

## Ion-Induced Nucleation: The Importance of Chemistry

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Experiments have shown that ions can substantially increase vapor-to-liquid nucleation rates. However, interpretation of these experiments is complicated by ambiguities arising from the manner in which the ions are produced. Several studies have concluded that water has a general preference for anions over cations. We show that specification of the ion's sign alone is insufficient to provide an understanding of the aqueous ionic cluster thermodynamics and that classical ion-induced nucleation theory does not treat the cluster physics properly to describe ion-induced nucleation accurately.

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Nucleation requires surmounting an activation barrier via rare event processes. The presence of trace species—especially ions—can reduce this barrier and increase the rate of formation of ionic embryos [1–23]. Considerable attention has been paid to the sign effect, the relative enhancement of nucleation rates due to an ion's sign, without reference to chemical identity [1–6,8,11–15]. Wilson discovered that x rays induced droplet formation in supersaturated water vapor. Employing suitable electric fields, he found that water prefers “anions” to “cations”—but the chemical identity of these ions was never determined. Subsequent ion-induced nucleation experiments have produced a variety of interesting results and interpretations, sometimes contradictory, depending on physical conditions, ion chemical identity, and electric field strength. The majority of these studies found that ion-induced nucleation is more favorable than homogeneous nucleation of the host vapor and confirmed a “negative” sign preference for water. These studies [1–6,8–15], however, produced ions via  $\gamma$  rays, x rays,  $\alpha$  particles, and nonresonant UV photoionization, resulting in a cascade of ions whose chemical identities and lifetimes were unknown [7].

Definitive experimental resolution of whether anions or cations enhance nucleation rates is difficult because it is not possible to simply change an ion's charge without altering its electronic structure and thus its chemical properties. Castleman and Tang [7] stated over 30 years ago “the sign of the charge is not the only prerequisite and even ions of like sign may nucleate at different supersaturation ratios. The interpretation of the data obtained in most ion-nucleation experiments is therefore very uncertain and appropriate account of the actual species is necessary in understanding the molecular nature of the nucleation phenomena.” This statement is in stark contrast to the conclusion [15] that “understanding the effect of ions would be very difficult, or even impossible, if the ion's specific chemical characteristics had a significant effect on their nucleating efficiency.” Further underscoring the importance of chemistry, Castleman suggested, based on electron affinities and ionization potentials, that halides and metals would be appropriate primary negative and positive ions,

respectively. Indeed, experimental data [24,25] on ionic hydrates explicitly demonstrate the sensitivity of monohydration enthalpies on an ion's chemical identity (for example,  $\text{Li}^+ = -34.0$ ,  $\text{Na}^+ = -24.0$ ,  $\text{K}^+ = -17.9$ ,  $\text{Rb}^+ = -15.9$ ,  $\text{Cs}^+ = -13.7$ ,  $\text{F}^- = -23.3$ ,  $\text{Cl}^- = -13.1$ ,  $\text{Br}^- = -12.6$ ,  $\text{I}^- = -10.2$ ; all energies in kcal/mol).

Theoretical approaches offer a means of isolating different effects, such as the sign of the ionic charge, while keeping all other factors constant. The first theory of ion-induced nucleation modified classical nucleation theory (CNT) [26] using the electrostatic model of Born [27] and Thomson [28] to yield classical ion-induced nucleation theory (CIINT) [29,30]. CIINT models cluster thermodynamics using the bulk liquid surface tension, density, and dielectric constant. Although CIINT does predict that ions have large effects on nucleation rates, it does not explicitly treat cluster chemical physics. Nadykto [23] addressed discrepancies between ion-induced nucleation experiments and CIINT by including a mean field charge-dipole free energy to account for the host vapor dipole interaction with the electric field of the seed ion. Although this effect may be important, it does not address the inherent limitations of CIINT. Moreover, it is unclear how these modifications could be validated against experimental results using chemically unidentified ions.

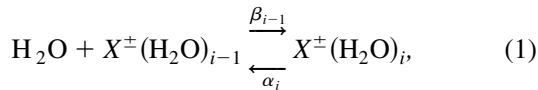
Molecular theory and simulation provide a means to examine the chemical nature of ions, not just the sign effect, on the nucleation process. Kusaka [17,18] predicted a sign effect for a simple attractive hard sphere molecule with multipole moments using a mean field density functional theory to compute the critical cluster reversible work. They found a sign preference resulting from an asymmetry in the electrostatic interaction. However, their approach is semiquantitative in model representation and theoretical treatment. Oh [20] performed Monte Carlo simulations of metastable water vapor to obtain the work of formation for aqueous ionic clusters in which only the sign of the ion was changed. Their studies concluded “generally” that water prefers anions—consistent with Wilson's early observations on unidentified “anions.” Furthermore, it is difficult to compare and contrast their

results because the ion's charge and repulsive core parameters were not held constant for each water model studied. Similarly, Brodskaya [21] used molecular dynamics to obtain the work of formation for aqueous ionic clusters and found results consistent with Oh [20]. Brodskaya and co-workers commented that "unfortunately, this work of formation does not alone provide an answer to the still unsolved problem of sign preference connected to water condensation on charged particles in atmospheric conditions." One aim of the present study is to show that the "sign effect" addressed in previous work is too simplistic to address the chemical physics of ion-induced nucleation.

Rather than asking whether anions or cations enhance nucleation rates, the relevant question is which specific properties of ions have the greatest influence on nucleation under specific conditions? In the present Letter we take the first step in answering this question by examining effects of an ion's chemical size as well as the sign of its charge and show that both have a significant effect on nucleation thermodynamics.

Our work uses dynamical nucleation theory (DNT), a novel molecular-based approach, to study multicomponent vapor-phase nucleation [31–33]. We compare DNT with CIINT and show that CIINT does not contain the essential chemical physics to understand ion-induced nucleation. From this, we conclude that any modifications to CIINT must be considered temporary expedients and that drawing general conclusions about sign preferences in ion-induced nucleation should be approached cautiously because the underlying chemistry can be quite complicated and extremely sensitive to the ion's identity.

In DNT the ion-induced nucleation mechanism is described by the addition and loss of H<sub>2</sub>O from ion-water clusters



where  $X^\pm$  denotes an ion of  $\pm$  sign,  $\beta_{i-1}$  is a condensation rate constant for addition of water to the cluster, and  $\alpha_{i-1}$  is an evaporation rate constant for loss of water from the cluster. Using detailed balance, the ratio of evaporation and condensation rate constants is related to the ratio of equilibrium populations of adjacent cluster sizes,  $N_i^{\text{EQ}}/N_{i-1}^{\text{EQ}}$ , and thereby to the Boltzmann weight of the cluster chemical potentials

$$\beta_{i-1}/\alpha_i = N_i^{\text{EQ}}/N_{i-1}^{\text{EQ}} = \exp(-\mu_{i-1,i}^{X^\pm} + \mu_1/k_B T), \quad (2)$$

where  $k_B$  is Boltzmann's constant,  $T$  is temperature, and  $\mu_1$  is the ambient water monomer chemical potential. Cluster chemical potentials are simply the differences in Helmholtz free energies  $A_i^{X^\pm}$  between adjacent-sized clusters

$$\mu_{i,i-1}^{X^\pm} \equiv A_i^{X^\pm} - A_{i-1}^{X^\pm} = \Delta A_{i,i-1}^{X^\pm}. \quad (3)$$

Therefore, cluster chemical potentials are fundamental quantities in understanding the molecular nature of nuclea-

tion phenomena. Using DNT, an extreme sensitivity of the kinetic parameters, and thereby nucleation rates, to the underlying molecular interaction potentials was discovered [34]. The sensitive nature of nucleation phenomena to slight variations in interaction energies is exemplified by recognizing that a systematic change of  $-0.5$  kcal/mole (well within zero-point-energy effects) in water cluster chemical potentials can alter the nucleation rate by 10 orders of magnitude [34].

The Helmholtz free energy  $A_i^{X^\pm}$  of an aqueous ionic cluster containing  $i$  water ( $w$ ) molecules and a single ion ( $X$ ) is obtained from the canonical partition function,  $Q_i^{X^\pm}$ . The cluster partition function is expressed as a configuration integral bounded by a spherical constraining volume of radius  $r_{\text{cut}}$  with the cluster center-of-mass fixed at the origin [31],

$$\begin{aligned} e^{-A_i^{X^\pm}/k_B T} &= Q_i^{X^\pm}(r_{\text{cut}}, T) \\ &= \frac{\gamma_w^i \gamma_X}{i!} \int d\mathbf{r}^{(i)} \exp[-U_i(\mathbf{r}^{(i)})/k_B T] \\ &\quad \times \prod_{j=1}^i \theta(r_{\text{cut}} - |\mathbf{r}_j - \mathbf{R}_i|). \end{aligned} \quad (4)$$

In this expression  $\gamma = (2\pi m k_B T/h^2)^{3/2}$ , where  $m$  is the mass of water ( $w$ ) or the ion ( $X$ ),  $h$  is Planck's constant,  $\mathbf{r}^{(i)} = \{\mathbf{r}_X, \mathbf{r}_1, \dots, \mathbf{r}_i\}$  are Cartesian coordinates of ion and water molecules in the ionic cluster,  $U_i$  is the interaction potential,  $\theta(x)$  is the Heaviside step function, and  $\mathbf{R}_i$  is the center-of-mass of the  $i$ -water ionic cluster. The *anharmonic* Helmholtz free energy of the aqueous ionic cluster is calculated via Monte Carlo simulations using the External Work Method by Reinhardt [32,35]. The External Work Method computes the free energy difference between the fully interacting cluster (with  $i$  water molecules and an ion) and the reference ideal gas cluster ( $U_i = 0$ ). The total cluster Helmholtz free energy is obtained by summing the free energies of the interacting cluster and the ideal gas cluster. Cluster chemical potentials were obtained at  $T = 243$  K, sampling 10–100's of millions of Monte Carlo steps, yielding a statistical uncertainty of 0.5 kcal/mol.

In this work we use the TIP4P potential [36] to describe water-water interactions and describe the ion-water interactions by Coulomb + Lennard-Jones (LJ) potentials. To study the dependence of the Helmholtz free energies on the ion size and  $q_X = \pm 1$ , two sets of parameters are considered: small (SM) with LJ parameters  $\sigma_X = 2.35$  Å,  $\epsilon_X = 0.13$  kcal/mol and large (LG) with parameters  $\sigma_X = 4.45$  Å,  $\epsilon_X = 0.10$  kcal/mol (the effect of the 0.03 kcal/mol difference in  $\epsilon_X$  parameters is negligible). It is well known that polarizability has an influence on ion-cluster structure and energetics. We anticipate that zero-point-energy effects will be just as important as polarization energy to the quantitative prediction of ion-induced nucleation rates. However, our focus here is on the more general features of ion-water interactions within a cluster

and how simple chemical differences can amount to profound influences on cluster thermodynamics. For the sake of illustration, we identify an ion chemically simply by the sign of its charge and its effective size.

In CIINT the distribution function,  $N_i^{\text{EQ}}$ , is related to the free energy of formation,  $W_i$  for an aqueous ionic cluster of  $i$  water molecules by

$$-k_B T \ln \left[ \frac{N_i^{\text{EQ}}}{C} \right] = W_i = -ik_B T \ln S + 4\pi r_i^2 \sigma - \frac{q_X^2}{2} \left[ 1 - \frac{1}{\epsilon_w} \right] \left[ \frac{1}{r_X} - \frac{1}{r_i} \right]. \quad (5)$$

In Eq. (5)  $S$  is the supersaturation (e.g., water monomer population divided by its equilibrium population),  $r_i$  is the radius of the whole cluster,  $\sigma$  is the bulk surface tension of water [37],  $\epsilon_w$  is the dielectric constant of water ( $\epsilon_w = 80$ ), and  $r_X$  is the ion radius, and  $C$  is a factor that depends on ion and H<sub>2</sub>O monomer concentrations. Note that the ion charge in Eq. (5) is squared, meaning there is no sign preference in CIINT. By assuming that water forms a liquidlike shell around the ion, the number of water molecules in the ionic cluster is  $i = 4\pi\rho_w[r_i^3 - r_X^3]/3$ , where  $\rho_w$  is the bulk density of water. Using Eqs. (2), (3), and (5), and  $\mu_1 - \mu_0 \equiv k_B T \ln S$  ( $\mu_0$  is the equilibrium water monomer chemical potential) in terms of the number of water molecules, the molecular-level chemical potentials can be compared with those from CIINT via

$$-\mu_{i,i-1} \approx -\frac{\partial W_i}{\partial i} - \mu_1 \approx [3i + 4\pi\rho_w r_X^3]^{-1/3} \left\{ -\frac{(32\pi)^{1/3} \sigma}{\rho_w^{2/3}} + \frac{q^2}{2} (4\pi\rho_w)^{1/3} \left[ 1 - \frac{1}{\epsilon_w} \right] [3i + 4\pi\rho_w r_X^3]^{-1} \right\} - \mu_0. \quad (6)$$

It is important to point out contributions from the two terms within braces in Eq. (6): the first term is negative (due to pure water surface tension) and the second term is positive (due to the ion). The limit of Eq. (6) as  $i \rightarrow \infty$  approaches the equilibrium chemical potential  $\mu_0$  for pure water corresponding to a vapor pressure of 0.38 torr [37] at 243 K.

The results in Fig. 1 show how the negative of the chemical potentials [Eq. (3)], for both SM/LG ions of  $\pm$  sign, vary with increasing number of water molecules. Also plotted in Fig. 1 is the CNT result for pure water and the CIINT results [Eq. (6)] for the limiting cases for ionic clusters where the lower (upper) dotted curve is for  $r_X = 10$  Å (0.1 Å). These radii were chosen to cover a broad range so as to include radii typically used for atomic and molecular ions. In the molecular calculations, the LJ size parameter ( $\sigma_X$ ) plays a similar role as  $r_X$  in CIINT. The molecular calculations display a negative curvature for the SM anion and cation whereas CIINT shows the opposite behavior. Note also the large differences in chemical potentials predicted from the molecular calculations versus those from CIINT—some differences are as large as 20 kcal/mol in a single monomer addition step. Our previous sensitivity studies on nucleation [33,34] found that tenths of a kcal/mol in each mechanistic step can have profound consequences on the nucleation rate. It is seen from Fig. 1 that *for the same*  $\sigma_X$ , water prefers the atomic anion to the cation—entirely consistent with Oh [20] and Brodskaya [21]. However, *for different effective sizes, this is not true*. Some examples serve to highlight the essential features of our analysis: H<sub>2</sub>O prefers (1) a small cation to a large anion, (2) a small anion to a large anion, and (3) a small cation to a large cation. These findings can be understood by considering the trade-offs between attractive and repulsive ion-water interactions. The small ion ( $\sigma_X = 2.35$  Å) has a smaller repulsive core allowing the water molecule to penetrate deeper into the Coulomb well, whereas the larger repulsive core ion ( $\sigma_X = 4.45$  Å)

does not allow water to sample the Coulomb well as deeply. For a given LJ size parameter, the sign effect can be explained by noting that there is no core repulsion placed on water's H atoms allowing the hydrogen positive charge to get closer to the anion. These simple examples underscore the importance of the details of the chemistry of small aqueous ionic clusters relevant in ion-induced nucleation. The insert to Fig. 1 shows at least two interesting features: (1) the cluster chemical potential size dependence is nonmonotonic and (2) the chemical potentials can cross each other. When the chemical potentials cross one another this means that the preference for the additional water molecule onto the  $i - 1$  cluster is reversed. Eventually, as water monomers are added to ionic clusters containing more water molecules, the chemical potential for the incoming water monomer should approach that for pure water clusters since the influence of the electric field of the screened ion will decrease with increasing cluster size. The insert shows that 40 water molecules are still not enough to reach this limit. Note also that the SM/LG anion chemical potentials and SM/LG cation chemical potentials track one another for the bigger clusters.

The present detailed analysis of aqueous ionic cluster chemical potentials, using ions of different size and sign, has shown that the chemical nature of ions in ion-induced nucleation phenomena must be considered in experiment and theory. Consequently, we suggest that future ion-induced nucleation experiments use a selective ion flow tube (SIFT) mass spectrometer [38] to produce well-characterized ions, and because nucleation is so sensitive to contamination [34,39], use an additional mass spectrometer to identify freshly nucleated clusters. CIINT and its modifications lack physical justification, and any agreement with experiment is, at best, fortuitous. DNT provides a theoretical formalism in which chemical potentials and rate constants can be systematically incorporated to build ion-induced nucleation kinetics mechanisms. Future work will address evaporation and condensation rate constants,

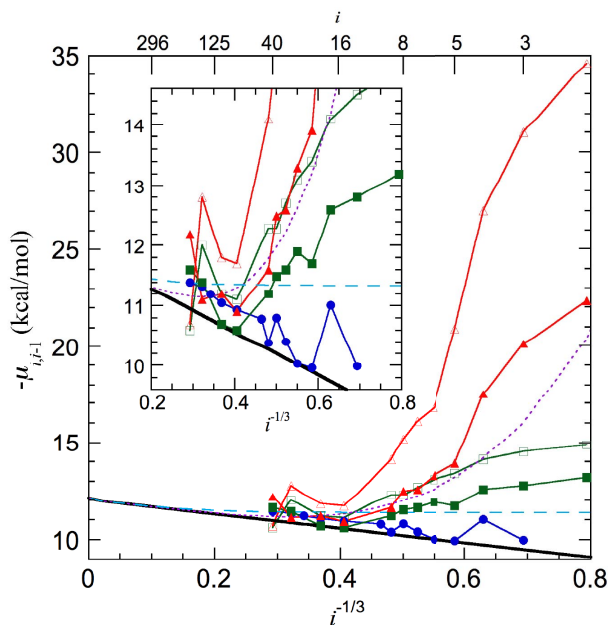


FIG. 1 (color online). Aqueous ionic cluster chemical potentials at  $T = 243$  K:  $X_{SM}^-(H_2O)_i$  (open triangles),  $X_{SM}^+(H_2O)_i$  (solid triangles),  $X_{LG}^-(H_2O)_i$  (open squares),  $X_{LG}^+(H_2O)_i$  (solid squares),  $(H_2O)_i$  (solid circles), CNT pure water (solid line), CIINT with ion radius  $r_X = 0.1$  Å (small-dashed curve), CIINT with ion radius  $r_X = 10$  Å (large-dashed curve). The insert provides an expanded view of the larger clusters.

molecular ions, polarizability, and zero-point-energy effects for aqueous ionic clusters.

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