Response to Referee #2

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

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

RC: Introduction section needs text on atmospheric relevance of surface charge on the aerosol. How one can interpret/use these results in the context of understanding atmospheric ice formation. Some text describing how varying pH of droplets can be used to understand about the surface charge (interface between droplet and substrate) is required. Few details (OH group orientation etc) are already described on page 8.

AC: The surface charge of a metal oxide surface is pH dependent. The higher the pH with respect to the point of zero charge (pzc) of the surface the more negative is the surface and vice versa (Kosmulski, 2001, 2009). This process is controlled by the degree of protonation and deprotonation of the surface and the adsorption of dissolved ions. It is has been shown that the acidic particulates (e.g. SO_4, and NO_3) from anthropogenic sources decrease the pH values in cloud and rain water (Castillo et al., 1983; Scott, 1978). On the other hand, it was reported that alkaline particulates can be observed in regions where soil is rich with alkaline components, e.g. Ca and Mg, (Khemani et al., 1985b). In these regions high pH values were observed in cloud and rain water (Khemani et al., 1985a; Khemani et al., 1987).

Since immersion freezing is based on aerosol particles immersed in water droplets in a cloud for a certain time, we expect that their surface charge may change due to the variation in the droplet pH. Since surface charge is one of the surface properties which influence its interaction with water molecules, we believe that such results will help in understanding one of the not well explored parameters of ice nucleation in the atmosphere.

We agree with the referee, this part was not clear in the text. We have attempted to remedy this by including a discussion in the Introduction.

RC: Experimental: Describe rate of cooling and step size experiment. Not clear if it is cooled for one degree and hold T constant. Brief description of the cold-stage needs to be included. In section 3, it is mentioned that rate of cooling is 5 deg/min, this rate is different than described above. How droplets were visualized, using microscope? What is the typical size of droplet as you used different solutions or they remained constant, and can any images showing before and after freezing events be added in the main text. There is camera shown in figure 1. More details particularly magnification and model name are needed. How frozen fraction was calculated. How do you define a spectra?

AC: We thank the referee for pointing that the description of the cooling SFG experiment was not sufficient. The sample was cooled by one degree, e.g. from T to T-1 °C, with a rate of 1°C/min and hold temperature constant for one and half minute. Afterwards, a spectrum was collected. Each spectrum took 30 sec integration time. The sapphire prism was placed in a copper adaptor which was fixed on the silver block of the Linkam cold-stage. Detailed description and drawing of the assembly of

the SFG measuring cell can be found in (Abdelmonem, 2017). The cold-stage can perform controlled heating and cooling ramps, applied to the silver block, at rates between 0.01 and 100 °C/min. Temperature stability of the cold stage is better than 0.1 K.

***NOTE:** We have used two cold-stages, one for the supercooled SFG experiments and one for the "cold-stage" experiments. We used the term "cold-stage experiments" for those of the freezing assay. This may be misleading and let the reader confuse what we are talking about. So, in the new version of the manuscript, we have referred to the "cold-stage experiment" by "droplet freezing assay setup"*

We have changed the text in the manuscript accordingly.

In section 3, the cooling rate, of 5 °C/min, was that of the cold-stage experiments (not the SFG experiments). The cooling rate doesn't change the results, however, since the acquisition rate of the cold-stage experiments is 8 frames per second, i.e. much faster than that of the SFG, so that we could use higher cooling rate.

As mentioned in the manuscript, the typical droplet size in the SFG experiments was roughly 15µl and difficult to keep constant from experiment to experiment. The typical droplet size in the cold-stage experiments was (0.21 $\pm$0.07) nL and kept constant for all experiments and solutions. This is why we rely on the cold-stage experiments to determine the median freezing temperature. We have added new panels to Fig. 1 and Fig.2 with images showing droplets before and after freezing events for SFG and cold-stage experiments respectively.

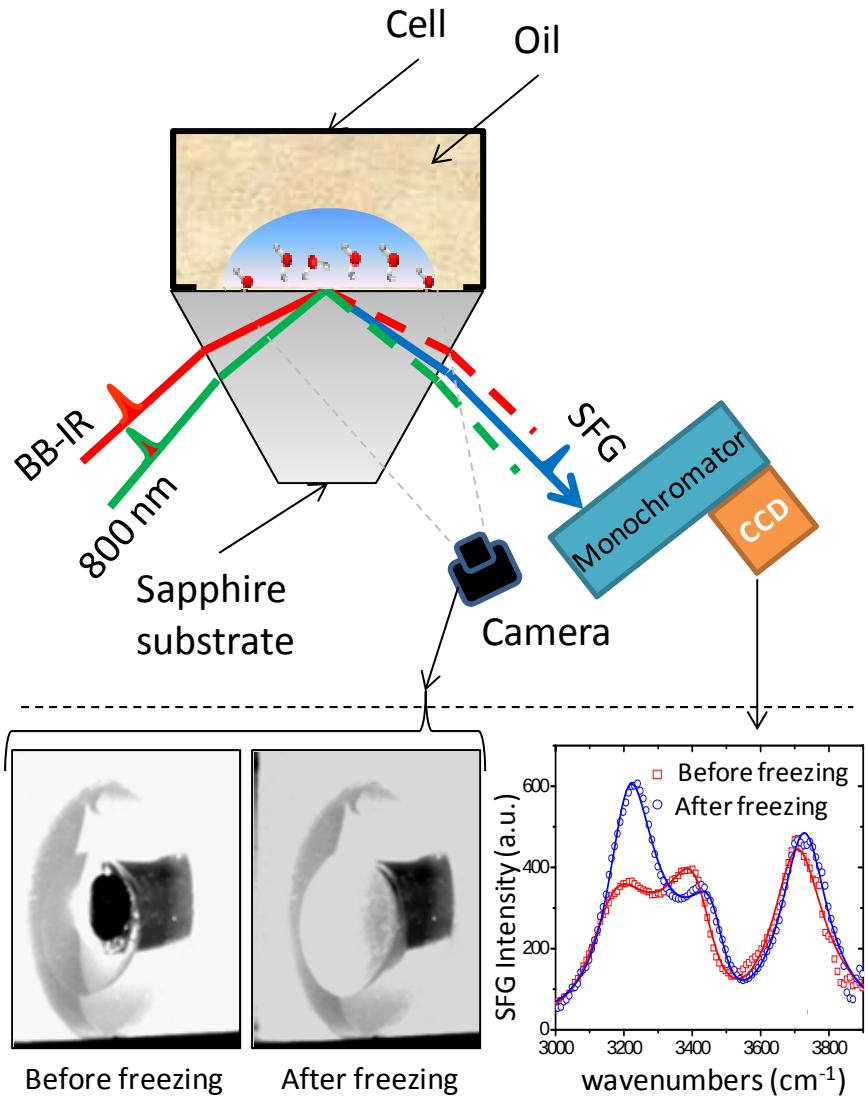

Figure 1. Upper panel: Schematic of the sample setup used in the SFG experiments. The SFG signal is generated in a co-propagating total internal reflection geometry at the spatial and temporal overlap of the incoming visible (800nm) and infrared (BB-IR) light, focused down to a ~100 µm diameter spot size. The camera (Guppy F-036 Allied Vision Technology with LINOS Macro-CCD Lens 0.14x (1:7) f4) is used to observe the droplet while placing it on the surface and filling the cell with oil, and to observe its status during the experiment. Lower panel: images of a typical drop on the substrate before and after freezing. Lower panel right: Typical water spectra before and after the freezing.

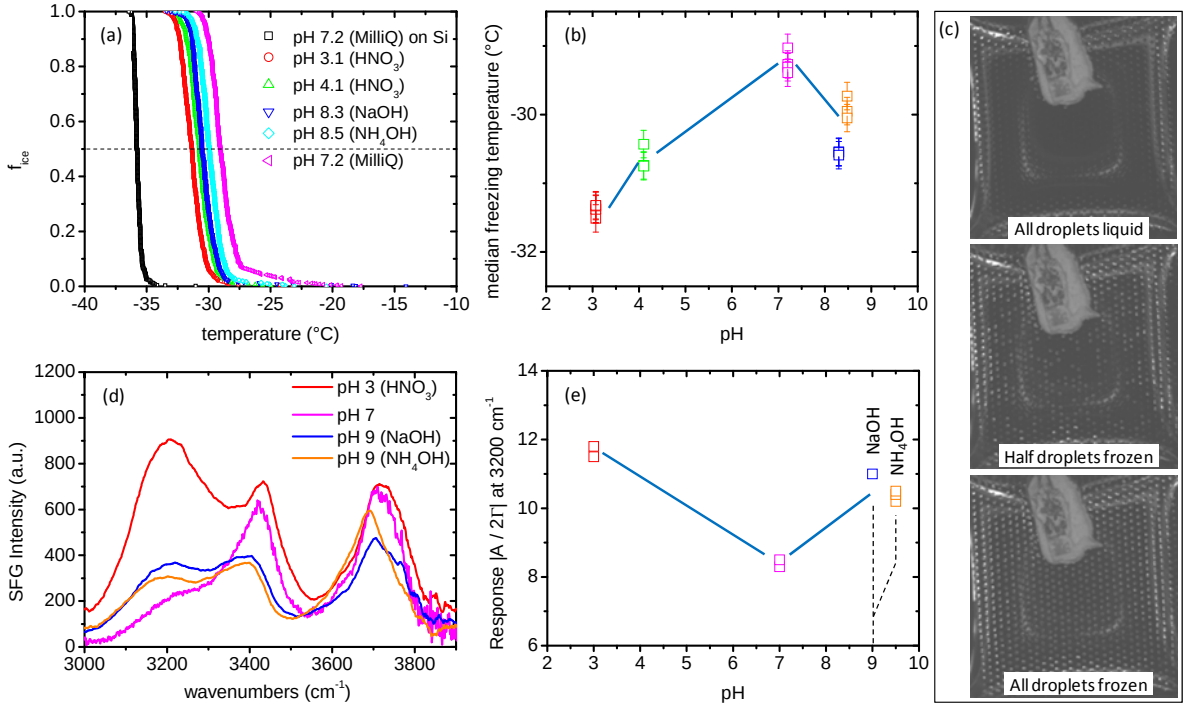

Figure 2. (a) Fraction of frozen droplets as a function of temperature of Sapphire (0001) surface in contact with different pH solutions. The black curve shows the data for water on a silicon substrate. (b) Freezing temperature as a function of pH of the different solutions for three independent experiments. ***(c)*** *Images of typical droplets on the substrate at different stages of the droplet freezing assay experiment. (d) SFG spectra of liquid water at the Sapphire (0001) surface, right before the nucleation event (see text for details); for fits, see Fig. 3. (e) Absolute value of the amplitude divided by width as a function of pH for the 3200 cm^{-1} resonance inferred from the data shown in (d). Different data points indicate data obtained from freshly prepared surfaces, recorded on different runs.*

Frozen fraction, in the cold stage experiments, is defined as the number of frozen droplets to the total number of droplets printed on the surface. In the SFG experiments, we probe only one droplet per run and the spectra at the solution water interface are collected as a function of temperature as described above.

The camera in figure 1 is Guppy F-036 Allied Vision Technology with LINOS Macro-CCD Lens 0.14x f4 and magnification (1:7). Specifications have been added to the caption of Fig.1

RC: Conclusion section is short and lacking many details. Describe what technique (because this is new about this work) was used, why alumina substrate was used and elaborate key results followed by the atmospheric implications. Remove any speculation and literature review text to add more clarity and improve readability.

AC: Indeed the conclusion was much shortened and assumed that the reader is familiar with the technique. The conclusion text has been expanded significantly to:

"The effect of surface charge on heterogeneous ice-nucleation ability of α-alumina (0001) surface has been studied by combining freezing assay and SFG characterizations. The droplet freezing assay

measurements allowed us to quantify the median freezing temperatures of the different solutions, while the SFG allowed us to probe the rearrangement of the water molecules at the interface on the molecular level. The use of an isolated water drop instead of a bulk solution in the SFG experiments ensured reaching the real heterogeneous nucleation point of the surface. Aluminum oxide can be used as a model surface of mineral aerosols and was reported as an atmospherically relevant aerosol. To study the effect of surface charge, which changes with the acidity or basicity of the cloud, on the immersion freezing, we studied the freezing of solution droplets of different pHs on the surface of α-alumina (0001). The selected range of pHs allowed us to study positive, neutral, and negative surfaces. The high pH solutions (positively charged surface) were frozen at temperatures higher than that of the low pH solutions (negatively charged surface) while the moderate pH (neutral surface) had the highest temperature of freezing defining optimum ice-nucleation conditions. The SFG spectra revealed substantial changes in the structure of the interfacial water upon freezing. Low pH solutions showed disordering while at moderate and high pH freezing yielded preferential orientation of water molecules. We found that water in contact with the α-alumina (0001) surface freezes most readily when the interfacial water molecules are not well-ordered which indicates that charge-induced surface templating is detrimental for ice nucleation on this particular surface, regardless of the sign of the surface charge. Understanding the role of charge on the ice-nucleation efficiency of metal oxides is important for heterogeneous ice nucleation in atmosphere, but may also impact other environmental and industrial applications."

RC: Page 2, line 14-15: Needs reference

AC: This part has been improved in the revised version and the references (Castillo et al., 1983; Scott, 1978; Khemani et al., 1985b; Khemani et al., 1985a; Khemani et al., 1987; Noone et al., 1988) are included.

The text is significantly changed to:

"Cloud pH may change depending on the concentration of acidic or alkaline particulates in atmosphere. It is has been shown that the acidic particulates (e.g. SO_4, and NO_3) from anthropogenic sources decrease the pH values in cloud and rain water (Castillo et al., 1983; Scott, 1978). On the other hand, it was reported that alkaline particulates were observed in the regions where soil is rich with alkaline components, e.g. Ca and Mg, (Khemani et al., 1985b). In these regions high pH values were observed in cloud and rain water (Khemani et al., 1985a; Khemani et al., 1987). The aerosol particle itself can have acidic or alkaline components absorbed on its surface which may dissolve in the water droplet and change its pH. The water droplet size affects the solute concentration (Noone et al., 1988) and hence pH. Since immersion freezing is based on aerosol particles immersed in water droplets in a cloud for a certain time, their surface charge may change due to the variation in the droplet pH because the surface charge of a metal oxide surface is pH dependent (Kosmulski, 2001, 2009). The higher the pH with respect to a specific pH, known as the point of zero charge (pzc) for which the surface is nominally neutral, the more negative is the surface, while the lower the pH with respect to the pzc the more positive is the surface. Surface charge is one of the surface properties which influence its interaction with water molecules, hence we believe that investigating the freezing-pH dependence will help in understanding one of the not well explored parameters of ice nucleation in the atmosphere."

RC: Page 2, Line 26-27: Elaborate and revise the sentence further.

AC: The original sentence is:

"Yang et al. have previously suggested from vibrational SFG spectroscopy that structured water at the interface may be required for efficient heterogeneous ice nucleation (Yang et al., 2011)"

The revised sentence is:

Yang et al. have previously suggested, from vibrational SFG spectroscopy at the water-mica interface for solutions with different molarities of sulfuric acid at room temperature, that structured water at the interface may be required for efficient heterogeneous ice nucleation (Yang et al., 2011). Yang et al. based this conclusion on the decrease in ordered water structure, at room temperature, and the corresponding reduced ice nucleation efficiency with the increase of sulfuric acid concentration in solutions in contact with the surface.

RC: Page 3, Line 1-3: Please add more specifics or details to understand why you want to take this particular approach.

AC:

Original sentence:

"In the current work, we ensure that we study specifically heterogeneous nucleation at the sapphire-water interface, by isolating water drops on the surface using silicon oil (Broadley et al., 2012; Hama and Itoo, 1956; Murray et al., 2011; Peckhaus et al., 2016)."

Revised sentence:

"To avoid early freezing which may be triggered by a different surface, as described above, in the current work, we ensure that we study specifically heterogeneous nucleation at the sapphire-water interface, by isolating water drops on the surface using silicon oil. Studying immersion freezing on isolated drops on a surface has previously been reported by several groups (Broadley et al., 2012; Hama and Itoo, 1956; Murray et al., 2011; Peckhaus et al., 2016). However, this is the first time where the freezing of an isolated drop on the surface is probed by SFG spectroscopy.

Page 3, Line 12: Revise the sentence.

AC:

Original sentence:

"For the first time in SFG experiments, the freezing of an isolated drop on the surface is probed."

This sentence was deleted after revising the former one (Page 3, Line 1-3 in the original manuscript)

RC: Page 4, Line 10-11: Revise the sentence.

AC:

Original sentence:

"The heterogeneous nucleation temperatures mentioned in the results and discussion section are those obtained from the cold-stage study."

Revised sentence:

"The heterogeneous nucleation temperatures reported in the "Results and Discussion" section were obtained from the cold-stage results shown, e.g., in Fig. 2a "

RC: Page 5, Line 11: pH 7.2 – is this water.

AC: Yes

Page 5, Line 26: : : :investigated: : :

AC: Corrected

RC: Page 8: Line 27. Can Fig 2c and d be included in Fig 4. These figure panels are not described until this point.

AC: One of the main points of the manuscript is the anti-correlation between median freezing temperature and SFG intensity; it is for this reason that we think it is important that panels 2b and 2d appear in one figure.

RC: Minor comments: Peckhaus 2016a and b are similar.

AC: Corrected

RC: Provide a space between references included within the text. Also a space is needed after 'period' located at the end of the sentence. See page 3, Line 10, 11.

AC: Done

RC: Supplement section is incomplete.

AC: We are not quite sure what the reviewer is referring to…

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