

Theoretical Prediction of Ion Clusters Relevant to the Atmosphere: Size and Mobility

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ABSTRACT

The clustering of water vapor about ions is important because of its relevance to atmospheric electrical processes. For this reason we have placed our emphasis particularly on the description of the size distribution (concentrations) and mobilities of the small ion clusters at various humidities. From our present theoretical study, we find that most of the hydronium ions H_3O^+ tend to associate with a small number of water molecules to form a hydrated ion cluster even at extremely low humidities in the range of 5×10^{-3} to 1%. At atmospherically more realistic humidities and at the room temperature, our computed number of water molecules in the hydrated ion clusters is predicted to be relatively small. It is then conjectured that ion-induced nucleation process (if it occurs) starts rather from the small hydrated ion clusters which initially existed even at extremely low humidities in the atmosphere. In addition, we also find that, in general, the hydrated ion clusters of small sizes corresponding to the mass range of 2–5 water molecules are responsible for the ion mobility range of $2\text{--}2.5 \text{ cm}^2 (\text{V s})^{-1}$. For reduced mobility below $2.0 \text{ cm}^2 (\text{V s})^{-1}$, the mass of the hydrated ion cluster is predicted to be greater than that of approximately five water molecules. The simultaneous estimation of size distribution and mobility aids us in better understanding observed mobility spectra and the nature of atmospherically important prenucleation clusters, including the information of their electric conductivities in the atmosphere.

1. Introduction

Ions are produced continually in the lower atmosphere as the result of ionization which occurs along the trajectory of high-energy cosmic rays and due to radioactivity (Israël, 1971; Chalmers, 1967). The life history of these ions prior to their ultimate recombination establishes the nature of the ion distribution at any point in time. This distribution has an important bearing on a number of atmospheric electrical processes.

The mass, polarizability, and molecular structure of an ion define its ability to drift in an electric field. This is characterized by mobility. The size distributions of the ions determine the rate at which the ions diffuse. This regulates rates of recombination, attachment to aerosols, and the electrical conductivity of the atmosphere. The ions participate in ion-molecule reactions and ion-induced nucleation (Castleman, 1979; Chan and Mohnen, 1980).

The most elementary of all pervasive processes through which ions grow involves the clustering of water molecules about the parent ion. This is not only one of the easiest processes to study experi-

mentally but it is also one of the most tractable processes to describe theoretically. It seems to be an important place to attempt a detailed theoretical explanation of the observed data in order to demonstrate the viability of molecular approaches in describing the properties of clusters.

Two fundamental problems arise particularly for molecular clusters. The first results from inadequacies in the usual ion mobility theory, by which the ion cluster is depicted as a polarizable charged sphere without internal degrees of freedom so that only elastic collisions are allowed. How well such a model represents reality is not known for the ion clusters. The second arises from difficulties in providing a consistent method of calculating the size distribution of the ion cluster. This paper addresses itself specifically to the latter problem.

In Section 2, we shall employ a statistical mechanical treatment of the hydrated ion clusters in order to determine the size distribution of the hydronium hydrate cluster $H^+(H_2O)_i$. The intermolecular interaction potential between the ion hydrate and the colliding gas molecule (or atom) is formulated for the ion mobility calculation. In Section 3 computed results using the theoretical method presented in Section 2 is given. The results are compared with the ion mobility measurements of others. In particular, the assignment of the hydrated ion cluster size to the ion mobility spectra will be discussed in detail. In addition, a description of the prenucleation proc-

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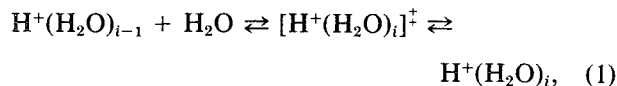
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ess will be presented in association with the size distribution.

The simultaneous estimation of the ion mobility and concentration is useful for the analysis of experimental mobility spectra. It is shown that atmospheric ion mobility spectra in the range of 2.0–2.5 cm² (V s)⁻¹ corresponds to small ion clusters whose masses are approximately equivalent to 2–5 water molecules. For mobility below 2.0 cm² (V s)⁻¹, the size of the hydrated ion cluster is predicted to be greater than approximately five water molecules.

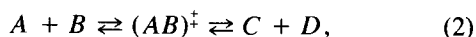
2. Theory: Statistical mechanical description of hydrated ion clusters and ion mobilities

The hydrated ions we consider here are assumed to consist of a parent ion which carries an elementary charge *e* surrounded by water molecules. The bimolecular association (forward process) and dissociation (reverse process) reaction is represented as



with *i* = 2, 3,

The first product hydronium ion is most likely to be left in an activated state. The activated cluster [H⁺(H₂O)_{*i*}][‡] is then subject to the reverse process (unimolecular decay) unless the gas pressure in the system is high enough to allow third-body collisions. Third-body collisions are necessary to remove the excess energy of the activated complex (cluster) to allow it to reach a thermally equilibrated state. On the other hand, at lower pressures, these clusters are subject to the general group exchange reaction of the type



where (AB)[‡] is the activated complex. In the domain of atmospheric interest, reactions of the type (1) are expected to be valid.

Thus, based on the reaction processes given in (1), the law of mass action is written

$$\frac{N_i}{N_{i-1}N_1} = \frac{q_i}{q_{i-1}q_1}, \quad (3)$$

where *N_i* and *q_i* are respectively the number and partition function of the *i* cluster, and *i* here refers to the total number of the water molecules in the cluster. We now rewrite expression (3) in the form

$$N_i = (N_{i-1}N_1/q_{i-1}q_1)q_i^0 \exp(-\Delta E_{i-1,i}/kT), \quad (4)$$

where

$$q_i^0 = q_i \exp(+\Delta E_{i-1,i}/kT) \quad (5)$$

and Δ*E_{i-1,i}* is the difference in binding energy between the *i* cluster and (*i* - 1) cluster, or stated differently, the binding energy added to the *i* cluster

due to the addition of another water molecule to the (*i* - 1) cluster.

Successive substitutions using (4) will yield

$$N_i = (N_0/q_0)(N_1/q_1)^i q_i^0 \exp(-\sum_j \Delta E_{j-1,j}/kT), \quad (6)$$

or

$$N_i = (N_0/q_0)(N_1/q_1)^i q_i^0 \exp(-\Delta E_{0,i}/kT). \quad (7)$$

Here Δ*E_{0,i}* is the total binding energy of the *i* cluster given by

$$\Delta E_{0,i} = \sum_{j=1}^i E_{j-1,j}. \quad (8)$$

Now we rewrite Eq. (7)

$$N_i = (N_0/q_0)N_1 \exp[-\Delta E_{0,i}/kT + \ln q_i^0 - i \ln q_1 + (i - 1) \ln N_1]. \quad (9)$$

If we divide both sides by the volume *V*, we obtain the number concentration or size distribution of the *i* cluster:

$$C_i \equiv N_i V^{-1} = (N_0/q_0)C_1 \exp[-\Delta E_{0,i}/kT + \ln q_i^0 - i \ln q_1 + (i - 1) \ln N_1]. \quad (10)$$

The total concentration of all the ion clusters is

$$C = \sum_j C_j = (N_0/q_0)C_1 \sum_j \exp[-\Delta E_{0,j}/kT + \ln q_j^0 - j \ln q_1 + (j - 1) \ln N_1]. \quad (11)$$

Now, the fraction of the number concentration *C_i* is written

$$f_i = C_i/C = (1/C') \exp[-\Delta E_{0,i}/kT + \ln q_i^0 - i \ln q_1 + (i - 1) \ln N_1], \quad (12)$$

$$C' = \sum_j \exp[-\Delta E_{0,j}/kT + \ln q_j^0 - j \ln q_1 + (j - 1) \ln N_1]. \quad (13)$$

The (relative) concentration ratio of the *i* cluster to the *j* cluster is then given by

$$\gamma_{i,j} \equiv f_i/f_j = \exp[-(\Delta E_{0,i} - \Delta E_{0,j})/kT + \ln(q_i^0/q_j^0) - (i - j) \ln q_1 + (i - j) \ln N_1]. \quad (14)$$

A more elaborate form of *C_i* in Eq. (10) is

$$C_i = (N_0/q_0)C_1 \exp\{-\Delta E_{0,i}/kT - \ln[(q_i^0/q_1^i)/q_i^0] - (i - 1) \ln S - (i - 1) \ln C_1^0\}, \quad (15)$$

in which

$$q_i^i = q_i^t q_i^r q_i^v, \quad (16)$$

$$q_i^{t'} = q_i^t V^{-1}. \quad (17)$$

Here *q_i^t* is the translational partition function, *q_i^r* the rotational partition function, and *q_i^v* the vibrational partition function of the *i* cluster. Other symbol definitions are as follows: *S* is the saturation ratio

and C_1^0 is the equilibrium concentration at the saturation ratio of $S = 1$. M_i is the mass of the i cluster given by

$$M_i = im + m_0, \quad (18)$$

where m is the mass of the water molecule m_0 that of the parent ion, k is the Boltzmann constant, and T is the absolute temperature.

The rearrangement of Eq. (15) yields

$$C_i = (N_0/q_0) \exp(-\Delta\phi_{0,i}/kT), \quad (19)$$

where

$$\Delta\phi_{0,i}/kT = \Delta E_{0,i}/kT + \ln(q_1^i)/q_1^i - i \ln S - i \ln C_1^0. \quad (20)$$

For large values of i , we obtain the energy of formation in dimensionless form,

$$\Delta\phi_{0,i}/kT \approx \Delta E_{0,i}/kT + (i-1) \ln q_1^i/q_1^i - i \ln S - i \ln C_1^0. \quad (21)$$

If we assume that the intramolecular vibrational frequencies remain constant with the cluster size i , we can write an explicit expression of the energy of formation,

$$\begin{aligned} \Delta\phi_{0,i} &= \Delta E_{0,i} + kT \ln \{ (M_i^i/M_i)^{3/2} [64\pi^5 (kT)^4 / h^6]^{i-1} \\ &\times [(I_i^a I_i^b I_i^c) / I_i^a I_i^b I_i^c]^{1/2} (\eta_i / \eta_i^i) \\ &\div \prod_{j=1}^{6(i-1)} [2 \sinh(h\nu_j^{\text{inter}}/2kT)]^{-1} \} - i \ln S - i \ln C_1^0, \quad (22) \end{aligned}$$

where I_i^α is the α th ($\alpha = a, b$ and c) component of the principal moment of inertia of the i cluster, η_i is the symmetry number, ν_j^{inter} is the intermolecular vibrational frequency and h , the Planck constant.

Now the intermolecular interaction potential between the i -hydrated ion cluster and the non-polar gas molecule or atom is given by

$$V = V_{H_2O,A} + V_{L,A}, \quad (23)$$

where the first term is the total interaction between the water molecules in the cluster and the gas phase molecule or atom A (Hagen *et al.*, 1975), i.e.,

$$V_{H_2O,A}(R) = \sum_{j=1}^i \{ 4\epsilon_a [(\sigma_a/x_j)^{12} - (\sigma_a/x_j)^6] - \alpha_A \mu_{H_2O}^2 / x_j^6 \}, \quad (24)$$

and the second term is the interaction between the center ion and the gas molecule or atom,

$$V_{L,A}(R) = 4\epsilon_b [(\sigma_b/R)^{12} - (\sigma_b/R)^6] - e\alpha_{H_2O}/2R^4 - \alpha_A \mu_1^2 / R^6, \quad (25)$$

where

$$\mathbf{x}_j = \mathbf{R} + \mathbf{r}_j, \quad (26)$$

with \mathbf{r}_j being the displacement vector between the

center of the i cluster and water molecule j , and \mathbf{R} the displacement vector between the i cluster and gas molecule or atom. ϵ and σ are the Lennard-Jone parameters (Hirschfelder *et al.*, 1954), and μ_{H_2O} and μ_A are the dipole moments of the water molecule and the gas molecule or atom, respectively. α_{H_2O} and α_A are the electric polarizabilities of the water molecule and the gas molecule or atom A.

For mathematical convenience, we write the first term of (23) in the form

$$V_{H_2O,A}(\mathbf{R}) = \int_a^{r_0} \left\{ 4\epsilon_a \rho \left[\left(\frac{\sigma_a}{|\mathbf{R} + \mathbf{r}|} \right)^{12} - \left(\frac{\sigma_a}{|\mathbf{R} + \mathbf{r}|} \right)^6 \right] - \frac{\alpha_A \mu_{H_2O}^2}{|\mathbf{R} + \mathbf{r}|^6} \right\} d\tau, \quad (27)$$

where ρ is the density of the i cluster, and r_0 and a are the effective radii of the i -hydrated ion cluster and ion by itself, respectively. $d\tau$ is the volume element. The choice of the spherical coordinates for the integration yields

$$\begin{aligned} V_{H_2O,A}(R) &= \frac{4}{5} \pi \epsilon_a \sigma_a^{12} \rho \left[\frac{1}{9} \left(\frac{1}{R_+^9} - \frac{1}{R_-^9} \right) - \frac{1}{8R} \left(\frac{1}{R_-^8} - \frac{1}{R_+^8} \right) \right] \\ &- (2\pi \epsilon_a \sigma_a^6 \rho + \alpha_A \mu_{H_2O}^2) \\ &\times \left[\frac{1}{3} \left(\frac{1}{R_-^3} - \frac{1}{R_+^3} \right) - \frac{1}{2R} \left(\frac{1}{R_-^2} - \frac{1}{R_+^2} \right) \right], \quad (28) \end{aligned}$$

where

$$R_+ = R + (r_0 - a), \quad (29)$$

$$R_- = R - (r_0 - a). \quad (30)$$

The ion mobility (McDaniel and Mason, 1973, pp. 139-140; Mason and Schamp, 1958) at low electric fields is given by

$$K = \frac{3e}{16} \left(\frac{1}{M_i} + \frac{1}{M_A} \right)^{1/2} \left(\frac{2\pi}{kT} \right)^{1/2} (N\Omega)^{-1}, \quad (31)$$

in first approximation. Here M_i and M_A are the masses of the i cluster and the gas molecule or atom A, respectively, N is the number density of the neutral gas. The collision integral Ω is given by

$$\Omega(T) = [2(kT)^3]^{-1} \int_0^\infty e^{-E/kT} E^2 Q(E) dE, \quad (32)$$

where the cross section $Q(E)$ is

$$Q(E) = 2\pi \int_0^\pi [1 - \cos\theta(b, E)] b db, \quad (33)$$

with the deflection angle given by

$$\theta(b, E) = \pi - 2b \int_{R_0}^\infty \frac{R^{-2} dR}{[1 - b^2/R^2 - V(R)/E]^{1/2}}. \quad (34)$$

Here E is the initial relative kinetic energy, b is the impact parameter, and R_0 is the distance of the closest approach between the i cluster and the gas molecule or atom. Finally, $V(R)$ is the intermolecular interaction potential described in Eqs. (23)–(25).

Now let us turn to the relevance of our present analysis [referring to Eqs. (23) through (34) above] of the hydronium ion hydrates in argon to the problem of ion mobility in the atmosphere. The electric polarizability and ionization potential are the basic physical properties which are used to characterize the long-range intermolecular interaction between ions (hydrated or not) and neutral non-polar molecules or atoms such as the argon, namely the induction and dispersion forces. At thermal energies ($\sim kT$), the collision cross sections are largely determined by the long-range part of the intermolecular force (Levine and Bernstein, 1974). We list below the values of the polarizability (McDaniel and Mason, 1973, pp. 344–345) and ionization potentials (Herzberg, 1950) of the buffer gas molecules N_2 and atom Ar: $\alpha_{Ar} = 1.64 \text{ \AA}^3$, $\alpha_{N_2} = 1.76 \text{ \AA}^3$, $I_{Ar} = 15.755 \text{ eV}$, and $I_{N_2} = 15.576 \text{ eV}$. Note the remarkable similarities between the two buffer gases. Thus, if we examine the long-range part of the intermolecular interaction force between the hydrated ion cluster $H^+(H_2O)_i$ and the buffer gas molecule, and compare this with that for the same hydrated ion cluster and the buffer gas, N_2 , they should be about the same if Ar is to be considered a reasonable buffer gas to use in experiments which are to represent the atmosphere. Thus, if both the long-range interaction potential and the reduced masses for the systems are close in values, the measured mobilities for the same ion in the two buffer gases should be nearly equal. We find the reduced masses of the two systems to be remarkably close

$$\mu_{H_3O^+, Ar} = \frac{M_{H_3O^+} M_{Ar}}{M_{H_3O^+} + M_{Ar}} \approx 0.09, \quad (35)$$

$$\mu_{H_3O^+, N_2} = \frac{M_{H_3O^+} M_{N_2}}{M_{H_3O^+} + M_{N_2}} \approx 0.08. \quad (36)$$

This finding is significant in that laboratory ion mobility measurements in argon gas can be used to simulate the atmospheric air.

However, for the sake of a numerical comparison with the analysis of reduced mobilities K_0 measured by Young *et al.* (1970), in the next section, we write the expression of the reduced mobility for the hydronium ion hydrates in argon,

$$K_0 = 35.9(\alpha\mu)^{-1/2} [\text{cm}^2 (\text{V s})^{-1}]. \quad (37)$$

This is the same equation that Young *et al.* used. This expression comes from the Langevin formula in the polarization limits (McDaniel, 1964) taking the polarizability of argon to be 1.64 \AA^3 . α is the

polarizability of the neutral gas in atomic units and μ is the ion-neutral reduced mass in atomic mass units.

3. Computed results and discussions

Recently, the reduced mobilities (between ~ 0.4 and $\sim 1.1 \text{ cm}^2 (\text{V s})^{-1}$) of the positive and negative ions of heavy (large) particles have been measured as a function of the saturated vapor temperatures by Henson (1978). In this present paper, we limit ourselves to the study of both relative size distributions (concentration ratio corresponding to the size of the hydrated ion cluster) and ion mobilities at various humidities below saturation. The computed values of the relative size distribution will be used to interpret the ion mobilities of the hydronium ion hydrate $H^+(H_2O)_i$ measured by Young *et al.* (1970).

We used Eq. (14) to estimate the relative size distribution. The evaluation of the total electronic binding energy $\Delta E_{0,i}$ was deduced from the use of the experimental enthalpies of Kerbarle *et al.* (1967). For simplicity, we used $I = 2/5\text{ima}^2$ with the radius of $a = 1.926 \text{ \AA}$ for the evaluation of the rotational part of the partition function (the choice of $a = 1.926 \text{ \AA}$ agrees with that of Abraham (1974) for 100 water molecules, that is, $kT \ln q'_{100} = 20.8kT$). The intermolecular vibrational frequencies of $H^+(H_2O)_i$ are not available in literature. For this reason we used the values of the six intermolecular vibrational frequencies available in the literature for $(H_2O)_2$. These frequencies are from the ab initio molecular orbital calculation of Curtiss and Pople (1975): They are 1) 536 cm^{-1} , 2) 452 cm^{-1} , 3) 204 cm^{-1} , 4) 185 cm^{-1} , 5) 118 cm^{-1} and 6) 81 cm^{-1} . For the water dimer, these results are in good agreement with other values including part of our frequency calculations (Suck *et al.*, 1979). For both $H^+(H_2O)_i$ and $(H_2O)_i$, the number of intermolecular vibrational frequencies increases by 6 with each additional water molecule. In reality, the intermolecular vibrational frequencies for $H^+(H_2O)_i$ are not the same as (expected to be higher than) those for $(H_2O)_i$. For this reason, we made several computer experiments with the choice of various sets of the vibrational frequencies in the range of $100\text{--}1000 \text{ cm}^{-1}$ to test the validity of our treatment. However, we find that the following discussions remain qualitatively unchanged.

We show the computed values of the relative size distributions (concentration ratios) in Table 1. Here the concentration ratios are scaled relative to the peak concentration at each partial vapor pressure and at the room temperature of 297 K. Note that the size of the ion cluster is predicted to generally increase with the pressure; at the lowest pressure of $4.0 \times 10^{-4} \text{ Torr}$ (0.5 ppm), the modal (peak) value is found at $i = 2$, i.e., the $H^+(H_2O)_2$ cluster. At the highest pressure of 16 Torr (21 000 ppm) shown in

TABLE 1. Computed concentration ratio σ at various pressures and at the temperature of 297 K (peak value is set as 1. Blanks are used for the small values of σ).

| H ₂ O ppm (Torr) | Concentration ratio σ for each size i | | | | | | | |
|--------------------------------|--|---------|---------|---------|---------|---------|---------|---------|
| | $i = 1$ | $i = 2$ | $i = 3$ | $i = 4$ | $i = 5$ | $i = 6$ | $i = 7$ | $i = 8$ |
| 0.5 (0.0004) | | 1 | 0.41 | | | | | |
| 1.5 (0.0011) | | 0.32 | 1 | | | | | |
| 2 (0.0015) | | 0.17 | 1 | | | | | |
| 160 (0.12) | | | 0.36 | 1 | 0.13 | | | |
| 300 (0.23) | | | 0.16 | 1 | 0.79 | | | |
| 1300 (1) | | | | 0.11 | 1 | 0.15 | | |
| 3500 (2.7) | | | | | 0.94 | 1 | 0.11 | |
| 7000 (5.3) | | | | | 0.24 | 1 | 0.41 | |
| 13 000 (10) | | | | | | 0.68 | 1 | 0.34 |
| 21 000 (16) | | | | | | 0.27 | 1 | 0.32 |

the table, the maximum concentration shifted toward $i = 7$, or $H^+(H_2O)_7$. It is interesting to note that the ion cluster size distribution is rather narrow at all the pressures. Such narrow size distributions have been observed from the mass spectroscopic measurements of $Pb^+(H_2O)_i$ by Castlemen and Tang (1972). Also in their study, they have found that as the humidity increased the modal position shifted toward larger sizes, still maintaining the very narrow width of the distribution. Our statistical mechanical method is expected to be superior to the classical theory of nucleation for the description of the clusters of molecular dimension where the definition of the surface term becomes meaningless.

Young *et al.* (1970) noted that their experimental ion currents agree qualitatively with calculations based on the equilibrium data of Kebarle *et al.* (1967) in that all ions except $H^+(H_2O)_3$ and $H^+(H_2O)_4$ constitute a negligible fraction of the observed current, for instance, at 0.4% water in argon at 3 Torr pressure. However, as they pointed out the measurement of Young *et al.* using drift tube techniques (Young *et al.*, 1970) showed a substantial disagreement with the thermodynamic equilibrium data of Kebarle *et*

al. in the ratios of $H^+(H_2O)_4$ to $H^+(H_2O)_3$. Our computed results of the ion concentrations are highly sensitive to the experimental accuracies of enthalpies or binding energies and to the estimations of normal vibrational frequencies. For instance, it is noted that the experimental enthalpies of DePaz *et al.* (1969, 1970) for the formation of $H^+(H_2O)_i$ do not precisely agree with those of Kebarle *et al.* (1967). Thus our statistical mechanical estimations should be considered to be of qualitative importance. Despite some uncertainties, particularly in the estimation of intermolecular vibrational frequencies, our computed ion concentrations agree qualitatively well with the thermodynamic equilibrium data of Kebarle *et al.* (1967) in the following sense: 1) The narrow range (three or four different sizes) of the ion cluster size in distribution is found at each water partial pressure; 2) gradual shifts to larger size distributions with the increase of water partial pressure is predicted; and 3) a similar continuous change in the size distribution with nearly equal cluster sizes at each water partial pressure is predicted, i.e., at water partial pressures between 1 and 10 Torrs, the measured range of $H^+(H_2O)_i$ clusters at 300 K is between

TABLE 2. Comparison with computed reduced mobility.

| Size i | Measured reduced mobility* [cm ² (V s) ⁻¹] | Computed reduced mobility** [cm ² (V s) ⁻¹] |
|----------|--|---|
| 1 | 3.0 | 3.00 |
| 2 | 2.5 | 2.46 |
| 3 | 2.2 | 2.24 |
| 4 | 2.0 | 2.12 |
| 5 | | 2.04 |
| 6 | | 2.00 |
| 7 | | 1.95 |
| 8 | | 1.93 |
| 10 | | 1.88 |
| 20 | | 1.80 |

* Measurements of Young *et al.* (1970) and their size assignments.

** Computed reduced mobility from Eq. (37).

TABLE 3. Assignment of cluster size i to the measured reduced mobility in the argon gas.

| H ₂ O ppm (Torr) | Reduced mobility K_0 vs size i [cm ² (V s) ⁻¹] | | | | | | Experiments |
|--------------------------------|--|-----|-------|-----|-------|-----|--------------|
| | K_0 | i | K_0 | i | K_0 | i | |
| 0.5 (0.0004) | 2.5 | 2 | 2.0 | 5 | 1.8 | 20 | ^a |
| | 1.8 | | | | | | ^a |
| 1.5 (0.0011) | 2.1 | 4 | 2 | 5 | 1.8 | 20 | ^b |
| 2.0 (0.0015) | 2.2 | 3 | | | | | ^a |
| 160 (0.12) | 1.9 | 8 | 1.8 | 20 | 1.6 | >20 | ^b |
| 300 (0.23) | 2.0 | 5 | 1.8 | 20 | 1.5 | >20 | ^a |
| 1300 (1) | 2.0 | 5 | 1.8 | 20 | | | ^b |
| 3500 (2.7) | 1.8 | 20 | 1.5 | >20 | 1.0 | >20 | ^a |
| 7000 (5.3) | 1.8 | 20 | 1.5 | >20 | 1.0 | >20 | ^a |

^a Measurements by Bricard *et al.* (1972).

^b Measurements by Thurman (1977).

$i = 5$ and $i = 8$, compared to our theoretical range between $i = 6$ and $i = 8$ at 297 K. However, it is to be noted that the relative size distributions do not agree well with each other. If the uncertainties in the estimation of intermolecular vibrational frequencies are removed, quantitative agreements in the ratios of the size distributions are expected to improve.

Based on the computed results (see Table 2) from Eq. (37) we assigned the sizes of the hydronium ion hydrates to the measured ion mobilities of Bricard *et al.* (1972) and of Thurman³ in Table 3. Some of the assignments are as follows: We assign the size of $i = 2$ to the reduced mobility $K_0 = 2.5$, $i = 3$ to $K_0 = 2.2$, $i = 4$ to $K_0 = 2.1$, and $i = 5$ to $K_0 = 2.0$. At 1.5 ppm, the reduced mobility of Thurman shows three different values: 2.11, 1.95 and 1.80 $\text{cm}^2 (\text{V s})^{-1}$, respectively, while only a single value of 1.8 $\text{cm}^2 (\text{V s})^{-1}$ was observed by Bricard *et al.* (1972) at the same pressure. Qualitative agreements are observed generally between the two measurements of Thurman and of Bricard *et al.* The computed ion mobilities from Eq. (37) are not expected to be accurate, particularly for large ion clusters. The effect of the inelastic contributions to the ion-neutral collisions was not taken into account in this equation. The clusters are weakly bound systems due to the relatively weak intermolecular force and they have a large number of internal degrees of freedom which can absorb or release energy during collision. Thus inelastic scattering should become increasingly important with increasing cluster size.

Judging from the drift tube measurements of Young *et al.* (1970) and the equilibrium data of Kebarle *et al.* (1967), the ion mobility measurements of Bricard *et al.* (1972) and Thurman (1976) at low H_2O partial pressures do not seem to show an agreeable trend in mobility spectra as a function of the ion cluster size. Our computed ion concentrations and mobilities as a function of the ion cluster size tend to more closely support the measurements of Young *et al.* Our results agree qualitatively well with the thermodynamic data of Kebarle *et al.* in the ion concentrations. In the future, it is to be explained why the ion mobility spectra measured by Bricard *et al.* and Thurman show discontinuous cluster size in the size distribution of the hydronium ion hydrates. It is also to be noted that their mobility measurements tend to show much larger cluster sizes than the measured values of Young *et al.* and Kebarle *et al.* even at extremely low H_2O vapor pressures.

In this paper, we have investigated both the size distribution and ion mobility of the clusters $\text{H}^+(\text{H}_2\text{O})_i$

at various humidities. Relatively good correlations were found between the measured mobility spectra of Young *et al.* and the cluster sizes assigned from the theoretical analysis of the relative concentrations of ion species. We find that the ion mobilities in the range 2.0–2.5 $\text{cm}^2 (\text{V s})^{-1}$ are due to the hydrated ion cluster size $i = 2-5$. These values are approximately equivalent to the total mass of the ions in the range of 2 to 5 water molecules. For the reduced mobilities below 2.0 $\text{cm}^2 (\text{V s})^{-1}$ the mass of the hydrated ions were predicted to be greater than that of five water molecules. The modal value of the cluster was predicted to consistently shift toward larger sizes as the humidity increases. However, the predicted concentrations were narrowly distributed, as is shown in Table 1. The computed ion mobility at each size agreed reasonably well with the cluster size assignment based on the concentration analysis.

The size of the ions determines the mobility. In turn, the electric conductivity is determined by the mobility and concentration. In this regard, our simultaneous evaluation of concentration and mobility is useful. In addition, the statistical mechanical method we developed here will show considerable potential for the future study of the energy of formation of prenucleation embryos for which the classical liquid drop model is generally believed to be of doubtful utility. Finally, the use of argon as a buffer gas for studying the mobility of ions in drift tubes may closely approximate the atmospheric ion mobility, as was discussed in Section 2.

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