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Electron impact ionization energies

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Abstract

Ionization energies (IEs) of 25 high temperature effusion-beam species, determined in this laboratory over a period of several decades from electron impact (EI) threshold measurements, are compared primarily with values obtained from photoelectron spectroscopy (PES). In a few instances, the comparisons include values obtained by other spectroscopic methods. The EI values were evaluated by the extrapolated voltage difference method and are assigned an accuracy of 0.10 eV, while the PES values are generally accurate to 0.01–0.02 eV. In the most straightforward cases, where the adiabatic and vertical IEs are coincident, the EI and PES values generally agree to within the lower accuracy of the EI results. Where molecular geometry changes lead to significant differences between adiabatic and vertical IEs, the EI values unexpectedly tend to agree with the adiabatic rather than the vertical IEs. Overall, the comparisons indicate that the Nier-Ingrahm type EI source is capable of reasonably accurate threshold IE measurements, within 0.10 eV, but the interpretation of the results in terms of specific ionic states is, of course, problematic. (Int J Mass Spectrom 197 (2000) 237–242) © 2000 Elsevier Science B.V.

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1. Introduction

The arrangement of a heated effusion-beam molecular source combined with mass spectrometric detection, pioneered by Chupka and Inghram [1] for the study of chemical speciation and thermodynamics of carbon vapor, has over the years provided a wealth of information about the thermochemistry of neutral and ionic species generated in molecular beams. This technique is sometimes referred to as Knudsen cell mass spectrometry (KCMS), and permits the study of many transient, radical species that are generated in the heated effusion cell under chemical equilibrium conditions. A large number of the selected values of dissociation energies of diatomic molecules listed by Huber and Herzberg [2] were determined by KCMS. Likewise, many of the ionization and appearance energies (IEs and AEs, respectively) listed in the NIST compilations [3–5] have come from EI data obtained by KCMS.

Since the Nier-Inghram [6,7] electron bombardment ion source used by Chupka and Inghram [1] (and by others with subsequent versions of this instrument) utilized the traditional hot-filament electron gun with its inherent energy spread, it was generally assumed that only qualitative IEs and AEs with accuracies of 0.3–0.5 eV at best could be obtained. Indeed, most investigators using the KCMS technique subscribed to this view, and made no attempt to explore the full capabilities of this EI source for ionization threshold measurements. Because KCMS provides a way to study many unusual transient, radical species, it seemed worthwhile to pursue the possibility of obtaining higher accuracy in such threshold measure-

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ments. As a result, we believe it is routinely possible to determine EI threshold IEs with an accuracy of 0.10 eV if certain procedures are followed. In this article we compare 25 IE values determined by the EI method in our laboratory over several decades with corresponding values from photoelectron spectroscopy (PES), which have an accuracy of 0.01–0.02 eV. In most instances, the PES values were reported subsequent to the EI values. Comparisons with IEs determined by other spectroscopic methods are also included in several instances. To our knowledge, the summary includes all published IE values with 0.10 eV accuracy from this laboratory for which corresponding PES values or others of similar accuracy are available.

2. Experimental

The electron impact ion source utilized in this work is essentially identical to that described by Chupka and Inghram [1], and by Inghram and Hayden [7]. An important feature of this source is that ionizing electrons emitted from the tip of the tungsten ribbon filament are highly collimated by two circular apertures 0.089 cm in diameter and 0.635 cm apart; the U-shaped tip of the filament is positioned about 0.06 cm from the first aperture. This feature tends to reduce the thermal-energy spread in the electron beam traversing the ionization region, and sharpens the features of the ion yield curves. With this source arrangement, for example, distinct breaks in the ion yield curve of O_2^+ due to onsets of known excited states of the molecular ion are readily apparent.

All electron impact IEs referenced here were evaluated from ion yield curves recorded automatically with an X–Y plotter, and interpreted by the extrapolated voltage difference method [8]. Pertinent features of the ion source and its operation in the recording of ion yield curves have been described previously, along with examples of the recorded curves and a discussion of various aspects of the interpretive process [9,10]. Checks with various reference standards have demonstrated that a threshold accuracy well within 0.10 eV can be attained [9]. Attention is focused on the sensitive region near threshold by recording and interpreting only that portion of the curve within about 2 eV of the zero-intensity baseline, or vanishing current, point. Molecular beam source conditions for generating the EI IE data tabulated here are described in the individual references for each determination.

3. Comparison of EI and PES results

Table 1 lists IE values for 25 species determined in this laboratory by the electron impact method as described previously, along with corresponding values from PES and other methods such as photoionization (PI), analysis of Rydberg series (Ryd), and thresholds of endothermic ion–neutral reactions (END). Comparisons of the EI values with PES results will be discussed first, followed by comparisons with other determinations of relatively high accuracy.

IE values determined from PES studies are generally of superior accuracy (0.01–0.02 eV), and have the important advantage of distinguishing between vertical and adiabatic thresholds. There are several weaknesses, however, in that PES spectral features cannot always be unambiguously associated with the correct neutral precursors, particularly for radical and unstable species prepared in reaction or excitation sources. And impurity bands are not always easily identified. EI values, which are ion-specific by virtue of mass separation, sometimes serve to support the subsequent PES threshold assignments.

In the photoelectron spectra of species for which there is no change in molecular geometry during ionization, the initial peak in the lowest energy band is the most intense, indicating that the vertical and adiabatic thresholds are coincident, as linked by the arrows in Table 1. For species of this type (BF, SiO, CS, SO, Al_2O, and TiO), the EI and PES IEs are in reasonably good agreement, within the lower accuracy (0.10 eV) of the EI determinations. This agreement is very gratifying, indicating that the EI values can be relied upon within 0.10 eV, when the type of ion source and the procedures referred to here are

Table 1
Comparison of IE values derived from electron impact studies, photoelectron spectroscopy, and other methods

	IE, eV						
			PES				
Species	EI (±0.10)	Ref.	Vertical	Adiabatic	Ref.	Other	Ref.
BF	11.06	[10]	→	11.12	[29]	11.115 (Ryd)	[30]
BCl	10.03	[19]				10.01 (PI)	[18,19]
SiO	11.58	[10]	→	11.61	[31]	11.58 (Ryd)	[32]
CS	11.39	[33]	→	11.33	[34,35]		
			→	11.34	[36]		
SO	10.28	[37]	→	10.31	[38]	10.29 (PI)	[39]
AgCl	10.06	[40]	10.08	(9.8)	[16]		
AlO	9.53	[37]				9.46 ± 0.06 (END)	[41]
Al_2O	8.20[a]	[37]	→	8.40	[42]		
FeO	8.71	[43]				8.90 ± 0.16 (END)	[41]
TiO	6.70	[44]	→	6.819	[46]		
			→	6.82	[45]		
CF	9.17	[47]	9.55	9.11	[48]		
CF_2	11.54	[49]	12.24	11.42	[50]	11.445 ± 0.025 (PI)	[15]
SF	10.09	[51]				10.16 ± 0.17 (END)	[52]
SF_2	10.29	[51]	10.31	10.08	[53]		
SCF_2	10.53	[51]	10.62	10.45	[54]		
			10.69	10.52	[55]		
			10.64		[56]		
GeO	11.10	[10]	→	11.25	[11]	11.25 (Ryd)	[14]
			→	11.25	[12]		
$MgCl_2$	11.58	[9]	11.80	(11.0)	[20]		
$CaCl_2$	10.33	[9]	10.99	(10.0)	[20]		
$SrCl_2$	9.70	[9]	10.49	(9.8)	[20]		
$BaCl_2$	9.18	[9]	10.05	(9.3)	[20]		
$CrCl_2$	9.99	[23]	9.97	(9.4)	[24]		
$FeCl_2$	10.63	[23]	10.34	(10.0)	[24]		
			10.45	(10.0)	[25]		
$CoCl_2$	10.75	[23]	10.60	(10.4)	[24]		
			10.51	(10.2)	[25]		
$NiCl_2$	11.38	[23]	11.23	(10.8)	[24]		
			11.34	(10.9)	[25]		
UF_4	9.96	[27]	10.32	9.51	[17]		

[a] Uncertainty ±0.15 eV.

utilized. Rydberg series values for BF and SiO, and the PI value for SO, provide strong support for the PES IEs.

For GeO, the PES spectrum is a bit more complex. Both Colbourn et al. [11] and White et al. [12] report the low energy band to be a sharp, intense peak at 11.25 eV which is overlapped by a less-intense broad band with vibrational structure, extending below 11 eV. Deconvolution of the two bands indicates that the sharp intense peak is associated with ionization to the X $^2\Sigma^+$ ground state of the ion, whereas the broad band is associated primarily with the A $^2\Pi$ excited state of the ion, with a vertical IE of 11.40 eV. Although White et al. [12] attribute the weak features below 11.25 eV to vibrational hot bands in excited neutral GeO, Colbourn et al. [11] initially interpreted this as a progression to a lower adiabatic threshold of the A $^2\Pi$ state; subsequently, this latter interpretation was revised [13] in favor of the hot band explanation. In any event, the relatively insignificant change in internuclear distance on ionization [11,12] is in accord with coincident adiabatic and vertical values for the first IE of GeO. Thus the EI value at 11.10 ± 0.10 eV is in fairly good agreement with the PES [11,12] and Rydberg series values [14] at 11.25 eV.

For those species in which neutral and ionic states have different molecular geometries, the more intense vertical IE lies somewhat higher in energy than the adiabatic threshold. In many instances, vibrational structure in the PES bands can be resolved so that the vertical and adiabatic components are readily differentiated. Of the species listed in Table 1, this clear differentiation between adiabatic and vertical IEs has been observed for CF, CF_2, SF_2, and SCF_2. Because electron impact ionization is considered to be a vertical process in the spirit of the Franck-Condon principle, one would expect that the EI IEs would be more in accord with the PES vertical IEs. Actually this is so only for SF_2. For the two most extreme cases, CF and CF_2, where the adiabatic and vertical IEs differ by 0.44 and 0.82 eV, respectively, the EI IEs are clearly more closely allied with the adiabatic values. The accurate PI threshold value [15] for CF_2, 11.445 ± 0.025 eV, is also in close agreement with the PES adiabatic IE, although photoionization is considered to be a vertical process as well. For SCF_2, the energy separation between vertical and adiabatic values is too small to be decisive and there is some scatter in the PES determinations, but the trend is toward agreement with the lower adiabatic values.

For AgCl, and for the alkaline earth and transition metal dichlorides in Table 1, vibrational structure was not resolved in the reported PES bands, and only vertical IEs were reported from the band maxima. From inspection of the reported bands, we have estimated the approximate adiabatic IEs from the onsets of the first ionizations, shown in parentheses in Table 1. These are only crude values for purposes of discussion, and reflect no input from any of the authors. Our EI value for AgCl agrees closely with the reported [16] vertical IE from PES, and is 0.26 eV higher than the estimated adiabatic value. For $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$, our EI IEs are uniformly lower than the PES vertical values, mostly by 0.7–0.8 eV. For all but $MgCl_2$, the EI values are definitely closer to the estimated adiabatic IEs. On the contrary, for $CrCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$ the EI IEs seem clearly more in accord with the PES vertical IE values; again there is some scatter in the PES values. With UF_4, both vertical and adiabatic IEs, separated by 0.81 eV, were evaluated [17] from the broad low-energy PES band. Our EI threshold IE is almost an average of these two values, but it is doubtful that any significance can be attached thereto.

For AlO, FeO, and SF, reasonably accurate IE values (±0.06 to 0.17 eV) have been determined from the translational energy dependence of the cross sections of endothermic ion-neutral reactions. As seen in Table 1, our EI values are in all instances in agreement with the END determinations, within the error limits. For the molecule BCl, an IE value can be derived from a photoionization threshold measurement [18] of the dissociative process

$$BCl_3 + h\nu \rightarrow BCl^+ + 2\ Cl + e$$

together with thermochemical data for BCl_3, BCl, and Cl and a correction for the internal energy of BCl_3 available for the dissociation process [19]. The corrected PI value of 10.01 ± 0.08 eV for IE(BCl) is in close accord with the EI value of 10.03 ± 0.10 eV, substantiating the stated accuracy of the latter.

4. Discussion

The comparisons described previously show clearly that the EI technique and interpretive method used here can yield useful IE values that are generally reliable to within 0.10 eV. For most diatomic molecules, with their small number of internal modes, the evidence is especially clear-cut and the results unambiguous. With polyatomic molecules, however, the impact energy may be distributed over a larger number of internal modes, thus complicating the interpretation of the threshold process. High resolution PES spectra are especially valuable in identifying the specific vibrational states of the ions involved, and the lack of such information is the major weakness of the EI method; with the latter, one can never be sure about the final state of the ion in the threshold process under study. Nevertheless, EI values that are accurate to within 0.10 eV are useful in the absence of more accurate determinations, and can be particularly helpful in the interpretation of PES spectra of unstable species prepared in reaction or excitation sources when the sample gas composition is uncertain. The mass selection feature of electron impact mass spectrometry does at least give positive chemical identification of the ion under study and removes any ambiguity about the species involved in the ionization process.

A surprising result of the EI/PES comparisons is the correlation of the EI threshold IEs of CF and CF_2 with the adiabatic IEs determined by PES rather than with the vertical IE values, which are distinctly different. Franck-Condon considerations would lead one to expect the EI values to correlate with the vertical IEs, since the Franck-Condon factors for ionization to the lowest vibrational states of CF^+ and CF_2^+ are expected to be very small because of the substantial geometry changes in the ionization process. The differences between adiabatic and vertical IEs of CF and CF_2, 0.44 and 0.82 eV, are well outside the error limit of ±0.10 eV for the EI values presented here, so it is unlikely that the correlation with adiabatic IEs in these cases can be ascribed to experimental error in the EI values. Furthermore, the close accord between the PI threshold IE [15] and the PES adiabatic IE of CF_2 indicates the same effect with PI.

In the metal chloride systems studied, where the EI IEs of the Ca, Sr, and Ba dichlorides are more closely in accord with the estimated adiabatic IEs from PES [20], it has been suggested [9] that geometry differences between neutrals and ions may account for the relatively high degree of EI fragmentation in the heavier alkaline earths. The ratio of parent to fragment ion, MCl_2^+/MCl^+, at 30 eV ionizing energy is 4.6, 0.29, 0.07, and 0.02 for Mg, Ca, Sr, and Ba dichloride vapors [9]. In this respect, the Ca, Sr, and Ba dichlorides are behaving more like CF and CF_2 noted previously, where ionization geometry changes are significant. On the other hand, the Cr, Fe, Co, and Ni dichlorides show relatively little EI fragmentation, with MCl_2^+/MCl^+ ratios ranging from 2.0 to 3.3 [21–23] and their EI IEs definitely correlate more closely with the PES vertical IEs [24,25].

In summary, the traditional "hot filament" EI ion source, when properly configured, is capable of routinely yielding threshold IEs with an accuracy of 0.10 eV but the interpretation of these IE values in terms of vertical or adiabatic transitions may be problematic. However, there are a number of such EI IE values for radical species such as BF_2 [26], UF_5 [27], GeCl [28], and the monochlorides of Cr, Fe, Co, and Ni [23] that will be useful until more accurate values are available.

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