Doubly charged ions in the electron ionization mass spectra of 4,6-di(substituted)amino *s*-triazines

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Abstract

Electron ionization mass spectra of the title compounds demonstrate intense peaks due to doubly charged ions. These ions have great analytical significance for the screening of these herbicides. The ions $[M–2CH_3]^{2+}$ reach 25%–30% of the base peak at 70 eV. The origin of these ions and their modes of fragmentation were studied through high voltage scans and mass analyzed ion kinetic energy spectroscopy on a reverse geometry double focusing mass spectrometer. The doubly charged parent ions of the title compounds behave like diradicals and undergo α cleavage reactions at the two substituted exocyclic amino groups with prevailing methyl loss. The $[M–2CH_3]^{2+}$ ions behave like characteristic even electron ions, either eliminating stable neutral molecules or undergoing Coulomb explosion into pairs of even electron ion products. Some of the products are characterized by proton transfer to a neutral molecule having a high proton affinity, notably the formation of CH_3NCH^+ from $[M–2CH_3]^{2+}$ in simazine. Similar reactions have been recently observed for multiply protonated biomolecules. Kinetic energy releases and interchange separations were determined for the Coulomb explosion reactions of the $[M–2CH_3]^{2+}$ ions. (Int J Mass Spectrom 192 (1999) 99–109) © 1999 Elsevier Science B.V.

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1. Introduction

4,6-di(substituted)amino *s*-triazines carrying in position 2 either a Cl atom, a methoxy group or an S-methyl substituent (see Scheme I) are used as herbicides. The best-known member of this group is atrazine which is used in huge quantities to destroy weeds in cornfields. It is usually applied to cultivated soils, at a rate of a few kilograms per hectare, in order to kill grassy weeds [1]. In high concentrations, it has been used to kill all of plant life, e.g. to create parking lots. Biochemically, it acts as a herbicide by blocking the operation of photosynthesis in the plant. Owing to their widespread use, triazines are considered potential water pollutants [2] and various methods for their analysis have been developed [3,4].

Interest in these compounds does not seem to wane despite having been in use for a long time. The triazines give excellent mass spectra under electron ionization (EI) conditions with the molecular ion

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Dedicated to the memory of a cherished colleague Robert R. Squires who passed away recently in the prime of life.
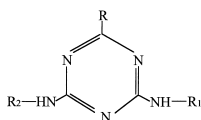
	M. W.	R	R_1	R_2
Atrazine	215	Cl	CH_2CH_3	$CH(CH_3)_2$
Simazine	201	Cl	CH_2CH_3	CH_2CH_3
Propazine	229	Cl	$CH(CH_3)_2$	$CH(CH_3)_2$
Terbutylazine	229	Cl	$C(CH_3)_3$	CH_2CH_3
Atraton	211	OCH_3	$CH(CH_3)_2$	CH_2CH_3
Prometon	225	OCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$
Prometryn	241	SCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$

Scheme 1.

often the base peak along with structure specific simple cleavage as well as rearrangement products.

The most interesting feature of the spectra is the presence of unusually abundant doubly charged odd mass fragments, mainly $[M–30]^{2+}$. Such fragments were described by Jorg et al. [5] who attributed them to the "loss of two methyl groups and two electrons . . .". They were also mentioned by Lamoureux et al. [6]. In abundance and alleged origin, namely the loss of $2e + 2CH_3$, they are like doubly charged fragments described by Silbiger et al. [7] in the electron impact mass spectra of some silazanes. Interestingly, other papers, besides reviews referring to [5], do not address the issue of the doubly charged ions in the EI spectra of *s*-triazines. Furthermore, these doubly charged ions were not observed in either the ion trap mass spectra or the collision-induced dissociation (CID) MS/MS ones studied with a Varian Saturn 4D ion trap [8].

Older type quadrupole mass analyzers might not be able to focus ions at half mass values and some benchtop mass spectrometers intended for low resolution work may be purposely designed to print only integer *m/z* values. This reasoning could serve as a partial explanation of the total absence of the doubly charged ions from published spectra such as the

Handbook of Mass Spectra of Organic Contaminants [9]. In spectra obtained using modern quadrupole mass filters, such as the Finigan 7000, doubly charged ions are observable [10]. However, doubly charged species in the mass spectra of the *s*-triazines were not mentioned by some authors who used sector mass spectrometers either. For example, Ross and Tweedy [11], claiming to have obtained virtually identical results to those of Jorg et al. [5], make no mention of doubly charged ions.

The objectives of our research to be described in this article were as follows. (1) The measurement of 70 eV mass spectra for a series of the *s*-triazines. We find this of analytical importance since the major existing compilations do not include the doubly charged ions. (2) A study of the origin and reactions of $[M–30]^{2+}$ ions in the spectra of *s*-triazines using mass analyzed ion kinetic energy (MIKE) spectra. (3) A search for other doubly charged, parent as well as fragment ions, which have not been reported earlier. (4) An attempt to bracket the appearance energies (AEs) for the formation of these ions. (5) The determination of kinetic energy releases (KERs) in Coulomb explosion experiments on these doubly charged ions and—from those—the intercharge distances.

2. Experimental

All the triazines studied were purchased from Riedel-de Haën (GmbH, Seelze, Germany) and were Pestanal grade analytical standards of >99% purity, with the exception of prometon, which was purchased from Ultra Scientific, North Kingston, RI. Mass spectra were run on several double focusing sector mass spectrometers including a VG analytical (Micromass UK) 70 SEQ, a VG VSE and a VG ZAB-2F reverse geometry instrument. The latter instrument was utilized for the MIKE, CAD, and KER measurements. Samples were introduced as solids using the standard direct probe inlet. Various electron energies were used and the representative spectra to be shown were obtained at 70 eV. A small number of experiments was carried out on a vacuum ultraviolet (VUV) photoionization mass spectrometer at the He resonance line of 21.21 eV.
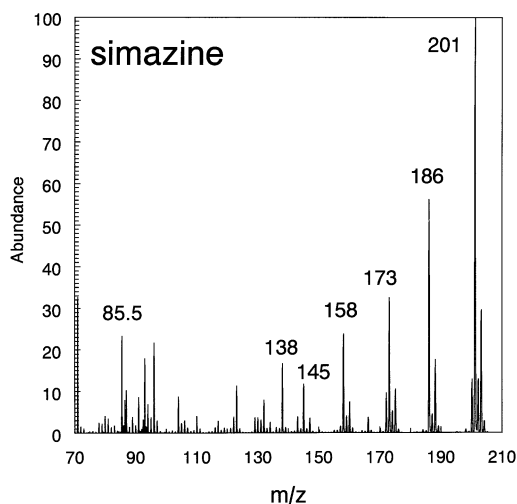
Fig. 1. 70 eV (VG ZAB-2F) mass spectrum of simazine.

3. Results and discussion

3.1. Mass spectra

A typical 70 eV EI mass spectrum is presented for simazine (Fig. 1). Fig. 2 shows that part of the mass spectrum where the doubly charged ions appear. Additional mass spectra are summarized in Table 1 (see Scheme I for identification of the various compounds). Only ions having an abundance of 5% or higher are shown, with the exception of the doubly charged ions, where the limit is 1%, in order to emphasize these ions). The presence of doubly charged fragment ions is observed in the spectra of all the triazines studied whether they are substituted by Cl, –OCH$_3$, or –SCH$_3$ at position 2. Jorg et al. [5] reported the $[M–2CH_3]^{2+}$ ions only in chlorine substituted triazines. Moreover, we find some ten doubly charged fragments in addition to $[M–30]^{2+}$ although of lower abundance. All of them result through cleavages of parts of the exocyclic substituents so that the triazine ring seems to be retained although large intercharge distances are observed upon Coulomb explosion (see Sec. 3.1) indicating ring opening for transition structures. It is important to emphasize the analytical advantage of the existence of doubly charged ions in triazines only, which makes identifi-
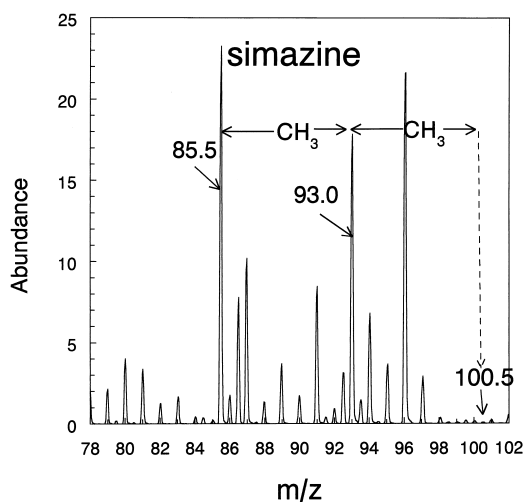

Fig. 2. Expanded region of the mass range for doubly charged ions in the 70 eV mass spectrum of simazine. Notice the weak doubly charged parent ion peak at *m/z* 100.5, the intense $[M–2CH_3]^{2+}$ peak at *m/z* 85.5, its ^{37}Cl isotope peak at *m/z* 86.5 and additional doubly charged peaks at *m/z* 92.5 and 93.5. The peak at *m/z* 93.0 has a strong contribution from doubly charged $[M–CH_3]^{2+}$ ions (see text).

cation of triazines in unknown water samples, when looking for pollutants, easier.

The singly charged ions analogous to the major doubly charged ones, namely $[M–2CH_3]^+$, are either absent in the spectra or of very low abundance. This agrees with the general trends of mass spectra of even and odd electron ions [12–14], whereby the even electron ion $[M–CH_3]^+$ does not tend to form a radical cation/neutral radical pair, because of the high energy requirements ("even-electron rule"). Similarly, it would not be expected for the doubly charged parent ion, which is an even electron ion, to undergo two consecutive CH$_3$ losses, but we will see in a coming section (Sec. 3.2) that this is what happens.

The ordinary mass spectra are not sensitive enough to allow observation of the doubly charged parent ion, however under conditions of high sensitivity, using a wide dynamic range, the doubly charged parent ion was observed for all the triazines studied, although at very low abundance (see Fig. 2). Furthermore, we found the doubly charged parent to be the ion of lowest appearance energy among the doubly charged ions and it is obviously the precursor for all the

Table 1
Mass spectra[a] of triazines

m/z	Atrazine %	Simazine %	Propazine %	Terbutylazine %	Atraton %	Prometon %	Prometryn %
62	10.5	15	20	15			
64			9.0	5.5			
67	5.5	10.5	13.5	8.0	5.5		
68	48.5	46	64.5	33	23.5	15	28
69	34.5	29.5	65	15	37.5	27	27.5
70	5.5	12.5	10		9.0		
71	33	39.5		28.5	18		
73		8.0					
74							16.5
79			21				
80		7.0					
81		10.5	11.5				
82			8.0		6.0		
83	7.0	12	31	23.5	17.5	10.5	12
83.5					2.0		
84			7.5		7.5		
85			13		15		16
85.5		30					
86.5		14	5.0				
87	7.0	15.5	14.5	7.5	5.0		
87.5			2.0				
88			6.0				
89		6.5	7.0				
89.5					1.0		
90.5					23		
91	6.5	19		7.0	5.0		5.0
92.5	18.5	8.5	2.5				
93	13.5	24.5	19	12.5	5.5		7.0
93.5	6.0	4.0	1.0				
94	12	13.5	33		13.5	7.0	9.5
95	5.5	11.5	13.5	5.0	6.5		5.5
96	17	35		17.5	13		
96.5						1.0	
97		13			7.0		
97.5					3.0	25	
98					14		
98.5			7.0		1.0		
99							8.0
99.5	1.5		58	16.0			
100			12.5		14.5	12.0	5.0
100.5	0.7		26	6.5			
101					7.5		
104	15.5	18	42.5	16			
105	9.5	8	27				
105.5							26
106	5.5	8	21	6.0			5.5
106.5			2.5				
107			14.5	5.5			
107.5			1.2				
108			13	6.0			
109			9.0				
110	6.5	11.5	20.5	6.5	7.0		11.5

(continued)

Table 1 *(continued)*

m/z	Atrazine %	Simazine %	Propazine %	Terbutylazine %	Atraton %	Prometon %	Prometryn %
111					13.5	6.0	10.5
112					14	9.0	
116							8.0
117		9.5					
122	14.5	9.0			13.5		
123	7.5	21.5			5.0		
123.5			2.0				
125					11.5	5.0	
126					16	6.5	
127							7.0
128					11.5		
129	5.5	9.0	14.5				
130	8.0	9.0	18.5	5.0			
131		8.5	12.5				
132	19	19	8.5	18.5			
134	6.0	7.5		7.5			
136	5.0		16.5	8.5	8.0		5.0
137			11.5		5.0		7.0
138	18.5	31	7.5	20.5	5.5		
139					29.5		
140					7.5		
141					30	26.5	5.5
142							9.0
143		11					
145	14	23	27.5	13.5			
146			14	5.0			
147		9.0	13.5	5.5			
152			28.5				13
153			6.5		16	12.5	7.0
154					35.5		
155					14		
157			10				14.5
158	20	37	5.5	19.5			
159		12	14.5				
160	6.5	18.5		7.5			
166		11			12.5		6.5
167		10					
168					26.5	55	
169					49.5	10.5	15.5
170			8.0		10		
172	23.5	25	75	17			
173	43	48	19	47			
174	12	15.5	45	22.5			
175	16.5	24	8.0	23			
176				8.0			
180					8.0	5.0	
182					9.0	6.0	
183					11	41	
184							63.5
185			5.0				14
186	9.5	65	30	7.0			7.0
187	7.0	12	68				

(continued)

Table 1 *(continued)*

m/z	Atrazine %	Simazine %	Propazine %	Terbutylazine %	Atraton %	Prometon %	Prometryn %
188		31	22.5				
189			33.5				
190			6.0				
194			8.5		7.0		
195							7.0
196					100		
197					25		
198			13		5.0		9.0
199							31.5
200	100	26	9.5				6.0
201	28	100					
202	49	27					
203	7.0	45.5					
207			6.0				
210					20.5	100	5.5
211					77	12	
212			10	5.5	17.5		
214	10	8.5	84	100			
215	57		36	21.5			
216	13		68.5	44.5			
217	22		16.5	9.0			
218	5.0						
224						10.5	
225						88.5	
226						11.5	65
227							11.5
228			28				6.0
229			100	43.5			
230			43	17.5			
231			74.5	21.5			
232			18	7.0			
240							12.5
241							100
242							50
243							14

[a] All of these mass spectra were run on a VG Analytical 70 SEQ instrument at the Israel Institute for Biological Research.

doubly charged fragment ions in the spectra. As an example for relative abundances we found for atraton (*m/z* 211) that the ion $[M–2CH_3]^{2+}$ at *m/z* 90.5 reaches up to ~23% of the base peak (*m/z* 196) in the 70 eV mass spectrum while the doubly charged parent ion at *m/z* 105.5 is only 0.04% of the base peak. The MIKE spectra could be studied for doubly charged parent ions, in spite of their very low abundances, as will be shown below. Ordinary mass spectra at high sensitivity, e.g. for simazine, demonstrated up to six consecutive H atom losses from the doubly charged parent ion.

Mass spectra, run at reduced electron ionizing energies, demonstrated that the nominal AE for the doubly charged ions was about 25 eV. However this value was very dependent on sensitivity. The AE was checked by running a mass spectrum for prometryn by photoionization mass spectrometry at 21.21 eV. The major singly charged ions observed in the 70 eV EI spectrum (Table 1), i.e. *m/z* 241, 226, 199, and 184

were all observed. However the doubly charged ion at *m/z* 105.5 which is 26% of the base peak in the EI spectrum is totally absent in the photoionization spectrum at 21.21 eV.

3.2. MIKE spectra and high voltage (HV) scans

The series of reactions leading to $[M–2CH_3]^{2+}$ and from these ions to other doubly charged fragments were studied via MIKE spectra and HV scans. The most abundant reactions observed were consecutive methyl radical losses and consecutive hydrogen atom losses and combinations of these. The $[M–2CH_3]^{2+}$ ions are to a very large extent formed by two consecutive methyl losses from the doubly charged parent ion and a single step elimination of ethane is totally ruled out. For example, a MIKE spectrum of low intensity observed for *m/z* 120.5 from prometryn, which is the doubly charged parent ion, demonstrates H loss, CH_3 and C_2H_3 losses. Fig. 3 reproduces the results of a HV scan on *m/z* 90.5 from atraton. It clearly indicates that the major precursor of *m/z* 90.5 is the ion at *m/z* 98, namely $[M–CH_3]^{2+}$ and the minor precursor is at *m/z* 91. This is a clear-cut indication that $[M–30]^{2+}$ is nearly 100% $[M–2CH_3]^{2+}$ formed by two consecutive CH_3 losses from the doubly charged parent ion. Similar results were observed for the other triazines. [See e.g. Eq. (1) for simazine.]

The doubly charged parent ion does not behave as a typical even electron ion but rather as a diradical. Ionization occurs to a large extent at the two exocyclic amino groups, each undergoing typical α cleavage reactions with methyl loss being the preferred reaction.

Additional doubly charged ions were identified as being due to consecutive cleavages. For example, *m/z* 83.5 in atraton is due to various combinations of consecutive ethylene, methyl radical, and hydrogen atom losses from the doubly charged parent ion, $[M–C_2H_4–CH_3–H]^{2+}$. It is not a ^{13}C isotope of a doubly charged *m/z* 83 ion.

The ions $[M–2CH_3]^{2+}$ undergo characteristic reactions in their MIKE spectra. The MIKE spectral
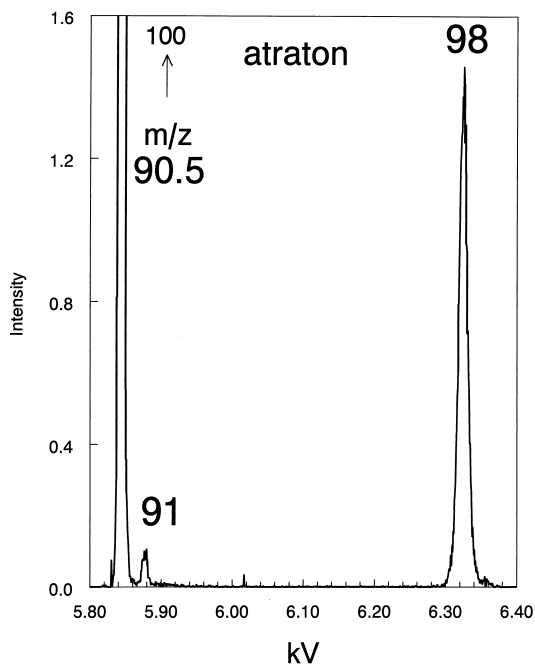

Fig. 3. A high voltage (HV) scan for the doubly charged ion $[M–2CH_3]^{2+}$, *m/z* 90.5, in atraton. The accelerating high voltage is scanned upwards to detect the precursor ions leading to *m/z* 90.5 in fragmentations taking place in the first field free region of the ZAB-2F.

ranges demonstrating lower *m/z* values than the parent *m/z* value are due to eliminations of neutrals and formation of doubly charged daughter ions. Eliminations of stable molecules are common. For example, atraton, for which $R_1 = CH(CH_3)_2$, undergoes elimination of acetylene from the $[M–2CH_3]^{2+}$ ion [Eq. (2)]. Prometryn, which has two exocyclic isopropyl substituents, undergoes a similar reaction. Further-
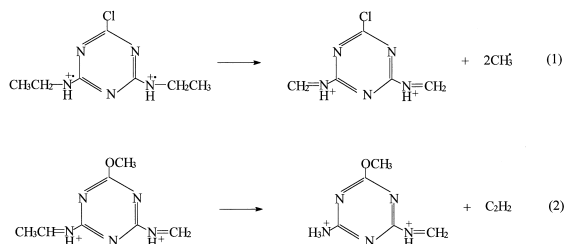
Scheme 2.

more, atraton, with R = OCH_3, undergoes CH_3OH elimination from $[M–2CH_3]^{2+}$ while prometryn, with R = SCH_3, undergoes CH_3SH elimination.

Spectral ranges in the MIKE spectra of $[M–2CH_3]^{2+}$ demonstrating higher *m/z* values than the parent ion *m/z* value are due to Coulomb explosion reactions. We have searched for common Coulomb explosion reactions for triazines having common structural features. We have found that atraton and prometon which have the same R substituent, namely R = OCH_3, both undergo a strong Coulomb explosion reaction due to CH_3^+ elimination:

$181^{2+} \rightarrow 166^+ + 15^+$ (in atraton) and $195^{2+} \rightarrow 180^+ + 15^+$ (in prometon). The methyl ion may originate from the OCH_3 group. Prometryn and propazine, which have two exocyclic isopropyl groups each, demonstrate strong $C_2H_3^+$ eliminations each: $199^{2+} \rightarrow 172^+ + 27^+$, in propazine, and $211^{2+} \rightarrow 184^+ + 27^+$, in prometryn. Other interesting Coulomb explosions are: $171^{2+} \rightarrow 129^+ + 42^+$, in simazine, where *m/z* 42 is probably CH_3NCH^+ and $211^{2+} \rightarrow 137^+ + 74^+$, in prometryn, where *m/z* 74 is possibly CH_3SCNH^+. It is interesting to note that the abundant Coulomb explosion reactions lead from an even electron ion to pairs of even electron ions. These reactions can obviously take place not only in the field free regions of the mass spectrometer but also inside the ion source and can contribute to singly charged ions observed in the 70 eV mass spectra of these compounds provided the discrimination effects against their detection are not too high.

3.3. Metastable peak shapes, kinetic energy releases, and intercharge distances

The metastable peak shapes for some of the Coulomb explosion reactions of the $[M–2CH_3]^{2+}$ ions were studied in greater detail. Results for simazine and atraton are reproduced in Figs. 4, 5, and 6. Dish-topped peaks are observed, which are characteristic of charge separation reactions of doubly charged ions. Such peaks can be deconvoluted to derive kinetic energy release distributions (KERDs) [15,16]. These distributions yield values for the most probable
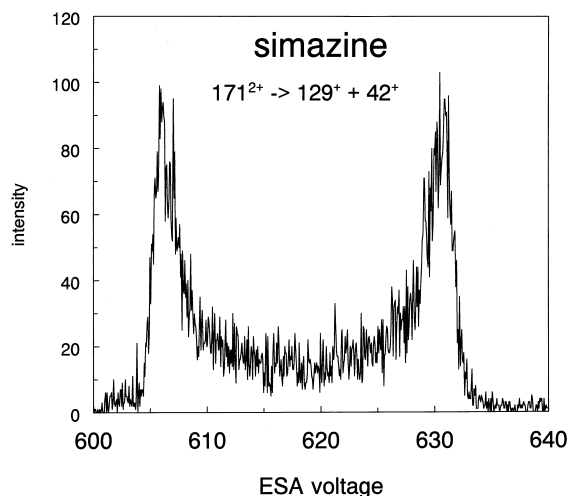
Fig. 4. The metastable peak shape for the indicated reaction of $[M–2CH_3]^{2+}$ in simazine taking place in the second field free region of the ZAB-2F. The electrostatic analyzer (ESA) voltage is scanned upwards from 400 V to observe Coulomb explosion reactions. The parent ion is transmitted in this case at an ESA voltage of 410 V. The peak observed is for the high mass ion fragment, *m/z* 129.

KER and for the average KER. We have adopted the easier, but less accurate method, of determining the KER from the distance between the horns of the metastable peak. For a generalized reaction [17]
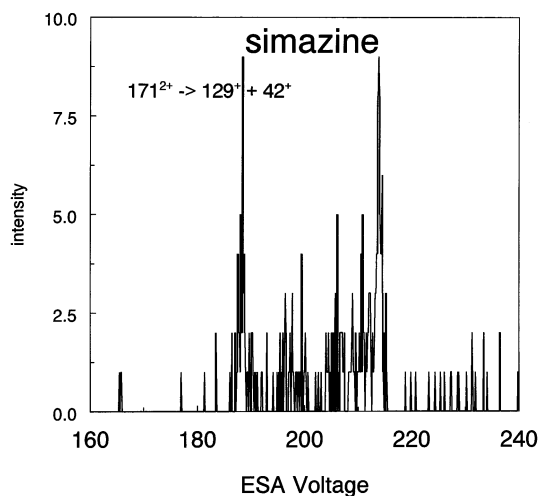
Fig. 5. The metastable peak shape for the indicated reaction in simazine. The parent ion is transmitted at an ESA voltage of 409 V. The peak observed is for the low mass ion fragment, *m/z* 42.
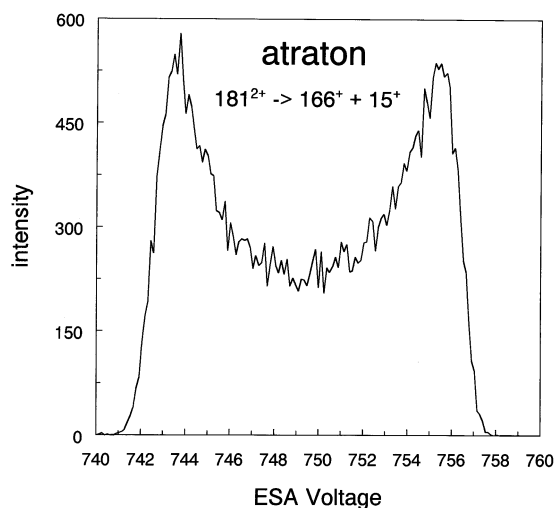
Fig. 6. The metastable peak shape for the indicated reaction of $[M–2CH_3]^{2+}$ in atraton. The parent ion is transmitted at an ESA voltage of 409.4 V corresponding to a laboratory ion energy of 7798 eV. The peak observed is the high mass ion fragment, m/z 166.

$$m_1^{2+} \rightarrow m_2^+ + m_3^+, \qquad (3)$$

$$T = \frac{m_1^2 \ \text{eV}}{16 \times 2m_2 m_3} \ (\Delta E/E_0)^2 \qquad (4)$$

where T is the KER, V is the accelerating voltage, E_0 is the electric sector voltage required to transmit stable ions formed in the source, and ΔE is the electric sector voltage width at the horns. The KER can be used to determine the intercharge distance (r) in the transition structure via [17],

$$r[\text{Å}] = 14.39/T[\text{eV}] \qquad (5)$$

Some of the values which we have deduced for the KERs and for the intercharge distances are summarized in Table 2. For example the values deduced for the CH_3CNH^+ elimination from $[M–2CH_3]^{2+}$ in simazine (Fig. 4) when monitoring m/z 129 are $T = 2.37$ eV and $r = 6.1$ Å. In this instance we were able to verify the results by measuring T (horns) for both of the ionic fragments of the reaction i.e. for m/z 42 formed together with m/z 129 in simazine (Fig. 5), and although the peak is much less intense and considerably more noisy than the one for the heavier fragment

Table 2
Kinetic energy releases and intercharge distances for Coulomb explosions of $[M–2CH_3]^{2+}$ ions

	Reaction		T (eV)	r (Å)
Prometryn	211^{2+}	$\rightarrow 137^+ + 74^+$	2.03	7.1
		$\rightarrow 168^+ + 43^+$	1.85	7.8
		$\rightarrow 183^+ + 28^+$	1.77	8.1
		$\rightarrow 184^+ + 27^+$	1.62	8.9
		$\rightarrow 196^+ + 15^+$	1.1	13
Simazine	171^{2+}	$\rightarrow 129^+ + 42^+$	2.40	6.0
		$\rightarrow 141^+ + 30^+$	1.6	9.0
Atraton	181^{2+}	$\rightarrow 166^+ + 15^+$	1.40	10.3

in Fig. 4, it lead to similar results, i.e. $T = 2.47$ eV and $r = 5.8$ Å. On the whole, the more symmetric the cleavage is, in terms of the fragment masses, the higher is the KER and the lower is the intercharge distance (see Table 2), as might be expected. For example, the least symmetric cleavage is the CH_3^+ elimination and the values deduced for it are $T = 1.4$ eV and $r = 10.3$ Å and $T = 1.1$ eV and $r = 13$ Å in the case of atraton (Fig. 6) and prometryn (Table 2), respectively.

The kinetic energy release of charge separation can be treated by the avoided crossing model of Gill and Radom [18]. A similar model has recently been applied in charge separation processes of highly charged fullerenes [19–21]. According to this model in the case of doubly charged ions, the transition structure is an avoided crossing of the repulsive state of AB^{2+} fragmenting to $A^+ + B^+$, and the attractive state $A^{2+} + B$. In this case, the KER should be equal to the ionization energy of A^+ minus the ionization energy of B, $T = IE(A^+) - IE(B)$. In the case of the triazines, some of the ionic fragments are unstable as neutrals and it makes more sense to assume that CH_3NCH^+ is formed, for example, by proton transfer to a receding CH_3NC fragment rather than by electron transfer from a neutral CH_3NCH. A similar situation exists for multiply protonated peptides [22–24]. A doubly charged peptide M bound to a base B can dissociate either to $MH_2^{2+} + B$ or to $MH^+ + BH^+$ and the competition between two such processes was studied in order to determine relative proton affinities and gas phase basicities of biopolymers [22–24]. A similar competition has not been observed for the

triazines, in other words both products were not observed in a single MIKE spectrum of a triazine. However, the spectra of several different triazines may be intercompared as follows: The proton affinity of CH_3NC is 201.4 kcal/mol, considerably higher than those of CH_3OH, PA = 181.9 kcal/mol and CH_3SH, PA = 187.4 kcal/mol [25]. As a result, $[M–2CH_3]^{2+}$ ions in atraton and prometryn eliminate neutral CH_3OH and CH_3SH, respectively, leaving behind doubly charged ions, and $[M–2CH_3]^{2+}$ ions in simazine eliminate CH_3NCH^+, i.e. undergo Coulomb explosion to two singly charged ions. The large intercharge distances calculated in some cases for the triazines, particularly for CH_3^+ eliminations, indicate that the transition structures, or the avoided crossings, correspond to open chain configurations, rather than to the original cyclic ones of the triazines. One has to bear in mind however that for polyatomic species, of the type discussed here, relation (5) holds only if all the available energy is released as translational energy of the products. If part of the energy is released as vibrational excitation of the two singly charged products, then the asymptotic electronic energy difference will be larger than the measured KER, and correspondingly, the crossing occurs at smaller interparticle separations than r in Table 2. Smaller values than the 6 Å determined for simazine would be more realistic for the suggested proton jump distance.

Some of the dish-topped peaks demonstrate a collisionally activated dissociation (CAD) peak near the center of the dish top, upon introduction of a collision gas into the second field free region of the ZAB-2F. This is seen for example in Fig. 7 for the reaction $171^{2+} \rightarrow 129^+ + 42^+$. Similar phenomena have been reported previously and have been ascribed to a charge exchange reaction preceding fragmentation in the presence of the collision gas so that the large Coulombic energy is not available for release [17]. Charge exchange produces a singly charged 171^+ ion; whether the neutral formed upon its fragmentation is CH_3NCH (M = 42) or a combination of H plus CH_3NC fragments remains an open question.
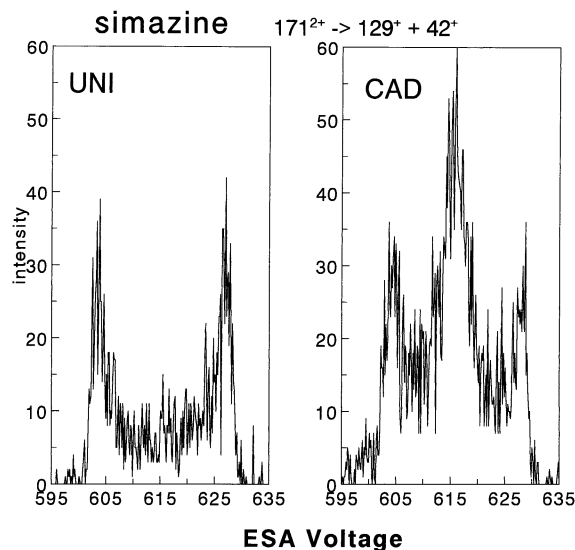

Fig. 7. Unimolecular (UNI) and CAD spectra for the indicated reaction in simazine.

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