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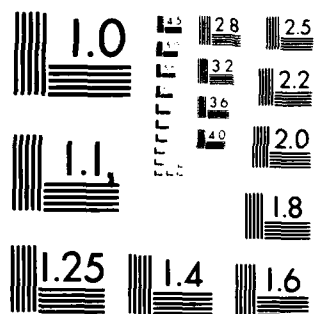
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THE KINETICS OF WATER ION CLUSTER DECOMPOSITION PROCESSES

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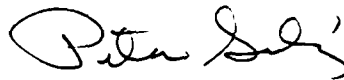
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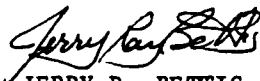


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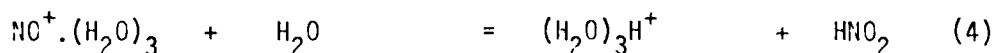
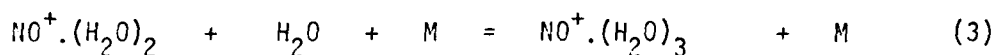
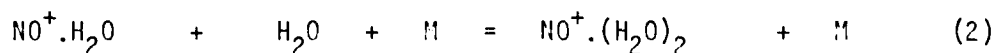
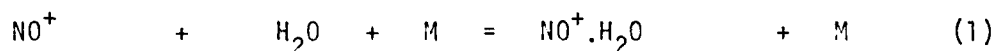


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A combined molecular beam-mass spectrometer system has been used to detect the presence of stable ion clusters. It has been found that relative metastable peak intensities provide the best indication of stability, and this is supported by results from the study of water and argon ion clusters. Some preliminary results on an experimental and theoretical study of doubly charged water clusters are also presented and discussed. In particular, it is suggested that the water molecules in these clusters are in a highly ordered		

Introduction.

It has now become recognised that water ion clusters play an important role as reaction intermediates in many of the ion - molecule processes associated with the chemistry of the upper atmosphere¹. From laboratory studies² it has been suggested that following the photo ionization of NO by solar Lyman α radiation, water ion clusters are generated by the following route



Because of the relatively low pressures in the D-region it is difficult to accommodate the above mechanism within the chemistry of the ionosphere. However, in the stratosphere where pressures are higher such processes may be possible. At these lower altitudes ionization through cosmic ray impact can also occur. To account for ion cluster formation in the D-region a mechanism based on switching reactions involving N_2 and CO_2 has been proposed³.

The contribution an individual ion cluster makes to the overall chemistry of the atmosphere depends on a number of factors: its mass and lifetime will determine its mobility, and these together with the cluster's concentration will influence both the rates of recombination and nucleation.

- 1) E. E. Ferguson, F. C. Fehsenfeld and D. L. Albritton, In 'Gas Phase Ion Chemistry', Vol. 1, M. T. Bowers, Editor, Academic Press, 1979.
E. E. Ferguson and F. Arnold, Chem. Rev., 14, 327 (1981).
- 2) E. E. Ferguson and F. C. Fehsenfeld, J. Geophys. Res. 74, 5743, (1969).
- 3) F. E. Ferguson, Rev. Geophys. Space Phys., 9, 997 (1971).



and the contribution the ion makes to the electrical conductivity of the atmosphere. Thus, the lifetime and/or structure of an ion cluster can have a decisive role in determining the part it plays in atmospheric chemistry.

Apart from the chemistry there is a further possibility that an ion cluster may act as an embryo in a nucleation sequence resulting in the formation of an aerosol droplet. Although there is no conclusive evidence to link specific ions with aerosol formation in the atmosphere, laboratory studies⁴ have shown that the presence of ions can influence the formation of ice particles. Also calculations by Mohnen et al⁵ suggest that species such as $H_3O^+ \cdot (H_2O)_n \cdot (H_2SO_4)_m$ could be candidates for aerosol formation.

Our initial objective in this project was to try and detect the presence of large stable water ion clusters. Kebarle et al⁶ have studied the ion equilibria $(H_2O)_{n-1}H^+ + H_2O = (H_2O)_nH^+$ up to $n = 8$, and their measurements of ΔG^0 , ΔH^0 and ΔS^0 indicate that $(H_2O)_4H^+$ constitutes the first solvation shell of the proton. The equilibrium nature of their experiment makes it difficult to generate and detect ion clusters larger than $(H_2O)_8H^+$. As will be seen, our experiment provides for the generation of species beyond $(H_2O)_{100}H^+$. However, this is done at the expense of any detailed thermodynamic information on these systems. It therefore becomes necessary to develop alternative criteria in order to assess the stability of a large ion cluster. An account of previous studies on large water ion clusters can be found in reference 7.

- 4) R. J. Anderson, R. C. Miller, J. L. Kassner, Jr. and D. E. Hagen, J. Atmos. Sci., 37, 2508 (1980).
- 5) L. Y. Chan and V. A. Mohnen, J. Aerosol Sci., 11, 35 (1980).
- 6) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough and M. Arshadi, J. Am. Chem. Soc. 89, 6393 (1967).
- 7) A. J. Stace and C. Moore, Chem. Phys. Letts, 96, 80 (1983).

Experimental section.

Neutral clusters are generated by the adiabatic expansion of a water vapour/argon mixture through a 50 μm orifice at station pressures up to 10 atm. During the course of this project a pulsed nozzle was built using a design based on a fuel injector⁸. The nozzle has been constructed in such a way that the action of the injector's pin serves to interrupt the gas flow at regular intervals. The movement of the pin can be controlled in the following ways:

- a) frequency: continuously variable from 1 to 20 Hz and from 10 to 200 Hz. Usually set at 100 Hz; but for large orifice sizes 20 Hz is used.
- b) fraction of the duty cycle during which the valve is open: continuously variable from 0 to 50%. The best signal - noise ratio is obtained when the valve is open for 50% of the duty cycle as this gives a mark - space ratio of one at the lock-in amplifier. For large orifice sizes the open - time is reduced to approximately 10%.
- c) valve opening current: continuously variable up to 1 amp. This controls the time taken by the valve to open. This aspect of the valve's behaviour has not yet been fully investigated.

The most difficult aspect of the construction process proved to be that of obtaining an effective seal between the pin and the orifice when the valve is in the closed position. Because the orifice is drilled in platinum (electron microscope apertures are used) it is not possible to lap this with the steel pin of the valve, as has been done previously⁸. The problem was solved by attaching a small rubber disc to the pin and using this to form the seal. A number of different rubbers and polymers

8) C. E. Otis and P. M. Johnson, Rev. Sci. Instr., 51, 1128 (1980).

were tested and the most effective proved to be KALREZ, a perfluoro-elastomer manufactured by Du Pont. The same 2mm disc has been in continuous use for 6 months in the presence of such gases and liquids as NH_3 , CS_2 , $(\text{CH}_3)_2\text{O}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_5\text{H}_5\text{N}$ and $(\text{CH}_3)_2\text{CO}$, with no evidence of deterioration. Only in the presence of formaldehyde does the polymer show some evidence of swelling.

The net result from using the pulsed nozzle is that we have been able to increase ion cluster intensities by at least a factor of 10. This has mainly been achieved through the use of higher stagnation pressures without having to increase the pumping capacity.

Following collimation with a skimmer the modulated cluster beam is ionized by electron impact and mass analysed on a modified A.E.I. MS 12 mass spectrometer. With the ion source accelerating potential set at 8 kV it is possible to mass select up to 1000 amu. At 1 kV, 3600 amu is possible. Figure 1 shows a typical water ion cluster mass spectrum run with a source potential of 4 kV. The intensity fluctuations are mainly due to changes in recorder sensitivity. In addition to providing relative ion cluster intensities, the mass spectrometer has also been used to monitor metastable peak intensities. If an ion has a lifetime in the range 10^{-5} - 10^{-6} s, there is a high probability that it will decompose in the field - free region between the ion source and the magnet. Under such circumstances the product ion is not properly focused by the instrument and is recorded as a diffuse peak at a non - integer position on the mass scale. Figure 2 summarizes this aspect of the experiment and figure 3 shows an example of a metastable peak for the unimolecular decomposition $(\text{H}_2\text{O})_{19}\text{H}^+ \rightarrow (\text{H}_2\text{O})_{18}\text{H}^+ + \text{H}_2\text{O}$.

Metastable peak analysis.

It is our ability to monitor metastable peaks which has provided much of the information on ion cluster kinetics and decomposition processes. Details of the application of metastable peak intensity data to the study of stable ion clusters are given in reference 7. We shall summarize the results here.

There are two measurements we can make on a metastable peak, these are width and intensity. The width provides a measure of the kinetic energy released during the decomposition which in turn is a reflection of the internal energy of the parent ion. The peak intensity is a measure of the fraction of those parent ions which have lifetimes within the range appropriate for decomposition in the field - free region. The intensity is approximately equal to the shaded area under the rate constant curve in figure 2. To calibrate our analysis⁷, use was made of the fact that $(\text{H}_2\text{O})_{21}\text{H}^+$ appears to be a particularly stable ion. Figure 4 shows the average kinetic energy released during the reaction $(\text{H}_2\text{O})_n\text{H}^+ \rightarrow (\text{H}_2\text{O})_{n-1}\text{H}^+ + \text{H}_2\text{O}$, plotted as a function of n . As can be seen the result for $(\text{H}_2\text{O})_{21}\text{H}^+$ displays no special feature which might differentiate it from the other ion clusters. Similar results were obtained for D_2O . Figure 5 shows a plot of the relative metastable peak intensities as a function of n . In this case it can be seen that the peak resulting from the decomposition which leads to the formation of the stable ion cluster is particularly intense. A similar result is obtained for H_2O ⁷. Finally, figure 6 shows the relative metastable peak intensities measured for the decomposition of argon ion clusters. From these results⁷ it was concluded that Ar_{19}^+ is a stable species. The average kinetic energy released as a function of cluster size has also been measured for the argon system; but these data have yet to be evaluated.

The conclusion from this study⁷ was that relative metastable peak

intensities can be used to establish the presence of stable ion clusters in those large systems where it is not possible to make thermodynamic measurements. The advantage of metastable peaks as opposed to ion cluster intensities is that the former are a function of an ion's reactivity and therefore should not be influenced by such factors as ionization cross - section or the presence of a stable neutral cluster.

Doubly charged ion clusters.

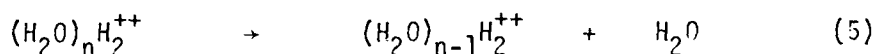
In figure 1 it can be seen that there are some low intensity peaks starting to appear at approximately $n = 18$ and situated between the main water ion cluster peaks. Using the water peaks as mass markers the general formula $(H_2O)_n H_2^{++}$ has been determined for these peaks, i.e. they are composed of two singly charged cluster units. Figure 7 shows an expanded portion of the mass spectrum in the region $n = 20$. The most interesting feature of these results is the sharp cutoff, with no doubly charged clusters being observed below $(H_2O)_{35} H_2^{++}$ (obviously $(H_2O)_{34} H_2^{++}$ may be present but hidden beneath $(H_2O)_{17} H^+$). Behaviour of this type has been observed by Sattler et al⁹ in Pb, NaI and Xe clusters, and they suggested that doubly charged clusters become unstable when the Coulomb repulsion between the positive charges is greater than the binding energy. Obviously, in $(H_2O)_{35} H_2^{++}$ this is not the case, but the loss of only two water molecules does create such a situation with the formation of $(H_2O)_{33} H_2^{++}$.

We have spent several months investigating doubly charged clusters and in particular those of water and D_2O (there is no isotope effect in the cutoff value). Much of our attention has been devoted towards trying to establish their fragmentation patterns through the observation of appropriate metastable peaks. It was felt that such a study might contribute towards our understanding of ionic repulsion in liquids and the transmission of electrostatic interactions through dense media (see below).

Figure 3 represents one of the best resolved mass spectra to date. Increasing the resolution unfortunately leads to a loss of sensitivity, and because the doubly charged clusters already have low intensities their metastable peaks can quite easily become lost in the noise. To provide some perspective within the spectrum, it should be noted that

9) K. Sattler, J. Muhlbach, O. Echt, P. Pfau and E. Recknagel, Phys. Rev. Letts. 47, 160 (1981).

the metastable peak is 0.94 amu away from the $(\text{H}_2\text{O})_{17}\text{H}^+$ peak, and that the distance between the latter and the $(\text{H}_2\text{O})_{35}\text{H}_2^{++}$ peak is 9 amu. There are two interesting features in figure 3 and we believe these are due to the presence of doubly charged clusters. First, the $(\text{H}_2\text{O})_n\text{H}^+$ peaks have a small shoulder approximately 0.25 amu to the right for $n > 16$ and secondly, the $(\text{H}_2\text{O})_{35}\text{H}_2^{++}$ peak has two components separated by approximately 0.25 amu. This behaviour together with the absence of any other identifiable peaks, metastable or otherwise, leads us to the conclusion that there are two possible decomposition routes for the doubly charged clusters, and these are:



$$k = j \quad \text{if } n \text{ even} \quad (a)$$

$$k = j+1 \quad \text{if } n \text{ odd} \quad (b)$$

For both reactions (5) and (6) the respective metastable peaks will lie very close to lower order parent peaks. For example, the process $(\text{H}_2\text{O})_{36}\text{H}_2^{++} \rightarrow (\text{H}_2\text{O})_{35}\text{H}_2^{++} + \text{H}_2\text{O}$ would give a metastable peak at 307.24 amu, which could account for the shoulder shown in figure 3.

Similarly, the reaction $(\text{H}_2\text{O})_{37}\text{H}_2^{++} \rightarrow (\text{H}_2\text{O})_{18}\text{H}^+ + (\text{H}_2\text{O})_{19}\text{H}^+$ would give peaks at 316.24 and 352.24, and one of these could account for the additional peak observed alongside the $(\text{H}_2\text{O})_{35}\text{H}_2^{++}$ ion. In option 6a above the metastable peak will have the same m/e position as a parent peak. We can eliminate the possibility in reaction (6) that $k \gg j$ by virtue of the fact that metastable peaks from such processes would be well separated from any of the main peaks.

In addition to the experimental work we have also been attempting to

model the doubly charged clusters in terms of the electrostatic interactions which exist between two positive charges. The simplest approach appears to be that of assuming the system consists of two point charges situated within a sphere of constant dielectric. The potential between the two charges is then given by ¹⁰

$$\phi = \sum_{n=0}^{\infty} \left[\frac{(\epsilon-1)(n+1)es^{2n}}{\epsilon(\epsilon n+n+1)a^{2n+1}} + \frac{e}{\epsilon s} \right] P_n(\cos\theta) \quad (7)$$

where a is the radius of the sphere, ϵ is the dielectric constant and s is the distance between either point charge and the centre of the sphere. For a given number of water molecules a can be calculated from the density of either ice or water (only 0.5 Å difference between them). This leaves s and ϵ as parameters. The value of s is limited by the fact that the two positive charges will most probably remain as far apart as possible, and may even lie quite close to the surface. The fact that only one or two water molecules means the difference between a stable and an unstable configuration, would suggest that ϕ has to vary quite rapidly as a function of s . So far we have only been able to achieve this type of behaviour with values of ϵ in the range 2 - 8. This in turn would indicate that the clusters are highly ordered structures and that substantial dielectric saturation is taking place.

We have now begun to investigate electronically similar systems, i.e. NH_3 , HF , CH_4 with a view to developing a more quantitative picture of the cutoff behaviour. In NH_3 , for example, no doubly charged clusters are observed below $(\text{NH}_3)_5\text{H}_2^{++}$. Obviously, the fragmentation pattern of these systems would help to establish the locations of the positive charges. To this effect we hope to develop a high-mass tandem mass spectrometer - molecular beam system where it should be possible to mass select

10) C. J. F. Bottcher, 'Theory of Dielectric Polarization', Vol. 1. Elsevier, Amsterdam, 1973.

individual doubly charged clusters and then mass analyse their fragmentation products. Such an instrument will also help in the study of singly charged clusters.

Conclusion.

We believe that the results obtained so far, illustrate that it is possible to detect the presence of stable ion clusters by monitoring metastable peak intensities for unimolecular reactions of the type $X_n^+ \rightarrow X_{n-1}^+ + X$. Unfortunately, the resolution of the present mass spectrometer is such that it is only possible to resolve metastable peaks below $n = 27$. It is anticipated that the development of a high-mass tandem mass spectrometer will help to remove this difficulty. Using the first magnet to select a particular ion cluster, it will then be possible to monitor decomposition, either unimolecular or collision-induced, in the 2nd field-free region with the second magnet. In this way it should be possible to detect the presence very large stable ion clusters. Such a mass spectrometer will also make a valuable contribution to our analysis of the doubly charged ion clusters.

Figure captions.

- 1) Typical mass spectrum of water ion clusters obtained using an ion source accelerating potential of 4 kV. The fluctuations are mainly due to changes in the recorder's sensitivity.
- 2) Schematic representation of the experiment and the conditions necessary for metastable peak formation.
- 3) Expanded section of the water ion cluster mass spectrum, illustrating a typical metastable peak and some features believed to be due to the presence of doubly charged ion clusters (see text).
- 4) The average kinetic energy released as a function of cluster size. E_t has been calculated from the width of the metastable peak at 22% peak height.
- 5) Relative metastable peak intensities as a function of cluster size for the reaction $(D_2O)_n D^+ \rightarrow (D_2O)_{n-1} D^+ + D_2O$. In each case the metastable peak intensity has been divided by the intensity of the respective parent peak.
- 6) Relative metastable peak intensities as a function of cluster size for the reaction $Ar_n^+ \rightarrow Ar_{n-1}^+ + Ar$.
- 7) Expanded section of the water ion cluster mass spectrum, illustrating the doubly charged clusters. The singly charged cluster sizes are labelled at the top of the figure and the doubly charged clusters are labelled above each peak.

Figure 1.

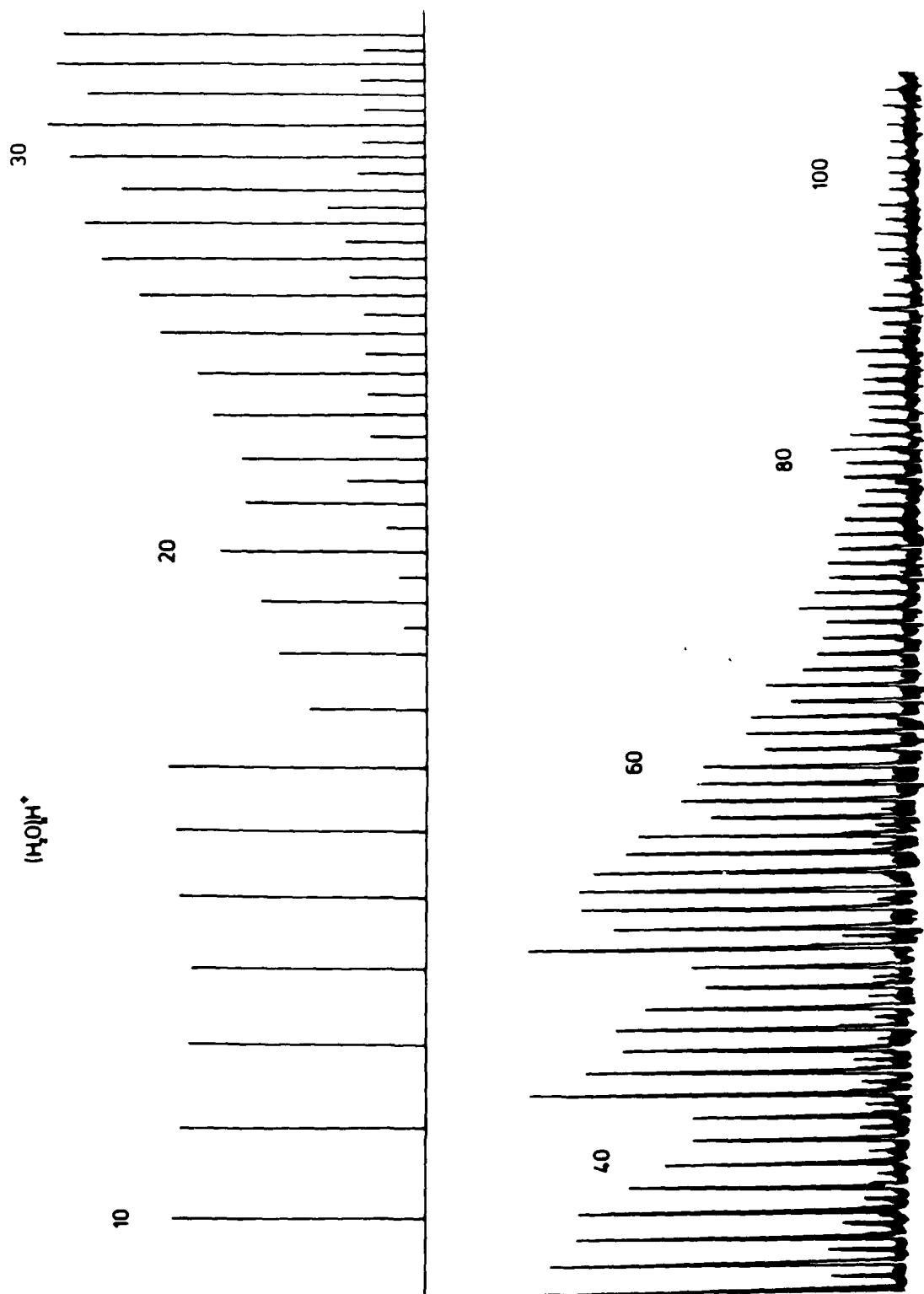


Figure 2.

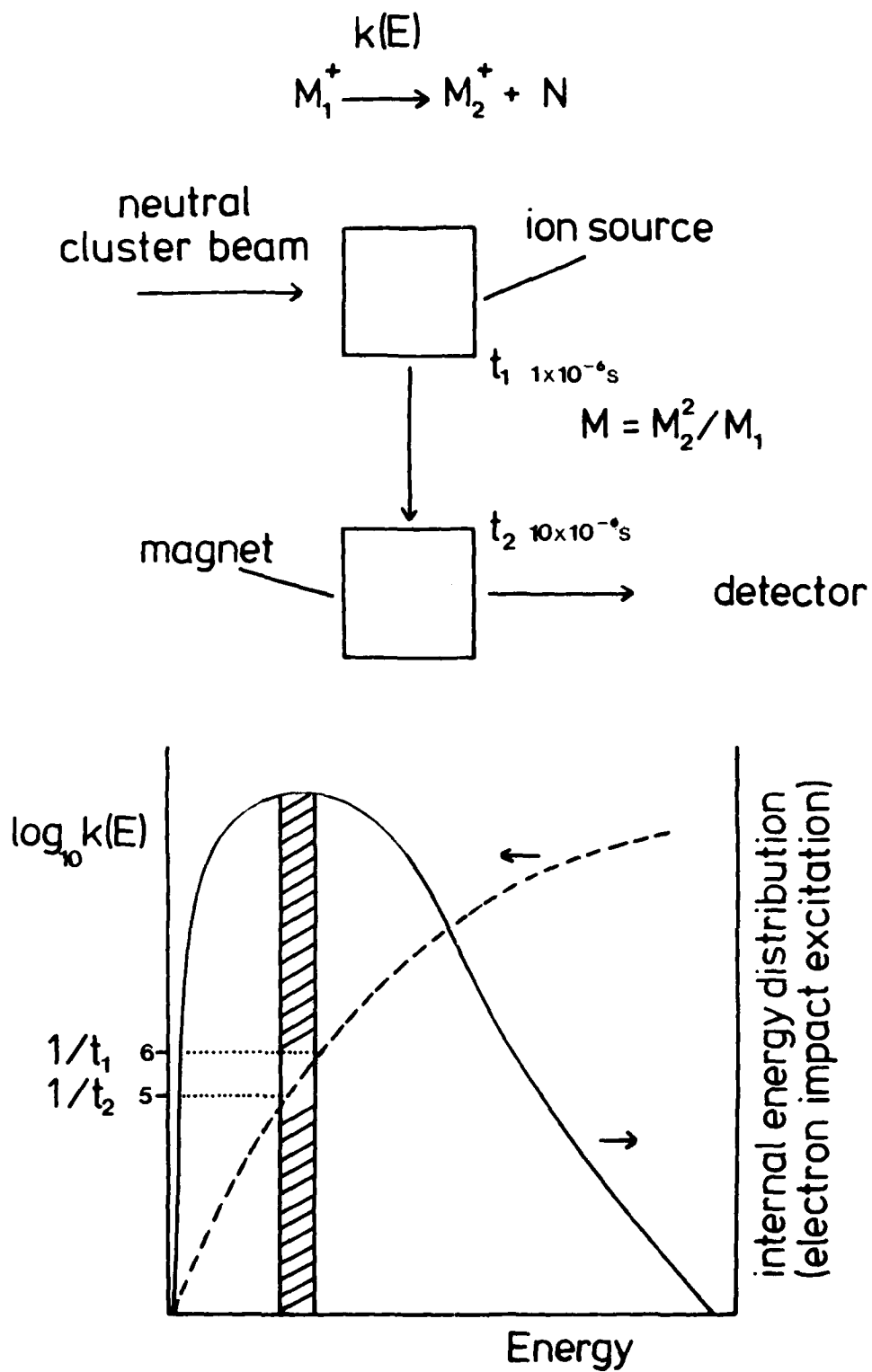


Figure 3.

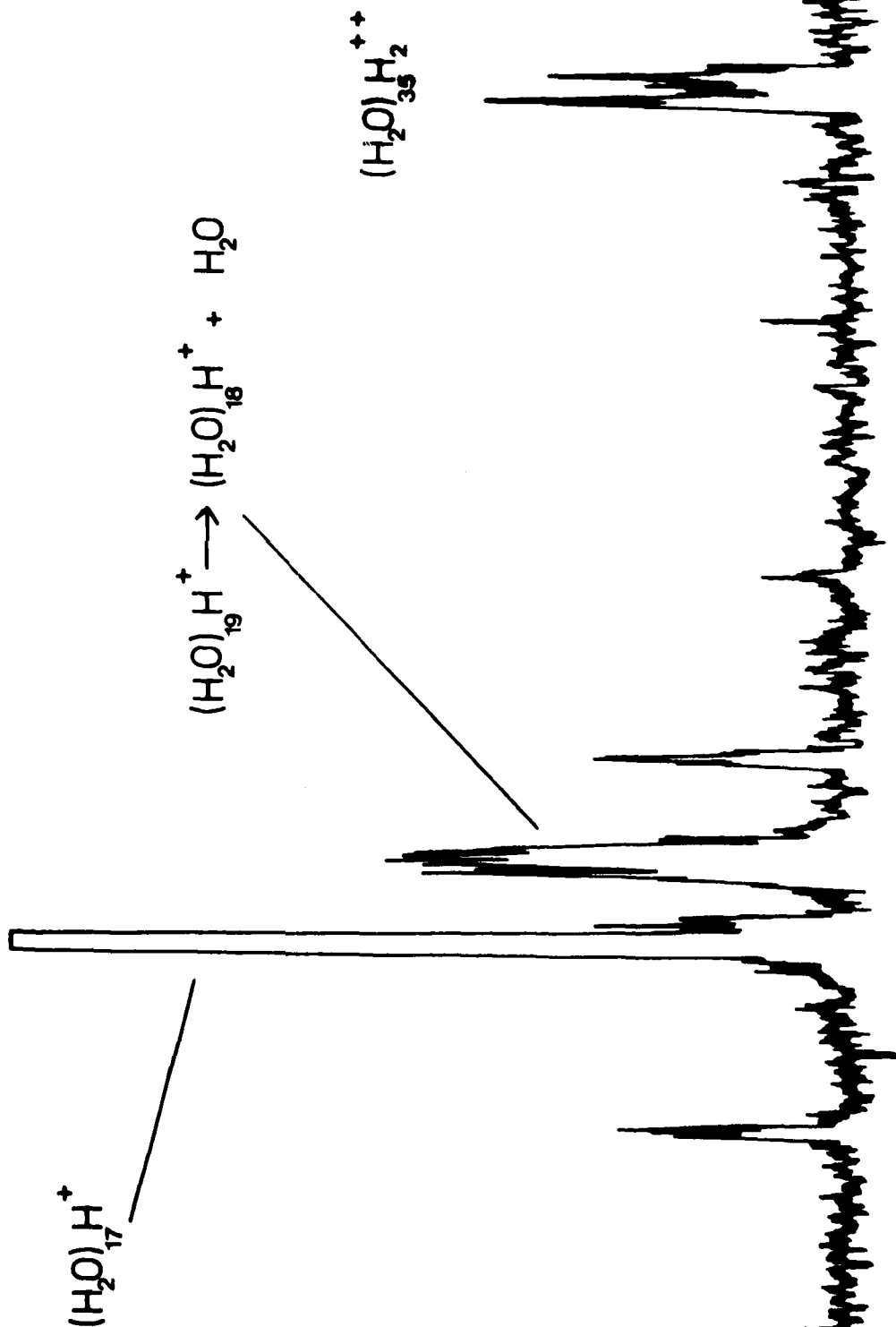


Figure 4.

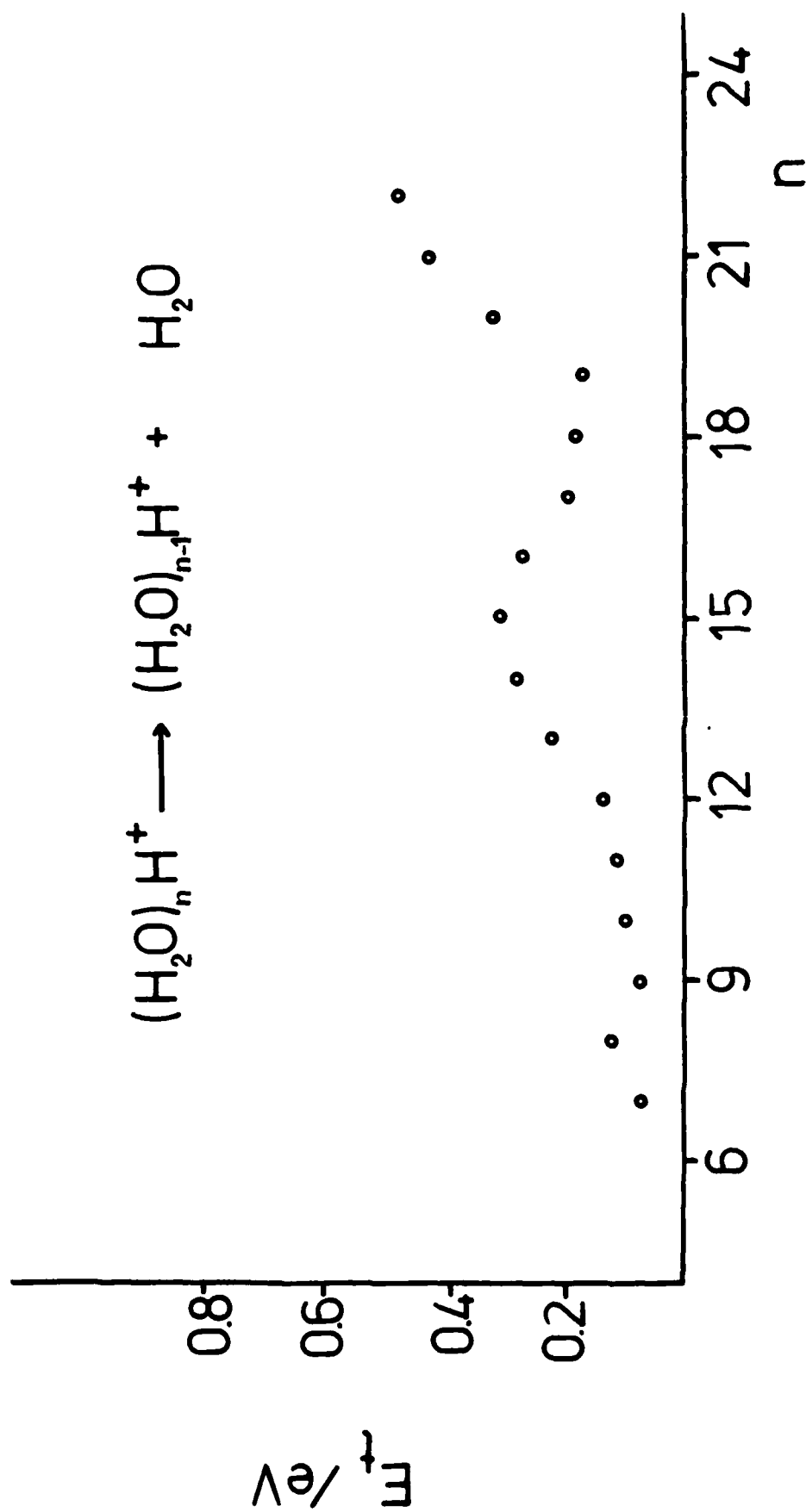


Figure 5.

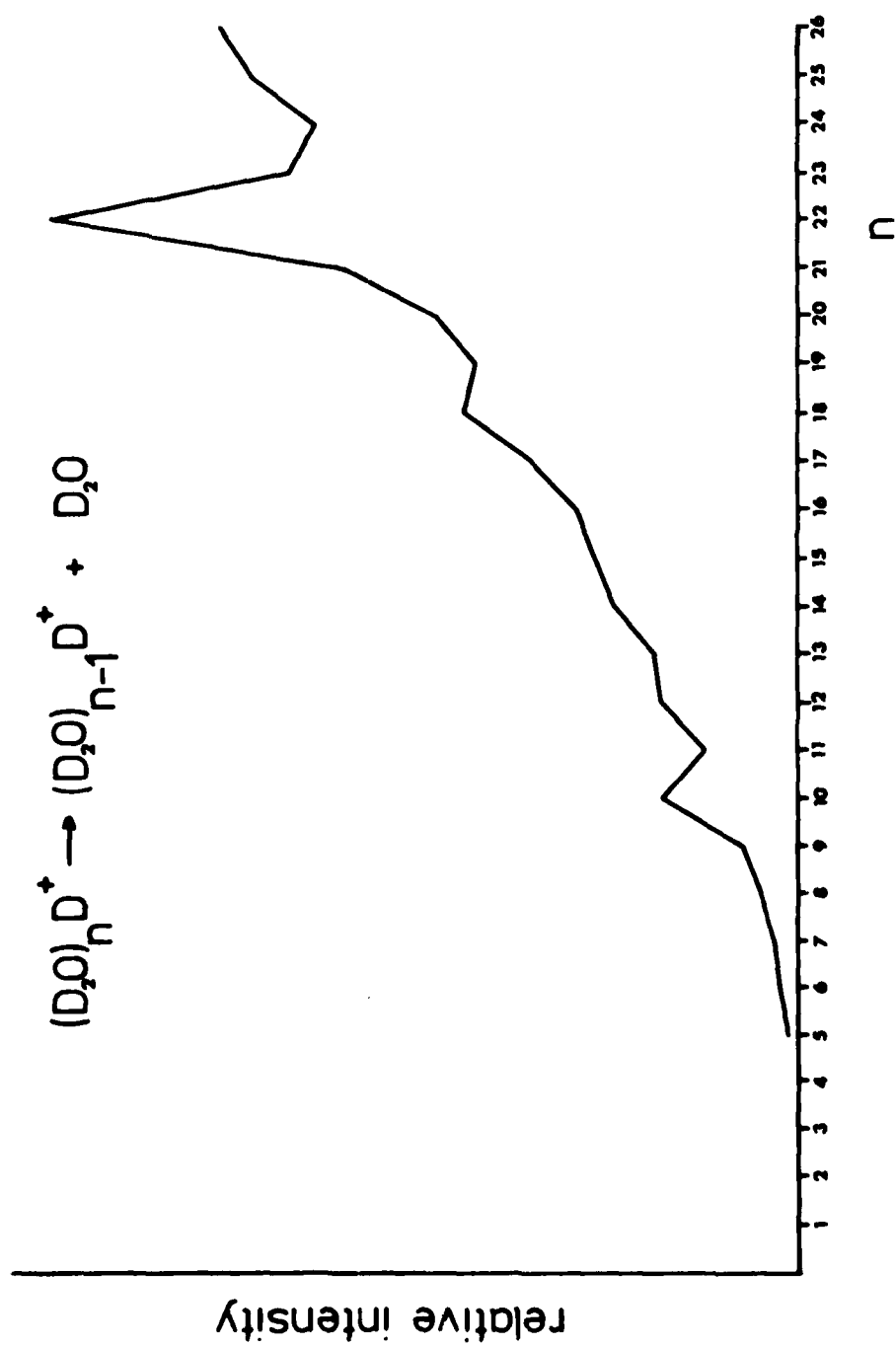


Figure 6.

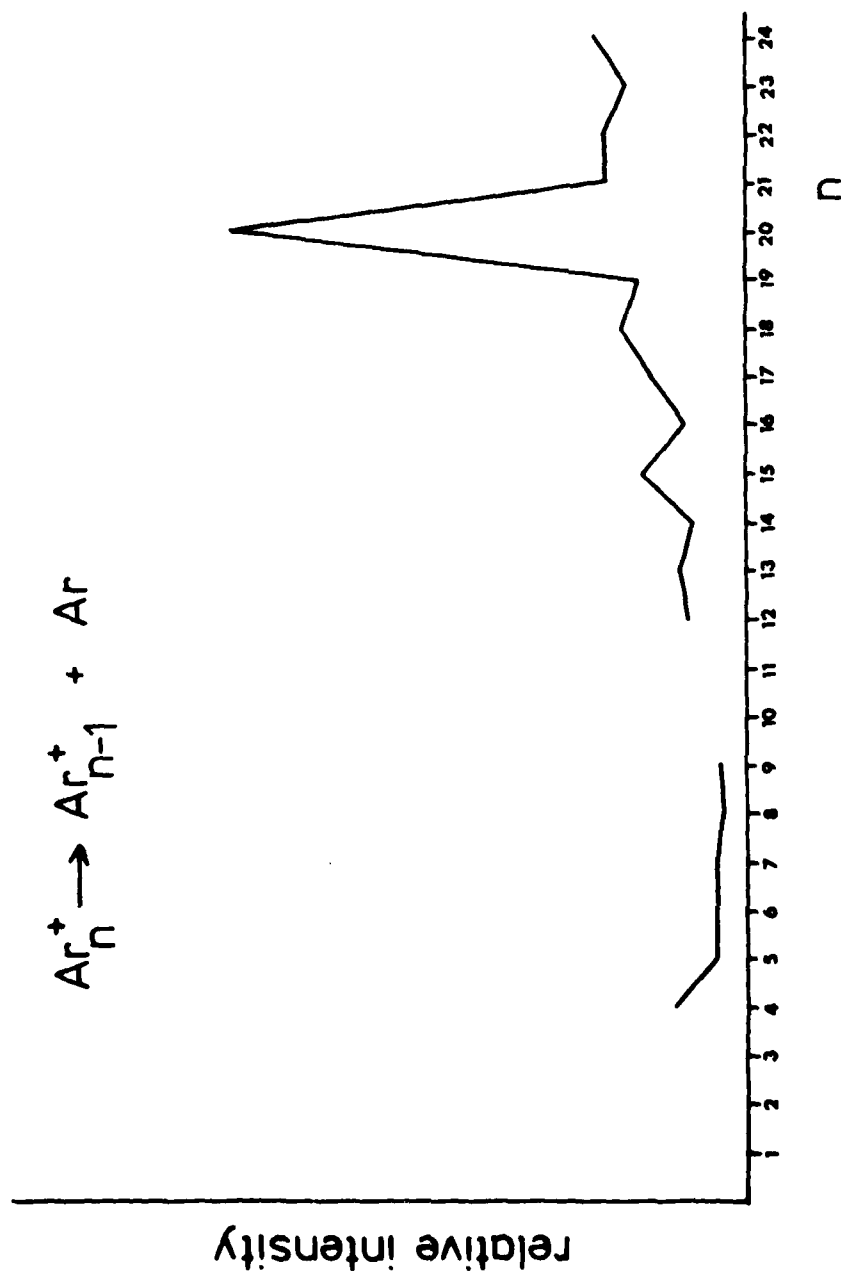


Figure 7.

