

Interactive comment on “Commentary on ”Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification” by Knopf et al.” by A. Tabazadeh

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I disagree with Dr. Koop in stating that the possibility of pseudo-heterogeneous freezing does not affect the conclusion of the Knopf et al. paper for the following reasons:

The rate of homogeneous freezing has the following form,

1. $J = C_{\text{exp}}(-\text{free energy}/kT)$ (please see Tabazadeh et al, J. Geophys. Res., 102, 23,845, 1997).
2. The surface tension of nucleus formation enters into the above exponential term, and this surface tension is further raised to the power of 3 in the above expression (see Tabazadeh et al. reference above).

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3. Now let's assume that the nucleus forms at the surface of the supercooled fluid and not in its bulk volume. In the case of a surface nucleus, the presence of a slight amount of organic contamination at the surface layer can change the surface tension. Let's say the surface tension is changed by just about 3 units. This slight change in surface tension can change the rate of freezing by nearly 12 orders of magnitude ($\exp(3^{**3})$).

4. Thus, one does not need a full layer of an organic coating to cause a dramatic change in the rate of nucleation. For example a 0.3 molar solution of propanol in water can change the surface tension of pure water by 3 units (see Figure 1 in Donaldson and Anderson, *J. Phys. Chem*, 103, 871, 1999). Based on the single particle data, discussed in my commentary, it seems highly unlikely that the Knopf et al. samples were devoid of organic contamination. Thus a slight change in the surface tension (just about 2 to 3 units) of their droplets is not an unlikely scenario, and this change could have efficiently hampered the nucleation process from occurring in their laboratory. Both anonymous referees agreed with me on this matter.

5. No where in the Knopf et al. paper a discussion is given to show that the droplet samples were pure samples, although the rates are reported for a homogeneous system, which implies that the samples must have been pure. No where in the Knopf et al. paper an attempt is made to measure the surface tension of the droplet to see whether or not the surface tension agrees with the surface tension of a pure system, which is presumably present in the pristine environment of the stratosphere. Thus I am not quite sure how Dr. Koop can state that their results are unaffected by the fact that the process of freezing may have occurred at the droplet surface. If the process of freezing occurs at the droplet surface, then this process could not have occurred under their laboratory conditions if the surface tension of the droplet under consideration in their laboratory had differed from the pure droplet system in the stratosphere by just about 2-3 units.

The title of the Knopf et al. paper states that they have studied a homogeneous process and that the stratospheric system CANNOT freeze homogeneously based on

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their data. My commentary argues that the system studied in their laboratory cannot be homogeneous, mainly because it is exposed to tropospheric air and that organic contamination is shown to be present in laboratory samples using quantitative mass spectrometry techniques. Therefore, drawing a conclusion about whether the real homogeneous system in the stratosphere will freeze or not based on their laboratory work is inaccurate. Thus, I disagree with the fact that they firmly state that the stratospheric system cannot freeze homogeneously. Both anonymous referees agree with me on this matter. I am not claiming that the stratospheric system will freeze homogeneously because we do not know at this point, and certainly more rigorous laboratory work is needed to resolve this issue, as I suggested in my commentary.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 827, 2003.

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