Answer to Michel J. Rossi

Thank you for your positive review of our manuscript and the helpful comments. Below we address your individual comments and describe the associated changes (in bold) that have been made in the revised manuscript version.

This paper deals with the formation and characterization of a thermodynamically stable polymorph of nitric acid dihydrate using a multidiagnostic approach within the well-known large coolable aerosol chamber (AIDA) equipped with various detection techniques including high-resolution 2D imaging of submicron and supermicron-sized ice particles in the presence of HNO3. This work is convincing, well-done with many quality control benchmarks and informative. The report is well organized, easy to follow, well written and represent a good compromise between sufficient detail and flow of presentation. The new aspect of this work, apart from the surprising discovery of fast growth conditions of β-NAD by heterogeneous nucleation in the presence of proxies of meteoric smoke aerosol particles, resides in the detailed analysis of the scattering properties of resulting solid α- and β-NAD aerosol particles resulting in a marked crystal shape of the two polymorphs. Time will tell whether or not the shapes of elongated needles (α-NAD) or compact spheroids (β-NAD) will explain the atmospheric lifetime or residence time of these aerosol particles in future real observations of given strata within the atmosphere in case β-NAD particles occur at all in nature. I propose the publication of this work in acp once my sparse comments will have triggered a suitable response by the authors.

In what follows I will submit the following comments/questions and remarks concerning the submitted manuscript in the hope to provide a line along which the authors may make changes to the manuscript:

• The displayed FTIR absorption spectra in Figures 5, 6, 8, 9, 10 and 11 are important spectral observables representing key elements in support of α- and β-NAD. However, in comparison to recent spectra, for instance by Iannarelli and Rossi (2015) recorded at nominally identical spectral resolution of 4 cm-1 the present spectra show relatively few details in comparison. Have the present FTIR spectra been smoothed in order to suppress small albeit potentially important details? I am aware that recording conditions (T and/or growth conditions, particle size distribution functions, scattering properties, etc.) may lead to minor frequency shifts and small differences in spectral appearance, but what are the reasons for the apparent lack of spectral details in the FTIR spectra? In cases where several FTIR spectra are shown in a stacked manner (for instance in Figure 5 or 6) it is unclear what the displacement of every superimposed spectrum (spectra b to e) is in terms of optical depth or absorption compared to the lowest. I assume that the labelled scale only applies to the lowest displayed absorption spectrum.

As mentioned in line 334, for technical reasons (to improve and speed up the convergence behaviour of the optimisation algorithm) we applied a weak smoothing function when retrieving the *k* spectrum. This was strictly limited to regions with broad absorption signals (e.g. not applied in the regime of the narrow 1038 and 812 cm^{-1} modes) and affected the *k* spectrum obtained (Fig. 8) and the calculations performed with this data set (Figs. 9 - 11). What we actually missed to report is that we corrected all the displayed measured spectra for imbalances in the gas phase CO_2 concentration between the reference runs before aerosol injection and the later sample runs in the wavenumber range from 2400 to 2280 cm^{-1}. We have added this information in line 202:

"All measured spectra displayed in this article were corrected for imbalances in the gas phase CO_2 concentration between the reference runs before aerosol injection and the later sample runs in the wavenumber range from 2400 to 2280 cm^{-1}."

A correction for water vapour signals (at 1600 and 3600 cm^{-1}) was not applied. The displayed NAD spectra were recorded at times when the transient increase in relative humidity after aerosol addition (see Fig. 4) had already subsided, so that the spectra were measured at similar relative humidity compared to the reference runs. This and the very low absolute water vapour concentration at low temperatures in the AIDA chamber made the H_2O correction obsolete.

The observation of higher feature detail in the spectra of Iannarelli and Rossi (2015) could also be due to the fact that these spectra show a progressive change in the signatures as HNO_3 was deposited on the ice films, and that the spectra also represent a superposition of two species, ice and NAT/NAD. Deconvolution was used to derive the pure NAD/NAT spectra, which could give rise to some features, as the pure substances in a mixture can undergo small frequency shifts.

We indeed missed an accurate description of the displacement applied to the stacked spectra in Figs. 5 and 6, thank you for pointing this out. Yes, the scale only refers to the lowermost spectrum and is therefore misleading for the other spectra. We therefore propose to change the labelling similar to the representation chosen by Grothe et al. (2004): We remove the label numbers and indicate by a bar in the panel the height of e.g. 0.02 optical depth (OD) units. The revised Fig. 5 would then look like (the upper part of Fig. 6 will be changed accordingly):
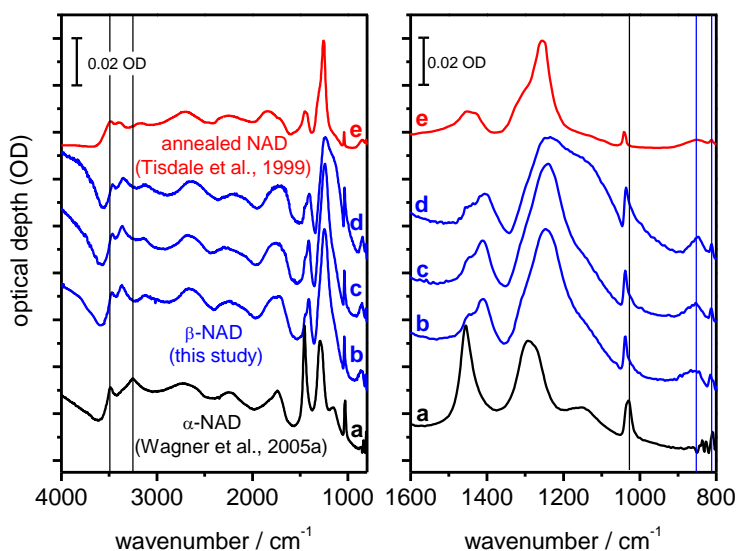
Added statement at the end of the figure caption:

"Individual spectra have been offset for clarity. The digitised absorbance spectrum (e) does not adhere to the optical depth scale and has been arbitrarily scaled to allow comparison with the AIDA measurements."

• Compared to the referenced precursor studies the present work clearly starts out with liquid droplets of HNO3/H2O aerosol, and it is this starting condition that enables the unambiguous observation of β-NAD when meteoric smoke proxies (Illite, MgFeSiO4) are used as seed crystals, otherwise α-NAD is observed for homogeneous freezing without ever ending up as stable β-NAD. This case corresponds to an immersion freezing event triggered by specific (solid) seed aerosol. On the other hand, we and others have exclusively observed the formation of α-NAD in case gas-phase HNO3 is deposited on a macroscopic ice surface without ever observing the conversion from α- to β-NAD. In this case the mechanism might be a case of condensation freezing on PSC II particles that are less prevalent compared to PSC Ia and Ib clouds. Even though the authors state this fact at the end of the article this difference seems to be important enough to alert the reader early on in the report. In addition, the bifurcation between NAT and NAD depends on the partial pressure (activity) of HNO3 at constant partial pressure of H2O vapor (Iannarelli and Rossi, 2015): by doubling the flow rate (concentration) of HNO3 we obtain NAD at the expense of α-NAT that converts to β-NAT with increasing temperature. It thus very well may be that NAD (including β-NAD) may never be accessed depending on the freezing mechanism. Relevant experiments on ice aerosol substrates may be performed in the AIDA chamber in order to test several growth mechanisms,

even if the partial pressure of H2O may be increase somewhat to artificially produce PSC II cloud particles.

We are happy to take up this suggestion, i.e. to emphasise the different nucleation pathways already at the beginning of the article, and have added the following paragraph at the end of our introduction in line 141:

"In anticipation of a later more detailed discussion of possible NAD/NAT nucleation mechanisms, we would like to emphasise here that our experiments address a particular heterogeneous nucleation process for β-NAT, i.e. immersion freezing induced by specific solid seed aerosol particles. This differs from other studies such as Iannarelli and Rossi (2015), where the deposition of HNO_3 vapour on pure H_2O ice led to the almost barrier-free growth of α-NAT and NAD. Iannarelli and Rossi (2015) also showed that the type of particles formed was sensitive to the partial pressure of HNO_3, with lower values favouring the formation of α-NAT. Depending on the freezing mechanism, neither α- nor β-NAD could therefore be accessible at all."

• My guess is that both OPC and SID-3 instruments were exposed to low temperatures. Did the authors encounter any temperature problems or other anomalies (calibration) in the vicinity of the measurement ports (inlet or optics)?

SID-3 is an airborne instrument that has been used frequently in aircraft campaigns in the stratosphere and is therefore robust for use at low temperatures (e.g. some optical components are heated to prevent condensation). No special adjustments were required for its use in the AIDA chamber. As the only precaution, when the SID-3 electronics were switched off and no longer generated internal heat, but the instrument was still exposed to low temperatures, we heated the stainless steel container in which the instrument was installed. We will include the information that the container was heatable in the revised manuscript version.

The OPC works with fibre optic technology, i.e. only the measurement cell (sensor unit) is exposed to low temperatures, while the electronics with light source and photomultiplier detector are located outside the insulating housing of the AIDA chamber (connected with optical fibres). Its use is therefore also specified for very low temperatures. We added a respective statement in line 228:

"The electronic unit of the OPC with light source and photomultiplier detector is located outside the insulating housing and is connected to the sensor unit with optical fibres."

• On line 350 what is the definition of the saturation ratio SNAD? Ratio of the activities of HNO3 to H2O water vapor? Please include the expression into the manuscript by mentioning why this was a calculated and not a measured parameter.

We propose to extend our description in line 350 as follows by now first explaining the definition of S_{NAD} and then our calculation method in more detail.

"S_{NAD} is the saturation ratio of the liquid phase with respect to solid NAD. Explicitly, it is the quotient between the activity product of the ions (H^+, NO_3^-) and the solvent (H_2O) in the liquid phase, i.e. $a(H^+) \cdot a(NO_3^-) \cdot a^2(H_2O)$, and the respective activity product in a solution saturated with respect to solid NAD (K_s) (Salcedo et al., 2001). Assuming that the liquid and the gas phase are at equilibrium, we first calculated the above activity product for the temperature and relative humidity conditions prevalent in the AIDA chamber with the E-AIM model (Clegg et al., 1998; Massucci et al., 1999). The formation of solid phases was hereby prevented. Afterwards, the activity product for NAD-saturated conditions, K_s, was computed according to the temperature-dependent function given in Eq. (A9) of Massucci et al. (1999). The ratio of these two activity products then yielded S_{NAD}."

More directly, the E-AIM model could also be fed with the composition of the nitric acid solution droplets obtained from the FTIR spectra to compute the activity product in the liquid phase (Stetzer et al., 2006; Möhler et al., 2006a). However, due to the rapid growth of β-NAD in the heterogeneous nucleation experiments, the recorded infrared spectra quickly showed an overlap of the signatures of the liquid HNO_3/H_2O solution droplets and the solid β-NAD crystals. An accurate determination of droplet composition was therefore not possible, so we constrained the E-AIM model to the measured relative humidity instead.

• What is the significance of the magenta window in the right and left hand panels of Figure 4: is it to highlight the change in time duration for reaching the peak of rh and the concomitant onset of aerosol particle nucleation?

The magenta-coloured frames indicate the duration of the injection of the mixed HNO_3 and H_2O carrier gases (in the case of the β-NAD experiment together with the seed aerosol particles). This is mentioned in line 348 in the article and in the figure caption.

• The linear depolarization results discussed in lines 491-497 are hard to rationalize in terms of differences of the shapes for α- and β-NAD. What is the physical reason for the three times larger depolarization ratio of β-NAD vs. α-NAD despite the more needle-like shape of the latter? This is somewhat counter-intuitive despite the invoked reference of Zhakarova and Mishchenko (2000) and may have far-reaching consequences for the interpretation of LIDAR atmospheric backscattering signals.

The scattering properties of needlelike and platelike particles are indeed "unique" and, therefore, "the weak depolarization capability of highly aspherical particles should be

taken into account during analysis of lidar depolarization measurements" (two quotes from the article by Zakharova and Mishchenko (2000). It is difficult to put this behaviour into a simple physical picture. Zakharova and Mishchenko (2000) found that some scattering parameters for the needlelike and platelike particles, such as the phase functions and the asymmetry parameters, are similar to those of surface-equivalent spheres. In other words, these parameters are determined by the value of the size parameter of the sphere having the same projected area as the aspherical particle. Other scattering parameters, however, such as the extinction efficiencies and the depolarisation ratios (linear and circular), are more sensitive to the value of the size parameter along the smallest particle axes, which can assume values below unity in the case of strong deviations from the spherical shape, even if the surface-equivalent-sphere size parameters are much larger. For these quantities, the scattering behaviour of needlelike and platelike particles is then typical of Rayleigh scatterers, i.e. they show much lower extinction efficiencies and lower depolarisation ratios compared to compact particles with the same surface-equivalent-sphere size parameters. This then leads to the important conclusion that the magnitude of the depolarisation ratio cannot be simply related to the degree of asphericity. We will expand the reference to Zakharova and Mishchenko (2000) (line 492) in the revised manuscript text as follows:

"Using ice crystals as an example, Zakharova and Mishchenko (2000) have shown that wavelength-sized needle- and plate-like particles, modelled as spheroids with aspect ratios of 0.05 and 20, have unique scattering properties. While some scattering parameters, such as the phase functions and the asymmetry parameters, are similar to those of surface-equivalent spheres, other quantities, such as the extinction efficiencies and the depolarisation ratios (linear and circular), resemble those of Rayleigh particles. In particular, such needle- and plate-like particles cause much less backscattering linear depolarisation than surface-equivalent particles with moderate aspect ratios of 0.5 and 2."