Response to reviewer 1

We thank the reviewer for their comments, which are reproduced below. Our response is in bold text.

This article describes the generation of a new set of spectroscopic parameters for NH3. It is careful and solid work, and the article is well written. The study seems quite complete other than the lack of temperature dependence, which could play a role in the analysis of atmospheric measurements somewhere other than near the surface; for example, with retrievals using MIPAS or ACE-FTS measurements in the upper troposphere where temperatures are quite different from 296 K.

Note that an analysis of temperature dependence is ongoing, with experimental measurements already completed. We will publish this work in due course.

The lack of temperature effects in the analysis might not be a major problem for pressure broadening parameters (in that pressure broadening temperature dependence information is already available in HITRAN for NH3 lines) or pressure shifts (in that it is typically assumed that pressure shifts have no temperature dependence). The biggest question might be the temperature dependence of speed dependence (through the parameter aw). Assuming that aw is constant as a function of temperature would imply that Γ0 and Γ2 have an identical temperature dependence, which may not be the case. This is not an issue that needs to be addressed in this paper, though.

Our version of Labfit does not include temperature dependence for the speed dependence parameter, but this is something that can be included in the program in future.

I am wondering if Γ2 values derived in this study (using the formalism in Eqs 8 and 9) can be directly used with the “quadratic speed dependent Voigt” formalism used elsewhere in the literature, expressed as the difference between two Voigt-like expressions. Software that uses line-by-line calculations seem more likely to employ the quadratic speed dependent Voigt formalism because it does not involve numerical evaluation of the integral over velocity, which should make it more efficient to calculate. This likely does not matter for IASI, CrIS, and TES (the suggested end users of the new parameters) because they presumably employ look up tables instead of line-by-line calculations, which means there would only be a one-time cost from the extra calculation requirements when populating the look up tables. I expect the two formalisms are compatible, differing only in the order of integration over velocity for the double integral associated with speed dependent Voigt (i.e., integrating over velocity first for “quadratic speed dependent Voigt” as compared to integrating over velocity second for the LabVIEW formalism described in the paper), but that is an assumption.

We think the two formalisms are equivalent. There are plans to perform a comparison in due course.

Note that a paper has been submitted (still under review) titled “New beyond-Voigt line-shape profile recommended for the HITRAN database by P. Wcislo et al” meant to guide future non-Voigt parameter usage in HITRAN. For speed dependent Voigt, the suggested “official HITRAN” line shape (the modified Hartmann Tran profile) will be the difference between two Voigt-like expressions.

Some people may continue to employ Voigt line shapes rather than switching to more accurate non-Voigt calculations. HITRAN has separate database streams for Voigt and non-Voigt, so you might want to consider what users will get if they request a set of Voigt profile parameters for NH3 from HITRAN after your data have been inserted. Will it be the older data set that contains no lines with non-Voigt parameters (and therefore none of your data)? Will it be your data for weaker lines and older data for the strongest lines (because the strongest lines use speed dependent Voigt in your data set)? Will it be all your data with non-Voigt parameters like speed dependence simply stripped out (which would make pressure broadening parameters too large, so I can't imagine them going that route)? If you want to completely replace the old NH3 parameters, you might need to consider providing HITRAN with two sets of parameters: a "Voigt set" and a "speed-dependent Voigt set." That would require extra work on your part, of course.

We do have a version of the fit without speed dependence, so providing two different linelists to HITRAN could be considered.

Nothing discussed here requires edits to the article. The only technical change I would suggest is to put the references in alphabetical order to make them easier to parse.

Yes, this will be done. Originally the references were numbered, but we forgot to reorder them once they were changed to the AMT format.

Response to reviewer 2

We thank the reviewer for their comments, which are reproduced below. Our response is in bold text.

This manuscript reports FT-IR measurements of spectroscopic line parameters of $^{14}NH_3$ and $^{15}NH_3$ in the 685 – 1250 cm^{-1} region covering their ν_2 band and more. In general, the spectrum fitting residuals look great, implicating the retrievals are high-precision.
As was pointed out in the manuscript, the NH_3 (ν_2) band is the strongest among its infrared bands. Furthermore, its rich spectrum makes it a valuable tracer of physical and chemical properties of diverse environments. Thus, the NH_3 ν_2 band has gained a lot of attention from atmospheric and planetary remote sensing communities.
However, its unusual strength makes it challenging to do precision measurements because their transitions are easily being saturated under a typical laboratory and optics setup. NH_3 is also well known to be a polar molecule, requiring special care to handling its gas sample transfer and minimizing any chance of possible cross-contamination, esp. with residual water in a supply line.
In this work, we note that their line positions, air-widths, air-shifts, and speed-dependence parameters have been characterized in an unprecedently high precision and accuracy through multispectrum fitting analysis software package that has repeatedly been validated by multiple projects. However, there are a couple of potential issues to be addressed.

[1] The experimental conditions and optics employed in the work are not sufficiently optimized for self-width and shift retrievals. Most of transitions from the ν_2 band are very strong. The highest NH3 sample pressure adopted was not more than 0.995 hPa for pure sample spectra and 1.29 hPa for Air-mixture spectra. According to Fig. 5(a) presenting all self-widths being no greater than 0.7 cm^{-1}/atm, the actual self-width contribution expected on the spectra obtained at

1.29 hPa is 0.0009 cm^{-1}, which corresponds to much less than the Doppler width, 0.0015 cm^{-1} near 1000 cm^{-1}. Moreover, many of the observed v2 transitions are near saturation for the pure sample spectra. Thus, the spectroscopic line shape parameter retrieval becomes even harder (because of the least constraining power from the observed spectrum in the saturated region). The validity of the self-line shape parameter retrievals should be argued more if the authors want to keep them as part of the measurements to be reported.

With regards to the experimental conditions, the focus of this work was for application to atmospheric measurements, so the "air" lineshape parameters are the most accurate. We did state in the manuscript section concerning self- and air-induced pressure shifts that the self parameters have larger errors because of the smaller range of NH_3 pressures in the analysis. We have now made this more clear. The HITRAN "self" parameters did not reproduce our pure measurements, so there was no alternative but to float them in the multispectrum fit. Further pure measurements at higher NH_3 pressures (with shorter pathlengths) would make it possible to determine more accurate self-width and shift values, but this wasn't within the scope of this work. Note also that the Doppler profile falls off from the line centre significantly faster than the Lorentzian profile, so the Lorentzian self widths can be determined from the wings of each line. The saturation issue will be addressed as part of the next point.

[2] Regarding line intensity measurement, one should put more weigh on their retrievals from pure sample spectra. Assuming that the air-mixture samples were prepared by adding Air to the existing pure sample in the cell (instead of preparing a pre-mixture sample gas), the sample mixing ratios of the admixture spectra are not intrinsically accurate because of contribution from the dead volume, i.e. any NH3 amount inside the protruding inlet value out of the cell body, as illustrated in Fig. 1. Therefore, line intensity measurements should count on the pure sample spectra. However, most transitions in the pure sample spectra are saturated. Authors should discuss more this weakness of their experimental conditions in the context of the measurement uncertainty estimates in Sec.4.1.

The line intensity calculation is driven by the pure NH_3 spectra in the fit. There are 5 of these, for which the lowest pressure (0.0171 hPa) NH_3 spectrum has no saturated lines; the transmittance of the strongest line is ~ 0.17. Therefore, each line has at least one, usually more, unsaturated pure measurements from which to derive intensities. It is the case that the lowest pressure measurements are less accurate, so we adjust these values in the fit so that the residuals align with those for the spectrum with the most accurate pressure (0.995 hPa). This adjustment is largely driven by unsaturated lines that are present throughout multiple spectra.

The reviewer might not appreciate that in a multispectrum fit, intensity information is also provided by the air-broadened spectra. The NH_3 mixing ratios for each air-broadened spectrum are adjusted in the fit to minimise the residuals (in order to agree with the intensities determined from the pure spectra), and these provide accurate relative intensities that feed into the fit.

Other miscellaneous items are listed below.
Title:
A compact title is suggested, for instance,

"Measurements of spectroscopic line parameters of 14NH$_3$ *and 15NH3 in the 685-1250 cm*$^{-1}$ *region for atmospheric remote sensing"*

We believe that our title is similarly compact – we chose to emphasise that new spectra are being taken and new line parameters determined, rather than focusing on both isotopes of ammonia.

Abstract:
Line#10: A few words and phrases are repeated in the first paragraph, e.g.
Delete "is a toxic pollutant" in the 1st sentence.
Delete "is one of the key pollutants" in the 2nd sentence.
Then, rearrange the paragraph.
Introduction:
Line#56: The word choice, 'defined', sounds odd. We suggest using 'characterized'.
Line#64: Instead of saying as "given arbitrary values of 0.5", we suggest stating it "set to be", which is more neutral.

Small changes have been made to the wording of the abstract and introduction to account for these comments.

Experimental details:

Line#95: *AgCl windows*
We are not sure whether AgCl windows is a good choice for use with a NH3 sample. There is a substantial chance of unwanted reactions between the AgCl windows and the NH3 sample gas. Was there any signal degradation from the contaminated windows while introducing and holding the NH3 sample into the cell? Authors should make comments on this, which will be useful to readers.

Our understanding is that AgCl and NH$_3$ **only react in aqueous solution. We tested the windows carefully and found that the mixtures were stable for many hours of scanning, with no signal degradation. We will include a comment on this in our final article.**

Lines#113-114: *"... empty cell spectra (taken at 0.03 cm-1 spectral resolution)...."*
This resolution of 0.03 cm^{-1} might be a typo of 0.003 cm^{-1}. In general, transmission spectra should be generated by point-by-point division between sample spectra and their corresponding empty spectra. Thus, if it was not a typo, authors should explain how the mismatched spectral resolution was handled when the transmission spectrum was generated. In particular, the mismatched resolution causes a serious line shape issue for the residual water features in the transmission spectra.

This wasn't a typo. The background resolution was 0.03 cm^{-1} **as reported. This is standard practice for many researchers in the field. Backgrounds recorded at 0.003 cm**$^{-1}$ **resolution are significantly noisier and this noise will be transferred to the transmission spectra when they are generated, impacting the quality of the fit. Instead, it is better to make use of backgrounds at lower resolution with less noise. The generation of the transmission spectra was handled by the Bruker OPUS program, which zero-fills the backgrounds to provide a point-by-point division on the grid of the single channel sample scans.**

There were no water features above the noise in the analysed spectral region, so no mismatch in resolutions to worry about. The water lines used for wavenumber calibration

lie outside this main region. In this case, the line positions were determined from the single channel sample scans without division by a background.

Analysis and data retrievals

Line#133: Define "I" in Eq.(2) and describe the source of the preceding constant, i.e. sqrt(ln2/π)/γ_D.

"I" is clearly defined in the text as the normalised Voigt lineshape with Rosenkranz line mixing. The preceding constant naturally falls out when taking the convolution of the Gaussian and Lorentzian profiles. It essentially comes from the Doppler part of the function. This is a well established equation and has been included on a number previous Labfit papers.

Table 4. $^{14}N^{1}H_3$ notation looks odd. We suggest deleting the superscript on H since ^2H and ^3H have their own designated notation, D and T, respectively.

It might look odd, but it is correct according to IUPAC.

Fig. 3 and throughout the manuscript, the ground state notation, 0, should be replaced by 'gs'.

We use '0' rather than 'gs' as our ground state notation to avoid confusion with the symmetry notation – 's' or 'a'.

Self- and Air-pressure-induced shifts.

Fig. 7: What are those up-and-down pattens on the shifts w.r.t. the K values for given J? Could it be related to an incomplete modeling of line mixing effects for the transitions within a given J manifold, although the fitting residuals with the Rosenkranz parameters look good as presented in Fig. 11.

Currently, it is unclear to us what the up-and-down patterns in the air-shifts with J are due to. We note that the reverse pattern is observed for the opposite symmetry transition (see Fig. S6b). It is possible that a full line mixing approach would better resolve the shifts, but this would require a considerable amount of additional work.

Supplements

Fig. S1(b): Remove the unit notation in the Y-axis. Fig S1(b) presents values of the retrieval errors ratioed to their retrievals. Thus, they have no dimension. Also, put them as in % for quick grasp.

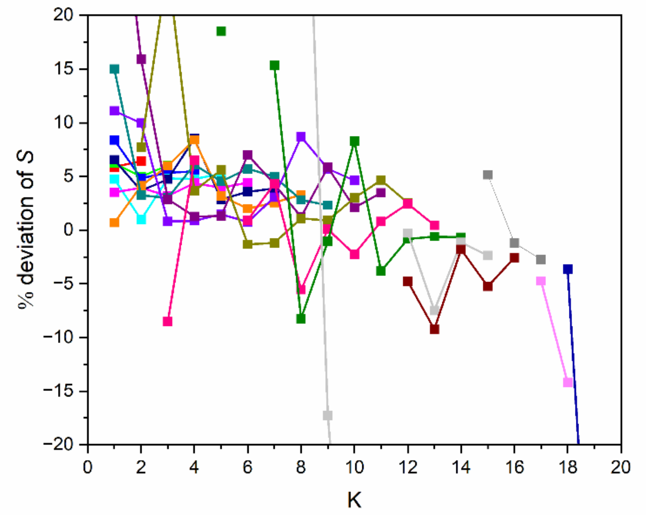
Fig. S2, S8, S13, S18, S23, S28, S30, S32(b): the same as above.

Yes, this was an oversight and will be corrected.

Fig. S3: Authors stated that "*For both cases, only lines with line intensity > 1 x 10-21 cm-1 / (molecule cm-2) are plotted*". It should be recalled, however, that strong lines are in near saturation in the pure sample spectra, thus more vulnerable to ill-determination of their intensity measurements. It is indeed interesting to see the %deviation decreased with increasing J and K whose transitions are in less chance of being saturated in the observed spectra. Also, recall that air-mixture spectra are sufficiently good for line shape parameter measurements, but not optimum enough for line intensity measurement because of such an intrinsic limitation on precision monitoring of the absorber sample pressure as stated above.

As explained earlier, this isn't quite true. Each line has at least one unsaturated pure measurement from which to derive intensities. Also, as explained earlier, relative intensity information is also provided by the air-broadened spectra. None of the air-broadened measurements are saturated. In our analysis the mixing ratios are adjusted to be compatible with the intensities derived from the pure measurements.

We note that in Fig. S3, whilst there does initially appear to be a decrease in % deviation of S with increasing J and K. In the plot in Fig. S3b, only lines of intensity *S* > 1 x 10^{-21} cm^{-1} / (mol. cm^{-2})) are included, as specified in the figure caption. The plot below shows the same data with the lower intensity lines now included; the decrease with K is more clear due to the inclusion of more lines with J > 11. HITRAN 2020 underestimates the line intensity for the low J/K lines, and overestimates the line intensity for the high J/K lines.



Furthermore, the plot below shows how the % deviation of S varies with line intensity, for the same Q branch of the same band plotted in Fig. S3. It is clear that the highest % deviations, positive and negative, are found where the line intensity is lower.

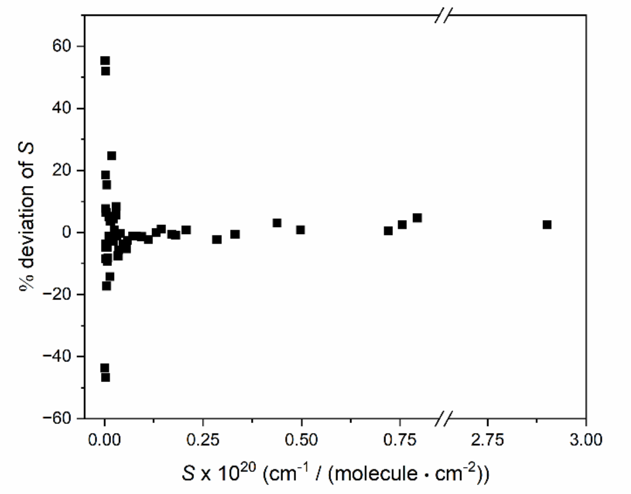


Table S7: transitions from v4(a) – v2(a) are reported.
Why not v4(s) – v2(s), whose transitions are of comparable intensities to their counterparts?

It is not possible to report ν4(s)←ν2(s) values, because the branches for this band lie outside our spectral region, at lower wavenumber than the 685-1250 cm-1 region that formed our study. We note that for the ν4 (a)←ν2 (a) transition, we are not able to report the full Q or P branch, because these also lie outside our spectral region. We refer the reviewer to Table 4 in the main body text, which details the transition bands, and their branches in ranges of J", that we were able to observe in our spectral region.

Fig. S6 and S12 report δair or δself for the transition $\nu2$←0. However, their numerical values are not included in Table S1 and S2. Explain what has happened to them?

Tables S1 and S2 only include lines for the ν2←0 transitions of lower spectral line intensity (< 1 x 10-21 cm-1 / (molecule cm-2)). The list of higher intensity lines, which includes the lines for which air- and self-shifts could be derived, is found in Tables 6 and 7 in the main body text. The headings of both Tables 6 and 7 reference that lower intensity lines are found in the supplementary information.