Response to Referee #1

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

RC: 1. In the Introduction section, it is suggested to have a briefly introduction on the SFG spectroscopy for readers who are not experts.

AC: Thanks to the referee to point out the necessity of considering those readers who are not expert in SFG. We have included, in the introduction, a brief general introduction to the technique. In addition, we have expanded the description of the experimental setup in the "Experimental" section. These changes in addition to the notes in the SI will help the readers with different backgrounds to understand the usefulness of the technique.

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: 2. P1, L25-27, this statement is not correct as the heterogeneous ice nucleation could also occur below -38 degree C.

AC: we have changed the phrasing accordingly, and now state that "homogeneous nucleation occurs typically at temperatures below -38° C".

RC: 3. P1, L30-32, the sentence is overstated. It is not conclusive yet on the existence of actual active sites that induce ice nucleation.

AC: In some special cases (K-rich feldspars, ice nucleating bacteria) the evidence is conclusive. Nevertheless, we have tempered the sentence.

Original sentence: "Ice nucleation occurs preferentially at microscopic active sites and is dominated by the nature of these sites rather than by the average behavior of the surface"

Revised sentence: "It is suggested that ice nucleation occurs preferentially at microscopic active sites and is dominated by the nature of these sites rather than by the average behavior of the surface"

RC: 4. P2, L2, Peackhaus et al 2016a and 2016b are in ACPD and ACP, respectively, final form should be cited?

AC: We thank the reviewer for pointing out this omission. We have corrected this oversight in the revised version.

RC: 5. P3, L15, how _-alumina (0001) substrate was selected or treated before the freezing experiments, from which manufacturer?

AC: This information was provided on P4, L18-26 in the original manuscript.

6. P3, L38, and Figure 1, in the SFG setup, what is size of the sample area where the signal was collected, since the water drop in these experiments were large and freezing of ice could be initiated at the interface outside the sampling area. In addition, the _-alumina (0001) should be homogenous and well cleaned.

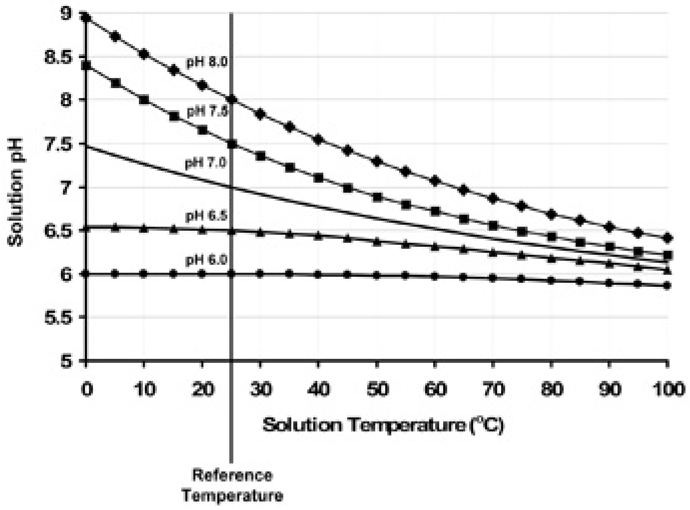
AC: The area sampled by the SFG beams is approximately 100 µm in diameter. It is indeed possible that nucleation occurs outside the sampled area, but since nucleation and growth across the droplet occur on a timescale short compared to the measurement time, this will not affect the results. We have included the information on the beam spot size in the caption of figure 1. The α-alumina (0001) was homogenous and well cleaned (details are giving in the experimental section, P4, L18-26 in the original manuscript).

7. P4, L20, what is “neat sapphire-c”?

AC: It is the *α-alumina (0001) cut. We probably should not have used double definitions. This has been corrected in the revised version.*

RC: 8. P4, L24-26, please provide more information to support this statement. What are the pH values at the temperature close to the point of freezing? P6, L10, what are the uncertainties for the pH of solutions used in SFG experiments?

AC: We assume that the referee means the sentence P5, L4-6 in the original manuscript where we speak about change of pH with cooling. It is hard to estimate the pH values at the freezing temperature. However, as stated in the link below, “the change in solution pH with temperature is controlled by the temperature-dependent dissociation constants. The effect of temperature on solution pH increases as the pH approaches the dissociation constant. For strong acids and bases, the dissociation constants are beyond the 0 to 14 pH range, so the primary effect is the water dissociation constant that is 1×10^{-14} at 25°C. Consequently, the effect of temperature is substantial for basic solutions” (see figure below).



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https://www.isa.org/standards-and-publications/isa-publications/intech-magazine/2009/december/web-exclusive-opportunities-for-smart-wireless-ph-conductivity-measurements/

In any case, the order of acidity strength of our solutions at room temperature doesn’t change at lower temperatures. For the experiments, what matters in the end, is the effect of pH on the surface charge. Since we measure the effect of surface charge on water structuring using SFG spectroscopy, the variation of the actual pH with temperature is not critical for the conclusions drawn from our work. We have included a brief discussion in the revised manuscript at the end of the Experimental section. We write:

“In addition, the pH is only tuned to change the surface charge, which is determined independently from the water alignment using SFG. Hence, knowledge of the precise temperature dependence of the pH is not required to correlate surface charge to freezing temperature.”

RC: 9. P8, L4-5, more detail description is needed for better understanding the use of this variable.

AC: This variable represents the strength of the oscillator normalized to the linewidth of the band, which provides a direct measure for the number density of the different surface groups. The sentence is revised in the new version of the manuscript.

Revised sentence: “Figure 4 depicts the amplitude divided by the width of each resonance ($\overleftrightarrow{A}_q/2\Gamma_q$). This variable represents the strength of the oscillator normalized to the homogeneous broadening of the band and thus is a measure for the number density of the different surface groups (Backus et al., 2012a; Li et al., 2015; Pranzetti et al., 2014).”

In addition, more details on the fitting variables are given now in the Introduction.

RC: 10. P8, L15, it is not clear what does “OH groups pointing with its H down to the bulk solution” mean? the OH groups near interface pointing away from the interface and into bulk solution?

AC: Yes. The word "down" is now replaced with "into" in the revised version

RC: 11. P8, for the most part of the discussion on surface charge or surface, it is not always clear referring to which surface or which side of the interface or water molecular layer. It will be informative and easy to understand these discussions if authors can provide an illustration.

AC: We thank the referee for this practical suggestion. In the revised version, we have included an inset in figures 3a, b, c and d to illustrate the net dipole orientations of water on the surface at different pHs (surface charges).

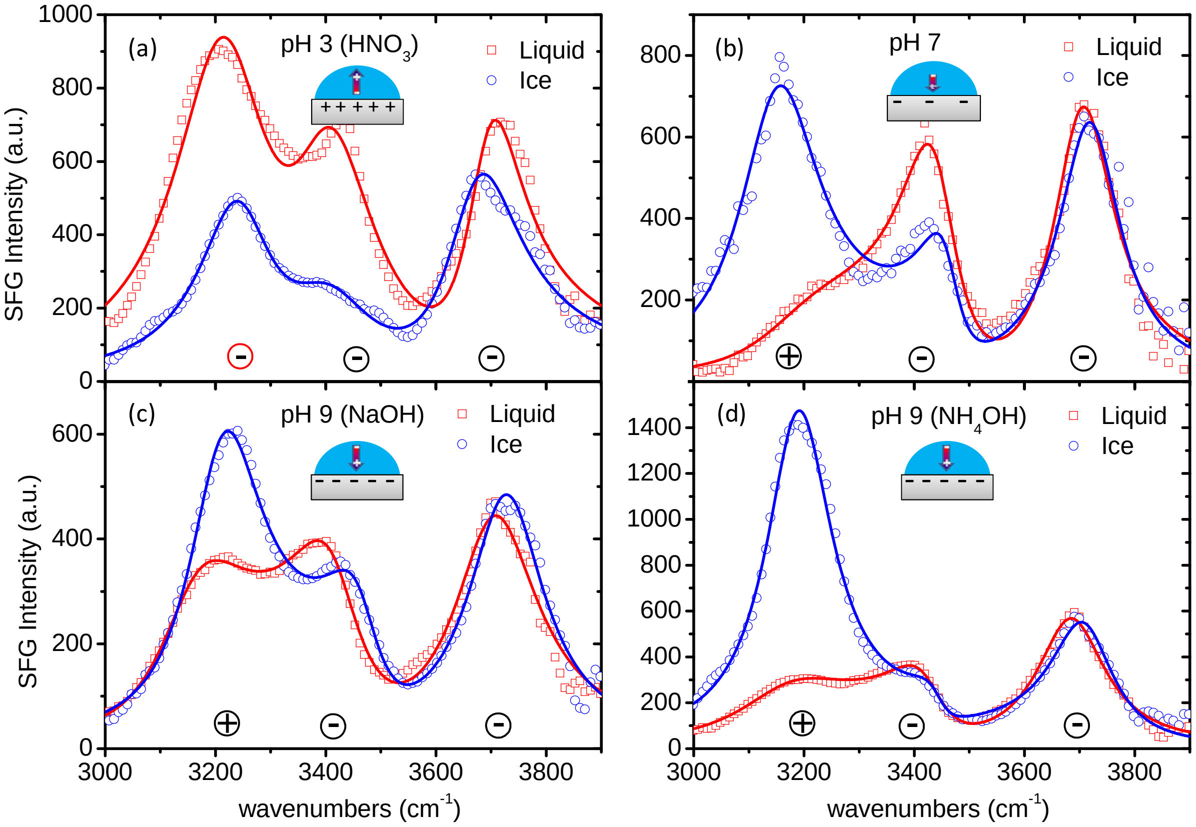

Figure 3. Measured (points) and fitted (lines) SFG spectra of α-Al2O3 (0001)/water interfaces collected in SSP polarization during the cooling cycles of (a) pH 3 - HNO3, (b) pH 7, (c) pH 9 - NaOH and (d) pH 9 - NH4OH. The spectra shown here are always the last and first spectrum right before (red) and immediately after (blue) the freezing event, respectively. The signs of the resonances are indicated by a circle with + or - sign (see SI for details). The insets in a, b, c and d illustrate the net dipole orientations (from O to H, as inferred from the low frequency peak) of water on the surface at different pHs (surface charges).

12. P9, L7-8, apparently, this sentence is over stated since it is possible that the conclusion is only applied for certain types of particles/surfaces and pHs.

AC: That's correct. We changed the sentence to "… charge-induced surface templating is detrimental for ice nucleation on this particular surface, regardless of the sign of the surface charge"