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## Charge Stripping Reactions in Mass Spectrometry: A Study of Diatomic and Triatomic Inorganic and Organic Ions

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Charge stripping reactions of the type  $m^+ + N \rightarrow m^{2+} + N + e^-$  have been studied for a variety of diatomic and triatomic inorganic and organic ions. Ionisation energies of the  $m^+$  ions,  $IE(m^+ \rightarrow m^{2+})$ , have been determined, most of them for the first time. The method is fast and straightforward; it is applicable to both molecular and fragment ions. The relative cross-sections for the charge stripping processes have been also determined; they show large variations from one species to another. Cases of possible interferences, which are fairly infrequent, are described and discussed.

### INTRODUCTION

Few double ionisation energies of organic molecules are known, as opposed to the large amount of information available on their single ionisation energies. This is the consequence of experimental difficulties associated with double ionisation energy determinations; a number of techniques have been suggested and employed, none of which is without certain limitations.

The method mostly used is electron-bombardment threshold measurement by mass spectrometry. Doubly-charged ions are produced in the ion source by the process:



The current due to  $M^{2+}$  ions is monitored as the ionising electron energy is decreased; the corresponding plot represents the ionisation efficiency curve for process (1). By extrapolating this curve down to threshold, the value of the double ionisation energy of  $M$  is obtained. There are a number of drawbacks which render the above procedure difficult and often unreliable: (i) the ionisation efficiency curve for process (1) follows a quadratic threshold law, which makes extrapolation inherently ambiguous; (ii) the abundances of doubly-charged ions are often very small, so that severe sensitivity problems are usually encountered; (iii) the presence of singly-charged ions of the same  $m/z$  ratio as the doubly-charged ion being investigated is often a further limiting factor, which requires resorting to measurement of ions containing  $^{13}C$ .

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An entirely different concept for the determination of double-ionisation energies by mass spectrometry is the double electron-transfer reaction<sup>1</sup>:



where  $A^+$  represents a high (several keV) translational energy ion (such as  $H^+$ ), and  $M$  represents a gaseous target. By measuring the translational energy change in reaction (2), and knowing the electron affinity of  $A$ , it is possible to obtain the double ionisation energy of the target  $M$ . The method is restricted to compounds which can conveniently be introduced into the collision region of a mass spectrometer and it cannot be applied to fragment ions. There is always a possibility that the doubly charged  $M^{2+}$  ions formed might fragment, thereby taking up more energy than required for removing two electrons; since  $M^{2+}$  ions are not collected (but rather the projectile  $A^-$  ions), it may be difficult to determine which process(es) have actually taken place.

A few attempts have been made to use Auger spectra for the determination of double ionisation energies. These experiments were hampered by the complexity of the Auger process in free molecules, which is an X-ray emission process, taking place between two states which are both excited. An inherent difficulty in the interpretation of Auger spectra is therefore the separation of contributions to the energy and line width from the two different states.<sup>2</sup>

In 1973, we suggested that charge stripping reactions of gaseous ions in a double focusing mass spectrometer could be utilized to obtain double ionisation energies.<sup>3</sup> In the reaction:



where  $m^+$  represents any singly charged ion formed in the ion chamber, and  $N$  represents an atom or molecule of a collision gas, the energy necessary to remove the second electron from  $m^+$  ions comes from its translational energy. Therefore, by precisely measuring the translational energy loss in process (3), the difference between the double and single ionisation energies of  $m$  can be obtained.

The charge stripping method has overcome most of the drawbacks associated with double ionisation energy determinations by the methods discussed above. In principle, any singly charged ion can be studied and its double ionisation energy determined; it is not limited to molecular ions (as is the double electron transfer method), nor does it require the production of doubly charged ions in the ion chamber directly from the neutral species (as does the electron bombardment threshold method). The power of the method is exemplified in the case of methane the double ionisation energy of which has been determined by the charge stripping method;<sup>4</sup> the electron impact method is not applicable to this case, since no doubly-charged ions are produced directly from the neutral species by electron bombardment.

Because doubly charged  $m^{2+}$  ions are collected, there is less ambiguity in interpretation of the energetics of the processes involved; thus, for example, processes in which  $m^{2+}$  ions take up excess energy and subsequently fragment, are not monitored under the experimental conditions employed and cannot cause interference. Typical abundances of  $m^{2+}$  ions formed in reaction (3) are lower by a factor  $10^4$ — $10^6$  than the abundance of corresponding singly charged ions, but, with modern detection systems, this rarely causes sensitivity problems. Finally, the experimental technique is fairly straightforward and the measu-

ments are very fast. The error margin of  $\pm 0.5$  eV may be considered quite adequate for double ionisation energy determinations.

In previous studies the charge stripping method has been applied to mono- and disubstituted benzenes,<sup>5</sup> rare gas ions<sup>6</sup> and monatomic halogen ions.<sup>7</sup> In most cases where literature values were available, the agreement between the charge stripping method and other methods of double ionisation energy determination was satisfactory. In the present study, we are reporting results obtained on a variety of simple (mostly diatomic and triatomic) organic and inorganic ions. The results on CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub>S protonated molecular ions, molecular ions and their fragment ions have been published elsewhere as a separate study.<sup>8</sup>

#### EXPERIMENTAL

All experiments were performed on a reverse geometry VG Micromass ZAB-2F double focusing mass spectrometer.<sup>9</sup> Standard experimental conditions have been described previously.<sup>5</sup> Nitrogen collision gas was employed in all cases.

If no loss of translational energy occurred in the charge stripping process (3), a peak would be recorded at an electric sector voltage E/2, where E represents the value at which the main beam of stable m<sup>+</sup> ions is transmitted. However, since some of the translational energy of m<sup>+</sup> ions is converted into internal energy to remove the second electron, the product m<sup>2+</sup> ions will be recorded at a smaller value of the electric sector voltage than E/2, by an amount of translational energy lost in the process.

Peaks due to the charge stripping processes usually exhibit fairly sharp onsets. The onset of each peak, corrected for the half-width of the corresponding peak due to the main beam of m<sup>+</sup> precursor ions measured at base line (to account for the initial energy spread of the ion beam), represents the minimum amount of translational energy lost in a particular process and has been denoted Q<sub>min</sub>. The process C<sub>7</sub>H<sub>8</sub><sup>+</sup> → C<sub>7</sub>H<sub>8</sub><sup>2+</sup> in toluene gives an abundant and well-defined signal; its value of Q<sub>min</sub> = 15.7 eV has been used for calibrating the energy scale throughout the measurements. In favourable cases, an accuracy of 0.2 eV can be achieved in the measurement of Q<sub>min</sub>; however, due to the poorer signal to noise ratio on some peaks, as well as the problem of maintaining all experimental parameters constant at all times, we estimate that the reliability of most measurements is of the order of  $\pm 0.5$  eV.

#### RESULTS AND DISCUSSION

The appearance of a typical charge stripping peak is exemplified by the process CO<sub>2</sub><sup>++</sup> + N<sub>2</sub> → CO<sub>2</sub><sup>2+</sup> + N<sub>2</sub> + e<sup>-</sup>, the peak from which is shown in Figure 1. The high energy side of the peak exhibits a fairly sharp slope; its extrapolation down to the base line yields a Q<sub>min</sub> value of 24.5 eV, which represents the minimum amount of translational energy loss in order to effect the charge stripping process. From the energetic point of view, the above reaction represents an isolated system in which the only source of energy for removing the second electron from the CO<sub>2</sub><sup>++</sup> ions is the ions' translational energy. Therefore, it can be postulated that

$$\begin{aligned} Q_{\min} &= \text{IE}(\text{CO}_2^{++} \rightarrow \text{CO}_2^{2+}), \text{ i.e. generally} \\ Q_{\min} &= \text{IE}(m^+ \rightarrow m^{2+}) \end{aligned} \quad (4)$$

(For the symbolism used, see Appendix). A more rigorous treatment of the energy balance of the general charge stripping reaction (3) has shown that part of the translational energy loss may be imparted to the collision gas molecule (as internal or translational energy) or can be carried away with the ejected electron.<sup>5</sup> If this were the case, the low energy side of the charge stripping peak would show some broadening, but the Q<sub>min</sub> value would not be affected. In fact, most of the charge stripping peaks are fairly symmetrical,

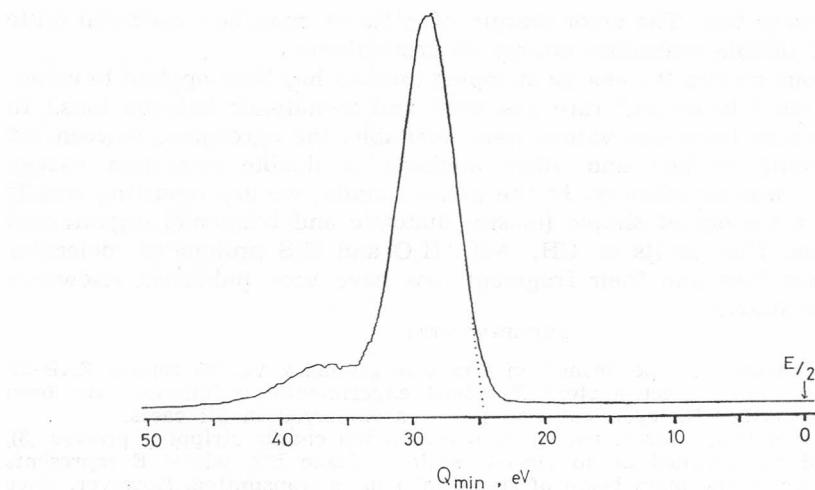


Figure 1. The charge stripping spectrum representing the process  $\text{CO}_2^{+*} + \text{N}_2 \rightarrow \text{CO}_2^{2+} + \text{N}_2 + \text{e}^-$ .

pointing to the fact that under our experimental conditions, the contribution from the processes in which either the collision gas or the electron take up translational energy is very small. On the other hand, all charge stripping spectra show evidence of electronic excitation of the nitrogen collision gas; in Figure 1, this is represented by an unresolved second peak centred some 8 eV below the main peak. (The first excited electronic states of N<sub>2</sub> lie 6.2 eV, triplet, and 8.5 eV, singlet, above its ground state).

So far, it has been assumed that both the m<sup>+</sup> and m<sup>2+</sup> ions involved in reaction (3) are in their ground states. Processes in which m<sup>2+</sup> is formed in an excited state would either contribute to the low energy side of the charge stripping peak (if m<sup>2+</sup> is stable enough to reach the detector), or else, the doubly charged ion would fragment and thus not be collected. In neither case would the Q<sub>min</sub> value be affected. However, if m<sup>+</sup> ions were present in excited states, the amount of translational energy loss necessary to remove the second electron would be smaller by the amount of excitation energy. The charge stripping reaction takes place a few microseconds after m<sup>+</sup> ions have been formed in the ion chamber; it seems reasonable to expect that after this time most of the excited m<sup>+</sup> ions would have fragmented. Thus, the m<sup>+</sup> ions that reach the collision cell would generally be expected to be in their electronic ground state. This concept has been experimentally proved for large organic ions;<sup>5</sup> all Q<sub>min</sub> values obtained, for which literature values were available for comparison, showed the validity of equation (4).

The results obtained for a variety of simple inorganic and organic ions are listed in Tables I and II.

Q<sub>min</sub> values for each ion are given in column 3; wherever available, literature values for IE (m<sup>+</sup> → m<sup>2+</sup>) are given in column 5 for comparison. It is interesting to note the fairly large disagreement between the various literature data for the same ion; this reflects the experimental difficulties and large error margins with most of the techniques employed, as discussed in the introduction to this paper. Under these circumstances, it is difficult to assess

the agreement of our values with those from the literature; nevertheless the fact that our  $Q_{\min}$  values are generally not lower than the corresponding literature  $IE (m^+ \rightarrow m^{2+})$  values, supports the validity of equation (4), i.e. the concept that  $m^+$  ions exist in their ground electronic states under our experimental conditions. However, the possibility of the existence of long-lived excited states cannot be ruled out; though their occurrence is infrequent for polyatomic ions, they have been observed in charge stripping experiments, notably in some simple halocarbon ions.<sup>11</sup> Their existence in monatomic ions, however, is well known and they have been studied in detail for rare gas ions<sup>6</sup> and halogen ions.<sup>7</sup>

The  $Q_{\min}$  values listed in Tables I and II span a large range between 14.1 eV (for  $Cl_2^+$ ) and 29.2 eV (for  $NO^+$ ). These energies, required to remove

TABLE I  
*Charge Stripping Data for Some Simple Inorganic Ions\**

Ion	Compound	$Q_{\min}/eV$	Relative cross-section		$IE (m^+ \rightarrow m^{2+}), eV$ (literature value <sup>a</sup> )
			$(m^{2+}/m^+) \times 10^6$		
$N_2O^{++}$	$N_2O$	24.0	0.04		23.5 <sup>e</sup> ; 24.4 <sup>d</sup> ; 25.7 <sup>h</sup>
$NO^+$	$N_2O$	29.2	2		26.5 <sup>c</sup> ; 30.1 <sup>d</sup> ; 30.6 <sup>f</sup>
$N_2^{++}$	$N_2$	27.6	b		27.3 <sup>c</sup> ; 27.5 <sup>d</sup> ; 27.7 <sup>e</sup> ; 27.9 <sup>f</sup>
$S_2^{++}$	Sulfur	17.8	b		b
$S_3^{++}$	Sulfur	16.5	b		b
$SOH^+$	$CH_2CH_2SO$	19.2	7		b
$SO^{++}$	$CH_2CH_2SO$	19.7	30		b
$HBS^{++}$	$BH_3S(CH_3)_2$	20.4	7		b
$BS^+$	$BH_3S(CH_3)_2$	18.0	5		b
$BH_3^{++}$	$BH_3S(CH_3)_2$	20.5	11		b
$SiH_2^{++}$	$(CH_3)_4Si$	17.7	182		b
$SiH^+$	$(CH_3)_4Si$	18.7	205		b
$PCl_3^{++}$	$PCl_3$	16.7	19		b
$PCl_2^{++}$	$PCl_3$	18.6	39		b
$PCl_1^{++}$	$PCl_3$	17.0	59		b
$TiCl_3^{++}$	$TiCl_4$	17.7	15		b
$TiCl_2^{++}$	$TiCl_4$	16.1	15		b
$TiCl_1^{++}$	$TiCl_4$	14.6	112		b
$HCl^{++}$	$CH_2Cl_2$	23.5	1	22.8 <sup>f</sup> ; 23.3 <sup>i</sup>	
$HBr^{++}$	$CH_2Br_2$	21.8	4	21.6 <sup>f</sup>	
$HI^{++}$	$CH_2I_2$	19.4	105	19.6 <sup>f</sup>	
$HI^{++}$	$CF_3CF_2I$	20.2	4	b	
$HgI_2^{++}$	$HgI_2$	17.2	2	b	
$HgI^+$	$HgI_2$	15.7	5	b	

\* Most of the literature data are in the form of double ionisation energies, i.e.  $IE (m \rightarrow m^{2+})$  values. The values of  $IE (m^+ \rightarrow m^{2+})$  given in this column were calculated as the difference  $IE (m \rightarrow m^{2+}) - IE (m \rightarrow m^+)$ , the values of the latter being taken from reference 10. <sup>b</sup> Data not available. <sup>c</sup> Reference 11. <sup>d</sup> Reference 1. <sup>e</sup> Reference 12. <sup>f</sup> Reference 13. <sup>g</sup> Reference 14. <sup>h</sup> Reference 15. <sup>i</sup> Reference 16.

TABLE II  
Charge Stripping Data for Some Simple Organic Ions

Ion	Compound	$Q_{\min}/\text{eV}$	Relative cross-section ( $m^{2+}/m^+$ ) $\times 10^6$	$IE (m^+ \rightarrow m^{2+})$ , eV (literature value <sup>a</sup> )
$\text{CO}_2^{+*}$	$\text{CO}_2$	24.5	7	22.6 <sup>f</sup> ; 24.2 <sup>j</sup> ; 24.3 <sup>h</sup>
$\text{CO}^{+*}$	$\text{CO}$	26.1	0.6	25.9 <sup>e</sup> ; 26.2 <sup>c</sup> ; 26.5 <sup>k</sup> ; 27.8 <sup>t</sup>
$\text{CS}_2^{+*}$	$\text{CS}_2$	18.0	115	16.9 <sup>h</sup> ; 17.4 <sup>l</sup>
$\text{CS}^{+*}$	$\text{CS}_2$	19.7	5	b
$\text{CSO}^{+*}$	$\text{CH}_2\text{CH}_2\text{SO}$	16.8	7	b
	$\begin{array}{ c c }\hline &   \\ \text{HCSI}^+ & (\text{CH}_3)_4\text{Si} \\ &   \\ &   \\\hline\end{array}$	17.2	88	b
$\text{CH}_2^{+*}$	$\text{iso-C}_4\text{H}_{10}$	19.8	b	b
$\text{CD}_2^{+*}$	$\text{CD}_4$	19.8	50	b
$\text{CF}_3^{+*}$	$\text{CF}_3\text{CH}_2\text{I}$	26.4	0.5	b
$\text{CF}_2^{+*}$	$\text{CF}_3\text{CH}_2\text{I}$	19.0	16	b
$\text{CF}^{+*}$	$\text{CF}_3\text{CH}_2\text{I}$	26.4	6	b
$\text{CCl}_3^{+*}$	$\text{CHCl}_3$	18.9	60	b
$\text{CCl}_2^{+*}$	$\text{CHCl}_3$	17.2	53	b
$\text{CCl}^{+*}$	$\text{CHCl}_3$	21.8	24	b
$\text{CBr}_3^{+*}$	$\text{CBr}_4$	18.1	9	b
$\text{CBr}_2^{+*}$	$\text{CH}_2\text{Br}_2$	15.2	18	b
$\text{CBr}^{+*}$	$\text{CH}_2\text{Br}_2$	20.2	9	b
$\text{CI}_2^{+*}$	$\text{CH}_2\text{I}_2$	14.1	12	b
$\text{CI}^{+*}$	$\text{CH}_2\text{I}_2$	19.0	6	b
$\text{CFI}^{+*}$	$\text{CF}_3\text{CH}_2\text{I}$	17.9	5	b

<sup>j</sup> Reference 17. <sup>k</sup> Reference 18. <sup>l</sup> Reference 19.  
(For other footnote explanations, see Table I.)

the second electron, are considerably higher than the corresponding single ionisation energies, which, of course, is an expected result. However, there does not seem to be a simple relationship between the values of  $IE(m \rightarrow m^+)$  and  $IE(m^+ \rightarrow m^{2+})$ ; for example, single ionisation energies of NO and  $\text{N}_2\text{O}$  are 9.25 eV and 12.90 eV, respectively; energies required to remove the second electron from  $\text{NO}^+$  and  $\text{N}_2\text{O}^+$  do not follow the above order, being 29.2 eV for  $\text{NO}^+$  and 24.0 eV for  $\text{N}_2\text{O}^+$ . A similar situation is encountered for  $\text{CCl}_3$  and  $\text{PCl}_3$ ; their  $IE(m \rightarrow m^+)$  values are 8.78 eV and 9.91 eV, respectively, their  $IE(m^+ \rightarrow m^{2+})$  values have been determined as 18.9 eV and 16.7 eV. One of the reasons for such behaviour may be the fact that  $\text{N}_2\text{O}^+$  and  $\text{PCl}_3^+$  are odd-electron ions, while  $\text{NO}^+$  and  $\text{CCl}_3^+$  are even-electron species; it is easier to remove an unpaired electron, and this is reflected in the «unexpectedly» low  $Q_{\min}$  values for  $\text{N}_2\text{O}^+$  and  $\text{PCl}_3^+$ .

It is also interesting to note that a homologous series of ions does not always behave in a predictable way. The  $Q_{\min}$  values in the series of ions  $\text{CH}_2^{+*}$  (19.8 eV),  $\text{CF}_2^{+*}$  (19.0 eV),  $\text{CCl}_2^{+*}$  (17.2 eV),  $\text{CBr}_2^{+*}$  (15.2 eV) and  $\text{CI}_2^{+*}$  (14.1 eV) do, however, show a smooth trend; the same is true for the series of ions from methane<sup>4,11</sup>  $\text{CH}^+$  (22.8 eV),  $\text{CH}_2^{+*}$  (19.6 eV),  $\text{CH}_3^+$  (18.9 eV) and  $\text{CH}_4^{+*}$  (17.9 eV).

In both these cases,  $Q_{\min}$  values decrease regularly with increasing the ion size, which is what one would expect. However, as seen in Table I, the  $Q_{\min}$  values for  $\text{TiCl}_3^+$ ,  $\text{TiCl}_2^{+*}$  and  $\text{TiCl}^*$  show exactly the opposite behaviour, increasing all the time with increasing ion size. To complicate matters further,  $Q_{\min}$  values for  $\text{PCl}_3^{++}$ ,  $\text{PCl}_2^{+}$  and  $\text{PCl}^{++}$  (Table I) show a different pattern again, the value for  $\text{PCl}_2^{+}$  now being the largest. Finally, the comparison of  $Q_{\min}$  values for  $\text{CX}_3^+, \text{CH}_2^{+*}$  and  $\text{CX}^+$  (where X = F, Cl or Br) show that the value for  $\text{CX}_2^{+*}$  is the smallest of the three for each halogen series. It seems obvious that other factors, besides ion size, are involved in determining the  $IE (m^+ \rightarrow m^{2+})$  values. In the case of phosphorus chlorides, as well as in the halocarbon ions mentioned above, the behaviour could again be rationalised as reflecting the odd-electron or even-electron character of the reacting ion, the former ones exhibiting the lower ionisation energies.

The shapes of the charge stripping peaks are a complex function of various phenomena that can take place (some of which have been mentioned earlier); they will also be very sensitive to alterations of experimental parameters, such as slit width and collision gas pressure, for example. The latter is the reason why peak width and peak abundance data, for experiments performed over a longer period of time, may not entirely compare, although care was taken to maintain all experimental conditions as constant as possible.

The charge stripping peaks of ions studied are generally quite narrow; measured at half-height, they would typically be some 20% wider than the corresponding peaks due to singly charged precursor ions, although cases were observed with broadening being anywhere between 10%—50%. The meaning and significance of these differences is currently being investigated.

The appearance of most charge stripping peaks is fairly symmetric in their upper portion, as opposed to the lower part of the peaks. The high energy side is most often a smooth curve which can easily be extrapolated to base line for  $Q_{\min}$  measurement; an example of such a case is the peak shown in Figure 1. Sometimes, however, a departure from linearity of this edge is observed, due to broadening of the peak stem; this is exemplified in Figure 2. The most plausible explanation for this effect is that it is due to the processes in which excited  $m^+$  ions are involved. In an extreme case of such behaviour when the number of excited ions is significant, and the excitation energy large enough, the peak due to the presence of excited states will become more or less resolved from the main peak representing the majority of the ions in their ground state. Such a case is shown in Figure 3; besides the peak at a  $Q_{\min}$  value of 29.2 eV, there is a small, partly resolved peak, some 6.5 eV higher in energy. It is interpreted as representing  $\text{NO}^+$  ions in an excited state; indeed, the first excited electronic state of  $\text{NO}^+$  lies some 7 eV above its ground state.

The main feature of the lower energy side of charge stripping peaks is the evidence of nitrogen collision gas excitation processes. The signal due to these processes is usually observed, as already mentioned, as a poorly resolved hump some 8 eV lower than the main charge stripping peak. It is interesting to note that this process shows a varying abundance, depending on the actual  $m^+$  ions involved. Figure 1 is typical of the most frequently occurring case, where the nitrogen excitation peak is of moderate abundance; Figure 4 represents two extreme cases, i.e. a) the case in which this peak is quite

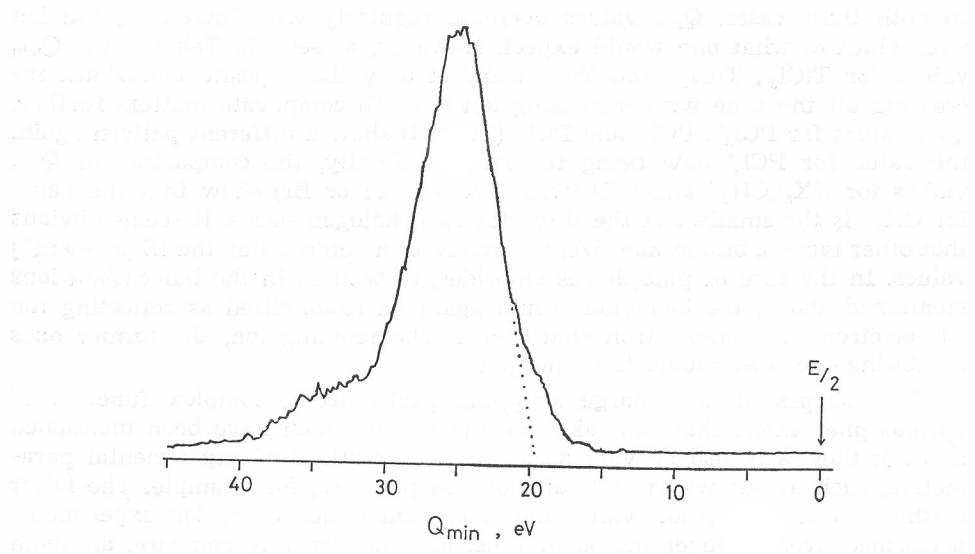


Figure 2. The charge stripping spectrum representing the process  $\text{CS}^+ + \text{N}_2 \rightarrow \text{CS}^{2+} + \text{N}_2 + \text{e}^-$ .

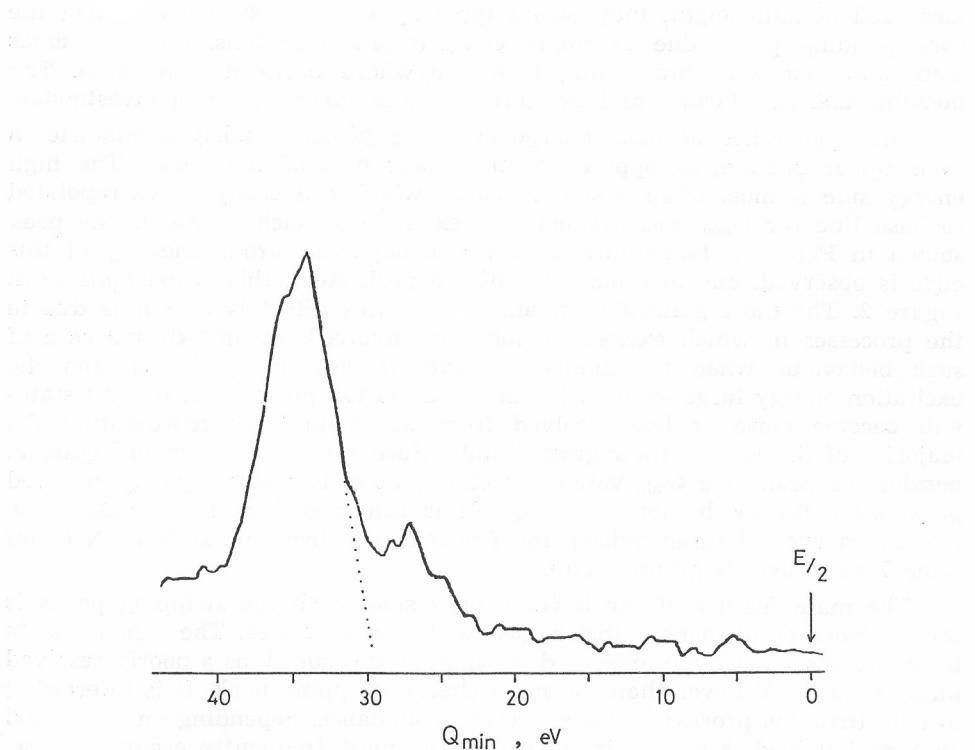


Figure 3. The charge stripping spectrum of NO<sup>+</sup> ions formed from iso-amyl nitrate. The small, partly resolved peak, represents processes in which excited NO<sup>+</sup> ions are involved.

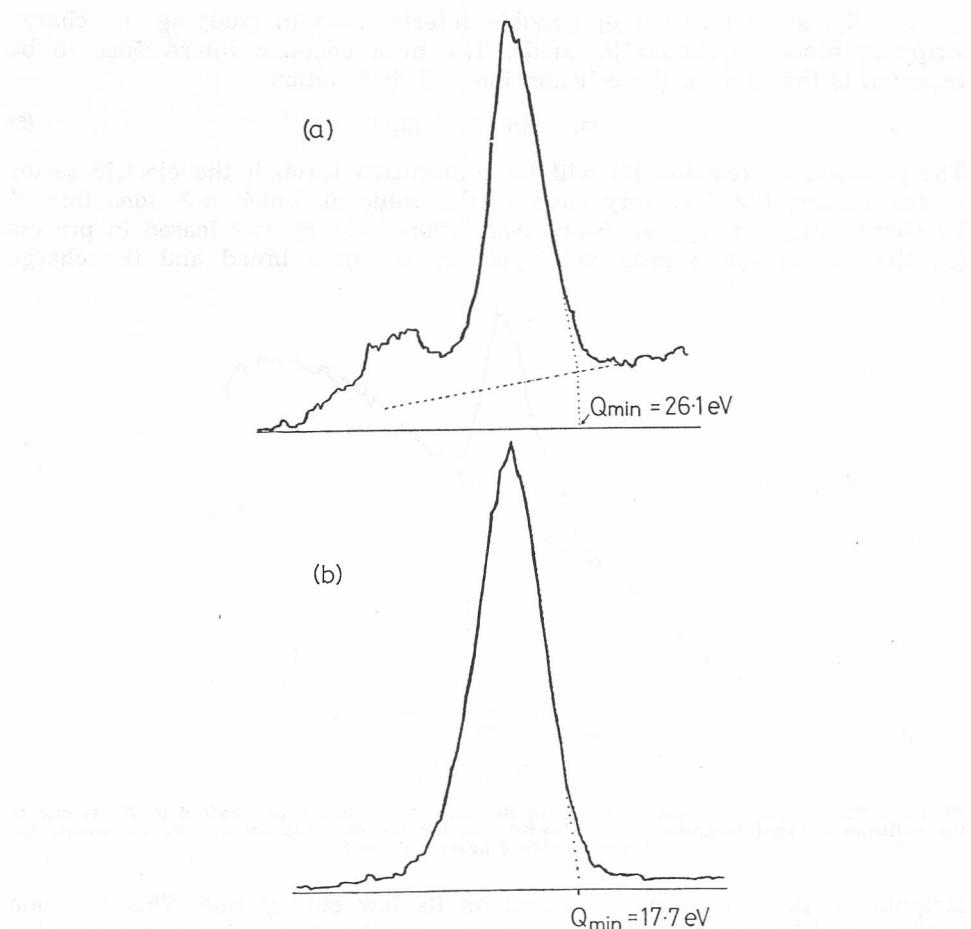


Figure 4. The charge stripping spectra of a)  $\text{CO}^+$  ions, showing a fairly well-resolved nitrogen collision gas excitation peak; and b)  $\text{TiCl}_3^+$  ions, with practically no evidence of the nitrogen excitation process.

significant and better resolved, and b) the case in which this peak is hardly noticeable.

The relative cross-sections for charge stripping have been expressed as the ratio of peak abundance  $m^{2+}/m^+$ , measured as peak heights. These values are given in column 4 of Tables I and II; they cover a large range between  $4 \times 10^{-8}$  (for  $\text{N}_2\text{O}^+$ ) and  $2 \times 10^{-4}$  (for  $\text{SiH}^+$ ). Since this cross-section is very sensitive to collision gas pressure variation, the values reported could differ by an estimated factor of 2 for measurements taken on different occasions. Irrespective of this uncertainty, the cross-sections for charge stripping processes exhibit remarkable differences. One factor that is important is the stability of the  $m^{2+}$  ion formed; only the stable product ions are used to estimate the charge-stripping cross-section so that a high percentage of product ions that rapidly undergo fragmentation will lead to a low, measured cross-section and vice-versa.

Finally, some mention of possible interferences in studying the charge stripping processes should be made. The most common interference to be expected is that due to the collision induced dissociation:



The products of reaction (5) will be transmitted through the electric sector at the voltage  $E/2$ , i.e. very close to the value at which  $m_1^{2+}$  ions formed by charge stripping appear. Since translational energy is released in process (5), the corresponding peak will typically be quite broad and the charge

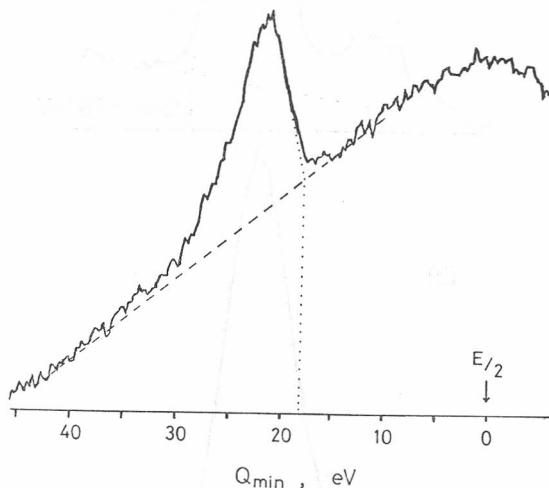


Figure 5. The charge stripping spectrum of  $S_2^{+}$  ions; the broad peak centred at  $E/2$  is due to the collision induced fragmentation  $S_2^{+} \rightarrow S^+ + S$ ; the narrow peak on its side represents the charge stripping process  $S_2^{+} \rightarrow S_2^{2+}$ .

stripping peak will be superimposed on its low energy side. This situation is illustrated in Figure 5; the broad peak centred at  $E/2$  is due to the collision induced decomposition  $S_2^{+} \rightarrow S^+ + S$ , while the narrow peak on its side represents the process  $S_2^{+} + N \rightarrow S_2^{2+} + N + e^-$ . In such cases, the  $Q_{\min}$  measurement for the charge stripping process is less reliable, but the magnitude of the interference will really depend on the relative abundances of the peaks due to the two processes. Consider the reaction  $CO^{+} + N \rightarrow CO^{+2} + N + e^-$ , shown in Figure 4a). Due to some nitrogen impurity in the CO gas used, the process  $N_2^{+} \rightarrow N^+ + N^-$  also takes place in the second field free region and is represented by a broad peak, but of low abundance, so the  $Q_{\min}$  measurement is not significantly affected in this case. On the other hand, the process  $O_2^{+} + N \rightarrow O_2^{2+} + N + e^-$  could not be studied at all due to the interference from the fragmentation reaction  $O_2^{+} \rightarrow O^+ + O$ , which gave an extremely strong signal, thus totally obscuring the charge stripping peak.

The other problem sometimes encountered may arise when two (or more) ions of the same nominal mass are present in the ion source. Under low mass resolution conditions, which we employed to gain sensitivity, both such ions are transmitted by the magnet, and, will, consequently, undergo charge

stripping. If  $Q_{\min}$  values for the two species are sufficiently different, two peaks will be recorded in the charge stripping spectrum. This situation is artificially illustrated in Figure 6; the measurement of interest is the process

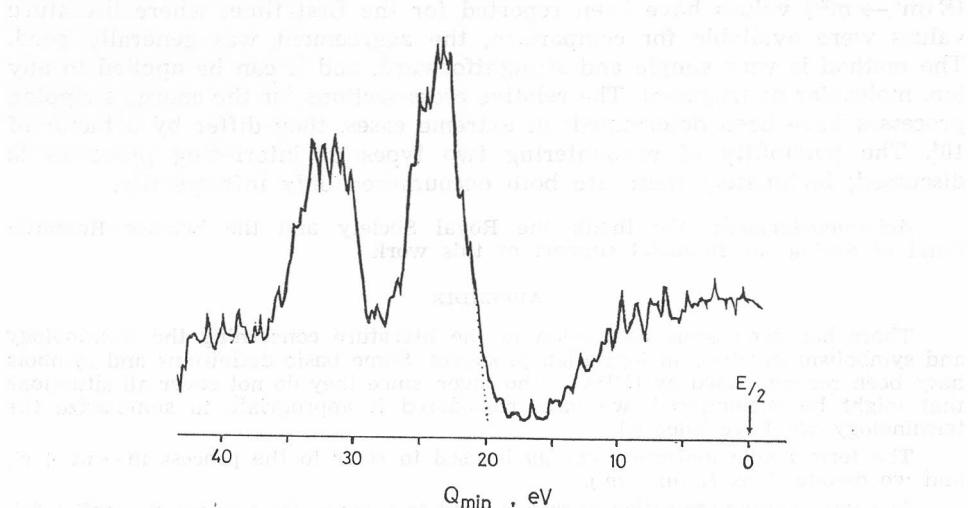


Figure 6. The complex spectrum obtained upon studying the  $m/z$  14 ions from iso-butane, with some air present in the ion source. The larger of the two charge stripping peaks is due to the process  $\text{CH}_2^{+} \rightarrow \text{CH}_2^{2+}$ , while the smaller one represents the process  $\text{N}^{+} \rightarrow \text{N}^{2+}$ . The broad peak at  $E/2$  is due to the fragmentation  $\text{N}_2^{2+} \rightarrow \text{N}^{2+} + \text{N}^{+}$ .

$\text{CH}_2^{+} \rightarrow \text{CH}_2^{2+}$  in iso-butane. The peak due to this process is represented by the large peak with  $Q_{\min} = 19.8$  eV. Simultaneously, some air was introduced into the source; as a consequence, the peak due to the process  $\text{N}^{+} \rightarrow \text{N}^{2+}$  also appeared in the spectrum, at  $Q_{\min} = 27.4$  eV. (The third peak, centred at  $E/2$ , is most probably due to the process  $\text{N}_2^{2+} \rightarrow \text{N}^{2+} + \text{N}^{+}$ ). However, if  $Q_{\min}$  values for the two species are fairly close, which can frequently be the case, the charge stripping spectrum will not show two resolved peaks, and the results become ambiguous, so it is very important to exercise the utmost caution to avoid such possibilities of error. For example, we used toluene as the standard for calibrating our energy scale; it was introduced into the source before and after each sample. If the pumping was not thorough enough, it was impossible to obtain reliable  $Q_{\min}$  values for certain ions, such as  $\text{CF}_2^{+}$  (due to interference from  $\text{C}_4\text{H}_2^{+}$ ), or  $\text{C}^{79}\text{Br}^{+}$  (due to interference from  $\text{C}_7\text{H}_7^{+}$ ), etc. While these problems can be avoided by exercising caution and checking for the background peaks, there will be cases, though not very frequent, where the above type of interference comes from within the sample itself. Thus, we have attempted some measurements on the sample  $\text{C}_5\text{H}_5\text{OBF}_4$ ; in particular, we were interested in the ion  $\text{BF}_3^{+}$ , but could not obtain its  $Q_{\min}$  value due to interference from  $\text{C}_4\text{H}_4\text{O}^{+}$  ions from the same sample. Likewise, no value could be obtained for  $\text{BF}^{+}$ , since its mass coincided with that of  $\text{H}_2\text{CO}^{+}$ . In certain cases this interference can be overcome by increasing the mass resolution; however, the consequent loss in sensitivity will often be the limiting factor.

### Conclusion

The charge stripping method has been used for obtaining the ionisation energies of a number of simple inorganic and organic ions. Most of the  $IE(m^+ \rightarrow m^{2+})$  values have been reported for the first time; where literature values were available for comparison, the agreement was generally good. The method is very simple and straightforward, and it can be applied to any ion, molecular or fragment. The relative cross-sections for the charge stripping processes have been determined; in extreme cases, they differ by a factor of  $10^4$ . The possibility of encountering two types of interfering processes is discussed; fortunately these are both encountered only infrequently.

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### APPENDIX

There has been some confusion in the literature concerning the terminology and symbolism involved in ionisation processes. Some basic definitions and symbols have been recommended by IUPAC;<sup>20</sup> however, since they do not cover all situations that might be encountered, we have considered it appropriate to summarize the terminology we have adopted.

The term *single ionisation energy* is used to refer to the process  $m \rightarrow m^+ + e^-$ , and we denote it as  $IE(m \rightarrow m^+)$ .

The term *double ionisation energy* is used to refer to the process  $m \rightarrow m^{2+} + 2e^-$ , and we denote it as  $IE(m \rightarrow m^{2+})$ .

Various *other ionisation energies* should be described by the same symbolism, e.g.  $IE(m^+ \rightarrow m^{2+})$ , which refers to the energy necessary to remove the second electron from  $m^+$  ions; or,  $IE(m^{2+} \rightarrow m^{3+})$ , which refers to the energy necessary to remove the third electron from  $m^{2+}$  ions, etc.

Terms such as *first ionisation energy* and *second ionisation energy* are ambiguous. (For example, second ionisation energy has been used to refer to the process in which a double charged ion is formed from the neutral molecule, but it can also mean the production of a singly charged ion in its excited state). We have, therefore, not used these terms, and have used instead, the terms *single ionisation energy* and *double ionisation energy* as indicated above.

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### SAŽETAK

**Reakcije otkidanja naelektrisanja u masenoj spektrometriji:  
ispitivanje dvoatomnih i troatomnih neorganskih i organskih jonova**

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Reakcije otkidanja naelektrisanja u sudarnim procesima u masenoj spektrometriji tipa  $m^+ + N \rightarrow m^{2+} + N + e^-$ , gdje  $m^+$  predstavlja bilo koji jon obrazovan u jonskom izvoru, a N atom ili molekul sudarnog gasa, proučene su za preko 40 vrsta dvoatomnih i troatomnih neorganskih i organskih ionova. Merenjem translatorne energije utrošene na otkidanje drugog elektrona iz  $m^+$  jona moguće je odrediti njegovu drugu ionizacionu energiju (potencijal). Vrednosti ovih energija poznate su za veoma mali broj uglavnom molekulskega jona; u ovom radu po prvi put su određene druge ionizacione energije za većinu ispitivanih uzoraka. Upotrebljena metoda je podjednako primenljiva i za molekulske i za fragmentne jone; ukazano je na izvore sporadičnih smetnji pri ovim određivanjima.

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