

# Multivalent Surface Cations Enhance Heterogeneous Freezing of Water on Muscovite Mica

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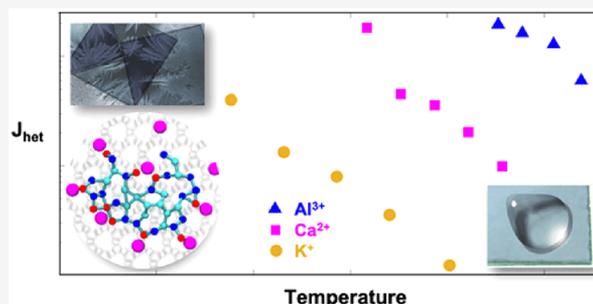
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**ABSTRACT:** Heterogeneous ice nucleation is a crucial phenomenon in various fields of fundamental and applied science. We investigate the effect of surface cations on freezing of water on muscovite mica. Mica is unique in that the exposed ion on its surface can be readily and easily exchanged without affecting other properties such as surface roughness. We investigate freezing on natural ( $K^+$ ) mica and mica in which we have exchanged  $K^+$  for  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Sr^{2+}$ . We find that liquid water freezes at higher temperatures when ions of higher valency are present on the surface, thus exposing more of the underlying silica layer. Our data also show that the size of the ion affects the characteristic freezing temperature. Using molecular dynamics simulations, we investigate the effects that the ion valency and exposed silica layer have on the behavior of water on the surface. The results indicate that multivalent cations enhance the probability of forming large clusters of hydrogen bonded water molecules that are anchored by the hydration shells of the cations. These clusters also have a large fraction of free water that can reorient to take ice-like configurations, which are promoted by the regions on mica devoid of the ions. Thus, these clusters could serve as seedbeds for ice nuclei. The combined experimental and simulation studies shed new light on the influence of surface ions on heterogeneous ice nucleation.



The formation of ice plays a central role in our daily life in areas as disparate as food preservation,<sup>1</sup> the global radiation budget,<sup>2</sup> and precipitation.<sup>3</sup> For example, the initial formation of ice in mixed phase clouds (i.e., both liquid water droplets and ice crystals are present) is governed by heterogeneous ice nucleation,<sup>4</sup> and mineral surfaces are one of the dominant sources of atmospheric ice nucleating particles.<sup>5</sup> Numerous laboratory experiments, simulations, and field studies have been conducted to explain the effect of these catalysts on ice nucleation.<sup>4,6–9</sup>

Despite these efforts, we still have no satisfactory understanding of the microscopic details of ice formation by different surfaces. An open question in this regard is the role of ions on heterogeneous ice nucleation. While recent studies<sup>10–13</sup> have shown that cations can affect ice nucleation, no clear picture has emerged. This has been hindered due to the other surface properties at play—for example, defects dominate ice nucleation behavior in feldspar, making it difficult to delineate ion-specific effects.<sup>14</sup> In other cases,<sup>11</sup> the ice nucleation occurred in a diffuse ion layer near a surface, where heterogeneous effects are conflated with the freezing point depression of a solution.<sup>15</sup> We use muscovite mica to avoid such issues and focus on cation effects on ice nucleation.

Mica offers the advantage that  $K^+$  on the surface can be readily exchanged for other ions<sup>16,17</sup> without changing other surface characteristics such as roughness. The ability to vary one factor (i.e., the ion on the surface) independent of other

characteristics of the substrate is unique in ice nucleation research. Further, mica also facilitates comparison between experiment and simulation, since when cleaved, the basal plane is almost atomistically smooth, reducing the influence of defects.<sup>18–20</sup>

Mica has been established as a rather ineffective ice nucleating agent,<sup>21–25</sup> though in very high concentrations, it catalyzes freezing at  $\sim -10$  °C.<sup>26</sup> The near atomic smoothness of the surface has facilitated studies into the mechanism of freezing via the interaction of water with the substrate, but no definitive conclusions have resulted.<sup>27–35</sup> In our study, we use a combination of experiments and molecular dynamics (MD) simulations to investigate the role of surface cations on the heterogeneous freezing of water. We study  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ , and  $Al^{3+}$ —cations that span a range of valency. Our results indicate that multivalent cations lead to enhanced freezing. Our results also show that the size of the ion affects freezing; in this paper, we focus on the intertwined effects of valency and the fraction of the surface not covered by ions.

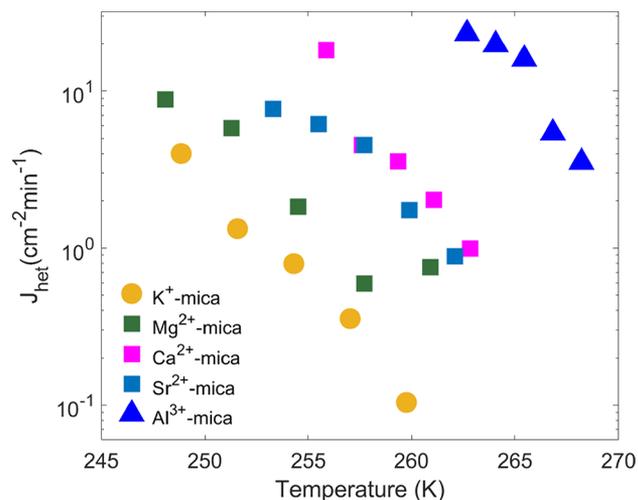
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Our simulations indicate that ice nucleation near the multivalent ions could be facilitated by the clusters of hydrogen bonded water molecules formed at these surfaces and anchored (and thus facilitated) by the water molecules in the hydration shell of the cations. These clusters have larger fractions of free water that can adopt ice-like configurations. Such ice-like configurations are promoted by the regions of mica devoid of the cations. These clusters could thus serve as seedbeds for ice nuclei. (We are unable to observe nucleation events on the surface in the simulations, because the time scale for nucleation on mica is very long.)

Figure 1 shows the heterogeneous freezing rate coefficient,  $J_{\text{het}}$ , of water on  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Al}^{3+}$ -mica surfaces.



**Figure 1.** Heterogeneous freezing rate coefficients on different ion exposed Asheville micas. Note that the time base is minutes.  $J_{\text{het}}$  increases with the valency of the exposed ion.

The data shown here is for mica from Asheville Mica Co. (A comparison among micas from different suppliers, details of the experimental procedure, and method of calculating  $J_{\text{het}}$  are in the Supporting Information (SI).) Clearly, the ion exchange reaction affects ice nucleation on the surface. The freezing curves are shifted to higher temperatures and higher nucleation rate coefficients for the divalent ion exposed surfaces; that trend is amplified further for the trivalent ion exposed surface that we tested. The data for the divalent ions suggest that the size of the ion may be playing a role. We focus on the effect of the ions' charge in this manuscript.

$J_{\text{het}}$  is the nucleation rate normalized by the contact area between the droplet and the substrate. We find that water spreads differently on untreated vs ion exchanged micas. Freshly cleaved mica is a hydrophilic surface. Water deposited onto the basal plane spreads such that its contact angle is approximately  $2^\circ$ .<sup>18,36</sup> This behavior changes dramatically upon ion exchange. We quantify this change through measurement of the surface area of a  $1 \mu\text{L}$  droplet deposited onto the mica surface. Results for the micas we tested are shown in Table 1. (See the SI for details.)

On the monovalent ion exposed surface (i.e., the  $\text{K}^+$ -mica), water spreads more than on the divalent and trivalent ion exposed surfaces. The wetting decreases in the order of  $\text{K}^+ > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+}$ . This trend is consistent with observations by Bera et al.,<sup>37</sup> who observed a change in the contact angle of droplets of aqueous chloride solutions on mica

**Table 1.** Surface Area of a  $1 \mu\text{L}$  Droplet on Different Ion Exposed Mica Surfaces

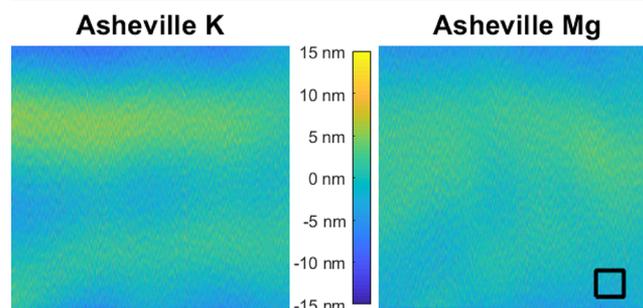
exposed ion	surface area of droplet ( $\text{cm}^2$ )	size of ion ( $\text{\AA}$ ) <sup>38</sup>	charge density of ion ( $\text{e}\text{\AA}^{-3}$ )
$\text{K}^+$	$0.31 \pm 0.01$	1.38	0.091
$\text{Sr}^{2+}$	$0.143 \pm 0.004$	1.18	0.291
$\text{Ca}^{2+}$	$0.131 \pm 0.005$	1.00	0.477
$\text{Mg}^{2+}$	$0.081 \pm 0.004$	0.72	1.279
$\text{Al}^{3+}$	$0.068 \pm 0.003$	0.535	4.677

immersed in alkane.  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{BaCl}_2$  solutions had the highest contact angles. Solutions with monovalent cations all had smaller contact angles.

$J_{\text{het}}$  and the surface area of the water droplet on different ion exposed mica surfaces can be correlated with the size and charge density of the cations, shown in Table 1. Larger cations are associated with a greater surface area of the droplet (i.e., the droplet spreads more) and in a shift of  $J_{\text{het}}$  to lower temperature. This is also reflected in the correlation with the charge density of the ion. Though we do not have a firm explanation for this behavior, we note that ions with a high charge density are associated with more tightly bound water molecules. Strong adsorption of ions to the mica surface and alteration of the hydration structure of water at the interface is one explanation for the change in the wetting behavior.<sup>37</sup>

Why does the ion substitution result in such a dramatic shift in the heterogeneous freezing rate coefficient? Surface roughness, or the presence of defects, can be the dominant factor in heterogeneous nucleation of crystals.<sup>39,40</sup> Previous work has shown that mica is remarkably smooth<sup>19</sup> and that ion substitution on the surface of mica does not result in an appreciable change in surface roughness,<sup>17</sup> but to investigate this possibility more quantitatively, we characterized surface roughness of  $\text{K}^+$  and treated micas using atomic force microscopy (AFM).

Our AFM images for  $\text{K}^+$ - and  $\text{Mg}^{2+}$ -mica are shown in Figure 2. The difference between the highest "peak" to the



**Figure 2.** False-color AFM images of  $10 \times 10 \mu\text{m}$  regions of the surface of an untreated, cleaved muscovite mica surface (left panel) and a sample of the  $\text{Mg}^{2+}$ -mica (right panel). The black square encompasses a  $1 \times 1 \mu\text{m}$  region.

lowest "valley" in these samples is less than 0.3% of the horizontal extent of the sample. The image makes it clear that the surface treatment did not meaningfully change the surface morphology. The only surface features that are present seem to occur on scales of at least several  $\mu\text{m}$ , and comparison between multiple samples shows that the  $\text{K}^+$  images are not consistently rougher or smoother on these scales than the images associated with the  $\text{Mg}^{2+}$  treated surfaces. Thus, dependence of freezing rates of cations cannot be explained from surface roughness

differences. More quantitative measures of surface roughness (or lack thereof) are described in the SI and given in Table 2.

**Table 2. RMS Roughness Measurements for Asheville K<sup>+</sup>- and Mg<sup>2+</sup>-Mica Samples<sup>a</sup>**

sample	full domain (nm)	(1.25 μm) <sup>2</sup> subdomains (nm)	box-filtered subdomains (nm)
K <sup>+</sup> -mica	2.58	1.24 ± 0.35	0.68 ± 0.05
Mg <sup>2+</sup> -mica	1.86	0.99 ± 0.16	0.66 ± 0.03

<sup>a</sup>Other measures of surface smoothness and the lack of change upon treatment are given in the SI.

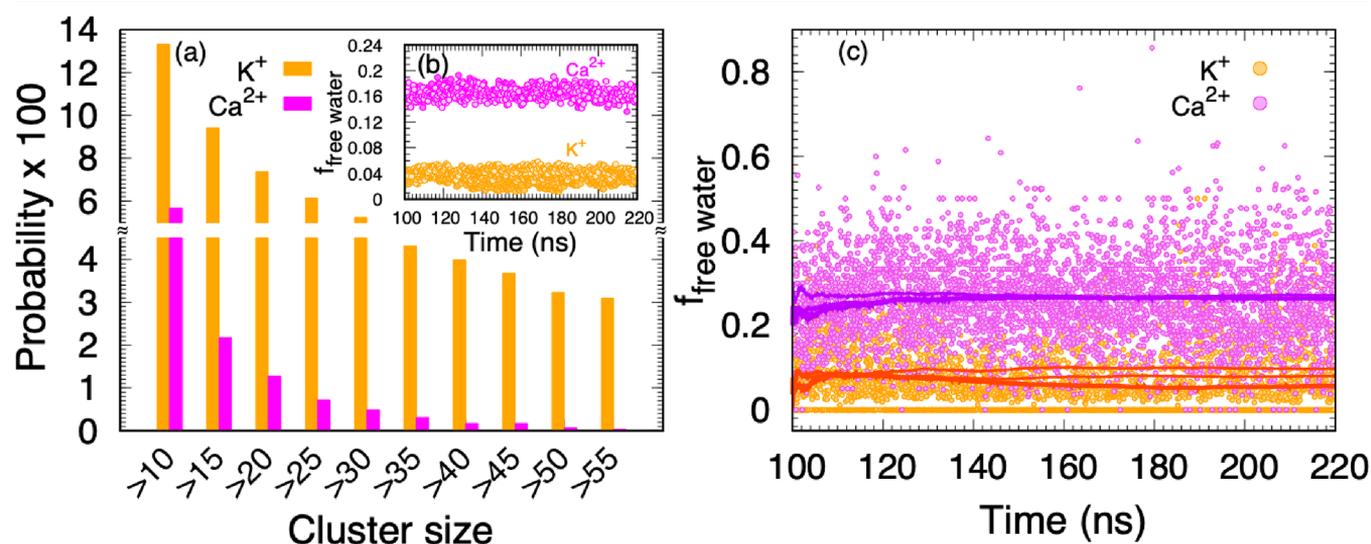
Having eliminated differences in surface roughness as a cause for the change in  $J_{\text{het}}$  we are left with the ions exposed on the surface as the most natural explanation. Ions at or near the surface have been proposed as important aspects of heterogeneous nucleation of ice. In a study of ice nucleation activity of a wide variety of substances, Shen et al.<sup>26</sup> found that fluorine phlogopite (a fluorine substituted mica) catalyzed freezing at temperatures as high as  $-1$  °C, higher than any of the other substances that they tested, including silver iodide. (Ground muscovite had a characteristic freezing temperature of  $-5.1$  °C in those tests.) They hypothesized that the fluorine ions stabilized water cages on the surface of the mineral, leading to a higher characteristic freezing temperature. This has also been indicated in studies of water on mica surfaces, where it has been hypothesized that the ice-like water structure is supported on mica. This has mostly been studied when few water layers are adsorbed on the mica surface.<sup>32,41,42</sup>

The influence of ions on water structure has also been proposed as a mechanism to explain the difference in freezing efficacy between K-feldspar and Na/Ca-feldspars.<sup>12</sup> In that case, the higher ice nucleation activity for K-feldspar is explained in terms of the mobility of water molecules in the vicinity of the ion. Zolles et al. argue that because potassium is larger, with a smaller charge density, it does not restrict and/or

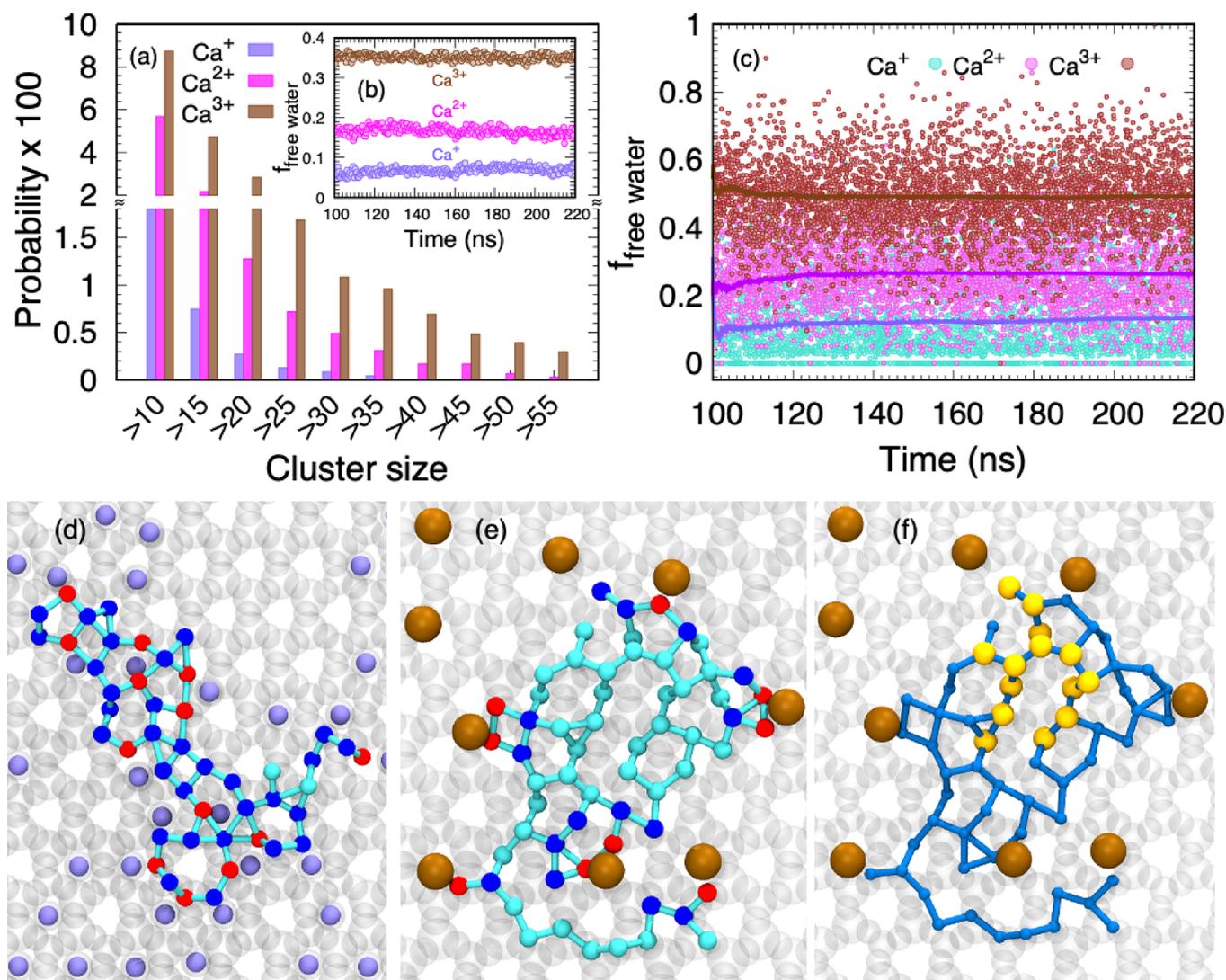
disrupt the structure of water as much as sodium or calcium, two other ions that can be present in feldspar; since water is tightly bound to the high charge density ions, it cannot reorient to adopt an ice-like structure, whereas water close to K<sup>+</sup> ions is not as tightly bound and can reorient to adopt an ice-like structure during nucleation. Similar arguments were employed in an attempt to explain the cation effects on ice nucleation observed on polyelectrolyte surfaces.<sup>10,11</sup>

To explore these ideas more completely, we used MD simulations to probe the water structure and dynamics near the mica surfaces with different cations. We performed simulations of water on K<sup>+</sup>-mica and Ca<sup>2+</sup>-mica at 243.5 K (see the SI for methodological details). Recent simulation studies of heterogeneous ice nucleation<sup>43–53</sup> have highlighted various factors such as lattice match, water orientation, and water–surface interaction energy to play an important role in catalyzing ice nucleation near surfaces. These studies have also demonstrated that the interfacial water structure and dynamics can provide insights into the observed experimental behavior of heterogeneous ice nucleation. For example, our previous studies indicate that orientations of interfacial water molecules in the metastable liquid phase can provide a measure of the ice nucleating propensity of a surface.<sup>51,52</sup> To this end, we calculated the distribution of water dipole orientations in the first few hydration layers. We did not observe any consistent trend, in contrast to those observed near kaolinite and AgI surfaces. This can arise either because of the heterogeneity of the surface coming from the cations or because the mica surfaces do not promote ice nucleation through facilitating ice favorable water orientations.

Nucleation on these surfaces is slow, precluding the possibility of observing ice formation in the simulations. For example, the nucleation on kaolinite is  $\sim 1000$  times faster than on mica.<sup>54,55</sup> At extreme supercooling, ice nucleation on kaolinite is observed in several hundred nanoseconds in straightforward MD simulations.<sup>49,52,56</sup> This implies that we would require several hundred microsecond long simulations to observe one nucleation event on mica. Due to limited



**Figure 3.** (a) Probability of observing clusters greater than a given size on the surface of Ca<sup>2+</sup>-mica and K<sup>+</sup>-mica. The data corresponds to a cutoff of 80% and an observation window of 2 ns for determining hydrogen bonded water molecules. See the SI for more details. (b) Fraction of free water ( $f_{\text{freewater}}$ ) within 0.8 nm of the surface as a function of time. (c) Fraction of free water in the largest cluster identified on Ca<sup>2+</sup>-mica and K<sup>+</sup>-mica surfaces as a function of time. The solid lines indicate the running averages for the three runs performed for each surface. The points represent data from one of the runs. The appearance of line at 0 is just the points at  $f_{\text{freewater}} = 0$  and not a running average.



**Figure 4.** (a) Probability of observing clusters greater than a given size on the surface of Ca-mica with various charges. The data presented here uses a cutoff of 80% and an observation window of 2 ns for determining hydrogen bonded water molecules. (b) Fraction of free water within 0.8 nm of the mica surface. (c) Fraction of free water in the largest cluster of hydrogen bonded water molecules. The solid lines indicate the running average. (d) Snapshot of the largest cluster identified on the Ca<sup>+</sup> surface. (e) Snapshot of the largest cluster identified on the Ca<sup>2+</sup> surface. (f) The same cluster as panel (e) with the ice-like water molecules marked using yellow spheres. Color code: gray: mica surfaces, slate blue: Ca<sup>+</sup> ions, sienna: Ca<sup>2+</sup> ions. Water molecules are shown as spheres; red: in ion first hydration shell, blue: in second hydration shell, cyan: free water, and yellow: ice-like water.

statistics of ice-like clusters, we instead focus on clusters of hydrogen bonded water molecules on the various surfaces. We hypothesize that formation of such clusters could facilitate the birth of ice nuclei. To eliminate the effect of thermal fluctuations on our cluster determination, we evaluate the clusters based on hydrogen bonds that exist for more than 80% of the time within a 2 ns observation window of the simulation. Note that in this criterion, the hydrogen bonds can break and reform but need to exist for at least 80% of the observation window (similar to the history-independent hydrogen bonds described in ref 57). Thus, we eliminate the bonds that might break or form for short periods of time through thermal fluctuations.<sup>57</sup> Geometric criteria of an O–O distance less than 0.35 nm and an  $\text{O}_{\text{donor}}\text{--H}_{\text{donor}}\text{--O}_{\text{acceptor}}$  bond angle greater than  $110^\circ$ <sup>58</sup> were used to identify hydrogen bonds between water molecules. Only the interfacial water molecules (within 0.8 nm of the surface) were considered for this analysis. Clusters were identified using Cytoscape network analysis

software<sup>59</sup> after the hydrogen bonded water molecules were identified. Results presented here are averaged over ten 2 ns observation windows from 200 ns long MD simulations. We tested the effect of the length of observation windows (0.5, 1, 2, and 5 ns) and the cutoff values for hydrogen bond existence (70, 80, and 90%) on the distribution of the cluster sizes. These parameters change the probability of observing various cluster sizes, but the relative trend between the different cations remains the same. Thus, the discussion provided here does not change with these parameters. Further details of the calculations and parameter sensitivity analysis are provided in the SI.

The distributions of the cluster sizes are shown in Figure 3. Interestingly, we find that larger clusters are more likely to form in case of K<sup>+</sup>-mica compared to Ca<sup>2+</sup>-mica. For instance, the probability of observing cluster sizes >45 water molecules is  $\sim 0.002$  for Ca<sup>2+</sup>-mica, while it is  $\sim 0.036$  in the case of K<sup>+</sup>-mica. This indicates that hydrogen bonded clusters alone are

insufficient to explain the experimental observations. It has been argued that ions hinder ice nucleation, because the tightly bound water molecules in their hydration shells cannot orient to give ice-like configurations.<sup>12</sup> Thus, we calculated the fraction of free water in the interfacial region as well as in the clusters of hydrogen bonded water molecules, where free water is defined as those water molecules that do not belong to the first or second hydration layer of the ions. The bounds of the first and second hydration layers were determined from the ion–water radial distribution functions obtained from simulations of single ions in water (see the SI). The amount of free water in the interfacial region (Figure 3(b)) is higher in the case of Ca<sup>2+</sup>-mica than K<sup>+</sup>-mica. Furthermore, the fraction of free water in the hydrogen bonded clusters is also consistently higher for Ca<sup>2+</sup>-mica (Figure 3(c)).

To evaluate this trend across valency, we performed simulations of hypothetical ions—K<sup>2+</sup>, K<sup>3+</sup>, Ca<sup>+</sup>, and Ca<sup>3+</sup>. The choice was guided by two reasons: First, no well-calibrated force field parameters are available for Al<sup>3+</sup> on mica. Thus, we did not perform simulations of Al<sup>3+</sup>-mica. Second, simulations of the hypothetical ions provide insights into the effect of charge on water structure (and cluster formation), while the size of the ions is unchanged. Results for Ca<sup>*i*</sup>, *i* = 1, 2, 3, are shown in Figure 4(a) (see the SI for results for K<sup>*i*</sup>, *i* = 1, 2, 3, mica, Figure S10). We observe that the probability of observing large clusters of hydrogen bonded water molecules increases with the charge. In addition, the fraction of free water in the interfacial region as well as the fraction of free water in the hydrogen bonded clusters increases with the valency of the cation. In fact, the fraction of free water is <0.2 in the case of Ca<sup>+</sup> but increases to >0.6 for Ca<sup>3+</sup>. Snapshots illustrate that the hydration shell water molecules act as anchors for the formation of large clusters. Based on our observations, we surmise that the slow dynamics of the water molecules in the hydration shell of the higher valency ions<sup>60,61</sup> contributes to the longer lasting hydrogen bonds and facilitates the formation of larger networks of water molecules. The higher valency also results in a larger fraction of free water, which will have faster reorientation times than hydration shell water molecules, enabling them to adopt ice-like conformations. Thus, these clusters could serve as seedbeds for ice nuclei. The trends observed suggest that Al<sup>3+</sup>-mica would have clusters of hydrogen bonded water molecules with a greater fraction of free water. Based on our hypothesis, this would result in a higher ice nucleation rate near Al<sup>3+</sup>-mica relative to Ca<sup>2+</sup>- and K<sup>+</sup>-mica, as observed in the experiments. We note that K<sup>+</sup>-mica does not follow this trend, indicating that other factors beyond valency might be at play. This will be probed in future work.

We further analyzed whether ice-like structures were observed in the clusters described above. We used a tetrahedrality-based criterion<sup>62,63</sup> to identify ice-like clusters (see the SI for further discussion). We found clusters of ice-like water molecules originating from the hydrogen bonded clusters, providing further support to our hypothesis. Stricter criteria for identifying ice-like molecules, like those used in a recently developed PointNet-based method,<sup>64</sup> also found ice-like particles in the hydrogen bonded clusters (see Figure S12). Lastly, we performed microsecond long simulations of the 3 × 3 nm<sup>2</sup> surface for Ca<sup>2+</sup>- and Ca<sup>3+</sup>-mica. Larger clusters of ice-like particles consistently form on Ca<sup>3+</sup>-mica relative to Ca<sup>2+</sup>-mica (see Figure S11).

What promotes the larger clusters of hydrogen bonded water molecules on surfaces with higher valency cations? It can be

surmised that the regions on the mica surface without ions promote these clusters. To investigate this, we created surfaces where the ions were shifted to a limited section of the surface (see Figure S13), thereby creating a large region of the mica surface devoid of cations. We performed simulations of water at 243.5 K on these surfaces. We observed that large clusters of hydrogen bonded water molecules and large clusters of ice-like particles formed on these surfaces. The clusters were primarily located in the region devoid of ions on the mica surface (Figures S14 and S15). This suggests that the regions of the mica surface without ions could promote the clusters and ice-like configurations.

Based on the simulation results presented here, we propose the following mechanism through which ions can enhance heterogeneous ice nucleation—the water molecules in the hydration shell of the ions provide anchoring for the formation of large clusters of hydrogen bonded water molecules in the interfacial region. With increasing valency, the fraction of free water (i.e., not belonging to the first or second hydration shell of the ions) increases in these clusters. This allows them to adopt ice-like conformations, which are facilitated by the regions on the mica surface devoid of ions, and could enhance the likelihood of the appearance of ice nuclei. Indeed, previous studies indicate that nucleation can proceed through large clusters with low crystallinity as well as small clusters with high crystallinity.<sup>65–68</sup> The former scenario appears to be enhanced on the mica surface. Investigations combining the MD simulations presented here with enhanced sampling techniques like forward flux sampling,<sup>69–72</sup> and transition interface sampling<sup>73,74</sup> are currently underway to further explore this hypothesis. While our focus is primarily on the effect of valency on ice nucleation on mica, some additional observations are noteworthy. Within the divalent ions, we observe that Mg<sup>2+</sup>-mica has a lower  $J_{\text{het}}$  than Ca<sup>2+</sup>- and Sr<sup>2+</sup>-mica. In simulations, K<sup>+</sup>-mica has larger clusters of hydrogen bonded water molecules than K<sup>2+</sup>- and K<sup>3+</sup>-mica. These observations suggest that other factors such as ion size can also affect ice nucleation.

In summary, by taking advantage of ion exchange on a near defect-free mica surface, we study the effect of cations on heterogeneous ice nucleation. Our experiments show that mica surfaces with a multivalent cation exposed on the surface are better ice nucleators, in the order of Al<sup>3+</sup> > Ca<sup>2+</sup> ≈ Sr<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup>. The data show that the size of the exposed ion affects the nucleation rate; here, we have focused on the linked effects of valency and the fraction of the silica surface exposed to water. Simulations show that the multivalent ions on the surface are associated with clusters of hydrogen bonded water molecules anchored by the ions and with a higher fraction of free water. To our knowledge, this is the first study to show such a clear correlation in both experiment and simulation for a naturally occurring substrate. These are also the first experiments to show unambiguously that multivalent cations on a surface promote ice nucleation; our simulations of this motivate a new mechanism for ice nucleation, wherein the hydration shells of the ions anchor large hydrogen bonded water clusters with a high fraction of free water, which can adopt ice-like configurations promoted by the underlying regions of a mica surface devoid of ions. These clusters could be precursors to the critical ice embryo. The studies have implications in understanding the role of ions in heterogeneous ice nucleation relevant to atmospheric chemistry as well as for the design of anti-icing surfaces.

## ■ ASSOCIATED CONTENT

## SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c02121>.

Variability of Micas from Different Sources, Ion Exchange, Surface Area of Droplets, Characterization of (Lack of) Surface Roughness, Ice Nucleation Experiments, Heterogeneous Freezing Rate Coefficient, Molecular Dynamics (MD) Simulations, Calculation of Hydrogen Bonded Clusters of Water Molecules, Single Ion in Water Simulations, Microsecond Long Simulations on Smaller Ca-Mica Surfaces, Clusters on  $K^{i+}$  ( $i = 1, 2, 3$ ) Mica Surfaces, Ice-Like Water Cluster Identification; and Simulations of Mica Surfaces with Shifted Ions (PDF)

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## Notes

The authors declare no competing financial interest.

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