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

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Atmospheric Chemistry and Physics Discussions

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

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I would also like to respond to some of the points made in A. Tabazadeh's answer (pages S304–S305).

To comment 1: In Tabazadeh et al. 2001 the parameterization of Salcedo et al. has been used at stratospheric saturation ratios, that is for $S_{\mathrm{NAD}} < 5$ and $S_{\mathrm{NAT}} < 30$. However, as very clearly and explicitly stated in the paper by Salcedo et al., these values are outside the validity range of the parameterizations:

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Salcedo et al., page 1436:
"*This equation is valid only for* $10 < S_{\mathrm{NAD}} < 30$*, because our experimental data fall within this interval.*"
page 1437:
"*This equation is valid for the interval* $50 < S_{\mathrm{NAT}} < 110$*.*"
Clearly, the parameterizations of Salcedo et al. were used outside their validity range by Tabazadeh et al. 2001. Not a single statement with respect to this point has been made in the paper by Tabazadeh et al. 2001. Instead, the parameterizations were linearly extrapolated to stratospheric conditions (as also correctly pointed out by both referees to the commentary under discussion), despite the fact that this is physically unreasonable within the framework of classical nucleation theory (as pointed out in the Knopf et al. 2002 paper).

To comment 3: I am surprised by A. Tabazadeh's statement that the Molina et al. 1993 Science paper convinced her that bulk solutions do not freeze at stratospheric conditions. The samples in the Molina et al. 1993 paper froze when containing significant amounts of HNO_3. One of the conclusions of this paper was that "*These liquid aerosols absorb significant amounts of* HNO_3 *vapor, leading most likely to the crystallization of nitric acid trihydrate (NAT).*" The first paper that showed, based on bulk experiments and Poisson statistics, that ternary stratospheric aerosols do not freeze readily under stratospheric conditions was a GRL paper by Koop et al. in 1995. This was followed up by a J.Phys.Chem. paper in 1997 that provided a detailed description of the statistical data treatment, additional data, and also a re-evaluation of the Molina et al. 1993 data to show that also these data are consistent with our 1995 conclusions that stratospheric aerosol droplets do not freeze readily via a homogeneous (volume-based) nucleation process.

However, neither the paper by Molina et al. 1993 nor our papers (Koop et al., GRL 1995, J.Phys.Chem. 1997) are discussed or referenced in the Tabazadeh et al. 2001

ACPD
3, S349–S351, 2003

Interactive Comment

paper, although they are at odds with the microphysical parameterization used in the paper. This was the one and only reason why we wrote “another” paper (Knopf et al., 2002) stating that bulk solutions show that homogeneous volume nucleation under stratospheric conditions is negligible. In that paper we show the reasons why the way the parameterization is used largely overestimates nucleation rates of ternary droplets in the stratosphere. We added some new data for medium size samples to show the smooth connection between the small droplet data by Salcedo et al. and our former bulk sample data (Koop et al. 1995, 1997). However, the Knopf et al. paper could have easily done without any new data, since the experimental data available were already sufficient to show that the nucleation rate parameterization largely overestimates nucleation rates at stratospheric conditions.

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