

***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***

**D. Knopf**

knopf@atmos.umnw.ethz.ch

Received and published: 28 March 2003

Part II of comment (4 page limit)

I agree with the second point mentioned by Tabazadeh et al. (2003) that the surface enrichment of  $\text{HNO}_3$  molecules of a small droplet is different from that of a large droplet. However, the size effect on surface enrichment occurs only in droplets with radii smaller than  $0.1 \mu\text{m}$ . Above this size surface enrichment reaches its bulk value and remains almost constant (Stuart and Berne, 1999) with increasing droplet

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

size. Therefore, a derived surface-based nucleation rate obtained by large droplets corresponds to that derived from droplets with a radius of  $0.1 \mu\text{m}$ .

Tabazadeh et al. (2002a) remarks that Molina et al. (1993) have already performed bulk freezing experiments. Also Koop et al. (1995, 1997) have measured upper limits of nucleation rate coefficients of NAD and NAT in bulk samples. If Tabazadeh et al. (2001) had used these data sets in the case of volume-based nucleation they would have obtained much higher nucleation activation energies of NAD and NAT and, therefore, much lower corresponding homogeneous nucleation rate coefficients under stratospheric conditions.

I want to remark that we are grateful to have received the preprints of Tabazadeh et al. (2002a, 2002b) and Djikaev et al. (2002). But this was after we had submitted our article to ACP. We agree with A. Tabazadeh that pseudo-heterogeneous nucleation is an exciting new way to see nucleation of atmospheric particles and, thus, should be investigated in more detail. However, this does not affect the conclusion of our paper (Knopf et al., 2002).

Djikaev, Y. S., Tabazadeh, A., Hamill, P., and Reiss, H., Thermodynamic Conditions for the Surface-Stimulated Crystallization of Atmospheric Droplets, *J. Phys. Chem. A*, *106*, 10 247–10 253, 2002.

Howard, P. H. and Meylan, W. M., *Handbook of Physical Properties of Organic Chemicals*, CRC Press, New York, 1997.

Jungwirth, P., 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, *Atmos. Chem. Phys. Discuss.*, *3*, S103–S104, 2003.

Knopf, D. A., Zink, P., Schreiner, J., and Mauersberger, K., Calibration of an Aerosol Composition Mass Spectrometer with Sulfuric Acid Water Aerosol, *Aerosol Sci. Tech-*

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

*nol.*, 35, 924–928, 2001.

Knopf, D. A., Koop, T., Luo, B. P., Weers, U. G., and Peter, T., Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification, *Atmos. Chem. Phys.*, 2, 207–214, 2002.

Knopf, D. A., Luo, B. P., Krieger, U. K., Koop, T., and Peter, T., Experimental and Theoretical Analysis with Respect to Surface-Induced Nucleation, Madrid, EAC 2003 Conference, submitted, 2003.

Koop, T., Biermann, U. M., Luo, B., Crutzen, P. J., and Peter, T., Do stratospheric aerosol droplets freeze above the ice frost point?, *Geophys. Res. Lett.*, 22, 917–920, 1995.

Koop, T., Luo, B. P., Biermann, U. M., Crutzen, P. J., and Peter, T., Freezing of  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  Solutions at Stratospheric Temperatures: Nucleation Statistics and Experiments, *J. Phys. Chem. A*, 101, 1117–1133, 1997.

Middlebrook, A. M., Thomson, David, S., and Murphy, D. M., On the Purity of Laboratory-Generated Sulfuric Acid Droplets and Ambient Particles Studied by Laser Mass Spectrometry, *Aerosol Sci. Technol.*, 27, 293–307, 1997.

Molina, M. J., Zhang, R., Woolridge, P. J., McMahon, J. R., Kim, J. E., Chang, H. Y., and Beyer, K. D., Physical-Chemistry of the  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  System-Implications for Polar Stratospheric Clouds, *Science*, 261, 1418–1423, 1993.

Salcedo, D., Molina, T., and Molina, M. J., Homogeneous Freezing of Concentrated Aqueous Nitric Acid Solutions at Polar Stratospheric Temperatures, *J. Phys. Chem. A*, 105, 1433–1439, 2001.

Saxena, P. and Hildemann, L. M., Water-Soluble Organics in Atmospheric Particles: A

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Critical Review of the Literature and Application of Thermodynamics to Identify Candidate Compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.

Stuart, S. J. and Berne, B. J., Surface Curvature Effects in the Aqueous Ionic Solvation of the Chloride Ion, *J. Phys. Chem. A*, 103, 10 300–10 307, 1999.

Tabazadeh, A., Commentary on "Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification" by Knopf et al.", *Atmos. Chem. Phys. Disc.*, 2003.

Tabazadeh, A., Jensen, E. J., Toon, O. B., Drdla, K., and Scheberl, M. R., Role of the Stratospheric Polar Freezing Belt in Denitrification, *Science*, 291, 2591–2594, 2001.

Tabazadeh, A., Djikaev, Y. S., Hamill, P., and Reiss, H., Laboratory Evidence for Surface Nucleation of Solid Polar Stratospheric Cloud Particles, *J. Phys. Chem. A*, 106, 10 238–10 246, 2002a.

Tabazadeh, A., Djikaev, Y. S., and Reiss, H., Surface crystallization of supercooled water in clouds, *Proc. Nat. Acad. Sci.*, 99, 15 873–15 878, 2002b.

---

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

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)