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Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification

D. A. Knopf, T. Koop, B. P. Luo, U. G. Weers, and T. Peter
Institute for Atmospheric and Climate Science, Swiss Federal Institute of Technology, Zurich, Switzerland

Abstract. The nucleation of NAD and NAT from HNO_3/H_2O and $HNO_3/H_2SO_4/H_2O$ solution droplets is investigated both theoretically and experimentally with respect to the formation of polar stratospheric clouds (PSCs). Our analysis shows that homogeneous NAD and NAT nucleation from liquid aerosols is insufficient to explain the number densities of large nitric acid containing particles recently observed in the Arctic stratosphere. This conclusion is based on new droplet freezing experiments employing optical microscopy combined with Raman spectroscopy. The homogeneous nucleation rate coefficients of NAD and NAT in liquid aerosols under polar stratospheric conditions derived from the experiments are $< 2 \times 10^{-5}$ cm^{-3} s^{-1} and $< 8 \times 10^{-2}$ cm^{-3} s^{-1}, respectively. These nucleation rate coefficients are smaller by orders of magnitude than the value of $\sim 10^{3}$ cm^{-3} s^{-1} used in a recent denitrification modelling study that is based on a linear extrapolation of laboratory nucleation data to stratospheric conditions (Tabazadeh et al., *Science*, *291*, 2591--2594, 2001). We show that this linear extrapolation is in disagreement with thermodynamics and with experimental data and, therefore, must not be used in microphysical models of PSCs. Our analysis of the experimental data yields maximum hourly production rates of nitric acid hydrate particles per cm^3 of air of about 3×10^{-10} cm^{-3} (air) h^{-1} under polar stratospheric conditions. Assuming PSC particle production to proceed at this rate for two months we arrive at particle number densities of $< 5 \times 10^{-7}$ cm^{-3}, much smaller than the value of $\sim 10^{-4}$ cm^{-3} reported in recent field observations. 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. This clearly shows that homogeneous nucleation of NAD and NAT from liquid supercooled ternary solution aerosols cannot explain the observed polar denitrification.

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