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High-resolution C 1*s* photoelectron spectra of methane, ethene, propene, and 2-methylpropene

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Vibrational fine structure in the C 1*s* photoelectron spectra of methane, ethene, propene, and 2-methylpropene has been observed using high-resolution synchrotron radiation. The degree of vibrational excitation is found to increase with the number of hydrogens attached to the core-ionized carbon atom, and this observation can be rationalized using a linear coupling intensity model. The vibrational structure can be accounted for almost quantitatively with the assumption that the primary vibrational excitation is stretching of the CH bond attached to the core-ionized carbon atom, using the results from methane to establish the intensities of the CH stretching vibrations in the other molecules. *Ab initio* calculations of the geometrical changes accompanying C 1*s* core ionization support this picture. The high resolution in these experiments makes it possible to determine the core-ionization energies of the inequivalent carbons in propene and 2-methylpropene, as well as the difference between the adiabatic and vertical ionization energies in all four molecules. *Ab initio* calculations of vertical binding-energy shifts using hole-state calculations show good agreement with those determined experimentally. [S1050-2947(97)08404-7]

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I. INTRODUCTION

Vibrational fine structure in core photoelectron spectra from molecules was first observed more than twenty years ago [1]. The C 1*s* core photoelectron spectrum of methane was then observed to be composed of at least three vibrational lines and it was possible to observe both the vertical and the adiabatic C 1*s* ionization energy of the molecule. The observation of the vibrational fine structure was achieved by technological developments of the spectroscopic technique at that time. These included a rotating aluminum $K\alpha$ anode source for excitation, monochromatization of the x rays using a spherically bent quartz crystal and enhancement of the performance of the electrostatic electron analyzer with a multichannel plate detector. The high resolution thus achieved revealed that vibrational excitation can contribute significantly to the line broadening in core photoelectron spectra.

The quartz-crystal monochromator has, in practice, a resolution limited to about 0.25 eV and no monochromatized Al $K\alpha$ excited gas phase spectrum has been reported with a total full width at half maximum (FWHM) of less than 0.30 eV. As a consequence, one has not even partly resolved vibrational fine structure in Al $K\alpha$ excited core photoelectron spectra of any molecule other than methane. Only line profiles have been observed. However, using synchrotron radiation and grazing-incidence grating monochromators, it has recently been possible to get a spectral linewidth substantially smaller than the one obtained with the crystal monochromator and still have intensity enough for core photoelectron spectroscopy [2–7]. Notably, the vibrational fine structure of the C 1*s* photoelectron line in carbon monoxide [3] and methane [4] has been observed at the X1 beamline in Brookhaven. Vibrational fine structure of core-ionized molecules has also been observed in experiments at the beamline in Wisconsin [5] and at the Daresbury Laboratory in the U.K. [6]. A very highly resolved C 1*s* spectrum of carbon monoxide [7] has recently been presented from beamline 51 at the MAX laboratory in Sweden [8].

We present here high-resolution C 1*s* photoelectron spectra of methane, ethene, propene, and 2-methylpropene, obtained using beamline 51 at the MAX laboratory. A major goal of this work has been to determine the different core-ionization energies for the inequivalent carbons in propene and 2-methylpropene. The differences in chemical reactivity of the double bond between ethene, propene, and 2-methylpropene as well as between the different carbons in propene and in 2-methylpropene provide a chemical incentive to investigate these core-ionization energies. Methane and ethene are simple compounds that provide prototypes for understanding the vibrational structure in the more complex molecules.

We have observed vibrational structure in all the C 1*s* photoelectron spectra and have been able to show that the dominant features of the vibrational profiles of these molecules arise from stretching of the CH bonds of the core-ionized carbon atoms. A linear coupling intensity model is found to account almost quantitatively for the vibrational

TABLE I. Experimental adiabatic and vertical C 1s ionization energies and comparison with calculated vertical chemical shifts relative to ethene. All values are in eV.

Molecule	Atom	I (adiabatic)[a]	I (vertical)[b]	ΔI (vertical)	ΔI (calc. vertical)[c]
Methane	C1	290.71[d]	290.91	0.09	0.01
Ethene	C1	290.75	290.82[e]	0.00	0.00
Propene	C1	290.18	290.25	−0.57	−0.59
	C2	290.69	290.73	−0.09	−0.14
	C3	290.67	290.81	−0.01	−0.02
2-methylpropene	C1	289.76	289.83	−0.99	−1.06
	C2	290.65	290.65	−0.17	−0.27
	C3	290.54	290.69	−0.13	−0.19

[a] Peak top position of the first member of the progression ($v=0$).

[b] Center of gravity of the intensity distribution.

[c] Core-hole state calculation.

[d] From Asplund *et al.*, Ref. [19].

[e] From Sæthre *et al.*, Ref. [14].

structure and makes it possible to obtain both the ''adiabatic'' and the vertical ionization energies for larger molecules. These are important for the comparison of core photoelectron shifts with chemical properties of molecules.

II. EXPERIMENTAL DETAILS

The x rays at beamline 51 at the MAX laboratory are produced by a short undulator, which is constructed to allow for very small magnetic gaps, down to 8 mm [9]. A modified SX-700 plane grating monochromator [10] produces a photon beam with a very narrow bandpass. The beam is refocused by a toroidal mirror in order to give high intensity in the sample compartment. The refocusing stage is also used for differential pumping, and the vacuum in the experimental chamber is effectively isolated from the monochromator. The electrons were energy analyzed using a hemispherical sector analyzer [11]. There is also an efficient differential pumping system in the analyzer itself. The pressure in the sample compartment can thus be kept as high as about 0.1 mbar, while still maintaining a base pressure below 10^{-5} mbar in the spectrometer.

Methane (99.95%), ethene (99.95%), propene (99.4%), 2-methylpropene (99.5%), and carbon dioxide (99.995%) were obtained from the ALFAX company and introduced into the inlet system without further purification.

For intensity reasons the spectra have been obtained 12–20 eV above the C 1s ionization threshold ($h\nu$=303 eV for methane and 310 eV for the other molecules). At these energies some postcollision effects [12] are present in our spectra. However, the influences from postcollision can be modeled empirically using suitable line profiles.

The resolution of the monochromator and electron spectrometer was set in order to reveal the finest possible details of the spectra, while keeping the recording times reasonable. For methane we used a 20-μm monochromator slit and 20-eV pass energy of the electron analyzer. In the case of ethene, propene, and 2-methylpropene, a 50-μm monochromator slit and 50-eV pass energy were sufficient, since the inherent structures are broader in these cases. The spectra were internally calibrated by mixing the sample gas with CO_2. The CO_2 gas could not be used as an absolute standard, since it was discovered that shape resonance effects gave enhanced vibrational broadening at the photon energy employed [13], thus influencing the vertical ionization energy of the calibrant. Instead, we refer all energies of ethene, propene, and 2-methylpropene to the vertical energy of ethene at 290.82 eV [14].

The numerical treatment of the data used the program package from Scienta [15]. With this, the spectra can be fit with pseudo-Voigt functions to represent the combined effects of lifetime width and experimental resolution, and a tail to low kinetic energies can be included to model the effects of postcollision interaction and unresolved, low-frequency vibrations. Special features of the fitting procedure for each molecule are described in more detail below.

The measured spectra are shown in Figs. 1–4. The lines, which represent fits to the data, are discussed in a subsequent section. The carbon 1s ionization energies derived from these spectra are given in Table I.

III. THEORETICAL CONSIDERATIONS

A. *Ab initio* calculations

Ab initio calculations of equilibrium geometry for the neutral molecules and the core-ionized species were performed using the GAUSSIAN-94 program package [16] and the $d95(d,p)$ basis. This is the Dunning-Huzinaga double-zeta basis set [17] augmented with p polarization functions, i.e., $(9s5p1d)/[4s2p1d]$ for C and N, and $(4s1p)/[2s1p]$ for H. For the core-ionized species, the equivalent core $(Z+1)$ approximation [18] was used. The geometries were optimized at the restricted Hartree-Fock level for both the initial and final states. There is good agreement between calculated and experimental initial-state geometries for these molecules. The calculated differences in bond lengths and bond angles are summarized in Tables II–IV.

Looking first at methane, in Table II, we note that core ionization is accompanied by a shrinkage of the CH bond by about 0.07 Å. This value is noticeably greater than that of about 0.05 Å, which has been found experimentally from fits to the vibrational structure in core-ionized methane [1,4,19,20]. Our experience is that this prediction of too

TABLE II. Calculated changes in bond lengths [r (Å)] and angles [ϕ (deg)] upon carbon 1s core ionization for methane and ethene.

Molecule	r	Δr	ϕ	$\Delta\phi$
Methane	C1 H1	−0.073		
Ethene[a]	C1 H1	−0.073	C1 C2 H2	−1.71
	C2 H2	0.001	C2 C1 H1	−0.08
	C1 C2	−0.057		

[a] In ethene C1 is the core-ionized atom. H1 refers to either of the two hydrogens attached to C1.

much bond shrinkage is a common failure of such calculations. Consequently, we can use these results only for qualitative guidance.

With this reservation in mind, we note a common feature of the calculated changes in bond length. This is that the bonds attached to the core-ionized carbon atom shrink by 0.03–0.07 Å, but other bond lengths change very little. The changes in bond angles are small. Thus, we expect that core ionization will produce vibrational excitation primarily in modes that are local to the core-ionized atom.

In order to obtain theoretical values of the core-ionization energies, calculations of the energies of the neutral and core-ionized molecules (at the optimized geometry of the neutral) were done at the restricted Hartree-Fock level with the MOLECULE-ALCHEMY programs [21] using the same basis set as above. The hole-state calculations for the core-ionized molecules were performed within the restricted open-shell Hartree-Fock approximation using the maximum overlap criterion [22]. Calculated vertical core-ionization energies were then obtained as the difference between the total energies of the final core-hole state and the initial closed-shell state. These so-called ΔSCF ionization energies take into account the redistribution of electrons after ionization. For present purposes, we are concerned only with the shifts of the 1s ionization energies relative to ethene. These are listed in Table I. For propene and 2-methylpropene, these results have been used to assist in the assignment of the spectra.

TABLE III. Calculated changes in bond lengths [r (Å)], angles [ϕ (degrees)], and dihedral angle [δ (degrees)] upon carbon 1s core ionization for propene. See drawing in text for numbering of the atoms.

Calculated		Ionization at	
parameter	C1	C2	C3
r	Δr	Δr	Δr
C1 C2	−0.049	−0.062	−0.011
C2 C3	−0.021	−0.028	−0.025
C1 H1	−0.074	−0.001	−0.002
C1 H2	−0.074	−0.002	−0.001
C2 H3	−0.002	−0.075	−0.008
C3 H4	−0.003	−0.005	−0.074
C3 H5	−0.001	−0.007	−0.075
ϕ	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$
C1 C2 C3	−1.21	0.88	−4.12
C2 C1 H1	0.24	−1.39	−2.20
C2 C1 H2	−0.27	−1.66	1.77
C1 C2 H3	−2.09	−0.92	7.20
C2 C3 H4	1.18	−2.31	0.12
C2 C3 H5	−2.33	−2.26	0.57
δ	$\Delta\delta$	$\Delta\delta$	$\Delta\delta$
C1 C2 C3 H5	1.38	−0.44	−0.57

TABLE IV. Calculated changes in bond lengths [r (Å)], angles [ϕ (degrees)], and dihedral angle [δ (degrees)] upon carbon 1s core ionization for 2-methylpropene. See drawing in text for numbering of the atoms.

Calculated		Ionization at	
parameter	C1	C2	C3
r	Δr	Δr	Δr
C1 C2	−0.042	−0.066	−0.011
C2 C3	−0.015	−0.032	−0.017
C1 H1	−0.076	−0.002	−0.003
C1 H2	−0.076	−0.002	−0.001
C3 H3	−0.003	−0.005	−0.074
C3 H4	−0.003	−0.007	−0.076
C2 C3′	−0.015	−0.032	−0.008
ϕ	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$
C1 C2 C3	−2.18	−0.02	4.50
C2 C1 H1	0.003	−1.33	−1.89
C2 C1 H2	−0.003	−1.33	−1.75
C2 C3 H3	0.76	−1.91	0.08
C2 C3 H4	−1.81	−2.14	0.48
C1 C2 C3′	−2.18	−0.02	7.11
C2 C3′ H3′	0.76	−1.92	−2.23
C2 C3′ H4′	−1.81	−2.14	0.70
δ	$\Delta\delta$	$\Delta\delta$	$\Delta\delta$
C1 C2 C3 H4	0.83	−0.38	−0.45
C1 C2 C3′ H4′	0.83	−0.38	−1.31

B. Analysis of vibrational structure

Understanding of the vibrational structure can be greatly simplified with two approximations. These are (1) that we can consider vibrational modes that are localized to the bonds attached to the core-ionized carbon, and (2) that the Franck-Condon vibrational intensities can be calculated using a linear coupling model [23,24].

Local modes

A full analysis of the vibrational structure would take into consideration the multidimensional problem of all of the normal modes of the core-ionized molecule. However, the theoretical calculations show that the major changes in geometry upon core ionization are in the bond lengths of the atoms attached to the core-ionized carbon—the carbon-hydrogen bonds and the carbon-carbon bonds. Moreover, they show that the CH stretching modes of the core-ionized molecules involve modes that are local either to the core-ionized carbon or to the unionized carbons. A simplification that is adequate for the present purposes is to treat the core-ionized center and its immediate neighbors as an isolated molecule. We then consider only the normal modes of this isolated molecule, which represent the actual localized normal modes of the whole molecule. Because of the large difference between CH and CC stretching frequencies, we can treat these modes separately. For the CH stretching, only the fully symmetric mode, A_1, is excited. Inspection of the experimental spectra shows that the vibrational envelope is dominated by a structure with a spacing characteristic of CH stretching frequencies. As a result, to a first approximation, we can consider the vibrational structure as being due to a single A_1 CH stretching mode.

Linear coupling model

A second simplification is introduced by noting that the CH vibrational frequencies for the core-ionized species are calculated to be within about 10% of those for the neutral molecules. In the case where these frequencies are identical, the Franck-Condon factors, $I(0\rightarrow v)$, for excitation from the ground vibrational state of the molecule to the v vibrational state of the ion are given exactly in the harmonic oscillator approximation by a Poisson function:

$$I(0\rightarrow v)=e^{-S}\frac{S^v}{v!}. \qquad (1)$$

From harmonic-oscillator wave functions one can show that

$$S=\frac{\delta^2\mu\omega}{2\hbar}, \qquad (2)$$

where δ equals the change in the equilibrium normal coordinate, μ the appropriate reduced mass for the normal mode, and ω the vibrational frequency of the normal mode. These equations can be obtained from the analytic expressions for harmonic-oscillator Franck-Condon factors given by Hutchisson [25] or from the linear coupling model developed by Cederbaum and Domcke [23] (which includes the approximations of no change in frequency upon core ionization and no coupling between normal modes).

S is related to the physical parameters of the molecule by Eq. (2). However, it has additional significance. First, S is the average value of v for the Poisson distribution and is, therefore, the average quantum number for the vibrational excitation. Correspondingly, $\hbar\omega S$ is the average vibrational energy of the Franck-Condon envelope and is equal to the mean vibrational excitation produced in the vertical core ionization. Second, S reflects the width of the vibrational distribution; the larger S is, the broader the distribution. Finally, S is equal to the ratio of intensities of the $v=1$ to $v=0$ peaks. As a result, a value of S can be easily estimated empirically from the spectrum.

Intensities of the CH *stretching frequencies*

From the measured spectra, Figs. 1–4, it can be seen that the vibrational progression is much more pronounced in methane than in ethene. Consideration of the simplifications discussed above shows that this difference arises directly from the different numbers of hydrogen atoms attached to the core-ionized carbon. As noted, the only vibrational mode of importance is the local A_1 mode, which involves equal changes, Δr, in the bond lengths of all of the hydrogen atoms attached to the core-ionized carbon. The change in the normal coordinate for this mode can be expressed in terms of the change Δr_i of the CH bond lengths:

$$\delta=\frac{1}{\sqrt{n}}\sum_{i=1}^{n}\Delta r_i=\sqrt{n}\Delta r, \qquad (3)$$

where n is the number of CH bonds around the core-ionized atom. Combining this expression with Eq. (2) gives

$$S=\frac{n\Delta r^2\mu\omega}{2\hbar}. \qquad (4)$$

Thus, S is proportional to the number of CH bonds, we expect (and find) that the Franck-Condon distribution broadens as we increase the number of hydrogen atoms attached to the core-ionized carbon. The relative intensity of the $v=1$ transition increases linearly with S and, therefore, linearly with n. The relative intensities of the transitions for higher values of v also increase with n, as can be readily calculated from Eq. (1).

An alternate approach to the same result can be obtained by considering the average vibrational excitation energy for the mode. The theoretical calculations show that the equilibrium bond length for each hydrogen atom connected to a core-ionized carbon atom is about 0.07 Å shorter than it is in the neutral molecule, and is the same regardless of how many hydrogen atoms there are. Core ionization, a vertical process, therefore produces an ion with stretched CH bonds. The total energy associated with this stretching, which is equal to the average vibrational energy, increases, therefore, in proportion to the number of hydrogen atoms attached to the core-ionized carbon. Since this energy is also equal to $S\hbar\omega$, S must also be proportional to the number of H atoms, just as we have seen in the simplified picture presented earlier.

This approach provides a convenient way to analyze the vibrational structure in the molecules we have studied. The value of S can be taken from the methane data and then used to determine the Franck-Condon factors to be used in fitting the other spectra. We will see below that this procedure allows us to represent the spectra well with a minimum number of free parameters.

IV. DISCUSSION

A. The methane C 1*s* photoelectron spectrum

The methane C 1*s* core photoelectron spectrum is shown in Fig. 1. One vibrational progression with three or more components is well resolved in this spectrum. Since the photon energy was only 12 eV above threshold, the line profiles are influenced by the postcollision effects. The line shapes cannot be modeled by a symmetric Voigt line profile and, as an approximation, we have used a pseudo-Voigt function with asymmetric tail, as available in the SCIENTA program package [15]. In Fig. 1 we have used four lines with the same asymmetry, Gaussian-Lorentzian mixing, and width (FWHM) and a constant background. The heights of the four peaks were free parameters. The position of the main peak and a single vibrational frequency were also free. In all, there are ten free parameters to fit this spectrum.

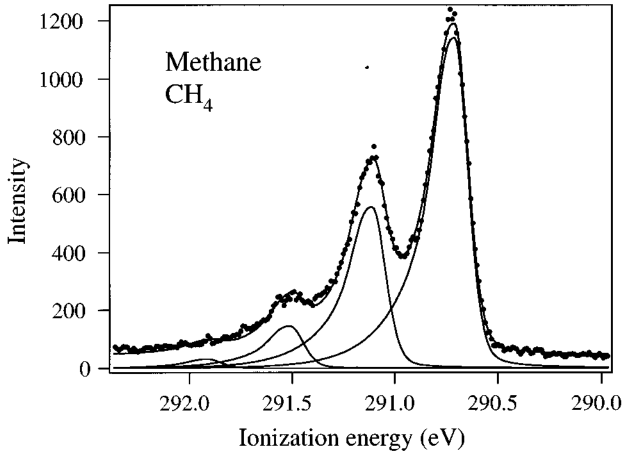


FIG. 1. The C 1*s* core photoelectron spectrum of methane obtained with synchrotron radiation at the MAX laboratory. The excitation energy was 303 eV.

The FWHM was found to be 219(10) meV. Both the electron spectrometer and the monochromator resolution at this setting are approximately 70 meV, giving a total instrument resolution of about 100 meV. The Doppler broadening is negligible at this low kinetic energy and therefore inherent effects (postcollision and lifetime broadening, etc.) dominate the line profiles.

We obtain the relative intensities of 1, 0.49, 0.13, and 0.03 for the transitions to the $v=0,1,2,3$ components in the progression. These values are in good agreement with earlier x-ray photoelectron spectroscopy (XPS) values [19,20]. To some extent, this result is surprising, since it is known that for the C 1*s* photoionization in CO, the Franck-Condon factors may vary with the excitation energy near the threshold [3], and one should therefore not expect a perfect agreement between XPS and synchrotron radiation results near the ionization threshold. The vibrational progression seen in Fig. 1 has been discussed earlier; it corresponds to the fully symmetric CH stretch mode in methane [1,19]. The observed energy difference between vibrational components is 400(10) meV. We do not see any evidence of anharmonicity.

The value of 0.49 for the relative value of the $v=1$ transition is used to determine a value of S for the CH stretch; this is then used to fix the value of S in the subsequent fits for the other molecules. Using $S=0.49$ and the linear coupling intensity model, we predict for methane 0.12 and 0.02 for the relative intensities of the $v=2$ and $v=3$ transitions, respectively, in good agreement with the observed values.

From the centroid of the vibrational spectrum and the value of 290.707 eV [19], we obtain a vertical ionization energy of 290.91 eV, which is in excellent agreement with the value reported by Thomas and Shaw [26]. These values are listed in Table I.

For the other molecules in this study, we can also find a difference between the vertical energy and the energy of the $v=0$ component in a CH stretch mode. We will call this latter energy adiabatic, although we are aware that other modes may contribute to the peak shape, with the result that the true adiabatic energy is at a lower ionization energy. However, the CH stretch frequency is much larger than other frequencies, so our notation is to some extent justified.

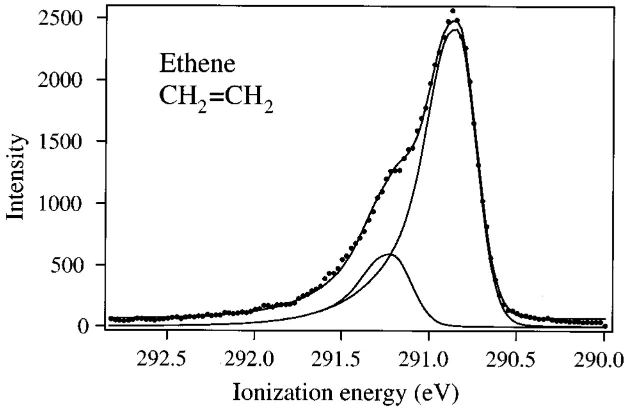


FIG. 2. The C 1*s* photoelectron spectrum of ethene. The spectrum was obtained with 310 eV excitation energy. The lines show the results of a least-squares fit to the data using results from methane to constrain the vibrational profiles. See text for details of the fitting procedure.

B. The ethene C 1*s* photoelectron spectrum

In Fig. 2 we present the C 1*s* photoelectron spectrum of the ethene molecule. It is apparent that there is vibrational structure on the high-ionization-energy side of this peak.

As in the case of methane, we have used the pseudo-Voigt function with an asymmetric tail to fit the spectrum. As noted, the profile is determined by three free parameters, but these are different for ethene than for methane because of different experimental conditions. The spectrum of Fig. 2 has been fit by using two such functions of identical (but variable) shape, allowing for an optimization of the energy positions and the intensity of the main peak. The intensity of the second peak is not a free parameter, but is determined using the linear coupling intensity model and the S value from methane. S for ethene is taken to be half the value of S for methane, since there are only two hydrogen atoms attached to the core-ionized carbon in ethene, but four in methane. A constant background is also included in the fitting process. There are, thus, 7 free parameters to fit this spectrum. The resulting FWHM of the lines is 359(10) meV. The energy difference between the lines is 368(10) meV.

The total instrumental resolution in the experiment is about 150 meV. Since the ethene data were obtained at a higher kinetic energy than was used for methane, the postcollision broadening is expected to be smaller than in the case of the methane. The large width of the fitted lines in Fig. 2 is therefore attributed to excitation of other vibrational mode(s).

In ethene there are three totally symmetric modes for the ground-state molecule: the totally symmetric C-H stretch mode, a CC mode, and a symmetric HCH bending mode. In the core-ionized molecule the corresponding modes are a local CH stretch, a CC stretch, and a local HCH bend. The latter two are at about half the frequency of the first. The *ab initio* calculations, summarized in Table II, indicate that all three of these modes are likely to be excited in core ionization. Because of its higher energy, the CH stretching mode is apparent in the spectrum as an obvious shoulder, but the other two modes are unresolved and are seen only in the additional width of the spectrum.

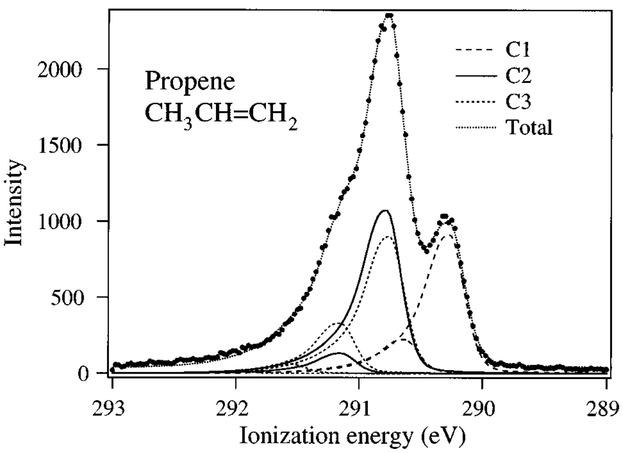


FIG. 3. The C 1*s* photoelectron spectrum of propene. The spectrum was obtained with 310 eV excitation energy. The lines show the results of a least-squares fit to the data using results from methane and ethene to constrain the vibrational profiles. See text for details of the fitting procedure.

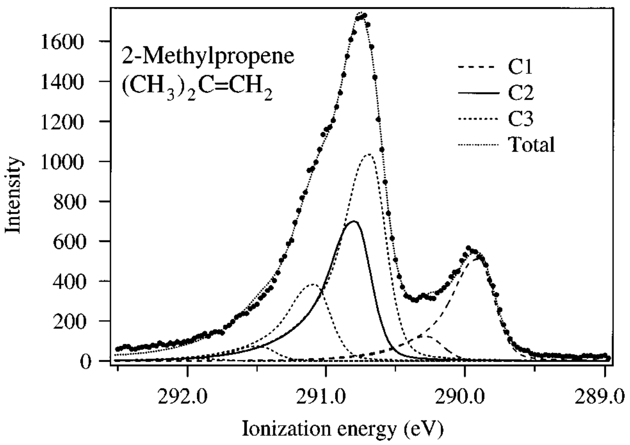


FIG. 4. The C 1*s* photoelectron spectrum of 2-methylpropene. The spectrum was obtained with 310 eV excitation energy. The lines show the results of a least-squares fit to the data using results from methane and ethene to constrain the vibrational profiles. See text for details of the fitting procedure.

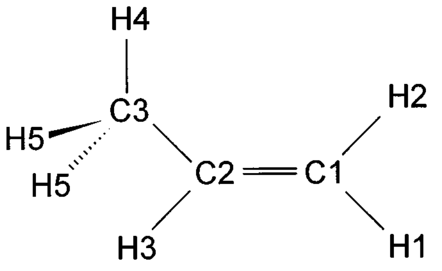
The energy difference of 368 meV between the vibrational fine structures is about the same as the energy of the totally symmetric CH stretch mode in the neutral molecule, which has an energy of 374 meV [27]. The calculations indicate a shortening of the CH bond by 0.07 Å and of the CC bond by 0.06 Å upon C 1*s* photoionization. Shortening of the bond usually implies a stronger bond and we therefore expect the vibrational energy to be larger than 374 meV in the core-ionized molecule. The fact that our observed difference is not larger than this can be attributed to unresolved contributions from the CC stretching and HCH bending modes. The $v=1$ contribution from these modes to the $v=0$ CH stretch peak will distort the position of this peak to higher apparent ionization energy, whereas the $v=2$ contribution of these modes will have almost the same energy as the $v=1$ CH stretching mode and will produce little effect on this peak position.

The adiabatic and vertical energies of ethene are summarized in Table I.

C. The propene C 1*s* photoelectron spectrum

The C 1*s* core photoelectron spectrum of propene is shown in Fig. 3. The spectrum was obtained under the same conditions as for ethene. There are three structures visible in the spectrum of Fig. 3. There is a resolved peak at a low binding energy of about 290.2 eV, a main structure with a maximum at about 290.7 eV, and a shoulder at around 291.1 eV.

Since the propene molecule contains three inequivalent carbon atoms, it is tempting to make a simple assignment of this spectrum in terms of three chemically shifted photoelectron peaks. However, such an analysis would neglect the presence of the vibrational fine structure, and we will here show that the chemical binding-energy shifts must be obtained with a consideration of the vibrational excitation of the core-hole states. We use the following labeling of the atoms:



The spectrum by itself does not give any clues as to how to assign the peaks. However, comparison with the spectrum for 2-methylpropene, Fig. 4, provides a first step. For both molecules the spectra are characterized by an almost resolved peak at low ionization energy and a larger peak at somewhat higher ionization energy. We note that in the spectrum for 2-methylpropene, which contains two methyl groups, the higher-energy peak is a more prominent feature than it is for propene. We can, therefore, conclude that the contribution from the methyl group is contained in this peak. From the overall areas we can also conclude that this peak contains contributions from one of the other carbons. Beyond this we must rely on the theoretical calculations, which show that C1 has a lower ionization energy than C2. We therefore assign the peak at low ionization energy to C1. This assignment is supported by comparison with similar measurements we have made on the three monochloropropene isomers.

The propene molecule has low symmetry (Cs) and has 21 nondegenerate normal vibrational modes. Several of these are active upon C 1*s* photoionization, and a strict analysis of the vibrational fine structure would be very complex. If we instead adopt the idea that local vibrational modes around the core-ionized atom are most important, especially the local CH stretching modes, we can use the linear coupling model and the value of *S* from the methane spectrum to predict the vibrational structure of the spectrum.

The propene spectrum has been fitted with the pseudo-Voigt function with an asymmetric tail, with three adjustable-shape parameters. The three total areas for C1, C2, and C3 are constrained by stoichiometry. However, it has been shown that the intensities of the C 1*s* lines are affected differently by shakeup; consequently, the relative intensities have been set to the theoretically predicted values: C1, 31.2%; C2, 33.1%; C3, 35.7% [28]. The relative heights of the vibrational structures within each of these groups are determined by the linear coupling model using the *S* value from methane (appropriately modified to reflect the number of hydrogen atoms attached to the core-ionized atom). The vibrational spacings are taken to be the same as for methane for the methyl carbon, C3, and the same as for ethene for the unsaturated carbons, C1 and C2. There are thus eight adjustable parameters, three for peak shape, one for background, one for overall intensity, and three for the adiabatic ionization energies of each of the three carbons.

The result of this fitting procedure is also shown in Fig. 3, where it can be seen that the correspondence between the fitted line and the experimental spectrum is quite good. The FWHM of the lines obtained from this analysis is 387(10) meV, almost the same as was found for ethene.

An important conclusion of the fitting procedure in Fig. 3 is that the shoulder at 291.1 eV is not directly due to the vertical binding energy of the C3 carbon atom. This structure is instead associated with excitation of the $v=1$ CH stretching modes from C2 and C3 ionization. The analysis shows that the adiabatic ionization energies for C2 and C3 are nearly the same. From these results, it is possible, for the first time, to estimate both the adiabatic and the vertical ionization energies for all the carbon atoms in this molecule. These energies are listed in Table I.

D. The 2-methylpropene C 1*s* photoelectron spectrum

The 2-methylpropene molecule also contains three chemically different carbon atoms. We use the following labeling:

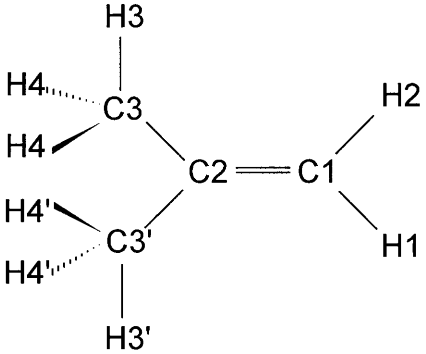


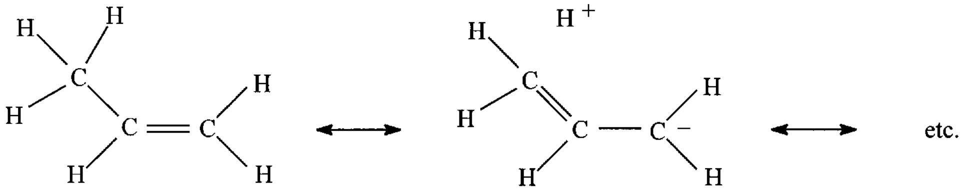
Figure 4 displays the C 1*s* core photoelectron spectrum of the molecule. At the lowest binding energy, 289.8 eV, there is a well separated peak, which we assign to C1, for the reasons outlined above. The dominant structure peaks at about 290.6 eV, with a shoulder and tail on the high-energy side. One should notice that the energy splitting between the structure at 289.8 eV and the peak maximum at 290.6 eV is substantially larger (by 0.3 eV) than in the case of the propene molecule. Also, there is considerable spectral intensity between these peaks.

We have applied the same type of analysis to this spectrum as was done for the propene molecule, with the same set of free parameters. The difference between the fits is partly stoichiometric, two methyl group C 1*s* profiles being used instead of one. The stoichiometric ratios were corrected to account for the influence of shakeup: C1, 22.4%; C2, 24.8%; C3, 52.9% [28]. In addition, the C2 line profile now consists of only one line, since this carbon no longer binds to a hydrogen atom and no local CH stretch progression exists for core ionization on this site. The resulting peak profile parameters are almost identical to those of propene, with a FWHM of 378(10) meV. As can be seen from Fig. 4, a reasonable fit is obtained, and again the shoulder at higher ionization energy is not due to the peak maximum of the C3 line but originates from the $v=1$ excited vibrational state in the C3 ionized system. As in the case of propene, the adiabatic C3 ionization energy lies very close to the C2 energy, which agrees with calculated energies (Table I). From the results of Fig. 4, we conclude that even for large molecules the vibrational profile may be analyzed, and reliable core ionization energy shifts obtained with high precision.

E. The ionization energies

There are several noticeable features of the ionization energies we have measured. First, the adiabatic ionization energy for a methyl/carbon varies only slightly from methane (290.71 eV), to propene (290.67 eV), to 2-methylpropene (290.54). Such trend as there is can be accounted for by a larger relaxation energy associated with the larger molecules. Second, addition of one or more methyl groups has only a small effect on the ionization energy of the carbon to which these are attached: for ethene we have ethene 290.75 eV, propene (C2) 290.69 eV, and 2-methylpropene (C2) 290.65 eV. These changes are again consistent with a larger relaxation energy associated with the larger molecules.

Third, and in contrast, the variation in the ionization energy for C1 in the unsaturated compounds is quite striking: ethene 290.75 eV, propene 290.18 eV, and 2-methylpropene 289.76 eV. This shift of about one eV is possibly associated with the existence of resonance forms such as



which shift charge from the methyl group to the C1 in propene. Similar but larger resonance effects will also be seen in 2-methylpropene. Such effects and other connections between these ionization energies and chemical properties will be discussed elsewhere [29].

As has been noted, the theoretical calculations of ionization energies were used as an aid in assigning the peaks in the propene and 2-methylpropene spectra. However, only the information that C1 has the lowest ionization energy was used. Comparison of the theoretical shifts with the experiment values in Table I shows that theory predicts all of the trends seen in the experimental results. The root-mean-square disagreement between theory and experiment is only 0.06 eV.

V. CONCLUSIONS

The C 1*s* core photoelectron spectra from methane and a series of alkene molecules have been recorded by using an advanced experimental setup at the MAX synchrotron radiation facility. The increased resolution has made possible a detailed study of the ionization energies from all carbon atoms in the alkene species. It has been shown that it is necessary to consider in detail the vibrational structure in the photoelectron spectra in order to obtain the ionization energies correctly. We have found that the vibrational structure in these molecules is due primarily to local modes involving stretching of the CH bonds attached to the core-ionized carbon atom. The degree of vibrational excitation increases with the number of these hydrogens.

A linear coupling intensity model has been presented in order to make possible analysis of complex spectra from large molecules. This has allowed us to use data from the photoelectron spectrum of C 1*s* in methane to predict accurately the vibrational structure in the spectra of ethene, propene, and 2-methylpropene. This procedure has also allowed us to obtain accurate ionization energies for very similar but nonequivalent carbon atoms in propene and 2-methylpropene.

The new precision in the determination of chemical shifts provides possibilities to use core-electron spectroscopy for the study of chemical properties of organic molecules. It is seen that the C1 ionization energies are strongly influenced by resonance effects involving methyl substituents at the C2 position.

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