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Atmospheric
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Discussions

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

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1. General Comments

Physical removal of nitric acid from the wintertime polar lower stratosphere (denitrification) is a key process in the seasonal evolution of stratospheric ozone, particularly in an atmosphere in which chlorine is enhanced by CFC emissions (Waibel et al., Science, 283, 2064-2069, 1999). Researchers have realised this for many years now, but have, as

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yet, struggled to provide a quantitative description of denitrification.

The Waibel et al. (ibid) study made a strong circumstantial argument for denitrification by nitric acid trihydrate (NAT) particles which had nucleated on ice particles. The denitrification scheme used, however, consisted of prescribed particle number densities and equilibrium vapour-solid mass partitioning. Tabazadeh et al. (Science, 291, 2591-2594, 2001) used laboratory data from Salcedo et al. (J. Phys. Chem., 105, 1433-1439, 2001) to suggest an alternative denitrification mechanism. In this alternative mechanism, NAT and nitric and dihydrate (NAD) solid particle formation occurs directly from supercooled ternary liquid droplets (and NAD subsequently converts to NAT). This mechanism does not require temperatures below the ice frost point. In the simulations reported, nucleation and growth of particles were calculated explicitly. The purpose of the present paper is to refute the Tabazadeh et al. paper on microphysical grounds. In doing so, the authors use a key piece of evidence, available to Tabazadeh et al. but not to Waibel et al.: the observation of very low number densities (of the order of 0.1 per litre) of large (about 15 micrometre diameter) NAT particles (Fahey et al., Science, 291, 1026-1031).

In general, this (Knopf et al.) paper is a very convincing refutation of the Tabazadeh et al. hypothesis. The arguments from nucleation theory against the Tabazadeh et al. hypothesis are rather obvious, but none the worse for that. They appear not to have been spotted by Tabazadeh and co-authors, and many who have cited that work, at least. Further arguments from experiment are also compelling, particularly when taken together with previous experimental work, as done here. The paper is very clearly written and laid-out.

2. Specific Comments

I am surprised that the authors don't refer to previous work on this topic from their own group - i.e. Waibel et al. (1999). At the very least I would expect the lay reader to be pointed back to the Waibel et al. paper in the conclusions of the current paper, since presumably one upshot of the Knopf et al. work is that the authors stand by the Waibel et al. results as the best simulation of denitrification to date, the Fahey et al. observations notwithstanding.

Page 672, line 1. Is there observational evidence in support of NAD in the atmosphere? I can't find it in the two papers cited.

Page 672, section 2. I guess I'm bound to say that σ_{sl} measurements ("values") are not available for any temperature (see MacKenzie, A. R., J. Phys. Chem., 101, 1817-1823, 1997).

Page 674 (top). Perhaps, for emphasis, it is worth giving the reader an impression of the sensitivity of the nucleation rate coefficient to any error in ΔG_{act}? At 191 K and $\Delta G_{act} = 27$ kcal/mol,
I reckon a 1 kcal/mol uncertainty in ΔG_{act} changes the nucleation rate coefficient by a factor of 14. Then for larger discrepancies, of n Kelvin say, the coefficient changes by a factor 14^n, of course.
Page 676, para 2. I agree that n^* is a conservative estimate of n, but simply by dint of the algebra in equation (4), using n^* instead of n cannot give you the highest possible J_{hom}, as appears to be implied.
Page 676, section 4. Why is a "slightly lower" value of the nucleation rate coefficient used?

3. Technical Comments

Abstract and throughout: might it help the reader who is skimming if it was made clear that the nucleation rate coefficients are given per cubic centimetre of solution, while the nucleation rates are given per cubic centimetre of air. A simple "cm^{-3} (solution) s^{-1}" would do.
Abstract: "...with thermodynamics and with experimental data", for

clarity?

Abstract, last sentence: isn't there a bit of a jump in the logic here? The connection between number densities observed in recent field observations and denitrification should be made.

Page 672, para 1. Couldn't the disagreement with bulk experiments be made explicit in a line or two, say by giving example freezing (or "not-frozen") temperatures? And wouldn't it be fair to indicate that you will give credit to the others who have worked on this on page 673 (i.e. "...with bulk experiments in our laboratory (... and see further references below).")?

Page 674, line 1. I don't think that the cell can be an "aerosol cell" unless it contains a suspension of particles in air. "Droplet cell" would be more correct, I think.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 669, 2002.

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