Response to Referee #3

We thank the reviewer for careful reading the manuscript and for the positive comments and suggestions. We have changed the manuscript accordingly. Please find below a detailed response.

RC: One substantial improvement to the paper would be to note the water activity for the various solutions used. While the emphasis is on pH and the resulting charge at the surface, noting aw would enable comparison with freezing point depressions as outlined in Koop et al. (2000). The statement on pg. 5, line 15 that the measured freezing temperature on Si wafers was the same for all pH solutions suggests that the water activity was very near 1 for all the solutions, but this should be confirmed.

AC: The median freezing temperature measurements for the pH solutions on a Si substrate could be used to estimate the water activity in the solutions. Applying Hildebrand and Scott equation (Miyawaki et al., 1997) and assuming temperature measurements accuracy of ± 0.2 K the water activity has been calculated to be within the range of 0.993 to 0.996. This confirms our statement that the solute effect on variation of the freezing temperature is negligible.

This information will be added to the "Results and Discussion" text of the revised manuscript.

NOTE: The modified text will be posted in a separate "Author Comment". This will be the revised manuscript with tracked changes upon comments from all referees.

RC: The principal conclusion that I draw from this paper is that surfaces can overtemplate water. This has been known for a long time. The authors cite Fletcher's paper from 1959, where he shows that increasing the order of water molecule's in a pre-critical embryo too much can actually decrease the probability of freezing. Fletcher showed that there is an appreciable entropic penalty for nucleation on the basal plane of silver iodide because it is polar. In contrast, the penalty for nucleation on a prism face is negligible. The prism face of silver iodide still acts as a template for the ice embryo, but the degree of alignment for the water dipoles is mitigated because ions of both signs are exposed. For this reason, I think the conclusion (page 9, lines 7-8) which reads "Apparently, charge-induced surface templating is detrimental for ice nucleation, regardless of the sign of the surface charge." should be softened. That statement may be true for this system, over this range of conditions, but I do not think it is appropriate to state it generally. (I concede that when taken together with the sentence just before that, this applies to corundum. Perhaps just add "on this surface" right after "ice nucleation" to reinforce the point.)

AC: We agree with the referee. This conclusion was overstated. The text is now softened to "....charge-induced surface templating is detrimental for ice nucleation on this particular surface, regardless of the sign of the surface charge."

RC: The conclusions in this paper suggest that for any pH other than 7, that the critical ice embryo forms in the second or third layer of molecules away from the surface. If the water molecules right at the surface are too tightly bound and/or constricted to allow them to adopt the ice lattice, doesn't that imply that other water molecules are the ones actually forming the embryo? It seems most likely

that it would be water molecules that were affected by the ordering imposed by the surface, but were perhaps still free to rotate and/or translate enough to adopt the ice lattice. Is there any indication of this in the data? (To be clear, I am not asking for an exhaustive re-analysis of the data. I am simply curious as to whether a signature like this could be gleaned from this data.)

AC: The reviewer raises a very interesting point. It is indeed not unlikely that the relatively mild templating occurring in water layers further from the surface (as evident from atomic force microscopy studies on similar systems) may be responsible for nucleation. Unfortunately, SFG does not allow to distinguish between contributions from different distances from the surface, so there is no reliable statement that we could make in this context.

RC: Pg. 2, lines 13-14: "The real influence of temperature and supersaturation on the interaction between water molecules and dust particle surface has not yet been explored." This is an overstatement. This has been extensively investigated. We don't have a definitive answer yet, but there are plenty of groups that have asked the question and contributed pieces to the puzzle.

AC: We totally agree that this sentence was an overstatement. It is replaced now by "The real influence of temperature and supersaturation on the interaction between water molecules and dust particle surface has been the focus of research since decades but remains debated."

Miyawaki, O., Saito, A., Matsuo, T., and Nakamura, K.: Activity and Activity Coefficient of Water in Aqueous Solutions and Their Relationships with Solution Structure Parameters, Bioscience, Biotechnology, and Biochemistry, 61, 466-469, doi: 10.1271/bbb.61.466, 1997.