

High-resolution carbon 1s photoelectron spectrum of ethene: *Ab initio* calculation of vibrational structure with dynamic localization of the core hole

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The vibrational structure in the carbon 1s photoelectron spectrum of ethene has been measured with a total experimental resolution of about 55 meV, significantly better than has been previously reported. The spectrum has been calculated using *ab initio* electronic structure theory with a localized core hole and the equivalent-cores approximation. Agreement between the calculated spectrum and measurements (taken 29 eV above the carbon 1s threshold) is excellent. This agreement indicates that there is dynamic localization of the core hole, even though the $1\sigma_g$ - $1\sigma_u$ splitting is not small. The theoretical method provides an approach that is useful for analyzing such spectra and also shows some of the pitfalls of attempting to fit complex vibrational spectra without guidance from theory. [S1050-2947(98)00101-2]

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I. INTRODUCTION

The shape of an inner-shell photoelectron spectrum for a molecule is influenced by several factors. For all such spectra, there are contributions from experimental resolution, lifetime broadening, and often vibrational structure. In molecules with inequivalent atoms of the same element, the spectrum will be the superposition of two or more spectra, each affected by the factors just mentioned, but at different positions on the energy scale. For inner shells other than s , there may be additional structure due to spin-orbit splitting and molecular-field splitting.

The vibrational structure is of interest in its own right, in that it provides information on geometry and bonding in the core-excited molecules. In many situations, however, one is interested in such quantities as lifetime broadening, ionization energies of inequivalent atoms, or molecular-field splitting. In these cases it is useful to have *a priori* knowledge of the vibrational structure as an aid to analyzing the spectra to obtain the desired information. *Ab initio* calculations provide a path to this information.

Accurate calculation of the vibrational structure requires accurate knowledge of the vibrational frequencies of the core-excited molecule and of the changes in bond lengths and bond angles that accompany core ionization. *Ab initio* calculations of the frequencies are, in general, not difficult if one makes empirical adjustments for the failures of the Hartree-Fock approach. The vibrational structure is, however, very sensitive to changes in bond lengths, and calculating this correctly provides a severe test of *ab initio* theory.

As an example, we consider the carbon 1s ionization of methane [1–9], which has a simple spectrum, consisting of a progression of lines arising from the symmetric carbon-hydrogen stretching mode. All analyses of the experimental data agree that there is a decrease of about 5 pm between the equilibrium bond length in neutral CH₄ and the core-ionized molecule [1–5,7,8]. Theoretical calculations give a range of

values from -4.1 to -7.2 pm for this change [4,10–13]. Although some theories predict the correct value, there is little correlation between the level of the theory and the accuracy of the prediction. A similar result has been seen by Siggel *et al.* [14] in a study of sulfur $2p$ ionization in several small molecules. They found that including the effects of electron correlation in their calculated spectra gave improved agreement for CS₂, worse agreement for SO₂, and no change for H₂S and OCS.

We have found a theoretical procedure that is relatively simple to use and gives an accurate prediction of vibrational structure in the core ionization of a number of hydrocarbons. In future [11] we plan to describe the successful application of this procedure to spectra taken with an experimental resolution between 113 and 140 meV for methane, deuteromethane, acetylene, deuterioacetylene, ethene, deuterioethene, and ethane. Here we outline the features of the procedure and show that it successfully accounts for a carbon 1s photoelectron spectrum of ethene recently acquired at the Advanced Light Source with a total experimental resolution of about 55 meV, close to the present state of the art for this kind of measurement. Moreover, this analysis shows that simple curve fitting of such complex spectra may not provide a reliable guide to the vibrational structure produced in core ionization.

Ethene was chosen for this study because it is rich in vibrational complexity, with at least three vibrational modes and their combinations contributing to the structure. It has been previously studied at lower experimental resolution by Köppe *et al.* [6], Sæthre *et al.* [9], and Kempgens *et al.* [15]. In addition, ethene has two equivalent carbon atoms and the question arises as to whether the core ionization should be treated as localized or delocalized. It has been suggested by Domcke and Cederbaum [16] that the inner-shell hole can be viewed as localized if the splitting between the $1\sigma_g$ and $1\sigma_u$ molecular orbitals is small, and evidence for such localization has been seen in the oxygen 1s ionization of CO₂

[17,18], where this splitting is of the order of 1 meV. However, in ethene we estimate this splitting to be of the order of 50 meV, which is not very small compared to typical vibrational energies (~ 200 meV). It is, therefore, of interest to see whether or not a localized model will work for this molecule.

II. EXPERIMENTAL PROCEDURE AND RESOLUTION

Measurements were made on Beamline 9.0.1 of the Advanced Light Source [19] at a photon energy of 320 eV, about 29 eV above the carbon $1s$ threshold. This energy was chosen to minimize distortion of the vibrational structure by resonances near threshold and distortion of the peak shapes by post-collision interaction, while still working in a region of energy where there was adequate intensity. This beamline receives its radiation from an undulator (U10) with a 10-cm period. It is equipped with a spherical grating monochromator that is, in principle, capable of a resolving power of about 10^4 . Photon absorption measurements to determine energy calibration and photon resolution were made in a parallel-plate ion-yield chamber. The photoelectron spectrum was measured in a spherical-sector electrostatic analyzer.

The resolution of the photon beam was determined by fitting a Voigt function to the photon absorption spectrum of the π resonance of CO. At a slit setting corresponding to a predicted resolution of 34 meV, we obtain a Gaussian contribution of 35 meV (full width at half maximum). The Lorentzian width of the principal line ($\nu=0$) is 103 meV, but this appears to have been broadened by sample thickness. The weaker lines ($\nu=1$ and 2) have widths of 78 and 82 meV, in reasonable agreement with the value of 85 meV reported by others [20]. The resolution of the electron-energy analyzer was determined by measuring the argon $3p$ photoelectron spectrum under conditions that the photon resolution was nearly negligible and the kinetic energy of the photoelectrons was the same as in the ethene measurement. Fitting the spectrum with Voigt functions gives a Gaussian contribution of 35 meV and a Lorentzian contribution of 10 meV, for an overall width of 41 meV.

Combining the components from the photon beam and the electron-energy analyzer gives an overall experimental function that is best described as a Voigt function with a Gaussian width of 50 meV, a Lorentzian width of 10 meV, or a total width of 55 meV. No physical significance should be attached to the Lorentzian component; use of the Voigt function appears to provide a better description of the experimentally measured resolution function than does the assumption of a Gaussian function.

Because of uncertainties in the energy calibration of the electron-energy analyzer, the photoelectron energy scale has been adjusted so that the peak corresponding to the adiabatic transition has the ionization energy of 290.75 eV reported by Sæthre *et al.* [9].

III. THEORETICAL PROCEDURES

A. Vibrational structure

We assume that, under the conditions of the experiment, the vibrational excitation can be predicted by using a simple Franck-Condon model. In this case, we require the bond

lengths, bond angles, normal modes, and vibrational frequencies of the initial and core-ionized molecules. For this we have used GAUSSIAN-94 [21] with the $D95(d,p)$ basis set at the $MP4SDQ$ level (that is, correcting for correlation effects using a fourth-order Møller-Plesset perturbation method, including single, double, and quadruple excitations). To describe the core-ionized species, we assume that the core hole can be treated as localized and, in addition, use the equivalent-cores approximation [22]; that is, the calculations were done for $\text{CH}_2=\text{NH}_2^+$ (but with nitrogen given a mass of 12 amu). In the predicted spectrum, the vibrational structure is extremely sensitive to the change in geometric parameters between the initial and final states. After analyzing spectra for a number of hydrocarbons [11] we found that good results were obtained by using the carbon basis set in place of the nitrogen basis set in the equivalent-cores calculation. It is to be noted that there is no justification for this procedure other than its apparent success. In the limit of a very flexible basis set, the result would be independent of the choice of basis set. Moreover, we anticipate that there are inherent errors in the equivalent-cores approach [23]. Here, however, our goal is to find a procedure that will describe the vibrational structure in a reliable way and our experience with the molecules mentioned above is that this procedure does that, although this success must in part be due to cancellation of errors.

The Gaussian calculations give all of the basic information needed and from these we can calculate the change in each normal coordinate. For core-ionized ethene there are five A_1 normal modes that might contribute to the vibrational structure, but the calculations show that only three of these are significant. In decreasing order of importance, these have fundamental frequencies of 165, 409, and 201 meV. We refer to these modes as ν_3 , ν_1 , and ν_2 , respectively. The character of each is considered in the discussion.

Once the changes in normal coordinates are known, Franck-Condon factors are calculated in the harmonic oscillator approximation for transitions from the (0,0,0) state of the neutral molecule to the $(\nu_1,0,0)$, $(0,\nu_2,0)$, and $(0,0,\nu_3)$ states of the core-ionized molecule. For these calculations we have used the vibrational frequencies noted above, which come from the Gaussian results, reduced by 10% [24,25]. The purpose of this correction is to account for inadequate treatment of correlation effects in the electronic structure calculations. Appropriate correction factors have been discussed by Radom and co-workers [24,25]. We note that reducing our calculated vibrational frequency for core-ionized methane by 10% gives a value of 397 meV, in good agreement with published experimental values of 391 meV [4] and 396 meV [6]. For the probability of excitation to a combination mode, (ν_1,ν_2,ν_3) , we take the product of the three corresponding single Franck-Condon factors; for the energy of the combination mode we use the sum of the energies of each of the contributing modes. From these results we generate the intensity and energy of all significant combinations. The final calculation includes 22 vibrational states, which account for 99.5% of the intensity.

B. The line shape

Because the excitation energy is only 29 eV above threshold, the intrinsic line shape is not Lorentzian, but is modified

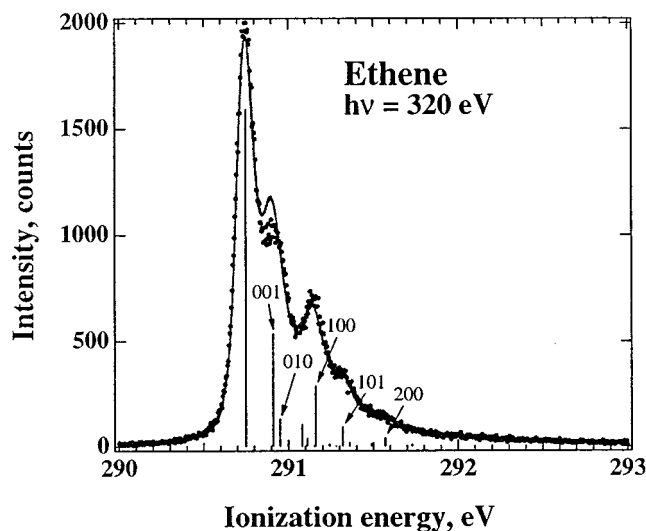


FIG. 1. Experimental and calculated photoelectron spectra for carbon 1s photoionization in ethene. The points show the experimental data. The vertical lines show the positions and intensities of 14 of the predicted vibrational transitions. Several of these are labeled with the appropriate vibrational quantum numbers. The solid line represents the predicted vibrational structure dispersed so as to show the combined effects of experimental resolution, lifetime, and postcollision interaction. The overall intensity and position of this line as well as a constant background have been fit to the experimental data by least squares. The data and the region used for fitting extend to both higher and lower energies than are shown here.

by postcollision interaction (PCI) between the low-energy photoelectron and the subsequent high-energy Auger electron. To approximate the PCI-modified line shape, we have used the theory of van der Straten, Morgenstern, and Niehaus [26] using a range of values for the natural linewidth between 70 and 110 meV.

The final spectrum is obtained from a convolution of the vibrational intensities with the PCI line shape and the resolution function. Spectra for different values of the linewidth were then fit to the experimental data with height, position, and constant background as adjustable parameters. The lowest value of χ^2 was obtained with a natural linewidth of 98 meV. This is to be compared with theoretical values of 95 and 89 meV, calculated by Coville and Thomas [27] and by Hartmann [28], respectively, and with an experimental value of 85 ± 10 reported by Kempgens *et al.* [15].

A comparison between the calculated and measured spectrum is seen in Fig. 1, where it is to be noted that the agreement is very good. Additional studies [11], at lower resolution, on other hydrocarbons show similarly good agreement. It is apparent that this method of calculating the spectra gives satisfactory results.

IV. DISCUSSION

A. Localization and delocalization

It is apparent that the vibrational excitation in the core ionization of ethene can be described by a model in which the core hole is localized, even though two carbons are equivalent. To obtain further insight into this phenomenon, we use an approach similar to that outlined by Domcke and

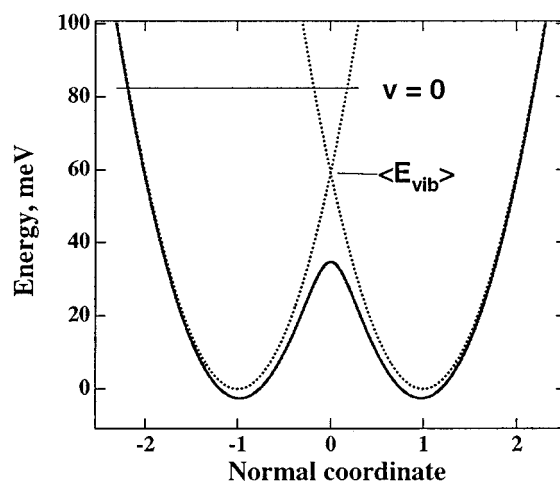


FIG. 2. Potential energy functions for localized (dotted) and delocalized (solid) models for the vibration of the bending mode of ethene at 165 meV (ν_3).

Cederbaum [16]. In the localized approach, the molecule is asymmetric, with the core hole located either on the left carbon or on the right carbon; the various bond lengths and bond angles are different on the left from what they are on the right, reflecting the different bonding of core-ionized and neutral atoms. The vibrations are relative to one or the other of these configurations. Taking a harmonic oscillator model gives the two dotted curves shown in Fig. 2, which represent the potential energy for one of the modes as a function of normal coordinate. Here the horizontal axis is the normal coordinate for one mode, normalized so that ± 1 on this scale corresponds to the difference in the coordinate between the equilibrium configuration of the neutral molecule and that of the core-ionized (localized) molecule. The potential energy at $Q=0$ is the difference in energy between the core-ionized molecule in its equilibrium configuration and in the configuration of the neutral molecule. Since the core-ionized molecule is created at $Q=0$, it has, on the average, a vibrational excitation energy approximately equal in magnitude to this difference (labeled $\langle \epsilon_{\text{vib}} \rangle$ in the figure). The horizontal line labeled “ $v=0$ ” shows the location of the lowest vibrational state for the left-hand potential relative to its zero; $\langle \epsilon_{\text{vib}} \rangle$ must be added to this to obtain the average vibrational energy relative to the zero of the potential. (In constructing these curves, we have used our calculations for the mode at 165 meV, for which $\langle \epsilon_{\text{vib}} \rangle$ was found to be 59 meV.)

In the delocalized picture we take linear combinations of these left and right configurations, thus allowing for the possibility that the core hole can be on either carbon. At the symmetry point we have two new energies, split about the average vibrational excitation energy by $\pm (\epsilon_g - \epsilon_u)/2$, where $\epsilon_g - \epsilon_u$ is the difference in energies between the g and u molecular orbitals of the 1s electrons. Given this splitting, the potential energy curves in the delocalized model are easily calculated as a function of normal coordinate. The curve for the lower of the two energies is shown as the solid line; this represents the adiabatic potential energy. (For this illustration we have taken the $g-u$ difference to be 49 meV, which is the difference in orbital energies obtained in a calculation using the 6-31G** basis set.)

Our comparison between experiment and theory shows that the localized potential gives an accurate description of the vibrational structure. How do we understand that the core-ionized molecule follows the localized potential rather than the delocalized one? The core-ionized molecule is created from a symmetric molecule, i.e., at $Q = 0$, where the two localized curves intersect. The electron is, however, removed from one or the other of the two carbons, left or right, and the molecule begins to vibrate according to one of the localized potentials, the left one, for example. In order for the molecule to explore the right-hand potential, the core hole must relocalize to the right carbon atom. The time for this relocalization is $\hbar/(\epsilon_g - \epsilon_u)$, whereas the time of a characteristic vibration is $\hbar/\epsilon_{\text{vib}}$, where ϵ_{vib} is the energy of a vibrational quantum. In CO₂, studied by Nordgren *et al.* [17] and by Kivimäki *et al.* [18], the hole delocalization time is about 200 times as long as the vibrational time, and the core hole cannot change its location during many vibrational periods. Thus the relevant potential is the localized one. This breakdown of the Born-Oppenheimer approximation, predicted by Domcke and Cederbaum [16], gives rise to what is known as dynamic core-hole localization.

For ethene, as studied here, the difference in times is not so pronounced. Our estimate of the $g-u$ splitting, 49 meV, is slightly less than $\frac{1}{3}$ of the vibrational energy, and the characteristic times are, accordingly, in the same ratio. Nevertheless, the vibrational structure is accurately predicted by the localized model. This result suggests a wider applicability of this model than might have been expected from the presentation of Domcke and Cederbaum [16], who emphasized that the $g-u$ energy difference must be close to zero.

B. The localized vibrational modes

We have seen that the core ionization of ethene can be treated as a localized excitation, with the result that the plane of symmetry perpendicular to the carbon-carbon bond of the ethene molecule is destroyed and the appropriate normal modes are those of CH₂=NH₂⁺ rather than those of ethene. However, the planes of symmetry that contain the carbon-carbon bond remain, and only those modes that are symmetric with respect to these planes will be excited in core ionization. In ethene there are five such modes—three A_g modes and two B_{3u} modes (Herzberg's notation [29]). These are two carbon-hydrogen stretching modes, two HCH bending modes, and the carbon-carbon stretching mode. There are five similar modes in the core-ionized molecule, all A_1 ; however, as noted earlier, the calculations show that only three of these are significantly excited.

The highest-energy mode (referred to here as ν_1) is calculated to be at 409 meV and results from carbon-hydrogen stretching. It produces the peak in the spectrum at an ionization energy of 291.15 eV. This feature is apparent in the spectra reported by Köppe *et al.* [6], Sæthre *et al.* [9], and Kempgens *et al.* [15]. The theoretical calculations show that this is almost exclusively a local mode, involving the in-phase stretching of the two hydrogens attached to the core-ionized carbon, as has been noted by Sæthre *et al.* [9]. Our predicted energy for this mode, 409 meV, is close to, but slightly lower than, that derived by Kempgens *et al.* [15] from their data, 424 ± 10 meV.

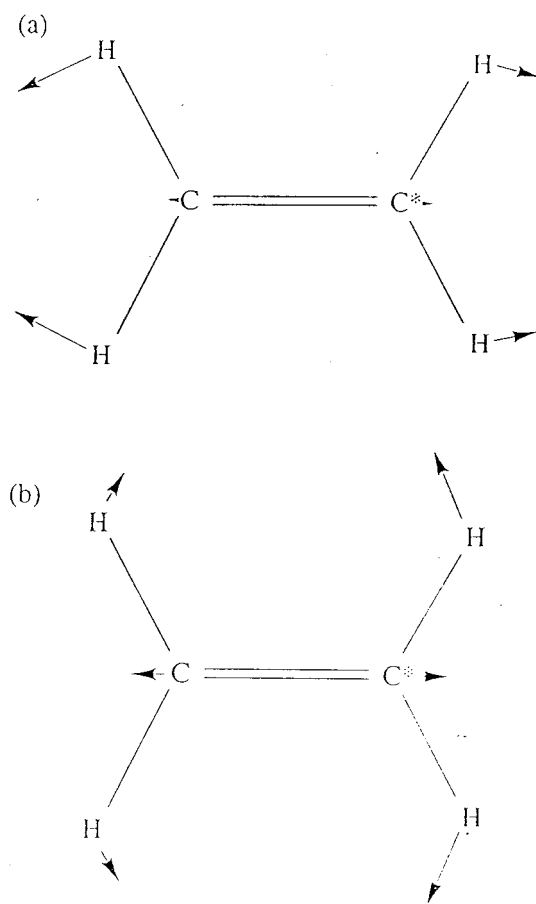


FIG. 3. Two of the predicted normal modes of core-ionized ethene. The asterisk indicates the core-ionized carbon. (a) HCH bending mode with $h\nu = 165$ meV, referred to in the text as ν_3 . (b) Carbon-carbon stretching mode with $h\nu = 201$ meV, referred to in the text as ν_2 .

The peak seen in Fig. 1 at an ionization energy of 290.9 eV is apparent as a shoulder in the spectra obtained by Köppe *et al.* [6] and Kempgens *et al.* [15] and as asymmetric broadening of the main peak in the results of Sæthre *et al.* [9] and Köppe *et al.* have attributed this to carbon-carbon stretching ($h\nu = 191$). The theoretical calculations show, however, that most of the intensity in this region comes from the mode referred to here as ν_3 , illustrated in Fig. 3(a), with a calculated energy of 165 meV. A smaller contribution (about 20% of the intensity in this region) comes from the mode illustrated in Fig. 3(b), ν_2 (201 meV). It is apparent from Fig. 3(a) that the major contribution involves predominantly HCH bending at the unionized carbon, with similar, but less pronounced, bending at the ionized carbon. The theoretical calculations [9] show a change in the equilibrium HCH bond angle of several degrees at the unionized carbon with a smaller change in angle at the ionized carbon. This change in geometry gives rise to the vibrational excitation that is observed at 290.9 eV. Carbon-carbon stretching plays only a small role in this mode according to our calculations, contrary to the conclusion drawn by Köppe *et al.*

Comparison of our analysis with those of Köppe *et al.* [6] shows the importance of having guidance from theoretical calculations in interpreting the data. Their analysis is based on the assumption that only two vibrational modes contribute

to the structure observed in the carbon 1s photoelectron spectrum of ethene—carbon-hydrogen and carbon-carbon stretching. From a comparison of the vibrational frequency that they have attributed to carbon-carbon stretching (191 meV) with the frequency for the similar mode in neutral ethene (201 meV), they concluded that the carbon-carbon bond is weaker and longer in the core-ionized molecule than in the neutral molecule. The theoretical analysis, however, shows, first, that three modes, rather than two, are significant and, second, that the main vibrational excitation in this energy region is the HCH bending mode, rather than the carbon-carbon stretching mode. Their conclusion about bond length change is, therefore, unjustified. The theoretical calculations of Saethre *et al.* [9], in fact, show a *shortening* of the equilibrium bond length by 5.7 pm upon core ionization,

Even with higher resolution, empirical fits of the experimental spectrum might not be able to determine the relative importance of HCH bending and CC stretching, since the

lifetime broadening (90–100 meV) will cause these peaks to overlap. As can be seen from the vertical lines labeled 001 and 010 in Fig. 1, the frequencies are not very different from one another and the spectrum will be fit almost equally well with various combinations of the two modes. The need for theoretical help in interpreting such spectra is apparent.

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