

Nuclear motion of a core-excited BF_3 molecule probed by subnatural-linewidth resonant Auger electron spectroscopy

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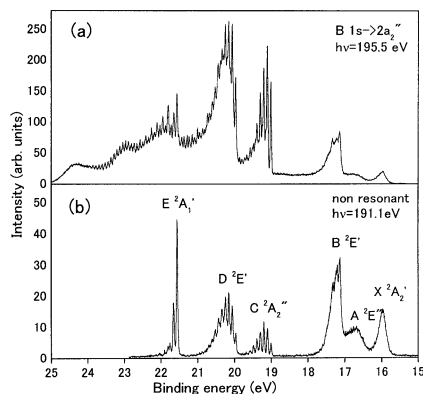
The boron trifluoride molecule BF_3 is a planar molecule of D_{3h} symmetry. When a B $1s$ electron is excited to the lowest unoccupied molecular orbital $2a_2''$, the molecule is expected to start deformation into trigonal pyramidal structure in C_{3v} symmetry. Molecular dissociation measurements indeed suggested that the deformation proceeded in the core-excited state.^{1,2} In the present study we have probed out-of-plane nuclear motion for the deformation of the core-excited state by means of resonant Auger spectroscopy.

First we have observed the B $1s \rightarrow 2a_2''$ excitation spectrum at the highest resolution (~ 20 meV band width) ever achieved. The spectrum exhibits a prominent peak whose width is broader (~ 250 meV) than the widths of other lines (~ 77 meV). This implies that the peak consists of more than one vibrational progressions that are not resolved owing to the lifetime width being larger than the vibrational separations. Thus one cannot confirm the out-of-plane motion in the excitation spectrum.

Note that the resonant Auger spectrum also includes the information of the nuclear motion in the core-excited state because the resonant Auger decay takes place along with this nuclear motion. We have recorded the resonant Auger spectrum at the B $1s \rightarrow 2a_2''$ excitation, with a high-resolution electron energy analyzer SES-2002 (Gammadata-Scienta), under the sub-natural-linewidth conditions, i.e. with the overall widths (~ 30 meV) smaller than the lifetime widths of the core-excited states (~ 60 meV). The spectrum (b) in Figure 1 is the direct photoemission

from the six valence orbitals in BF_3 , whereas spectrum (a) is recorded at the B $1s \rightarrow 2a_2''$ resonance. The electron emission for the C, D, and E bands is strongly enhanced by the B $1s \rightarrow 2a_2''$ excitation, suggesting that the participator Auger decay takes place. In the resonant enhanced spectrum, one can see long progressions of the out-of-plane vibrations. The highly excited out-of-plane vibrations in the Auger-final states are direct reflection of the highly excited out-of-plane vibrations in the core-excited state.

Figure 1. Valence-electron spectra of BF_3 (a) after



excitation of the B $1s \rightarrow 2a_2''$ state and (b) direct photoemission.

1. Simon *et al.* Chem. Phys. Lett. **238**, 42 (1995).
2. Ueda *et al.* Phys. Rev. A **52**, R1815 (1995).

Vibronic coupling in the core-excited states in BF_3 and BCl_3 molecules probed by the ultrahigh-resolution angle-resolved ion yield spectroscopy

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Boron trifluoride (BF_3) and trichloride (BCl_3) have been used as boron sources for the chemical vapor deposition (CVD) of thin films including boron-doped silicon. Both electron beam and X-ray irradiation can be employed to provide the selective area processing. Monochromatic irradiation in the region of B $1s$ excitation may give additional selectivity in the photochemical deposition (see for example [1]). Characterization of the initially formed excited states is crucial for elucidation of the deposition mechanisms, from the initial absorption through bond breaking to the formation of thin films.

BF_3 and BCl_3 are highly symmetrical polyatomic molecules that belong to the D_{3h} point group, and the angle-resolved ion-yield measurement comes into play for identification of the core-excited states. Thus, in the present study we have investigated the angular distribution of the fragment ions ejected after B $1s$ excitation of BF_3 and BCl_3 molecules to probe the nuclear motion in the core-excited states, i.e., vibronic coupling.

The experiments were performed on the c branch of the soft X-ray photochemistry beamline BL27SU at SPring-8. Using a pair of energetic ion detectors of retarding potential type mounted in the direction parallel (0°) and perpendicular (90°) to the polarization vector, we measured yield curves of energetic ions (with $KE \geq 6.4$ eV). We also measured the total ion yield (TIY) curve simultaneously.

The dipole-allowed transitions are $A_1' \rightarrow$

A_2'' and $A_1' \rightarrow E'$. "Symmetry-resolved" yield spectra were obtained according to the procedure described in Ref. [2]. Figure 1 shows the total and symmetry-resolved ion yield spectra of BF_3 in the B $1s$ excitation region. The prominent peak observed at 195.5 eV has been assigned to the B $1s \rightarrow 2a_2''$ transition. We can clearly see the e' symmetry component as well as the $2a_2''$ component contributes to this peak. The lowering of symmetry arises from a molecular deformation by the excitation into the $2a_2''$ state. As shown in the inset of Fig. 1, two small bands can be observed in the region 198–201 eV. The band at 198.2 eV stems from the $3sa_1'$ transition, which is dipole-forbidden transition and occurs as a result of the vibronic coupling with the $2a_2''$ state. The analysis is in progress and the further results will be presented elsewhere.

- 1) R. A. Rosenberg *et al.*, *Appl. Phys. Lett.* **58**, 607 (1991).
- 2) Y. Shimizu *et al.*, *J. Chem. Phys.* **107**, 2415 (1997).

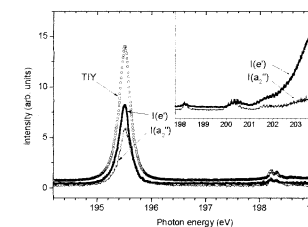


Figure 1: Total and symmetry-resolved yield spectra of photofragment ions of BF_3 in the B $1s$ excitation region.