

Interactive comment on “Unravelling the microphysics of polar mesospheric cloud formation” by Denis Duft et al.

Anonymous Referee #1

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I have just seen the manuscript "The heterogeneous nature of polar mesospheric cloud formation" by Duft, Nachbar and Leisner (DNL). They report water uptake experiments on iron-silicate nanoparticles for various particles sizes and water supersaturation ratios at 128-152 K. This manuscript is part of a series of works by the same three authors - three manuscripts were published in 2016 and 2018, and two manuscripts are reported as submitted. The latter were not available to me at the time of this review. The main conclusion is that noctilucent clouds may form under the experimental conditions in the mesosphere below supersaturations that are typically observed in Earth's upper atmosphere. A secondary conclusion that has already been reported in their earlier manuscripts is that amorphous solid water (ASW) rather than crystalline ice I (cubic, hexagonal or stacking-disordered) condenses on such smoke particles. Finally,

C1

they claim that charge effects or sunlight absorption by the particles is of minor relevance for the formation of mesospheric clouds. An impressive number of almost 200 experiments under different conditions has been performed. However, the data themselves are not convincing, and I have also doubts about the model used to interpret the data as detailed below: 1) My major concern is on the nature of the condensed ASW. The authors treat ASW as if it was a well-defined phase, just like a crystalline phase. However, it is well known that the nature of ASW deposits differs very much depending on the growth conditions. ASW is usually a highly microporous materials. Porosities can be close to 0 or up to 80%, specific surface areas can be between almost 0 and several hundred m²/g. Furthermore, ASW is well known to take up background gases very efficiently and incorporate them into its pores, burying them into its bulk. In fact, some of the micropores in ASW are large enough to take up the whole iron-silicate particle of length scale 1-3 nm in a single pore. Some of this is described by Kay and co-workers (Science 283 1999) as well as by Mayer and Pletzer (J. Phys. Colloques 48 1987 and Nature 319 1986). Unfortunately, any kind of characterization of the ASW particles in terms of porosities, uptake of background gas or additional Fe-Si nanoparticles is missing in this work. Still the authors use specific values in their modelling, e.g., a density of 0.93 g/ml in order to determine the water coverage and wet particle radius. How would the model be affected if the density was much lower than that because of a high porosity within ASW? Even more troublesome is the saturation water vapor of ASW (S_{ASW}) used in equation (1) of the model. The vapor pressure of ASW maybe much smaller than the one parameterized by Nachbar et al. due to the incorporation of foreign atoms/molecules into the ASW matrix - which automatically implies that the supersaturations given by DNL maybe very different from what they assume in their model. Also the internal porosity and surface corrugation may have a large impact on the vapor pressure. No critical analysis with respect to these uncertainties is discussed in their model. The values they have chosen seem to be taken as granted and are not critically discussed or given the possibility for a range of values for different individual ASW particles - in particular there is no anal-

C2

ysis how the results would change if S_{ASW} and the density were different. 2) The data themselves show a very large scatter. For example in Fig.3 the desorption energies for the SiO₂ nanoparticles in the range of 0.3-0.5 nm⁻¹ scatter more or less randomly between 38.5 and 40.0 kJ/mol. With equal justification one could fit a line independent of particle size or that even shows larger desorption energies for smaller particles. The fit given by DNL hinges mainly on the 4 data points between 0.5 and 0.7 nm⁻¹, whereas the other roughly 40 data points do not show any trend. That is, there is a large uncertainty associated with the size-dependent desorption energies deduced from Fig.3 that is not at all reflected in the error-bars in Fig.4. Why is the error-bar for the curvature-independent desorption energy for SiO₂ and Fe₂O₃ in Fig.4 of similar size, even though the data points for Fe₂O₃ particles scatter much less around the fitted line? A problem that goes hand in hand with this inappropriate fit is the surface-tension deduced from the slope in Fig.3: why is the surface tension for SiO₂ half of the one found for Fe₂O₃ or Fe₆₅Si₃₅O₃₀₀? One would expect very similar values for all three types of nanoparticles - which demonstrates that the values deduced from Fig.3 are associated with a huge error, much larger than the "+/- 18 mN/M" given by DNL. In my opinion the data for SiO₂ do not even allow to exclude a surface tension below 0. Similarly, also in Fig.5 the scatter of the data is unacceptably large. I believe this huge scatter reflects that S_{ASW} can not be defined in the straightforward way assumed by DNL. In fact, S_{ASW} needs to be defined individually for each particle, depending on density, curvature and porosity of each deposit. This task is obviously unfeasible, but this still does not validate the use of an invalid assumption. 3) I did not understand from this manuscript why the authors believe that charges do not play a role. Which experimental finding allows for this statement? This needs to be elaborated. Even though the mesosphere contains mostly positively charged ions such as N₂⁺, NO⁺, O₂⁺,... I would also be interested to see what role negative ions (electrons) might play. Can the authors rule out an influence of electrons on the formation of noctilucent clouds? As the manuscript stands now, I do not feel that it reports important new physics or chemistry that goes beyond what DNL have published in their recent papers on this

C3

topic. The manuscript needs to take into account uncertainties in the model and the nature of the formed ASW with much more care.

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C4