Determination of Electron Impact Ionization and Appearance Potentials

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Summary We show that a general formula may be applied to electron-impact ionization efficiency curves to determine the ionization or appearance potential of an ion without subjective assessment of ionization behaviour near threshold.

SEVERAL methods are currently used to determine ionization or appearance potentials from ionization efficiency curves measured with conventional electron-impact ion sources, either by mathematical[1] or empirical[2] procedures which attempt to allow for the effect of the wide spread of electron energies. However, most of these methods make assumptions which have little or no experimental support, and are likely to give results having significant systematic errors.[3] The low signal-to-noise ratios of ionization efficiency curves measured by manual methods also accentuate the difficulty of determining accurate ionization and appearance potentials. Much better signal-to-noise ratios are readily obtained using a fairly simple computer-aided data acquisition system together with mathematical smoothing techniques.[4] Accurate ionization and appearance potentials can be measured using nearly monoenergetic electron beams,[5] or a Fourier-transform deconvolution procedure,[6] to remove the effect of the electron energy spread from electron impact ionization efficiency curves, but these techniques require sophisticated apparatus to produce good results.

If the data obtained with conventional ion sources are plotted (Figure) against the ionizing voltage (V) as the ionization efficiency i(V) divided by its first derivative i′(V), distinct advantages are gained over the other methods[1,2] for determining appearance potentials. This 'critical slope' function $i(V)/i'(V) = [d \ln i(V)/d(V)]^{-1}$, has units of electron volts and no arbitrary normalization

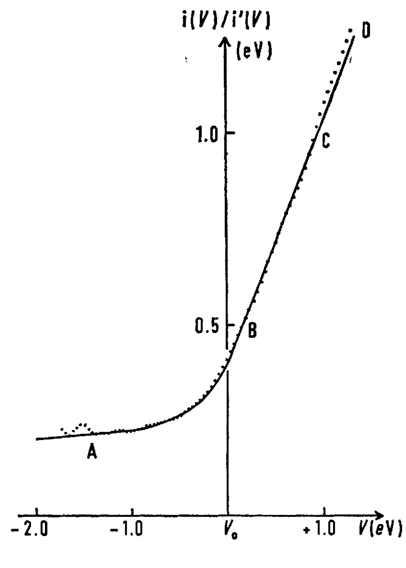

FIGURE. Experimental (·) and calculated (———; $p = 2$, $r = 1$, $q = 5{\cdot}8$, $s = 1{\cdot}5$) i(V)/i′(V) curves for argon.

procedure is necessary to fix the absolute value of the ordinate scale. Furthermore it provides a sensitive means of detecting and allowing for variations in the shapes of ionization efficiency curves due to differences in the ionization cross-sections of different ions. We have measured experimental $i(V)/i'(V)$ curves for several different types of ions and they all show the same general features. Just above onset they curve slowly upwards from a value near 0·2 eV (Figure; AB), becoming linear at energies greater than about 2 eV above the onset (Figure; BC). This linear region often extends over a few electron volts, but for some ions its slope gradually increases after 1 eV or more (Figure; CD).

For electrons of ionizing voltage (V) with thermal energies (U), theoretical ionization efficiency curves may be computed numerically from the convolution integral[7] (1) if the forms of the ionization probability function, $p(E)$, and

$$i(V) \propto \int_0^\infty p(E)m(U)\mathrm{d}U, \; E = V + U \quad (1)$$

the electron energy distribution, $m(U)$, are known. Substituting the parametric functions (2) and (3) into (1),

$$m(U) = U^p \exp(-qU^r) \quad (2)$$

$$p(E) = \begin{cases} (E - V_0)s, & E = V + U \geqslant V_0 \\ 0 & , E < V_0 \end{cases} \quad (3)$$

where V_0 is the true appearance potential, we have been able to simulate accurately the experimental $i(V)/i'(V)$ curve over the whole threshold region (Figure; AC). The parameters p, q, r, s, and V_0 may be determined objectively using a general least-squares computer programme to obtain the best fit between the calculated and experimental curves. For a standard ion source with a tungsten filament on an A.E.I. MS902 mass spectrometer and using a trap current of 20 μA, we find approximately $p = 2{\cdot}0$, $r = 1{\cdot}0$, $q = 5{\cdot}8$. A good fit cannot be obtained if $m(U)$ is assumed to be a simple Maxwellian distribution with $p = r = 1$ and $q = 1/kT$. The calculated $i(V)/i'(V)$ curves show that the parameter s, giving the effective threshold law near threshold may be easily determined from the slope of the linear region (Figure; BC) which equals $1/s$. Even for the relatively small range of measurements we have made so far, we find that s varies markedly for different types of ions. For example, $s \simeq 1{\cdot}5$ (Ar^+, Xe^+), 1·5—2·0 (molecular ions), 1·5—3- (fragment ions), 1·0—1·5 (metastable ions).

The true appearance potential (V_0) may also be determined by an alternative and simple procedure. At $V = V_0$ we have shown that formula (4) holds. Since p,q,r are instrumental parameters and appear to remain fairly constant over a period of time, they can be used in subsequent work once they have been determined, and only s

$$i(V_0)/i'(V_0) = \left\{\Gamma\left(\frac{s+p+1}{r}\right)\right\} \Big/ s(q)^{1/r}\,\Gamma\left(\frac{s+p}{r}\right) \quad (4)$$

needs to be measured from the slope of the linear region of the experimental $i(V)/i'(V)$ curve as described above. Thus the appearance potential is immediately obtained from the $i(V)/i'(V) - V$ curve (Figure) by reading off the voltage at which $i(V)/i'(V)$ equals the critical slope calculated from (4) using values of the gamma functions obtained from mathematical tables.[8] To obtain absolute ionization or appearance potentials, the nominal ionizing voltage (V) must be calibrated with any reference ion whose ionization potential is known accurately. It is unnecessary for the sample and reference ions to have ionization efficiency curves of the same shape.

The good fits obtained between the calculated and experimental curves show that functions (2) and (3) adequately describe the threshold behaviour of ionization efficiency curves measured with conventional mass spectrometer ion sources. This new method is straightforward to use and makes no arbitrary or subjective assumptions about the electron energy distribution or the effective threshold law, unlike most other methods of determining electron impact ionization or appearance potentials. As an example of the results obtained, the difference between the ionization potentials of argon and xenon was measured as 3·59($\pm$0·05) eV at $i(V_0)/i'(V_0) = 0{\cdot}40$ eV, to be compared with 3·629 eV obtained by spectroscopic methods.[9]

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