

### [Point-to-point answers to the comments of SC #1](#)

*The author is grateful to Dr. Hugo K Christenson for his interest in the work and also for his valuable comments and constructive recommendations.*

SC: 1. The two-step nucleation process postulated by Campbell et al. in 2013 involved various organic liquids crystallising from vapour on mica surfaces, but only in surface features such as cleavage steps, cracks and pockets. A later study (Campbell et al., 2017)) has confirmed the two-step process for the organic liquids, and strongly suggested a two-step process for water and ice, although conclusive proof could not be obtained for water and ice.

*AC: Indeed, the discussion on the two-step process by (Campbell et al., 2013) in page 2 line 6 requires more details about the work. This will be considered in the revised version of the manuscript. The author would also like to thank Dr. Christenson for drawing the attention to the very recent work by Campbell et al. on the two-step process (Campbell et al., 2017). This work will also be considered in the revised manuscript.*

SC: 2. The material used by Layton and Harris in their 1963 paper (the reference is incomplete) was not muscovite mica but synthetic fluorophlogopite, which is similar in structure but has the hydroxyl groups replaced by fluorine. Moreover, neither is a metal oxide as stated in the abstract, but they are both layered aluminosilicates.

*AC: Thanks for this clarification. The difference between the two micas as well as the corrected citation will be included in the revised manuscript.*

SC: 3. The basal (cleavage) plane of mica consists of distorted hexagons of oxygen atoms, and there are no Si or Al atoms in the outermost layer. Moreover, the hydroxyl groups are below the oxygen hexagons, so there are none available for hydrogen bonding to adsorbed water molecules. This is explained in a recent review (Christenson and Thomson, 2016) which gives numerous references to the original literature on the structure determination of muscovite mica by X-ray diffraction.

*AC: Probably the sentence in the manuscript was not clear enough (will be revised). Indeed, a cleaved mica surface exhibits a distorted hexagons of oxygen atoms in the outermost layer (Ostendorf et al., 2008) which are doubly coordinated with Si/Al atoms. My hypothesis is as follow: 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 SHG signal can mainly originate from the surface hydroxyl groups (dangling-OH) which are naturally pointing out from the surface. A strong SHG signal was detected from the mica-air interface at 110 °C and under purging of N<sub>2</sub> gas before starting the cooling. The bulk hydroxyl groups cannot contribute to this signal. To my knowledge, the presence of free surface hydroxyl groups on mica is poorly discussed in literature. I could find only two articles discussing hydroxyl groups on mica basal plane: 1) 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 wrote: "Deuterated water (D<sub>2</sub>O) was used in the SFG*

*experiments to avoid confusion of the hydroxyl stretch modes in the spectrum from both water and mica". This should mean that they observed a signal from those species (surface OH) in the OH vibrational region and, for this reason, they moved to the OD vibrational region. 2) 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).*

*Since one in four Si in the tetrahedral layers is randomly substituted for Al (Christenson and Thomson, 2016), 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 point-of-zero-charge (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.*

SC: 4. The simulation by Odelius et al. (1997) suggested that the mica surface is covered by a network of hydrogen bonds between water molecules only, with no free water hydroxyls. However, these results have been called into doubt by more recent simulations (Wang et al., 2005; Malani and Ayappa, 2009), and in a density-functional study that found no evidence of 2D-ice on mica, but that the properties of water on the surface are dominated by hydration of potassium ions (Feibelman 2013).

*AC: The author is thankful for this clarification and probably referring to this work in the last paragraph was not correct (will be removed in the revised version).*

SC: 5. The study of air-cleaved mica and water vapour (as is the case here for the measurements in water vapour) is complicated by the fact that the surface potassium ions are free to diffuse along the surface (as potassium carbonate), which may even result in the formation of crystallites on the surface in dry conditions. This was first shown by Christenson and Israelachvili in 1987, and was discussed in Balmer et al., 2008. The implications for studying mica in humid atmospheres was summarised in the 2016 review mentioned under point 3. Mica immersed in bulk water does not suffer from these problems, of course, as any potassium carbonate dissolves and the nature of the surface ions is determined by the pH and any residual electrolyte in the solution. The mobility of the potassium ions (as potassium carbonate) does not necessarily alter dramatically any measurement of average surface properties, as is the case with SHG, and at high humidities the potassium will be widely dispersed across the surface. However, the surface mobility of the potassium will necessarily decrease at lower temperatures, and there may be a dependence on the history of the mica surfaces. To summarise, it should be borne in mind that what is adsorbed to the mica surface is a thin film of aqueous potassium carbonate, the concentration of which varies with humidity and temperature, rather than pure water.

*AC: As written in the original manuscript, P. 3, L. 23, the laser power was reduced to allow observable signal but not destroy the index-matching gel. The fluctuation in the signal due to reducing the laser power limited the sensitivity of the system to monitor minor changes which may arise from pre-adsorption of sub-monolayers or even few monolayers at temperatures higher than the dew point or freezing point. The thickness of the water layer at the time of collecting the signal is expected to be in the order of 1  $\mu\text{m}$  (will be explained in the revised version) which should allow the potassium to be*

widely dispersed across the surface. In addition, the sample was washed several times in the cell and kept in either dry  $N_2$  gas or humid air. The humid air was obtained from continuously  $N_2$ -purged MQ water as described in the SI. It is also expected, under these conditions, that the  $K^+$  ions are totally replaced by  $H^+$  ions. Studying monolayer film needs experimental arrangements which are not available in our Lab at this moment.

**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.**

#### References:

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