



HAL
open science

The ammonia absorption spectrum between 3900 and 4700 cm⁻¹

Patrice Cacciani, P. Čermák, J. Vander Auwera, Alain Campargue

► **To cite this version:**

Patrice Cacciani, P. Čermák, J. Vander Auwera, Alain Campargue. The ammonia absorption spectrum between 3900 and 4700 cm⁻¹. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2021, pp.107961. 10.1016/j.jqsrt.2021.107961 . hal-03433182

HAL Id: hal-03433182

<https://hal.science/hal-03433182>

Submitted on 17 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Journal of Quantitative Spectroscopy and Radiative Transfer

The ammonia absorption spectrum between 3900 and 4700 cm⁻¹

--Manuscript Draft--

Manuscript Number:	JQSRT-D-21-00512R1
Article Type:	VSI:HITRAN2020
Keywords:	Ammonia; NH ₃ ; absorption spectrum; 2.3 μm atmospheric window; HITRAN
Corresponding Author:	Alain Campargue Centre National de la Recherche Scientifique Saint Martin d'Hères, FRANCE
First Author:	Patrice Cacciani
Order of Authors:	Patrice Cacciani Peter Cermak Jean Vander Auwera Alain Campargue
Abstract:	<p>Room temperature absorption spectra of ammonia have been recorded by high-resolution Fourier transform spectroscopy in the range 3900-4700 cm⁻¹ at four pressures (13, 46, 140, and 304 Pa). The investigated spectral region overlaps the important 2.3 μm atmospheric transparency window. 8419 absorption lines were retrieved from the recorded spectra. Line intensities range between 1×10⁻²⁵ and 1.6×10⁻²⁰ cm/molecule. The rovibrational assignments, relying on the position and intensity agreement with the C2018 theoretical line list, were validated by the systematic use of Lower State Combination Difference (LSCD) relations. 6052 transitions were assigned to 51 vibrational bands of the main isotopologue, 14 NH₃, and 625 transitions of the 15 NH₃ minor isotopologue were identified. Overall, the assigned transitions represent over 99.8% of the integrated absorption at room temperature in the region. The upper state empirical energy of a total of 2287 rovibrational levels of 14 NH₃ were derived. Among them, 1870 are newly reported. The achieved quality of the LSCD relations indicates that the accuracy of the derived energy levels is better than 0.001 cm⁻¹. Comparison with the HITRAN2020 list shows that the present results will be valuable in improving the ammonia spectroscopic databases in the region, both in terms of completeness and accuracy of the line positions and line intensities. A recommended line list for ammonia in natural isotopic abundance is provided for the studied region.</p>
Suggested Reviewers:	<p>Robert Hargreaves robert.hargreaves@cfa.harvard.edu</p> <p>Keeyoon Sung Keeyoon.Sung@jpl.nasa.gov</p> <p>Sergey Yurchenko s.yurchenko@ucl.ac.uk</p> <p>Volker Ebert Volker.Ebert@ptb.de</p>
Response to Reviewers:	see the file "Answers to the reviewers.docx"

Response to the reviewers

Ref: JQSRT-D-21-00512

The ammonia absorption spectrum between 3900 and 4700 cm^{-1}

We thank the two reviewers for their useful comments which were taken into account as detailed below.

-Reviewer 1

In this manuscript, P. Cacciani, P. Čermák, J. Vander Auwera and A. Campargue present measurement and analysis of spectra of NH_3 -14 and NH_3 -15 in the range 3900-4700 cm^{-1} , with 8419 new line positions reported together with intensities. Out of these 8417 transitions, 6677 lines are assigned: 6052 lines of NH_3 -14 are provided with full ro-vibrational assignment, while 625 line of NH_3 -15 have the rotational assignment only. The latter is due to the insufficient accuracy of the existing theoretical predictions.

In my opinion, this is an excellent experimental work that reports new important experimental high-resolution spectroscopic data for two isotopologues of ammonia. From the theoretical point of view, this work is a good example of the paradigm shift in the experimental analysis from effective Hamiltonians to empirical variational calculations in cases where the former fail due to a large number of interacted vibrational bands. The latter are commonly based on refined potential energy surfaces and ab initio dipole moments. It is only recently that the accuracy of such variationally computed line lists became sufficiently high to be useful for analysis of experimental spectra of vibrationally excited manifolds. The manuscript is perfectly suited for the JQSRT readership. The experimental line list is provided as part of this work. All details of the experiment and analysis are carefully explained making this work reproducible. It is also well written and I don't have anything to suggest. I recommend publishing it as it is. It will be interesting to see if this work will stimulate a new empirical line list for NH_3 -15, so much needed to support this and future experimental data on this molecule.

We thank the reviewer for his/her positive comments

-Reviewer 2

The authors present their study on the spectrum of ammonia for the 3900 - 4700 cm^{-1} region. This spectral range has been shown to be incomplete in the spectral databases (e.g., HITRAN) and limited spectroscopic studies for this region has restricted the number of transitions that can be provided from energy level networks (e.g., MARVEL). This work is therefore a very welcome analysis of the 3900 - 4700 cm^{-1} region of ammonia that significantly expands the number of assigned lines for $^{14}\text{NH}_3$ (as well as $^{15}\text{NH}_3$). The authors have supplied detailed supplementary material (and uncertainty considerations) that will be valuable in refining ab initio calculations and improving spectroscopic networks, and will help to increase the accuracy of spectroscopic databases for this range. The paper is very well written and will be of interest to the JQSRT readership. There are some minor comments below that can be addressed before publication.

Abstract: "C2018" is quoted in the abstract, but the full reference is preferable (i.e., Coles et al. 2018) We changed "C2018" to "Coles et al. 2018" in the abstract.

Page 4: "limited to 80X cm^{-1} " what is meant by the "X"?

It should be "80 cm^{-1} ". It is now corrected

Done

Figure 6 caption and text: While the description explains the assignment process it could benefit for some additional clarity. For example, it may help readers to state that panel "B" demonstrates that resulting assignments of this line for the caption. Also, a further reference to the previous work by the same authors (Ref. [18]) could be included as this provides additional details of the assignment methodology.

The reviewer is right: our caption was not sufficiently explicit. We have added to the caption of Fig. 6: "For the (A) tentative assignment, five C2018 transitions are predicted but no LSCD coincidences are found neither in our line list nor in available databases. For the second tentative assignment (B), two of the three predicted LSCD lines are present in our list, one of them being also in Beale's list [17]. The third predicted line is obscured by the wing of strong neighboring lines and represented with the dashed line. The (B) upper state leads to unambiguously assign the considered line to $2\nu_2^s + \nu_3^1(J = 7, K = 7, \Gamma_{tot} = A_2'') \leftarrow \nu_2^s(J = 6, K = 6, \Gamma_{tot} = A_2')$."

Page 13: Regarding the unassigned lines, what is the likely explanation that the (relatively) strong lines in Figure 7 for C2018 are not able to be assigned? Is this possibly due to the matching criteria being too narrow for the C2018 accuracy? Or maybe the experimental lines are blended? Where there instances where a potential assignment could have multiple possible assignments? For example, in the process presented in Figure 6, were there examples when both possible assignments provided a successful assignment?

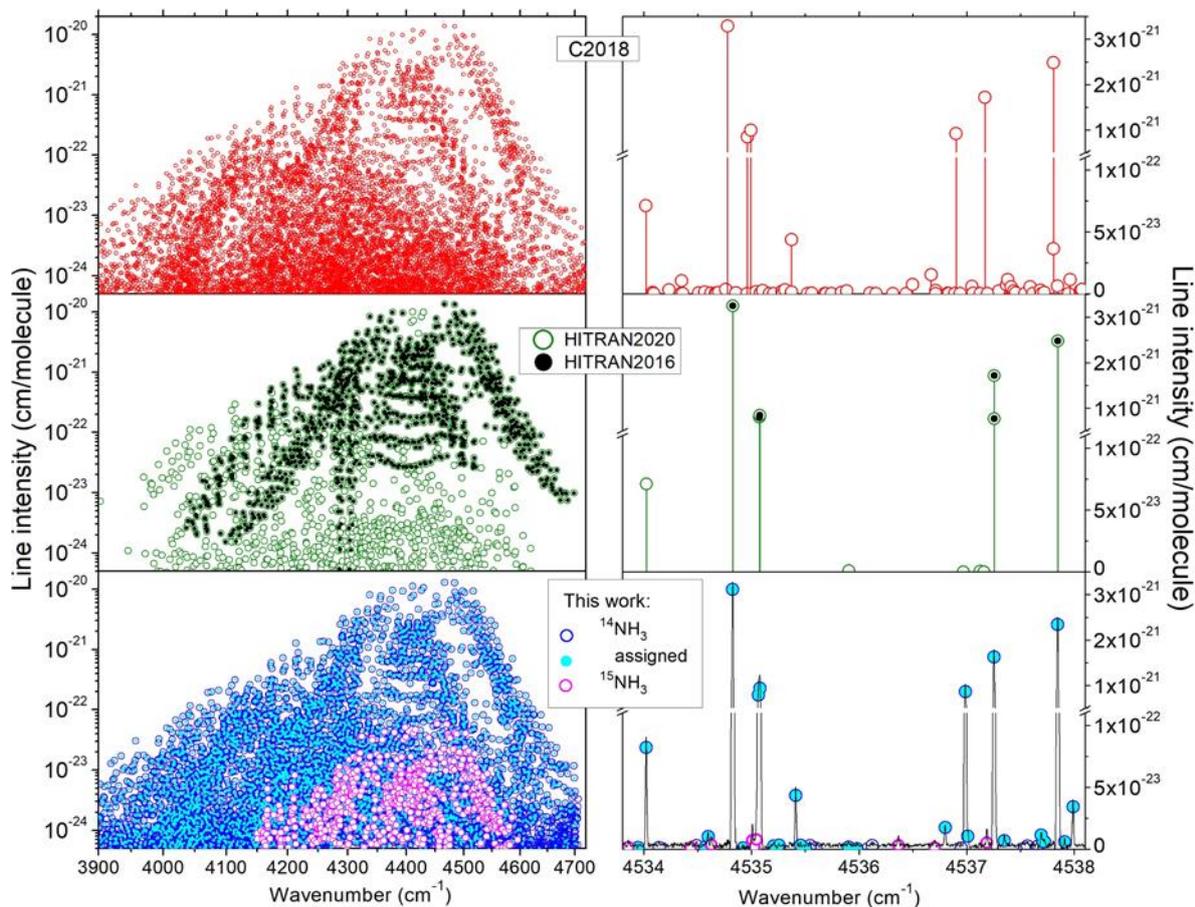
We did important efforts to decrease the number of unassigned lines. As a result, the strongest unassigned lines have an intensity smaller by three orders of magnitude compared to the strongest lines in the region. Different reasons can explain the C2018 calculated lines which could not be identified in the spectrum. The most obvious reason is that the corresponding experimental partner is hidden by a stronger line and that was missed when assigning this line. This kind of situation was possible to detect when LSCD is found for the two components (see in the Supp Mat all the double assignments where extra line distant by $1\text{E-}5 \text{ cm}^{-1}$ is generated in order to fill the two assignments). If no LSCD is found, it is difficult to detect such situation.

We cannot exclude that the agreement criteria used to pair C2018 and experimental lines was too strict in some particular situations. For instance, local resonances could lead to perturbation of the line position or to intensity transfers i.e. "anomalous" line intensities.

Finally, if several candidate exist but the good assignment cannot be unambiguously discriminated, no assignment was proposed.

Figure 8: This figure is good at showing the overall improvements for the new work. However it is not clear why some of the points on the zoomed regions contain lines, while others do not. It would be interesting to include the spectrum as an overlay for the C2018 and HITRAN zoomed regions (as done for "this work"). This would help to emphasize the intensity/positions differences for lines in these works.

We have made the stick spectra visible on all the panels (see revised fig. below). The inclusion of a spectrum simulation does not add significant information.



Section 5b: The authors compare to their previous analysis between 4275-4356 cm^{-1} . Were the assignments consistent for all lines between the present and previous works (except for the outliers described in the text)?

Except for the outliers described in the text, the two sets of assignments are consistent.

Figure 10/11 and correspond text: Sometimes Ref. [16] is used to refer to MARVEL, whilst other times it is Ref. [14].

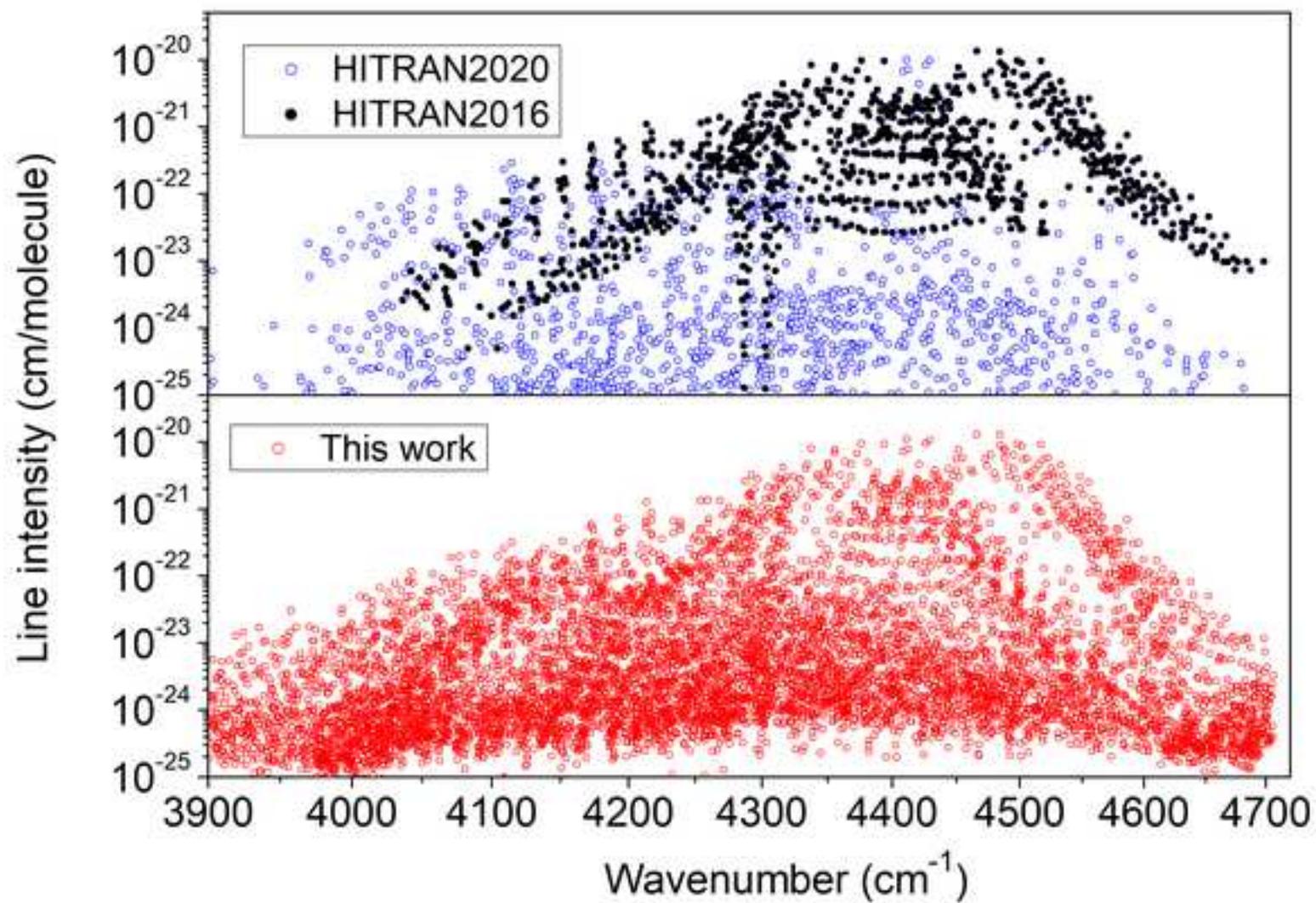
Ref. [14] is the suitable reference for the MARVEL energy levels that we used for comparison. It has been corrected in the text:

Figure 10 compares our empirical energies and the MARVEL energies reported in Ref. [146], as well as the predicted C2018 values. The number of empirical upper-state energies in the region has been

We hope that the amended version is now suitable for publication in JQST.

Highlights

- Room temperature Fourier transform absorption spectra of ammonia were recorded at four pressures in the 2.3 μm atmospheric window.
- 7794 $^{14}\text{NH}_3$ and 625 $^{15}\text{NH}_3$ transitions were identified in the 3900 - 4706 cm^{-1} region.
- The theoretical spectra available in the literature and lower state combination difference relations were used to assign the $^{14}\text{NH}_3$ lines.
- For $^{14}\text{NH}_3$, 6052 transitions were assigned to 51 vibrational bands providing 2287 experimental energy levels with 1870 new ones.
- The assigned transitions representing over 99.8% of room temperature $^{14}\text{NH}_3$ integrated absorption in the region will be valuable to improve spectroscopic databases.



The ammonia absorption spectrum between 3900 and 4700 cm^{-1}

P. Cacciani ¹, P. Čermák ², J. Vander Auwera ^{3#} and A. Campargue ^{4*}

¹ *Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers, Atomes et Molécules, 59000 Lille, France*

² *Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia*

³ *Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), C.P. 160/09, Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, B-1050 Brussels, Belgium*

⁴ *Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

Key words: Ammonia; NH₃; absorption spectrum; 2.3 μm atmospheric window; HITRAN

* Corresponding author: Alain.Campargue@univ-grenoble-alpes.fr

Senior research associate with the F.R.S.-FNRS (Belgium)

Abstract

Room temperature absorption spectra of ammonia have been recorded by high-resolution Fourier transform spectroscopy in the range 3900-4700 cm^{-1} at four pressures (13, 46, 140, and 304 Pa). The investigated spectral region overlaps the important 2.3 μm atmospheric transparency window. 8419 absorption lines were retrieved from the recorded spectra. Line intensities range between 1×10^{-25} and 1.6×10^{-20} $\text{cm}/\text{molecule}$. The rovibrational assignments, relying on the position and intensity agreement with the C2018 theoretical line list (Coles et al. 2018), were validated by the systematic use of Lower State Combination Difference (LSCD) relations. 6052 transitions were assigned to 51 vibrational bands of the main isotopologue, $^{14}\text{NH}_3$, and 625 transitions of the $^{15}\text{NH}_3$ minor isotopologue were identified. Overall, the assigned transitions represent over 99.8% of the integrated absorption at room temperature in the region. The upper state empirical energy of a total of 2287 rovibrational levels of $^{14}\text{NH}_3$ were derived. Among them, 1870 are newly reported. The achieved quality of the LSCD relations indicates that the accuracy of the derived energy levels is better than 0.001 cm^{-1} . Comparison with the HITRAN2020 list shows that the present results will be valuable in improving the ammonia spectroscopic databases in the region, both in terms of completeness and accuracy of the line positions and line intensities. A recommended line list for ammonia in natural isotopic abundance is provided for the studied region.

1. Introduction

Ammonia is an essential component in various astrophysical and terrestrial objects, including the Earth's atmosphere. Therefore, understanding its infrared absorption spectra is a prerequisite for accurate monitoring of these environments. However, this task is complicated by the tangled structure of its rovibrational spectra driven by the complex interaction between its six vibrational modes (two of them being doubly degenerated). Although extensive experimental studies [1–9] have been reported and used to elaborate the ammonia line list in the HITRAN2016 database [10] and its recent update HITRAN2020 [11] (available online, <https://hitran.org>), important deficiencies in terms of completeness and accuracy remain. The present work is devoted to the 3900–4700 cm^{-1} spectral range of importance for atmospheric monitoring of ammonia because it coincides with the 2.3 μm atmospheric window, and the ammonia absorption is strong in this region.

The HITRAN line list in the 4000–4700 cm^{-1} range was elaborated based on the original work of Urban et al. [1] in 1989 by Fourier Transform Spectroscopy (FTS) with a 0.005 cm^{-1} spectral resolution. Several transitions belonging to the $\nu_1+\nu_2$ and the $\nu_2+\nu_3$ bands were reported together with tentative assignments of the $\nu_2+2\nu_4$ parallel and perpendicular bands. However, only the first two bands with reliable assignments were retained for the HITRAN database since its 1996 edition [12]. In the following editions, the list remained essentially unchanged [3,13]. The most significant update was performed in the recent 2020 edition [11] and consisted of the addition of a large number of transitions from the hybrid CoYuTe list [14] (**Fig.1**). The CoYuTe list was generated based on the most recent potential energy surface – C2018 [15]. Although this variational list is quite accurate with a good intensity agreement with experiment, the calculated line positions do not attain the experimental accuracy (see *e.g.* [6,9]). Therefore, to achieve experimental accuracy, where possible, the variational line positions were replaced by their empirical counterparts generated using the MARVEL algorithm [16]. For the HITRAN2020 edition, it was decided to add to the HITRAN2016 dataset only CoYuTe transitions for which both the lower and upper levels have empirical energies and corresponding to line intensities larger than 1×10^{-25} $\text{cm}^2/\text{molecule}$ [11]. The overview comparison of the HITRAN2016 and HITRAN2020 lists presented in **Fig. 1** shows the important increase of the amount of data obtained through the process in the spectral region targeted in this work. In particular, transitions of the $\nu_2+2\nu_4$, $L_4 = 0$ and $L_4 = 2$ bands with A and E symmetry, respectively, partially reported in Urban's paper [1], are now included. Also, the HITRAN2020 list includes many weak lines, particularly hot band transitions with upper levels determined from cold band transitions at higher energies.

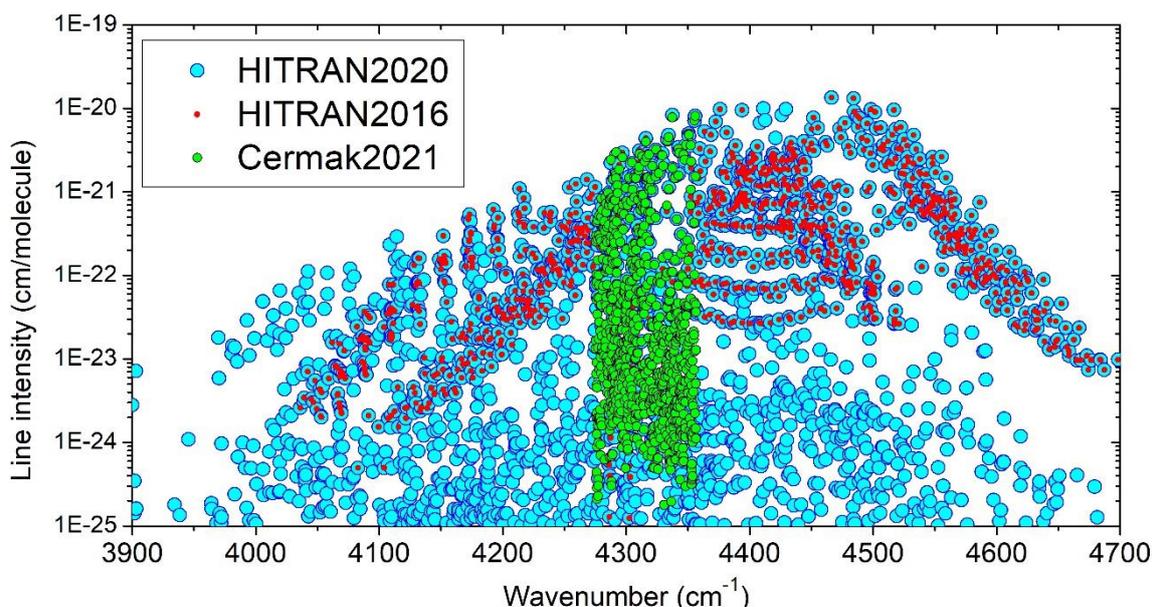


Figure 1.

Comparison of the HITRAN2016 [10] and HITRAN2020 [11] line lists (red dots and cyan symbols, respectively). The recent absorption line list obtained using a VECSEL in the 4275-4356 cm^{-1} range is superimposed for comparison [18] (green circles - see Text).

An experimental work of interest for the present study was recently reported by Beale et al. [17]. Spectra of ammonia in the 2400-5500 cm^{-1} region were recorded at temperatures from 295 to 973 K using FTS with a 0.01 cm^{-1} spectral resolution. Many high- J transitions were identified from this experimental list. Still, due to its lower accuracy, this study was used neither for direct inclusion in the HITRAN2020 list nor for determining the MARVEL energy levels [11, 16].

Finally, very recently, a Vertical External Cavity Surface Emitting Laser (VECSEL) was used to record the high-resolution ammonia spectra in the 4275-4356 cm^{-1} interval (~ 2295 - 2339 nm) at temperatures from 160 to 296 K [18]. Although the spectral coverage of the laser was limited to 80 cm^{-1} , several hundreds of new $^{14}\text{NH}_3$ transitions could be assigned. The comparison of the VECSEL line list to the HITRAN lists is included in **Fig. 1**. It shows that although the most intense lines missing in HITRAN2016 were added in HITRAN2020 (*e.g.* around 4400 cm^{-1}), a number of transitions with line intensities around 1×10^{-23} cm/molecule were measured with the VECSEL but are absent in HITRAN2020. They mostly correspond to newly determined upper energy levels. Let us mention that, as a result of the limited laser coverage, part of the new assignments was obtained by applying Lower State Combination Differences (LSCD) relations to VECSEL line positions and line positions reported by Beale et al. [17]. Thus, Beale's list was found particularly valuable to confirm the assignments of the VECSEL list [18]. Finally, the assigned lines represent 99.9% of the integrated absorption in the region of the VECSEL recordings.

The VECSEL study [18] has illustrated the capability to significantly improve the existing experimental lists with a simple differential absorption spectroscopy setup. The present work aims to cover a wider region, from 3900 to 4700 cm^{-1} by FTS with similar sensitivity.

The paper is organized as follows. The following section describes the experimental setup and the conditions of the recordings. The fitting process and construction of the line list are presented in section 3. Section 4 describes the assignment process before discussing the results and comparison to previous experimental and theoretical line lists (section 5).

2. Experimental details

Four unapodized absorption spectra of ammonia in natural abundance (Aldrich, stated purity $\geq 99.99\%$) were recorded with a Bruker IFS 120 (upgraded to 125) HR high-resolution Fourier transform spectrometer (FTS). The instrument was fitted with a tungsten source, an entrance aperture set to 0.8 mm, a CaF₂ beam splitter, a high pass (in wavenumber) filter with a cut-off at about 2900 cm⁻¹, and an InSb detector cooled down to 77 K. The spectra were recorded in the range 3900 to 5600 cm⁻¹ at room temperature [295.6 (1.0) K], stabilized by an air-conditioning system. The samples were contained in a Pyrex White-type cell, set to provide an absorption path length of 13.86 (4) m and closed by CaF₂ windows. The sample pressures were measured with a MKS Baratron 390HA capacitance manometer of 10 Torr full-scale range, temperature stabilized at 45°C and characterized by an accuracy of reading conservatively assumed to be 0.5%. The ammonia pressures, averaged over the time required to record the interferograms, are listed in **Table 1**. Their uncertainties, also provided in this Table, were estimated as the sum in quadrature of half of the peak-to-peak variations of the pressures measured during the recording of the interferograms and the 0.5% accuracy of reading of the gauge. All the interferograms were recorded with a maximum optical path difference (MOPD) of 90 cm, corresponding to a spectral resolution of 0.01 cm⁻¹. The number of interferograms averaged to yield the single beam spectra is also provided in **Table 1**. The single beam spectra were interpolated four times. **Figure 2** presents the spectra corresponding to the lowest and highest ammonia pressures.

Table 1.

Average pressures of ammonia (P) and number of co-added interferograms (#). The numbers between parentheses are the uncertainties of measurement, provided in the units of the last digit quoted (see Text for details), and σ_P is the relative uncertainty.

P/Torr	P/Pa	$P_{\text{corr.}}/\text{Pa}^a$	$\sigma_P/\%$	#
0.109 (6)	14.5 (8)	13.2 (1.5)	11.0	294
0.348 (8)	46.4 (1.1)	46.0 (1.1)	2.3	283
1.053 (33)	140.4 (4.4)		3.1	270
2.28 (8)	304. (11)		3.5	180

^a Values corrected by comparison of a set of line intensities retrieved from the different spectra (see text for details)

The two lower ammonia pressures deserve the following comment. The pressures measured for these two spectra are outside the last decade of the gauge used (*i.e.*, 1 – 10 Torr), in which the accuracy of reading stated by the manufacturer applies. To estimate the actual pressures associated with these two spectra, ammonia lines observed in the four spectra were fitted simultaneously, varying the two lowest

pressures and keeping the two higher pressures fixed to the values reported in **Table 1**. These measurements showed that the average pressures of 14.5 and 46.4 Pa listed in **Table 1** should be decreased to 13.2 and 46 Pa, respectively. The uncertainty reported in **Table 1** for the corrected lowest pressure is doubled to conservatively account for this change.

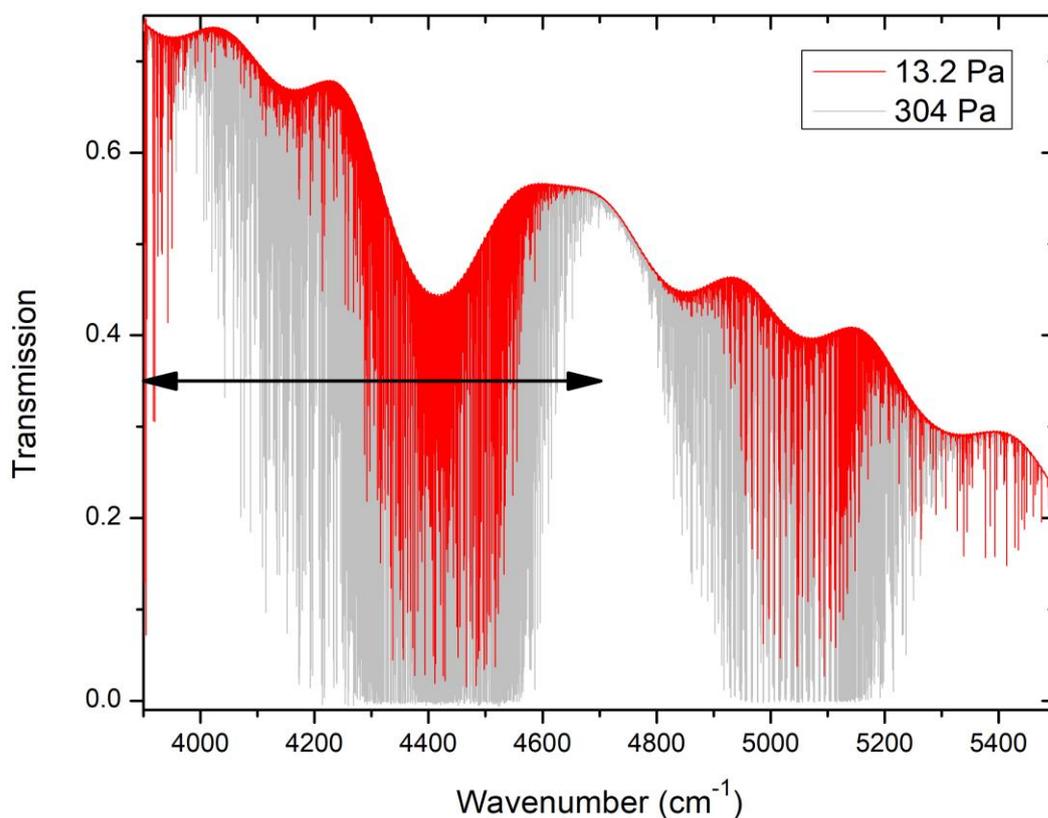


Figure 2

Overview of two of the Fourier transform absorption spectra of ammonia in natural isotopic abundance recorded in the present work with the resolution of 0.01 cm^{-1} . They correspond to the lowest (13.2 Pa) and highest (304 Pa) ammonia pressures (see Table 1). The absorption path length was 13.86 (4) m, and the temperature was 295.6 (1.0) K. The arrows specify the region of the present analysis.

To calibrate the wavenumber scale of the ammonia spectra, an absorption spectrum of nitrous oxide was also recorded at the same experimental conditions and an average pressure of about 0.2 Torr. It resulted from the co-addition of 120 interferograms. To determine the value of the calibration factor C (such that $\nu_{\text{ref}} - \nu_{\text{obs}} = C \nu_{\text{obs}}$) to be applied to the ammonia line positions, the positions of N_2O lines observed in the range $4360 - 5140\text{ cm}^{-1}$ were measured in the spectrum interpolated four times using the program WSpectra [19], giving each line a Gaussian line shape and including instrumental effects as fixed contributions. The measured positions ν_{obs} of 259 N_2O lines having intensities larger than 10^{-22} or $10^{-23}\text{ cm}^2/\text{molecule}$ (below and above 4820 cm^{-1} , respectively) were then matched to reference line positions ν_{ref} available in the HITRAN2016 database [10] (uncertainties in the $10^{-3} - 10^{-4}\text{ cm}^{-1}$ range).

The root means square (RMS) deviation of the linear fit of the (meas. – ref.) position differences was $4.1 \times 10^{-5} \text{ cm}^{-1}$.

3. Line list construction

3.1. Line parameter retrieval

Line positions and line intensities were retrieved using a multiline fit of the spectra. The fit was performed assuming a simple Voigt function as line profile, thus, including in an effective way the Instrument Line Shape (ILS). In practice, the spectrum was divided into successive 4 cm^{-1} wide spectral segments for which a low-order polynomial was adjusted to account for the baseline. The absorbance was then obtained and fitted with a standard nonlinear Levenberg-Marquart algorithm [20] as a sum of Voigt profiles. The Lorentzian and Gaussian components of the Voigt profile were assumed to be identical for all the peaks within each 4 cm^{-1} wide segment and adjusted freely during the fit. The reason not to fix the Gaussian width to the corresponding Doppler value was to account for the ILS contribution to the line shape, so the best measurement of the peak surface was achieved. **Figure 3** shows an example of spectrum fit. For the two lowest pressure spectra at 13.2 and 46 Pa, the observed Lorentzian width is dominated by the apparatus function contribution, which has an estimated Half-Width at Half Maxima (HWHW) of 0.0034 cm^{-1} compared to the Lorentzian HWHM of 0.0001 and 0.0003 cm^{-1} for the two spectra, respectively (considering a typical HITRAN self-pressure broadening coefficient value of $0.5 \text{ cm}^{-1}/\text{atm}$). For the spectrum at 304 Pa, the Lorentzian HWHM is up to ten times larger and approaches the self-broadening value. The fitted value of the Gaussian width was found slightly above the calculated value of the $^{14}\text{NH}_3$ Doppler broadening, confirming a small contribution of ILS. Constraining peak widths across the fitted segments helped to disentangle blended lines, as they produced a distinctive pattern in the fit residuals [18].

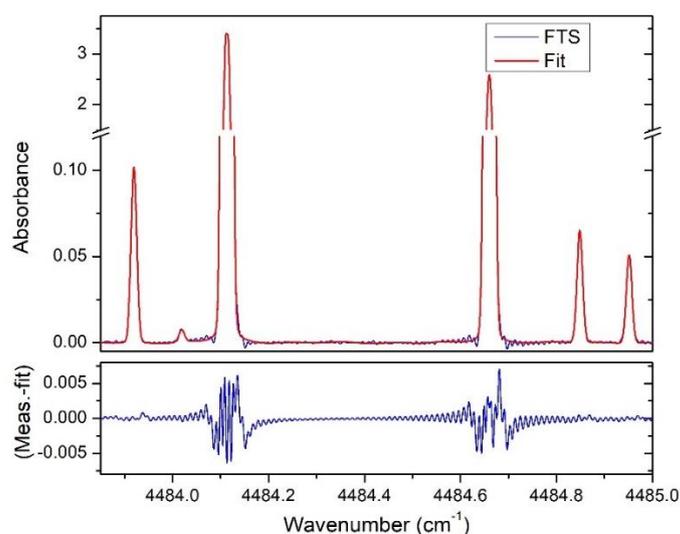


Figure 3.

Example of the fit of the experimental spectrum at 13.2 Pa around 4484 cm^{-1} . The resulting absorbance was fitted as a sum of Voigt line profiles. The FTS apparatus function is responsible of oscillations and “ghost” peaks observed in the blue side of the line in the (Meas. – fit) residuals (lower panel).

Our data treatment without explicit account of the ILS has two drawbacks. First, a minor problem is the remaining pattern from the ILS observed in the fit residuals (**Fig. 3**). As the ILS exhibits a slight asymmetry, the residuals showed a satellite peak on the blue side of the strong fitted lines. Special care was taken not to confuse this artifact with an actual weak line. Second, our approximate treatment of the ILS led to underestimated line intensities, especially for strong lines [7].

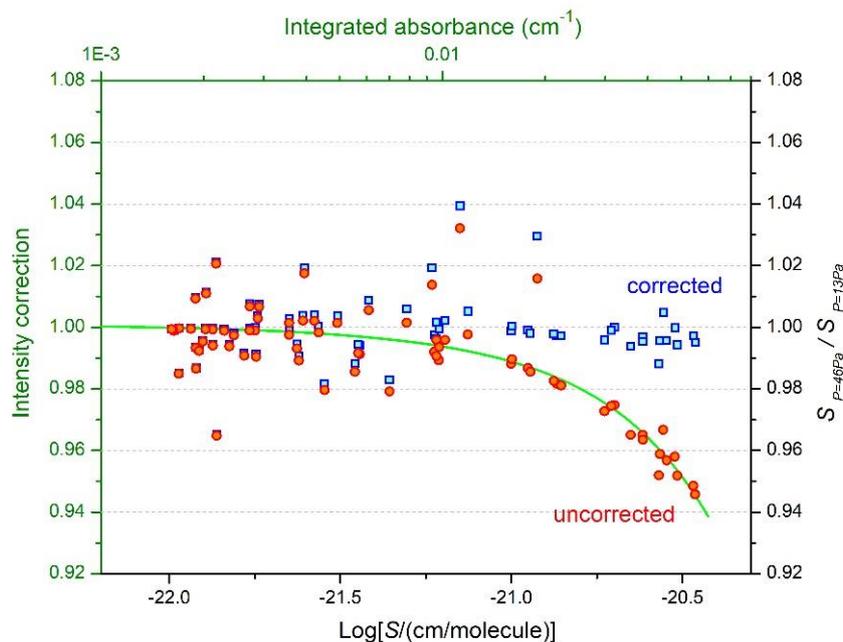


Figure 4.

Line strength correction curve *versus* integrated line absorbance. The curve was derived from a specific study of synthetic spectra. Its effect is shown by plotting the ratio of uncorrected and corrected intensities derived from the spectra at 13.2 and 46 Pa (orange and blue symbols, respectively). The displayed 0.0015-0.058 cm^{-1} integrated absorbance range corresponds to line intensities ranging from 9.7×10^{-22} to 3.7×10^{-21} $\text{cm}/\text{molecule}$ in the 46 Pa spectrum and 2.8×10^{-22} to 1.1×10^{-21} in the 13.2 Pa spectrum.

A specific study was conducted to quantify this impact by comparing our fitting results to the correct ones obtained by a direct fit of the transmittance, including the ILS. The actual ILS was measured by fitting twelve strong N_2O lines observed in the 4391 – 4434 and 4710 – 4747 cm^{-1} intervals of the spectrum used for calibration (see section 2), interpolated 16 times, with an algorithm being developed in Brussels [21], drawn from the method proposed by Boone and Bernath [22]. This ILS was convoluted with the transmittance of a single line to obtain a synthetic experimental spectrum. The simulated line was chosen with typical Gaussian and Lorentzian widths corresponding to the room temperature 13.2 Pa spectrum (0.00025 cm^{-1} and 0.0062 cm^{-1} for the Lorentz and Gauss HWHM, respectively). Afterward, the integrated line absorbance was retrieved in the same way as used for the true experimental spectrum and compared with the one used as the input for the simulation. Following this procedure and varying the line intensity, the correction curve displayed in **Fig. 4** was determined for integrated absorbances ranging from 0.0015 cm^{-1} to 0.058 cm^{-1} (corresponding to line intensities of 3.34×10^{-21} and 1.29×10^{-20} $\text{cm}/\text{molecule}$, respectively, for the 13.2 Pa spectrum). On the considered range, it led to a correction increasing up to 5.5 % for the strongest lines ($\sim 10^{-20}$ $\text{cm}/\text{molecule}$). **Figure 4** also shows how

this correction can be tested within the experimental spectra. The retrieved line strengths of the transitions, whose integrated absorbances range from 0.0015 cm^{-1} to 0.058 cm^{-1} in the spectrum at 46 Pa, are compared to their values in the spectrum at 13.2 Pa where their integrated absorbances are three times lower. Applying the correction curve, the ratios show an average value around 1 with a spread of about 2%. The flatness of the points distribution in **Fig. 4** validates the use of the correction curve.

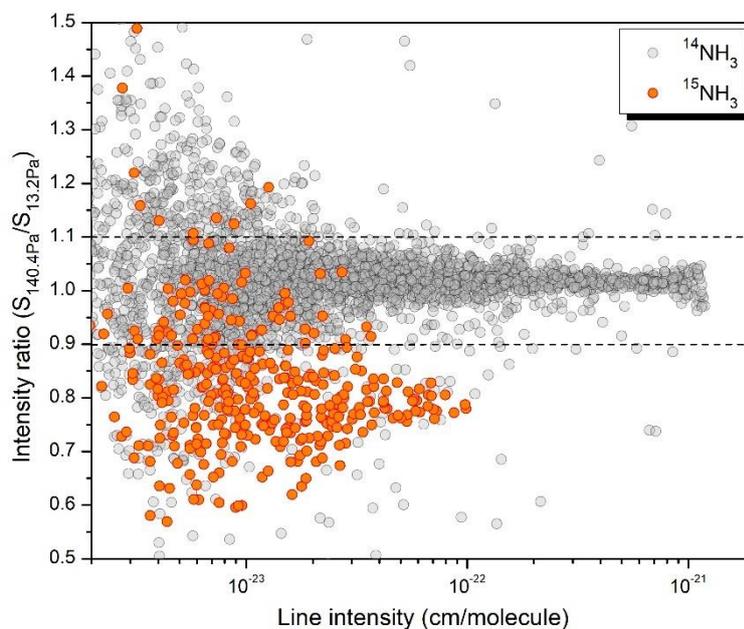


Figure 5.

Ratios of the intensities derived from the 140.4 Pa spectrum to those of the 13.2 Pa spectrum in the range 1.8×10^{-24} - 1.2×10^{-21} cm/molecule. The intensity ratio transitions of the $^{15}\text{NH}_3$ lines (orange symbols) are spread around 0.8 (see text for details).

Considering the maximal deviation of around 4% and the pressure measurement uncertainty (**Table 1**), we can safely estimate the absolute line intensity uncertainty below 10%. To better understand the overall accuracy of line intensities, the ratio between the intensities derived from the two spectra at 140.4 and 13.2 Pa is plotted in **Fig. 5**. We can see that the most accurate values are for the lines with intensities around 5×10^{-22} cm/molecule (better than 5%), and the 10% uncertainty is kept for the lines above 2×10^{-23} cm/molecule. Also, as described below, due to desorption, the $^{15}\text{NH}_3$ lines show roughly a 20 % increase of abundance in the 13.2 Pa spectrum compared to the 140.4 Pa one, leading to an average intensity ratio of about 0.8.

3.2. Global line list

In the global experimental list provided as a Supplementary Material, the experimental position and intensity of each line rely on one of the four recorded spectra which is indicated. The lowest pressure spectrum (13.2 Pa) provides most of the entries because it is the only one for which the strongest lines are not saturated (the most intense line around 4460 cm^{-1} has a peak transmittance of 3%, corresponding to an integrated absorbance of 0.058 cm^{-1}). The spectrum at 140 Pa was also completely analyzed in the

4000 – 4600 cm^{-1} region. The lines on the low- and high-energy regions 3900 – 4000 cm^{-1} and 4600 – 4700 cm^{-1} used the two highest pressure spectra.

A number of water vapor lines (present as an impurity) were observed in the spectra, mostly in the low energy range. The water lines were removed manually by comparison with the HITRAN2016 line list [10]. Finally, the resulting ammonia experimental list includes 8419 lines with intensity ranging between 1×10^{-25} and 1.3×10^{-20} $\text{cm}/\text{molecule}$. About 5800 of them have an intensity larger than 1×10^{-24} $\text{cm}/\text{molecule}$. Next, we focused on the identification of the lines due to the $^{15}\text{NH}_3$, minor isotopologue. To the best of our knowledge, no accurate $^{15}\text{NH}_3$ list is available in the literature in the studied region, except for a small spectral interval from 4275 to 4356 cm^{-1} [6]. Luckily, we had at our disposal a FT spectrum of ^{15}N enriched ammonia recorded five years ago [23] with the same setup as used for the present recordings. Although only a raw peak list was constructed, it was sufficient to identify 625 $^{15}\text{NH}_3$ lines. The $^{15}\text{NH}_3$ lines are marked in the experimental list provided as Supplementary Material. The comparison to the $^{15}\text{NH}_3$ intensity values included in Ref. [6] reveals a significant ^{15}N enrichment. While the natural abundance of $^{15}\text{NH}_3$ is 3.661×10^{-3} , from the measured intensities, we obtain a relative abundance of about 5.7×10^{-3} in the spectrum recorded at 140 Pa. This enrichment is the result of the past of the cell: a small fraction of the $^{15}\text{NH}_3$ molecules injected five years ago for the ^{15}N enriched spectra recordings remains adsorbed on the cell walls and slowly desorbed or exchanged with the main $^{14}\text{NH}_3$ species. Note that in the present work, the cell was first filled at a pressure of 500 Pa and, after equilibration, the four spectra listed in **Table 1** were recorded successively by decreasing pressure steps from 330 to 13.2 Pa Torr. Due to the continuous exchange between $^{15}\text{NH}_3$ adsorbed on the cell walls and $^{14}\text{NH}_3$ in the gas phase, a significantly higher enrichment (6.8×10^{-3}) was evidenced for the last recorded spectra (at 13.2 Pa) compared to the 140 Pa spectrum. It leads to the average intensity ratio of about 0.8 observed in **Fig. 5**. Finally, scaling the measured intensities to the absolute intensities from Ref. [6], a list of $^{15}\text{NH}_3$ transitions was constructed and included in the recommended list for ammonia in normal isotopic abundance which is provided as a Supplementary Material.

4. Rovibrational assignments

Following our recent analysis [18], the C2018 variational list of $^{14}\text{NH}_3$ was used as a primary source for the rovibrational assignment of the $^{14}\text{NH}_3$ experimental line list. Although a hybrid CoYuTe line list [14] exists – where empirical line positions (when available) were substituted to variational line positions – the C2018 was preferred for two reasons. First, for an independent comparison with previous experimental datasets, we preferred to use the purely theoretical predictions (C2018) of the CoYuTe list as starting point of our assignments. Second, the method of branches based on the (generally smooth) rotational dependence of the (obs.-calc.) line position differences within a given vibrational branch was used for the assignment. It allowed us to assign new transitions belonging to the same branch by inter-

or extrapolating the available positions differences. The application of the method of branches to the hybrid CoYuTe list would have made the procedure more complicated.

The C2018 rovibrational labeling uses 13 quantum numbers: ν_1 , ν_2 , ν_3 , ν_4 , L_3 , L_4 , inv , $\Gamma_{vib.}$, J , K , $\Gamma_{rot.}$, N_B , $\Gamma_{tot.}$. ν_i are the vibrational normal-mode quantum numbers corresponding to the ν_1 symmetric stretch, ν_2 symmetric bend, ν_3 the antisymmetric stretch, ν_4 antisymmetric bend, respectively. $L_3=|l_3|$ and $L_4=|l_4|$ are the corresponding vibrational angular momentum quantum numbers, $inv=a/s$ is the inversion symmetry (asymmetric/symmetric or odd/even), and $\Gamma_{vib.}$ is the symmetry of the vibrational motion. J is the total angular momentum quantum number, $K=|k|$ is the projection of the total angular momentum on the molecule-fixed axis z , and $\Gamma_{rot.}$ is the rotational symmetry. Finally, $\Gamma_{tot.}$ stands for the total symmetry of the eigenstate, and N_B is the block counting number used during the generation of the C2018 list.

In our previous analysis of the NH_3 spectrum [18], several spectra at different temperatures were recorded, and the assignment procedure benefited from information on the lower state energies. Here spectra were recorded at a single temperature, and thus only the line position and line intensity (ν_{exp} , S_{exp}) were used for comparison to the C2018 predictions. The following constraints were applied to search for coincidence between our global experimental line list and the C2018 calculated list: $|\delta\nu| = |\nu_{exp} - \nu_{calc}| \leq 1 \text{ cm}^{-1}$ and $0.5 \leq S_{exp}/S_{calc} \leq 2$. For a given measured line, the C2018 coincident lines were searched following the procedure combining intensity considerations and LSCD relations described in detail in Ref. [18] and illustrated in **Fig. 6**. Shortly, the empirical upper state energy, E_{emp} , was calculated from the experimental wavenumber and the lower state energy taken either from Cacciani et al. [24] for ground and ν_2 vibrational states or from MARVEL2020 list [16] for the other bands. For each C2018 candidate, the transitions sharing the same upper state were identified in the C2018 list. Their wavenumbers were adjusted using the determined E_{emp} value and the corresponding MARVEL2020 lower state energy value. To confirm (or not) the assignment, the obtained transitions with adjusted line position and C2018 line intensity were searched in the experimental lists. Let us mention that the LSCD partners were searched not only in the region under analysis (3900-4700 cm^{-1}) but also in the higher 4700-5500 cm^{-1} range of the recordings (see **Fig. 2**). Additionally, the line lists from HITRAN2020, Beale et al. [17,25] and our previous work [9] were considered in other spectral regions, taking into account their respective accuracy on the line positions. In the case of this work, Ref. [9] and HITRAN list, we used the wavenumber criterion of $\pm 0.003 \text{ cm}^{-1}$. For Beale et al. [17,25], a less strict value of $\pm 0.006 \text{ cm}^{-1}$ was adopted. The LSCD search used an agreement between the FTS and C2018 line intensities within a factor of two. On the other hand, stronger lines by factor two and more were accepted but considered rather as screening lines and not the searched transition itself. In this case, lines beyond the wavenumber criteria were examined in order to check whether their wing has sufficient intensity at the predicted wavenumber to hide the searched transition.

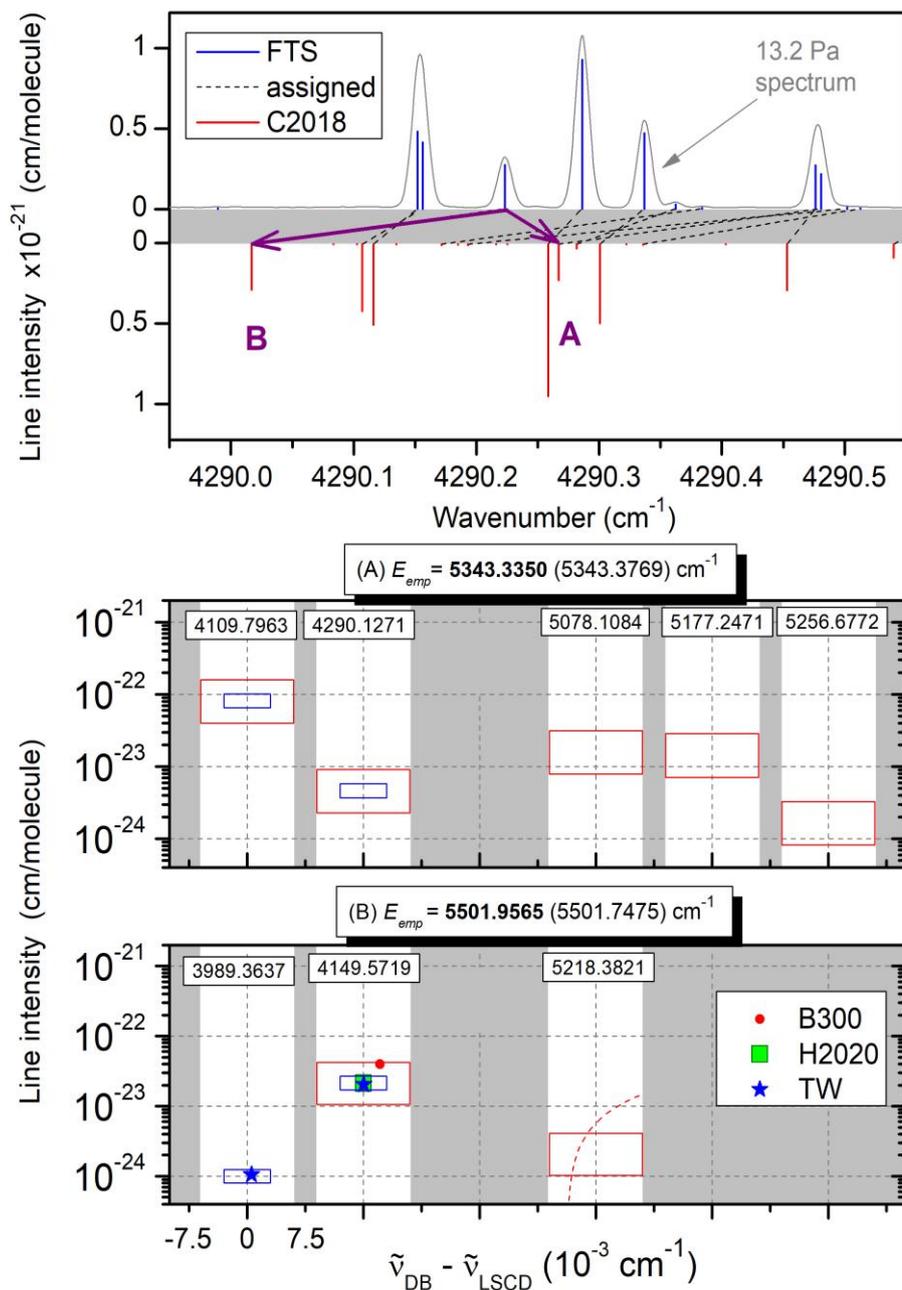


Figure 6

Illustration of the procedure used to assign the experimental line at $4290.2233 \text{ cm}^{-1}$. The two most probable assignments – (A) and (B) – are considered. For each of this assignment, the C2018 LSCD partners are shown in a single graph row if their line center and intensity fall within estimated error bars of the different databases considered: our experimental list (This work), HITRAN2020, and the FTS list by Beale et al. (B300). The LSCD upper state energy, common for all combination transitions, is indicated on the top of the row with its C2018 counterpart position in parenthesis. The calculated line center is given for each LSCD partner. For each database, the peak match criteria are represented with a target rectangle of the same color with dimensions fixed by the estimated value of the position and intensity error bars. Scatter points are indicated in the case of matching.

For the (A) tentative assignment, five C2018 transitions are predicted but no LSCD coincidences are found neither in our line list nor in available databases. For the second tentative assignment (B), two of the three predicted LSCD lines are present in our list, one of them being also in Beale's list [17]. The third predicted line is obscured by the wing of strong neighboring lines and represented with the dashed line. The (B) upper state leads to unambiguously assign the considered line to $2\nu_2^s + \nu_3^1 (J = 7, K = 7, \Gamma_{\text{tot}} = A_2'') \leftarrow \nu_2^s (J = 6, K = 6, \Gamma_{\text{tot}} = A_2')$.

Figure 6 illustrates the application of the LSCD procedure for an unassigned line at 4290.2233 cm⁻¹. Applying the above position and intensity criteria to the set of C2018 lines, the C2018 lines at 4290.26683 and 4290.0168 cm⁻¹, (A) and (B), respectively, are identified as possible candidates. For each of them, the corresponding empirical position of the LSCD partners are indicated on the lower panels. For the closest transition, (A), five C2018 transitions are predicted (the transition itself is also included on the graph) and searched, but no LSCD coincidences are found neither in our line list nor in available databases. For the second tentative assignment (B), two of the three predicted LSCD lines are present in our list, one of them being also in Beale's list [17]. From the examination of the spectra, it appeared that the third LSCD partner is small and obscured by a much stronger line (a dashed line represents its wing in the figure). Therefore, the experimental line at 4290.2233 cm⁻¹ must be unambiguously paired with the calculated hot-band transition (B) - the corresponding assignment is $2\nu_2^s + \nu_3^1(J = 7, K = 7, \Gamma_{tot} = A_2'') \leftarrow \nu_2^s(J = 6, K = 6, \Gamma_{tot} = A_2')$.

As a complementary assignment procedure, the method of branches was used. The (obs.-calc.) wavenumber differences within a given vibrational branch are expected to vary slowly with the rotational quantum numbers. This expected tendency was used to confirm the LSCD assignments and assign new lines missing LSCD partners.

Overall, 6052 out of 7794 transitions were assigned to 51 ¹⁴NH₃ vibrational bands listed in **Table 2**. The obtained assignments are included in the experimental list provided as Supplementary Material. The assigned transitions represent 99.8% of the integrated intensity in the region. **Figure 7** compares the set of unassigned lines to that of the C2018 lines with no experimental counterpart. All unassigned lines have an intensity smaller than 10⁻²³ cm/molecule, to be compared to intensities of 1×10⁻²⁰ cm/molecule for the strongest lines in the studied region.

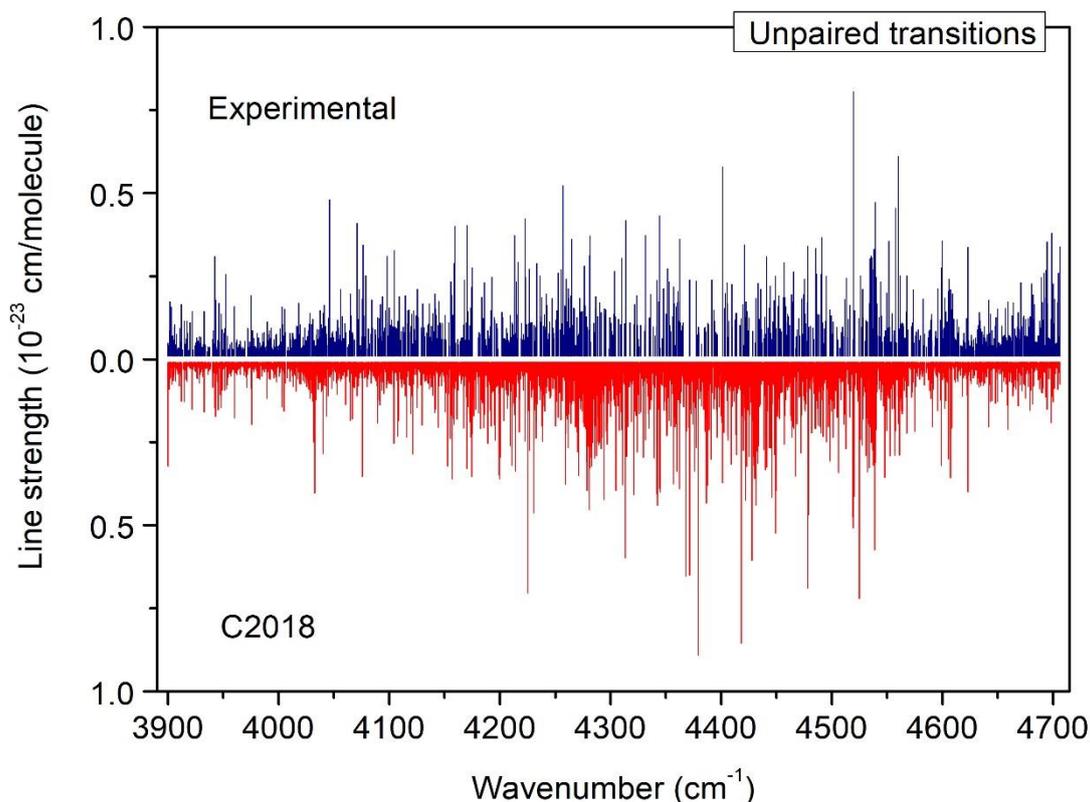


Figure 7

Comparison between the experimental lines left unassigned and the C2018 calculated lines with intensities larger than 10^{-25} cm/molecule, having no experimental counterpart.

5. Comparison to literature

5.1. The HITRAN and C2018 lists

As mentioned in the introduction, the HITRAN2016 list in the considered region was limited to $^{14}\text{NH}_3$ and relied mainly on the work of Urban et al. [1]. In the recent 2020 edition of the ammonia HITRAN list [11], the CoYuTe line list was considered but only for new bands absent in the HITRAN2016 edition [10]. The comparison of the HITRAN2016 and HITRAN2020 lists included in **Figs. 1 and 8** shows the important extension of the amount of data due to the CoYuTe line list (the number of transitions was doubled compared to HITRAN2016). Let us recall that the added CoYuTe lines are the C2018 lines with position empirically adjusted according to MARVEL energy levels. The comparison of the HITRAN2020 and C2018 lists displayed in **Fig. 8** indicates that many lines are absent in the HITRAN2020 dataset because their upper energies were not experimentally determined. The HITRAN2020 intensity cut-off in the region was fixed to 1×10^{-25} cm/molecule at 296 K. The comparison with our line list indicates that most of the C2018 lines with intensity above this cut-off are presently measured. The expanded spectral region around 4536 cm^{-1} presented on the right panels of **Fig. 8** illustrates the large number of weak lines newly measured. Our $^{14}\text{NH}_3$ assigned line list includes about four

times more lines than the HITRAN2020 list. Note that some lines with intensity larger than 1×10^{-22} cm/molecule are absent from the HITRAN2020 list. The statistical comparison of the different datasets is presented in **Table 3**.

Regarding the $^{15}\text{NH}_3$ isotopologue, when scaled to the natural abundance (**Fig. 8**), the strongest lines have intensity up to 6×10^{-23} cm/molecule around 4450 cm^{-1} . Thus, they represent a non-negligible contribution to the absorption in the studied range.

Table 3.

Statistics and integrated absorption in various databases for ammonia in the $3900\text{-}4706 \text{ cm}^{-1}$ spectral range (intensity cut-off of 1×10^{-25} cm/molecule at 296 K).

	HITRAN2016	HITRAN2020	This work		Beale2017	CoYuTe (C2018)
			$^{14}\text{NH}_3$	$^{15}\text{NH}_3$		
Transitions	1129	2250	7794	625	2689	12703
Assignments	973	2128	6052	0	398	12703
Intensity sum ($\times 10^{-19}$ cm/molecule)	8.56×10^{-19}	9.239	9.75	0.0334	8.88	10.2

As mentioned previously, there is an overall good agreement between the experimental and C2018 intensities. Nevertheless, band-by-band comparison reveals some systematic deviations. **Figure 9** shows the full data and highlights three vibrational bands: $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, and $\nu_2 + 2\nu_4$, $L_4 = 2$. Average intensity ratios of 0.97, 0.95, and 1.02, respectively, are obtained, the differences being significant compared to the experimental uncertainties. Note the dispersion of the intensity ratios at the 1% level in the case of the two strongest bands ($\nu_1 + \nu_2$ and $\nu_2 + \nu_3$), indicating that the uncertainty on our measured intensities is significantly smaller than 5 %, at least for these two bands. The same intensity comparison is also presented for the HITRAN2020 list. On the same scale, a more extensive spread of points is observed even for strong lines. Also, we can point out the underestimated intensities of the $\nu_1 + \nu_2$ band.

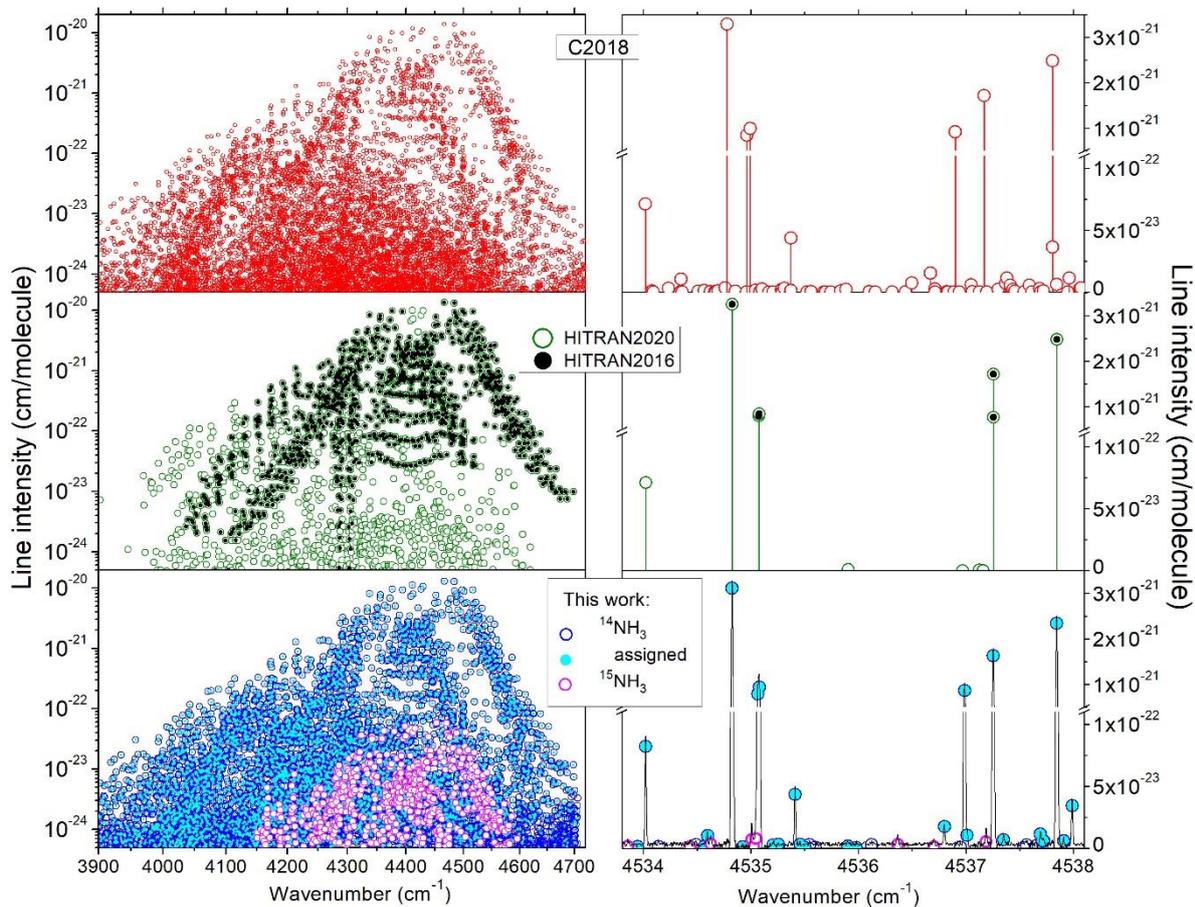


Figure 8.

Left panels: Overview comparison of line lists of ammonia in the 3900-4700 cm^{-1} region: C2018 variational line list (upper panel), HITRAN2016, and HITRAN2020 lists (middle panel) and our FTS experimental list (lower panel). The $^{15}\text{NH}_3$ measured intensities have been scaled to correspond approximately to the natural isotopic abundance (see text for details).

Right panels: Comparison over a small spectral interval around 4536 cm^{-1} . Note the lines added in the HITRAN2020 line list using the MARVEL energy levels on the middle panel. The lower panel, including the FTS experimental spectrum at 140 Pa, illustrates many weak newly measured lines.

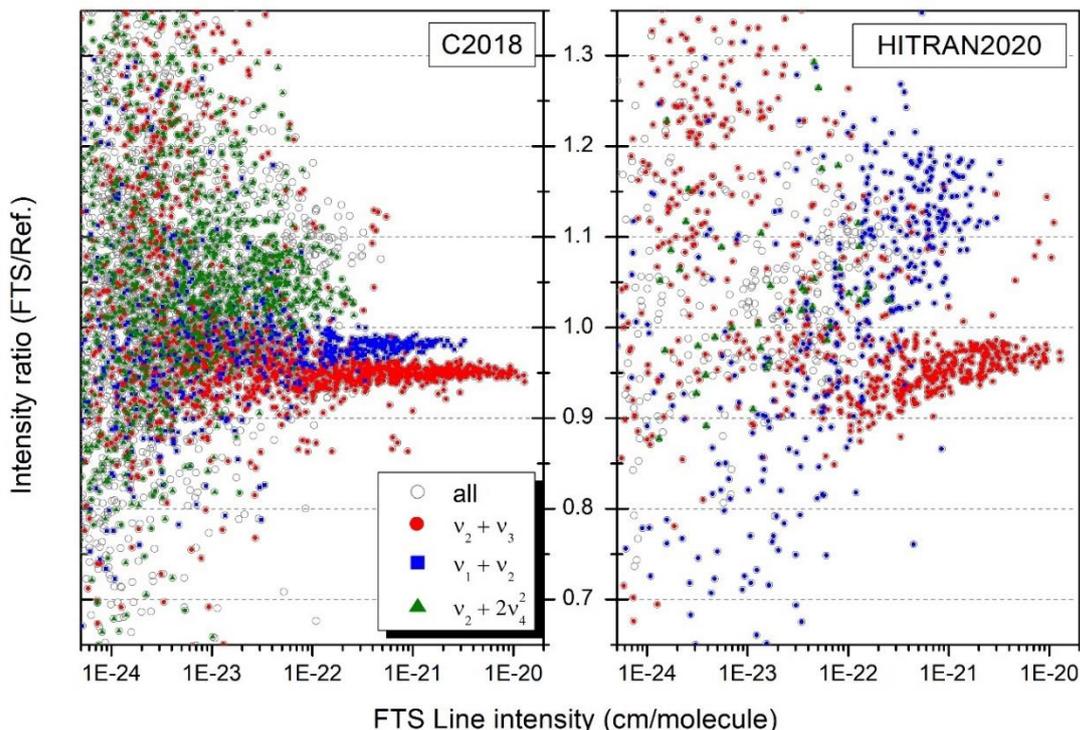


Figure 9.

Ratios of the $^{14}\text{NH}_3$ line intensities measured in this work in the $3900 - 4706 \text{ cm}^{-1}$ spectral region to the corresponding values of the C2018 and HITRAN2020 line lists. The intensity ratios corresponding to the $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, and $\nu_2 + 2\nu_4$, $L_4 = 2$ bands are distinguished.

5.b. VECSEL line list ($4275\text{-}4356 \text{ cm}^{-1}$)

It is interesting to compare the results of our previous work [18], using laser spectroscopy with a VECSEL source in a limited range of $4275\text{-}4356 \text{ cm}^{-1}$, to the present FTS results. In this region, 807 transitions were measured with the VECSEL and 1056 by FTS, indicating a similar sensitivity of the two experimental setups (the absorption pathlength was 6.92 m [18] to be compared to 13.86 m in the present study). The comparison of the line positions reveals minor deviations with a general tendency to decrease from $+0.001$ to -0.001 cm^{-1} with increasing wavenumber over the range. A few observed outliers correspond to doublets – experimental lines assigned to two C2018 transitions. For some doublets, the VECSEL results have benefited from smaller Doppler broadening at low temperatures [18]. On the other side, the broad FTS spectrum allows for a more extensive application of the LSCD relations. For the intensity ratios, considering only the transitions with line intensity larger than $10^{-23} \text{ cm/molecule}$, an average value of 0.97 is obtained. This is the same number as obtained for the HITRAN $\nu_2 + \nu_3$ band, as this band was used as a reference for the intensity calibration of the line intensities reported in Ref. [18].

5.c. Upper energy levels. Comparison to MARVEL and C2018 values

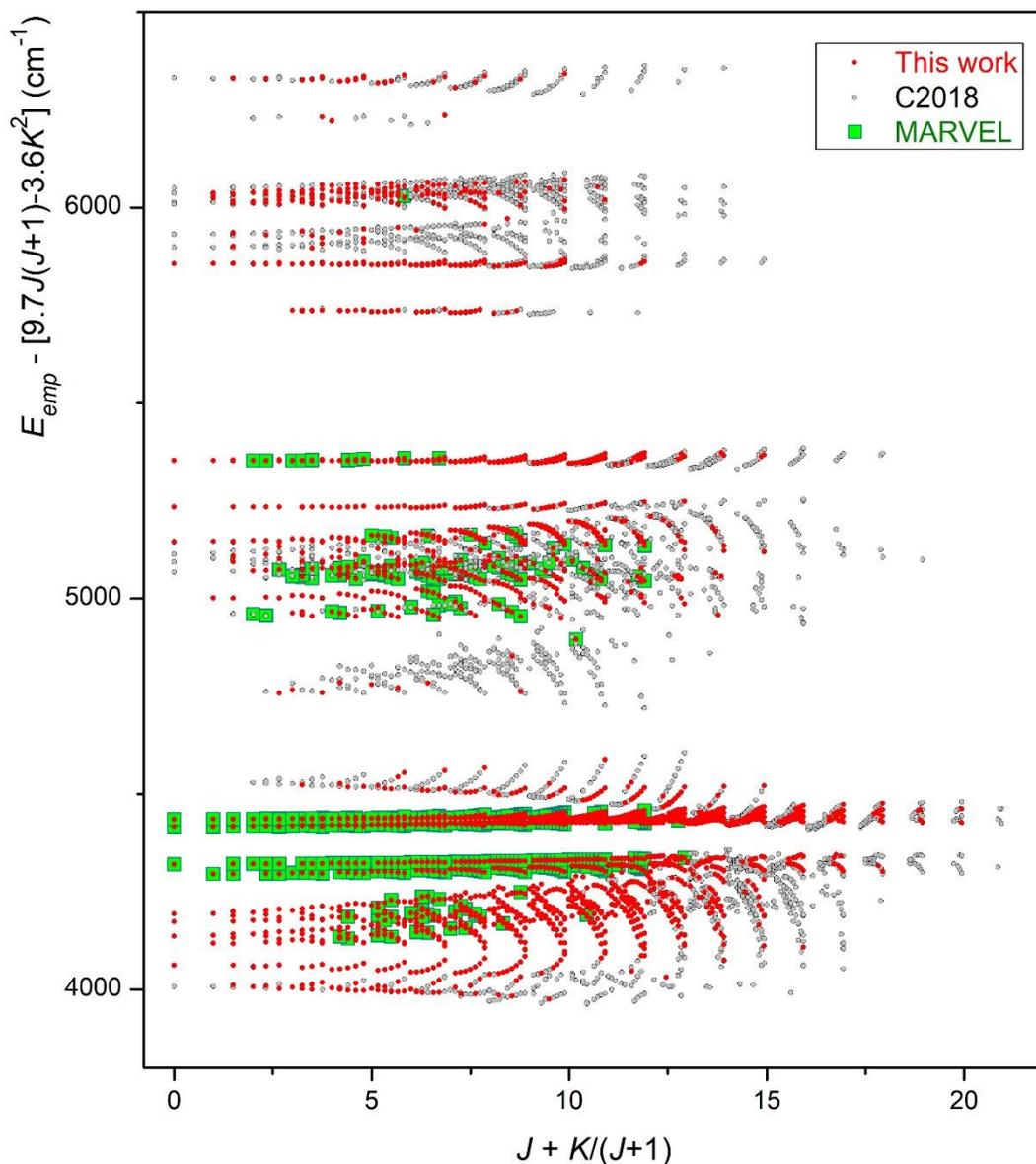


Figure 10.

Overview comparison between the set of MARVEL energy levels (green squares) [14] and the set of upper energy levels presently derived from the analysis of the $^{14}\text{NH}_3$ spectrum between 3900 and 4706 cm^{-1} (red dots). The plot includes the C2018 calculated values (grey symbols). For the sake of clarity, the average rotational term $[9.7 \times J(J+1) - 3.6K^2]$ was subtracted from each energy.

The upper state empirical energies of 2287 $^{14}\text{NH}_3$ rovibrational levels were derived from the assigned list by adding the lower state energies to the measured line positions. We adopted the values used in the previous work for the lower state energies (533 in total). For the ground and $v_2 = 1$ states, the energy was taken from Cacciani et al. [24], and MARVEL energies [16] were used for the $v_2 = 4$ and $v_4 = 1$ states. Depending on the number of transitions sharing the considered upper state, some determinations relied on up to 10 measured transition wavenumbers. The complete list, including the average value and standard deviation, is given in a separate Supplementary Material. The

MARVEL2020 energies are listed for comparison, when available. In the case of multiple determinations, the *rms* deviation of the obtained energy gives an insight into the uncertainty of the measured transition wavenumbers. An average *rms* value of $5 \times 10^{-4} \text{ cm}^{-1}$ with a spread of $5 \times 10^{-4} \text{ cm}^{-1}$ was obtained for the entire set of energy levels. These values give an estimate of the precision of our line center determinations. The accuracy of the derived energies was further improved as follows. Instead of a simple average, weighted and trimmed averages were applied when possible depending on the number, n , of transitions sharing the same upper level. For $n = 2$, a weight corresponding to the logarithm of the transition intensity was used. The trim at 30% was applied with higher values of n . As a result, the *rms* and spread were decreased to $2 \times 10^{-4} \text{ cm}^{-1}$ and $3 \times 10^{-4} \text{ cm}^{-1}$, respectively. From these considerations, we conclude that the accuracy of the empirical upper state energies is better than 10^{-3} cm^{-1} .

Figure 10 compares our empirical energies and the MARVEL energies reported in Ref. [14], as well as the predicted C2018 values. The number of empirical upper state energies in the region has been increased four times as a result of the identification of new bands and the extension to higher J values of the rotational structure of known bands (1841 of 2287 derived rovibrational levels are new). An exception is the vibrational state $\nu_3 = \nu_4 = 1$ that is less represented in our work because only components of the hot band $\nu_3 + \nu_4 - \nu_2$ lie in our range (the $\nu_3 + \nu_4$ cold band transitions are located in the 4700-5300 cm^{-1} range).

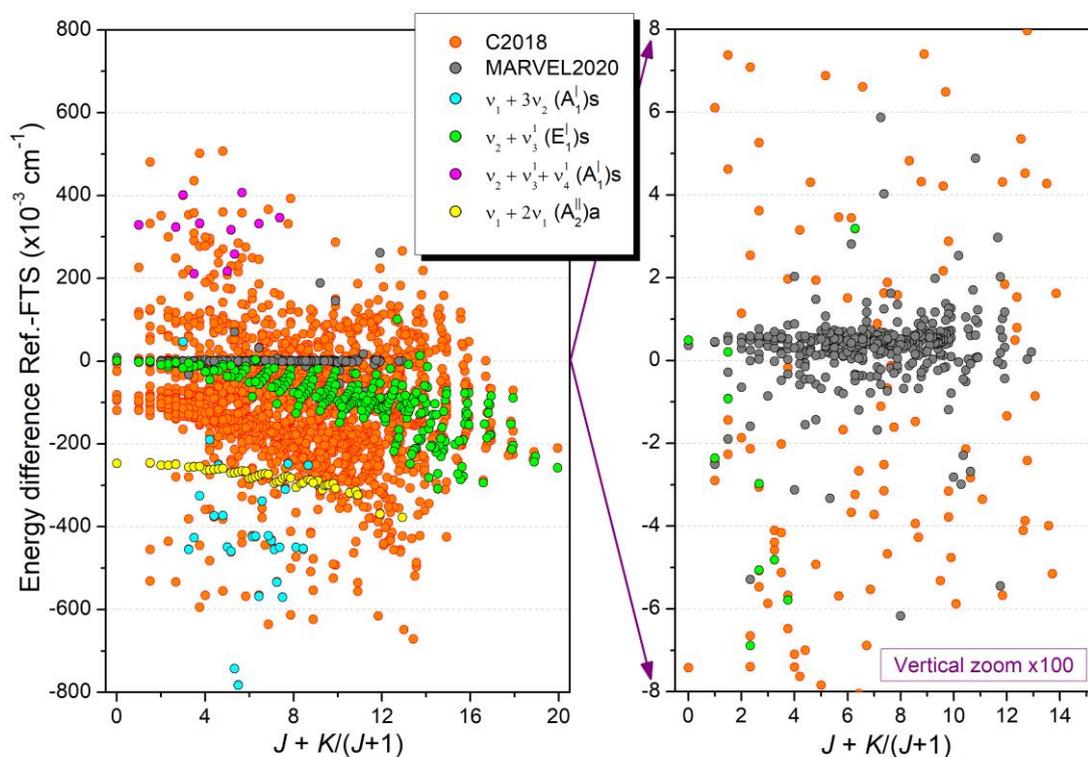


Figure 11. Difference between the MARVEL [14] and C2018 energies of the upper levels and the corresponding values derived in the present work.

Figure 11 presents the differences between the upper state energies measured in this work, calculated by C2018 and present in MARVEL, *versus* the rotational numbers factor $J+K/(J+1)$. A small systematic overestimation of $5 \times 10^{-4} \text{ cm}^{-1}$ is evidenced for the MARVEL energies, probably related to the frequency calibration of the original data by Urban et al. [1], and a larger dispersion is observed above 5300 cm^{-1} corresponding to hot bands transitions. Regarding the C2018 variational energy values, the deviations are more significant, on the order of a few tenths of cm^{-1} , with a general tendency to be underestimated.

5. Conclusion

The characterization of the ammonia room temperature absorption spectrum has been significantly improved between 3900 and 4700 cm^{-1} , relying on low-pressure absorption FTS spectra at room temperature. As a result, the amount of assigned transitions has been increased to about 7800 lines. The current HITRAN2020 list, resulting from a MARVEL extension of the previous HITRAN2016 list (about 1100 transitions), provides 2250 transitions in the considered region. The transitions assigned by comparison with the C2018 theoretical list and supported by systematic checking of Lower State Combination Difference (LSCD) relations, belong to 51 bands and bring over 99.8% of the integrated absorption in the region. In addition, 1870 new upper energy levels were determined with accuracy better than 0.001 cm^{-1} .

As main outcome of the present work, we provide as a Supplementary Material a recommended list of 8419 transitions for ammonia in natural isotopic abundance. The $^{14}\text{NH}_3$ line positions were calculated using our best empirical determination of the upper energy levels. Line intensities are FTS values. In the case of $^{15}\text{NH}_3$ transitions, the experimental intensities were scaled to coincide with the natural $^{15}\text{NH}_3$ isotopic abundance.

The studied spectral interval intersects the $2.3 \text{ }\mu\text{m}$ atmospheric transparency window corresponding to a region of low water vapor absorption. The presently reported results might be important for analyzing the weak lines in high sensitivity spectra of water vapor in the $4200\text{-}4600 \text{ cm}^{-1}$ region. Indeed, ammonia is generally present in water vapor as an impurity with sub-ppm concentration (see for instance, [26-28]). The improvement of spectroscopic databases in the region will help to discriminate NH_3 lines among the numerous weak water vapor lines of the $2.3 \text{ }\mu\text{m}$ transparency window.

The HITRAN2020 line list of ammonia shows similar deficiencies in the nearby $4700\text{-}5400 \text{ cm}^{-1}$ region [11]. Therefore, based on the present FTS recordings (**Fig. 2**), we plan to perform a similar analysis and extend our experimental list and assignments up to 5500 cm^{-1} .

Acknowledgments

This work is a contribution to the CPER research project CLIMIBIO. The authors thank the French Ministère de l'Enseignement Supérieur et de la Recherche, the Hauts de France Region and the European Funds for Regional Economic Development for their financial support to this project. This work was also supported by the joint Slovak-Czech-French Danube Region project (DS-FR-19-0050) and the Slovak Research and Development Agency (contract number APVV-19-0386).

Table 2: Statistics and integrated absorption of the various vibrational bands contributing to the $^{14}\text{NH}_3$ spectrum between 3900 and 4706 cm^{-1} . The bands are ordered according to their C2018 integrated intensities.

Vibrational band	Upper state ^a	C2018			This work			Int. ratio ^h %	$\langle \delta \rangle^i$ (cm^{-1})
		E_0^b (cm^{-1})	Nb ^c	Band Int. ^d ($\text{cm}/\text{mol.}$)	Nb ^e	J_{\min}/J_{\max}^f	Band Int. ^g ($\text{cm}/\text{mol.}$)		
$3\nu_2 + \nu_3^1$ (E') s	031010	4416.9	1081	4.18E-19	792	0/19	3.98E-19	99.96	0.08
$3\nu_2 + \nu_3^1$ (E'') a	031010	4435.4	1106	4.11E-19	783	0/19	3.91E-19	99.96	0.06
$\nu_1 + \nu_2$ (A ₁ ') s	110000	4294.5	659	6.71E-20	361	1/17	6.57E-20	99.8	0.11
$\nu_1 + \nu_2$ (A ₂ '') a	110000	4320.0	642	6.33E-20	355	0/16	6.19E-20	99.8	0.07
$2\nu_2 + \nu_3^1$ (E') s $\leftarrow \nu_2$	021010	5144.9	539	1.10E-20	322	0/14	1.04E-20	98.7	0.21
$2\nu_2 + \nu_3^1$ (E'') a $\leftarrow \nu_2$	021010	5353.0	502	7.85E-21	302	0/14	7.42E-21	98.2	0.14
$\nu_2 + 2\nu_4^2$ (E'') a	010202	4192.9	970	1.00E-20	610	0/14	1.03E-20	98.1	0.09
$\nu_2 + 2\nu_4^2$ (E') s	010202	4135.8	932	7.87E-21	587	0/14	8.18E-21	97.9	0.13
$\nu_2 + 2\nu_4^0$ (A ₂ '') a	010200	4173.1	531	8.36E-21	339	0/14	8.85E-21	99.1	0.02
$\nu_2 + 2\nu_4^0$ (A ₁ ') s	010200	4115.9	479	7.01E-21	319	1/15	7.54E-21	99	0.03
$\nu_1 + 2\nu_2$ (A ₁ ') s $\leftarrow \nu_2$	120000	5000.2	200	1.43E-21	121	1/12	1.38E-21	97.1	0.18
$\nu_1 + 2\nu_2$ (A ₂ '') a $\leftarrow \nu_2$	120000	5233.8	203	8.91E-22	107	0/12	8.34E-22	92	0.28
$3\nu_2 + \nu_4^1$ (E'') a	030101	4530.6	568	7.50E-22	142	3/14	5.80E-22	77.9	0.04
$3\nu_2 + \nu_4^1$ (E') s	030101	4007.6	319	2.09E-22	116	1/12	1.78E-22	64.4	0.07
$3\nu_2 + \nu_3^1$ (E') s $\leftarrow 2\nu_2$	031010	5856.1	262	4.77E-22	128	0/11	4.09E-22	84.3	0.15
$3\nu_2 + \nu_3^1$ (E'') a $\leftarrow 2\nu_2$	031010	6331.3	184	1.06E-22	27	1/9	4.36E-23	38.3	0.12
$3\nu_2 + \nu_3^1$ (E') s $\leftarrow \nu_4$	031010	5856.1	96	2.57E-23	8	5/11	5.59E-24	21.6	0.18
$4\nu_2$ (A ₂ '') a	060000	4061.6	199	4.48E-22	110	0/12	4.65E-22	95	0.01
$2\nu_2 + 2\nu_4^2$ (E'') a $\leftarrow \nu_2$	020202	5113.3	323	2.04E-22	54	1/11	9.33E-23	41.4	0.36
$2\nu_2 + 2\nu_4^2$ (E') s $\leftarrow \nu_2$	020202	4773.8	47	1.54E-23	3	4/8	4.09E-24	24.7	0.4
$2\nu_2 + 2\nu_4^0$ (A ₂ '') a $\leftarrow \nu_2$	020200	5093.6	198	1.67E-22	49	1/10	1.07E-22	52.9	0.25
$2\nu_2 + 2\nu_4^0$ (A ₁ ') s $\leftarrow \nu_2$	020200	4756.9	31	1.41E-23	2	5/6	2.79E-24	19.4	0.21
$2\nu_2 + 2\nu_4^0$ (A ₁ ') s	020200	4756.9	33	2.54E-23	5	2/6	7.55E-24	34.5	0.17
$\nu_2 + \nu_3^1 + \nu_4^1$ (E') s $\leftarrow \nu_4$	011111	6012.9	216	1.51E-22	56	1/10	8.92E-23	54.9	-0.05
$\nu_2 + \nu_3^1 + \nu_4^1$ (E'') a $\leftarrow \nu_4$	011111	6036.5	197	1.39E-22	50	1/10	7.53E-23	57.2	-0.1
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₂ '') s $\leftarrow \nu_4$	011111	6008.0	139	8.51E-23	9	2/7	1.11E-23	22	-0.33
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₁ '') a $\leftarrow \nu_4$	011111	6033.7	135	8.20E-23	21	1/9	3.08E-23	35.7	-0.22
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₁ ') s $\leftarrow \nu_4$	011111	6024.3	110	5.16E-23	13	1/7	1.49E-23	26.5	-0.32
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₂ '') a $\leftarrow \nu_4$	011111	6049.6	102	4.71E-23	9	3/6	1.11E-23	20.1	-0.25
$\nu_2 + \nu_3^1 + \nu_4^1$ (E'') a $\leftarrow 2\nu_2$	011111	6036.5	17	3.28E-24	2	8/9	1.38E-24	19.9	0.01
$4\nu_2 + \nu_4^1$ (E') s $\leftarrow \nu_2$	030200	5104.9	188	9.63E-23	29	3/8	4.58E-23	46.9	0.23
$\nu_1 + \nu_4^1$ (E'') a $\leftarrow \nu_2$	100101	4956.9	113	8.00E-23	44	3/9	5.40E-23	70.8	0.04
$\nu_1 + \nu_4^1$ (E') s $\leftarrow \nu_2$	100101	4955.8	18	1.22E-23	3	7/13	4.38E-24	30.1	-0.02
$\nu_1 + \nu_4^1$ (E'') a	100101	4956.9	13	2.95E-24	2	10/11	7.47E-25	20.2	0.04
$\nu_1 + \nu_4^1$ (E') s	100101	4955.8	11	2.88E-24	4	10/11	1.60E-24	57.4	-0.02
$\nu_3^1 + \nu_4^1$ (A ₁ '') a $\leftarrow \nu_2$	001111	5052.7	105	7.44E-23	14	5/12	3.17E-23	44.4	0
$\nu_3^1 + \nu_4^1$ (E'') a $\leftarrow \nu_2$	001111	5053.2	148	5.39E-23	48	3/13	3.24E-23	55.8	0.02
$\nu_3^1 + \nu_4^1$ (A ₂ '') a $\leftarrow \nu_2$	001111	5067.7	81	5.36E-23	33	7/9	3.89E-23	77.7	0.11
$\nu_3^1 + \nu_4^1$ (E') s $\leftarrow \nu_2$	001111	5052.6	23	2.39E-23	5	6/8	3.48E-23	80.9	0.05
$\nu_3^1 + \nu_4^1$ (A ₂ ') s $\leftarrow \nu_2$	001111	5052.0	44	1.15E-23	4	6/10	4.80E-24	21.6	0.02
$\nu_3^1 + \nu_4^1$ (A ₁ ') s $\leftarrow \nu_2$	001111	5067.8	20	7.48E-24	2	5/7	5.90E-25	15.3	0.04

$\nu_3^1 + \nu_4^1$ (E') s	001111	5052.6	6	1.65E-24	3	12/13	1.11E-24	64.2	0
$\nu_3^1 + \nu_4^1$ (E'') a	001111	5053.2	7	1.41E-24	1	11/11	3.02E-25	15.5	-0.03
$\nu_1 + \nu_2 + \nu_4^1$ (E') s $\leftarrow \nu_4$	110101	5897.8	132	3.77E-23	4	1/4	2.90E-24	6.4	-0.48
$\nu_1 + \nu_2 + \nu_4^1$ (E'') a $\leftarrow \nu_4$	110101	5930.8	136	3.69E-23	12	1/7	7.63E-24	17.4	-0.32
$3\nu_4^1$ (E') s	000301	4799.2	66	2.02E-23	1	10/10	2.85E-25	1.0	0.2
$\nu_1 + 3\nu_2$ (A ₁ ') s $\leftarrow 2\nu_2$	130000	5737.9	41	1.68E-23	23	3/8	1.11E-23	67.6	0.42
$\nu_1 + 3\nu_2$ (A ₂ ') a $\leftarrow 2\nu_2$	130000	6230.3	11	1.94E-24	13	3/6	8.48E-25	40.7	0.6
$\nu_1 + 3\nu_2$ (A ₁ ') s $\leftarrow \nu_2$	130000	5737.9	28	8.52E-24	3	3/6	6.66E-24	64.9	0.42
$3\nu_4^3$ (A ₁ ') a $\leftarrow \nu_2$	000303	4843.0	3	3.44E-24	1	8/8	2.99E-24	93.5	0.16
$6\nu_2$ (A ₁ ') s $\leftarrow \nu_4$	060000	6043.4	7	1.56E-24	1	8/8	7.03E-25	23.2	0.11
Sum ^j			12221	1.02E-18	6048		9.74E-19	99.8	
Others ^k			482	1.12E-22	1744		1.34E-21		
Total ^l			12703	1.02E-18	7792		9.75E-19		

Notes

^a Vibrational labeling: $V_1V_2V_3V_4L_3L_4$ where $V_{i=1-4}$ are the vibrational normal mode quantum numbers corresponding to the ν_1 symmetric stretch, ν_2 symmetric bend, ν_3 the antisymmetric stretch, ν_4 antisymmetric bend, respectively.

$L_3=|l_3|$ and $L_4=|l_4|$ are the vibrational angular momentum quantum numbers of the ν_3 and ν_4 modes, respectively.

^b Energy of the lowest level of the upper vibrational state (corresponding generally to $J=K=0$) as calculated in the C2018 list [18]. In the case of the hot bands, the $J=K=0$ value of the lowest state was subtracted.

^c Number of lines of the corresponding band with C2018 intensity larger than 1×10^{-25} cm/molecule.

^d Sum of the C2018 intensities larger than 1×10^{-25} cm/molecule

^e Number of lines of the corresponding band assigned in the studied spectrum

^f Minimum and maximum values of the rotational quantum numbers of the assigned lines

^g Sum of the experimental intensities of the considered band

^h Ratio of the sum of the C2018 intensities of the transitions identified in the studied spectrum by the total C2018 intensity of the considered band.

ⁱ Average value of the (exp.- C2018) position differences of the considered band

^j Sum of the intensities of the listed bands

^k For the experimental list of transitions, "others" correspond to the intensity sum of the unassigned transitions, while for the C2018 line list, it corresponds to the total intensity of the predicted vibrational bands with intensity smaller than the smallest observed band.

^l Sum of the two above values corresponding to the total C2018 intensity (intensity cut off of 1×10^{-25} cm/molecule) and all the measured absorption lines.

References

- [1] Urban Š, Tu N, Narahari Rao K, Guelachvili G. Analysis of high-resolution Fourier transform spectra of $^{14}\text{NH}_3$ at 2.3 μm . *J Mol Spectrosc* 1989;133:312–30. doi: 10.1016/0022-2852(89)90195-1.
- [2] Brown LR, Margolis JS. Empirical line parameters of NH_3 from 4791 to 5294 cm^{-1} . *J Quant Spectrosc Radiat Transf* 1996;56:283–94. doi: 10.1016/0022-4073(96)00041-6.
- [3] Down MJ, Hill C, Yurchenko SN, Tennyson J, Brown LR, Kleiner I. Re-analysis of ammonia spectra: Updating the HITRAN $^{14}\text{NH}_3$ database. *J Quant Spectrosc Radiat Transf* 2013;130:260–72. doi: 10.1016/j.jqsrt.2013.05.027.
- [4] Cacciani P, Čermák P, Cosléou J, Khelkhal M, Jeseck P, Michaut X. New progress in spectroscopy of ammonia in the infrared 1.5 μm range using evolution of spectra from 300K down to 122K. *J Quant Spectrosc Radiat Transf* 2012;113:1084–91. doi: 10.1016/j.jqsrt.2012.02.026.
- [5] Cacciani P, Čermák P, Cosléou J, Romh J El, Hovorka J, Khelkhal M. Spectroscopy of ammonia in the range 6626–6805 cm^{-1} : using temperature dependence towards a complete list of lower state energy transitions. *Mol Phys* 2014;112:2476–85. doi: 10.1080/00268976.2014.924653.
- [6] Čermák P, Hovorka J, Veis P, Cacciani P, Cosléou J, El Romh J, et al. Spectroscopy of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ in the 2.3 μm spectral range with a new VECSEL laser source. *J Quant Spectrosc Radiat Transf* 2014;137:13–22. doi: 10.1016/j.jqsrt.2014.01.005.
- [7] Vander Auwera J, Vanfleteren T. Line positions and intensities in the 7400–8600 cm^{-1} region of the ammonia spectrum. *Mol Phys* 2018;116:3621–30. doi: 10.1080/00268976.2018.1467054.
- [8] Svoboda V, Rakovský J, Votava O. New insight on ammonia 1.5 μm overtone spectra from two-temperature analysis in supersonic jet. *J Quant Spectrosc Radiat Transf* 2019;227:201–10. doi: 10.1016/j.jqsrt.2019.01.030.
- [9] Cacciani P, Čermák P, Béguier S, Campargue A. The absorption spectrum of ammonia between 5650 and 6350 cm^{-1} . *J Quant Spectrosc Radiat Transf* 2021;258:107334. doi: 10.1016/j.jqsrt.2020.107334.
- [10] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, et al. The HITRAN2016 Molecular Spectroscopic Database. *J Quant Spectrosc Radiat Transf* 2017;203:3–69. doi: 10.1016/j.jqsrt.2017.06.038.
- [11] Gordon IE, Rothman LS, Hargreaves RJ, Hashemi R, Karlovets EV, Skinner FM, et al. The HITRAN2020 molecular spectroscopic database. *J. Quant. Spectrosc. Radiat. Transfer* 2021, *in press*.
- [12] Rothman LS, Rinsland CP, Goldman A, Massie ST, Edwards DP, Flaud J-M, et al. The HITRAN Molecular Spectroscopic Database and HAWKS (HITRAN atmospheric workstation): 1996 edition. *J Quant Spectrosc Radiat Transf* 1998;60:665–710. doi: 10.1016/S0022-4073(98)00078-8.

- [13] Kleiner I, Tarrago G, Cottaz C, Sagui L, Brown LR, Poynter RL, et al. NH₃ and PH₃ line parameters: the 2000 HITRAN update and new results. *J Quant Spectrosc Radiat Transf* 2003;82:293–312. doi: 10.1016/S0022-4073(03)00159-6.
- [14] Coles PA, Yurchenko SN, Tennyson J. ExoMol molecular line lists – XXXV. A rotation-vibration line list for hot ammonia. *Mon Not R Astron Soc* 2019;490:4638–47. doi: 10.1093/mnras/stz2778.
- [15] Coles PA, Ovsyannikov RI, Polyansky OL, Yurchenko SN, Tennyson J. Improved potential energy surface and spectral assignments for ammonia in the near-infrared region. *J Quant Spectrosc Radiat Transf* 2018;219:199–212. doi: 10.1016/j.jqsrt.2018.07.022.
- [16] Furtenbacher T, Coles PA, Tennyson J, Yurchenko SN, Yu S, Drouin B, et al. Empirical rovibrational energy levels of ammonia up to 7500 cm⁻¹. *J Quant Spectrosc Radiat Transf* 2020;251:107027. doi: 10.1016/j.jqsrt.2020.107027.
- [17] Beale CA, Hargreaves RJ, Coles P, Tennyson J, Bernath PF. Infrared absorption spectra of hot ammonia. *J Quant Spectrosc Radiat Transf* 2017;203:410–6. doi: 10.1016/j.jqsrt.2017.02.012.
- [18] Čermák P, Cacciani P, Cosléou J. Accurate ¹⁴NH₃ line-list for the 2.3 μm spectral region. *J Quant Spectrosc Radiat Transf* 2021:107861. doi: 10.1016/j.jqsrt.2021.107861.
- [19] MR Carleer, WSpectra: a Windows program to accurately measure the line intensities of high-resolution Fourier transform spectra, in *Remote Sensing of Clouds and the Atmosphere V*, edited by J.E. Russel, K. Schäfer, and O. Lado-Bordowsky, Vol. 4168 (Proceedings of SPIE – the International Society for Optical Engineering, Barcelona, Spain, 2001), p. 337.
- [20] Wojdyr M. Fityk: a general-purpose peak fitting program. *Journal of Applied Crystallography* 2010; 43 (5 part 1) 1123-28. doi: 10.1107/S0021889810030499
- [21] Bertin T, Vander Auwera J. Adaptation to high resolution of an algorithm to retrieve the instrument line shape of a fourier transform spectrometer. *Int. Symp. Mol. Spectrosc.*, 2021, p. TM06.
- [22] Boone CD, Bernath PF. The instrumental line shape of the atmospheric chemistry experiment Fourier transform spectrometer (ACE-FTS). *J Quant Spectrosc Radiat Transf* 2019;230:1–12. <https://doi.org/10.1016/j.jqsrt.2019.03.018>.
- [23] Čermák P, Hovorka J, Veis P, Patrice C, Cosléou J, Khelkal M, et al. Analysis of ¹⁵NH₃ absorption spectra in the 2.3 μm atmospheric water window. *24th Int. Conf. High Resolut. Mol. Spectrosc.*, 2016.
- [24] Cacciani P, Cosléou J, Khelkhal M, Tudorie M, Puzzarini C, Pracna P. Nuclear spin conversion in NH₃. *Phys Rev A* 2009;80:042507. doi: 10.1103/PhysRevA.80.042507.
- [25] Beale CA, Wong A, Bernath P. Infrared transmission spectra of hot ammonia in the 4800–9000 cm⁻¹ region. *J Quant Spectrosc Radiat Transf* 2020;246:106911. doi: 10.1016/j.jqsrt.2020.106911.

- [26] Leshchishina O, Mikhailenko SN, Mondelain D, Kassi S, Campargue A. An improved line list for water vapor in the 1.5 μm transparency window by highly sensitive CRDS between 5852 and 6607 cm^{-1} . *J Quant Spectrosc Radiat Transf* 2013;130:69–80. doi: 10.1016/j.jqsrt.2013.04.010.
- [27] Mikhailenko SN, Mondelain D, Karlovets EV, Kassi S, Campargue A. Cavity ring down spectroscopy of ^{17}O enriched water vapor near 1.73 μm . *J Quant Spectrosc Radiat Transf* 2019;222–223:229–35. doi: 10.1016/j.jqsrt.2018.10.027.
- [28] Vasilchenko S, Tran H, Mondelain D, Kassi S, Campargue A. Accurate absorption spectroscopy of water vapor near 1.64 μm in support of the MEthane Re- mote LIdar missioN (MERLIN). *J Quant Spectrosc Radiat Transf* 2019;235:332–42. doi: 10.1016/j.jqsrt.2019.06.027.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

P. Cacciani: Investigation, **P. Čermák:** Investigation, **J. Vander Auwera:** Investigation, **A. Campargue:** Investigation



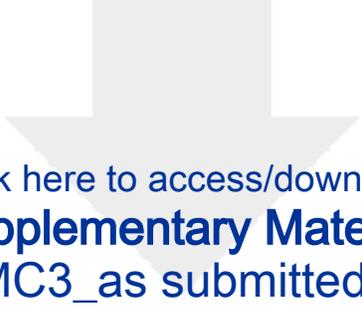
Click here to access/download
Supplementary Material
MMC1_as submitted.txt





Click here to access/download
Supplementary Material
MMC2_as submitted1.txt





Click here to access/download
Supplementary Material
MMC3_as submitted.txt

