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Adiabatic and vertical carbon 1s ionization energies in representative small molecules

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Abstract

Adiabatic and vertical carbon 1s ionization energies are reported for methane (CH_4), ethane (CH_3CH_3), ethene (CH_2CH_2), ethyne (HCCH), carbon monoxide (CO), carbon dioxide (CO_2), fluoromethane (CH_3F), trifluoromethane (CHF_3), and tetrafluoromethane (CF_4) with an absolute accuracy of about 0.03 eV. The results are in good agreement with earlier values but are measured with higher resolution and accuracy than has previously been available. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

For over 30 years, core-ionization energies have been the subject of many experimental and theoretical investigations. The reason for this interest is that these ionization energies relate directly to properties of fundamental chemical significance such as the charge distribution in a molecule, the electron withdrawing power of substituents, and the ability of a molecule to accept or supply charge at a particular site. Of particular interest have been carbon 1s ionization energies because of the rich and important chemistry of carbon-containing compounds.

A requirement for such measurements to be useful is that they be accurate, and in the early days of electron spectroscopy techniques were developed to provide accurate measurements. At the most basic level these involved use of characteristic X-rays whose energies were accurately known together with neon or argon as calibration gases to establish the kinetic energy scale of the analyzer [1–4]. Other approaches have measured the shift in electron kinetic energy relative to a calibrant for which the absolute ionization energy is known [5,6]. The accuracy that can be obtained is better than 0.05 eV, and measurements made at different laboratories usually agree well within this uncertainty. The limitation of using characteristic X-rays is, however,

the resolution, and for a molecule the measurement represents an average over the vibrational profile, or, in other terms, the vertical ionization energy.

The availability of high-brightness, high-resolution sources at third-generation synchrotrons has made it possible to resolve, at least partially, the vibrational structure for a number of small molecules. Thus, it is now possible to determine not only the vertical but also the adiabatic ionization energy. Moreover, the narrow lines and high intensity available with synchrotron radiation open the possibility of improving the absolute accuracy of the earlier measurements. With synchrotron radiation, however, the accuracy with which the photon energy is known is not high. For a given setting of the monochromator, the apparent photon energy may change from one day to the next by a large fraction of an electron volt. Also away from the photon-energy region for which the monochromator has been calibrated, the photon energy may be absolutely in error by an electron volt or more. Thus, for accurate measurements of ionization energies, it is necessary to include an internal standard for which the ionization energy is well known.

A useful standard for calibration of a carbon 1s photoelectron spectrum is the argon $2p_{3/2}$ line. Since argon is monatomic, there is no vibrational excitation and the vertical and adiabatic energies are identical. The ionization energy is known with an accuracy of about 0.02 eV; reported values range from 248.60 to 248.63 eV [1,2,7–11]. This is only 40–50 eV away from the range of carbon 1s ionization energies. We report here the results of measurements in which we have used this line to calibrate the carbon 1s photoelectron spectra for nine compounds: methane (CH_4), ethane (CH_3CH_3), ethene (CH_2CH_2), ethyne (HCCH), carbon monoxide (CO), carbon dioxide (CO_2), fluoromethane (CH_3F), trifluoromethane (CHF_3), and tetrafluoromethane (CF_4). The carbon 1s ionization energies for these molecules span most of the range of known carbon 1s energies, from about 291 to 302 eV. Since these spectra are, to one degree or another, vibrationally resolved, we have been able to determine both the adiabatic and vertical ionization energies. These energies are of interest in their own right for the chemical information that they provide and for comparison with theoretical calcula-

tions. In addition they provide potential calibration standards for future measurements.

2. Experimental procedures

The measurements were made using Beamline 10.0.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratory at a photon energy of 330 eV. This beamline receives its radiation from an undulator (U10) with a 10-cm period. It is equipped with a spherical-grating monochromator that is capable of a resolving power of greater than 10^4; this was set to provide a resolution of 40 meV for the photoelectron measurements. Measurements of the photon absorption spectrum for the argon $2p_{3/2}$ to 4s transition and for the carbon monoxide carbon 1s to 2p transition indicated that the actual resolution of the photon beam was about 50 meV.

The electron spectra were measured with a Scienta SES-200 spectrometer [12]. This was set to have a pass energy of 40 eV, and the entrance slit of the analyzer was chosen to give an expected resolution of 40 meV. Measurements of the xenon 5s photoelectron spectrum indicated that the resolution of the analyzer under these conditions was actually about 60 meV. All measurements were made with the analyzer perpendicular to the beam direction and at an angle of 54.7° to the polarization direction.

Combining the contributions from the photon bandwidth, the spectrometer resolution, and the Doppler broadening gives an expected resolution for the carbon 1s spectra of 88 meV. Least-squares fits to the spectra (discussed below) with the resolution as one of the fitting parameters give results that are consistent with this.

The actual voltages applied to the Scienta analyzer were measured with a digital voltmeter and were found to differ slightly from the nominal voltages. Corrections of about 6 mV were made to the nominal voltages on the basis of these measurements.

The photoelectron spectra have been fit by least squares using a fitting function that includes the effects of post-collision interaction (PCI) and experimental resolution [13]. To represent the PCI effect, we have used Eq. (12) of van der Straten et al. [14], which is expected to be valid in the energy

region we have studied. This is convoluted with a Gaussian to represent the experimental resolution.

The experimental spectra and the fits for the nine molecules are shown in Fig. 1. In this figure, the circles represent the data and the solid lines indicate the least-squares fits. Specific features of the fits are discussed in the following paragraphs.

For the argon $2p_{3/2}$ spectrum there is only one peak, and the fitting is straightforward. For the molecules, however, there is vibrational structure, and each molecule presents unique challenges. For methane, carbon monoxide, and carbon dioxide, only one vibrational mode (CH or CO stretching) is excited. For the first two, the vibrational structure is sufficiently well resolved that the spectra can be fit with a progression with peak heights and positions all as free parameters. For carbon dioxide, which is

not well resolved, the energy spacing between the peaks has been fixed at 165.6 meV [15].

For ethane, two vibrational modes are excited, CH stretching and HCC bending [16–18], and the spectrum can be fit well with three peaks representing the $v=0$, 1 and 2 excitations of the CH stretching mode plus three more representing the $v=1$ bending mode in combination with each of the first three peaks. We have used two different fitting procedures for ethane. In one, all 12 parameters describing the positions and intensities are free. In the other, the positions and intensities of the (1,1) and (2,1) peaks relative to the (1,0) and (2,0) peaks are constrained to be the same as for the (0,1) peak relative to the (0,0) peak. The energies obtained from the two procedures are essentially the same. For ethene, the same set of six peaks contribute significantly to the spectrum
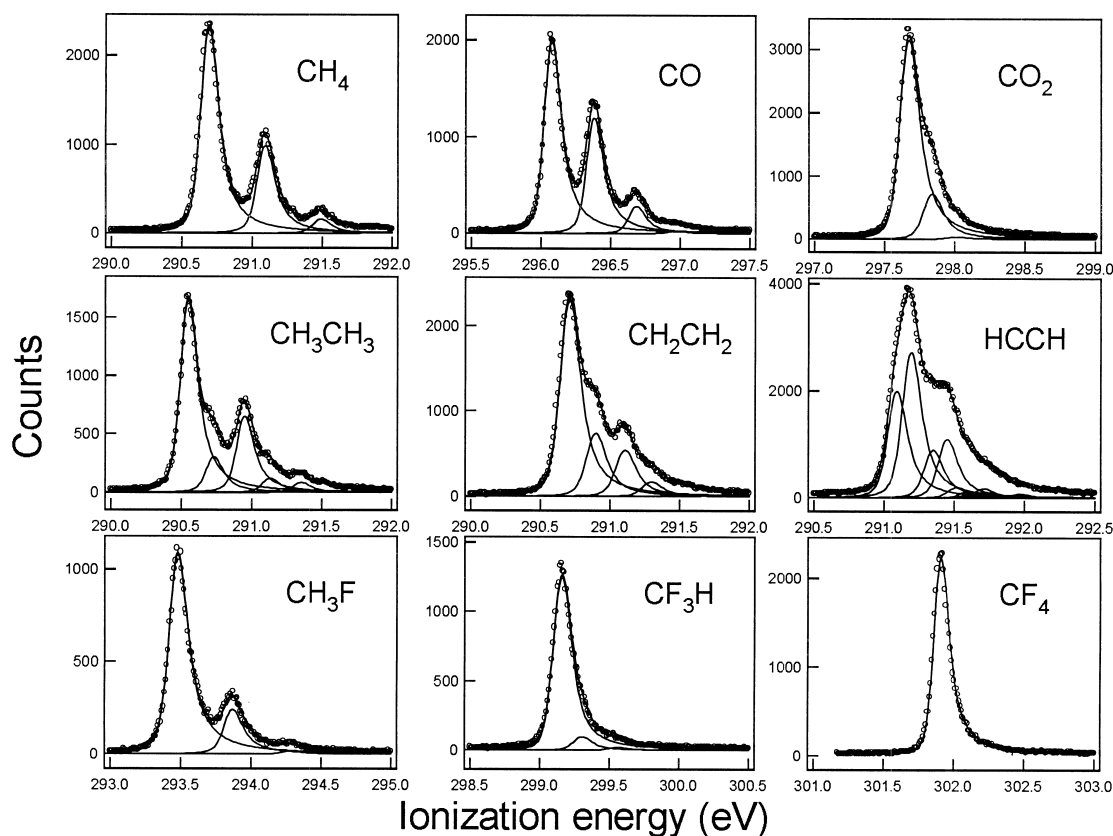

Fig. 1. Carbon 1s photoelectron spectra of the molecules studied here. The circles show the data and the lines show least-squares fits to the data.

[16,19], but in this case a completely free fit is not possible, and the peaks have been constrained in the same way as for ethane.

For ethyne, the spectrum is complicated by the significant splitting between the $^2\Sigma_g$ and $^2\Sigma_u$ states and by the prominence of CC stretching (which is almost absent in ethane and ethene). For this molecule, we have constrained the relative positions of the 11 peaks to be given by the values determined by a theoretical analysis of this spectrum [20]. The relative intensities of seven of the 11 peaks were also constrained in the same way. Comparison of the experimental spectrum with the theoretical prediction (which does not include the effect of anharmonicity) shows that too much intensity is predicted for the $v=2$ and 3 states of the CC stretching mode. As a result, an average vibrational energy (and, hence, the vertical ionization energy) that is based on the theoretical predictions is too high. To correct for this, we have allowed the total intensity for each of these two states to vary freely in the fit. Although this choice influences the vertical ionization energy derived from the fit, it has negligible effect on the adiabatic energy.

For tetrafluoromethane there is also only one vibrational mode expected to be excited, but the excitation is so weak that it is impossible to distinguish between vibrational excitation and a low-kinetic energy tail produced by PCI. For this molecule, we have made three fits, one assuming no vibrational excitation, one assuming that there is a $v=1$ peak shifted 100 meV from the main peak, but with intensity as a free parameter, and one assuming that there is a $v=1$ peak with free position and intensity. The effect of these different assumptions on the position of the adiabatic peak ($v=0$) is to shift it by only 3 meV, which is insignificant. The results of the fit assuming no vibrational excitation have been used. Trifluoromethane is, like tetrafluoromethane, somewhat ambiguous. The PCI tail obscures the weak vibrational structure, but there is some evidence for a contribution from the $v=1$ peak of the CH stretching mode. From the fits, the position of the adiabatic peak is almost independent of assumptions about the presence or absence of vibrational excitation. The data presented here are based on a fit in which the $v=1$ peak of the CH stretching mode is constrained to be displaced from

the $v=0$ peak by 400 meV (typical CH stretching frequency), but is unconstrained in intensity. In addition the fit allows for a weak CF stretching mode. Fluoromethane is fit with a single progression that corresponds to CH stretching.

The fitting procedure gives the nominal kinetic energy of the adiabatic peak in each molecular spectrum and of the $2p_{3/2}$ peak in the argon spectrum. These cannot be used directly to determine the ionization energies, however, since neither the absolute kinetic energy nor the absolute photon energy is known accurately. On the other hand, the difference between the kinetic energies is accurately known, and this can be combined with the known $2p_{3/2}$ ionization energy (taken to be 248.629 eV [8]). Thus, the carbon 1s ionization energy, I_C, is given by the expression:

$$I_C = 248.629 + \Delta_K + \Delta_R \qquad (1)$$

where Δ_K is the difference in the measured kinetic energies (argon minus carbon) and Δ_R is the difference in the recoil energies imparted to the remaining ion. Values of the adiabatic carbon 1s ionization energies determined in this way are given in Table 1.

From the vibrational profiles that are obtained from the fits, we can also calculate the average ionization energy, which can be equated to the vertical ionization energy. These values are also given in Table 1.

3. Discussion

3.1. Comparison with other values

Previously reported values of the adiabatic ionization energies are based on X-ray photoelectron spectroscopy [21], X-ray spectroscopy [9], and electron-energy-loss spectroscopy [22]. The results of such measurements are compared in Table 1 with the results of our measurements. For four of the seven comparisons, the agreement between our results and those reported by others is within 0.02 eV. For ethene, our result agrees with that of Tronc et al. [22] nearly within the uncertainty of their measurement. For ethyne, the ionization energy is 291.179 eV for the $^2\Sigma_g$ ionic state and 291.128 eV for the average of

Table 1
Adiabatic and vertical carbon 1s ionization energies (eV) (uncertainties in the last digit are given in parentheses)

Molecule	I_C (adiabatic)			I_C (vertical)		
	This work	Other work	Ref.	This work	Other work	Ref.
Methane	290.689	290.707(3)	[21]	290.844	290.83(2)	[24]
		290.76(3)	[22]		290.91(5)[a]	[25]
					290.85(3)	[33]
Ethane	290.545			290.714	290.71(2)	[24]
					290.75(5)[a]	[25]
					290.70(5)	[26]
					290.70(5)[b]	[27]
Ethene	290.695	290.74(4)	[22]	290.823	290.82(5)	[26]
					290.88(5)	[28]
					290.85(3)	[33]
Ethyne	291.128 (avg)[c]	291.20(3)	[22]	291.249[c]	291.2(1)	[27]
	291.179 ($^2\Sigma_g$)				291.14(10)	[30]
Carbon monoxide	296.069	296.05(3)	[22]	296.229	296.24(3)	[3]
					296.28(3)	[33]
Carbon dioxide	297.664	297.66(4)	[22]	297.699	297.69(14)	[1]
		297.651(10)	[9]		297.71(5)	[2]
					297.76(4)	[33]
Tetrafluoromethane	301.898			301.898	301.96(5)	[2]
					301.96(5)	[31]
					301.86(5)[a]	[25]
					301.93(3)	[33]
Fluoromethane	293.478			293.557	293.6(1)	[32]
Trifluoromethane	299.143			299.159	299.1(1)	[32]
					299.24(5)[b]	[27]

[a] 0.18 eV has been added to the results given in Ref. [25], since they used a value of 248.45 for the argon $2p_{3/2}$ ionization energy rather than the value of 248.629 used here.

[b] The ionization energies from Ref. [27] are given relative to that in tetrafluoromethane. We have obtained absolute values by combining these with our value for tetrafluoromethane. The quoted uncertainties include those given in Ref. [27] as well as the uncertainty in our value for tetrafluoromethane.

[c] Unweighted average for the $^2\Sigma_g$ and $^2\Sigma_u$ states.

the $^2\Sigma_g$ and $^2\Sigma_u$ states. The value given by Tronc et al. [22] of (291.20 eV) agrees with our value for the $^2\Sigma_g$ ionic state within the uncertainty they have given. Their value is based on an extrapolation of the Rydberg series, and it is not clear which state is reached by this extrapolation. For methane, the value given by Tronc et al. [22] differs from both our value and that given by Asplund [21] by twice the uncertainty that they have indicated.

The adiabatic ionization energies we have measured are also consistent with a set of measurements that we have made at the Advanced Light Source using a different procedure [23]. In these experiments we have measured the carbon 1s photoelectron spectra of the first six compounds listed in Table 1 simultaneously with the spectrum of tetrafluoromethane. The measurements give the difference between the ionization energies of these compounds and that of tetrafluoromethane. The differences are consistent with the values of the ionization energies listed in Table 1 to within 0.02 eV.

Previous measurements of vertical ionization energies come primarily from X-ray photoelectron spectroscopy. In some cases, only shifts between the ionization energy of interest and that of a reference compound have been measured. Selected values are listed in Table 1 for comparison with our results [1–3,24–33]. For the most part, the agreement between our results and those reported previously is quite good. The average deviation between our vertical ionization energies and the earlier values is −0.01 eV, indicating that any systematic difference

between our measurements and the older ones is small. The root-mean-square difference between our results and the earlier ones is 0.05 eV, which is the same as the average of the uncertainties quoted by the earlier workers.

3.2. Uncertainty of the measurements

The general agreement between our results and those reported earlier indicates that the accuracy of the measurements is quite good. However, not only do our measurements depend on the accuracy with which the argon $2p_{3/2}$ ionization energy is known, but so also do many of the other measurements that have been reported. Thus, the uncertainty in our measurements is at least as great as the uncertainty in the argon ionization energy. The uncertainty quoted for this by Nordgren et al. [8] is 0.01 eV. However, the range of values that have been reported for this quantity is about 0.03 eV [1,2,7–11]. It seems more conservative to assign an uncertainty of 0.02 eV. In addition to this, there is a contribution from other systematic as well as random errors. Comparison of the values given in Table 1 with ionization-energy differences that we have measured [23] suggests that this should be about 0.02 eV — see the second paragraph of Section 3.1. Combining these uncertainties leads to an overall uncertainty in the absolute ionization energies of 0.03 eV. The relative uncertainty between one ionization energy and another is less than this, but how much less we cannot say. As a result, we give the values in Table 1 to three decimal places to allow for the possibility that the uncertainty in the relative numbers is in the third place.

Acknowledgements

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