

Nuclear Motion of Polyatomic Molecules Probed by High-resolution Resonant Auger Spectroscopy

When an inner-shell electron of an atom composing a molecule is promoted to an unoccupied molecular orbital, a resonant Auger decay takes place on a femtosecond time scale. Within this short time scale, however, nuclear motion can proceed in the core-excited state. Nuclear motion in a polyatomic molecule is of particular interest because multi-dimensional nuclear motion may be mediated by core excitation. The nuclear motion caused in the core-excited state then mediates nuclear motion in the Auger final states and thus may govern dissociation pathways.

The nuclear motion in the core-excited state proceeds in competition with the resonant Auger decay and thus should be reflected in the resonant Auger spectrum. To probe the nuclear motion in the core-excited state as well as in the Auger final state in the resonant Auger spectra, we installed a high-resolution electron spectroscopy apparatus on beamline **BL27SU** [1]. The apparatus consists of a state-of-the-art SES2002 electron energy analyzer (Gammadata-Scienta), a gas cell, and a differentially pumped experimental chamber, and allows us to observe the resonant Auger spectra of gaseous molecules with an unprecedented resolution when they are combined with a high-resolution soft X-ray monochromator at BL27SU [2].

We present here two typical showcases of our observations; the resonant Auger spectra of the boron trifluoride molecule BF_3 [3] and those of the water molecule H_2O [4].

The BF_3 molecule in the ground state has a planar structure of D_{3h} symmetry, whereas it has trigonal pyramidal structure of C_{3v} symmetry in the core-excited state in which a B 1s electron is promoted to the lowest

unoccupied molecular orbital $2a_2''$. We probed out-of-plane nuclear motion for the deformation from D_{3h} to C_{3v} following the core excitation, by means of resonant Auger spectroscopy.

The spectrum (b) in Fig. 1 represents the direct photoemission from the six valence orbitals in BF_3 , whereas the 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 resonantly enhanced spectrum, one can see long progressions of out-of-plane vibrations in the Auger final states. The highly excited out-of-plane vibrations are a direct reflection of the out-of-plane nuclear motion in the core-excited state.

The H_2O molecule has a bent structure of C_{2v} symmetry. The two lowest unoccupied molecular orbitals $4a_1$ and $2b_2$ are the antibonding counterparts of the two OH bonding orbitals $3a_1$ and $1b_2$. The O $1s^{-1} 4a_1$ core-excited state is known to be dissociative, whereas the O $1s^{-1} 2b_2$ core-excited state has a shallow potential minimum so that the vibrational structure can be seen in the O $1s \rightarrow 2b_2$ resonance [5]. We demonstrated that one can control the two-dimensional nuclear motion of the Auger final state by changing the nuclear

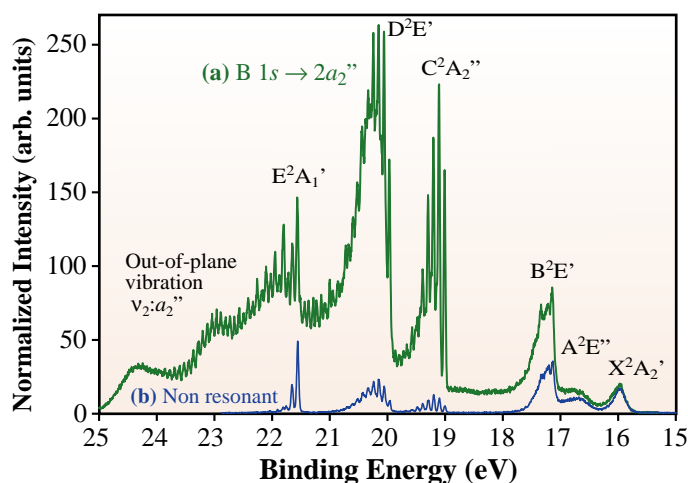


Fig. 1. Valence-electron spectra of BF_3 (a) after excitation of the B $1s^{-1}2a_2''$ state and (b) direct photoemission.

motion in the $O\ 1s^{-1}\ 2b_2$ core-excited state.

The electron spectra recorded at four photon energies across the $O\ 1s \rightarrow 2b_2$ resonance are presented in Fig. 2. Here the largest contribution to the spectral width comes from the Doppler width due to the thermal motion of the sample molecules. The spectra cover the binding energy region 17.0–20.0 eV, where the electron emission from the $1b_2$ orbital is present. The bottom spectrum (a) represents the direct photoemission spectrum, whereas the other three spectra (b), (c), and (d) are recorded approximately at the energies of the $(\nu_1, \nu_2) = (0,0)$, $(1,0)$ and $(2, 0)$ vibrational components, respectively, of the $O\ 1s \rightarrow 2b_2$ band. When the Auger final state is populated via the $O\ 1s \rightarrow 2b_2$ $(0,0)$ excitation (spectrum (b)), the vibrational structure of the ν_2 mode with spacing of ~ 200 meV is partially resolved. The vibrational structure, however, becomes less resolved at the $O\ 1s \rightarrow 2b_2$ $(1,0)$ and $(2,0)$ excitations (spectra (c) and (d)). To discover the reason for this, we carried out *ab initio* calculations. The results show reasonable agreement with the experimental spectra as can be seen in Fig. 2. It is clear from the *ab initio* spectra that more and more vibrational components with a mixture of the ν_1 and ν_2 modes are populated with the increase in the excitation energy. In this way we confirm that it is possible to control the two-dimensional nuclear motion in the $1b_2^{-1}$ Auger final state by tuning the incident energy to different portions of the $O\ 1s^{-1}\ 2b_2$ core-excited state.

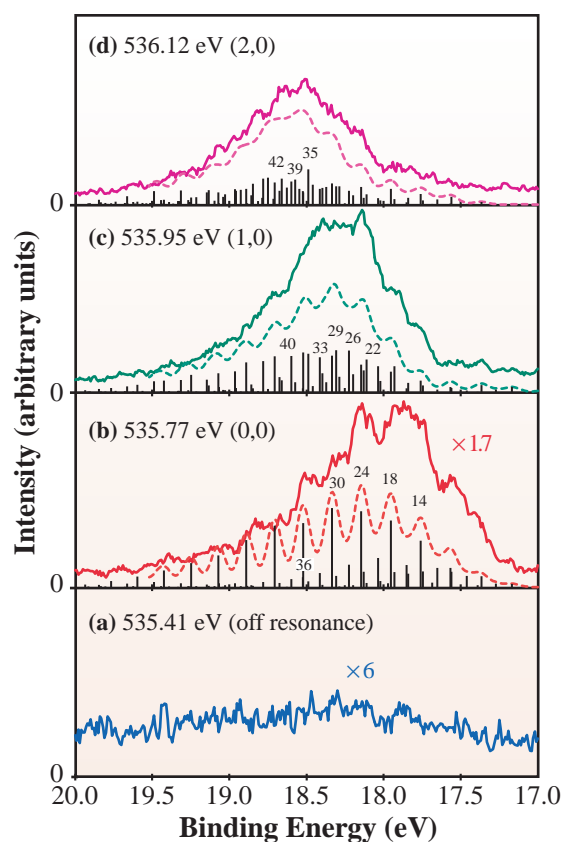


Fig. 2. Measured and calculated resonant Auger spectra of H_2O decay to the $1b_2^{-1}$ Auger final state at various excitation energies across the $O\ 1s \rightarrow 2b_2$ band, continuous and dashed lines. The calculated vibrational components are represented by vertical bars.

References

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