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Comment on "Clustering of Water on Hydrated Protons in a Supersonic Free Jet Expansion"

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COMMENTS

Comment on "Clustering of water on hydrated protons in a supersonic free jet expansion"

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Recently Searcy and Fenn[1] reported results of a molecular beam experiment, evidencing the nature of clustering of water molecules on positive ions. The clusters were assumed to be $H^+(H_2O)_n$. Ions were produced by corona in an environment saturated with water vapor, the ions were subjected to a free jet expansion wherein the ions experienced a state of supersaturation, and finally the resulting cluster-ion beam was mass analyzed with a quadrupole mass filter for the size range $1 \leq n \leq 29$. One of the more interesting results was a rather remarkable peak at a mass corresponding to 21 molecules.

Another experiment bearing on the same problem was made by Lin.[2] His experiment examined a free jet expansion of water vapor whereupon a beam of neutral water clusters was formed. The neutral clusters were subsequently ionized with a low energy electron beam upon entrance into a quadrupole mass filter operating at an unusually low frequency so that large masses could be observed. Lin also observed a striking anomaly at a mass corresponding to 21 water molecules. Searcy and Fenn speculated that the peak they observed and the anomaly Lin observed was indicative of a cluster exhibiting pronounced stability. Such a cluster might be attributed to the formation of a clathrate cage structure: a pentagonal dodecahedron with a water molecule at each corner and a single water molecule at the center.

We would like to comment on several aspects of these two papers and on some correlations between them. First, we would like to point out that the increased stability of the 21 molecule cluster based on the clathrate structure has been predicted by a molecular cluster theory. During the past six years a molecular model for water clustering associated with the nucleation process has evolved in this laboratory.[3–11] The model emphasizes the tetrahedral coordination of the hydrogen bonding between water molecules which leads to the pentagonal dodecahedron being a basic building block for small clusters of water molecules. The energy of formation for various sized clusters shows distinct minima at those sizes corresponding to closed cage structures, e.g., 20, 35, 47, ... molecules for clusters whose cages are unoccupied and 21, 37, 50, ... molecules for clusters all of whose cages are occupied with either a neutral molecule or an H_3O^+ ion. These numbers bear some similarity to the *magic numbers* associated with the structure of nuclei.

Until now we have not attempted to attach too much significance to the minima in the free energy associated with such magic numbers, because we felt that when the configurational entropy was properly handled, it would have a significant smoothing tendency,[9] and to some extent this is true. Sporadic bond breaking and making is undoubtedly more important in larger clusters and probably inhibits observation of the larger magic number clusters. However, it seems particularly significant to us that the experimentally observed stability of the 21 molecule cluster seems to be important evidence supporting the basic concepts used in the model for the case where the bond energy is large compared with the effective internal temperature of the cluster. We believe that Searcy and Fenn's and Lin's data provide at least one essential element of experimental verification of the molecular approach to the theory of nucleation which investigators in this Center have been developing.

A few words should be said about a major difference between Searcy and Fenn's work and that of Lin. Searcy and Fenn's data are characteristic of an equilibrium size distribution resulting from clustering on ions, i.e., a peak is reached corresponding to the minimum in the free energy of formation curve.[12] Lin's data is charac-

teristic of an equilibrium or steady state size distribution corresponding to homogeneous nucleation, i.e., the number density shows a general exponential decrease as size increases. The fact that a peak is seen at size 21 rather than at size 20 gives evidence that the filled cage structure is favored over the empty cage structure even for the case of homogeneous nucleation. It is not clear, however, that the system is representative of either the equilibrium or the steady state; another possibility is that the data represents some frozen transient state. As we have pointed out, the size 21 cluster is probably relatively stable against both growth as well as decay.[11] It could very well be a bottleneck in the kinetics associated with steady state nucleation.

We also wish to point out that the results shown in Searcy and Fenn's paper represent the cluster distributions which exist at the location of the quadrupole filter and not necessarily the distributions characteristic of the supersaturated region in the free jet. The clusters formed in the supersaturated region will possess internal vibrational energy characteristic of the gas temperature somewhere near the end of the collisional regime of the jet. These internal vibrations can interfere constructively[11] and can result in the spontaneous evaporation of water molecules from the cluster as it travels through the low pressure region between the free jet and the quadrupole filter. Clusters having one or more monomers which are only singly bonded to the rest of the cluster would be the most susceptible to this loss process. Clusters just above the 21 molecule size would be expected to fit into this category. They should quickly decay down to the more stable 21 molecule structure. The large peak at 21 represents clusters of that size formed in the supersaturated region plus larger clusters which were formed there and which might have subsequently decayed down to the 21 molecule size during their transit to the quadrupole filter.

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Reply to comment by Kassner and Hagen

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We apologize for our not being aware of some of the earlier theoretical predictions for the enhanced stability of the water cluster with 21 water molecules. In general, we agree with the statements made by Kassner and Hagen, but we would like to emphasize certain points and to point out that our data can be approximated by a simple kinetic model.[1]

The similarities between our data[2] and those of Lin[3] are greater than appearances would suggest. Both sets of data represent frozen transient states, and neither represents equilibrium. The clustering environment changes so rapidly in small supersonic nozzles that the clusters cannot possibly be in equilibrium with the ambient gas. Not even rotational degrees of freedom manage to relax as fast as translational energy.[4-6] This lack of local thermodynamic equilibrium makes it dangerous to draw parallels between the shape of the cluster distributions and theories of nucleation that assume local thermodynamic equilibrium. However, we doubt that there is any evaporation loss for these clusters after leaving the free jet. The time spent in free flight for a particular cluster is less than the time spent in the free jet. Calculations reported previously[1] indicate no decay of a smaller cluster in the equilibrium distribution during the expansion, and the decay rate for larger clusters should be even slower. These things considered, we think the cluster distributions observed by the quadrupole are truly representative of those at the terminal mach number position in the free jet.

Our data appear to be characteristic of equilibrium distributions simply because a limited number of clus-

