Point-to-point answers to the comments of Referee #2

The author would like to thank the referee for his time reading the manuscript and for the recommendations and suggestions.

RC: (1) The author stated that "the SHG signal is originated from the nonresonant OH stretching vibrations at the interface". (Line 8 on page 4) This statement does not make sense. A nonresonant signal is by definition not to be associated with a particular vibrational mode.

AC: Indeed the statement "the SHG signal is originated from the nonresonant OH stretching vibrations at the interface", in page 2 line 19, is incorrect. The author has clarified this oversight failure in an earlier quick Author Comment on the discussion form because he expected that it may influence the general evaluation of the referees and the readers. This wording failure should however become clear to the reader when reaching to page 6 line 9 when the author started discussing interpretations in terms of "electric dipolar contribution" as an origin of the signal.

This oversight will be corrected in the revised version.

RC: (2) Mica is birefringent. As the laser beam goes through the mica, its polarization may not be linear any more. "The advantage of using SM polarization combination is its dependence on only one non-vanishing nonlinear susceptibility tensor element (line 33 on page 3)" is likely not what has happened in the experiment.

AC: Before starting the measurements, the polarization of the water SHG signal was analyzed and found to have the expected maxima at S and P polarizations. (Will be explained in the revised version)

RC: (3) The index-matching gel of unknown chemical composition is a concern. While the gel helps to obtain the TIR condition, the gel/mica and gel/sapphire interfaces may produce SHG signal. The author may want to look into the freezing temperature of the gel too.

AC: The author would like to thank the referee for pointing out this missing information.

The IMG was obtained from Thorlabs (source and specifications will be mentioned in the revised version). The Flash point is > 220 °C. However, the freezing point is not specified by the manufacturer but tested in the lab. At least the gel was not frozen until -45 °C.

As already mentioned in the original manuscript, P. 3, L. 11 – 13, the influence of the temperature dependence of the optical properties of the index-matching gel, sapphire prism and mica on the SHG signal was studied before starting the series of measurements. There was no significant effect of the changes in the optical properties of these media on the detected signal within the range of freezing temperatures observed in the study. The Figure below (Fig. R2.1) shows the SHG at mica-N_2 gas interface in the range of freezing temperatures mentioned in the manuscript.
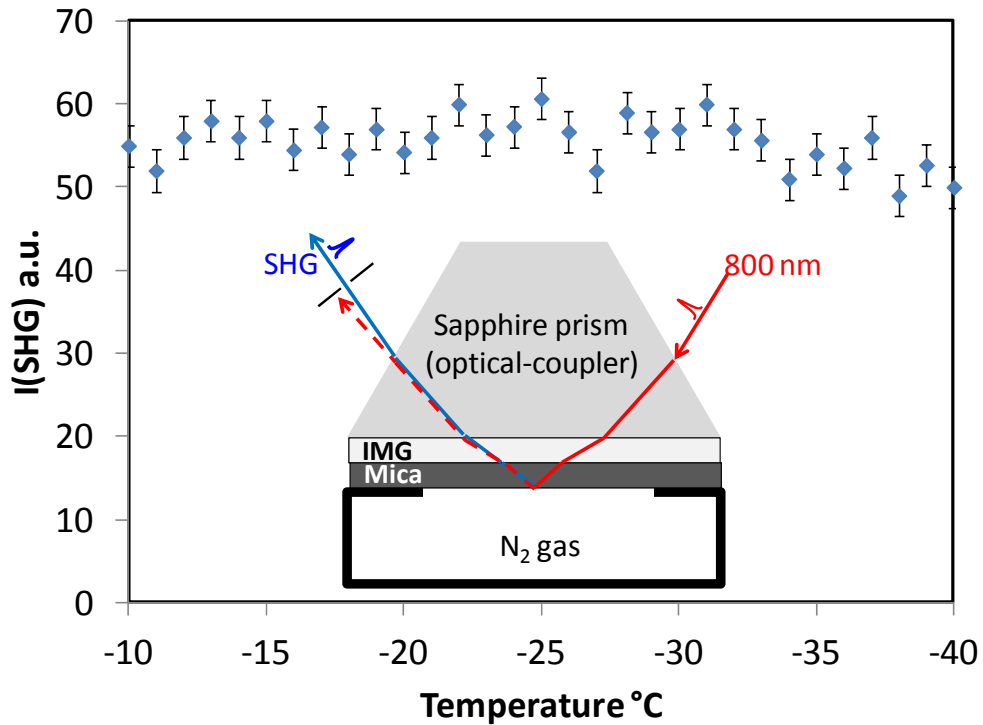
Figure R2.1: SHG at mica-N_2 gas interface in the range of freezing temperatures observed in the study. The cell, shown in Figure S2 in the original SI, was filled with ultrapure N_2 gas (99.9999 %).

Figure R2.1 and the corresponding text will be added to the SI of the revised manuscript.

(4) Figure 1 and 2 should be real-time plots similar to Figure 3.

During the experiments, except for those of Figure 3, the signal was collected, averaged and stored as a function of the state of condensation, deposition, freezing, or formation of bulk. There was no need to record the data as a function of time. However, Fig. 3 is a special case because it was intended to report on the detected transient ice formed upon immersion freezing. Anyways, in the Figure below (Fig. R2.2), I show some screen shots of typical SHG signal and temperature changes in time, and show the points where the signal was collected and averaged.
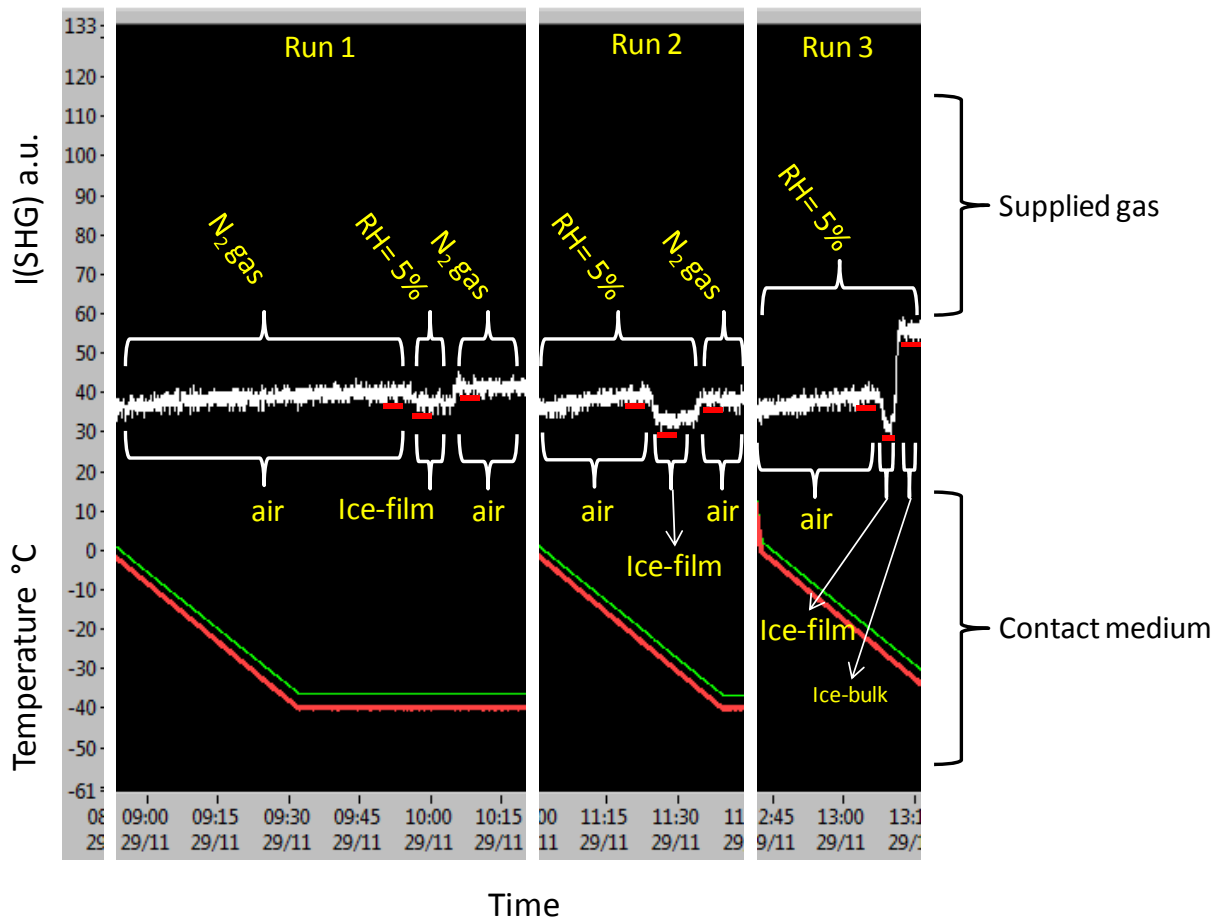
Figure R2.2: Screen shots of typical signal and temperature changes in time during arbitrary cooling processes. The white line shows raw SHG data. The short red dashes below the SHG data show the points where the signal was collected and averaged. The red and green lines show the temperatures of the sample bottom and sample top respectively.

Figure R2.2 shows three examples of three arbitrary experiments (Runs):

Run1: The cell was purged continuously with N$_2$ gas while cooling the sample down to -40. There is a small gradual change in the signal due to the changes in the temperature dependent optical constants. The cell was then purged with humid air which resulted in a formation of an ice-film by deposition. Finally, the cell was purged again with N$_2$ gas which resulted in sublimation of the ice film.

Run2: The cell was purged with humid air (RH=5%) while cooling the sample down until the formation of an ice film and then the cell was purged by N$_2$ gas which resulted in film sublimation.

Run3: The cell was purged with humid air (RH=5%) while cooling the sample down until the formation of an ice film. Purging the cell with humid air was continued until the formation of bulk ice.

All experiments of deposition freezing were done in a similar way as described above. Figures 1 and 2 in the manuscript show the averaged signal at each event and the error bars on the figures show the fluctuation in the data points among all repeated experiments.

This part will be included in the revised manuscript.

(5) Terms such as "liquid (film)", "liquid (bulk)", "transient ice", "stable ice" used in Figure 2 should be experimentally defined.

This is a very good point and was missing in the original manuscript. The border between a film at the solid-air interface and a bulk (ice or water) was defined experimentally by the point where the intensity of a TIR reflected light from the solid-air interface drops due to the violation of TIR condition when the refractive index of the contact medium changes drastically from that of air ($n_a=1$) to one of those of water or ice ($n_{w\ or\ i} > 1.3$). Whether the contact medium is ice or liquid, this was defined by the strong light scattering, observed at a CCD camera placed close to the detection path (Fig. R2.3), when the ice is formed. This camera was missing in Fig. S1 in the SI of the original manuscript and will be added in the revised version.

After immersion freezing, there was a rapid increase in the signal and then slow decrease. The maximum after the rapid increase was defined as the "transient ice" data point. After reaching a maximum, the signal was decreasing with time until stabilized after certain time. This stabilized signal was defined as the "stable ice" data point
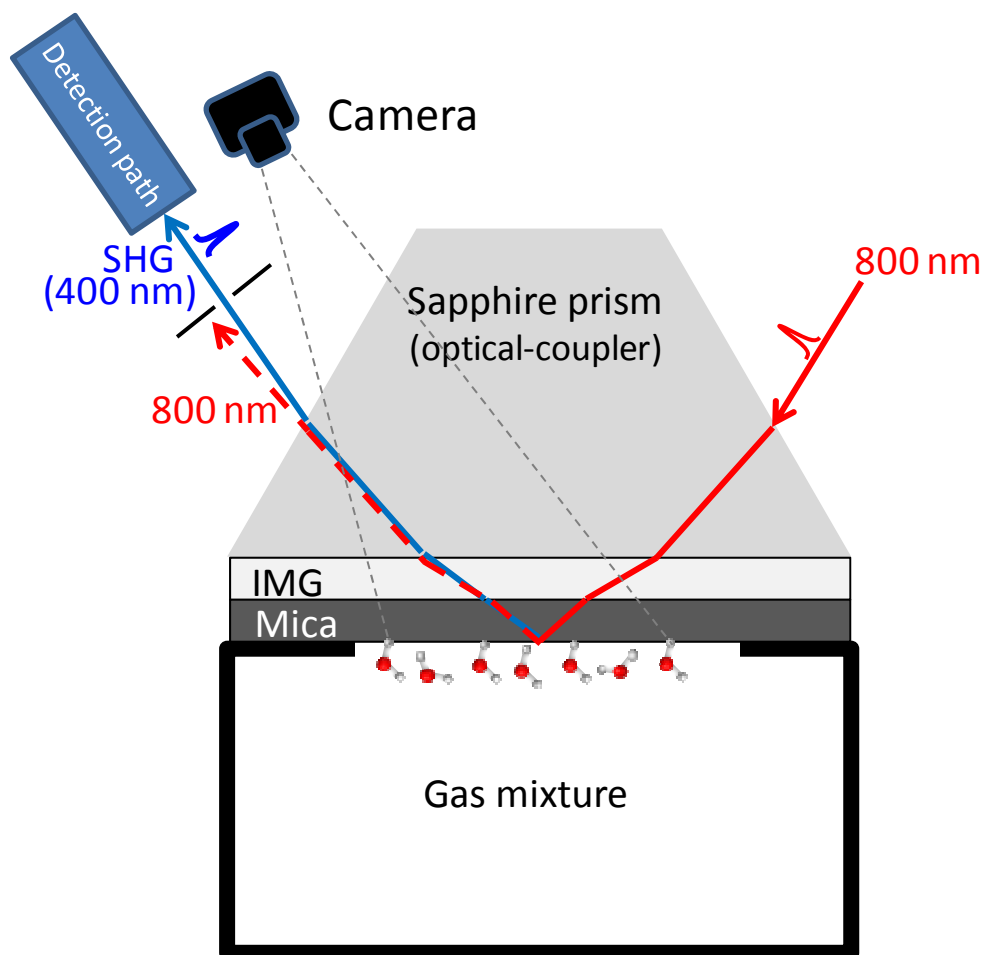

Figure R3.3: The same as Fig. S1 but with including the CCD camera (Guppy F-036 Allied Vision Technology with LINOS Macro-CCD Lens 0.14x (1:7) f4)

The text in the manuscript and SI will be changed correspondingly.

(6) The cooling rate dependence should be investigated.

The results and conclusion were limited to the given cooling rate. Investigation of the influence of cooling rate was not planned in this work. However, the cooling rate dependence was tested in immersion freezing on sapphire surface using SFG in different study (under publication). It was found that the different cooling rates do not change the spectroscopic results.

(7) One fundamental issue of SHG is that SHG intensity can be difficult to interpret. For example, why is there a _80% SHG drop from the "air" to the "bulk liquid" in Figure 2? What does the SHG measure?

This is indeed a good question. The SHG signal is mainly produced by all polarizable species within the SHG-active region as long as the inversion symmetry is broken. The polarizable species at the surface are the water molecules and the surface OHs. The contribution of water molecules are limited by the penetration depth. The experiments were carried out in total internal reflection geometry with an incident angle of 15° from air to the prism side*. The SHG-active region is limited by the penetration depth of the evanescent wave in the second medium (air, liquid water or ice). The calculated penetration depths are about 130 nm, 328 nm, and 253 nm for air, liquid water bulk, and ice bulk as contact media respectively. (This part will be added to the discussion in the revised version).

* Note: there was a typo in the corresponding incidence angles at the interfaces in the original manuscript. This will be corrected in the revised version.

The 80% drop of the signal was explained in the final paragraph of page 6 in the original manuscript. However, the author agrees with the referee that this part was not well explained in the manuscript. Here is a more detailed discussion:

"Since SHG response reflects the overall arrangements of the polar entities at the interface between two isotropic media (Fordyce et al., 2001; Goh et al., 1988; Luca et al., 1995a), signal intensity is expected to increase when a single (or few non-centrosymmetric) layer(s) of water or ice is(are) formed at the surface. It is clear from Figures 1 and 2, however, that SHG intensity decreases upon deposition freezing, condensation, and growth of liquid layers by diffusion. This can be explained by phase interference between two signals originating from two different interfacial groups of opposite dipole moments: surface-OH points out of the surface and water points to the surface. A cleaved mica surface exhibits a disordered hexagonal arrangement of Si- (partly Al-) doubly coordinated O atoms in the outermost layer (Ostendorf et al., 2008). As an aluminosilicate mineral, this surface may protonate immediately in contact with the ambient air (forming silanol and aluminol groups at the surface). In this case, the mica-dry air signal can mainly originates from the surface hydroxyl groups (dangling−OH) which are naturally pointing out from the surface. Since mica surface is inherently negatively charged, the interfacial water will point to the surface and thus have a phase opposite to that of the surface−OH groups, as was reported by Shen and co-workers (Zhang et al., 2008) on negatively charged surfaces. This well explains the ostensible decrease in the overall signal upon deposition and condensation. When the surface of mica is covered with bulk water of a pH (~ 7) relatively higher than the point-of-zero-charge (pzc) of the surface, it becomes totally deprotonated (no free−OH). Under this condition the SHG signal comes exclusively from the interfacial water molecules between the surface and liquid-bulk. This defines a new reference of the signal generated at the new interface (liquid-solid rather than gas-solid). The increase of the signal afterwards indicates more structuring of either the interfacial water before freezing, like shown in (Abdelmonem

et al., 2015) or the interfacial ice after freezing like shown here. It is worth to mention that, the presence of free surface hydroxyl groups on cleaved mica is poorly discussed in literature. Miranda et al. have indirectly referred to their (hydroxyl groups) existence in their work on mica-water vapor interface using SFG (Miranda et al., 1998). They used deuterated water (D_2O) in the SFG experiments to avoid confusion of the hydroxyl stretch modes in the spectrum from both water and mica. Maslova et al. have discussed it a bit explicit in their work on surface properties of cleaved mica and they assumed that hydroxyl groups of the basal plane are not reactive (Maslova et al., 2004). One in four Si in the tetrahedral layers of mica is randomly substituted for Al (Christenson and Thomson, 2016). The result is that the majority of the surface hydroxyl groups of a cleaved basal plane are silanol and therefore the surface deprotonation is mostly determined by silica. The pzc value of silica lies between its respective isoelectric points (pH 2-3, (Hartley et al., 1997; Iler, 1979; Scales et al., 1992)) and hence the silanols in silica (Si-OH) deprotonated totally in the presence of neutral water."

The final paragraph in the manuscript will be changed correspondingly.

(8) Some conclusions made in the manuscript are not well supported by the SHG data. For example, line 8 on page 4: "The coincidence of the SHG signals of the thin ice film formed in DF2 and DF3 indicates identical structuring of water on the surface in two step deposition freezing regardless of the onset temperature." SHG simply cannot provide the structural information of water. The same SHG intensity does not necessarily mean the same water structure.

SHG is electric dipole forbidden in the centrosymmetric bulk media and therefore SHG has been widely used as the spectroscopic probe for molecular orientation, structure, and spectroscopy of different interfaces (Richmond et al., 1988; Goh et al., 1988; Goh and Eisenthal, 1989; Zhao et al., 1993; Conboy et al., 1994; Luca et al., 1995b; Eisenthal, 1993; Eisenthal, 1996; Antoine et al., 1997; Fordyce et al., 2001; Zhang et al., 2005; Pham et al., 2017). The SHG response relates to the overall arrangements of the water (or more general interfacial) entities (Goh et al., 1988; Luca et al., 1995b; Fordyce et al., 2001). However, probably the sentence "... indicates identical structuring..." is overstated. This sentence will be tempered in the revised manuscript.

Finally the author would like to thank the referee again for his valuable comments which helped to improve the manuscript. The author would also like to emphasize that the aim of the work was to demonstrate the worthwhile of investigating different ice nucleation processes and water structuring upon freezing on the molecular-level using SHG spectroscopy. The manuscript is considered as a cornerstone of future complementary studies involving other surfaces, and other techniques to precisely investigate the layer thickness, the surface morphology effect, the cooling rates ...etc. Probably a better title of the manuscript could be "Direct molecular level characterization of different heterogeneous freezing modes on mica – Part 1"

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.

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