

## Evidence of Two Stable Forms of Doubly and Triply Charged Water Cluster

A. J. Stace

*School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, Sussex, United Kingdom*

(Received 21 December 1987)

By means of the supersonic expansion technique in conjunction with a high-resolution mass spectrometer, two separate forms of doubly and triply charged water cluster have been observed. The doubly charged clusters have been identified as  $(\text{H}_2\text{O})_n^{2+}$  and  $(\text{H}_2\text{O})_n\text{H}_2^{2+}$ , and the triply charged as  $(\text{H}_2\text{O})_n\text{H}^{3+}$  and  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$ . Coulomb explosion imposes a minimum value of  $n$  below which each form is unstable, and that value is different for each of the four types of multiply charged cluster.

PACS numbers: 34.90.+q, 35.20.Gs

A feature common to many ion-cluster mass spectra is the existence of a size restriction, below which multiply charged clusters are not observed.<sup>1-7</sup> When the repulsive Coulomb interaction between the two (or more) positive charges becomes greater than the binding energy responsible for holding the cluster together the cluster becomes unstable. As might be expected, the minimum size for a cluster composed of atoms or molecules bound by weak van der Waals interactions is much larger than that for a cluster bound, for example, by hydrogen bonding. Echt<sup>7</sup> has demonstrated that there is a semiquantitative correlation between minimum stable size and the boiling point ( $T_b$ ) of the bulk material. Such a relationship is not unexpected; Trouton's rule provides a link between  $T_b$  and the heat of vaporization, and the magnitude of the latter reflects atomic or molecular binding energy.

For singly charged clusters, there is mass spectrometric evidence that both water<sup>8</sup> and ammonia<sup>9</sup> ion clusters can exist in two separate forms, either protonated or nonprotonated. However, in all the experiments to date on multiply charged clusters,<sup>7</sup> just one stable form for each type of ion has been identified. The purpose of this Letter is to report the results of a series of experiments on water ion clusters in which two types of doubly and triply charged cluster have been identified. The experiments have been performed on an apparatus where a supersonic nozzle has been combined with an ultrahigh-resolution mass spectrometer. The latter is a VG Instruments Inc. ZAB-E double-focusing, reverse geometry instrument, which when operated with an ion source voltage of 8 kV has an upper mass limit of 10000 amu and a resolution in excess of 100000. However, because the ion clusters of interest in the present experiments have comparatively low intensities, it was not possible to operate the mass spectrometer under conditions which maintained both high resolution and sensitivity. Hence, most of the results reported here were obtained with the resolution set at approximately 3000.

The supersonic nozzle system consists of two differentially pumped chambers; an expansion chamber which houses the nozzle and a collimation chamber

which is separated from the former by a skimmer 1 mm in diameter. The expansion chamber is evacuated with a 8000-l-s<sup>-1</sup> diffusion pump, backed with a mechanical booster and a rotary pump. The collimation chamber is evacuated with a 2000-l-s<sup>-1</sup> diffusion pump. Figure 1 shows a schematic diagram of the apparatus. Under typical operating conditions, the pressure in the expansion chamber is  $5 \times 10^{-4}$  Torr, in the collimation chamber it is  $2 \times 10^{-6}$  Torr, and in the ion source of the mass spectrometer the background pressure remains below  $1 \times 10^{-6}$  Torr. To minimize the possibility of ion signal attenuation by collision-induced processes within the flight tube of the mass spectrometer, the background pressure in that region is maintained below  $8 \times 10^{-9}$  Torr.<sup>10</sup> Neutral water clusters were generated by the expansion of a water-vapor-argon mixture at a pressure of approximately 5 atm, through a 150- $\mu\text{m}$ -diam pulsed nozzle operating at approximately 20 Hz. Phase-sensitive detection is used to monitor the ion-cluster spectra.

Figure 2 shows a small section of a mass spectrum recorded for water ion clusters. The spectrum shows the presence of two very intense singly charged ion clusters,

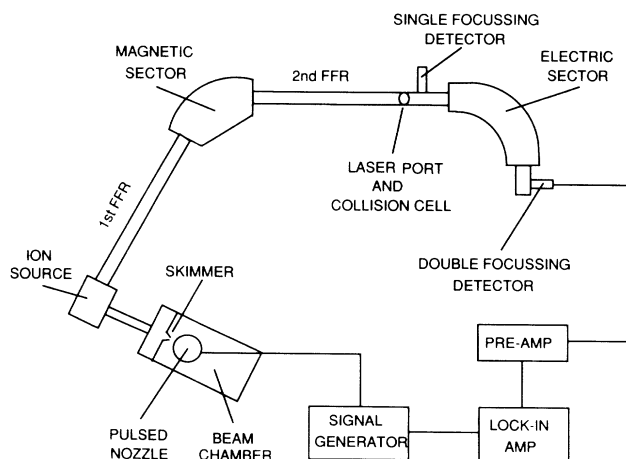


FIG. 1. Schematic diagram of the cluster-beam mass spectrometer apparatus.

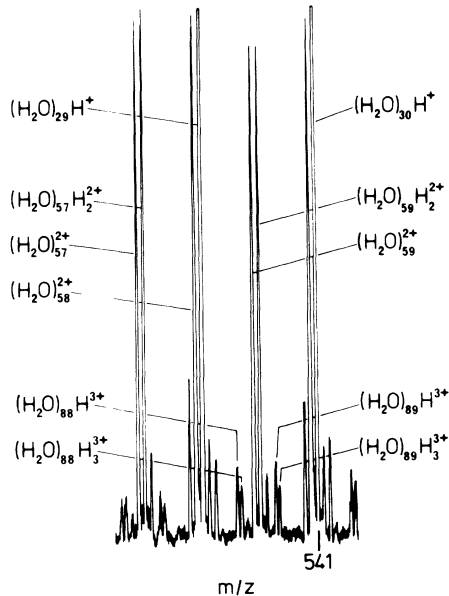


FIG. 2. Section of a mass spectrum recorded following the adiabatic expansion of a water-vapor-argon mixture at 5 atm. The various singly, doubly, and triply charged ion clusters are labeled.

$(\text{H}_2\text{O})_{29}\text{H}^+$  and  $(\text{H}_2\text{O})_{30}\text{H}^+$ . For reasons which will become obvious, it was not possible to detect the nonprotonated form<sup>8</sup> of the above ions in this region of the spectrum. Between each pair of singly charged ions there are two ion peaks, which from their nominal masses correspond to  $(\text{H}_2\text{O})_n^{2+}$  and  $(\text{H}_2\text{O})_n\text{H}_2^{2+}$ . In a previous study of doubly charged water clusters,<sup>4</sup> there was no evidence of the nonprotonated form of the ion. It is possible that a combination of the mass limit, i.e., as imposed by the Coulomb explosion, and the fact that the experiments were performed on a mass spectrometer with a comparatively low resolution contributed to such ions not being identified in earlier experiments. Because the nonprotonated form of the doubly charged cluster is not equivalent to two singly charged protonated units, it is also possible to identify the presence of even-sized doubly charged clusters of the form  $(\text{H}_2\text{O})_n^{2+}$ . In Fig. 2, the ion cluster  $(\text{H}_2\text{O})_{58}^{2+}$  is shown. Previously, the existence of such ions has always been inferred either from the fact that the odd-sized ions are present<sup>1-7</sup> or from the observation of fragmentation products.<sup>6</sup> In support of the proposal that we are observing even-sized doubly charged clusters [as opposed, for example, to  $(\text{H}_2\text{O})_n^+$  clusters], Fig. 3 shows a section of that region in the mass spectrum where the doubly charged water clusters disappear through Coulomb explosion. It can be seen that the behavior of the even-sized  $(\text{H}_2\text{O})_n^{2+}$  clusters as a function of  $n$  closely follows that of the odd-sized doubly charged water clusters. That there appears to be a residual ion peak beyond the Coulomb cutoff, suggests that there is an  $(\text{H}_2\text{O})_n^+$  component associated with the

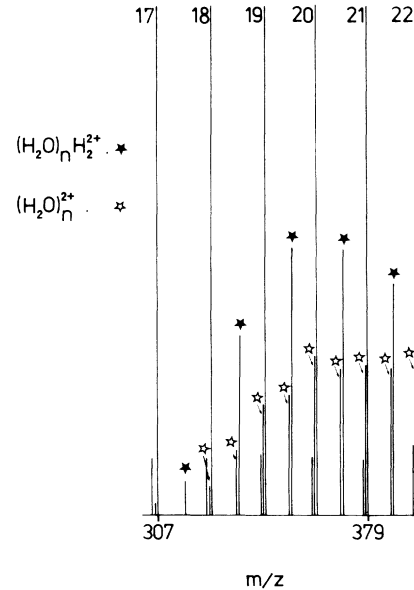


FIG. 3. Section of a mass spectrum of water ion clusters in the region where Coulomb explosion imposes a size restriction on doubly charged clusters. The sizes of singly charged  $(\text{H}_2\text{O})_n\text{H}^+$  clusters are given at the top of the figure. Odd-sized doubly charged clusters are denoted by a filled star, even sized by an open star.

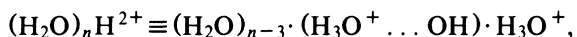
$(\text{H}_2\text{O})_n^{2+}$  clusters.

Further examination of Fig. 2 reveals the presence of a third series of ions. From their positions, relative to those ions we have already identified, these additional clusters are triply charged, and according to their nominal masses, they would appear to correspond to the formulas  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$  and  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$ . From Fig. 2 it is obvious that there is less than 1 amu separation between the ions, and a difference of two protons would separate adjacent triply charged clusters by  $\frac{2}{3}$  amu.

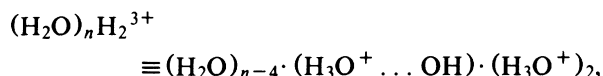
To acknowledge the stability of the  $\text{H}_3\text{O}^+$  unit ( $\Delta H$  for the reaction<sup>11</sup>  $\text{H}_2\text{O}^+ + \text{H}_2\text{O}^+ \rightarrow \text{H}_3\text{O}^+ + \text{OH}$  is  $\approx -20$  kcal mol<sup>-1</sup>), singly charged clusters of the form  $(\text{H}_2\text{O})_n\text{H}^+$  should, strictly speaking, be written as  $(\text{H}_2\text{O})_{n-1} \cdot \text{H}_3\text{O}^+$ . By analogy, I would suggest that the ions  $(\text{H}_2\text{O})_n\text{H}_2^{2+}$  and  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$  could be assigned configurations of the form  $(\text{H}_2\text{O})_{n-2} \cdot (\text{H}_3\text{O}^+)_2$  and  $(\text{H}_2\text{O})_{n-3} \cdot (\text{H}_3\text{O}^+)_3$ , respectively. The presence of the  $\text{H}_3\text{O}^+$  units would then serve to stabilize the clusters by contributing to the hydrogen bond network. However, it would then have to be assumed that the positive charges do not reside on the surface of a cluster. The short-range order imposed by the charges through  $\text{H}_3\text{O}^+$  units in the form of, for example, the stable  $(\text{H}_2\text{O})_3 \cdot \text{H}_3\text{O}^+$  moiety,<sup>12</sup> would imply that they are situated below the surface to a depth of at least one molecule.

To account for the other two types of multiply charged cluster,  $(\text{H}_2\text{O})_n^{2+}$  and  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$ , I shall adopt similar considerations to those presented by Shinohara,

Nishi, and Washida<sup>8</sup> to explain the stability of nonprotonated, singly charged clusters. From calculations,<sup>13,14</sup> it has been proposed that the dimer ion  $(H_2O)_2^+$  has a structure which closely resembles that of a proton transfer complex between an oxonium ion and a hydroxyl radical, i.e.,  $H_3O^+ \dots OH$ . Obviously, the validity of the assumption that such a structure is also present in clusters of the general form  $(H_2O)_n^+$  must remain in question until further calculations have been carried out on large ion clusters. However, the extension of such a complex to the larger clusters does have its attractions, in that structures similar to those proposed for the protonated clusters can now be utilized for nonprotonated species. Thus, for the above multiply charged clusters I would propose that  $(H_2O)_n^{2+}$  adopts the structural form  $(H_2O)_{n-4} \cdot (H_3O^+ \dots OH)_2$ , and that  $(H_2O)_n H^{3+}$  has the structure  $(H_2O)_{n-5} \cdot (H_3O^+ \dots OH)_2 \cdot H_3O^+$ . It is interesting to note that the two other possible variations,



and



do not appear to be stable. This suggests that single protons are stabilized by the  $H_3O^+$  unit, i.e.,  $(H_2O)_n H^+$ ,  $(H_2O)_n H_2^{2+}$ , and  $(H_2O)_n H_3^{3+}$ , but that multiply charged clusters containing nonprotonated ions require the unit  $(H_3O^+ \dots OH)_2$  to be present.

In Fig. 2 the two different types of doubly charged cluster are shown to have approximately equal intensities; however, this is not the case in most other regions of the mass spectrum (see Fig. 3). Figure 4(a) shows a plot of the ratio  $(H_2O)_n^{2+}/(H_2O)_n H_2^{2+}$  for  $n$  in the range 35-121. The minimum stable size for the protonated doubly charged cluster is  $(H_2O)_{35} H_2^{2+}$ , but that for the nonprotonated form is  $(H_2O)_{36}^{2+}$ . For values of  $n$  close to the minimum size, the protonated form is the more intense; but beyond  $n=70$  the nonprotonated, doubly charged clusters dominate. It is not immediately clear why this should be the case. If we equate intensity with stability as, for example, is done with inert-gas ion clusters,<sup>15,16</sup> then it could be concluded that, as the sizes of the clusters increase, the nonprotonated form becomes the more stable. Taking this analysis a step further, one can use the mass spectrometer to examine any differences between the ions in terms of their fragmentation behavior. Changes in relative stability appear to be reflected in the unimolecular fragmentation patterns of ion clusters.<sup>17</sup> Figure 5 shows a mass-analyzed ion kinetic energy<sup>18</sup> spectrum of the ions  $(H_2O)_{57}^{2+}$  and

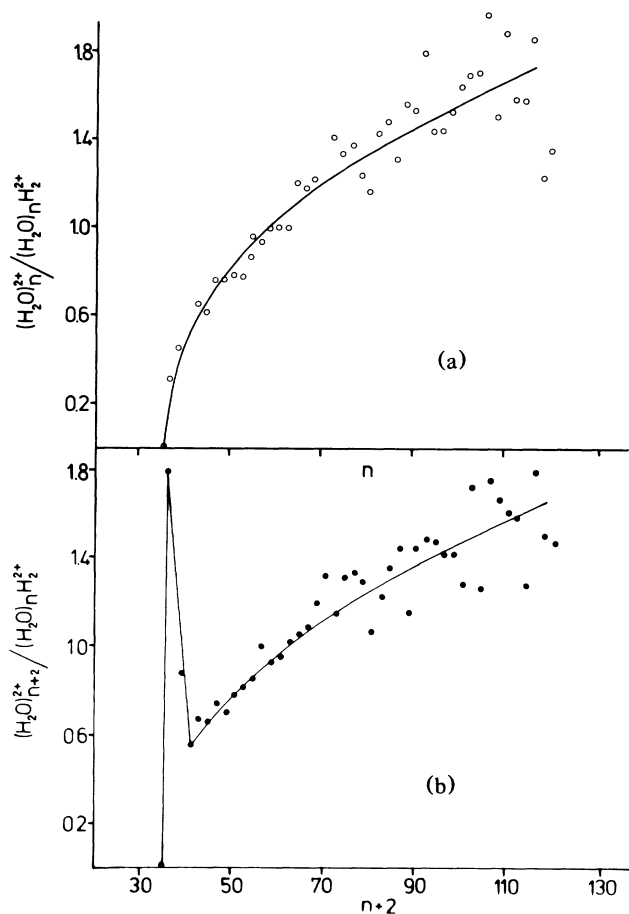


FIG. 4. (a) Plot of the intensity ratio  $(H_2O)_n^{2+}/(H_2O)_n H_2^{2+}$  as a function of cluster size. (b) Plot of the intensity ratio  $(H_2O)_{n+2}^{2+}/(H_2O)_n H_2^{2+}$  as a function of cluster size. Note the cluster size is now given as  $n+2$ .

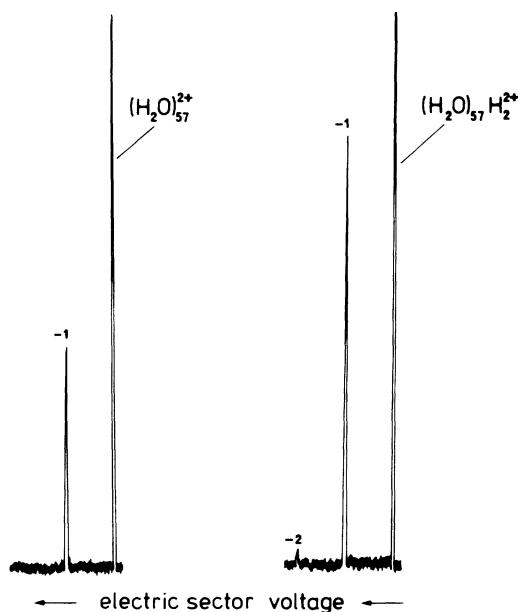


FIG. 5. Measured unimolecular fragmentation patterns for the ion clusters  $(H_2O)_{57}^{2+}$  and  $(H_2O)_{57} H_2^{2+}$ .

$(\text{H}_2\text{O})_{57}\text{H}_2^{2+}$ . To obtain a mass-analyzed ion kinetic energy spectrum, the magnet is set such that it transmits each of the ions in question, and the electric sector voltage is then scanned so that those ions fragmenting in the field-free region (FFR) between the magnetic and electric sectors (2nd FFR in Fig. 1) are detected. It would appear from Fig. 5 that, of the two types of doubly charged water cluster, the protonated form is slightly more reactive. This observation supports my proposal that the nonprotonated form of the clusters is the more stable. With use of the conclusions reached above regarding the structures of the clusters, the intensity data presented in Fig. 4(a) can be evaluated in a slightly different way. If we bear in mind that the cluster  $(\text{H}_2\text{O})_n^{2+}$  can also be written as  $(\text{H}_2\text{O})_{n-4} \cdot (\text{H}_3\text{O}^+ \dots \text{OH})_2$  and that  $(\text{H}_2\text{O})_n\text{H}_2^{2+}$  can be written as  $(\text{H}_2\text{O})_{n-2} \cdot (\text{H}_3\text{O}^+)_2$ , it is perhaps worth considering a plot of the ratio  $(\text{H}_2\text{O})_{n+2}^{2+}/(\text{H}_2\text{O})_n\text{H}_2^{2+}$ , which should allow for the additional two water molecules the nonprotonated cluster requires to form the  $(\text{H}_3\text{O}^+ \dots \text{OH})_2$  complex. The result is shown in Fig. 4(b). While the conclusion regarding behavior for large values of  $n$  remains the same, there is now a sharp change in relative intensity below  $n=41$ , which again favors the nonprotonated form of the cluster as the more stable. A search for quadruply charged water clusters may help to establish a reason for the stability of the different species. To be consistent with the doubly and triply charged clusters, the quadruply charged ions should adopt the forms  $(\text{H}_2\text{O})_n^{4+}$ ,  $(\text{H}_2\text{O})_n\text{H}_2^{4+}$ , and  $(\text{H}_2\text{O})_n\text{H}_4^{4+}$ .

Finally, I should comment on the Coulomb explosion limits for the triply charged clusters. The lower limit for  $(\text{H}_2\text{O})_n\text{H}^{3+}$  is  $n=83$ , whereas that for  $(\text{H}_2\text{O})_n\text{H}_3^{3+}$  is  $n=82$ . Although the ion signals are quite weak, it would appear (see Fig. 2) that as  $n$  increases, clusters containing a single proton, i.e., a possible  $(\text{H}_3\text{O}^+ \dots \text{OH})_2$  unit, become more intense than those containing three protons. The ratio of the minimum stable sizes,  $n_{\text{crit}}^{3+}:n_{\text{crit}}^{2+}$ , is equal to 2.34; this value agrees very well with the 2.3 predicted for spherical charged clusters.<sup>19</sup>

The author would like to thank the Science and Engineering Research Council, United Kingdom, for the award of an equipment grant, the Nuffield Foundation for the award of a research fellowship, and Mr. J. E. Upham for assistance with the experiments.

<sup>1</sup>K. Sattler, J. Muhlbach, O. Echt, P. Pfau, and E. Recknagel, Phys. Rev. Lett. **47**, 160 (1981).

<sup>2</sup>S. S. Lin, Rev. Sci. Instrum. **44**, 516 (1973).

<sup>3</sup>D. Dreyfuss and H. Y. Wachman, J. Chem. Phys. **76**, 2031 (1982).

<sup>4</sup>A. K. Shukla, C. Moore, and A. J. Stace, Chem. Phys. Lett. **109**, 324 (1984).

<sup>5</sup>D. Kreisle, K. Leiter, O. Echt, and T. D. Mark, Z. Phys. D **3**, 319 (1986).

<sup>6</sup>K. Leiter, D. Kreisle, O. Echt, and T. D. Mark, J. Phys. Chem. **91**, 2583 (1987).

<sup>7</sup>O. Echt, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. N. Khanna, NATO Advanced Study Institute, Series B, Vol. 158 (Plenum, New York, 1987), p. 623.

<sup>8</sup>H. Shinohara, N. Nishi, and N. Washida, J. Chem. Phys. **84**, 5561 (1986).

<sup>9</sup>H. Shinohara, N. Nishi, and N. Washida, J. Chem. Phys. **83**, 1939 (1985).

<sup>10</sup>A. J. Stace, P. G. Lethbridge, J. E. Upham, and M. Wright, J. Chem. Phys. **88**, 483 (1988).

<sup>11</sup>R. D. Levin and S. G. Lias, *Ionization Potential and Appearance Potential Measurements, 1971-1981* (U.S. GPO, Washington, DC, 1982).

<sup>12</sup>M. D. Newton, J. Chem. Phys. **67**, 5535 (1977).

<sup>13</sup>L. A. Curtiss, Chem. Phys. Lett. **96**, 422 (1983).

<sup>14</sup>S. Tomoda and K. Kimura, Chem. Phys. **82**, 215 (1983).

<sup>15</sup>O. Echt, K. Sattler, and E. Recknagel, Phys. Rev. Lett. **47**, 1121 (1981).

<sup>16</sup>H. P. Birhofer, H. Haberland, M. Winterer, and D. R. Worsnop, Ber. Bunsenges. Phys. Chem. **88**, 207 (1984).

<sup>17</sup>A. J. Stace and C. Moore, Chem. Phys. Lett. **96**, 80 (1983).

<sup>18</sup>R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, *Metastable Ions* (Elsevier, Amsterdam, 1973).

<sup>19</sup>D. Tomanek, S. Mukherjee, and K. H. Bennemann, Phys. Rev. B **28**, 665 (1983).