

The investigation by Woiwode et al. (2016) represents an improved and updated reinterpretation of spectroscopic data on the existence of NAT particles in the Arctic lower stratosphere. However, the whole evidence is based on the symmetric nitrate deformation band $\nu_2=\delta_s(\text{NO}_3^-)$, which is in general the weakest band of the overall mid-infrared spectrum of nitric acid hydrates. Also, the differences between the ν_2 bands of NAT (α , β) and NAD (α , β) are rather small. These differences may also be caused by different crystal structures or different morphologies and textures of the very same phase. This might be worth to be mentioned in the text. Unless concomitant changes in other parts of the mid IR spectrum are not conclusively observed, minor changes in one of the IR absorptions alone constitute weak evidence for the reasons cited above.

The authors have detected highly aspherical NAT particles, which are in accordance with lab experiments (XRD, ESEM) and Avrami calculations by Grothe et al. (2006) and Tizek et al. (2004). The main aspect ratio is 1:10 or 10:1. The authors should however indicate clearly if they assign these ratios to needles or platelets? Are optical calculations able to distinguish between these alternatives?

Only recently Weiss et al. (2016) have shown that α -NAT has a much lower heterogeneous nucleation barrier than β -NAT, where ice acts as the heterogeneous nucleus. In a lab experiment, HNO_3 was deposited from the gas phase onto an ice film and the outcome was a pure α -NAT film on top of the ice substrate – similar findings are also reported by Gao et al. (2015). This is important in view of the here presented findings, since Grothe et al (2006) found long needles with an aspect ratio of 1:10 only in the presence of ice. On the other hand platelets with a much smaller aspect ratio were found in experiments without ice. So the straightforward conclusion would be that the history of the here observed NAT particles should have involved a heterogeneous nucleation step of α -NAT on ice and a subsequent transformation of α -NAT into β -NAT. It would be interesting to note if the presence of ice can be confirmed by limb emission spectra.

Additionally, Tizek et al. (2004) found a stabilization of α -NAT in ice matrices. The phase transition was so much hindered by the ice that at about 200 K α -NAT could still be observed for several hours. It might be worth to check for the presence of α -NAT in the here presented spectra. Iannarelli and Rossi (2016) have estimated an enthalpy difference of 6 ± 20 kJ/mol between α - and β -NAT in favor of the latter which just about corresponds to the enthalpy difference between diamond and graphite, also in favor of the latter, with one significant difference, namely that the barrier in the carbon system is very high in contrast to the nitric acid trihydrates. However, the phase transition occurs in both systems with differing rates owing to differences in the corresponding barriers. An interesting situation arises in α -NAT because the enthalpy of evaporation of HNO_3 is lower than in β -NAT by 32 ± 20 kJ/mol, but this difference is more than compensated by the increased stability of the H_2O network which results in the small, but probably significant enthalpy difference in favor of β -NAT.

The authors discuss a possible transformation of NAD into NAT. In Tizek et al. (2004) and Grothe et al. (2008), we have performed corresponding laboratory experiments. We may underline that we have observed α -NAD transforming into β -NAD and the respective melting of β -NAD. However, a phase change from α -NAD or β -NAD into β -NAT was of extremely low significance and should be kinetically and thermodynamically unfavorable. Also from a stoichiometric point of view, one may conclude that this would include the formation of nitric acid monohydrate or pure nitric acid, which are rather unlikely on thermodynamic grounds. Again a transformation from α -NAT into β -NAT is the most reasonable process, which also fits the observations of Weiss et al. (2016) and Gao et al. (2015).

In this context, one might also remember the AIDA experiments performed by Stetzer et al. (2006) where no NAT but α -NAD formation had been observed. The reason might be well involved HNO_3 concentrations that were larger than required for NAT formation and so led to NAD. Only recently Iannarelli and Rossi (2015) could show in laboratory experiments that increased HNO_3 concentrations exposed to pure ice spontaneously led to NAD.

References

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