Core Level Energy Splitting in the C 1*s* Photoelectron Spectrum of C_2H_2

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The partially resolved vibrational fine structure on the C 1*s* photoelectron line of C_2H_2 clearly differs from that of other small hydrocarbon molecules such as CH_4, C_2H_4, and C_2H_6. This is attributed to photoionization from the two $1\sigma_g$ and $1\sigma_u$ core orbitals of C_2H_2, which can be described as the symmetric and antisymmetric linear combinations of the C 1*s* orbitals. According to our analysis they are split by 105 ± 10 meV, a result which is in good agreement with calculation. [S0031-9007(97)04424-4]

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In recent years there has been considerable progress in molecular *K*-shell spectroscopy of small molecules. Continuous improvements in soft x-ray monochromator design for synchrotron radiation sources [1] have led to a much higher experimental resolution than has been possible with conventional sources [2]. This has yielded, for example, more information on linewidth and on nuclear motion following the creation of a *K*-shell vacancy. It has recently become possible, for example, to identify the excitation of nontotally symmetric modes and characteristic nonadiabatic effects in systems with several equivalent core levels [3–8]. A phenomenon closely linked to the nonadiabatic effects in these systems is the occurrence of several near-degenerate core-hole configurations. Each of them corresponds to a hole in a particular symmetry-adapted core orbital, and the near degeneracy arises simply from the strong spatial localization of the constituent atomic orbitals of which the symmetry-adapted (molecular) orbitals are composed. In principle, it should be possible to show experimentally that these states are not quite degenerate. The splitting can occur in both ionization and absorption spectra, but for the latter case only one of the states may be observed because of dipole selection rules. On the other hand, no such selection rules exist for photoelectron spectra where, in principle, the complete manifold of near-degenerate states should be seen. In the present Letter we report the first experimental identification of such a core level energy splitting, namely, in the C 1*s* photoelectron spectrum of C_2H_2.

Ethyne (acetylene) C_2H_2, which is isoelectronic with CO and N_2, is the simplest triply bonded hydrocarbon. It has been extensively studied, both theoretically and experimentally, as the prototypical alkyne. Particular attention has been paid to the valence level photoelectron spectrum [9]; the core level region has also been investigated both with laboratory sources [10] as well as at variable energy with synchrotron radiation [11]. The ethyne molecule is linear and belongs to the point group $D_{\infty h}$. The C-C bond length is 1.204 ± 0.002 Å [12] in the ground state.

The photoelectron spectrum of C_2H_2 was measured on the X1B undulator beam line at the National Synchrotron Light Source (NSLS) in Brookhaven [13]. The photoelectron spectra were measured with a stationary, angle-resolving magic-angle cylindrical mirror analyzer (CMA), the axis of which is collinear with the incoming synchrotron radiation beam. In this geometry the total intensity, integrated over all angles around the axis, is independent of the angular distribution of the photoelectrons and the degree of light polarization. A description of the spectrometer has been published previously [14]. The high resolution measurements of the C 1*s* main line (over 20 spectra at different photon energies) were recorded with a constant CMA pass energy of 10 eV, giving an electron kinetic energy resolution of ~80 meV. The photon energy resolution ranged from 60 to 80 meV, depending on the slit settings and photon energy. Figure 1 shows the main line C $1s^{-1}$ photoelectron spectrum of C_2H_2 measured at 313 eV. At first sight, the spectrum resembles that of the diatomics CO [15,16] and N_2 [17], or of CH_4 [18–20], and appears simple enough to be described using a single

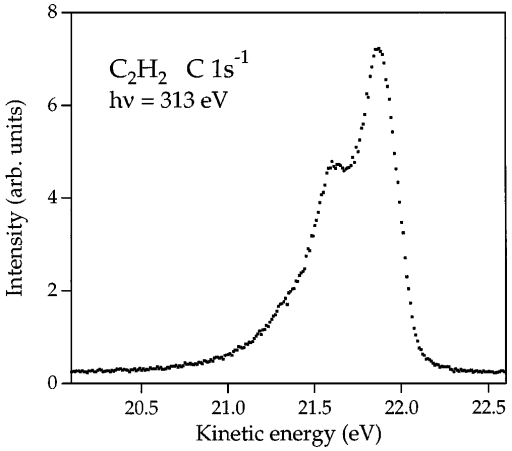

FIG. 1. The C 1*s* photoelectron line of C_2H_2 measured at a photon energy of 313 eV.

vibrational progression. On the basis of the usual interpretation of photoelectron spectra based on the Franck-Condon principle, however, one would expect both the totally symmetric C-C and C-H stretching modes to appear. In Fig. 1, the well resolved shoulder on the left is situated about 240 meV from the peak maximum. This is approximately the energy of the totally symmetric C-C stretch in the ground state, 248 meV [21]; it is unlikely to be due to the symmetric C-H stretch which has an energy of about 400 meV in small hydrocarbons.

For the analysis of the vibrational structure a fit routine was optimized to take into account up to 3 vibrational progressions with 4 quanta for each. (The C_2H_2 molecule possesses 2 doubly degenerate bending modes, ν_4 and ν_5, with fundamental frequencies of 76 and 90 meV [21], respectively. These, in principle, could also play a role in the vibrational fine structure. Modes ν_4 and ν_5 have, however, Π symmetry and to a first approximation are not expected to appear in the C $1s^{-1}$ photoelectron spectrum.) To reduce the number of free parameters in the fit, the C $1s$ photoelectron spectra of molecules showing distinct vibrational structure, such as CH_4 and CO, were measured under the same experimental conditions. The photon energy and the electron energy resolution extracted from these spectra were used in the fit routine. However, over a large photon energy range the photoelectron spectrum of C_2H_2 could not be fitted satisfactorily with 1, 2, or even 3 vibrational progressions. The results, contrary to all expectations, actually indicated the presence of another line contributing to the width of the lowest binding energy feature in the photoelectron spectrum, the 2 lines being separated by about 100 meV.

In order to study further the fine structure on the C $1s$ photoelectron line of C_2H_2, it was compared with that of CH_4, C_2H_4, and C_2H_6. The 4 molecules were measured under the same experimental conditions, i.e., identical photon energy, the same slit settings of the monochromator, the same pass energy, and almost the same number of counts. These spectra recorded at 338 eV photon energy are presented in Fig. 2. The spectral features in the C $1s$ spectrum of C_2H_2 are broader than those in CH_4, C_2H_4, and C_2H_6, all of which show a distinct peak about 400 meV from the main line due to the excitation of the C-H stretching vibration. Its relative intensity appears to decrease with the number of hydrogen atoms. The C_2H_4 and C_2H_6 spectra also contain another, less conspicuous vibrational feature about 200 meV from the main line which arises from the excitation of the C-C stretch. In contrast to the C-H stretch, its intensity is greater in C_2H_4 than in C_2H_6. The spectrum of C_2H_2 does not fit in with the general trends in the series. In particular, its low binding energy flank is not coincident with those of the other 3 molecules, but gives rise to the maximum at a higher relative binding energy. Furthermore, spectra measured at other photon energies show an identical behavior.

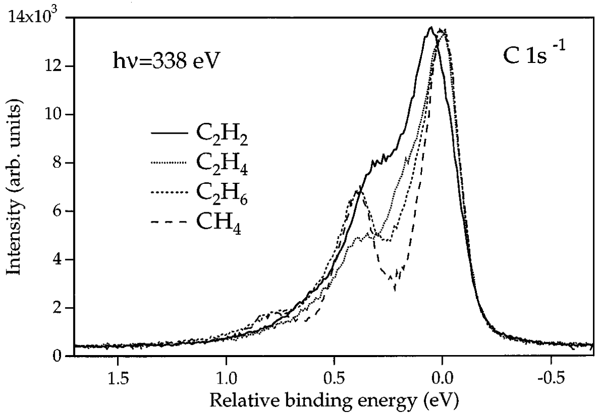

FIG. 2. Superposition of the C $1s$ photoelectron spectra of C_2H_2, C_2H_4, C_2H_6, and CH_4 measured under identical experimental conditions (the same photon energy 338 eV, the same slit settings of the monochromator, the same pass energy for the analyzer, and almost the same number of counts). The spectra are shown on a relative binding energy scale scaled to the low binding energy flank.

The presence of 2 main lines follows from elementary theoretical considerations. There are 2 almost degenerate core orbitals $1\sigma_g$ and $1\sigma_u$, which are associated with the symmetric and antisymmetric linear combination of the atomic $1s$ carbon orbitals, respectively.

$$\Psi\sigma_g = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2), \qquad \sigma_g \text{ symmetry},$$

$$\Psi\sigma_u = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2), \qquad \sigma_u \text{ symmetry}.$$

The core hole states of ethyne thus occur in pairs of nearly degenerate states of g and u symmetry. We have determined this energy splitting between the 2 core hole states in the C $1s^{-1}$ C_2H_2 ion by *ab initio* calculations, approximating the core hole energies by the negative of the corresponding molecular orbital energies (Koopmans' theorem). Two different basis sets have been employed in the calculations, one being of double zeta type, including a set of polarization functions, the other belonging to Dunning's improved "correlation consistent" basis sets and included up to f functions on carbon and up to d functions on hydrogen (cc-pVTZ basis [22]). The difference in the core orbital energies obtained is 98 and 101 meV, respectively.

The experimental energy splitting has been extracted from an elaborate fit procedure based on the minimization of a "reduced" χ^2 function (χ^2_{red}), which is similar to that in the usual least squares fit procedure, but includes a variable for the number of free parameters [23]. This method provides results of higher precision by reducing the uncertainty of mutually correlated experimental parameters. For the final analysis of the C $1s$ photoelectron line of C_2H_2, we selected 4 spectra measured at relatively high photon energies (337, 347, 360, and 370 eV) and fitted them simultaneously keeping all the parameters except intensity fixed. The χ^2_{red} was then determined at different values for the parameter of interest. The results for the energy splitting of the main line doublet and lifetime broadening of the core-ionized state are shown as a contour plot in Fig. 3; the minimum corresponds to an energy splitting of 105 ± 10 meV and a lifetime broadening of 90 ± 10 meV. The other parameters such as vibrational spacings were determined using the same procedure. The first vibrational energy is found to be 270 ± 12 meV for the C-C mode (ν_2) and 415 ± 15 meV for the C-H mode (ν_1); the intensity of the latter is very low. The higher vibrational frequency for the ionic state of 270 meV compared to 248 meV for the neutral ground state indicates that the equilibrium internuclear distance is shorter in the ionic state. The approximation of Nicholls [24] applied to the resulting Franck-Condon factors gives an equilibrium internuclear distance of $R_e = 1.158$ (± 0.004) Å between the 2 carbon atoms which is 0.046 Å shorter than in the neutral ground state.

The photoelectron spectrum of C_2H_2 at another photon energy (338 eV) is presented in Fig. 4(a). The parameters derived above were used; only the vibrational branching ratio were fitted. (Note the skewed line shapes which are used to account for the effect of post-collision interaction [25,26]; see, e.g., Refs. [15,17,18]. Another spectrum measured near threshold at 298 eV and fitted using the same set of parameters is shown in Fig. 4(b). The fit is not as good, although in this the monochromator bandwidth and lifetime broadening were not fixed. As a result of the various above-threshold resonances [11,27] at this photon energy it appears that the excitations from $1\sigma_g$ and $1\sigma_u$ initial states are no longer of equal weight [28,29]; i.e., the intensity ratio of the 2 components of the doublet is dictated by dipole selection rules. The fit shows that the intensity of the low kinetic energy component of the doublet is overestimated.

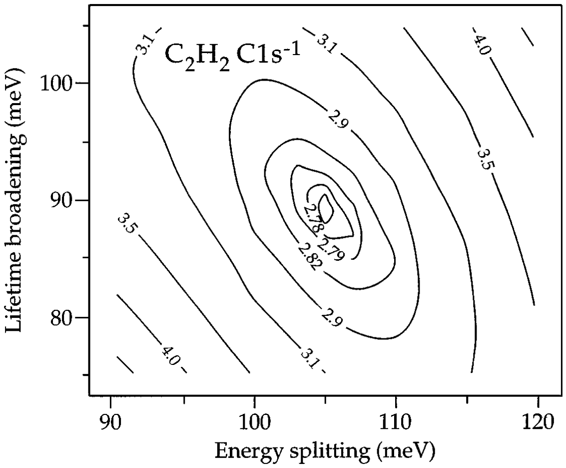

FIG. 3. Contour plot of χ^2_{red} curves with the energy splitting varied along the abscissa and the lifetime broadening along the ordinate. The contours show a clear minimum corresponding to an energy splitting of 105 ± 10 meV and a lifetime broadening Γ of 90 ± 10 meV. Four C 1s photoelectron spectra measured at photon energies well above threshold were fitted simultaneously.

We now briefly compare these findings with other systems containing near-degenerate core-hole states. The reason for the different behavior of the C $1s^{-1}$ states of ethene and ethane, for example, can be found with the aid of *ab initio* calculations for C_2H_4 [7]. Owing to the longer C-C bond (1.337 Å) [12] compared to ethyne, the energy splitting between the 2 core-hole states turns out to be in the range 20–30 meV. For ethane with its even longer C-C bond (1.536 Å) [12] the splitting will be correspondingly smaller. Thus, for both ethane and ethene the core energy splitting is well below the lifetime broadening, which is of the order of 85 ± 15 meV. In the case of the C $1s \rightarrow \pi^*$ excitations in ethene [3,4,6,7] and ethyne [5,30] as well as the O $1s^{-1}$ ionization in CO_2 [8,31], emphasis has been put on the phenomenon of core-hole localization and excitation of nontotally symmetric vibrational modes. It turns out that these phenomena play only a minor role in the C 1s ionization of ethyne. Additional *ab initio* calculations have been performed which reveal that the asymmetric C-H stretching mode as well as both bending modes (ν_4 and ν_5) are hardly excited in the C $1s^{-1}$ photoelectron band.

In conclusion, we have shown that the energy splitting between nearly degenerate core orbitals cannot be

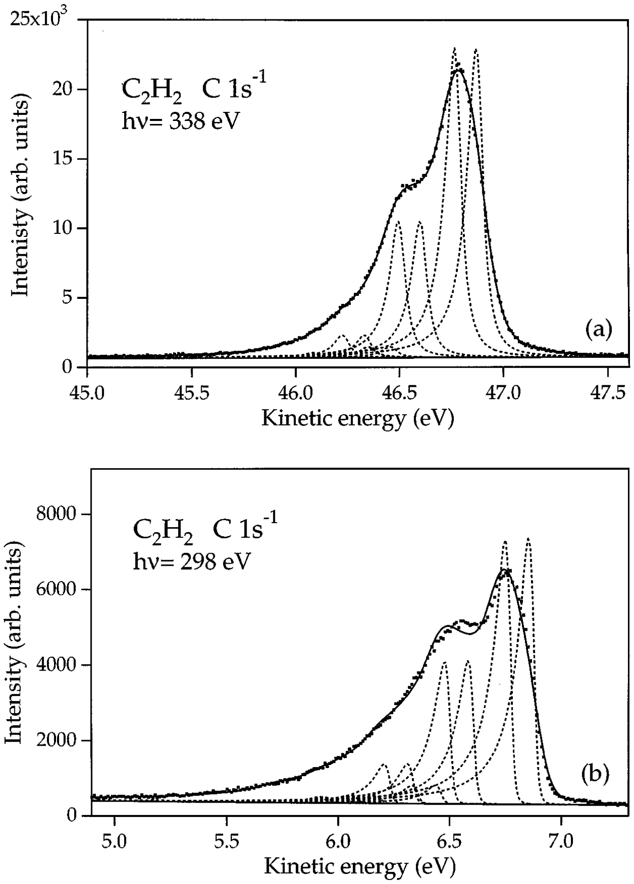

FIG. 4. C 1s photoelectron spectrum of C_2H_2 measured at (a) $h\nu = 338$ eV and (b) 298 eV. Note the high quality of the fit of spectrum (a) considering that, apart from the intensities, all parameters are fixed: energy splitting, lifetime broadening, monochromator bandwidth, and vibrational spacings.

neglected, if the vibrational fine structure on a core level photoelectron line is to be properly understood. In C_2H_2 this core energy splitting amounts to 105 ± 10 meV, which, although smaller than the vibrational energies of the ν_1 and ν_2 stretching modes, exceeds the lifetime broadening of the C $1s^{-1}$ state (90 ± 10 meV). Similar effects, but usually smaller, are also expected to occur in core ionization spectra of other molecules containing equivalent atoms.

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