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Atmospheric Chemistry and Physics Discussions

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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The idea that pseudo-heterogeneous nucleation might occur in liquid aerosol particles in the atmosphere and/or the laboratory is very intriguing and I fully agree with A. Tabazadeh that this possibility should be explored further, both experimentally and theoretically. However, the possibility of pseudo-heterogeneous nucleation does not affect the conclusions drawn in the paper by Knopf et al. [2002]. In this comment, I will focus on the topics that are relevant to the conclusion of the paper by Knopf et al. [2002]. Specific points regarding surface nucleation etc. will be discussed in a separate comment.

The main conclusions of the paper by Knopf et al. [2002] was that homogeneous (volume-based) nucleation rate coefficients are too small to be important for stratospheric denitrification. However, most of the commentary by A. Tabazadeh is dealing with the issue of whether or not the experiments of Knopf et al. [2002] are suitable to infer pseudo-heterogeneous (surface-based) nucleation rates for application at stratospheric conditions. So in that sense the comments by A. Tabazadeh are not directly related to the paper by Knopf et al. [2002].

A. Tabazadeh questions the suitability of the experiments presented in Knopf et al. [2002] who suggested that the results of the paper by Tabazadeh et a. [2001] are erroneous. However, even without these new experiments, the Knopf et al. paper shows that the main problem of the Tabazadeh et al. [2001] paper was a linear extrapolation of the Gibbs activation energy to stratospheric conditions at which the parameterization is not valid (see also my other comment.) This alone is enough to show that the PSC production rates were overestimated in Tabazadeh et al. [2001]. However, in her commentary, A. Tabazadeh did not address this criticism.

Furthermore, even if surface nucleation occurred in the experiments, our conclusion are not affected. The observed nucleation rate in our experiment is the sum of the homogeneous (volume-based) nucleation rate coefficient times the sample volume and the pseudo-heterogeneous (surface-based) nucleation rate coefficient times the sample surface S (see eq. 1 in Tabazadeh et al. J.Phys.Chem.A 2002):

$$\omega_{\mathrm{obs}} = J_{\mathrm{v}} \cdot V + J_{\mathrm{s}} \cdot S \tag{1}$$

In our evaluation we assumed that all of the observed nucleation events were due to homogeneous nucleation (i.e. assuming J_{s} equals zero). This yields an upper limit to J_{v}:

$$J_{\mathrm{v}} \leq \frac{\omega_{\mathrm{obs}}}{V}\,, \tag{2}$$

i.e. the homogeneous nucleation rate coefficient is smaller than the quoted values de-

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rived from ω_{obs}/V. Now, if we include J_{s}, equation 2 becomes:

$$J_{\mathrm{v}} \leq \frac{\omega_{\mathrm{obs}} - J_{\mathrm{s}} \cdot S}{V} \tag{3}$$

So if indeed pseudo-heterogeneous nucleation at the surface of our samples occurred in our experiments, $J_{\mathrm{s}} \cdot S$ is positive, and the upper limit of J_{v} would be even smaller. Since J_{v} in Eq. 3 is always smaller than J_{v} in Eq. 2, we have reported the conservative (too large) value of J_{v} in the paper by Knopf et al. [2002]. Since these (too large) values are already much too low to be of stratospheric importance, the conclusions of the paper by Knopf et al. [2002] that "homogeneous nucleation is insufficient" remains valid, irrespective of whether pseudo-heterogeneous nucleations occurred in our experiments or not.

It is clear that Tabazadeh et al. have other reasons to believe that homogeneous nucleation does not occur in the stratosphere (but rather pseudo-heterogeneous nucleation). But this does not imply that our approach and conclusions to show that homogeneous nucleation in the stratosphere does not occur (but some other process) are "wrong" and "faulty". Arguments against a hypothesis do not become invalid just because additional arguments have been found.

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