Dynamics of Solvation-Induced Structural Transitions in Mesoscopic Binary Clusters

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Ion solvation dynamics following collision of K^+ with mesoscopic water-ammonia aggregates is investigated. Two processes determine the postcollision state of the clusters: First, a morphological transformation from a structure characterized by a solid water core and a liquid-phase ammonia sheath into a dumbbell-shaped cluster composed of a liquid water droplet attached to an ammonia subcluster containing the solvated ion. Second, evaporation cools the cluster during and after the morphological change and this evaporative cooling is quantitatively characterized by determining the size-dependent rate constants for these complex clusters.

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Ion solvation dynamics in bulk liquids has been the topic of experimental and theoretical studies for many years and its analog in molecular clusters has attracted attention more recently. The availability of new experimental information [1–3] as well as the fact that mesoscale molecular clusters have properties distinct from both few-molecule clusters and bulk fluids have contributed to interest in this area. In this Letter we examine the mechanisms that govern the solvation dynamics that occurs after a metal ion collides with a binary polar molecule cluster. Binary clusters present a number of interesting features, most notably, those related to the competitive coordination of the two "solvent" species to the ionic solute. Even in the absence of a solute, such binary clusters may exhibit a number of equally interesting competitive effects, such as superficial vs bulk states and total segregation vs full mixing, depending on the specific details of the Hamiltonian and the relative concentration of the components [4,5]. Recent molecular beam experiments on singly charged metal ions dissolved in water-ammonia clusters [1] lead one to ask how the ionic solute is incorporated in the originally neutral cluster and what morphological changes of the aggregate take place as the solvation proceeds [6]. We show that the solvation dynamics has two different relaxation contributions: (i) the selective ionic solvation by one component leads to a significant morphological change in the overall cluster structure and (ii) selective cluster evaporation, which presents features distinct from that in simpler clusters.

Using molecular dynamics techniques, we investigate the solvation dynamics of a K^+ ion in a water-ammonia cluster following the collision of the ion with the binary cluster and investigate the mechanism of the cluster structural rearrangement that leads to the final solvation state. The states of the cluster prior to the collision (upper panel) and at a later time after structural changes have taken place (lower panel) are shown in Fig. 1.

Water molecular interactions were described by the three-site simple point charge model [7] and ammonia as a rigid four-site molecule [8]. Solute-solvent potentials were taken from Ref. [9]. Initial conditions for the precollision states were chosen in the following way: 200 configurations were generated from a canonical ensemble [10] obtained by selecting configurations every 10 ps from a long trajectory at $T_i \approx 110$ K. Under these

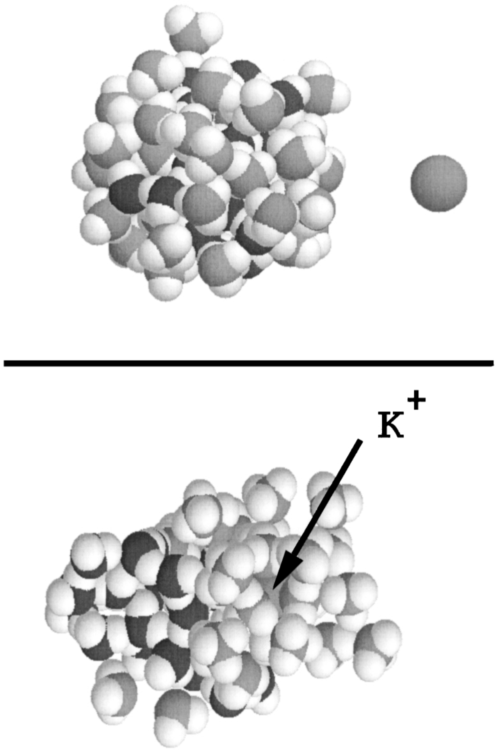

FIG. 1. Two configurations of a [25:43] water(black)-ammonia(light gray) cluster. The ion is rendered in dark gray. The top panel is a precollision state where the cluster is spherical with a water core and ammonia sheath. The bottom panel shows the dumbbell-shaped morphology with the K^+ ion fully solvated by ammonia.

conditions, the initially neutral target binary cluster comprises a stable solid water nucleus surrounded by a sheath of liquid-phase ammonia. Energetic factors determine the morphology of these small, low-temperature clusters: since the attractive water (w) and ammonia (a) interaction energies satisfy $\epsilon_{ww} > \epsilon_{wa} > \epsilon_{aa}$ one expects [4], as observed, a water core surrounded by an ammonia sheath [11]. Two initial water-ammonia cluster compositions were studied: [25:25] (partial coverage of the water core by ammonia) and [25:43] (total coverage). The initial ion-cluster relative separation was taken to be 50 Å. The impact parameter, measured from the cluster center of mass, and the relative velocity of the ion with respect to the center of mass of the cluster, define the remaining collision initial conditions [12]. We explored three projectile energies: 2, 1, and 0.025 eV; these energies are representative of low-energy molecular beam experiments (1–2 eV) and for a reaction taking place in atmospheric conditions, respectively. The dynamics of the collision process was microcanonical.

Figure 2 shows the time dependence of the temperature of the cluster. Immediately following the collision, a few ammonia molecules initially located in the vicinity of the impact region evaporate as a result of momentum transfer from the ion. One can see that the first evaporated ammonia molecules have kinetic energies which are significantly higher than those of the cluster constituents. However, the main source of the postcollision thermal energy release occurs in the initial portion of the solvation relaxation, which lasts on the order of 1 ps. During this initial stage the cluster is far from thermal equilibrium and the temperature of the water nucleus is significantly lower than that of the ammonia. Subsequent to this initial stage, the solvation process exhibits a much slower diffusive character during which thermal equilibrium of the entire aggregate is achieved after ≈7–8 ps. Two processes occur during the solvation: (i) a steady selective evaporation of ammonia molecules responsible for the gradual cooling of the aggregate [13] and (ii) a morphological change driven by the preferential ionic solvation by ammonia molecules [14] which "slip" from the water nucleus and form a subcluster around the ion (cf. lower panel of Fig. 1) leading to a dumbbell-shaped cluster consisting of two fused liquid droplets, with the ion located in the ammonia subcluster. This morphological change can be understood on simple energetic grounds: it is more favorable for the ammonia molecules to participate in ion solvation than in the formation of weaker interfacial ammonia-water interactions.

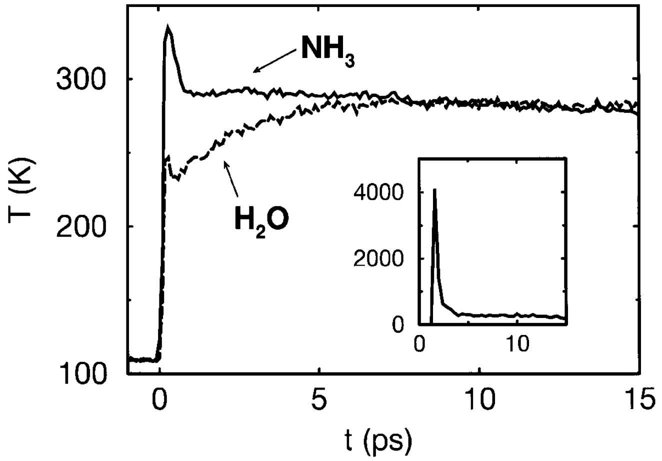

FIG. 2. Temperatures of water and ammonia vs time for a [25:43] cluster following a collision with 2 eV K$^+$ ion. The inset shows the time evolution of the translational temperature of the evaporated ammonia molecules. The zero of time is defined as the instant when the relative velocity of the ion with respect to the center of mass of the cluster attains its maximum value.

In the second part of the diffusive regime, for $t >$ 8 ps, evaporation takes place from a local thermal equilibrium state of the cluster. Surprisingly, despite the gradual change from spherical to cylindrical symmetries, we found no evidence of a preferential angular dependence in the directions of the evaporated ammonia. Evaporation in this regime can be viewed as a sequence of first order processes, $C_N \xrightarrow{k_N} C_{N-1}$, where a cluster with N ammonia molecules, C_N, converts to a cluster with one less ammonia molecule. Evaporation both of small and large single-component clusters has been studied extensively [15–17]. While the general activated form of the rate constants k_N has been discussed, here we explicitly compute these quantities in order to fully characterize the relaxation process. The rate constants k_N were obtained as follows: for each ensemble of clusters we determined the distribution of survival times of the clusters of size N, i.e., the time required for a cluster of size N to form an $N - 1$ cluster. In agreement with first order kinetics, we found that the distribution of lifetimes for every size N is exponential with time constant k_N; moreover, we found that after the transient period the single particle kinetic energy distributions are Maxwellian characterized by average temperatures T_N. It is noteworthy that the evaporation from a cluster with a complex internal structure that indergoes a morphological change can be described by such a simple dynamical model. Figure 3 shows the temperatures T_N vs N for two different relative kinetic energies of the collision partners. The variation of T_N with N is the same in both cases [18]. The magnitude of the rate and temperature dependence of k_N can be analyzed by assuming a transition state model,

$$k_N^{TS}(T_N) = \frac{k_B T_N}{h} f(N) e^{\frac{\Delta S^\dagger}{k_B}} e^{-\frac{\Delta E^\dagger}{k_B T_N}}, \tag{1}$$

where $\Delta E^\dagger$ and $\Delta S^\dagger$ are the energy and entropy differences between the transition state of the evaporating ammonia and the ammonia molecules in a cluster containing 25 water molecules and N ammonia molecules at the ensemble average temperature T_N. The factor $f(N) \propto N^\gamma$ accounts for the modification of the entropic and energetic terms due to the existence of a surface [19]. The

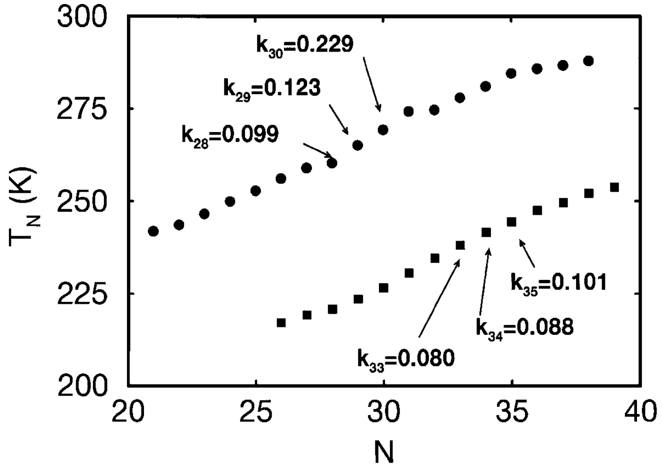

FIG. 3. Local equilibrium cluster temperatures vs cluster size N for two different collision energies: 2 eV (circles) and 0.025 eV (squares). Some typical values of the rate constants k_N (in ps^{-1}) for intermediate size aggregates are also shown.

temperature dependence of k_N is shown in Fig. 4. From linear regressions of the two curves, we obtained values of $\Delta E^\dagger/k_B = 4100 \pm 200$ and 4400 ± 150 K and $(k_B T_N/h)\exp(\frac{\Delta S^\dagger}{k_B}) = 2.2 \times 10^5$ and $2.4 \times 10^5\ \mathrm{ps}^{-1}$, for simulations corresponding to collision energies of 0.025 and 2 eV, respectively. When compared to the temporal prefactor $k_B T_N/h \approx 1\ \mathrm{ps}^{-1}$, the latter values indicate a large contribution from the activation entropy due to significant loss of local order when an ammonia molecule passes from the liquid cluster into the vacuum. To gain insight into the orders of magnitude of the computed thermodynamic quantities, as a first approximation one can assume that the condensation process has no barrier. Then $\Delta E^\dagger$ should be equal to the binding energy ΔE_b of an evaporating molecule. Experimental values of $\Delta E_b/k_B$ for protonated ammonia clusters are intermediate between 3000–6000 K [20] and compare favorably to those for $\Delta E^\dagger$ obtained from the slopes of Fig. 4. Incidently, the much larger magnitude of ΔE_b for water (see Ref. [1]) is consistent with the fact that water molecule evaporation was rarely observed. Note that the computed value of $\Delta S^\dagger/k_B \approx 12$ is quite close to the vaporization entropy of pure ammonia under normal conditions, $\Delta S_{\mathrm{vap}}/k_B = 11.7$, a fact that would suggest that the presence of the ion does not introduce a significant change in the entropy of the mesoscopic ammonia phase, compared to the bulk value.

The remaining dynamical aspect to consider is the cluster morphological change. To quantitatively monitor this transition an order parameter, the distance between the centers of mass of water and ammonia subclusters, $d(t)$, was introduced. The time evolution of $\Delta d(t) = d(t) - d(\infty)$ and the average number of ammonia molecules remaining in the cluster $N(t)$ are shown in Fig. 5. Note that although the morphological change occurs during the cooling evaporation process, the dynamics of $d(t)$ is not strongly coupled to the evaporation process: in Fig. 5 we also present a second set of curves for a collision with a completely frozen binary cluster. The highest temperature attained in this case is ≈200 K and was sufficiently low to preclude substantial evaporation of ammonia. A structural transformation with similar dynamical characteristics is nevertheless observed and is driven by the ionic solvation dynamics.

An equation of motion in the form of a generalized Langevin equation for the order parameter d may be derived. Consider the final phase segregated cluster and imagine changing d from its average value $\langle d \rangle$. The evolution equation for $\delta d = d - \langle d \rangle$, averaged over a

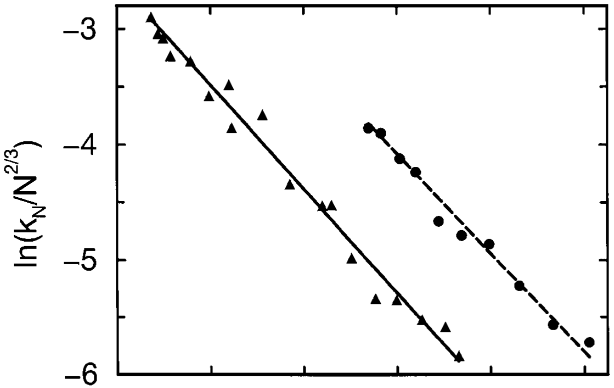

FIG. 4. Temperature dependence of the rate constants. The triangles (collision energy of 2 eV); circles (0.025 eV). The ensembles start with a [25:43] water-ammonia cluster at 110 K. γ was assumed to be 2/3 (see Ref. [19]).

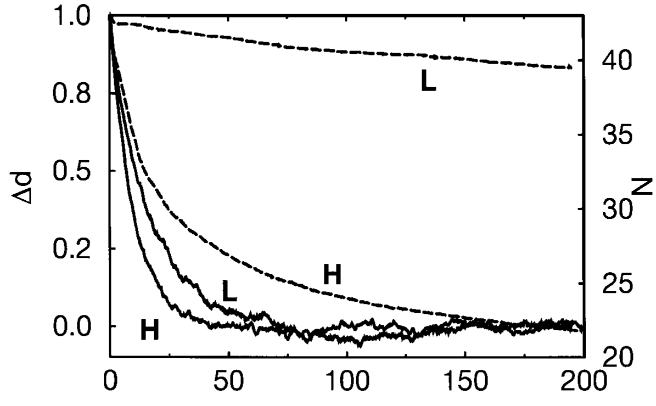

FIG. 5. Normalized nonequilibrium relaxation of $\Delta d(t)$ for collisions between a [25:43] target cluster at $T_i = 110$ K with a 2 eV ion (solid line, H) and at $T_i = 10$ K with a 0.025 eV ion (solid line, L). The corresponding ammonia cluster populations are also shown (similar labeling with dashed lines, ordinate on right).

nonequilibrium ensemble with a fixed initial value of δd is [21]

$$\frac{d\langle \delta d(t)\rangle_{\text{ne}}}{dt} = -\int_0^t d\tau\, K_d(\tau)\, \langle \delta d(t-\tau)\rangle_{\text{ne}}\,, \qquad (2)$$

where $K_d(t)$ is the rate kernel. For such small deviations from equilibrium, the time autocorrelation function of d satisfies the same equation of motion, in accord with Onsager's regression hypothesis. Assuming that the characteristic decay time τ_d of d is much longer than that of its flux, τ_f (verified by direct simulation), the time evolution of $\langle \delta d(t)\rangle_{\text{ne}}$ takes the form of a simple exponential decay with time constant k_d given by

$$k_d = \int_0^{\tau^*} K_d(t)\, dt \approx \langle (\delta d)^2\rangle^{-1} \int_0^{\tau^*} \langle \dot{d}(t)\dot{d}(0)\rangle\, dt\,. \quad (3)$$

Here τ^* is such that $\tau_f \ll \tau^* \ll \tau_d$. We computed the flux autocorrelation function in the equilibrium segregated state by monitoring its fluctuations. From its time integral, k_d, we find $\tau_d = k_d^{-1} \approx 20$ ps. This result is in good agreement with $\tau_d \approx 15$ ps determined from the exponential decay of $\Delta d(t)$ in the structural transformation following the collision with the ion [22]. Since, to a good approximation (cf. Fig. 5), the evolution of $d(t)$ follows a simple exponential law for the entire time domain following the ion collision, and the time constants are in accord, the evolution equation appears to hold beyond the near equilibrium regime. On time scales where d does not vary significantly, the dynamical part of k_d has the same form as that of the *mutual* diffusion coefficient of a binary mixture.

The results presented here show that ion solvation dynamics in binary molecular clusters requires consideration of concepts related to binary fluid phase separation and evaporative cooling, both of which present distinctive features. The processes described in this paper could be probed in time-resolved studies of size-selected clusters.

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[18] The curves are displaced by a temperature gap $\Delta T_N \approx \Delta E/c_N$, where ΔE is the difference in total energy of the clusters in the two simulations and c_N is the cluster heat capacity.

[19] Dimensional analysis shows that $f(N)$ should be $\propto N^{2/3}$ for evaporation from a sphere of N ammonia molecules; if ammonia forms a monolayer layer coating the water nucleus, $f(N) \propto N$. Because of changes in the cluster during the evaporation process, it is difficult to assign a definite value to γ. Both $\gamma = 2/3$ and 1 yield good correlation coefficients for linear fits of $\ln[\frac{k_n}{N^\gamma}]$ vs T_N^{-1}.

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