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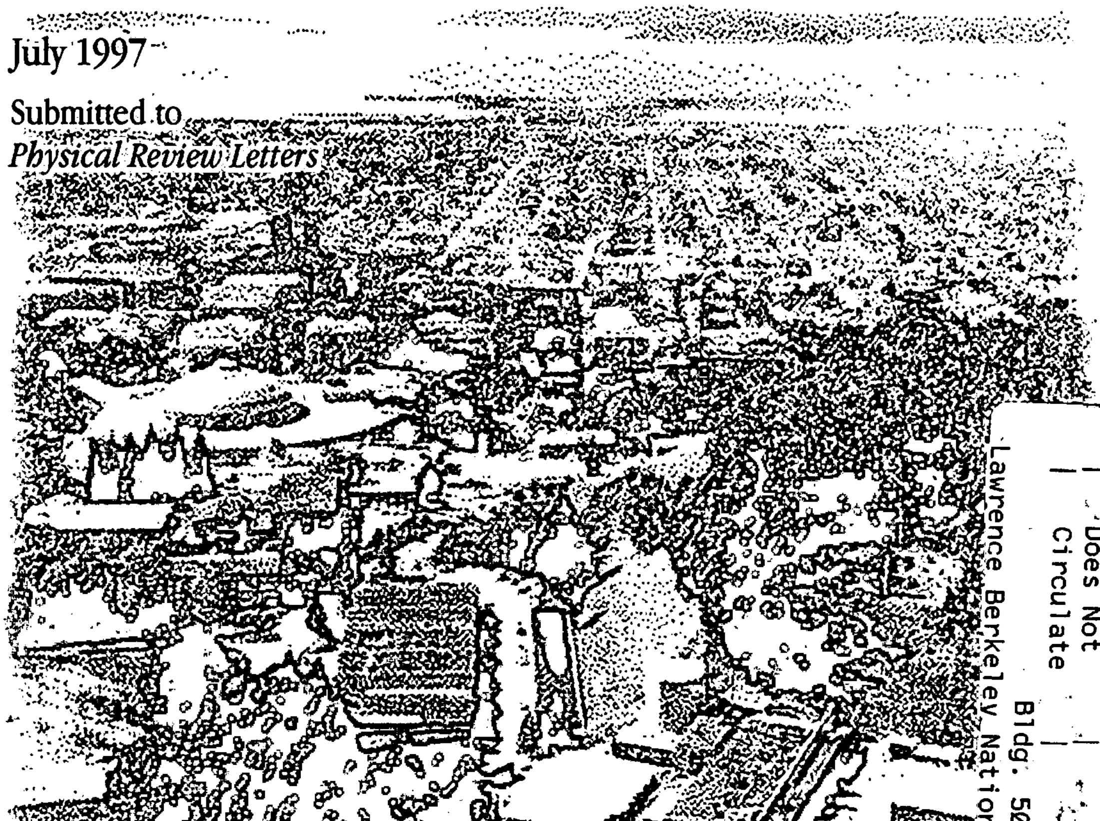

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HIGH-RESOLUTION CARBON 1S PHOTOELECTRON SPECTRUM OF ETHENE. AB INITIO CALCULATION OF VIBRATIONAL STRUCTURE

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High-Resolution Carbon 1s Photoelectron Spectrum of Ethene. Ab Initio Calculation of Vibrational Structure

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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 and the equivalent-cores approximation. Agreement between the calculated spectrum and measurements (taken 29 eV above the carbon 1s threshold) is excellent. This 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.

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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 CH_4 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 no apparent 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 CS_2, worse agreement for SO_2, and no change for H_2S 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 a future paper[11] we will describe the successful application of this procedure to spectra taken with an experimental resolution between 113 and 140 meV for methane, acetylene, deuteroacetylene, ethene, deuteroethene, 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 does 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 3 vibrational modes and their combinations contributing to the structure. It has been previously studied at lower resolution by Köppe et al[6] and by Sæthre et al.[9]

Experimental procedure and resolution

Measurements were made on Beamline 9.0.1 of the Advanced Light Source[15] 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 the σ resonance 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 (v=0) is 103 meV, but this appears to have been broadened by sample thickness. The weaker lines (v=1 and v=2) have widths of 78 and 82 meV, in reasonable agreement with the value of 85 meV reported by others.[16] 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 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]

Theoretical procedures

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[17] with the D95(d,p) basis set at the MP4SDQ level. To describe the core-ionized species, we use the equivalent-cores approximation;[18] that is, the calculations were done for $CH_2{=}NH_2^+$ (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.[19] 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 v_3, v_1, and v_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 $(v_1,0,0)$, $(0,v_2,0)$, and $(0,0,v_3)$ 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%.[20] We assume that the probability for excitation to a combination mode, (v_1,v_2,v_3), is equal to the product of the three corresponding single Franck-Condon factors and that the energy of the combination mode is 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.

The line shape. Because the excitation energy is only 29 eV above threshold, the intrinsic line shape is not lorentzian, but is modified by post-collision 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,[21] using a range of values for the natural line width 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 line width 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 line width of 98 meV. This is to be compared with theoretical values of 95 and 89 meV, calculated by Coville and Thomas[22] and by Hartmann,[23] respectively.

A comparison between the calculated and measured spectrum is seen in Figure 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.

Discussion

To a reasonable approximation, core-ionization of ethene can be regarded 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 $CH_2=NH_2^+$ 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[24]). 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 lower resolution spectra reported by Köppe et al.[6] and by Sæthre et al.[9] The theoretical calculations show that this is almost exclusively a local mode, involving the symmetric motion of the two hydrogens attached to the core-ionized carbon, as has been noted by Sæthre et al.[9]

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 as asymmetric broadening of the main peak in the results of Sæthre et al.[9] Köppe et al. have attributed this peak to carbon-carbon stretching ($h\nu = 191$ meV) and have proposed that contributions from the HCH bending mode can be ignored. 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 Figure 2a, with a calculated energy of 165 meV. A smaller contribution (about 20% of the intensity in this region) comes from the mode illustrated in Figure 2b, ν_2, (201 meV). It is apparent from Fig. 2a 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 assumption made by Köppe et al.

Comparison of our analysis with that 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, in fact, show a shortening of the equilibrium bond length by about 4 pm upon core ionization.

Even with higher resolution, empirical fits of the experimental spectrum would 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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Figure captions

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 post-collision 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.

Fig. 2. 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.

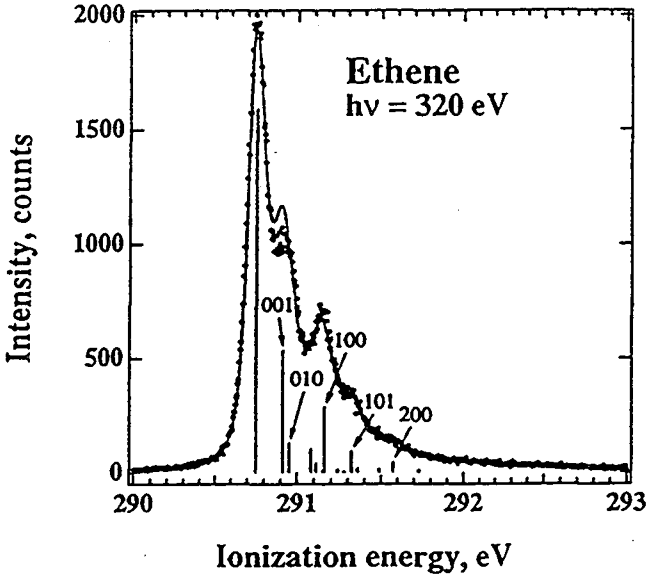

Fig. 1

High-Resolution Carbon 1s Photoelectron Spectrum of Ethene. Ab Initio Calculation of Vibrational Structure J. Bozek, T. X. Carroll, J. Hahne, L. J. Sæthre, J. True, and T. D. Thomas

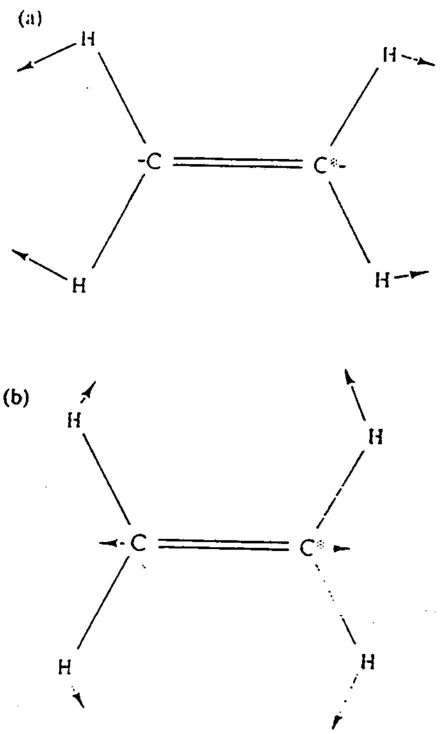

Fig 2

High-Resolution Carbon 1s Photoelectron Spectrum of Ethene. Ab Initio Calculation of Vibrational Structure J. Bozek, T. X. Carroll, J. Hahne, L. J. Sæthre. J. True, and T. D. Thomas

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