

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

**D. A. Knopf et al.**

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### 1. Specific Comment:

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.

Reply:

We will add the following sentence:

p. 678, l. 12: Therefore, other NAD/NAT formation mechanisms such as heterogeneous NAT nucleation on ice particles are required to explain polar denitrification

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(Waibel et al., 1999).

(Waibel, A. E., Peter, Th., Carslaw, K. S., Oelhaf, H., Wetzel, G., Crutzen, P. J., Pöschl, U., Tsias, A., Reimer, E., Fischer, H.: Arctic Ozone Loss Due to Denitrification, Science, 283, 2064–2069, 1999.)

## 2. Specific Comment:

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.

Reply:

We agree and will change and add the following sentences:

p. 670,l. 26: Field measurements have shown that PSCs can be composed of liquid supercooled ternary solutions (STS) and nitric acid trihydrate (NAT) (Schreiner et al., 1999; Voigt et al., 2000). In addition, nitric acid dihydrate (NAD) has been suggested to exist in PSCs based on laboratory experiments (Worsnop et al., 1993).

(Worsnop, D. R., Fox, L. E., Zahniser, and M. S. Wofsy: Vapor Pressures of Solid Hydrates of Nitric Acid: Implications for Polar Stratospheric Clouds, Science, 259, 71-74, 1993.)

## 3. Specific Comment:

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

Reply:

We agree and will change the sentence to the following one:

p. 672, l. 9: Since measured values for  $\sigma_{sl}$  and  $\Delta G_{dif}$  are not available (MacKenzie,

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1997),  $\Delta G_{act}$  can be determined from experimentally observed nucleation rate coefficients by solving Eq. 1 for  $\Delta G_{act}$ :

#### 4. Specific Comment:

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  $\Delta G_{act}$ ? At 191 K and  $\Delta G_{act} = 27$  kcal/mol, I reckon a 1 kcal/mol uncertainty in  $\Delta G_{act}$  changes the nucleation rate coefficient by a factor of 14. Then for larger discrepancies, of  $n$  Kelvin say, the coefficient changes by a factor  $14n$ , of course.

Reply:

We will add the following sentence:

p. 672, l. 23: ..in each case. Note that an underestimation of  $\Delta G_{act}$  by 1 kcal mol<sup>-1</sup> increases the corresponding homogeneous nucleation rate coefficient by a factor of 14.

#### 5. Specific Comment:

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.

Reply:

We do not agree on this point. Our conservative estimate  $n^*$  is LARGER than  $n$ , i.e.  $n^* > n$  (see p. 675, l. 14). Hence, equation 4 does indeed always yield the highest possible  $J_{hom}$ -value. We will add another sentence to illustrate the physical relevance of  $n^*$ :

P. 675, l. 7: ...(Koop et al., 1997) – i.e., if the experiments were repeated an infinite number of times the observed number of nucleation events will be smaller than  $n^*$  in 99.9 % of the cases.

#### 6. Specific Comment:

Page 676, section 4. Why is a "slightly lower" value of the nucleation rate coefficient used?

Reply:

In the original publication J values were estimated using the average radius of the particles. The 'modified' J values are based on a more rigorous calculation: The authors calculated the size distribution of the particles using Mie scattering theory and a least squares analysis, and the 'modified' J values were calculated using this size distribution (Allan Bertram, personal communication).

1. Technical Comment:

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<sup>-3</sup> (solution) s<sup>-1</sup>" would do.

Reply:

We will add cm<sup>-3</sup>(air) every time production rates are used.

2. Technical Comment:

Abstract: "...with thermodynamics and with experimental data", for clarity?

Reply:

We will make this change.

3. Technical Comment:

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.

Reply:

We will add the following sentence:

p. 670, l. 21.: In addition, the nitric acid hydrate production rate inferred from our data is much smaller than that required to reproduce the observed denitrification in the modelling study mentioned above.

#### 4. Technical Comment:

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.)")?

Reply:

The following sentences will be added:

p. 671, l. 10: ...in disagreement with bulk nucleation experiments performed at stratospheric conditions (Koop et al., 1997). For example, according to the nucleation formulation an aqueous ternary solution of 41.2 wt% HNO<sub>3</sub> and 3.9 wt% H<sub>2</sub>SO<sub>4</sub> and 1 cm<sup>3</sup> in volume is predicted to freeze at 249.0 K. In contrast, in experiments such samples did not freeze down to temperatures of 190 K (Koop et al., 1995). Also, the formulation is in disagreement with aerosol experiments of aqueous nitric acid solutions (Anthony et al., 1997; Bertram and Sloane, 1998a, b; Bertram et al., 2000; Salcedo et al., 2001).

#### 5. Technical Comment:

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.

Reply:

We agree.

Aerosol cell will be changed in droplet cell.

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