

COMMENTS

Comment on “Do NAD and NAT Form in Liquid Stratospheric Aerosols by Pseudoheterogeneous Nucleation?”

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In a recent article, Knopf¹ strongly warns the atmospheric modeling community, both in the abstract and in the body of the paper, not to use parametrizations of nitric acid nucleation rates that we published in 2002² (referred to as TDHR from hereon). In this Comment, I make a few clarifications of what was actually discussed in TDHR with regard to both the validity of our published nucleation rates and whether such rates should be used in modeling studies in the future.

Before discussing the above matters, I emphasize that the main message of the TDHR paper was to introduce the novel idea of “surface nucleation” and to provide experimental evidence for this new hypothesis. In Knopf’s paper no new experimental or theoretical studies are presented to debate the main conclusion published in TDHR, regarding surface nucleation in aqueous HNO₃. In fact, a number of recent experimental and theoretical studies,^{3–8} not discussed in Knopf’s introduction, provide support for the general idea of surface nucleation.

Overall, the focus of Knopf’s paper appears to be centered in showing that nucleation rate functions published in TDHR are not applicable to more dilute solutions found in the stratosphere. We have stated, at least in seven different places in TDHR, that our published rates are for concentrated solutions and may not apply to the stratospheric system. In TDHR, we stated a number of different reasons as to why our rates may not extrapolate properly, all of which are discussed in depth in the paper. Thus the main finding of Knopf’s paper, that TDHR rates may not extrapolate properly to the stratosphere, is not surprising, based on all the caveats we discussed in the paper. In addition, Knopf argues that TDHR rates are flawed because at NAT and NAD melting points, the rates do not tend to zero. This argument is invalid because the rates were fitted over a range of compositions where S values are well above 10. Therefore, it is unreasonable to expect TDHR rates to extrapolate to zero at the melting point because no data were available at low S values to influence our fit at or near $S = 1$. Also, it is unreasonable to even expect nucleation rates to equal zero at NAT and NAD melting points, as stated and emphasized by Knopf. Due to its functional dependence, the classical formulation of nucleation rate theory, which we have used in our work, will always yield a finite value for rates at $S = 1$ or even $S < 1$. Thus one often relies on intuition to disregard finite values of rate at $S < 1$. The fact that our nucleation rates at $S = 1$ are nonzero does not violate any laws of thermodynamics, regarding melting of bulk phases, as implied by Knopf.

Also, there is no inherent problem in using TDHR rates for modeling studies in the stratosphere. In fact, we have used

TDHR rates in the past to conduct microphysical simulations for comparisons against observational data (ref 31 in Knopf’s paper). What we and other researchers (refs 28–34 in Knopf’s paper) have found is that TDHR rates are apparently too high, by a factor of 10–100, when compared against observational data. We have suggested, in one of our papers (ref 31 in Knopf’s paper), that this may be corrected by increasing the free energy term provided in TDHR by about 8–12%. Frankly, considering that the stratospheric drop system is more dilute and contains H₂SO₄, as compared to laboratory solutions used in TDHR to parametrize the rates, a factor of 10–100 difference between estimated and required rates to match the observations seems quite reasonable. Thus I strongly disagree with Knopf’s statement in the abstract, “In addition, a parametrization of pseudoheterogeneous nucleation of NAD and NAT suggested recently (Tabazadeh et al. *J. Phys. Chem. A* 2002, 106, 10238–10246) has been analyzed, showing that this parametrization should not be used in stratospheric modeling studies”. On the contrary, I suggest that modified rates, where free energies are 10% higher than originally reported in TDHR, are suitable for use in modeling studies.

It is important to note that none of the approaches currently used (refs 28–34 in Knopf’s paper) to compare calculated polar cloud properties against observational data are fully interactive 3-dimensional models. Thus, the lack of agreement between calculated and observed cloud properties may be related, at least to some extent, to factors other than just nucleation rates emphasized by Knopf. Such factors include full treatments of gravity and lee waves, full treatments of small-scale realistic updrafts and downdrafts in clouds, full 3D treatments of coupled nucleation–growth–sedimentation in clouds, etc. Particularly, for stratospheric ternary drops, fast cooling and warming cycles (associated with gravity and lee waves) will prevent ternary solutions to reach equilibrium in the stratosphere. Thus, I caution against using the simple logic put forward in Knopf’s papers to exclude homogeneous nucleation in the stratosphere.

Knopf compares observed and calculated particle number densities to eliminate homogeneous surface nucleation as a viable pathway. The problem with this approach is that observed number densities are influenced by the many factors mentioned above, whereas Knopf’s calculated number densities are only influenced by a single nucleation rate equation applied under an equilibrium assumption. Considering disequilibrium compositions for ternary drops, S values will show a range of variations around equilibrium mean values. Particle number densities, generated by surface nucleation, are most influenced by the spread of S values at the high end of the distribution and not by equilibrium mean values. The nucleation rate has an exponential dependence on composition or S values. Therefore, a short period of time spent at higher S values (lets say hours) can generate many more particles than a long period of time spent under lower equilibrium S values (weeks as assumed by Knopf). Knopf presents no arguments as to why maximum equilibrium S values, maintained over a period of 4 weeks, are appropriate to use in his calculations to derive particle number densities. Most studies use full microphysical models to derive cloud number densities (refs 28–34 in Knopf’s paper) for valid

comparisons against observational data. Thus, I strongly doubt Knopf's approach, as stated in the abstract, "If maximum NAD supersaturation persisted for 4 weeks in the polar stratosphere the corresponding NAD particle number densities are estimated to be about $6 \times 10^{-6} \text{ cm}^{-3}$. These particle number densities are 3 orders of magnitude lower than particle number densities recently observed in the stratosphere", can generate a reasonable particle number density to compare against observational data. In closing, I strongly disagree with the firm tone used in Knopf's paper to disregard surface nucleation simply because his approach is too simplistic to support such firm conclusions.

References and Notes

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