Breaking of Ground-State Symmetry in Core-Excited Ethylene and Benzene

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The observation of C-H bending and C-C and C-H stretching vibrational levels in high-resolution C $1s^{-1}\pi^*$ photoabsorption spectra of ethylene and benzene demonstrates that, within the validity of the Franck-Condon principle, both molecules have broken symmetry in this core-excited state. A simple model based on the antibonding character of the π^* electron, and on the local rehybridization of the bonding orbitals on the excited C atom, is utilized to explain our observations and to show that both core-excited molecules become nonplanar. Our results also show that the core hole is localized on the excited carbon atom.

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The vibrational structure associated with electronic transitions in molecules has been extensively studied to investigate the internuclear potential of the excited molecule, and its dependence on the electronic charge distribution.[1] These studies have concentrated mostly on valence excitations.[1] The vibrational structure of core-to-bound transitions is, however, of particular interest. The localized nature of the core wave function offers a unique means to investigate how the molecule rearranges itself, modifies its symmetry,[2] and relaxes in the vicinity of the excited atom.

Investigation of the vibrational structure of core-to-bound excitations has so far been restricted mostly to diatomic molecules composed of light elements,[3] and to theoretical calculations on more complex systems such as C_2H_2 and C_2H_4.[2,4] The intrinsic lifetime broadening of core excitations and the experimental resolution of the available excitation sources and detectors have limited the number of observable vibrational modes, and prevented detailed studies.

In this Letter we report on the C $1s^{-1}\pi^*$ photoabsorption spectra of ethylene and benzene, measured with unprecedented photon-energy resolution. Comparing the spectra of C_2H_4 and C_6H_6 with those of C_2D_4 and C_6D_6, three different vibrational frequencies are identified as due to the C-H bending, the C-C stretching, and the C-H stretching modes. The excitation of the C-H bending mode provides compeling evidence that in both molecules the ground-state symmetry is broken. Furthermore, the C-H stretching frequency of both molecules is higher than in the ground state, while that of the C-C stretching mode is found to be smaller; this indicates that the internuclear potentials have been modified along these two bonds from their ground-state values, differently in each case. A simple model shows that these results are related to the antibonding character of the excited π^* electron, and to the fact that the presence of this excited electron favors the sp^3 hybridization, so that the two excited molecules are no longer planar. These conclusions compare well with a theoretical calculation performed on the ethylene molecule.[4] Our analysis indicates that the in-plane symmetry is also reduced, supporting the view that the C 1*s* core hole is localized on the photoexcited carbon atom.[5]

The C 1*s* photoabsorption spectra were measured using the new Bell Laboratories *Dragon* soft-x-ray beam line at the National Synchrotron Light Source with photon energy resolution of 30 meV full width at half maximum (FWHM).[6] The spectra were measured by total-electron-yield detection in ultrahigh vacuum on condensed high-purity C_2H_4, C_2D_4, C_6H_6, and C_6D_6 gases. No chemical reaction of dissociation of the condensed gases was detected.

Figures 1 and 2 show the C $1s^{-1}\pi^*$ photoabsorption spectra of C_2H_4, C_2D_4, C_6H_6, and C_6D_6. The observed fine structure is due to vibrational excitations associated with the $1s^{-1}\pi^*$ electronic transitions. These two sets of spectra are very similar, and are both dominated by four features, labeled as 0, *A*, *B*, and *C*. Their energy positions, referenced to peak 0, are listed in Table I. The energy positions of peaks *B* and *C* can be precisely determined. Feature *A*, clearly observed in benzene, is less prominent in ethylene. It is obvious, however, that the spectra of C_2H_4 and C_2D_4 are different from each other in the region of this feature, and that this difference must be associated with the change in the hydrogen mass. This is the important conclusion necessary for the subsequent discussion. An estimate of the energy position of feature *A* was made by fitting the spectra in the energy range of features 0, *A*, and *B*. We used Lorentzians of equal width but different intensities and positions, convoluted with a Gaussian representing the instrumental bandwidth of 30 meV FWHM.[7] The Lorentzian FWHM was found to be 110±10 meV for both molecules. Interestingly, such a lifetime width of the C $1s^{-1}\pi^*$ state is almost 2 times larger than that of theoretical predictions for the isolated carbon atom.[8] Table I also lists the energies of the various ground-state

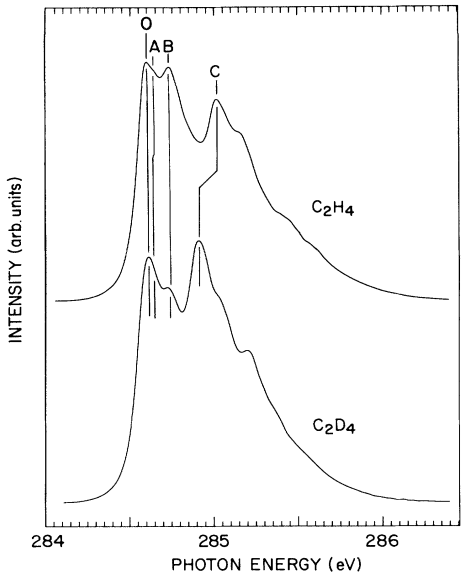

FIG. 1. C $1s^{-1}\pi^*$ photoabsorption spectra of condensed C_2H_4 and C_2D_4. Peak positions are indicated by the solid lines and labeled as explained in the text.

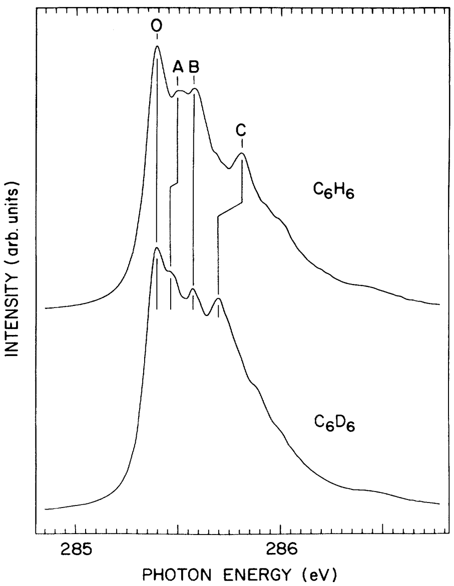

FIG. 2. C $1s^{-1}\pi$ photoabsorption spectra of condensed C_6H_6 and C_6D_6. Peak positions are indicated by the solid lines and labeled as explained in the text.

vibrational modes of the two molecules.[9] These modes have been divided into five groups, identified by the characteristic motion of a C-C or C-H atom pair; some are listed by an energy range obtained from the lowest and highest frequencies if more than one mode belongs to the considered group. This division has been made to emphasize the differences in the characteristic energy of the various vibrations.

By comparing the spectra of the hydrogenated and deuterated molecules one can distinguish the vibrational excitations characteristic of the C-H atom pair from those of the C-C pair. Peak 0 corresponds to the C $1s^{-1}\pi^*$ electronic transition with no vibrational excitations. As shown in Figs. 1 and 2, peak *C* and feature *A* shift towards lower energies when hydrogen is replaced by deuterium, while the energy of peak *B* is unchanged. When referenced to peak 0, the energies in the hydrogenated and deuterated molecules of features *A* and *C* are in a ratio consistent with the different masses of the two isotopes. This behavior indicates that these two excitations are predominantly associated with the C-H pair, while peak *B* is due to a C-C mode.

To interpret this vibrational structure, we will assume the Born-Oppenheimer approximation to be valid. The initial- and final-state total molecular wave functions can then be expressed as the product of the electronic and

TABLE I. Summary of the energy positions of features *A*, *B*, and *C* in C_2H_4, C_2D_4, C_6H_6, and C_6D_6. These energies are relative to peak 0. The various ground-state modes of these molecules are given after they have been divided into groups labeled by the characteristic motion of the C-C or C-H atom pair. The C-C bending modes in benzene, observed at frequencies below 70 meV, have been omitted.

Molecule	Peak *A* (meV)	Peak *B* (meV)	Peak *C* (meV)	C-H out-of-plane bending (meV)	C-H in-plane bending (meV)	C-C symmetric stretch (meV)	C-C *non*-totally symmetric stretch (meV)	C-H stretch (meV)
C_2H_4	70(20)	150(15)	415(15)	100–120^a	165–180^a 125–150^a	200	⋯	375–385^a
C_2D_4	60(20)	140(15)	325(15)	75–100^a	125–135^a 90–120^a	190	⋯	280–290^a
C_6H_6	105(10)	180(15)	420(15)	85–120^a	130–145^a	125	185–200^a	380
C_6D_6	80(10)	180(15)	310(15)	65–100^a	100–110^a	115	180–195^a	285

[a] The energy interval refers to the lowest and highest frequency of the considered atom-pair vibrational motion (Ref. 9).

nuclear wave functions. We will also use the plausible assumption that for core-to-bound excitations the electronic dipole transition is insensitive to the nuclear coordinates in a small range around the equilibrium positions of the initial- and final-state internuclear potentials (nonresonant vibronic coupling).[2] Within these two approximations, the Franck-Condon principle is valid, and the optical transition matrix element is composed of two factors: the dipole operator between the initial- and final-state electronic wave functions and the overlap between the initial- and final-state nuclear wave functions.[2] This last term, the Franck-Condon (FC) factor, determines the observed vibrational structure. The FC factor between different vibrational states is different from zero if the ground-state and excited-state nuclear eigenfunctions are no longer orthogonal to each other as a consequence of a change in the internuclear potential. It is obvious then that the observed vibrational structure yields direct information on modifications of the molecular symmetry.

We first consider the ethylene results. The ground-state frequencies listed in Table I are much higher than the thermal energy of the condensed molecules, and therefore the initial vibrational state is always the ground state. It then follows that peaks *B* and *C* are due to the excitation to the first level of the C-C and C-H stretches, while feature *A*, observed at energies below 100 meV, can only be assigned as the excitation to the first vibrational level of a *non*-totally symmetric C-H bending mode. Comparison of our measured values with those in the ground state reveals that while the C-H stretching frequency is increased, the C-C stretching frequency is decreased. This behavior indicates that in the C $1s^{-1}\pi^*$ excited state, the C-H and C-C bonds are, respectively, stronger and weaker than in the ground state. This result implies an anisotropic change of the internuclear potential. Using the well accepted view that an increase (decrease) in bond strength corresponds to a decrease (increase) in bond length, we also conclude that the C-C and C-H bonds are, respectively, longer and shorter than in the ground state. A *non*-totally symmetric C-H bending mode, with energy similar to that of feature *A*, can only be observed if the symmetry of the molecule is broken. This is a general property of a normal mode, derived from the fact that its wave functions for the ground state and for the first excited state have even and odd symmetry with respect to the equilibrium position of the normal coordinate. The FC factor, consequently, is different from zero only if the equilibrium positions are different in these two states. For totally symmetric modes, like the C-C stretch, this difference does not alter the symmetry of the molecule.[10] If, on the contrary, this mode is *non*-totally symmetric, the molecular symmetry is broken.[10] In our case, the identification of feature *A* as a *non*-totally symmetric C-H bending mode indicates that in core-excited ethylene the broken symmetry is associated with a change in the C-H bond direction.

To investigate and understand more of this symmetry breaking in core-excited molecules, we now consider the benzene results. We observe that, similarly to the absorption features, also the ground-state vibrational frequencies are similar to those of ethylene. Feature *A*, with its clearly observable isotope effect, indicates that in benzene as well there is the excitation of a C-H bending mode, and the breaking of the ground-state symmetry. Furthermore, as in ethylene, the C-H stretch (feature *C*) is stiffer than in the ground state. The assignment of the C-C stretching mode, however, is more involved than in ethylene because of the greater number of C-C modes in this larger molecule. A possible assignment for peak *B*, observed at ~180 meV, is the totally symmetric C-C stretching mode, which has a ground-state frequency of ~120 meV. A problem with this interpretation is that the difference between the ground state and the measured value is too large, even larger than that observed for the C-H stretches of either molecule. It is also difficult to reconcile this ~60-meV blueshift with the opposite ~50-meV redshift that we previously observed for the C-C stretch of ethylene. These difficulties are removed when peak *B* is assigned to a *non*-totally symmetric C-C stretch that has a ground-state frequency of ~190 meV.[9] According to this interpretation, the observation of a *non*-totally symmetric C-C mode indicates that the sixfold in-plane symmetry of benzene is also broken. This provides strong evidence that the C 1*s* core hole is localized on the photoexcited C atom.

Further support for this localized picture is given by the facts that the C-H stretching frequencies are very similar for benzene and ethylene in both ground and excited states, and that the values of the excited state are comparable to that of the ground state of N-H.[11] This is a direct consequence of the core hole being localized on one carbon atom, which behaves as an equivalent nitrogen core. On the contrary, the delocalized picture, in which the positive charge per carbon atom would be 3 times larger in ethylene than in benzene, would predict a larger C-H bond stiffening in ethylene.

Our mode assignments and conclusions compare extremely well with a theoretical calculation on the vibrational structure of the C $1s^{-1}\pi^*$ excitation in C_2H_4.[4] Here, it is shown that the C-C bond is weakened and the C-H bond is strengthened in the final state, and that a predicted twist of the CH_2 group on the excited C atom breaks the planar symmetry of the molecule. To understand the mechanism leading to this behavior, we suggest a model that relates the vibrational structures to the antibonding character of the π^* orbital and to the localization of the core hole.

The filling of an antibonding π^* orbital between two atoms in simple molecules is known to weaken the bond. Conversely, the attractive potential of a core hole induces a bond stiffening. Among these two competing effects, the π^*-induced bond weakening is generally dominant. This can be seen, for example, in diatomic molecules where the bond strength monotonically decreases between CO, NO, O_2, and F_2, in correspondence with the increase in occupation of the π^* orbital and in the positive nuclear charge.[12] We suggest that a similar mechanism is responsible for the C-C bond weakening of excited ethylene and benzene. This effect is smaller in benzene because here the π^* electron is shared by at least two C-C bonds while in ethylene there is only one C-C bond.

An alternative way to describe this process is by noticing that the C atoms in ethylene and in benzene have the sp^2 bonding configuration because the C $2p_z$ orbitals are half filled. In the core-excited case, however, the presence of an electron in the π^* orbital localized on the core hole decreases the C-C bonding due to the π bonding orbital, and favors the formation of a lone pair in the $2p_z$ orbital of the excited carbon atom. An obvious consequence of this process is a C-C bond-strength reduction (reduced π bonding), while the C-H bond remains essentially undisturbed. The C-H bond stiffening is then simply due to the core-hole attraction.

Another consequence of the formation of a lone pair in the $2p_z$ orbital of the excited C atom is that the planar sp^2 configuration of the orbitals of this atom becomes unstable with respect to the tetrahedral sp^3 configuration. The breaking of the planar symmetry of the two excited molecules is then a natural consequence of this rehybridization mechanism. This simple argument supports the assignment feature *A* to an out-of-plane C-H bending mode, which is excited because the C-H bond equilibrium direction is no longer in the molecular plane. Moreover, this rehybridization mechanism suggests that the ground-state symmetry breaking is a general consequence of core excitations into π^* orbitals of polyatomic molecules.

In conclusion, improved experimental conditions allowed us to observe the complex vibrational structure of polyatomic molecules. We showed, within the Franck-Condon principle, the breaking of the ground-state symmetry in the C $1s^{-1}\pi^*$ excited state of ethylene and benzene. Changes in C-C and C-H bond strength, as well as in the C-H bond direction, were related to the antibonding character of the π^* electron and provided evidence for the core-hole localization. This work demonstrates that the study of the vibrational structure of core-excited molecules can offer detailed information on the excited-state internuclear potential. Furthermore, the core-hole localization emphasizes the site specificity of this kind of experiment and its utility for the systematic study of the geometric, electronic, and vibrational properties of core-excited systems.

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[10] See, e.g., R. Bauman, *Absorption Spectroscopy* (Wiley, New York, 1962), pp. 535–537.

[11] See, e.g., Ref. 9, p. 289. The N-H stretching frequency is typically 420 meV.

[12] See, e.g., Ref. 9, p. 287.