The Referee has raised some important points which we gladly clarify. We list here our answers to the Referee's questions structured along the relevant topics.

SHG in more details and SHG vs. SFG

The second-harmonic generation (SHG) technique can provide insight into the interfacial molecular properties at an interface between two isotropic media. Its response relates to the overall arrangements of the water (or more general interfacial) entities. The resulting signal arises from the surface dipole contribution as well as from some contribution of higher-order terms from the bulk, the electric quadrupole and the magnetic dipole terms. No vibrational states are excited here (fundamental at 800 nm, SHG at 400 nm). Non-resonant SHG provides orientational measurement of the non-straddle-type of interfacial water molecules (Zhang et al., 2005). Shen's group demonstrated systematically in the early 1980s that surface SHG can be treated as radiation from a nonlinear polarization sheet induced by an incoming wave at the surface, besides comparable quadrupole contributions (see (Shen, 1989) and other references from Shen therein). The dipolar part should strongly depend on the absolute orientation of the water molecules (which belong to C_{2v} symmetry), whereas the quadrupolar contribution should only be weakly dependent on this (Goh and Eisenthal, 1989;Goh et al., 1988). In short, the sum over the surface dipole moments is structure dependent, the higher the ordering of the molecules the higher the overall dipole response.

SFG on the other hand includes scanning over the different vibrational bands of the species at the interface. In case of water, one can observe the development of the so-called "ice-like" and "liquid-like" water components at 3200 and 3420 cm^{-1}, respectively. Band positions and widths are related to the bonding-debonding states (Du et al., 1993;Richmond, 2001). This will yield deeper insight into how the water molecules behave at the specific interface under cooling. In that sense, SFG allows more detailed information on the interfacial water molecules.

Possibility of different source of signal increase on Mica

SHG is monolayer sensitive. Secondary layers may have an indirect effect on the signals by affecting this first layer. However, this would not change our interpretation that the surface can induce water structuring upon temperature change. Other sources were also considered. As written on page 5270 - line 10, the temperature profiles "were applied to sapphire/N2 and mica/N2 (i.e. solid/gas) interfaces to assure that the change in the refractive indices of the substrates and IMG with temperature has no significant effect on the resulting SHG signal in the range of temperatures applied in this work".

The temperature difference between both signal drops

We cannot attribute the temperature difference between both signal drops to anything since we know that ice formation is initiated somewhere else and furthermore here we do not discuss the onset temperature at all. We believe and report (and here we rely on the camera) that the ice

formation is initiated at a joint between the measuring cell and the surface (mica or sapphire). This we aim to avoid with the new sample/cell design.

Is a pre-structuring of the water layer on mica the only interpretation for the earlier freezing on mica?

So far we have no alternative interpretation and our suggested interpretation is confirmed by the theoretical work of (Lupi et al., 2014;Lupi and Molinero, 2014) on similar systems. The planned SFG experiment might further help to confirm or deny this interpretation.

Is the area enclosed by the vertical trend line of the laser signal during freezing and the curve alteration due to the latent heat is proportional to the mass of ice being formed? For what reasons should both areas be the same as in your experiment?

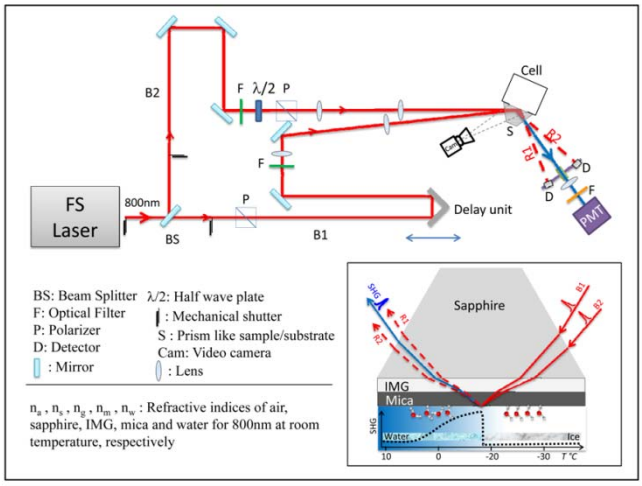
That's a good point. The vertical drop corresponds to the difference between signals of water/substrate and ice/substrate interfaces. The latent heat is related to the amount of water frozen at the interface which has the same contact area in both cases (cell opening), same sensor positions, same cooling source. There can be small differences due to the difference in material properties involved in the heat transfer from the interface to the sensors (like substrate itself, and IMG in case of mica) and the exact positions of the temperature sensors. We will keep this point in mind in future experiments and make sure that identical conditions prevail to quantify the amount of water frozen immediately.

Rewrite the results and discussion section giving the focus more on the pre-ordering.

In the light of the comments above, our pre-activation interpretation should be clear. We will try to include these notes in the final version of the manuscript.

Figure 1

The symbol of the lenses is included in the legend. However turning the inset upside down doesn't result in the same orientation that is shown in the schematic presentation. The inset includes a schematic plot which illustrates the behavior of the signal. When we tried to rotate the inset, the output was awkward.


B2
F λ/2 P
Cell
S
F
P
FS Laser
800nm
BS
B1
Delay unit
D
D
F
PMT
BS: Beam Splitter
F: Optical Filter
P: Polarizer
D: Detector
: Mirror
λ/2: Half wave plate
: Mechanical shutter
S : Prism like sample/substrate
Cam: Video camera
: Lens
n_a , n_s , n_g , n_m , n_w : Refractive indices of air, sapphire, IMG, mica and water for 800nm at room temperature, respectively
Sapphire
IMG
Mica
Water
Ice
SHG
10
0
-20
-30
T °C

References

Du, Q., Superfine, R., Freysz, E., and Shen, Y. R.: Vibrational spectroscopy of water at the vapor/water interface, Phys. Rev. Lett., 70, 2313-2316, 1993.

Goh, M. C., Hicks, J. M., Kemnitz, K., Pinto, G. R., Heinz, T. F., Eisenthal, K. B., and Bhattacharyya, K.: Absolute orientation of water molecules at the neat water surface, J. Phys. Chem., 92, 5074-5075, 10.1021/j100329a003, 1988.

Goh, M. C., and Eisenthal, K. B.: The energetics of orientation at the liquid-vapor interface of water, Chemical Physics Letters, 157, 101-104, http://dx.doi.org/10.1016/0009-2614(89)87216-1, 1989.

Lupi, L., Hudait, A., and Molinero, V.: Heterogeneous Nucleation of Ice on Carbon Surfaces, Am. Chem. J., 136, 3156-3164, 10.1021/ja411507a, 2014.

Lupi, L., and Molinero, V.: Does Hydrophilicity of Carbon Particles Improve Their Ice Nucleation Ability?, J. Phys. Chem. A, 118, 7330-7337, 10.1021/jp4118375, 2014.

Richmond, G.: STRUCTURE AND BONDING OF MOLECULES AT AQUEOUS SURFACES, Annual Review of Physical Chemistry, 52, 357-389, doi:10.1146/annurev.physchem.52.1.357, 2001.

Shen, Y. R.: Optical Second Harmonic Generation at Interfaces, Annual Review of Physical Chemistry, 40, 327-350, doi:10.1146/annurev.pc.40.100189.001551, 1989.

Zhang, W.-k., Zheng, D.-s., Xu, Y.-y., Bian, H.-t., Guo, Y., and Wang, H.-f.: Reconsideration of second-harmonic generation from isotropic liquid interface: Broken Kleinman symmetry of neat air/water interface from dipolar contribution, J. Chem. Phys., 123, 22471301 - 22471311, doi:http://dx.doi.org/10.1063/1.2136875, 2005.