

## ***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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Knopf et al. (2002) have shown that the extrapolation of nucleation activation energies of NAD and NAT derived by laboratory experiments (Salcedo et al., 2001) to stratospheric conditions (Tabazadeh et al., 2001) leads to physically unreasonable homogeneous nucleation rate coefficients at stratospheric temperatures and concentrations. Knopf et al. (2002) also presented upper limits of the homogeneous nucleation rate coefficients of NAD and NAT (this corresponds to lower limits of the nucleation activation energies) derived from newly obtained experimental data and previously published data. The analysis yields NAD and NAT production rates which

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are 5 orders of magnitude lower than the ones used in the stratospheric denitrification modelling study presented by Tabazadeh et al. (2001).

Before I want to answer the comments given by Tabazadeh et al. (2003), I want to emphasize that the critics of Tabazadeh et al. (2003) regarding pseudo-heterogeneous nucleation in our samples do not affect the conclusion on volume dependent homogeneous nucleation in Knopf et al. (2002). Knopf et al. (2002) analyze a volume-based nucleation parameterization given by Tabazadeh et al. (2001) which is at odds with volume-based theory and corresponding experiments. Both articles Knopf et al. (2002) and Tabazadeh et al. (2001) only deal with volume-based nucleation.

Nevertheless I want to comment on the statements given by Tabazadeh et al. (2003). Tabazadeh et al. (2003) states that the large droplets of our experiments are more easily surface contaminated than small droplets and, therefore, surface-induced nucleation is influenced or even inhibited. Small droplets with a radius  $0.1 \mu\text{m}$  have  $1.3 \cdot 10^6$  molecular surface sites compared to  $1.3 \cdot 10^{14}$  molecular surface sites of a particle with a radius of  $0.1 \text{ cm}$ . Therefore, less ambient gaseous contaminants are needed to influence the surface composition of smaller droplets.

It has also to be taken into account that even surface active species dissolve into the aqueous phase (see also comment by Jungwirth (2003)). Using mass spectroscopy Middlebrook et al. (1997) detect  $0.02 \text{ wt}\%$  of organic contaminants in  $0.2 \mu\text{m}$  particles in a laboratory environment. These impurities were assigned to organic substances such as ethylene, acetylene, and butane, which have solubilities in water of about  $0.001\text{--}0.01 \%$  (Howard and Meylan, 1997). It was suspected that also formaldehyde was an organic impurity which is very soluble in water (Saxena and Hildemann, 1996). A droplet of  $10 \mu\text{l}$  volume contains about  $10^{21}$  molecules of which  $10^{14}$  reside at the droplet surface. From this and the solubility mentioned above it can be concluded that at least  $0.00001 \times 10^{21} = 10^{16}$  organic molecules can be dissolved in the volume. In equilibrium, the organic molecules will be distributed equally throughout the droplet, hence, only a fraction of the organic molecules will be sitting on the droplet surface.

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Therefore, the assumption of “surface-clean” large droplets may not be wrong, if we analyze our nucleation data with respect to pseudo-heterogeneous nucleation (Knopf et al. 2003).

Only by using mass spectroscopy techniques which can be calibrated with respect to the compounds in the aerosol particles (Knopf et al. , 2001) the purity of the particles can be determined. From the above mentioned reasons we cannot conclude that no contamination occurred in our sample preparation but this applies also to other laboratory nucleation studies. Since Tabazadeh et al. (2003) suggests that every terrestrial laboratory is contaminated also the nucleation data used to derive the pseudo-heterogeneous nucleation parameterization may be influenced by contaminants. Thus, the nucleation parameterization given by Tabazadeh et al. (2002a) may describe an artificial nucleation process.

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