugate momentum to $Q$. The frequency $\omega$ is estimated from other experiments to be $\sim 0.086$ eV [26]. For the core-excited states, we consider the quasi–Jahn-Teller coupling between the $1s^{-1}2a''_2$ and $1s^{-1}3a'_1$ states through the $a''_2$ symmetry vibration. Then the Hamiltonian $H_{es}$ for the core-excited states is described by

$$H_{es} = H_i + H L + H_{JT},$$

where

$$H_i = \epsilon_i \{2a''_2/2a''_2\} + (\epsilon_i + \Delta)\{3a'*/3a'\},$$

$$H_L = \frac{1}{2} P^2 - E_0 \exp \left[ - \frac{1}{2} \frac{\omega^2}{E_0} Q^2 \right],$$

$$H_{JT} = SQ \exp \left[ -(Q/\rho)^2 \right] \times \{2a''_2/(3a'_1) + [3a'_1/(2a'')].$$

In the above equations the $2a''_2$ core-excited state at $\epsilon_i$ interacts with the $3a'_1$ excited state located at $\Delta$ above $2a''_2$ through the quasi–Jahn-Teller coupling $H_{JT}$, where the coupling strength $S \exp \left[ -(Q/\rho)^2 \right]$ is assumed to be decreased by a Gaussian function with its full width at half maximum represented by $\rho \sqrt{\ln 2}$ as $Q$ increases. The second term of Eq. (4) describes the unperturbed vibational potential, which can be approximated by a harmonic potential with a curvature $\omega_0$ near $Q = 0$, but deviates from it because the bond becomes looser for large $Q$. The potential value of $H_L$ at the origin is described by $E_0$. The parameter values are chosen so as to reproduce the XAS and RAES consistently.

In the final state, the system is separated into two parts describing the ion and the Auger electron states. The final state of the PAES is considered to be stable near the origin of $Q$ since there is no $2a''_2$ electron anymore. On the other hand, the final state of the SAES is unstable because the quasi–Jahn-Teller coupling is still active. For the sake of simplicity, we assume that the final state Hamiltonian $H_f$ for the ion has the same functional form as $H_L$ and $H_{es}$ for the PAE and SAE processes, respectively, except for the difference in the parameter values.

We calculate the RAES using the Kramers-Heisenberg formula

$$S(\Omega_1, \epsilon_k) = \sum_{\phi_f} \sum_{\phi} \frac{\langle \phi_f, \epsilon_k | T | \phi \rangle \langle \psi | g \rangle}{E_{\phi} - E_{\phi'} - \Omega_1 - i\Gamma(1s)} \times \delta (E_{\phi_f} + \epsilon_k - \Omega_1 - E_{\phi'}),$$

where the excitation photon energy is denoted by $\Omega_1$, the kinetic energy of the Auger electron is denoted by $\epsilon_k$, and $|\psi\rangle$ and $|\phi\rangle$ are the eigenstates for $H_{es}$ and $H_f$ with the energies $E_{\phi}$ and $E_{\phi'}$, respectively. The ground-state energy is represented by $E_g$ and $\Gamma(1s)$ is the damping factor due to the B $1s$ core-hole lifetime. The ground state $|g\rangle$ is represented by the direct product of the electronic ground state $|g\rangle$, and the vibration vacuum state $|0\rangle$, because the energy quantum of the $a''_2$ vibration is too large to be excited at room temperature. The core-excited state $|\psi\rangle$ has been expanded by the vibronic basis functions.
\[ |\psi\rangle = \sum_{i,n} |i\rangle_{G} \otimes |n\rangle_{V} \] (7)

\[ (i = 1s^{-1}2a''_{1}, 1s^{-1}3a'_{1}; n = 0, 1, \ldots), \] (8)

where \( |n\rangle_{V} \) is the number-state basis functions of the harmonic oscillator of \( H_{V} \). The Hamiltonian \( H_{G} \) is diagonalized in the vector space represented by the above basis functions. In the final state, we neglect the couplings between the different electronic states \( j \) for simplicity, so the wave functions are obtained simply by solving the eigenvalue problem for each adiabatic potential.

The dipole-transition operator \( \mathcal{P} \) for the incident x-ray photon is written, within the Condon approximation, as

\[ \mathcal{P} = |1s^{-1}2a''_{1} \rangle_{EE} \langle g| + |g\rangle_{EE} \langle 1s^{-1}2a''_{1}|, \] (9)

except for irrelevant factors. The dipole-forbidden transition \( |g\rangle \rightarrow |3a'_{1}\rangle \) would gain intensity through the vibronic interaction. The Auger transition operator \( \mathcal{T} \) is described by

\[ \mathcal{T} = \sum_{i,j} M_{ij} |j\rangle_{EE} \langle i| + |i\rangle_{EE} \langle j| \] (10)

\[ (i = 1s^{-1}2a''_{2}, 1s^{-1}3a'_{1}; j \text{ is the final electronic state}), \] (11)

where the magnitude of the Auger transition elements \( M_{ij} \) is assumed to be independent of the vibrational coordinate. The value of \( M_{ij} \) should be calculated from state to state by taking into account the multiplet coupling, the fine structure of which is smeared out by the insufficient experimental resolution. For simplicity, we neglect the effect of the multiplet coupling and treat \( M_{ij} \) as parameters determined in the following way. The dependence on the intermediate state \( i \) (= \( 1s^{-1}2a''_{2}, 1s^{-1}3a'_{1} \)) is neglected and the dependence on the final state \( j \) is determined so as to reproduce the observed intensity ratio of the emission bands. This is a rather crude approximation, but is sufficient to investigate the gross features of the Auger line shape. Note that the matrix elements for the Auger transition are not as sensitive to the symmetry of the state compared to those for the optical transition.

We have carried out the actual calculation by expanding the state vectors in a series of number-state basis functions of the harmonic oscillator with the number of states up to 300. We have confirmed the convergence of the expansion by observing that the spectral shape does not change anymore even if we increase the number of basis functions. Since the potential shape in the intermediate state is not so strongly dissociative in the present case, the expansion by the basis function of the harmonic oscillator is sufficient to describe the SAES final state where the potential shape is assumed to be more dissociative since the domain of the motion of the wave packet in the intermediate state is confined near \( Q = 0 \) and since all we need is to mimic the potential shape of the final state around this region, as can be seen from the Frank-Condon principle. In the case that the potential shape in the intermediate state is strongly dissociative and the lifetime is fairly long, it might be more appropriate to take a set of basis functions that has a continuous spectrum [6].

**III. RESULTS AND DISCUSSION**

First we show the calculated results of the B 1s XAS in Fig. 1, where the experimental results in the vicinity of the B 1s \( \rightarrow 2a_{2}^{\pi} \) resonance [17] are also shown in the inset. A slight asymmetric feature of the main peak corresponding to the \( 1s^{-1}2a_{2}^{\pi} \) core-excited state and the dipole-forbidden transition to the \( 1s^{-1}3a'_{1} \) core-excited state 2.6 eV above the main peak in the experiment are satisfactorily reproduced in the calculation.

The adiabatic potentials for the core-excited states along \( Q \) are shown in Fig. 2, where the solid and the dashed lines of the upper two curves are for the \( 1s^{-1}2a''_{2} \) and \( 1s^{-1}3a'_{1} \) core-excited states, respectively, and the unperturbed potentials for the excited states are also shown by the dotted lines. The adiabatic potentials of the lowest final states for the PAES and SAES are also shown in the same figure, where they are

![Fig. 1. Calculated B 1s x-ray absorption spectra. The origin of the abscissa is taken at the main peak position. The experimental result [17] is also shown in the inset.](image1)

![Fig. 2. Adiabatic potentials along Q for the core-excited states and for the final states for the participator and spectator Auger emission spectra (PAES and SAES).](image2)
drawn so as to coincide at $Q=0$. The values of parameters used in the calculation are listed in Table I. The potentials for the $1s^{-1}2a_2^\sigma$ and $1s^{-3}3a_1^\sigma$ states strongly repel each other near the origin by the quasi–Jahn-Teller coupling between them, so that the lowest core-excited state becomes unstable at the origin. The wave function of the ground state is well localized around the origin $Q\approx 0$, so the absorption intensity mainly comes from the transition to the lower branch near the origin because of its large dipole-allowed $1s^{-1}2a_2^\sigma$ component around the origin. The asymmetry of the main peak having a tail toward the low-photon-energy side is a consequence of the instability against the $a_2^\sigma$ vibrational motion in the $1s^{-1}2a_2^\sigma$ core-excited state.

The calculated PAES and SAES are shown in Figs. 3 and 4, respectively, where the experimental results by Simon et al. [18] are also shown for comparison. In the figures the spectral intensities are plotted versus binding energies $E_B = \Omega_1 - \epsilon_k$. Both the theoretical and experimental spectra are given for three different excitations: for the B $1s^{-2}2a_2^\sigma$ resonance peak and 200 meV lower and higher than the resonance peak, as indicated by the arrows in Fig. 1.

The PAES consists of three major peaks for the $1a_2^\pi$, $2e'$.

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**TABLE I.** Parameter values used in the calculation.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta$ (eV)</th>
<th>$\omega_c$ (meV)</th>
<th>$E_0$ (eV)</th>
<th>$S$</th>
<th>$\rho$</th>
</tr>
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<tr>
<td>$1s^{-1}2a_2^\sigma$</td>
<td>2.4</td>
<td>93</td>
<td>1.78</td>
<td>5.5</td>
<td>12</td>
</tr>
<tr>
<td>PAES</td>
<td>89</td>
<td>1.335</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAES</td>
<td>2.4</td>
<td>47</td>
<td>$-0.89$</td>
<td>5.5</td>
<td>12</td>
</tr>
</tbody>
</table>

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![Figure 3](image-url)  
**FIG. 3.** (a) Calculated and (b) experimental results of the PAES. The results for the excitation at the B $1s^{-2}2a_2^\sigma$ resonance peak and 200 meV lower and higher than the resonance peak are shown in (a) by the solid, short-dashed, and long-dashed lines, respectively. Those for the experimental results are shown by the solid line, open circles, and closed triangles, respectively.

![Figure 4](image-url)  
**FIG. 4.** (a) Calculated and (b) experimental results of the SAES. See the caption of Fig. 3 for further details.

and $2a_1^\sigma$ one-valence-hole final states, as shown in Fig. 3(a). It should be noted that the PAES has a tail toward the higher-binding-energy side, while such a long tail has not been observed for the corresponding photoemission peaks (not shown in the figure; see Ref. [18]).

The appearance of the tail in the PAES is interpreted within a semiclassical picture in the following manner. Owing to the large fluctuation amplitude of the transition energy, which is roughly estimated by the width of the absorption band, the coherence of the vibration in the ground state is maintained in the transition to the $1s^{-1}2a_2^\sigma$ excited state even in the case of the monochromatic excitation. The subsequent nuclear motion can be viewed as an evolution of the wave packet along the adiabatic potential surface. Immediately after the excitation, the B atom moves quite slowly along the potential surface of the lower branch and then is accelerated to move toward the equilibrium point. Since the kinetic energy of the Auger electron corresponds to the energy difference of the adiabatic potentials between the intermediate and final states, the Auger kinetic energy decreases while the B atom moves along the lower branch of the adiabatic potential in the core-excited state. This makes a tail toward the low-kinetic-energy side. Thus we may call the long tail part in the PAES dynamical Auger emission.

It should be noted that the tail toward the lower-kinetic-energy side in the PAES is an analog of the tail in the lower-photon-energy side of the hot luminescence in the strongly coupled vibronic system [27,28]. Indeed, Tanaka and Kayanuma [11] explained such a tail in the RXES following the C $1s$ excitation in diamond observed by Ma et al. [12] as the hot luminescence associated with the wave packet of the vibrational mode undergoing the $T_d\rightarrow C_{3v}$ distortion.

The intensity of the dynamical Auger emission is roughly proportional to the inverse of the time derivative of the
Frank-Condon energy for the evolving wave packet [29], as is well known in the spectral line-shape theory of collisionally broadened absorption/emission lines (see, for example, Ref. [30] and references cited therein). Therefore, it may have a peak structure at the point where the slopes of the two potential-energy curves become the same and also at the stationary point of the oscillation of the wave packet. One can notice in Fig. 3 that there are weak shoulder and satellite structures around 22.4 eV and at 23.6 eV, respectively. These structures correspond to the electron emission in the vicinity of the minimum point of the adiabatic potential for the $1s^{-1}2a_2^*$ excited state, at which the two potential-energy curves become nearly parallel each other. The shoulder around 22.4 eV and the satellite at 23.6 eV are accompanied by the $2e'$ and the $2a_1^*$ peaks, respectively, and the separation between the peak and the satellite is about 2.25 eV. These satellite structures are more clearly seen in the experimental results previously found by Ueda et al. [18]. The contribution of the electron emission from the outer turning point of the adiabatic potential of the $1s^{-1}2a_2^*$ excited state also lies between the main peak and these satellites.

On the other hand, such a long tail toward the higher-binding-energy side cannot be seen in the SAES. Instead, a short tail toward the lower-binding-energy side appears, as shown in Fig. 4. The reason for this is because the adiabatic potential for the SAES final state is more dissociative than in the core-excited state, as shown in Fig. 2, so the energy difference between the intermediate and the final states slightly increases with $Q$. The dissociative nature of the adiabatic potential for the SAES final state is consistent with the experimental fact that the B ion ejection to the out-of-plane direction is observed [14,15].

It should be noted that this short tail toward the higher-kinetic-energy side in the SAES is an analog of a tail toward the higher-photon-energy side in the RXES predicted by Gel’mukhanov and Ågren when the final state of the RXES is more dissociative than the core-excited state [6].

Consider the excitation energy dependence of the PAES and SAES. It is found from Fig. 3 that there is a linear dispersion between the incident photon and the electron kinetic energies or, in other words, the binding energies are independent of the incident photon energy, in the PAES, while there seems to be no correlation between them in the SAES as seen in Fig. 4. The prominent peak in the PAES corresponds to the Rayleigh-like decay process, where the coherence is maintained throughout the whole process. Such a Rayleigh-like process has a strong correlation between the incident photon and Auger electron kinetic energies. This is quite analogous to the behavior of the Rayleigh component in the resonant light scattering of a strongly coupled vibronic system [28].

The binding energies of the SAES peaks show a linear dependence on the photon energy (see Fig. 4): Kinetic energies of the SAES peaks are nearly constant. This photon-energy dependence (nondispersive effect) is a consequence of the fact that the potential-energy surfaces of the SAES final states are nearly parallel to that of the intermediate core-excited state in the vicinity of the origin and therefore unstable along $Q$. The early decay leading to these peaks occurs perpendicular downward in the configuration coordinate space (Fig. 2) because of the orthogonality of the vibrational states and thus the loss of the potential energy in the excited state is compensated by that in the final states.

We now discuss the lifetime effect on the RAE (PAE) process in order to illustrate how the dynamical aspect of the nuclear motion is reflected in the RAES (PAES). In Fig. 5 we show the calculated PAES for different core-hole lifetimes, where $\Gamma(1s) = 64$ meV corresponds to an approximately realistic situation [31]. It is found that the tail part grows in intensity as the core-hole lifetime becomes longer. The reason for this is because the B atom can travel more and more in the core-excited state as the core-hole lifetime becomes longer and as a consequence the contribution of the dynamical Auger emission increases. In this way, the tail part of the PAES directly represents the dynamical motion of the B atom in the core-excited state in conformity with the notion of the dynamical Auger emission.

Finally, we briefly consider the relation between the photon-energy dependence and the lifetime effect. Gel’mukhanov and Ågren [6] introduced a concept of the duration time of the coherent second-order quantum process $\tau = (\Omega^2 + \Gamma^2)^{-1/2}$, where $\Omega$ is the detuning of the excitation energy and $\Gamma$ is the lifetime broadening. This concept was successfully applied to explain and/or predict the excitation energy dependence (detuning effects) in the RXES and RAES. For example, Nordgren and co-workers [24,25] demonstrated that, in the resonant x-ray Raman scattering in the CO$_2$ molecule, the symmetry breaking due to the Jahn-Teller coupling in the core-excited states is gradually suppressed with the increase in the detuning energy $\Omega$, as a consequence of the shortening of the duration time. Björnholm et al. [5], on the other hand, demonstrated that, in the RAES of the HCl molecule, the electron emission from the atomic fragment Cl is suppressed and accordingly the molecular contribution to the RAES is increased with the increase in $\Omega$, as a consequence of the shortening of the duration time.

If we apply the concept of the duration time of Gel’mukhanov and Ågren to the present case, the detuning effect studied in Fig. 4 should be equivalent to the lifetime effect studied in Fig. 5. A careful inspection in the calculated PAES indeed reveals that the detuning induces the effect equivalent to the shortening of the lifetime, i.e., the suppression of the tail part of PAES in the present case. In the experiment by Simon et al. [19], however, the change of the
excitation energy is limited and thus the change of the intensity of the tail part is not clearly seen with a change of the excitation energy.

**IV. CONCLUSION**

We have calculated quantum mechanically the B 1s XAS and the RAES in the BF\(_3\) molecule. The XAS and RAES are calculated as first-order and second-order quantum processes, respectively. The B 1s core-hole lifetime is longer than the vibrational time and thus there is enough time for the B atom to move along the potential surface toward the new equilibrium point, and the Auger emission takes place while this atomic motion is going on. The 1s\(^{-1}\)2a\(_g^*\) core-excited state is coupled with the 1s\(^{-1}\)3a\(_1^*\) state through the antisymmetric a\(_g^*\) vibration, which induces the movement of the B atom toward the out-of-plane direction in the core-excited state. This atomic motion promotes the B ion ejection toward the out-of-plane direction. It has been shown that the overall features of the XAS and RAES are well reproduced by a simple vibronic model that takes into account the quasi–Jahn-Teller interaction. We conclude that the out-of-plane dissociation mode of the B atom is triggered by the vibronic instability in the early stage of the core-excited state in the presence of the excited electron in the 2a\(_2^*\) orbital. The present analysis strongly suggests the usefulness of the resonant Auger emission spectroscopy as a tool to investigate the nuclear motion of molecules in the initial stage of dissociation induced by the core excitation. By a comprehensive analysis of the emission spectra as a second-order process and combined with the analysis of the ion spectra, we can obtain a great deal of information about the shape of adiabatic potentials in the core-excited state and in the valence excited ionic states as well. A more elaborate calculation of the adiabatic potentials in the excited states should be done in the future and should be compared with those proposed here. It will also be worthwhile to extend the experimental study of high-resolution resonant Auger spectroscopy to other molecules.

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