

Bond-Length-Dependent Core Hole Localization Observed in Simple Hydrocarbons

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Soft x-ray-emission spectroscopy is applied to measure the amount of dynamic symmetry breaking in core-excited acetylene, ethylene, and ethane. Large variations are observed between the molecules and are rationalized in terms of the different C-C bond lengths: Shorter bond lengths give smaller symmetry breaking. The results also indicate that asymmetric modes are important for all the systems studied, in contradiction to previous assumptions in literature.

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Resonant soft x-ray-emission spectroscopy (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 decays by emission of an x-ray photon to a final, valence-excited state (spectator transition) or to the electronic ground state (participator transition). For homonuclear diatomics these electronic transitions are parity selective; i.e., the electron filling the core hole must originate from an orbital of the same parity as the one to which the core electron was promoted, in the ultrasoft x-ray range, as firmly proven by measurements on O₂ and N₂ [1,2]. However, measurements on polyatomic molecules have shown that the dipole selection rules based on symmetries of the involved *electronic* states can break down [3]. Symmetry breaking occurs when nontotally symmetric vibrational modes couple near-degenerate allowed and forbidden excited electronic states of different symmetry [4]. Such coupling perturbs the line shape or fine structure observed in x-ray absorption and photoelectron spectra [5–11]. In soft x-ray emission this coupling and the accompanying core-hole localization leads to the appearance of “forbidden” transitions [3,12]. This makes SXES a powerful method for detecting and even quantifying vibronic coupling and symmetry breaking. In this paper we demonstrate this by analyzing soft x-ray emission spectra from three hydrocarbon molecules: acetylene, ethylene, and ethane.

The experiments were performed at the Advanced Light Source in Berkeley, California, using the undulator beam line 7.0 [13]. A description of the SXES grating spectrometer can be found in Refs. [14,15] and of the experimental setup, e.g., in Refs. [1–3]. The spectrometer contributes around 0.4 eV at FWHM to the width of the peaks in the spectra. The bandpass of the synchrotron beam was about 0.2 eV at FWHM. The spectrometer was mounted parallel to the polarization vector of the synchrotron light.

Emission spectra from C₂H₂, C₂H₄, and C₂H₆ are shown in Figs. 1–3. An obvious trend is observed going from

acetylene to ethane. The acetylene spectra are strongly dependent on the excitation energy, with the relative intensities of the peaks changing in a systematic manner. Ethylene also shows quite large intensity variations; however, the changes are more complex in this case. In contrast, all the ethane spectra, with the exception of the spectrum in Fig. 3a, are very similar.

The role of the C-C bond length in the C₂H₂, C₂H₄, C₂H₆ series can be analyzed considering the dimensionless vibronic coupling (VC) parameter

$$\lambda = \frac{\langle u|U'|g\rangle}{\Delta E} \sim e^{R_e/2a}, \quad (1)$$

upon which the amount of symmetry breaking or the degree of core-hole localization is dependent. Here $|u\rangle$ and $|g\rangle$ are the nearly degenerate symmetry related core orbitals with energies ϵ_u and ϵ_g , respectively. $\Delta E = \epsilon_u - \epsilon_g$ and $U' = (\partial U/\partial Q_u)_0$ with U being the VC operator and Q_u the normal coordinate. The denominator of the expression for λ contains the small energy difference of the core orbitals which depends exponentially on the separation R_e of the carbons and on the spatial extent a of the core orbitals. Slow variations with bond length in the numerator in Eq. (1) can be neglected. Qualitatively this can be understood by considering the fact that the numerator depends on the potential surfaces, which vary appreciably only over a distance of at least the size of an atom, whereas the denominator is sensitive to changes of the size of the $1s$ orbital. This simple expression thus predicts that a single bonded species like ethane, which has a comparatively long bond distance, is more likely to break symmetry than a triple bonded species like acetylene, with a smaller bond distance, and that oxygen containing symmetric molecules are more likely to break symmetry than carbon containing ones of the same size. The same conclusion is reached in [23], where the connection between core-hole localization and bond length is discussed. For C₂H₂, C₂H₄, and C₂H₆, R_e and ΔE are 1.208, 1.339, and 1.536    [24], and 0.1084, 0.0449, and

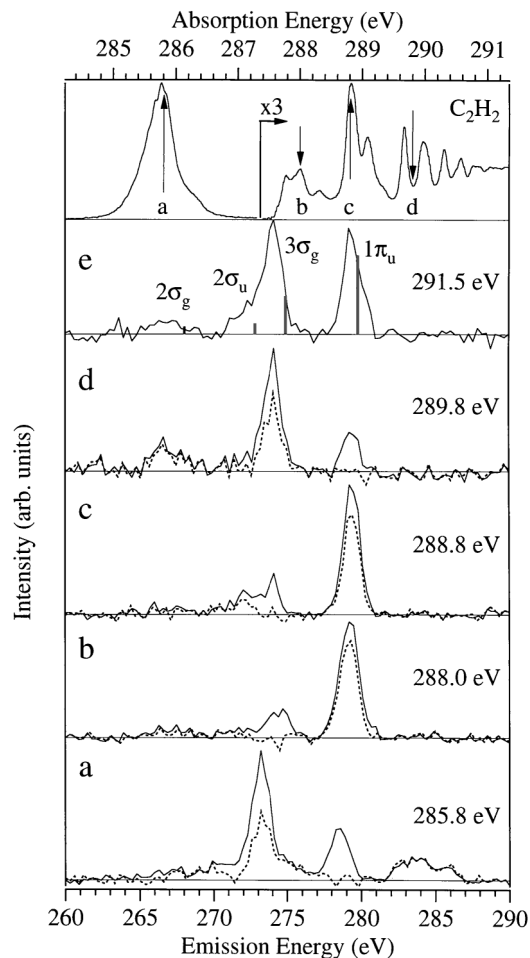


FIG. 1. C_2H_2 . (top) Absorption spectrum from Ref. [8]. [(a)–(e)] Full lines: Emission spectra recorded at the excitation energies marked by arrows in the top panel. The transitions are labeled by the valence orbital from which the deexcitation takes place. Dotted lines: Difference spectra obtained as described in the text. The bars in the nonresonant spectrum (e) are determined by intensities obtained from Hartree-Fock calculations and vertical energies obtained from photoelectron spectra [16–18].

0.0161 eV, respectively. ΔE was obtained from Hartree-Fock calculations. An experimental value of 0.105 eV for acetylene is given in Ref. [9]. This shows that ΔE differs by as much as an order of magnitude due to the different C-C bond lengths for the three molecules.

In the case of complete symmetry breaking (and with neglect of screening and polarization effects [25]), the relative intensities in the resonant spectra are the same as in the nonresonant spectra, for which the excitation is to the ionization continuum and the parity selection rule does not normally affect the spectra [2,26]. However, in many cases the symmetry breaking is only partial, with peaks of “correct” symmetry still being relatively more intense. To characterize quantitatively the symmetry breaking we assume that the experimental spectrum differs from the “ideal” spectrum with strict selection rules only because of VC. The intensity difference $\Delta I = I_R - kI_{NR}$ between

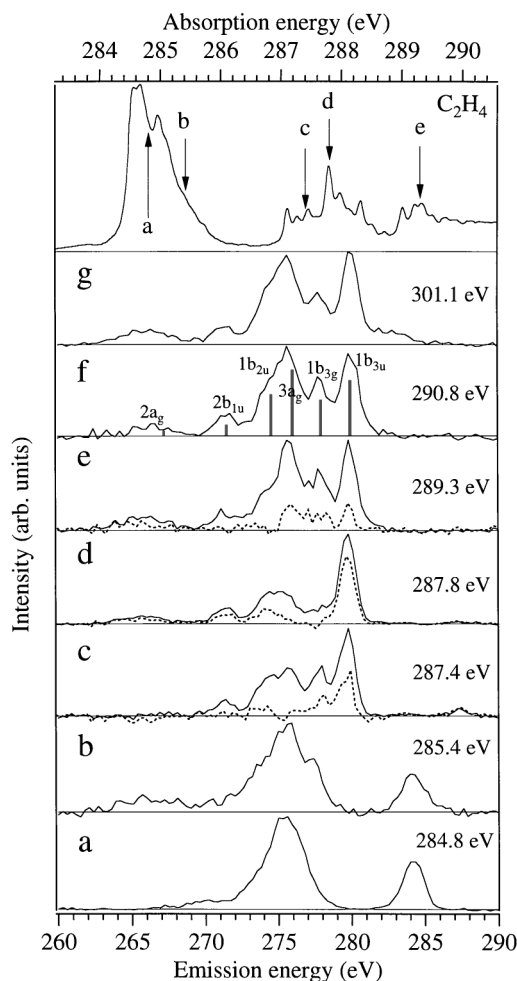


FIG. 2. C_2H_4 . (top) Absorption spectrum from Ref. [6]. [(a)–(g)] As in Fig. 1. Experimental energies for the calculated intensities from [19,20].

normalized resonant and nonresonant spectra, with the appropriate factor k , gives the symmetry preserved part of the spectrum. The coefficient k is maximized under the constraint that the difference spectrum should not contain any negative features. The factor k gives a measure of the symmetry breaking and $1 - k$ the “purity” of the resonant spectrum.

The procedure devised above can become problematic for excitations to a valencelike level (often the first unoccupied level only) since the energies and intensities of the emission peaks may then be strongly affected by the spectator electron due to screening. Electrons in Rydberg orbitals, on the other hand, give only small screening effects. Care must still be taken when Rydberg resonances of different parities overlap since the symmetry selectivity of the core excitation may then be lost.

Absorption spectra [5,6,8,9], with arrows indicating the energy positions at which emission spectra were recorded, are shown in the top panels of Figs. 1–3. Assignments of the absorption features are listed in Table I. Resonant and nonresonant emission spectra are shown below the absorption spectra. In the nonresonant emission spectra in

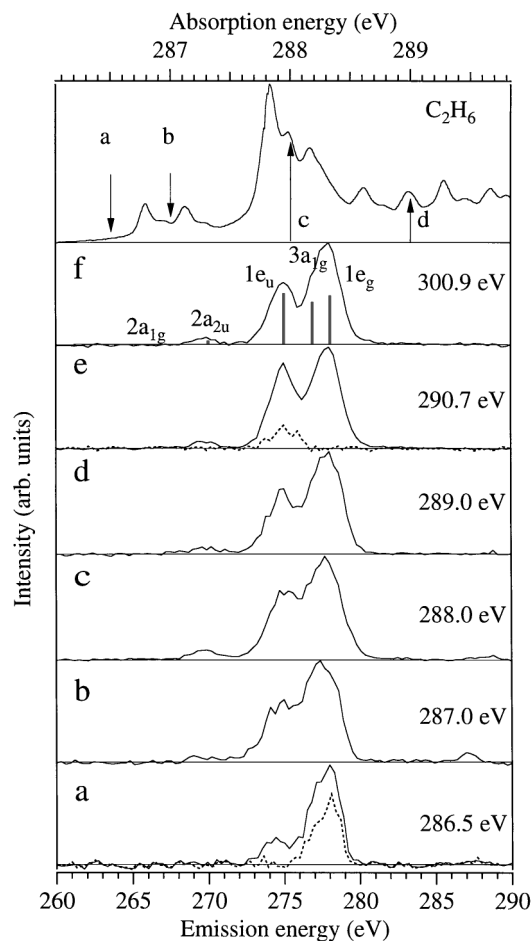


FIG. 3. C_2H_6 . (top) Absorption spectrum from Ref. [5]. [(a)–(f)] As in Fig. 1. Experimental energies for the calculated intensities from [21,22].

Figs. 1e, 2f, and 3f the transitions are labeled by the valence orbital from which the deexcitation takes place. To help identify the transitions, intensities calculated by the Hartree-Fock method have been inserted as bars in the nonresonant spectra. The dotted lines are the difference spectra obtained as described above. The percentages given in Table I are the obtained purities, $1 - k$, measured as the areas of the difference spectra. The error margins for the obtained values are 5%–10%.

Acetylene (C_2H_2) is linear in the ground state and belongs to the $D_{\infty h}$ symmetry group. The electron configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$ $^1\Sigma_g^+$. Two features dominate the nonresonant emission spectrum in Fig. 1e: one at 279 eV corresponding to a transition from the $1\pi_u$ valence orbital and one at 274 eV mainly from the $3\sigma_g$ orbital. Compared to the nonresonant spectrum there is a marked decrease in intensity of the forbidden peaks for all resonant excitations. The large selectivity is confirmed by the difference spectra, which give a purity of 50%–60% for Rydberg excitations.

The ground state of ethylene (C_2H_4) belongs to the D_{2h} symmetry group and the electron configuration is $(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2$

TABLE I. Absorption resonances to which the excitation energy was tuned to obtain the emission spectra and the purities of the emission spectra.

Label	Unoccupied orbital	Purity	Ref.
C_2H_2			
a	$1\pi_g$	45%	[11]
b	$3p\sigma_u$	60%	[11]
c	$3p\pi_u$	60%	[11]
d	$3d\pi_g$ or $4s\sigma_g$	50%	[11]
e	K edge		[27]
C_2H_4			
a	$1b_{2g}$		[7]
b	$1b_{2g}$		[7]
c	$4a_g(3s)$ + possibly $3p(u)$	20%	[5,7]
d	$2b_{2u}(3p)$	50%	[5,7]
e	$4p(u)$ + possibly $4s(g)$	25%	[5]
f	K edge		[27]
g	just above double excitation and σ_u shape		[28]
C_2H_6			
a	about 0.3 eV below $3sa_{1g}$	45%	[5]
b	$3sa_{1g}$	0%	[5,29]
c	$3pa_{2u}$	0%	[5,29]
d	$3d + 4s(g) + \sigma_u$	0%	[5]
e	K edge + σ_u shape	10%	[27,28]
f	nonresonant		

1A_g . Spectra 2a and 2b were obtained by exciting to the $1b_{2g}$ valence orbital. The high-energy peak (at 285 eV) represents the participator transition. Because of large screening effects these spectra do not resemble the nonresonant one in Fig. 2f. The energy shift compared to the nonresonant spectrum of the forbidden $1b_{3u}$ transition is estimated to be up to 2.9 eV, and it is possible that it contributes to the broad band in the spectra. Spectra c and d appear very different from each other although the excitation energy differs by only 0.4 eV. The purity is 20% and 50%, respectively. We attribute the apparently lower purity of spectrum c to the fact that both the $3s(g)$ and $3p(u)$ resonances were excited. Overlapping resonances of different parity also explains the intensity distribution in spectrum e which is only slightly different from that in the nonresonant spectrum. Spectrum g is excited just above the double excitation threshold and the shape resonance, with a resulting satellite contribution to the spectrum.

Ethane (C_2H_6) belongs to the D_{3d} point group in its ground state and has the electron configuration $(1a_{1g})^2(1a_{2u})^2(2a_{1g})^2(2a_{2u})^2(1e_u)^4(3a_{1g})^2(1e_g)^4$ $^1A_{1g}$. The nonresonant emission spectrum in Fig. 3f consists mainly of two partly resolved features of different parity: one corresponding to transitions from gerade orbitals at 278 eV and one from the $1e_u$ ungerade orbital at 275 eV. Spectrum a was obtained by detuning the excitation energy about 0.3 eV below the first absorption resonance. As described in [3,12] detuning leads to a quenching of the symmetry breaking. In spectrum a the forbidden ungerade

transitions are suppressed and the purity is as high as 45%. Spectra *b-d* do not show any clear selectivity. Spectrum *e* was obtained by exciting on the σ_u shape resonance. Though the purity factor is small, 10%, a distinct $1e_u$ peak is seen in the difference spectrum. Thus, a small symmetry selectivity is observed for excitation to the shape resonance but practically none for the Rydberg excitations.

In the literature there are various assignments of the vibrational modes excited in the three molecules. For acetylene, bending modes are strongly excited in the C $1s-\pi^*$ absorption spectrum [8,11] due to the Renner-Teller effect. Such modes have also been observed for C $1s-3p\pi_u$ excitation. This type of vibrations is connected with "valence shell" VC, which does not lead to core-hole localization. For ethylene, vibrations of both core-hole localizing and valence shell type have been observed in the C $1s-\pi^*$ absorption peak [6,7]. However, in the ethylene case the core-hole localizing modes are the stronger non-totally symmetric modes. These modes are also observed in ionization of C_2H_4 according to [10], in contradiction to the assignment given in [30], where only symmetric modes are assumed. In the ionization of C_2H_2 and C_2H_6 , there are only symmetric modes, according to [9] and [31], respectively. However, in all the molecules the symmetric and the antisymmetric C-H stretches have very similar vibration frequency [24] and are therefore hard to distinguish, especially when only a curve fit is used as in [30,31]. Therefore, calculations are necessary for a correct interpretation of ionization spectra, as was also pointed out in [10]. In this respect the situation is very different for SXES. Because of the parity selection rule it can be seen immediately from the spectra that asymmetric vibrations are excited in all of them. We thus explain the contradiction between our assignments and those of [30,31] as being due to the small difference in vibrational frequency of the two modes.

Valence shell VC is expected to have a large excitation energy dependence, unlike "core shell" VC (the core-hole localizing type). In the spectra shown here the variation in the purity factors for each molecule is small, with the exception of ethylene. As already mentioned, the apparently large variation in ethylene can be explained to be due to overlapping absorption resonances. This indicates that valence shell VC is less important for the symmetry breaking observed in SXES. Since vibrations connected with valence shell VC are often "slow," this also agrees with the time-dependent consideration that within the limited duration time for the x-ray scattering process, symmetry breaking along high frequency, and therefore fast, modes are more likely to be observed by SXES than those along low-frequency modes [3,12,32].

Out of the considered series of molecules, the single bonded ethane molecule has the longest distance between the symmetry related carbon atoms and is indeed the one for which symmetry breaking is most apparent. In the triple bonded acetylene molecule symmetry is preserved to a much higher degree. The double bonded ethylene molecule, with an intermediate bond length, appears to have a

symmetry breaking somewhere in between the others. A large difference in the amount of symmetry breaking between the molecules is thus demonstrated, showing that symmetry breaking is not always complete for core excitation in polyatomic symmetric molecules and that the degree of symmetry breaking is sensitive to the bond length between the symmetry related atoms.

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