Bond-length-dependent core-hole localization

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Polyatomic symmetric molecules may have their symmetry broken when they are core excited. Symmetry breaking occurs because asymmetric vibrations can couple near-degenerate, core-excited states of different symmetry. In resonant soft x-ray emission spectroscopy (SXES), also known as resonant inelastic x-ray scattering (RIXS), this coupling and the accompanying core-hole localization lead to the appearance of "forbidden" transitions. In our experiments at the ALS, RIXS spectra from acetylene, ethylene, and ethane molecules show that the amount of symmetry breaking, and thus dynamic vibronic coupling, in a core-excited molecule is bond-length dependent [1].

Resonant SXES is based on a two-photon scattering process: an incoming x-ray photon excites a core electron, which results in a transition to an intermediate core-excited state. The intermediate state then decays by emission of an x-ray photon to a final valence-excited state or to the electronic ground state. The resonant SXE spectra were recorded at Beamline 7.0.1 with a grating spectrometer. Owing to the low fluorescence yield in this energy range and the low density of gas-phase targets as compared to that of solid samples, the high brightness of the ALS and the good focus of Beamline 7.0.1 were necessary for carrying out these experiments.

Figures 1, 2, and 3 show absorption spectra and resonant and nonresonant SXE spectra for acetylene, ethylene, and ethane, respectively. For acetylene (Figure 1a) the excitation was to the unoccupied $1\pi_g$ orbital. If the parity selection rule were strictly valid, only dexcitations from gerade (g) valence orbitals would be seen. In the emission spectrum, however, both the allowed transition from the $3\sigma_g$ and the forbidden transition from the $1\pi_u$ orbitals are seen. However, the relative intensity of the forbidden transition is greatly reduced , as compared to that in the nonresonant spectrum in Figure 1e, showing that the selection rule is still partially valid. The same is true for the spectra in Figures 1b–d.

For ethane, on the other hand, Figure 3 shows that the relative intensities of gerade and ungerade (u) transitions in all spectra are practically the same as in the nonresonant case, so the selection rule is broken. Figure 3a is an exception, since the forbidden transitions are reduced. In this case, the excitation energy was detuned below the first absorption resonance. As we have shown previously, detuning leads to a quenching of the symmetry breaking [5]. The spectra of ethylene in Figure 2 are more complicated than those of acetylene and ethane, representing an intermediate case between large symmetry conservation and large symmetry breaking.

In summary, the large suppression of the forbidden peaks in the resonant acetylene spectra, as compared to those in the nonresonant spectrum, indicates that symmetry is preserved to a large degree, whereas the ethane spectra show almost complete symmetry breaking. The different behavior is due to the different bond lengths. A shorter bond length means a larger energy splitting between the gerade and ungerade core orbitals, which in turn gives a smaller vibronic coupling and less symmetry breaking [6]. The energy splittings for acetylene (shorter bond length) and ethane (longer bond length) differ by an order of magnitude, which is why the effect can be seen so clearly.

This is one example of how the symmetry selectivity of resonant SXES can be used to study the behaviour of molecules during the x-ray scattering process. It can be used in a similar way to study the electronic structure and the dynamics of the scattering process in other situations.
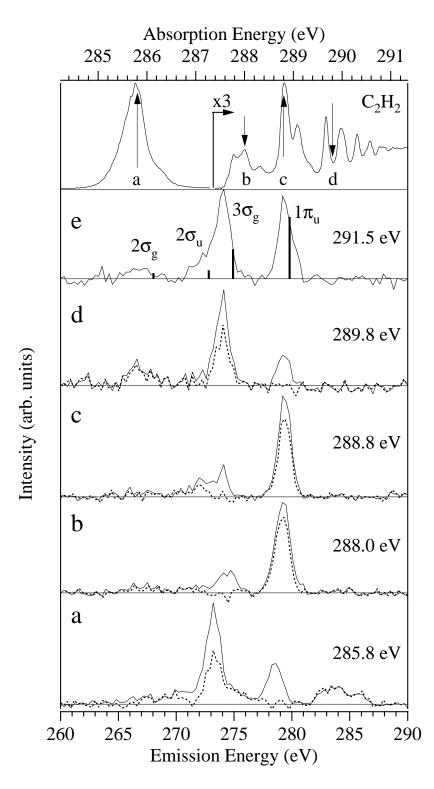

Figure 1. Absorption, resonant SXE, and nonresonant SXE spectra of C_2H_2. (top) Absorption spectrum from Ref. [2]. Spectra (a–e) Emission spectra recorded at the excitation energies marked by arrows in the top panel. The transitions are labelled by the valence orbital from which the deexcitation takes place.
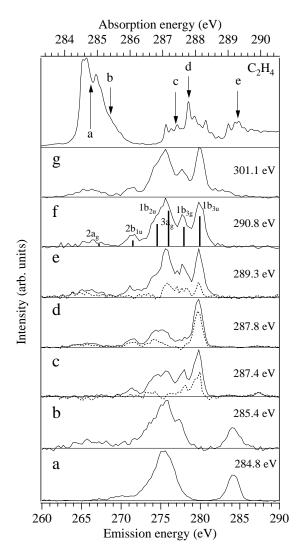
Figure 2. Absorption, resonant SXE, and nonresonant SXE spectra of C_2H_4. (top) Absorption spectrum from Ref. [3]. Spectra (a–g) As in Figure 1.
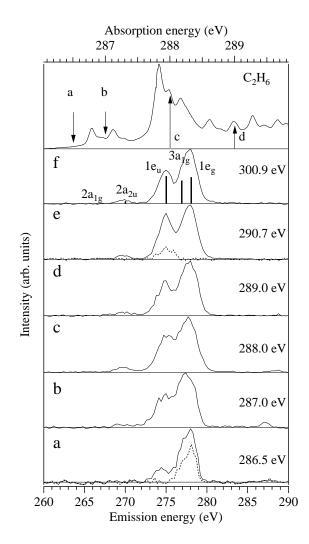

Figure 3. Absorption, resonant SXE, and nonresonant SXE spectra of C_2H_6. (top) Absorption spectrum from Ref. [4]. Spectra (a–f) As in Figure 1.

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