RC: 1) The document is in a poor state of editing, with many grammatical errors that substantially distract from evaluating it.

AC: As the author is not a native English speaker the manuscript was revised by the "language service department" at the KIT before submission. Anyways, if the journal requires professional lingual editing by the journal itself or somewhere else, the author will certainly consider that.

RC: 2) The document contains false statements re: the origin of the SHG response. The system is probed off resonance, which means that all terms contributing to the response are purely real. Statements like "the SHG signal is originated from the the nonresonant OH stretching vibrations at the interface" are simply incorrect and reflect a fundamental misunderstanding of the signal generation process by the author. The signal is produced by all polarizable species within the SHG-active region. Unfortunately, the SHG active region is neither characterized nor defined in this work, making the signal interpretation at best appear as creative writing.

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. However, it should be clear that this is not a "fundamental misunderstanding of the signal generation process by the author" but rather an oversight, wording failure, mixed with the definition of water stretching signal in SFG. This should 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)

The polarizable species at the surface are the water molecules and the surface OHs. 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.

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

RC: 3) The interference that is briefly alluded to in the final paragraph is not quantified, even though the changes in the SHG responses shown in the three figures are produced by said interference, in addition to changes in surface potential that occur during the experiments. The author is encouraged to read and understand the recent work on nonlinear optical interference in thin-layer systems by Massari (J. Phys. Chem. Lett., 2016, 7 (1), pp 62–68) and on the chi(2) and chi(3) phase interference by Wang, Geiger, and Eisenthal (Nature Communications, 7, 13587, 2016).

AC: The referee speaks here about the "Two-Interface Problem" and refers to the work of Massari (J. Phys. Chem. Lett., 2016, 7 (1), pp 62–68). Certainly, the author ignored this effect, and the mentioned paper is not relevant to the presented work, for the following reasons:

1. *The mentioned work describes the interference between two resonant signals generated at the two interfaces (on two sides) of a well controlled thin-film prepared for an organic thin-film field-effect transistor. <u>The two interfaces are well within the focal volume of the pump beams.</u>*

2. *The signal interference occurs between two oppositely oriented groups, of the same type, at both sides of the thin-film*

3. *In contrast, ice (or liquid) -film growth on a surface is completely different. The growth depends mostly on the atmosphere saturation for a given temperature and pressure, and the thermal conductivity of the substrate material. When the air is supersaturated, the growth rate is very fast after nucleation and is very difficult to control.*

4. *In the presented work the second interface (ice-air or water-air) is not within the focal volume of the pump beam (please remember that the signal in the presented work was collected in TIR geometry) and the non-resonant signal is coming exclusively from the first interface (water-solid or ice-solid) due to the following: Under the thermodynamical conditions of the presented work, the ice (or water) layer thickness exceeds 1 μm within 1 sec which is far beyond the penetration depth of the evanescent field (see values above). The author would like to draw the attention of the referee to a related details on the growth velocity of a solidification front normal to the ice surface in the Supplementary Materials of the work of one of our KIT groups (Kiselev et al., 2016). These calculations were taken from numerous works of Libbrecht (Libbrecht, 2003; Libbrecht, 2005). These articles will be cited in the revised version along with the corresponding discussion. For calculations of growth due to condensation, the reader is referred to the Aerosol Calculator Program (Excel) by Paul Baron which is based on equations from (Willeke and Baron, 1993; Hinds, 1999; Baron and KlausWilleke, 2001). These will also be cited in the revised version with the corresponding discussion.*

The referee has also referred to the great paper on Phase-referenced nonlinear spectroscopy of the α-quartz/water interface by Wang, Geiger, and Eisenthal (Nature Communications, 7, 13587, 2016) which shows that the absorptive (imaginary) and dispersive (real) terms of chi(2) chi(3) may mix. Again the author sees no significant relevance[†] to the presented work for the following reasons:

1. *Regardless of the interesting role of the anisotropy of α-quartz to generate phase-referenced SHG signal, the mentioned paper discusses two extreme pHs (pH 3 and pH 11.5 which have 8.5 orders of magnitude hydrogen ion activity factor) and different ionic strengths. In contrast, in the presented work, neither the pH nor the ionic strength was changed. The author used deionized water with pH ~ 7.*

2. *The change of pH with temperature is very trivial for neutral water (e.g. from pH 7 at 25 °C to pH 7.47 at 0 °C). In addition, this does not mean that water becomes more alkaline at lower temperatures because in the case of pure water and according to the Le Châtelier's principle there are always the same concentration of hydrogen and hydroxide ions and hence, the water is still neutral (pH = pOH) even if its pH changes. The pH 7.47 at 0°C is simply the new reference of neutral water pH at 0 °C.*

3. *Assuming that the surface potential has an influence on the background signal, this will not change even if the pH changes with temperature. It was found that the surface potential*

values of the muscovite basal plane (the surface under study) is pH independent in the range from pH 5.6 to 10 (Zhao et al., 2008).

† Probably the author should have mentioned the chi(3) mechanism for interfacial potential-induced SHG which is an important factor in such experiments and has been originally established by the group of Eisenthal (Zhao et al., 1993; Ong et al., 1992). This will be considered in the revised manuscript.

RC: 4) The work requires additional information on ice layer thickness, on the uniformity of the ice layers across the 2 mm laser spot, and it requires verification wether the SHG signal depends quadratically on input power. The polarization states of the SHG responses during the various stages of the experiments should also be determined.

AC: As mentioned above, the ice layer thickness exceeds the penetration depth of the evanescent field at the time when the signal was collected. The exact thickness cannot be determined in this setup, however it does not change the probed signal. (Will be mentioned in the revised manuscript)

At the deposition, and also condensation, events the signal was not collected until it became stabilized and therefore, it was assumed that the ice layer is uniform at the surface covered by the laser spot. (Will be mentioned in the revised manuscript)

It was verified that $I(400) \propto I(800)^2$. (Will be mentioned in the revised manuscript)

As mentioned in page 3 line 26m, the SHG was collected S-polarized.

RC: 5) Connections of any results and/or discussion presented to the scientific motivation provided are not made except for two generic statements ("They provide novel molecular-level insight into different ice nucleation regimes..." and "Investigating the structuring of water molecules upon freezing next to solid surfaces is crucial to many scientific area...") which are broad and sweeping. In sum, this work is far too preliminary to be reconsidered. As such, this reviewer recommends rejection, with the hope that the author will write a new document that addresses the points made above in a new submission elsewhere.

AC: Certainly, 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. This has been successfully demonstrated although conclusive description of ice nucleation on mica has not been obtained which is not expected at this stage. The manuscript is more like a "letter" or "short communication". However, ACP does not provide an individual category for particularly short papers because the process of peer review and publication in ACP is inherently efficient and rapid for all types of manuscripts without artificial length restrictions. A complementary study involving other techniques and sophisticated studies will follow this paper which is considered as a cornerstone for future studies. 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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