Abdelmonem et al.

The manuscript submitted by Abdelmonem et al. examines the effects of freeze-melt processes on the aqueous chemistry at silica surfaces at low pH. The experiments were performed in an environmental cell in conjunction with second-harmonic generation spectroscopy. Abdelmonem et al. found a water ordering-cooling dependence that improved continuously and they proposed that water ordering is a result of the dissolution of the silica surface and that this process causes the improved ice nucleation of aged silica samples. The manuscript is interesting but focused mostly on SHG measurements. Therefore it seems more relevant for a more physical chemical journal and in the current form the conclusions of the SHG measurements and their relevance and connection for atmospheric research are not evident.

Scientific significance: 3
Scientific quality: 2
Presentation quality: 3

Points to be addressed:

General discussion:

SHG probes the average of the ensemble of all water molecules underneath the heterogeneous silica sample. Yet, ice nucleation on α-quartz surfaces was shown to occur at only a few locations which were associated with micron-size surface pits. (Holden et al. 2019 Science Advances). The authors should include this important point into the manuscript so that the readers can better put the SHG results in perspective. The authors should also think about possible topographical changes on the silica due to pH 3 treatment as this might also be able to explain the improved ice nucleation. The authors might also want to consider providing evidence whether their silica substrates become better ice nucleators with time.

Introduction:

p.3. l. 5- The discussion about the pH solubility of silica is not presented in great clarity and it is not directly clear why pH 3 is relevant for atmospheric conditions. When reading the introduction it seems that higher alkaline pH would be much more relevant.

p.3 l. 42 “molecular level” this statement should be altered. In the presented experiments a large ensemble of water molecules are probed the term molecular-level might be misleading.

Experimental:

p.4 l. 15 Are there any information on the surface roughness or homogeneity of your silica samples?

p.4. l. 34 “the incident angle was adjusted to 1 degree above the critical anlge of TIR to guarantee a TIR condition in the studied temperature range. Why was +1 degree chosen and why would the incident angle change? Which effect would the changing angle of incident have on your data?

p.4 l. 35 Were the Fresnel factors corrected for the effect of temperature? Does it affect the silica measurements?

Results and discussion:

Does the volume stay the same during the longer successive runs and are evaporation effects possible/considered?

p. 6 Fig. 2: The light grey scan and the turquoise scan were cut after 1500 s without an explanation. Full data sets should be shown.

p.8 Fig.4: Fig4b and c seem identical. It would be much more convincing if they would add a point at 2000 s to see how this signal changes as a function of cycles. From the data presented in Figure 2 it seems that except for Run 1 the intensities look comparable.

p.8 Fig. 4 Are there any indications from your data that the onset of the freezing occurs at earlier timings when the samples are aged?

p.9 l. 1-5 Control experiments at lower temperature, not RT would be helpful since the pH depends on the temperature.

p.9 l. 41 The statement "the older the sample" is somewhat ambiguous. Were the experiments performed on multiple independent samples? Or one silica prism and the age of the sample refers to the number of cycles the sample was exposed to. The number of used silica samples and the number of independent experiments should be added to the materials section.

p.10 l. 8 What is the experimental evidence that the prism that orders water better is also a better ice nucleator? Were any experiments performed? Couldn't the ageing process and the contact with acid also just roughen the surface and that is the reason why it nucleates better?

p.10 Fig.5 Since the observed effect is not very pronounced. It would be good toadd error bars in the Figure or provide information on how reproducible the trend is.

p.11 l. 15 The results of the following study should be added to the discussion. Rehl et al. 2019 New Insights into $\chi(3)$ Measurements: Comparing Nonresonant Second Harmonic Generation and Resonant Sum Frequency Generation at the Silica/Aqueous Electrolyte Interface, JPCA.

p.13 l. 33 Is there an explanation why the ice signal shows such strong variations.

p. 13. l. 35 Is it possible to estimate the thickness of the liquid film? I would assume this could provide very useful information as one could estimate the pH of this solution which should be much lower due to the freeze concentration and likely dissolves the silica even faster.

p. 14 l. 28 "this study is expected to benefit"… The connection of the results of the current study and its implications for atmospheric research are not clear.