Mass Spectroscopic Study of Some Novel Water Clusters: 
\((\text{H}_2\text{O})^+_n; n > 3\)

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Received April 16, 1986

A near atmospheric pressure ion source with a \(\beta\)-emitter as electron source is used to inject ions into a supersonic water expansion. Cluster ions of the structure \((\text{H}_2\text{O})^+_n\) have been observed for \(n\) up to 8. For \(n > 3\) these cluster ions cannot be obtained by ionization of water clusters in vacuum, but they can be grown in the cold environment of a supersonic beam. Extremely clean conditions are necessary for the observation of these cluster ions. The data can be explained by assuming that the local potential minimum calculated for the \((\text{H}_2\text{O})^+_2, n = 2\), potential hypersurface exists also for \(n > 2\). The model developed to explain these data is similar to that proposed for ionized rare gas clusters.

PACS: 36.40.+d; 35.20.Wg

Introduction

If one ionizes an isolated water cluster by electron or photon impact, the first step:
\[ \text{e}^- + (\text{H}_2\text{O})_n \rightarrow (\text{H}_2\text{O})^+_n + 2\text{e}^- \]  
will very rapidly be followed by an ion-molecule half-reaction occurring in the cluster:
\[ (\text{H}_2\text{O})^+_n \rightarrow \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{n-2} + \text{OH}. \]  
This has been known and studied since a long time. The literature has recently been reviewed by Märk and Castleman [1]. The vibrational excitation caused by the formation of the strongly bound \(\text{H}_3\text{O}^+\) ion in the cluster leads to subsequent evaporation of water molecules as observed by Echt et al. [2] and Stace and Moore [3]. Only by working at low electron energies (15 eV) Klots and Compton [4] were able to observe a signal on \((\text{H}_2\text{O})^+_2\), its intensity being only 1% of \(\text{H}_3\text{O}^+ (\text{H}_2\text{O})_2\). Because of its obvious atmospheric and radiological importance the ionization of water and clustering around water ions has been studied by many different groups [1–7].

We report here, that under some special conditions the second step, according to (2), can be suppressed. In this case intact \((\text{H}_2\text{O})^+_n\) clusters can be produced. After completion of this work we learned, that Shinohara et al. [8] have studied photoionization of \((\text{H}_2\text{O})_n\text{Ar}_m\) clusters and have observed \((\text{H}_2\text{O})^+_n\) clusters, too. They explain their results by the cooling of the vibrationally excited ionized water cluster by evaporation of Ar atoms. The cluster ion \((\text{H}_2\text{O})^+_n\) can be trapped in a local minimum of the potential energy hypersurface, and reaction (2) cannot proceed, at least not on the timescale of the experiment. For the \((\text{H}_2\text{O})^+_2\) dimer ion this minimum is known to exist from experimental [9] and theoretical [10, 11] work. In another as yet unpublished result Ozaki et al. have reported \((\text{D}_2\text{O})^+_n\) clusters from electron impact ionization of \((\text{CO}_2)_n (\text{D}_2\text{O})_m\) clusters [12].

While developing an ion source [13–15] for negatively charged water clusters, \((\text{H}_2\text{O})^-_n\), we observed that one of the tried sources also gave the respective positively charged clusters [16]. The experimental technique and the way the clusters are formed are very different from those of Shinohara et al. [8].
Experiment

It was assumed for a long time, that neither \((\text{H}_2\text{O})^+_n\) nor \((\text{H}_2\text{O})^-_n\) could be obtained by interaction of electrons with free water clusters [1-22]. Several sources were therefore built in this laboratory, in which electrons could be introduced into the high pressure part of a supersonic expansion. The idea behind this unusual set-up was the speculation that the inability to form positively or negatively charged \((\text{H}_2\text{O})_n\) clusters might indicate different geometries of the neutral and ionized species. Introducing an electron or an \(\text{H}_2\text{O}^+\) ion into a cooling supersonic beam would perhaps permit their synthesis. This speculation turned out to be essentially correct. A modified design is used presently for negative cluster ions \([14, 15]\), because of the severe impurity problems discussed below.

Experience with an early version showed that the mass spectra are very sensitive to minute concentrations of impurities in the ion source \([13]\). All water samples were therefore purified by ion exchange and double distillation. After transfer to the gas inlet system the water is carefully degassed by repeated freeze, pump, thaw cycles. The source shown in Fig. 1 is an all-metal construction, which can be heated to 400 °C. The ion source contains a low energy beta-emitter, \(^{63}\text{Ni}\), as an electron source. The maximum electron energy is 66 keV. Its activity of 15 mCi corresponds to about \(6 \times 10^8\) decays/s. Taking into account secondary electron emission one calculates that about 50 ion pairs per primary electron or about \(10^{10}\) ion pairs per second are produced at a water pressure of 100 Torr. Only \(10^{-4}\) or less of this current goes through the nozzle hole, which has a diameter of 0.08 mm. We suspect that an ion has to be formed very near the nozzle exit, in order to be swept by the expanding gas into the expansion. Most of the clustering around the ion will occur in the expansion. The newly formed cluster ions are cooled by the cold environment of the expanding jet. The ions are accelerated by 40 V to a skimmer, transferred to a second differentially pumped chamber, mass selected by a quadrupole, and counted. The quadrupole is mass tuned by a linear voltage ramp, which is obtained from a precision 14-bit digital-to-analog converter. It is stepped through the desired mass range by a microprocessor, which also provides the channel advance pulses to a multichannel analyzer recording the mass spectrum. In this way an accurate, reproducible, and digitally controlled mass calibration of the quadrupole is possible. Total ion intensities are \(10^6\)/s or less, while the neutral intensity is 12 orders of magnitude higher. High pressure ion sources have been used earlier with similar impurity problems \([17–21]\).

Results

Figure 2 shows a typical mass spectrum from a neat water expansion. The spectrum was taken after baking the nozzle assembly to 200° C overnight and taking the precautions described above. The less intense series corresponds to \(\text{H}_2\text{O}^+ (\text{H}_2\text{O})_n^-\) ions, while the higher peaks are identified as \((\text{H}_2\text{O})^-_n\). The latter ions have only very recently been observed for \(n > 3\) under very different conditions \([8, 12]\). Formerly \([4]\) they were assumed to be unstable for \(n > 3\). The maximum in the mass distribution in Fig. 2 depends on stagnation temperature and pressure. The highest value of \(n\) observed so far is \(n = 8\). No effort was made to extend the measurements to higher \(n\) values, which should be possible.

The overall shape of the mass spectrum is unusual. A roughly exponential fall off of the intensity with cluster size is generally observed for ionization of neutral clusters, whereas in the high pressure ion source with supersonic beam combination of Fig. 1 roughly...