Nuclear Motion of Core Excited BF_3 Probed by High Resolution Resonant Auger Spectroscopy

M. Simon, C. Miron, N. Leclercq, and P. Morin
LURE, Batiment 209d, Universite Paris-Sud, 91405 Orsay Cedex, France
and CEA/DRECAM/SPAM, CEN Saclay, 91191 Gif/Yvette Cedex, France

K. Ueda and Y. Sato
Research Institute for Scientific Measurements, Tohoku University, Sendai 980-77, Japan

S. Tanaka[1] and Y. Kayanuma[2]
[1]*CIAS, Osaka Prefecture University, Sakai 593, Japan*
[2]*College of Engineerings, Osaka Prefecture University, Sakai 593, Japan*
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High resolution resonant Auger spectroscopy applied to the core excitation of BF_3 reveals that the kinetic energy of the spectator Auger electrons stays constant when the photon energy is scanned through the B $1s \rightarrow 2a_2''$ resonance, whereas the kinetic energy of participator Auger electrons shows a linear photon energy dependence. These nondispersive and dispersive effects are theoretically reproduced using a quasi-Jahn-Teller model and by treating the Auger emission process as a coherent second-order quantum process. [S0031-9007(97)04506-7]

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The study of core excitation of atoms and molecules is an active field which benefits from fast developments in technologies of soft x-ray monochromators and synchrotron radiation sources. It is now possible to observe the evolution of a deexcitation process following the resonance excitation with a resolution smaller than the natural width of the core excited states. Then, the resolution of the deexcitation spectrum is determined by the convolution of the bandwidth of the excitation energy and the bandwidth for the energy analysis of the deexcitation spectrum [1,2]. Such resonance measurements provide evidence of the breakdown of the two-step model in which the excitation and the deexcitation processes are treated separately. The breakdown of the two-step model is clearly seen in the linear dispersion of kinetic energy of the resonant Auger electrons as a function of photon energy scanning through the resonance. This effect has been recently addressed both theoretically and experimentally, known as "Auger resonant Raman" [1,2].

Another interesting aspect is a strong lifetime dependence in the resonant Auger emission spectral shape in molecules. If the lifetime of a core excited state is longer than a period of molecular vibrations, the natural width is smaller than the vibrational spacing and the excitation to a specific vibrational level will occur for a sharp bandwidth of the incident photon. In this situation, the deexcitation spectrum can be approximately described by a Franck-Condon factor between the core-excited state and final states of the decay. On the other hand, if the lifetime is shorter than the vibrational period, one can no longer say which vibrational level is excited, and a coherent nuclear motion will be induced as a result of interference between excited vibrational levels. When the lifetime is not much shorter than the vibrational period, this nuclear motion will be reflected in the Auger electron spectral shape. In other words, the resonant Auger electron spectroscopy may become a probe of the ultrafast dynamical process of the core-excited state during the core hole lifetime. Such high resolution studies have been reported only for diatomic molecules so far [3–5].

In this Letter, we report nuclear motion of a polyatomic molecule probed by high resolution resonant Auger electron spectroscopy. The main difference between polyatomic molecules and diatomic molecules is that the relevant potential energy surfaces are multidimensional, and thus the molecular shape or the symmetry can be changed for each state allowing specific effects stressed in this Letter. The polyatomic molecule concerned here is BF_3, a plane molecule of D_{3h} symmetry in its ground state. The B $1s$ excitation (absorption) spectrum shows a strong resonance B $1s \rightarrow 2a_2''$ below the B $1s$ ionization threshold [6]. Extensive study on this resonance and its decay dynamics [7–10] revealed that the molecule deforms to the C_{3v} pyramidal structure following the B $1s \rightarrow 2a_2''$ excitation in competition with electronic decay. The aim of the present study is to *see* this nuclear motion with high-resolution resonant Auger spectroscopy.

We first explain the idea of the experiment. The effective width of the B $1s \rightarrow 2a_2''$ resonance is $\sim$400 meV. The lifetime broadening of the B $1s$ is $\sim$80 meV or less. According to the core equivalent model, the core-excited BF_3 geometry can be approximated to CF_3. The stable geometry of the B $1s^{-1}2a_2''$ core-excited state is known to be C_{3v}, where the B atom is out of plane [9], and thus the out-of-plane vibrations (ν_2:a_2'' symmetry) are expected to be highly excited via the $1s \rightarrow 2a_2''$ excitation. The effective width of the resonance is therefore considered as a width of the envelope of out-of-plane vibrational progression containing many unresolved highly excited vibrations: the interval of the adjacent vibrational levels may be a little smaller than the natural width of the $1s^{-1}\ 2a_2''$ state. In this situation, the change of the photon energy corresponds to the change of a location of a wave packet created on the potential surface of the $1s^{-1}\ 2a_2''$ core-excited state. Then a dynamical motion of the wave packet, or a nuclear motion of the molecule, should be revealed in the deexcitation spectrum observed with a sufficiently high resolution.

The experiment has been carried out at the SA31 bending-magnet beam line of SuperACO. A plane-grating monochromator installed in this beam line was used with entrance and exit slits of 0.1 mm, giving a photon bandwidth of 200 meV at 200 eV. This bandwidth is smaller than the effective width of ~400 meV for the B $1s \rightarrow 2a_2''$ resonance and thus allows us to selectively excite a part of the resonance, or a bunch of vibrationally excited states.

The electron analyzer used for this experiment is described in detail elsewhere [11]. Only a brief account is given here. The analyzer is a double toroidal type which combines the advantages of the cylindrical mirror analyzer (high acceptance angle) and the hemispherical analyzer (plane focus for a broad kinetic energy range). A retarding lens system of four conical elements focuses the electron beam on the conical entrance slit of the first tore. The electrons are dispersed and focused by a set of two tores, on a plane perpendicular to the analyzer symmetry axis, where a set of three microchannel plates is mounted together with a position sensitive detector of resistive anode type. The measurements have been carried out at a pass energy of 20 eV. The electron energy resolution is 200 meV.

Figure 1(a) shows the observed resonance Auger spectra. Here spectral intensities of photoelectron emissions are plotted versus binding energy $\mathrm{BE} = h\nu - \mathrm{KE}$, where $h\nu$ is the photon energy and KE is the electron kinetic energy. The photon energies employed for the excitations are the energy of the resonance peak (195.5 eV) and 200 meV lower and higher than the resonance peak energy.

Six outer valence photoelectrons are partially resolved in the spectra of Fig. 1(a). The resonance enhancement is significant for $1a_2''$, $2e'$, and $2a_1'$, as noticed previously [8], indicating the occurrence of the participator Auger decay. The electron emissions at the binding energies ~28–37 eV in Fig. 1(a) correspond to the spectator Auger decay, whose final states have two holes in the outer valence orbitals localized at two different F sites and one electron in the $2a_2''$ orbital [8,12]. There are three recognizable peaks, but many multiplet structures in the two-hole one-electron final state are actually involved there.

The binding energies of the participator Auger peaks are constant irrespective of the excitation photon energy: kinetic energies of the participator Auger peaks show a linear dependence on the photon energy. This linear dispersion can also be seen in the atomic spectator lines.

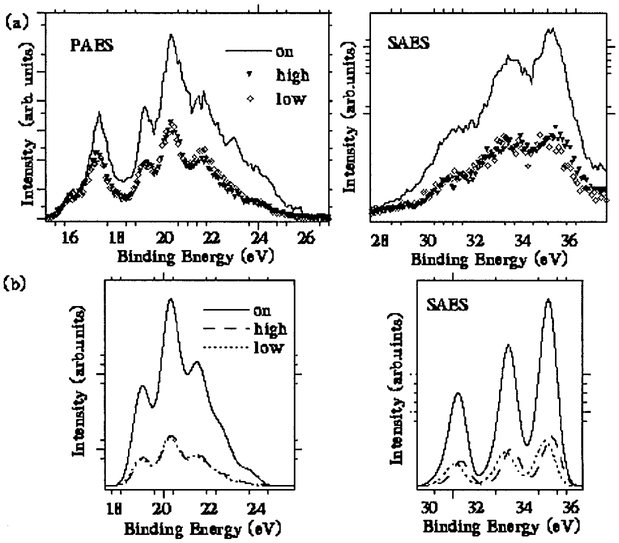

FIG. 1. The observed (a) and calculated (b) resonance Auger spectra. The participator and spectator Auger spectra are shown in the left hand and right hand panels, respectively. The results for the excitation at B $1s \rightarrow 2a_2''$ resonance and for 200 meV lower and higher than the resonance peak are shown.

In case of atoms, since there is no energy dissipation mechanism and/or dephasing mechanism, this is quite reasonable: the resonant Auger process can be regarded as a pure Raman scattering. In the case of molecules concerned here, however, the linear dispersion correlation between the Auger kinetic energy and the photon energy may disappear due to the conversion of the energy to the vibrational degrees of freedom. We can explain this *dispersive effect* qualitatively within a semiclassical picture, using the adiabatic potential surface along the out-of-plane vibration mode with $a_{2''}$ symmetry, the coordinate of which is designated by $Q_{a_{2''}}$ hereafter. The adiabatic potentials are shown in Fig. 2. Note that, in the case of participator Auger decay, the final state adiabatic potential is assumed to be stable at the origin whereas the core-excited state is unstable there. In the semiclassical picture, the Auger emission signal gains intensity mainly at the turning points of the classical motion of the wave packet and also at the points where the potential curves for the initial and the final state become parallel. The prominent peak which shows the dispersive effect corresponds to the decay at the inner turning point near the origin where the excitation takes place. The prompt decay to the Auger final state prohibits the nuclear motion to respond to the potential change, as if it were frozen around the ground state configuration. This is quite analogous to the behavior of the Rayleigh component in the resonant light scattering of a strongly coupled vibronic system [13] and is a salient feature of coherent second order processes.

The assumption of the minimum of the potential surface at the origin along $Q_{a_2''}$ in the final state is supported by the previous photoelectron-photoion coincidence study

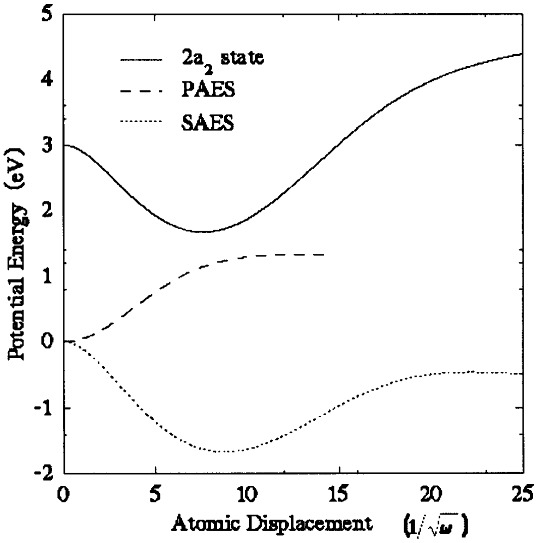

FIG. 2. The adiabatic potential surfaces along the out-of-plane vibration mode with a_2'' symmetry for the core excited $1s^{-1}2a_2''$ state (solid line), the participator Auger final state (dashed line), and the spectator Auger final state (dotted line). The origin of the potential energy is shifted arbitrary for each line.

[7], which showed that the states with one outer valence hole predominantly dissociate into $BF_2^+ + F$ and thus the dissociation is within the molecular plane. The fact that outer valence photoelectrons excited by the He line source do not show significant out-of-plane vibrations [14] also implies that the potential surfaces of these states are stable at the origin along $Q_{a_2''}$.

Another interesting point is the appearance of the tail on the higher binding energy side (i.e., lower kinetic energy side of the emitted electron) in the spectra, as noted previously [8]. This is direct evidence that the deexcitation occurs while the B atom is moving out of the plane. The participator Auger spectrum of O_2 [3] shows a similar tail and is interpreted by the deexcitation in the course of the stretching of the bond in the excited state. The nuclear motion we are probing here is molecular deformation from D_{3h} to C_{3v}. A tail structure of equivalent origin has been observed in the resonant light scattering of the F centers in alkali halides [15] and is called a hot luminescence. The mechanism responsible for the tail in the resonant Auger spectrum discussed here may be called *dynamical Auger emissions*. If the lifetime of the core-excited state were long enough for the molecule to vibrate many times, the electronic decay would take place predominantly also in the vicinity of the potential minimum of the core-excited state, where the potential curve is parallel to the final state (see Fig. 2). The observed participator spectrum, however, does not show such a significant peak corresponding to the decay there, implying that the lifetime is shorter than the vibrational period.

Let us now turn to the energy dependence of the spectator Auger peaks in Fig. 1(a). The binding energies of the spectator peaks show a linear dependence on the photon energy: kinetic energies of the spectator Auger peaks are nearly constant. This photon energy dependence (*nondispersive effect*) implies that the potential surfaces of the spectator Auger final states are nearly parallel to that of the intermediate core-excited state in the vicinity of the origin, and therefore unstable along $Q_{a_2''}$. The early decay leading to these peaks occurs perpendicularly 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. Previous coincidence measurements [9,10] showed that the energetic B^+ is ejected following the spectator Auger decay, supporting the idea that the potential surfaces of the spectator Auger final states are unstable along $Q_{a_2''}$.

In order to confirm our conjecture described so far, we have carried out theoretical calculations. We consider a quasi-Jahn-Teller coupling between the $2a_2''$ and $(3s)3a_1'$ excited states through the $Q_{a_2''}$ out-of-plane vibrational mode and obtain vibronic states solving the energy eigenvalue problem. Then we calculate resonant Auger emission spectrum treating the Auger emission process as a coherent second-order quantum process (i.e., Raman process).

The Hamiltonian for the initial state is written by

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

where Q denotes the coordinate of the $Q_{a_2''}$ vibrational mode, and P is the conjugate momentum to Q. The frequency ω is $\sim$0.089 eV. For the B $1s^{-1}2a_2''$ core-excited state, we consider the following Hamiltonian H_{ex}:

$$H_{\mathrm{ex}} = H_{\mathrm{el}} + H_L + H_{\text{J-T}}, \tag{2}$$

where

$$H_{\mathrm{el}} = \epsilon_c |2a_2''\rangle\langle 2a_2''| + (\epsilon_c + \Delta)|3a_1'\rangle\langle 3a_1'|, \tag{3}$$

$$H_L = \frac{1}{2}P^2 - E_0 \exp\left[-\frac{1}{2}\frac{\Omega^2}{E_0}Q^2\right], \tag{4}$$

$$\begin{aligned} H_{\text{J-T}} = {} & SQ\exp[-(Q/\rho)^2] \\ & \times \{|2a_2''\rangle\langle 3a_1'| + |3a_1'\rangle\langle 2a_2''|\}. \end{aligned} \tag{5}$$

In the above equations, $|2a_2''\rangle$ state at ϵ_c interacts with $|3a_1'\rangle$ state located at Δ above $|2a_2''\rangle$ through the quasi-Jahn-Teller coupling $H_{\text{J-T}}$.

In the final state, the system is separated into two parts, the ion and the Auger electron. The final state Hamiltonian for the ion, H_f, is assumed to have almost the same form as H_L and as H_{ex}, for the participator and spectator Auger emission processes, respectively.

The resonant Auger spectrum is calculated by using the Kramers-Heisenberg formula:

$$\begin{aligned} S(\Omega_1, \epsilon_k) = {} & \sum_{\phi}\left|\sum_{\psi}\frac{\langle\phi, \epsilon_k|\mathbf{T}|\psi\rangle\langle\psi|\mathbf{P}|g\rangle}{E_\psi - E_g - \Omega_1 - i\Gamma(1s)}\right|^2 \\ & \times \delta(E_\phi + \epsilon_k - \Omega_1 - E_g), \end{aligned} \tag{6}$$

where the kinetic energy of the Auger electron is denoted by ϵ_k, and the $|\psi\rangle$ and $|\phi\rangle$ are the eigenstates for $H_{\rm ex}$ and H_f with the energies E_ψ and E_ϕ, 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 dipole transition operator for the incident x-ray photon is $\mathbf{P}$ and the Auger transition operator is described by $\mathbf{T}$. Various Auger transition elements are determined so as to reproduce the experimental results. We convolute this spectra by a Gaussian taking into account the effects of the experimental resolution and the final state lifetime. Here we neglect all the multiplet structures for simplicity.

In Fig. 1(b), we present the results of the calculated participator and spectator Auger emission spectra for comparison with the experimental results. The calculation reproduces well the dispersive and nondispersive characters in the participator and spectator Auger peaks, respectively. In Fig. 2, we show the adiabatic potential surfaces along $Q_{a_2''}$ for the B $1s^{-1}2a_2''$ core-excited state and the participator and spectator Auger final states. The potential surfaces for core-excited state and the spectator Auger final state are unstable at the origin, whereas the potential surface of participator Auger final state is stable. The present calculation confirms our conjecture about the origin of the dispersive/nondispersive effects of participator/spectator Auger peaks described above. We can also see that each of the calculated participator Auger spectra has a tail towards the higher binding energy side. In the calculation of the spectra seen in Fig. 1(b) the lifetime width is 64 meV. We have also calculated the spectra varying the lifetime width $\Gamma(1s)$ in the range between 20 and 200 meV and found that the satellite peak ascribed to the Auger emission from the point in the vicinity of the excited potential minimum increases its intensity at ~2.3 eV above (in binding energy scale) the main peak with the decrease in the lifetime width, whereas the intensity in the tail decreases rapidly with the increase in the lifetime width. Thus, the present calculation confirms that the tail of the participator Auger spectrum indeed corresponds to the dynamical Auger emission reflecting the dynamical nuclear motion in the core-excited state.

In conclusion, high resolution resonant Auger spectroscopy following the B $1s \rightarrow 2a_2''$ excitation of BF_3 allows us to point out a new effect, specific of polyatomic molecules: the observation of dispersive/nondispersive lines as issued from participator/spectator states. It has been interpreted in terms of bound/unbound shape of the relevant potential curves of the ions along the $Q_{a_2''}$ coordinate, as shown by theoretical calculations. The tail in the participator Auger spectrum is ascribed to a dynamical Auger emission which illustrates the survival of the core-excited state against wave packet motion along the ion potential surface. It is thus shown that resonant Auger spectroscopy provides direct information not only on potential surfaces but also on nuclear dynamics.

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