Probing symmetry breaking upon core excitation with resonant x-ray fluorescence

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Resonantly excited x-ray fluorescence spectra of the benzene molecule are presented and analyzed in terms of symmetry-selective resonant scattering processes. The sharp frequency dependency that is observed can be understood from strict parity and symmetry-selection rules operating in the full D_{6h} point group symmetry. The experimental results prove that the electronic symmetry is not broken for the lowest unoccupied level involved in the resonant x-ray emission process.

During the development of high-resolution core-electron spectroscopies there has been an ongoing discussion on the possibility of core hole state symmetry breaking and core hole localization. Arguments have been put forward on a theoretical or on a computational basis, many of them resting on localization and instabilities of Hartree-Fock or of other electronic structure methods [1–8]. Although it is an accepted fact that without additional interactions, such as vibronic coupling, the symmetry must be restored for the exact electronic core hole state wave function, direct experimental evidence has been lacking to prove just that. The introduction of high-brightness synchrotron radiation sources has opened new possibilities to measure *resonant* core-electron spectra [5] and thereby reach conclusions on this issue by purely experimental means. Resonant x-ray emission provides such a possibility because the dipole character of the absorption and emission leads to simple selection rules also for the full scattering process [4].

The resonant x-ray emission processes can be represented as

$$A + \hbar\omega \rightarrow A(k^{-1}\nu) \rightarrow A(n^{-1}\nu) + \hbar\omega', \qquad (1)$$

where indices k, n, and ν denote levels defined by core, occupied, and unoccupied molecular orbitals, respectively; ω and ω' are the frequencies of incoming and emission photons. $A(k^{-1}\nu)$ denotes the core-excited state, in which an electron from the core orbital k has been selectively excited to the unoccupied orbital ν following the dipole selection rule. $A(n^{-1}\nu)$ is the optical excited state, where the core hole k^{-1} has been filled by electrons from the valence orbitals n through the emission process. It can easily be understood that the x-ray emission process provides a direct probing tool to detect the symmetry of the core-excited state $A(k^{-1}\nu)$ by applying strict dipole selection rules. These can be obtained in a one-step formulation [4] of the process or in a two-step picture [6] where the dipole selection rules of absorption and emission steps are combined. For instance, if electrons from core orbital k with parity g have been excited into an unoccupied orbital with parity u, only those valence orbitals with parity u can be observed in the x-ray emission spectrum when the symmetry is not broken. A direct experimental observation of symmetry breaking can thus be obtained by recording x-ray fluorescence spectra where the individual core-excited states are resonantly excited.

In this paper we present the resonant x-ray emission spectrum (RIXS) of benzene. We focus first on those transitions, the energies of which are *experimentally* known, by combining observed x-ray absorption (XAS) and optical excitation (OPT) energies through the relation

$$E_{RIXS} = E_{XAS} - E_{OPT}. \qquad (2)$$

For the lowest core-excited level involving the $1e_{2u}$ orbital we find that the D_{6h} symmetry selection rules are obeyed without symmetry breaking. In the last part of the paper we present simulations that also analyze the nonresonant spectrum and those higher-lying resonant spectra that cannot be derived by relation 2 because of the lack of experimental data.

The experiments were performed at beamline 7.0 of the Advanced Light Source, Lawrence Berkeley Laboratory [9]. This beamline comprises a 5-m, 5-cm-period undulator and a 10.000-resolving-power spherical grating monochromator covering the spectral range from 100 to 1300 eV.

Condensed benzene was obtained by dosing the sample gas onto a liquid-nitrogen-cooled copper surface. The sample was purified by a freeze-pump sequence prior to exposure. The dosing was performed at a pressure of 1×10^{-6} mbar, as measured with the system's ion gauge, at a base pressure of 5×10^{-9} mbar for about 10 min by using a nozzle placed about 10 mm from the cooled copper surface. The temperature of the substrate was about $-160\,°C$ during the whole experiment and the obtained benzene film was very thick, as inferred from its visible color. The film only appeared close to the nozzle, indicating a higher local dosing pressure there than mentioned above. The soft-x-ray fluorescence was recorded in the polarization plane and was normal to the inci-
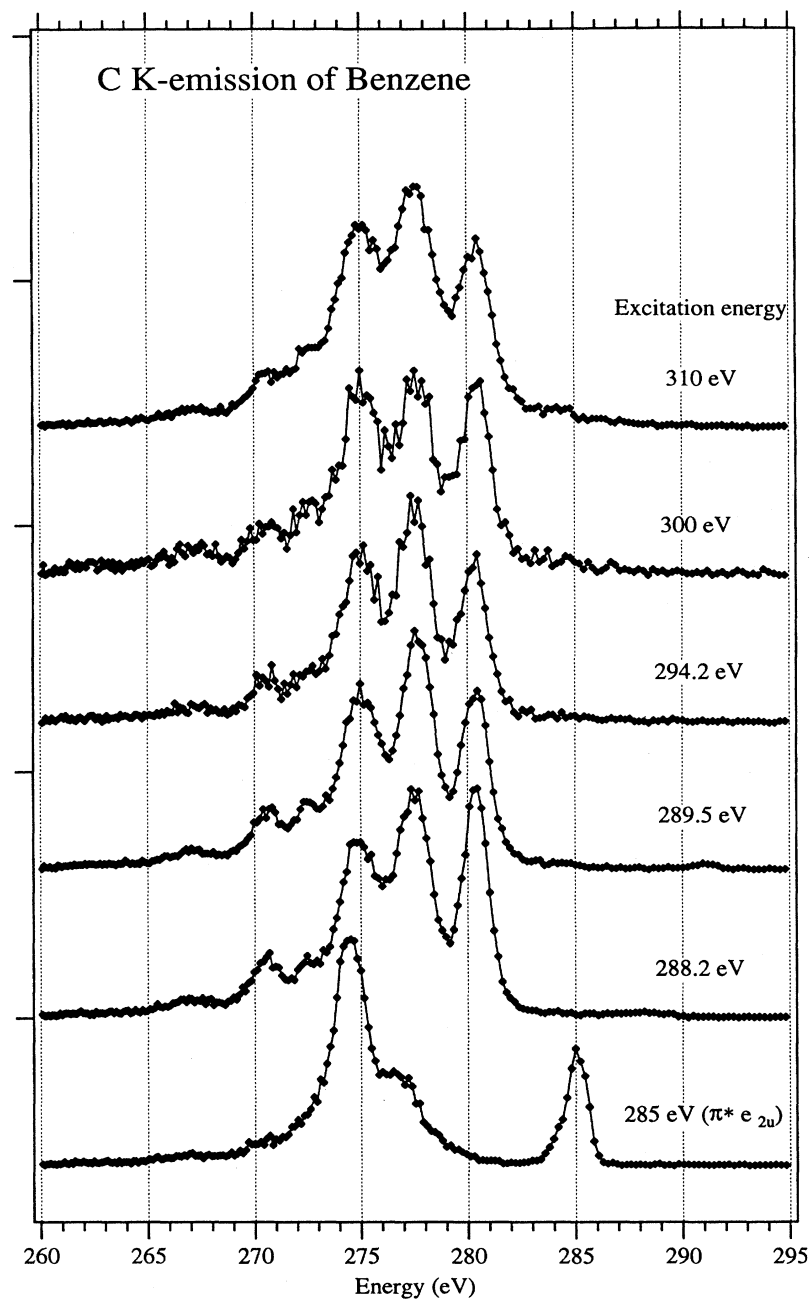
FIG. 1. Resonant x-ray emission spectra of benzene recorded at various resonance absorption peak energies.

dent photon beam, using a high-resolution grazing-incidence grating spectrometer with a two-dimensional detector [10]. The sample was oriented so that the incident photon beam impinged at an angle of 60° relative to the surface normal, in order to suppress effects due to self-absorption. The band-pass of the incident photon beam was set to 0.22 eV in the emission measurements, and the fluorescence spectrometer resolution was 0.45 eV. The energy scale of the x-ray emission spectra was calibrated by using the elastic peak and copper metal $L_{II,III}$ emission lines recorded in the third order of diffraction.

Figure 1 presents the resonant x-ray emission spectra of benzene together with the nonresonant x-ray emission spectrum. The resonant spectra correspond to excitation energies for which resonances are observed in the x-ray absorption spectrum [11,12]. The latter spectrum is heavily dominated by absorption at 285 eV to the first unoccupied MO of e_{2u} symmetry [12]. The other absorption resonances are much
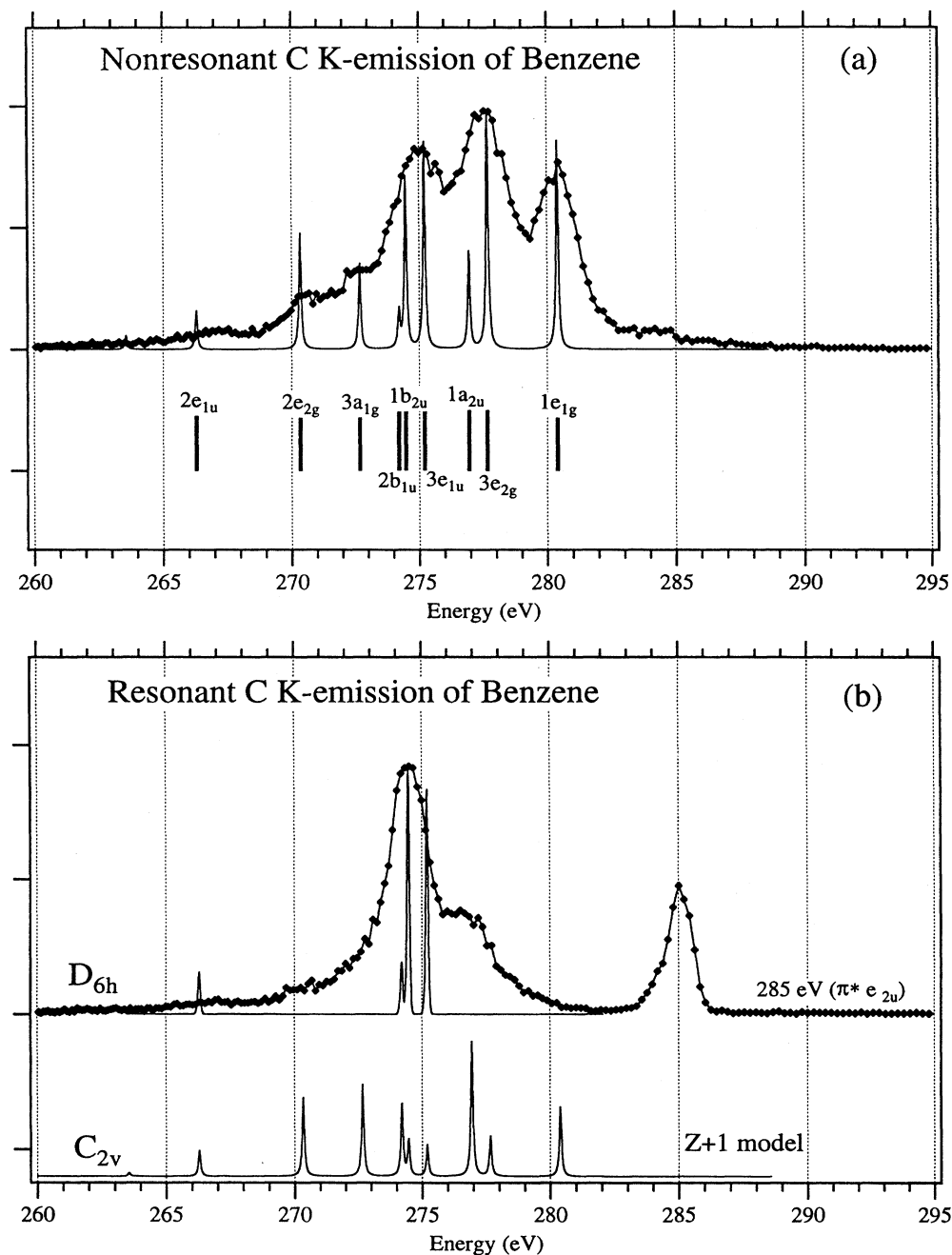
FIG. 2. A comparison between simulated and experimental spectra of benzene. Computed spectra inserted as narrow bands (determined only by the core-excited-state lifetime of $\Gamma = 0.15$ eV and the linewidth of incoming photons, $\gamma = 0.05$ eV). (a) Nonresonant x-ray emission. Bottom panel gives a molecular-orbital assignment. (b) Lowest unoccupied molecular-orbital resonant x-ray emission spectrum. Top panel shows simulations within D_{6h} restricted symmetry; bottom panel, within the C_{2v} broken symmetry, using a $Z+1$ model.

weaker and apparently well separated in energy from this absorption feature. This is in accordance with the fact that the elastic peak is represented strongly only in the 285-eV fluorescence spectrum; see Fig. 1. It is also seen that the inelastic resonant x-ray emission spectrum excited at 285 eV is quite different from spectra generated at higher absorption resonances.

Out of the four core orbitals of benzene, $1a_{1g}$, $1e_{1u}$, $1e_{2g}$, and $1b_{2u}$, only one, the $1e_{2g}$ orbital, can connect through the dipole operator with the $1e_{2u}$ level that corresponds to the first core-excited resonance at 285 eV. If this core-excited state maintains the same symmetry as the ground state (D_{6h}), the dipole character of the soft-x-ray emission selects electrons exclusively from valence orbitals

with symmetries b_{1u}, b_{2u}, e_{1u}, and e_{2u} to fill the $1e_{2g}^{-1}$ core hole. All orbitals with parity g would be unobservable in the emission spectrum. The highest occupied molecular orbital of benzene is the $1e_{1g}$ orbital [13,14]. Using experimental data for the vertical x-ray [12] and optical [15] absorption energies, we place the resonant x-ray band(s) $1e_{2g}^{-1}1e_{2u}^{1}\rightarrow 1e_{1g}^{-1}1e_{2u}^{1}$ in the 2 eV interval of 278–280 eV (corresponding to the $1e_{1g}^{-1}1e_{2u}^{1}$ configuration states $^{1}B_{2u}$, $^{1}B_{1u}$, and $^{1}E_{1u}$ of the optically excited benzene molecule [15]). However, as seen in Fig. 1, no intensity is observed in this energy interval. The corresponding transitions are allowed in the C_{2v} broken symmetry representation (and indeed emerge strongly in the simulated C_{2v} spectrum; see below). Full D_{6h} symmetry is thus preserved in the 285-eV resonant x-ray emission spectrum, and the notation of a symmetry-restricted core-excited state must be retained. This is an experimental verification of symmetry restriction in a spectroscopic process involving core electrons at symmetry related atoms.

Other features of the presented spectra are examined by means of simulations. These are based on a frozen-orbital one-particle description of the RIXS process and have been successively employed before, even for systems as large as C_{60} [7] and C_{70} [8]; the full results for benzene and for substituted benzenes will be published elsewhere [16]. The present analysis is restricted to the pure resonant inelastic part of the scattering process. It assumes randomly oriented benzene molecules and detection and polarization directions as described above.

The nonresonant spectrum serves as a high-energy convergence limit for the resonant spectra. The energies of this spectrum are given by experimental energies as shown by Eq. (2) when replacing E_{OPT} by the valence photoelectron energies [13,14]. The simulation of the nonresonant spectrum serves, therefore, as a calibration for benzene of the employed method. As seen in Fig. 2 the features are well reproduced by the simulations. The six bands observed in the nonresonant spectrum at 280.4, 277.5, 275, 273.7, 270.3, and 266.3 eV can thus be assigned to x-ray transitions involving the $1e_{1g}$, $3e_{2g}+1a_{2u}$, $3e_{1u}+1b_{2u}+2b_{1u}$, $3a_{1g}$, $2e_{2g}$, and $2e_{1u}$ orbitals, respectively, following also the experimental ultraviolet photoemission spectroscopy assignments [13,14]. The latter two bands are weak because of the $2s$ character of the corresponding molecular orbitals and presumably also because of the breakdown of the molecular-orbital picture with accompanying correlation state splittings [14].

Having established the interpretation of the nonresonant spectra, we simulate the 285-eV resonance x-ray emission spectrum in the symmetry-broken, localized (C_{2v}), and symmetry-restricted (D_{6h}) representations. The resonant x-ray emission spectrum should in general be treated in a one-step model; however, for the case presented here, the two-step model gives the same conclusions (the differences between one-step and two-step models have been discussed analytically and numerically in detail in Ref. [17]). The results, shown in Fig. 2, together with the corresponding experimental spectrum, strongly support the experimental evidence of symmetry restriction in the 285-eV spectrum; the 2-eV interval of 278–280 eV receives significant intensity in the C_{2v} simulations (these are performed by means of the

$Z+1$ approximation), so much so, in fact, as to make the 285-eV spectrum look very much like the nonresonant spectrum. This actually also follows from simple symmetry considerations. In the C_{2v} point group, the core orbital has symmetry a_1, and the $1e_{1g}$ orbital is split into a_2 and b_1 orbitals, the latter connecting with the core a_1 orbital. Full localization and symmetry breaking will give nonresonantlike frequency-independent RIXS spectra, in clear contrast to what is observed in Fig. 2.

The resonant x-ray emission spectrum excited at 285 eV simulated in D_{6h} symmetry is also shown in Fig. 2. The main feature at 275 eV of the experimental spectrum receives contributions from the $3e_{1u}+1b_{2u}+2b_{1u}$ orbitals. A conspicuous feature of the resonant x-ray emission spectrum recorded at 285-eV excitation is the high-energy shoulder around 277 eV. This shoulder is located close to, but slightly redshifted from, the forbidden a_{2u} and e_{2g} transitions, as predicted by the calculations. One possible explanation for this incoherent contribution to the resonant x-ray emission spectrum is that vibronic coupling effects introduce small admixtures of electronically symmetry-forbidden transitions (here a_{2u} and e_{2g}) in the resonant x-ray emission spectrum.

One observes that resonant x-ray emission spectra recorded at photon energies of 288.2 eV and up are quite nonresonantlike. These excitation energies refer to the second and higher features in the absorption spectrum [12] and are all associated with close-lying resonance levels. Strict electronic symmetry selection for the resonant x-ray emission process also predicts different appearances of the spectra referring to this composite molecular-orbital region [4]. The similarity of these spectra and the nonresonant spectrum must be seen as effects of "tail excitation" (a delicate matching between the excitation photon function and the widths and spacings of close-lying resonance levels) and of vibronic coupling. Both these effects originate in the close proximity of states in this region. It is well known that vibronic interaction, the so-called pseudo-Jahn-Teller effects, operate for core hole states of molecules containing an element of symmetry, the antisymmetric coupling of the gerade and ungerade O $1s^{-1}$ states of CO_2 being the most conspicuous example [18]. However, the question of whether this interaction causes a real electronic localization presents an elaborate dynamic problem [19] and lies beyond the scope of the present paper.

In conclusion, using benzene we have demonstrated the symmetry-selective character of resonant x-ray emission and indicated that this spectroscopy is potentially rich for electronic structure investigations. We have given experimental evidence of a case, namely, the lowest core-excited, $1e_{2u}$, level of the benzene molecule, when this symmetry selectivity is enforced in the full, nonbroken, point-group symmetry of the molecule. The corresponding resonant x-ray fluorescence spectra can only be understood by assuming delocalized core electrons and electronically delocalized core hole states. It was pointed out that in the symmetry-broken, localized representation, the fluorescence spectra become completely frequency independent, in clear contrast to the experimental observation for benzene. It was shown that fluorescence spectra referring to higher resonant levels are quite nonresonantlike.

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