

Vibronic Coupling and Core-Hole Localization in K -Shell Excitations of Ethylene

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A new high-resolution measurement of the C $1s$ near-edge photoabsorption spectrum of the ethylene molecule is reported. An analysis of the vibrational structure in the C $1s$ - π^* band indicates strong excitation of non-totally-symmetric modes and the importance of vibronic coupling. The latter phenomena provides a mechanism for core-hole localization in the final state.

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The availability of intense synchrotron radiation and recent advances in soft-x-ray monochromator design have made it possible to measure second-row K -shell photoabsorption spectra of molecules with unprecedented resolution and signal-to-noise ratio.^{1,2} In particular, the vibrational fine structure of K -shell transitions can be examined in greater detail. An interesting object for such high-resolution studies is photoabsorption in molecules with two or more equivalent core-level sites. Here the promotion of K -shell electrons to an unoccupied valence orbital gives rise to nearly degenerate excited states which in turn can couple vibronically through modes of appropriate symmetry. We will show here that this characteristic vibronic coupling mechanism, which has been disregarded in previous K -shell excitation studies, plays an important role in such situations. Its effect is reflected by a novel type of symmetry breaking resulting in effectively localized core holes and a rich vibrational fine structure. In such a case the interpretation of the observed vibrational structure cannot be based on the usual Born-Oppenheimer (BO) adiabatic and Franck-Condon (FC) approximations but must include a proper treatment of the coupling between the electronic and nuclear motion.

An exemplary case of equivalent-core-level excitation is the C $1s$ - π^* transition in ethylene, which recently has been reexamined by Ma *et al.*¹ and Rabus *et al.*² for the condensed species C_2H_4 and C_2D_4 with distinctly higher resolution than in previous experimental work.³⁻⁵ To interpret the details of the observed vibrational structure in the C $1s$ - π^* band these authors assume the validity of the BO approximation and attempt to correlate peaks in the spectral profile with excitations of selected vibrational modes.

In this Letter we report on a new high-resolution measurement of these spectra recorded in the gas phase and

give an analysis of their vibrational structure in terms of a vibronic model that fully accounts for the vibronic coupling between the two nearly degenerate (equivalent-core-level) states. The resulting theoretical spectrum shows strong excitation of non-totally-symmetric modes and differs considerably from that expected according to the usual BO and FC analysis. Further, it allows us to specify quantitatively the extent of core-hole localization and symmetry breaking in the excited-state manifold.

The measurements were performed using the Bell Laboratories "Dragon" high-resolution soft-x-ray monochromator at the National Synchrotron Light Source, Brookhaven.⁶ The photon energy range from 280 to 300 eV has been covered in this study with a resolution of 40 meV. The absorption spectra were obtained by means of the transmission method with a 10-cm-long gas cell.⁷ By monitoring the light intensity transmitted through the cell with and without the gas, features due to the transmission function of the optical system can be removed from the spectrum.

Calculations of (vertical electronic) excitation energies and oscillator strengths at various nuclear geometries were performed using a complete second-order approximation [ADC(2)]⁸ for the polarization propagator. The application of this method to molecular K -shell excitation has been described previously.⁹ Details of the present calculations will be published elsewhere.¹⁰ A previous theoretical study of K -shell excitations in ethylene has been performed by Barth *et al.*¹¹

Figure 1 shows the high-resolution C $1s$ photoabsorption spectrum of C_2H_4 in an 8-eV energy range below the C $1s$ ionization threshold (290.5 eV). The broad feature at ≈ 285 eV corresponds to the C $1s$ - π^* core-valence transition, while the peaks above 287 eV are associated with C $1s$ Rydberg excitations converging to the K edge. The present spectra show significantly more

structure than those of previous studies;³⁻⁵ in particular, the Rydberg peaks above 287 eV have been measured for the first time at high resolution. The C 1s- π^* band is similar to the corresponding spectrum of the condensed species measured with the electron yield technique.^{1,2} The calculated excitation energies for the first three dipole-allowed transitions, $1b_{3u}(C1s)-1b_{2g}(\pi^*)$, $1b_{3u}(C1s)-4a_g$, and $1a_g(C1s)-2b_{2u}$ at the ground-state equilibrium geometry (D_{2h} symmetry, molecule in the x - y plane, CC bond along x axis) are 284.8, 287.1, and 287.7 eV, respectively. Compared with the centroids of the corresponding bands the theoretical results are uniformly too small, but only by about 0.2 eV. In the following we focus on the vibrational structure of the C 1s- π^* band.

In the symmetric nuclear configuration the two equivalent C 1s sites give rise to two almost degenerate core orbitals $1a_g$ and $1b_{3u}$, corresponding to the symmetric and antisymmetric linear combinations of the atomic 1s orbitals. According to the possibility of exciting an electron into the $1a_g$ or $1b_{3u}$ orbital, the C 1s excitations of ethylene occur in pairs of nearly degenerate states of g and u symmetry. For example, the pair of singlet C 1s- π^* excitations is ${}^1B_{1u}(1b_{3u}-1b_{2g})$ and ${}^1B_{2g}(1a_g-1b_{2g})$, their calculated energies differing only by 0.02 eV. Although only the excitations to the u states are dipole allowed (in D_{2h} symmetry), the g states come into play if a coupling between the g and u states can occur via vibrational modes of suitable symmetry. For the case of C 1s- π^* excitations there are two modes (ν_{11} , ν_{12}) of b_{3u} symmetry (u modes) that may couple the two states ${}^1B_{1u}$ and ${}^1B_{2g}$. Including also the three totally-symmetric a_g modes (g modes) ν_1 , ν_2 , and ν_3 , the vibronic Hamiltonian \hat{H}_c associated with the two-state vibronic coupling problem of the C 1s- π^* excitations may be formulated as follows:¹²

$$\hat{H}_c = \hat{H}_0 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} E_g + \sum_{r=1}^3 \kappa_{gr} Q_{gr} & \sum_{s=1}^3 \lambda_s Q_{us} \\ \sum_{s=1}^3 \lambda_s Q_{us} & E_u + \sum_{r=1}^3 \kappa_{ur} Q_{gr} \end{bmatrix}. \quad (1)$$

Here a matrix notation has been adopted where the rows

$$\hat{S}^\dagger \hat{H}_c \hat{S} = \hat{H}_0 \mathbf{1} + \begin{bmatrix} E_0 + \sum_r \kappa_r Q_{gr} + \sum_s \lambda_s Q_{us} & 0 \\ 0 & E_0 + \sum_r \kappa_r Q_{gr} - \sum_s \lambda_s Q_{us} \end{bmatrix}, \quad (3a)$$

where \hat{S} is the unitary operator

$$\hat{S} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}. \quad (3b)$$

This transformation corresponds to a change from symmetry-adapted or delocalized core-hole states to localized core-hole states. According to Eq. (3a) the vibrational motion is governed by states with localized rather than delocalized core holes. Each of these two states contains an equal admixture of the dipole-allowed

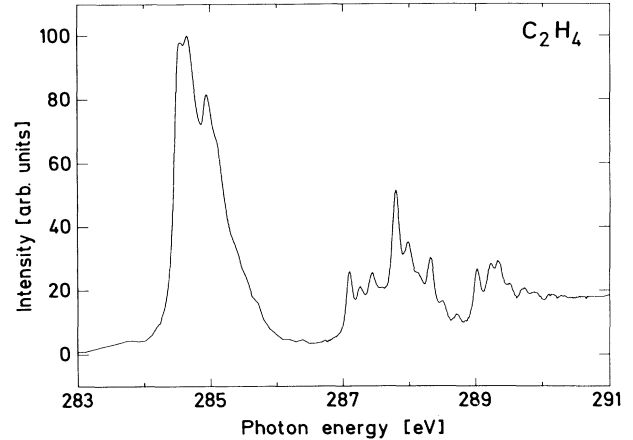


FIG. 1. C 1s photoabsorption spectrum of ethylene in the energy range below the ionization threshold. Experimental resolution ~ 40 meV.

(and columns) refer to the excited states ${}^1B_{2g}$ and ${}^1B_{1u}$, respectively, taken as diabatic electronic states.¹³ The first part of \hat{H}_c represents the unperturbed harmonic vibrational motion in the molecular ground state, that is, prior to the excitation process. The second part accounts for the (linear) differences between ground- and excited-state potential surfaces. The parameters used here are the vertical-electronic excitation energies E_g and E_u (at the ground-state equilibrium geometry) for the ${}^1B_{2g}$ and ${}^1B_{1u}$ states, respectively, the diagonal coupling coefficients κ_{gr} and κ_{ur} ($r=1-3$), and the vibronic (nondiagonal) coupling coefficients λ_s ($s=1,2$). Q_{g1-3} and $Q_{u1,2}$ denote the normal coordinates associated with the modes $\nu_1-\nu_3$ and ν_{11}, ν_{12} , respectively.

The vibronic coupling problem defined by Eq. (1) can easily be solved for the case of exact degeneracy of the electronic states.¹² We then have

$$E_g = E_u = E_0, \quad (2a)$$

$$\kappa_{gr} = \kappa_{ur} = \kappa_r, \quad (2b)$$

and \hat{H}_c can be diagonalized according to

${}^1B_{1u}$ state (with the delocalized core hole). Therefore, each localized state leads to the same spectral intensity distribution, with excitation of both even and odd quanta of the non-totally-symmetric modes ν_{11} and ν_{12} . More explicitly, the spectrum is given by a convolution of Poisson distributions for both the g and the u modes, with excitation strengths $f_{gr} = \kappa_r^2 / 2\omega_{gr}^2$, $r=1-3$, and $f_{us} = \lambda_s^2 / 2\omega_{us}^2$, $s=1,2$ (see, for example, Ref. 14).

Figure 2 shows the pair of excited-state potential

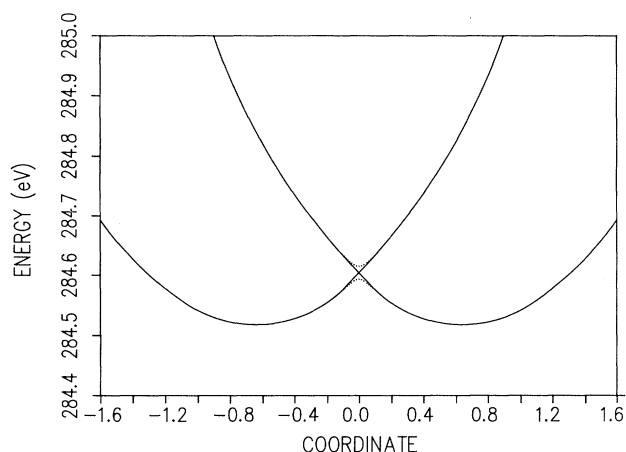


FIG. 2. Potential-energy curves of the two interacting C $1s-\pi^*$ core excited states of ethylene as a function of the asymmetric C-H stretching (dimensionless) normal coordinate Q_{u1} . Solid lines: potential energies of the diabatic states of Eq. (3), corresponding to localized core vacancies. Dashed lines: potential energies of the adiabatic states, obtained by diagonalizing the potential matrix of Eq. (1) with a finite energy split $E_g - E_u = 0.022$ eV.

curves obtained by distorting the molecule along one non-totally-symmetric coordinate, say, Q_{u1} . The dashed lines represent the adiabatic potentials of the Hamiltonian (1). At $Q_{u1} = 0$ these curves exhibit a narrow avoided crossing ($E_g - E_u = 0.02$ eV) and correspond to states with delocalized core holes of g and u symmetry. In the vicinity of such a weakly avoided crossing the nuclear motion is well known¹³ to be subject to diabatic potentials given by the solid lines in Fig. 2. These diabatic states are just the states with localized core holes for all nuclear geometries according to Eqs. (3a) and (3b).

In the actual calculations of the C $1s-\pi^*$ excitation spectra, it also proved necessary to consider the torsional mode ν_4 . This mode is not involved in the vibronic coupling mechanism and the linear diagonal coupling coefficients vanish for symmetry reasons. However, higher-order coupling terms here can lead to excitation of even quanta in accordance with the FC picture. In view of the shallow double-minimum shape of the excited-state torsional potential curve¹¹ a substantial excitation of the ν_4 mode is to be expected. To account for the torsional motion the Hamiltonian (1) was augmented by the part

$$\hat{H}_v = \left[-\frac{\omega_4}{2} \frac{\partial^2}{\partial Q_4^2} + \sum_{n=1}^4 c_n Q_4^{2n} \right] \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad (4)$$

where the coefficients c_1, \dots, c_4 were chosen as -1.12×10^{-2} , 1.55×10^{-3} , 9.58×10^{-5} , and 3.02×10^{-6} . Since \hat{H}_c and \hat{H}_v commute, the full spectrum can be obtained by convoluting the separately calculated spectra of \hat{H}_c and \hat{H}_v .

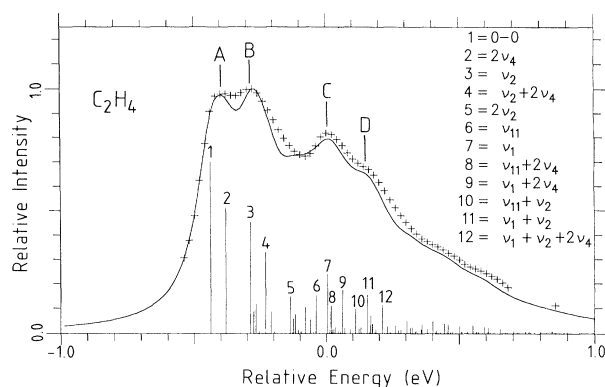


FIG. 3. Comparison of the experimental (crosses) and theoretical (solid line) C $1s-\pi^*$ band in the core excitation spectrum of C_2H_4 . The theoretical band envelope has been obtained by convoluting the line spectrum with Lorentzians of width FWHM=0.14 eV. The coupling constants for the individual modes are (frequencies in parentheses, all quantities in eV) $\kappa_1 = 0.323$ (0.441), $\kappa_2 = -0.234$ (0.150), $\kappa_3 = -0.098$ (0.170), $\lambda_{11} = 0.254$ (0.398), and $\lambda_{12} = 0.032$ (0.182).

Ab initio values for the coupling constants $\kappa_1, \kappa_2, \kappa_3$ and λ_1, λ_2 were extracted from the variations of the calculated excitation energies with different geometries. The calculated energy split $\Delta = E_g - E_u = 0.02$ eV is considerably smaller than the frequencies involved which justifies use of the degenerate-state approximation of Eq. (2). The final result shown in Fig. 3 was obtained using slightly adjusted values for some of the *ab initio* coupling constants and frequencies. The approximation $E_g = E_u$ does not noticeably change the resulting vibronic spectrum in the case of ethylene as was tested by treating the full Hamiltonian (1) with nonvanishing values of $E_g - E_u$ (and $\kappa_g - \kappa_u$). A more detailed report on the present calculations will be published elsewhere.¹⁰

Figure 3 shows a comparison between the final theoretical and the experimental C $1s-\pi^*$ absorption spectrum of C_2H_4 . The theoretical line spectrum has been convoluted with Lorentzians of 0.14 eV FWHM to simulate the effect of apparatus resolution (~ 0.04 eV) and lifetime broadening (~ 0.1 eV). The resulting envelope is in very good agreement with the experimental curve. While—especially for higher energy—many lines contribute to the spectral profile, a few of the major features can be assigned individually. The first peak *A* corresponds to the 0-0 transition and the excitation of two quanta of the torsional mode ν_4 . The peaks *B*, *C*, and the shoulder *D* each contain the various lines indicated in Fig. 3. The non-totally-symmetric modes are not explicitly resolved, but they strongly influence the widths and heights of the observed peaks. In particular, without the contribution of the coupling mode ν_{11} peak *C* almost disappears. A similar good agreement between theory and experiment is obtained for C_2D_4 using scaled parameters according to the usual L -matrix relationship.¹⁵

The vibrational excitation reflects concomitant changes in the molecular geometry upon core excitation. We find here a symmetric decrease of the C-H distance by 0.06 a.u., an increase of the C-C distance by 0.19 a.u., a symmetric decrease of the HCH angle of 6° , a torsional angle of 25° , and asymmetric changes of the C-H distance and the HCH angle of ± 0.06 a.u. and $\pm 1.5^\circ$, respectively. The torsional angle comes out in good agreement with the calculation of Barth *et al.*¹¹ The near equality of symmetric and asymmetric C-H bond-length changes implies that the C-H bond length decreases by $2 \times 0.06 = 0.12$ a.u. at the site with the localized core vacancy and by virtually zero at the other site.

The theoretical analysis given here of the C $1s-\pi^*$ photoabsorption band in ethylene proves that the observed spectral profile emerges from a manifold of vibronic states associated with both the ${}^1B_{3u}$ and the ${}^1B_{1g}$ electronic states, although for the latter dipole selection rules forbid a vertical-electronic transition from the ground state. Strong dynamical (non-BO) effects as a result of vibronic coupling via the non-totally-symmetric C-H bending mode ν_{11} and, to a lesser extent ν_{12} , determine the spectral distribution of the final vibronic states and lead to a substantial asymmetric planar distortion of the excited molecule. An additional non-planar-symmetry lowering is introduced by the torsional motion. While a twisted final-state conformation is not specific to the case of *K*-shell excitation and has indeed been observed previously in valence-electron excitation and ionization, the symmetry breaking by an asymmetric in-plane distortion is a characteristic effect in the excitation of equivalent-core-level electrons. Via this symmetry breaking a dynamical localization of the core hole is achieved; i.e., the potentials governing the vibrational motion are those of states with localized rather than delocalized core holes. The simple theoretical model considered in this Letter even allows a quantitative analysis of the ethylene C $1s-\pi^*$ absorption band. In fact, the experimental spectrum can only be understood with the aid of quantum chemical and dynamical calcu-

lations. This is the first time that vibronic coupling has been unambiguously established in *K*-shell absorption spectroscopy. In view of the much higher resolution now attainable in the soft-x-ray region, this result is likely to have important implications for many other systems.

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