

Energetics of the Charge-stripping Process from Negative Ions. A New Method for the Estimation of Electron Affinities

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Summary A negative ion A^- with a high translational energy may be converted into a non-decomposing ion A^+ after a glancing collision with a neutral molecule; if both A^- and A^+ are in their ground state, the translational energy difference (ΔE) between A^- and A^+ equals the sum of the electron affinity (E.A.) and the ionisation energy (I.E.) of A , and if the I.E. is known, measurement of ΔE provides a method for the estimation of the E.A. to within an estimated accuracy of 0.4 eV.

electrostatic sector (placed between the main electrostatic analyser and the electron multiplier), which increases the signal: noise ratio and limits the possibility of the detection of artefact peaks.³

Five systems, for which I.E. and E.A. values are known, have been studied, and the results are summarised in the Table. The translational energy profiles for the two ions in the reaction $CN^- \rightarrow CN^+$ are shown in the Figure. Experimental conditions were as follows: electron energy 50 eV

ANY non-decomposing negative ion may be converted, in a field-free region of a mass spectrometer, into a positive ion by the collision process $A^- + N \rightarrow A^+ + N + 2e^-$.¹ The majority of A^+ ions are formed in excited states and fragment to produce an intense spectrum of fragment positive ions, but in a number of cases, peaks corresponding to A^+ itself may be observed in small abundance.¹ Such peaks tend to be more pronounced for small negative ions, and are formed exclusively for monatomic species, particularly negative halide ions.^{1,2} Polyatomic ions A^- , having survived for at least 5×10^{-6} s in order to reach the collision region, will normally be in the electronic ground state. The energy required for the conversion $A^- \rightarrow A^+$, if both ions are in their ground state, will equal the sum of the electron affinity (E.A.) and the ionisation energy (I.E.) of A . The energy ΔE required to effect this transformation must originate from the ion translational energy of A^- .

Ion translational energy measurements were carried out with a V.G. Micromass ZAB 2F mass spectrometer, in which the magnetic and electric sectors are arranged such that the ion beam traverses the magnetic sector first.² The instrument is equipped with a beam lock circuit which enables the selected ion to be held without shift over the whole period of the measurement,² a collision cell (placed in the field-free region between the magnetic and electrostatic sectors),² a modified VG 2000 series data system which controls the electrostatic sector voltage and acquires and processes mass analysed ion kinetic energy (MIKE) spectra,² and a second

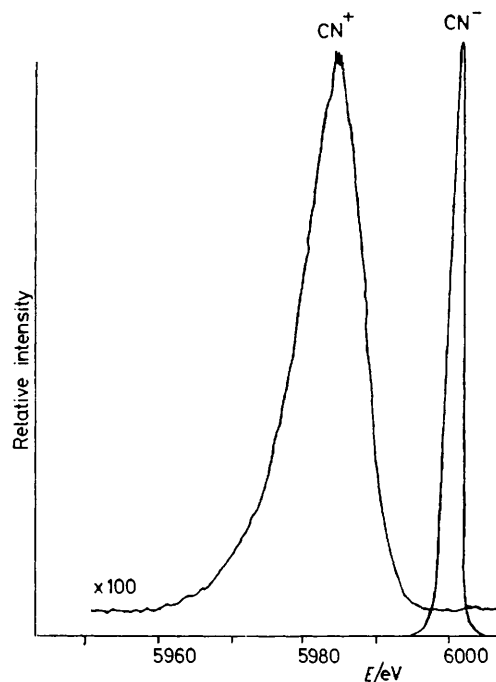


FIGURE. Ion translational energy spectra of CN^- and CN^+ for the charge inversion reaction $CN^- + He \rightarrow CN^+ + He + 2e^-$. The peak for CN^+ is a time-averaged signal from five scans.

TABLE. Ion translational energy differences (ΔE) for processes $A^- \rightarrow A^+$.

Process ^a	Precursor molecule	I.E. of A ^b (eV)	E.A. of A (eV)	I.E. + E.A. (calculated)	ΔE (± 0.5 eV) ^c (measured)
$Cl^- \rightarrow Cl^+$	CCl_4	12.97 ± 0.01	3.613 ± 0.003^d	16.6	16.15^e
$S^- \rightarrow S^+$	CS_2	10.36 ± 0.01	2.05 ± 0.01^f	12.4	12.1^e
$CN^- \rightarrow CN^+$	MeCN	14.2 ± 0.3	3.7 ± 0.2^g	17.9	17.5^e
$CS_2^- \rightarrow CS_2^+$	CS_2	10.08 ± 0.01	$\begin{cases} 0.6 \pm 0.2^h \\ 1.0 \pm 0.2^i \end{cases}$	$\begin{cases} 10.7 \\ 11.1 \end{cases}$	11.4^e
$NO_2^- \rightarrow NO_2^+$	PhNO ₂	9.95 ± 0.01	2.4 ± 0.05^j	12.2	12.6^e
$S_2^- \rightarrow S_2^+$	Rhombic S	9.4 ± 0.05	$> 2.0^k$		11.55^l

^a The efficiency of conversion is *ca.* 1% in all cases. ^b Ref. 4. ^c The value in parentheses (± 0.5 eV) is the energy range obtained for each set of measurements. No allowance has been made for possible systematic instrumental bias or other potential sources of error. ^d R. S. Berry and C. W. Riemann, *J. Chem. Phys.*, 1963, **38**, 1540. ^e Each value is the mean of four measurements carried out on different days. ^f N. S. Buchel'nikova, *Usp. fiz. Nauk*, 1958, **65**, 351. ^g I. N. Bakulina and N. I. Ionov, *Zhur. fiz. khim.*, 1959, **33**, 2063. ^h H. Dispert and K. Lacmann, *Chem. Abs.*, 1976, **85**, 25553. ⁱ R. N. Compton, P. W. Reinhardt, and C. D. Cooper, *J. Chem. Phys.*, 1975, **63**, 3821. ^j E. Herbst, T. A. Patterson, and W. C. Lineberger, *J. Chem. Phys.*, 1974, **61**, 1300. ^k Ref. 5. ^l Mean of eight measurements, standard deviation 0.38 eV, and probable error ± 0.25 eV.

(negative ions produced by dissociative secondary-electron capture), accelerating voltage -6 kV, sample pressure (source) 5×10^{-7} Torr, and pressure of collision gas (He) in cell *ca.* 10^{-3} Torr. The magnet is set to transmit the appropriate negative ion, the ion focusing controls are adjusted so that the ion beam is centrally transmitted throughout the analyser system, and the slits are set to give an energy resolution of 3000. The focusing controls remain the same when the electrostatic sector controls are reversed to allow the transmission of the product positive ion. The energy profiles (*e.g.* Figure) are determined by scanning the voltage of the main electrostatic sector over the appropriate range.

The ΔE values in the Table are the energy differences between the maxima of the two peaks. The correspondence between the ΔE values and the values of the parameter (I.E. + E.A.) demonstrates (i) that a simple relationship exists between the translational energy lost and the minimum internal energy necessary to effect the charge-inversion reaction, (ii) that there is no significant instrumental bias in the results as shown by comparison of the present results with values from the literature that were obtained by other methods, and (iii) that the majority of non-decomposing positive ions are formed in electronic ground states. However, each positive ion peak has a high energy tail (*e.g.* Figure), showing that a proportion of higher energy

states are probably also involved, even though no discrete fine structure was observed in any case.

Electron affinities are not always simple to determine; the method outlined here allows an estimation of the E.A., since values of the I.E. are generally available. As a demonstration, the system $S_2^- \rightarrow S_2^+$ was chosen for study since the E.A. of S_2 is known only to be greater than 2.0.⁵ The estimated E.A. of S_2 (see Table) is 2.15, the mean of eight determinations (standard deviation 0.38, probable error ± 0.25 eV). The error in ΔE , and therefore in E.A., could be reduced if the experiment was fully automated to allow statistical averaging of multiple determinations. Although this is a simple and convenient method for the estimation of E.A. it cannot produce the accuracy given by certain other techniques. The most accurate method remains laser photoelectron spectroscopy which often yields values of E.A. to an accuracy better than ± 0.01 eV.^{4,6} The present technique is, however, of wider application and can readily be performed on high-performance double-focusing mass spectrometers.

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