Formation of the distribution of cluster ions in a molecular beam

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Measurements of the energy distribution of water cluster ions in a molecular beam show that the distributions of ions with "magic numbers" of molecules which have been reported previously are formed during the disintegration of metastable cluster ions.

The nonmonotonic size distribution of the microscopic droplets of atomic dimensions—clusters—which are formed during the adiabatic expansion of xenon in a supersonic flow, were first studied in detail by Echt *et al.*[1] in 1981. A molecular beam obtained from a supersonic flow was ionized by electron impact; the distribution of the resulting cluster ions in the atoms was measured by a mass spectrometer. Estimates show that the numbers of atoms in a cluster (the so-called "magic numbers") which correspond to the local maxima of the measured distribution function coincide with the numbers which would be required to fill stable spherical shells in a neutral cluster. The independence of the magic numbers from the energy of the ionizing electrons was taken as experimental confirmation that the ionization of neutral clusters is not accompanied by changes in the size distribution.[1] This explanation of the experimental results forces a reexamination of the macroscopic model for the nucleation of a new phase in the classical theory of first-order phase transitions, which otherwise gives a good description of all experimental data.

There is also some question regarding the validity of interpreting the observed distributions as structural features of neutral molecular clusters. In the first place, not all of the magic numbers which have been predicted have been observed experimentally, and some "extra" numbers have been observed.[2] Second, experiments on the scattering of cluster molecular argon beams have demonstrated a significant fragmentation of neutral clusters during electron impact.[3] The fraction of clusters that dissociate depends only very weakly on the energy of the ionizing electrons, so that the independence of the magic numbers from the electron energy is not evidence that the neutral clusters survive the ionization. Clearly, the most direct experiment would be to measure the time evolution of the size distribution of the clusters after ionization. However, since it has been shown experimentally[4] and theoretically[5] that small clusters of inert gases with more than one elementary charge break up very rapidly, in a time on the order of 10^{-10} s, because of the Coulomb repulsion of like charges, it has been assumed that the dissociation of excited ion clusters cannot be observed.[5] It has recently been observed,[6] however, that the distribution function of the cluster ions, which form during the ion bombardment of a crystal surface, is a smooth distribution when

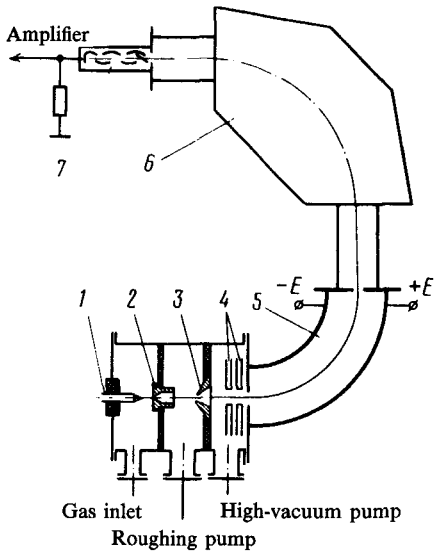

FIG. 1.The experimental arrangement. Nozzle 2 is a conical nozzle with a geometric Mach number of 4 and with a throat diameter of 0.6 mm. The ion acceleration distance (the distance between diaphragm 3 and accelerating electrode 4) is $L = 4$ cm.

the measurements are taken 0.2×10^{-6} s after the formation of the ions, and it has characteristic magic numbers when measurements are taken after 70×10^{-6} s.

In the present experiments we observed the disintegration of clusters and measured the energy distribution and relaxation time of the size distribution in a molecular beam of ion clusters of water formed during condensation on ions in a supersonic flow. The experimental arrangement is shown in Fig. 1. The ions are formed in a coronal discharge near a sharp point 1 in air at atmospheric pressure. The water vapor density corresponds to the saturation level at room temperature; the discharge current is 5 μA. The condensation on the ions occurs in a supersonic flow of air cooled adiabatically during expansion through nozzle 2 into the first vacuum chamber. The cluster ion beam is transported through a conical diaphragm 3 into a high-vacuum region. A potential difference $U_0 = 2.5$ kV is applied between this diaphragm and accelerating electrode 4. The beam is focused onto the entrance slit of an electrostatic analyzer 5, which is a cylindrical capacitor. By varying the potential difference (E) between the plates of this capacitor, we can deflect to the exit slit beam ions differing in mass but having the same energy, determined by E. If an ion cluster decays over the acceleration distance $L = 4$ cm, the energy of the daughter ions will be smaller than eU_0. The mass spectrum of the clusters of a given energy is measured beyond sector magnetic analyzer 6. The ion current is measured by a multiplier 7. This experimental arrangement differs from all others which have been used to study ion clustering[1-4,6] in that it allows independent measurements of the energy and the mass, so that the origin of an ion can be determined.

Figure 2 shows the intensities of lines in the mass spectrum of water cluster ions, $H^+(H_2O)_n$, versus n for ions with various energies: 2500 V (●), 2480 V (◑), and 2450 V (◐). The energy width of the analyzer window, $\epsilon = 20$ V, is measured when the ions are accelerated with respect to the supersonic flow by a potential difference $\Delta U > 100$ V between nozzle 2 and diaphragm 3, and the formation of ion clusters becomes

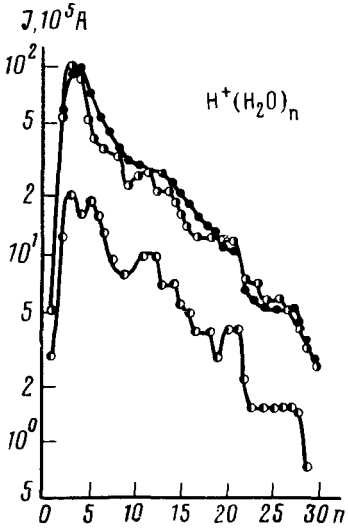

FIG. 2. Intensities of lines in the mass spectrum of $H^+(H_2O)$ ions versus n for several ion energies: ●—2500 eV; ◑—2480 eV; ◐—2450 eV.

impossible. We see that as the fraction of daughter ions is increased, a distribution with the magic numbers $n^* = 3, 5, 11, 13, 17, 21$ is formed; i.e., the numbers are the same as those which are ordinarily observed during the ionization of neutral clusters.

Figure 3 shows energy distributions of the $H^+(H_2O)_n$ ions for $n = 1$–5. Nearly all the ions with $n = 1$ and 2 form during the disintegration of larger clusters. The ions with $n \geqslant 5$ are mother ions; i.e., the probability for the decay

$$H^{Z+}(H_2O)_N \rightarrow H^{(Z-1)+}(H_2O)_{N-n} + H^+(H_2O)_n, \quad (1)$$

where Z is the charge of the primary cluster, decreases rapidly with increasing n. The maxima of the distributions at energies above the width of the window of the energy analyzer are related to the formation of a given ion during the disintegration of pri-

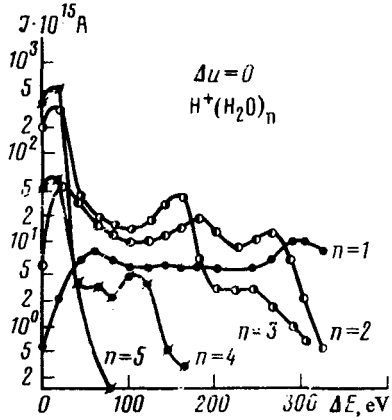

FIG. 3. Intensities of lines in the mass spectrum of $H^+(H_2O)_n$ ions, for $n = 1$–5, versus the difference (ΔE) between the energy to which the energy analyzer is tuned and the accelerating potential $U_0 = 2500$ V. The potential difference between nozzle 2 and diaphragm 3 (Fig. 1) is $\Delta U = 0$.

mary ions with $Z = 1, 2, \ldots$; with increasing Z, the maximum on each curve shifts down the energy scale. Assuming that the decrease in the density (ρ_N^{Z+}) of ions of size N over the acceleration distance is described by

$$\rho_N^{Z+} = \rho_{0N}^{Z+} \sum_{n}^{n} \exp(-t/\tau_{n,Z}), \tag{2}$$

where $\tau_{n,Z}$ is the scale time for disintegration by process (1), we can use the energy dependence in Fig. 3 to calculate $\tau_{n,Z}$. For $n = 1$, for example, we can use (2) to write an expression for the energy dependence of the intensity of the line corresponding to the ion $H^+(H_2O)$:

$$J(\Delta E) = \rho_{01}\exp(-\Delta E/\epsilon) + \sum_{N,Z}\left[1 - \exp\left(-\sqrt{\frac{2mNL^2\Delta E}{Ze^2U_0^2\tau_{1,Z}^2}}\right)\right]\sqrt{\frac{2(eU_0 - \Delta E)}{m}}, \tag{3}$$

where m is the mass of a water molecule. From the experimental results we have $\rho_{01} \ll \Sigma\rho_{0N}$. Taking $\bar{N} = 50$ as an estimate, we find the maxima of expression (3); comparing with the measured values of ΔE (Fig. 3), we find $\tau_{1,1} = 2\times10^{-6}$ s for the disintegration of singly charged ions,

$$H^+(H_2O)_{\bar{N}} \rightarrow (H_2O)_{\bar{N}-1} + H^+(H_2O) \tag{4}$$

and we find $\tau_{1,2} = 0.6\times10^{-6}$ s for the disintegration of doubly charged ions,

$$H^{2+}(H_2O)_{\bar{N}} \rightarrow H^+(H_2O)_{\bar{N}-1} + H^+(H_2O)\ . \tag{5}$$

From Fig. 3 we see that the disintegration times $\tau_{n,Z}$ decrease with increasing n and Z; i.e., the distribution of water cluster ions forms as a result of the disintegration of excited ion clusters in a time of about 2×10^{-6} s [according to the slowest process, (4)]. The disintegration occurs through the evaporation of $H^+(H_2O)_n$ ions from the original clusters. The binding energy of the $H^+(H_2O)$ ion in a singly charged cluster is estimated from the Frenkel' formula and the measured disintegration time to be about 0.25 eV, and the observed decrease in the lifetime of the multiply charged clusters is attributed to a decrease in the ion binding energy due to the Coulomb repulsion of like charges.

In summary, the distributions with magic numbers that are observed in experiments of this sort are formed during the disintegration of ion clusters with a large internal energy. These distributions do not depend on the mechanism for the formation or excitation of these clusters, and they do not characterize the distribution of neutral clusters that are formed during spontaneous condensation, before they are ionized in one way or another.

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