

## ***Interactive comment on “Homogeneous nucleation rates of nitric acid dihydrate (NAD) at simulated stratospheric conditions – Part II: Modelling” by O. Möhler et al.***

### **Anonymous Referee #2**

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#### General comments:

This is an excellent paper presenting new data for the homogeneous nucleation process of the low-temperature modification of nitric acid dihydrate ( $\alpha$ -NAD). Activation energies for the nucleation process in supercooled binary solutions have been investigated at different molar ratios and temperatures. The activation energies were calculated from nucleation rates measured in the AIDA aerosol chamber or taken from the literature. A micro-physical process model shows that volume-based and surface-based nucleation rates overestimate NAD formation, but if NAD nucleates then the volume-based process is more likely than the surface-based. This comes also clear

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from the companion paper Stetzer et al. (2006). Both papers are important contributions to the discussion of the phase composition of solid particles in polar stratospheric clouds (PSC). I recommend this paper for publication in ACP after some minor revisions.

#### Specific comments:

Moehler et al. (2006) observed the nucleation of sub-micron sized droplets in the nitric acid molar ratio between 0.26 and 0.28. Tizek et al. (2002) found a dominance of  $\alpha$ -NAD in the same concentration region in their X-ray diffraction experiments - the paper should be quoted. By all means, both modifications of NAD are metastable phases and also the supersaturated solution from which the nucleation process occurs has to be considered as a metastable state. Therefore, I recommend avoiding the wording "thermodynamic equilibrium" in the text (see p. 2125, 2133), which certainly is not the case for any of these particles. The nucleation of a metastable phase is rather controlled by kinetics than by thermodynamics. This is a consequence worded by Ostwald's step rule - you should mention Ostwald in the discussion. Under these non-equilibrium conditions the structure of  $\alpha$ -NAD nuclei is more similar to the short-range order of the supersaturated liquid than the nuclei of any other phase. Thus, the activation barrier is lowest for  $\alpha$ -NAD. However, when the structures of the liquid and of the germ converge to each other with increasing supersaturation then the free surface energy (or surface tension) between both is inherently reduced. By no means, it can be considered as constant, but it depends on concentration and temperature. Therefore, it is not aiming to describe the free interface energy as a constant as the authors did - eq. 4 shows that the activation energy depends on the third power of the free interface energy. I would expect that the authors control at least for an upper and lower limit value of the free interface energy - Prenni et al. (1998) derived only the half value and also Turnbull (1950) derived a value which is 10% lower.

I agree with the authors that for low supersaturations, approaching one, the activation energy steeply increases and for high supersaturation decreases. However, the

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same as A. Tabazadeh, I have a problem regarding a plot of pure supersaturation dependence, since supersaturation is a function of both temperature and concentration. Thus, the plot in figure 1 is very ambiguous. I may be mistaken, but might it be that the experimental values in figure 1 follow two different hyperbolic functions, one between  $S=1$  and  $S=5$ , another between  $S=5$  and  $S=10$ , and for  $S>10$  the progression appears linear - is this a reasonable consequence of the dependences discussed above? I also agree that error bars for the experimental values are desirable.

There has been a very recent publication of Knopf (2006), who derived the same conclusions concerning pseudo-heterogeneous nucleation as you did - you should quote him. Additionally, I may note that volume-based nucleation is a prerequisite of the classical nucleation theory.

Minor comments:

Page 2123, line 9: remove the question mark. Page 2134, line 26: remove the question mark Page 2143, table 1: headline: "...nucleation rates  $J$  of  $\alpha$ -NAD" body: which dimension has  $\Delta G_{act}, V$ ? foot: present a legend for the meaning of the parameters. Page 2146, fig. 3, 4, 5: explain in the figure captions the meaning of the horizontal lines in the sections (a) and (b). Page 2149, fig. 6: the label " $dN/dlogd$ " is overlapping with "100" of the color code.

References Knopf, D. A.: Do NAD and NAT Form in Liquid Stratospheric Aerosols by Pseudoheterogeneous Nucleation?, J. Phys. Chem. A, 110(17), 5745-5750, 2006.

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