

Interactive comment on “Direct molecular level characterization of different heterogeneous freezing modes on mica” by Ahmed Abdelmonem et al.

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I have read with interest the recent contribution of A. Abdelmonem to Atmospheric Chemistry and Physics Discussions. Second-harmonic generation (SHG) spectroscopy has the potential to be a powerful tool for investigating freezing at interfaces. However, there are a number of points regarding the mica surface and previous work with mica that should be taken into consideration in any revised manuscript. In particular, these points may lead the author to reconsider some of his interpretation of the results.

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

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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.

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.

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.

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).

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

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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.

New references Christenson, H. K. and Thomson, N. H.; The Nature of the Air-cleaved Mica Surface, *Surf. Sci. Rep.* 71, 367-390, 2016. Christenson, H. K. and Israelachvili, J. N.: Growth of Ionic Crystallites on Exposed Surfaces, *J. Colloid Interface Sci.* 117, 576-577, 1987. Campbell, J. M., Meldrum, F. C. and Christenson, H. K.; Observing the Formation of Ice and Organic Crystals in Active Sites, *Proc. Natl. Acad. Sci. USA*, 114, 810-815, 2017. Feibelman, P. J.; K⁺-hydration in a low-energy two-dimensional wetting layer on the basal surface of muscovite, *J. Chem. Phys.* 139, 074705, 2013. Wang, J., Kalinichev, A. G., Kirkpatrick, R. J. and Cygan, R. T.; Structure, Energetics, and Dynamics of Water Adsorbed on the Muscovite (001) Surface: a Molecular Dynamics Simulation, *J. Phys. Chem. B* 109 2005, 15893-15905, 2005. Malani, A. and Ayappa, K. G.; Adsorption Isotherms of Water on Mica: Redistribution and Film Growth, *J. Phys. Chem. B* 113 1058-1067, 2009.

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