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CLUSTER IONS OF WATER OBSERVED BY LIQUID IONIZATION MASS SPECTROMETRY

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Cluster ion distributions were measured and stable ions were observed at m/z 379 (21 molecules), 505, 73, and 181. Significant effects of a high electric field and temperature of a needle on the ion abundances strongly suggest that water vapor in argon under the atmospheric pressure condenses on the needle and ionization occurs at the liquid surface where cluster molecules of water exist.

In recent years considerable attention has been directed to studies on the properties of weakly bound clusters of molecules. Studies of clusters involving water molecules are particularly important since they provide insight into the nature of hydrogen bonded systems. In an early study of water by means of a supersonic free jet expansion with mass spectrometry,1) unusual stability was observed at a mass 379 corresponding to 21 water molecules. Other experiments2 - 4) involving the secondary ion mass spectrometry of ice,5) also show evidence for the same stability under a variety of conditions. It has been suggested that the 21st cluster consists of a clathrate of 20 water molecules about a central molecule.6,7)

Liquid ionization (LI) mass spectrometry is a method for measuring a liquid at atmospheric pressure8,9) and has been applied to cluster ions.10) This paper describes cluster ions of water observed by this (LI) method.

The instruments used are two LI mass spectrometers, one is the same as previously reported9) and the other is an improved one with a large pinhole (diameter : 250 µm) built by JEOL LTD.11)

Cluster ions of water, $(H_2O)_nH^+$, are usually observed as a back ground in the instrument. The base peak appears at m/z 73 or 91 and the largest n-value is 8 or so at normal operating conditions for organic samples (for the improved instrument with a thick needle and V_E of 1.5 - 1.6 kV). When a high voltage (V_E) is applied to a needle (sample holder)9) and the vapor pressure of water is high, a mass spectrum like Figure 1 is obtained using the improved instrument. This spectral pattern represents a typical cluster ion distribution at room temperature with a high V_E (2.0 kV in Fig.1). The base peak at m/z 379 corresponds to the 21st cluster ion known by its unusual stability.1 - 7) Larger ions with n more than 44 may be produced but in contrast, the largest cluster ion obtained using the previous instrument (diameter of the pinhole : 25-30 µm) was the 23rd cluster.

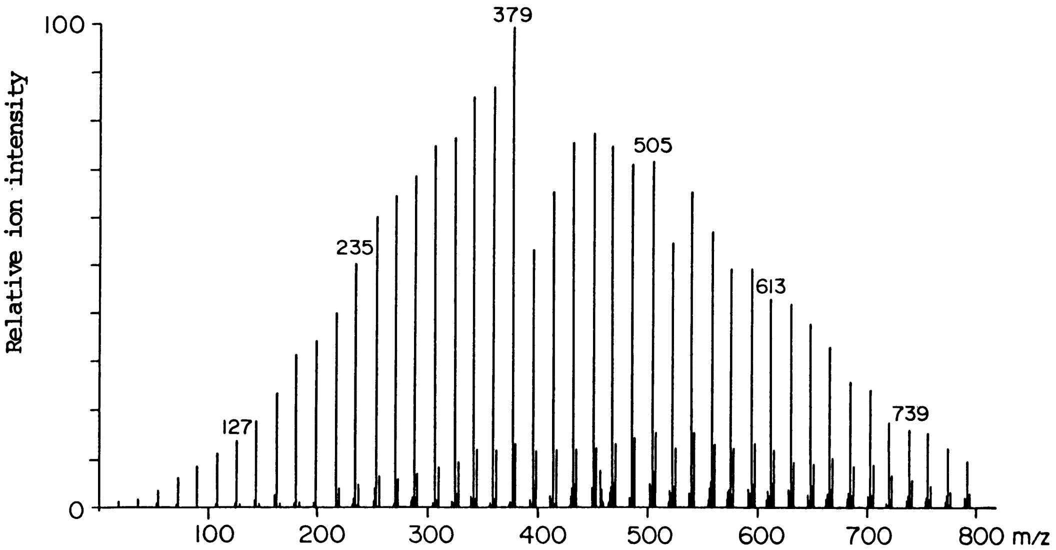

Fig. 1. Cluster ion distribution of water at room temperature (25 °C). V_E : 2.0 kV, Diameter of the needle tip : about 80 µm.

When water is introduced into the ion source by placing a wet tissue paper inside the side tube (port for sample introduction), cluster ion distribution is nearly reproducible. Vapor pressure estimated is about 18 Torr in Fig. 1.

Significant effect of V_E on the ion abundances is shown in Fig. 2. The ion abundances increase with the V_E, especially for larger cluster ions. A needle with a sharpe edge lowers V_E value for the same effect.

When the needle is heated, the cluster ion distribution shifts toward smaller n-values as shown in Fig. 3 that is an example measured at 90 °C. It is interesting to note that the base peak at m/z 181 corresponds to $(H_2O)_{10}H^+$ ion which may be a half of the clathrate with 20 molecules,[6,7] consisting of three pentagonal rings, and is observed rather at heating. A study of the effect of temperature gives us useful information. The results will be described in detail elsewhere. The stability of ion at m/z 505 (28 molecules) seen in Fig. 1 has been reported[7] but not of the ion at m/z 181.

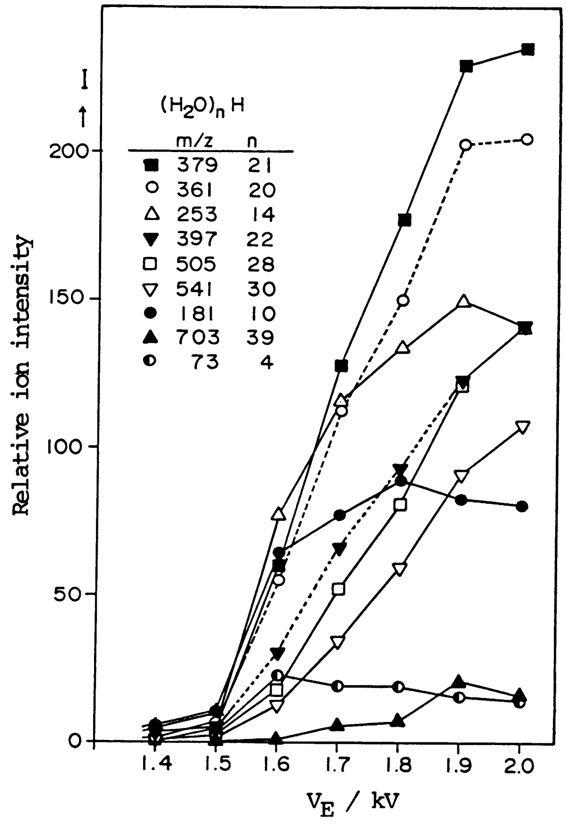

Fig. 2. Ion currents - voltage (V_E) curves for main cluster ions of water.

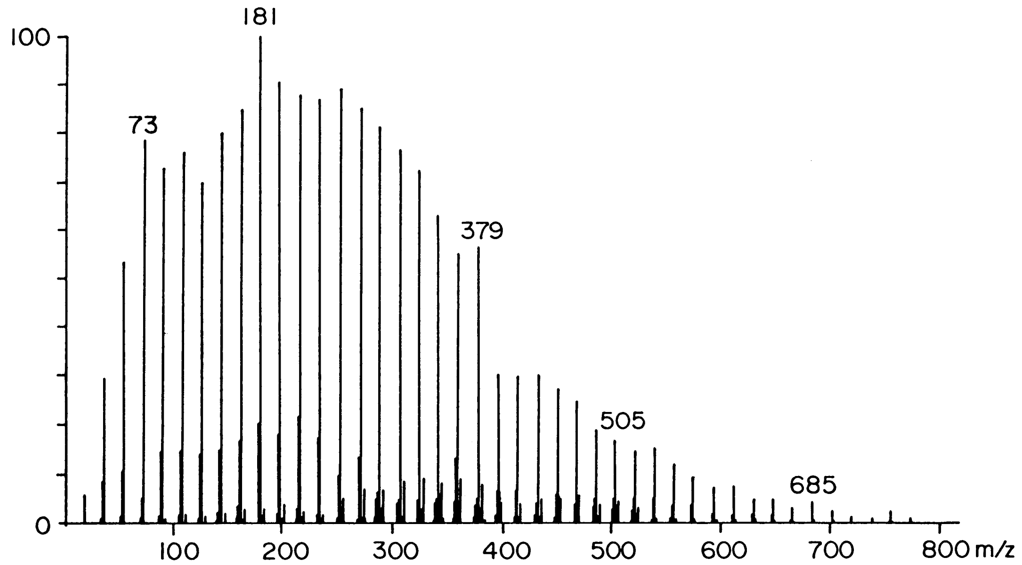

Fig. 3. Cluster ion distribution of water at needle temperature of 90 °C.

The results indicate that cluster ion distributions depend on the electric field (due to V_E), temperature and position of the needle tip. Low vapor pressure of water and a narrow pinhole limit the size of the largest ion.

Three mechanisms were assumed to account for the ionization of water. Namely, (a) Penning ionization of cluster molecules, (b) field ionization of water by a high V_E, and (c) field ionization of metastable argon (Ar^*) producing Ar^+ followed by charge transfer reactions from Ar^+ to water molecules.

Ionization energy (IP) of H_2O is high (12.6 eV), but large clusters may have lower IP than the internal energy of Ar^* (11.7 eV) so that cluster ions may be partly produced by process (a). Without the corona discharge (no Ar^*), no cluster ions are observed with V_E below 2.2 kV. At $V_E = 2.34 \pm 0.07$ kV, however, the abundant cluster ions appear suddenly to give a mass spectrum similar (but larger ions are slightly more abundant) to that shown in Fig. 1. Therefore, process (b) did not contribute to the results in this paper. At V_E between 1.3 – 1.6 kV (Fig.2), the currents (I) of small ions increase sharply with V_E. The slope (m) of the log I versus log V_E curve was about 5 or 6 using a sharp needle. Similar current-voltage characteristics such as $I - V^m$ have been observed by field ionization (in vacuum) for He (m : 30), heptane (m : 16) and so on.[12] Such characteristics and the IP of Ar^* (4.0 eV) indicate that ionization of Ar^* occurs to produce Ar^+ ions and then charge transfer reactions result in cluster ions, that is, process (c) may be responsible for ion formation, especially at lower V_E. The contribution of process (a) has not yet been estimated, but it would be understood from IPs of water clusters measured by utilizing process (b) (i.e., field ionization at atmospheric pressure).

Three processes were also assumed to account for cluster ion formations. Namely, (d) cluster ions are directly produced at the surface of liquid water condensed on the needle tip, (e) cluster ions are produced by ion-molecule reactions between H_2O^+ ion and water molecules in the gas phase at atmospheric pressure, and (f) condensation of cluster ions occurs in a vacuum just outside of the pinhole by a supersonic jet expansion of water vapor in argon.

The process (f) is a typical technique for producing a cluster beam in a vacuum. However, process (f) and also process (e) is unlikely to be responsible for the cluster ion formation, because it is impossible to explain the significant effects of V_E and temperature (Figs. 2 and 3) and the effect of position of the needle tip. If the needle tip was moved toward out of the right position, the cluster ion distribution shifted to smaller n, resulting in a mass spectrum similar to Fig.3. Larger cluster ions would be produced at positions closer to the tip surface. Figure 2 indicates that a higher V_E is required to detect larger cluster ions. This is reasonable for process (d), because a higher V_E provides a higher electric field to capture electrons emitted from large clusters through a thicker layer of water and to promote desorption of larger ions from the surface of liquid water. These functions of the needle with high V_E are very important to detect ions produced by Ar^* in the LI method.

Condensation of water on the neele tip has been observed even in a vacuum.13) Therefore, water vapor in atmospheric Ar must condense easily on any surfaces in the ion source. Thus these results strongly suggest that the ionization occurs by process (c) (and (a)) at the surface of liquid water condensed on the needle tip (process (d)). Further clustering or dissociation of ions produced on the needle tip may occur and are still being studied. Observation about the intense peaks at m/z 379 and 505 with small maximums such as at m/z 451 is consistent with observations by other methods. In conclusion, the method is useful for obtaining information about cluster ions and the liquid surface where a variety of cluster molecules of different sizes may move around.

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