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The ammonia absorption spectrum between 4700 and 5650 cm⁻¹

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Abstract

Room temperature absorption spectra of ammonia were recorded by high-resolution Fourier transform spectroscopy in the 4700-5600 cm⁻¹ range at four pressures (13, 46, 140, and 304 Pa). Additionally, we use an existing Kitt Peak spectrum to extend the analysis up to 5650 cm⁻¹. In total, 9110 absorption lines with intensity ranging from 1×10^{-25} to 1.6×10^{-20} cm/molecule were retrieved, for the two principal isotopologues. Another Kitt Peak spectrum was used to identify 505 ¹⁵NH₃ transitions within the experimental line list. The rovibrational assignments of the ¹⁴NH₃ lines relied on the position and intensity agreement with the C2018 theoretical line list (Coles *et al.* JQSRT 2018;219 199–212) and were validated by the systematic use of Lower State Combination Difference (LSCD) relations. In the process, a number of intensity transfer between nearby transitions were identified. Finally, 6562 transitions were assigned to 61 vibrational bands of the main isotopologue, ¹⁴NH₃, representing over 99.8% of the C2018 integrated absorption at room temperature in the region. The upper state empirical energy of a total of 2215 rovibrational levels of ¹⁴NH₃ were derived. Most of them are newly reported. The comparison with the current HITRAN2020 list is discussed. 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 [1, 2]. This task is made difficult by numerous interactions between its six vibrational modes and the internal inversion motion.

The current work is part of the analysis of the ammonia high resolution spectrum recorded by Fourier Transform Spectroscopy (FTS) in the 3900-5600 cm⁻¹ range. The low energy part of the range, from 3900 to 4700 cm⁻¹, was covered in our previous contribution [3], while the remainder of the data set, up to 5600 cm⁻¹, is analyzed in the

9 current work. The present FTS data are complemented with an existing Kitt Peak FTS spectrum in the weak absorbing
10 5600-5650 cm^{-1} interval, in order to fill the gap up to our previous analysis of the 5650-6350 cm^{-1} range [4].

11 The HITRAN line list [5] in the considered range is based on the study of a FTS spectrum recorded at Kitt Peak
12 with a 0.011 cm^{-1} spectral resolution [6]. The spectrum is dominated by the $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ bands centered at 4956
13 cm^{-1} and 5050 cm^{-1} , respectively. The upgrade of the HITRAN database from 2016 [7] to 2020 [5] has increased
14 the number of $^{14}\text{NH}_3$ transitions from 1875 to 2493 while the $^{15}\text{NH}_3$ dataset in the region has remained unchanged.
15 The overview of HITRAN2020 list is presented in the upper panel of Fig. 1. About 620 new transitions of $^{14}\text{NH}_3$
16 included in HITRAN2020 were not observed but transferred from the hybrid CoYuTe list created by adjusting the
17 line positions predicted from the C2018 potential energy surface [8] according to empirical energy levels determined
18 using the MARVEL algorithm [9]. For the HITRAN2020 edition [5], it was decided to add to the HITRAN2016
19 dataset [7] only the CoYuTe transitions for which both the lower and upper levels have empirical energies and their
20 calculated line intensities are larger than 1×10^{-25} $\text{cm}^2/\text{molecule}$. In our region, the added transitions include several hot
21 band transitions for which the upper levels were determined from ground state transitions, thus at higher energy [10].
22 Their intensities are generally less than 3×10^{-24} $\text{cm}^2/\text{molecule}$ which was the intensity cut-off of the HITRAN2016
23 list. Among the $^{14}\text{NH}_3$ transitions, 1255 are given with full assignment of the lower and upper states, whereas no
24 or incomplete assignment is given for 1201 transitions. Experimental intensities have been kept for the transitions
25 transferred from HITRAN2016, whereas C2018 calculated intensity values [11] are given for the added transitions.

26 Regarding the previous experimental studies in our region, in addition to Ref. [6], it is worth mentioning the
27 recent work of Beale *et al.* [12]. These authors reported an analysis of ammonia FTS spectra recorded at different
28 temperatures from 295 to 973 K with a 0.01 cm^{-1} spectral resolution. Due to its lower accuracy, this study was used
29 neither for the HITRAN2020 update nor for the derivation of new MARVEL energy levels [11]. Nevertheless, it is a
30 very useful source for the application of Lower State Combination Differences (LSCD) relations used for validation
31 of our quantum assignments [4].

32 As the experimental setup, conditions of the recordings, fitting process and construction of the line list were de-
33 tailed in Ref. [3], they are briefly recalled in the two next sections. Section 4 describes some aspects of the assignment
34 process before discussing the results in particular the occurrence of intensity transfers between resonant lines.

35 2. Experimental details

36 Four room temperature FTS absorption spectra of ammonia were recorded at ULB with a Bruker IFS 120 (up-
37 graded to 125) in the 3900-5600 cm^{-1} range (Fig. 2). The experimental conditions of the measurements are summa-
38 rized in Table 1.

39 In the 5600-5650 cm^{-1} interval where the ammonia absorption is very weak, an existing Kitt Peak spectrum with
40 reference 900308R019 (KP1) was analyzed. Also, a second Kitt Peak spectrum (Ref. 930826R016, KP2 in Table 1)
41 recorded with a $^{15}\text{NH}_3$ enriched sample was treated to identify the $^{15}\text{NH}_3$ transitions.

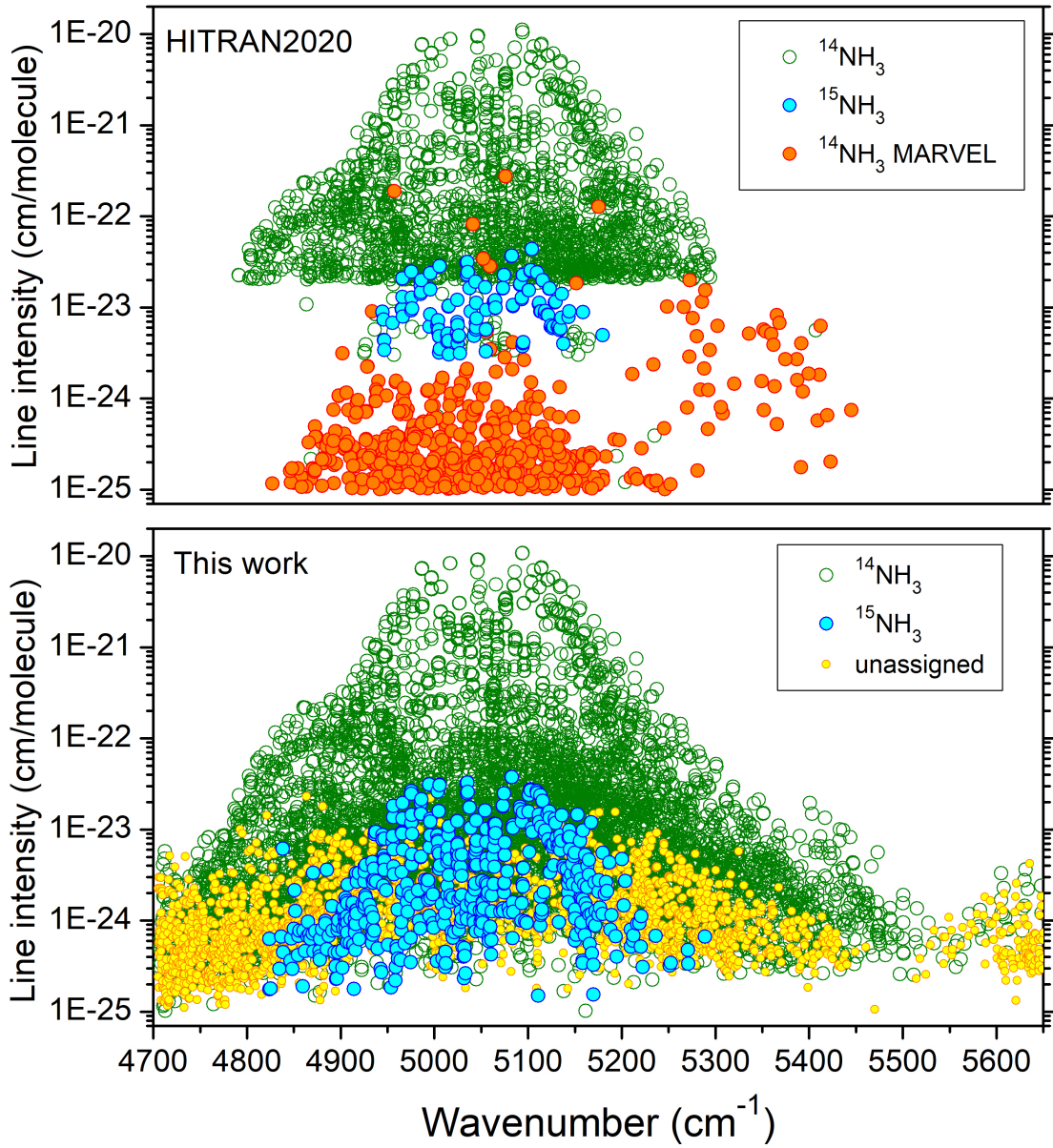


Figure 1: *Upper panel*: Overview of the HITRAN2020 transitions of $^{14}\text{NH}_3$ (green and orange) and $^{15}\text{NH}_3$ (cyan) in the studied region. $^{14}\text{NH}_3$ transitions were added using MARVEL algorithm (orange). *Lower panel*: Ammonia transitions measured in the present work: $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ (green and cyan circles, respectively), and unassigned (yellow circles).

Table 1: Experimental parameters of the four FTS spectra used in this work.

Spectrum	p (Torr)	p (Pa)	$c_{^{15}\text{N}}$ (%)	L (m)	R (cm^{-1})
TW1	0.109 (6)	13.2 (1.5)	0.78		
TW2	0.348 (8)	46.0 (1.1)	0.68	13.86 (4)	0.003
TW3	1.053 (33)	140.4 (4.4)	0.62		
TW4	2.28 (8)	304.0 (11.0)	0.54		
KP1 (Ref. 900308R019)	0.52	69.3		193	0.01
KP2 ($^{15}\text{NH}_3$ - Ref. 930826R016)	2.0	167.	99.64	16	0.01

Notes: For the four spectra studied in this work (TW1-TW4), p is the average pressure (the numbers between parentheses are the uncertainties of measurement, provided in the units of the last digit quoted,

L is the interaction pathlength and R is the spectral resolution used for the recording. $c_{^{15}\text{N}}$ is the estimated value of the $^{15}\text{NH}_3$ relative abundance (the natural value is 0.37%).

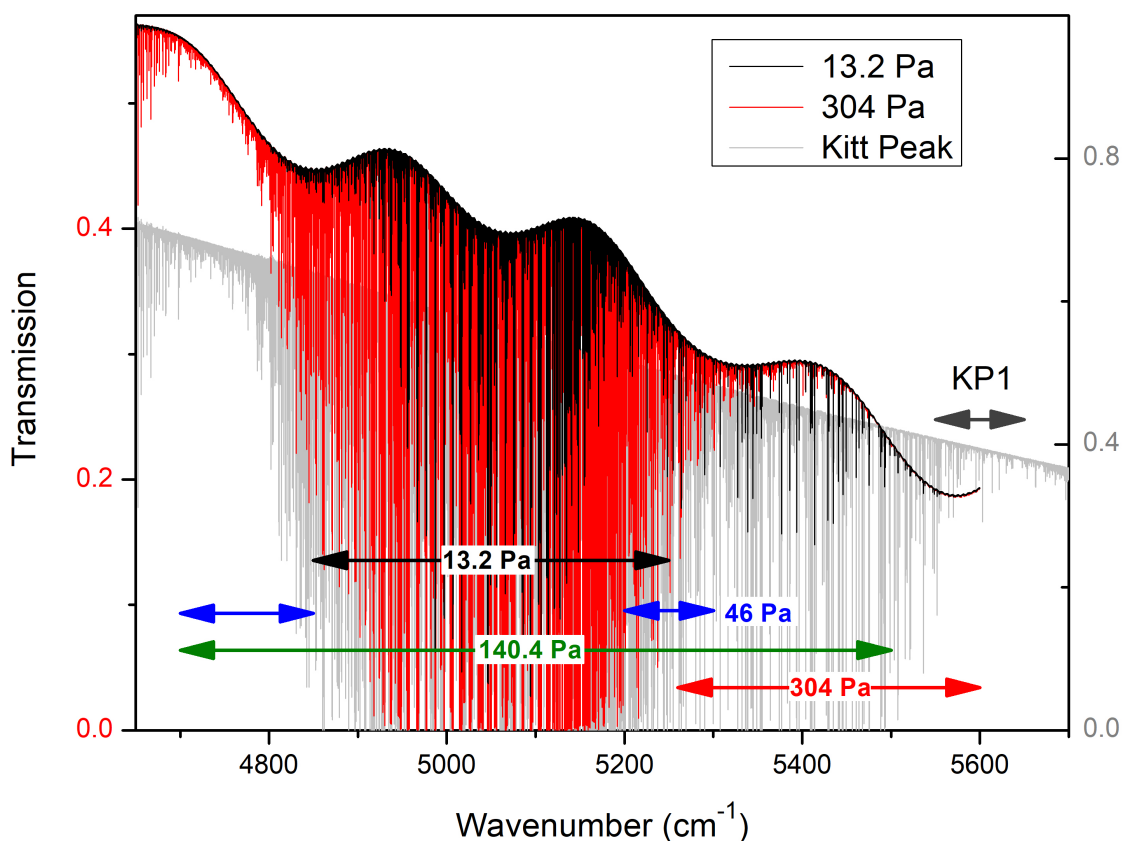


Figure 2: Overview of the Fourier transform absorption spectra of ammonia recorded in the present work with the resolution of 0.003 cm^{-1} . The arrows mark the spectral intervals of the spectra used in the analysis. In the $5600\text{-}5650 \text{ cm}^{-1}$ interval, the Kitt Peak spectrum (KP1) with Ref. 900308R019 was used.

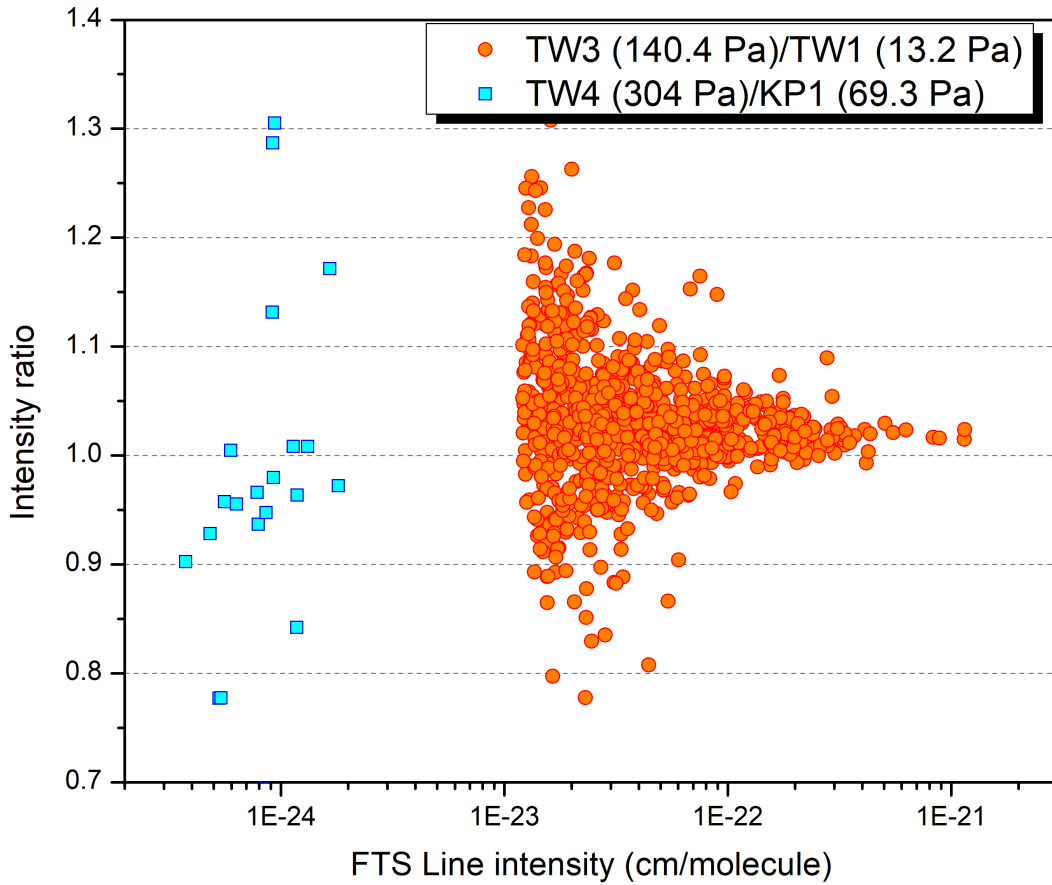


Figure 3: Ratios of the intensities derived from the 140.4 Pa spectrum to those of the 13.2 Pa spectrum (orange dots) for isolated transitions in the 1.2×10^{-23} - 1.2×10^{-21} cm/molecule range. $^{15}\text{NH}_3$ transitions were removed from the comparison. Intensity ratios between the KP1 Kitt Peak spectrum and the 304 Pa spectrum are plotted for a few weak lines below 5600 cm^{-1} (cyan dots). They are used for the intensity calibration of the $5600\text{-}5650 \text{ cm}^{-1}$ interval.

3. Line list construction

Line positions and line intensities were retrieved using a multi-line 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). The Lorentzian and Gaussian components of the Voigt profile were assumed to be identical for all the lines and adjusted in the fit. The fitted value of the Gaussian width was found slightly above the calculated value of the $^{14}\text{NH}_3$ Doppler broadening (FWHM 0.015 cm^{-1}), confirming a small contribution of ILS. Constraining the line widths helped to disentangle blended lines.

In Ref. [3], it was demonstrated that our data treatment neglecting the ILS leads to underestimated line intensities in case of strong absorbance, and the correction of this bias was presented. The same process was applied in the current range. As a test of the correction and consistency of the intensity values in this new range, Fig. 3 plots the

52 ratio of intensities retrieved from different sources. The intensities from the 140.4 Pa spectrum are compared to those
53 retrieved from of the 13.2 Pa spectrum. For the KP1 data in the 5550-5600 cm^{-1} interval, the intensity ratio between
54 the 304 Pa and the KP1 spectra is presented for a few lines. Isolated lines were preferred for the comparison (minimum
55 position separation of 0.03 cm^{-1}). The oscillator strength spans over two decades between 1.2×10^{-23} and 1.2×10^{-21}
56 $\text{cm}/\text{molecule}$ (in order to correspond to absorbances not too small at 13.2 Pa spectrum and not too large at 140.4 Pa).
57 On average, a small overestimation of 1.5% is noted between 1.2×10^{-22} and 1.2×10^{-21} $\text{cm}/\text{molecule}$ for the 140.4 Pa
58 spectrum and the root mean square deviation less than 5% in the whole range. This confirms the efficiency of the
59 applied correction and allows for using either spectrum. To construct the global line list, we selected at least two
60 spectra for each spectral interval, according to the absorption amplitude (see Fig. 2): the 13.2 Pa spectrum was used
61 from 4850 to 5250 cm^{-1} , the 46 Pa spectrum in 4700-4850 cm^{-1} and 5200-5300 cm^{-1} regions, the 140.4 Pa in the
62 4700-5500 cm^{-1} range, the 304 Pa spectrum from 5260 to 5600 cm^{-1} and, the KP1 spectrum in the 5550-5650 cm^{-1}
63 range. The comparison between the 304 Pa and the KP1 spectra in the range 5550-5600 cm^{-1} was used to calibrate in
64 intensity the latter (Fig. 3).

65 Several water vapor lines (present as an impurity) were also observed in the spectra, accidentally hiding some
66 ammonia lines above 5200 cm^{-1} . They were removed manually or subtracted from the spectrum by comparison
67 with the HITRAN2020 line list [5]. Finally, the resulting ammonia list includes 9110 lines with intensity ranging
68 between 1×10^{-25} and 1.3×10^{-20} $\text{cm}/\text{molecule}$ including 505 $^{15}\text{NH}_3$ transitions (see lower panel of Fig. 1). In case
69 of superposition of a $^{14}\text{NH}_3$ line and a $^{15}\text{NH}_3$ line (or a water line), the intensity of the interfering line was carefully
70 estimated and subtracted in order to minimise its impact on the retrieval of the $^{14}\text{NH}_3$ line intensity.

71 As mentioned in Ref. [3], the FTS spectra under analysis do not correspond to the ammonia natural isotopic
72 abundance but are enriched in the $^{15}\text{NH}_3$ isotopologue due to previous recordings with ^{15}N enriched gas samples. The
73 $^{15}\text{NH}_3$ transitions in the different spectra were identified by comparison with a Kitt Peak spectrum highly enriched
74 in $^{15}\text{NH}_3$ (Ref. 930826R016, $p = 2.00$ Torr, $T = 23.8$ °C, $L = 2.4$ m with CO for calibration). The $^{15}\text{NH}_3$ relative
75 abundance corresponding of our FTS spectra has been estimated in two ways: using the absolute intensities obtained
76 in Ref. [13] already used in Ref. [3] or by comparison with the calculated intensity values of Ref. [14]. The two results
77 agree and lead to the relative abundance values included in Table 1. The $^{15}\text{NH}_3$ abundance increases from 0.54%
78 (340 Pa) to 0.78% (13.2 Pa) to be compared to a natural value of 0.366% [5]. As the four spectra were recorded
79 successively by decreasing steps of the pressure, the isotopic ratio increased, due to the progressive desorption of
80 $^{15}\text{NH}_3$ adsorbed on the walls of the cell and exchanges with ammonia in natural isotopic abundance initially injected
81 in the cell. Note that the estimated value of the $^{15}\text{NH}_3$ abundance in the various analyzed spectra was used to scale
82 the $^{15}\text{NH}_3$ line intensities accordingly, and the reported intensity values correspond to the natural abundance.

83 4. Rovibrational assignments

84 Following our recent analysis [1, 3, 4], the C2018 variational list of $^{14}\text{NH}_3$ [11] was used as a primary source for
85 the rovibrational assignment of the experimental line list. The C2018 rovibrational labeling uses 13 quantum numbers:

86 $\nu_1, \nu_2, \nu_3, \nu_4, L_3, L_4, \tau_{inv}, \Gamma_{vib}, J, K, \Gamma_{rot}, N_B, \Gamma_{tot}$ where ν_i are the vibrational normal-mode quantum numbers, $L_i = |l_i|$
87 are the corresponding vibrational angular momentum quantum numbers, $\tau_{inv} = a/s$ is the inversion symmetry, and
88 Γ_{vib} is the symmetry of the vibrational motion. J is the total angular-momentum quantum number, $K = |k|$ is the
89 projection of the total angular momentum on the molecule-fixed axis z , and Γ_{rot} is the rotational symmetry. Finally,
90 Γ_{tot} stands for the full symmetry of the eigenstate, and N_B is the block counting number used during the generation of
91 the C2018 list. Let us recall that only J and Γ_{tot} are exact quantum numbers, the others are approximate ones which
92 describe helpfully the level considering its true wavefunction and how this wavefunction is projected on the basis set.
93 In each (J, Γ_{tot}) subspace, the diagonalization process gives the eigenvalues and eigenstates which correspond to the
94 energy levels, ordered by increasing energy and with a rank number N_B . In this context, let us mention the work of
95 Huang *et al.* who have processed the same type of calculations, using a refined potential surface [15, 16]. The quality
96 of the predicted energy positions is claimed to be improved compared to C2018 but the transition intensities are not
97 provided.

98 The assignment process has been described in detail in our previous contributions [1, 3]. Coincidences between
99 the experimental and C2018 lists were searched automatically with the constraints $\delta\nu = |\nu_{exp.} - \nu_{calc.}| \leq 1 \text{ cm}^{-1}$ and
100 $0.5 \leq S_{exp.}/S_{calc.} \leq 2$. For a given measured line, the C2018 candidates were tested using LSCD relations combined
101 with intensity considerations. It means that the LSCD candidate partners were also subjected to the intensity screening
102 with a similar criterion as for the initial C2018 match. For the search of LSCD relations, different studies extending
103 from 3900 to 6500 cm^{-1} were considered [3, 4, 5]. The method of branches was used to complement the assignment
104 procedure [3]. The (obs.-calc.) wavenumber differences within a given vibrational branch are expected to vary slowly
105 with the rotational quantum numbers. This expected tendency was used to confirm the LSCD assignments and for
106 transitions missing LSCD partners. In some cases, the application of the LSCD relations leads to an assignment of two
107 or more C2018 predicted transitions to a single experimental line. In such a case, the original line was artificially split
108 into the corresponding number of independent transitions with positions shifted by a negligible value of $1 \times 10^{-5} \text{ cm}^{-1}$.
109 The intensities of these new transitions were obtained by affecting to each transition the fraction of the measured total
110 intensity following the predictions of the C2018 line list.

111 Overall, 6562 out of 8610 transitions were assigned to 61 $^{14}\text{NH}_3$ vibrational bands listed in Table 2. In this table,
112 the vibrational bands are defined by the vibrational quantum labels: $\nu_{1,2,3,4}, L_{1,2}$ and Γ_{vib} (the τ_{inv} label has been
113 added). The line assignments are included in the list provided as a Supplementary Material. Considering the C2018
114 intensities, the assigned transitions represent 98.9% of the total integrated intensity in the region.

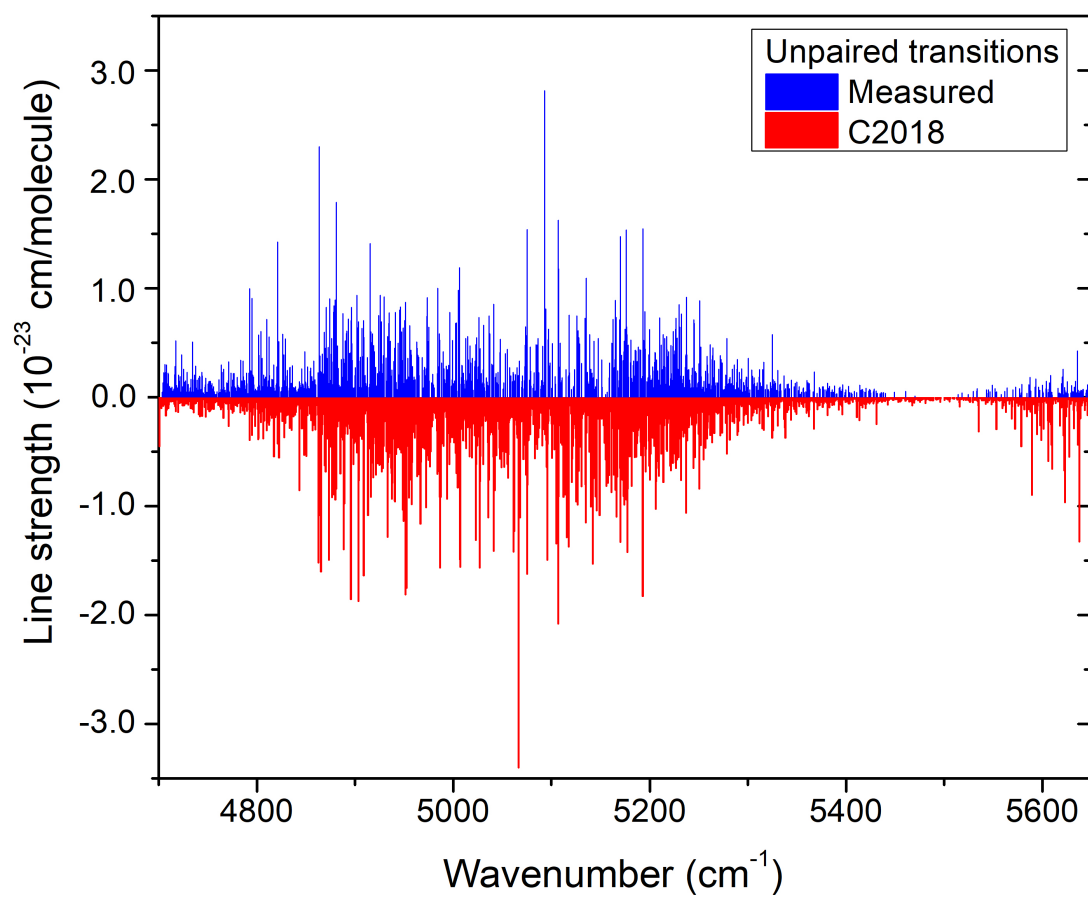


Figure 4: Comparison between the experimental lines left unassigned and the C2018 calculated lines of $^{14}\text{NH}_3$ with no experimental counterpart.

Table 2: Statistics and integrated absorption of the various vibrational bands contributing to the $^{14}\text{NH}_3$ spectrum between 4705 and 5650.3 cm^{-1} . The bands are ordered according to their C2018 integrated intensities.

Vibrational band ^a	C2018			This work			Int. ratio ^h (%)	$\langle \delta \rangle^i$ (cm^{-1})
	E_0^b (cm^{-1})	Nb^c	Band Int. ^d ($\text{cm}/\text{molecule}$)	Nb^e	J_{min}/J_{max}^f	Band Int. ^g ($\text{cm}/\text{molecule}$)		
$\nu_3^1 + \nu_4^1$ (E') s	5052.6	1508	3.15E-19	911	0/17	3.16E-19	99.8	0.03
$\nu_3^1 + \nu_4^1$ (E'') a	5053.2	1480	3.07E-19	909	0/17	3.08E-19	99.8	0.02
$\nu_1 + \nu_4^1$ (E') s	4955.8	1063	2.15E-20	564	0/14	2.18E-20	97.9	0.01
$\nu_1 + \nu_4^1$ (E'') a	4956.9	1021	2.08E-20	525	0/15	2.11E-20	97.9	0.06
$\nu_3^1 + \nu_4^1$ (A ₁ ') s	5067.8	552	1.56E-20	337	1/13	1.60E-20	98.8	0.04
$\nu_3^1 + \nu_4^1$ (A ₂ ') a	5067.7	546	1.32E-20	324	0/13	1.33E-20	98.3	0.06
$\nu_3^1 + \nu_4^1$ (A ₂ ') s	5052.0	577	6.62E-21	297	2/12	6.45E-21	96.2	0.01
$\nu_3^1 + \nu_4^1$ (A ₁ ') a	5052.7	585	6.21E-21	299	2/13	6.12E-21	96.3	0.00
$4\nu_2 + \nu_4^1$ (E') s	5104.9	638	5.86E-21	161	4/11	5.42E-21	92.9	0.20
$2\nu_2 + 2\nu_4^0$ (A ₂ ') a	5093.6	402	5.03E-21	109	3/13	6.20E-21	96.0	0.17
$\nu_2 + \nu_3^1 + \nu_4^1$ (E') s $\leftarrow \nu_2$	5080.4	485	4.28E-21	257	0/14	4.20E-21	96.2	-0.05
$\nu_2 + \nu_3^1 + \nu_4^1$ (E'') a $\leftarrow \nu_2$	5104.1	467	3.25E-21	241	0/14	3.20E-21	95.6	-0.10
$2\nu_2 + \nu_3^1$ (E') s	5144.9	706	2.89E-21	279	1/14	2.96E-21	86.3	0.21
$\nu_1 + 2\nu_2$ (A ₁ ') s	5000.2	448	2.47E-21	186	1/12	3.32E-21	92.0	0.19
$2\nu_2 + 2\nu_4^2$ (E'') a	5113.3	314	1.25E-21	58	4/15	1.06E-21	86.6	0.35
$2\nu_2 + \nu_3^1$ (E'') a	5353.0	651	1.08E-21	368	0/12	9.92E-22	89.8	0.15
$3\nu_4^1$ (E') s	4799.2	496	9.91E-22	42	4/16	4.02E-22	38.8	0.15
$3\nu_4^1$ (E'') a	4801.4	452	5.48E-22	13	3/16	7.24E-23	14.4	-0.09
$3\nu_4^3$ (A ₂ ') s	4840.9	262	4.95E-22	52	2/10	3.46E-22	60.9	0.19
$3\nu_4^3$ (A ₁ ') s	4841.6	245	4.94E-22	46	1/13	4.16E-22	57.9	0.12
$3\nu_4^3$ (A ₂ ') a	4843.4	204	4.23E-22	30	0/12	4.08E-22	57.6	0.16
$3\nu_4^3$ (A ₁ ') a	4843.0	251	3.95E-22	27	6/11	1.51E-22	54.3	0.10
$3\nu_2 + \nu_3^1$ (E') s $\leftarrow \nu_2$	4923.6	266	3.86E-22	121	1/11	3.11E-22	74.2	0.15
$\nu_1 + 2\nu_2$ (A ₂ ') a	5233.8	207	3.12E-22	58	0/12	1.94E-22	73.7	0.28
$2\nu_2 + 2\nu_4^0$ (A ₁ ') s	4756.9	163	1.80E-22	20	1/10	9.07E-23	48.0	0.16
$2\nu_2 + 2\nu_4^2$ (E') s	4773.8	294	1.71E-22	4	5/9	6.60E-24	3.0	0.16
$2\nu_2 + \nu_3^1 + \nu_4^1$ (E') s $\leftarrow 2\nu_2$	5119.8	179	1.67E-22	23	2/8	6.51E-23	38.7	-0.20
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₂ ') a $\leftarrow \nu_2$	5117.2	159	1.56E-22	31	2/10	1.04E-22	59.6	-0.22
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₁ ') s $\leftarrow \nu_2$	5091.8	159	1.50E-22	38	3/9	1.02E-22	63.8	-0.29
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₁ ') a $\leftarrow \nu_2$	5101.2	156	1.39E-22	33	2/9	7.75E-23	43.7	-0.20
$\nu_2 + \nu_3^1 + \nu_4^1$ (A ₂ ') s $\leftarrow \nu_2$	5075.6	113	1.20E-22	22	4/8	9.06E-23	63.6	-0.22
$\nu_1 + \nu_2 + \nu_4^1$ (E'') a $\leftarrow \nu_2$	4998.4	206	1.14E-22	25	1/9	4.55E-23	28.7	-0.33
$\nu_1 + \nu_3^1$ (E') s $\leftarrow \nu_4$	4982.5	267	1.09E-22	5	4/7	6.42E-24	5.8	0.02
$\nu_1 + \nu_2 + \nu_4^1$ (E') s $\leftarrow \nu_2$	4965.4	196	9.84E-23	15	2/10	2.37E-23	23.3	-0.36
$\nu_3^1 + 2\nu_4^2$ (A ₂ ') a $\leftarrow \nu_4$	5025.8	103	8.53E-23	1	6/6	1.58E-24	1.6	0.17
$\nu_3^1 + 2\nu_4^2$ (A ₁ ') a $\leftarrow \nu_4$	5025.4	81	5.67E-23	1	4/4	1.96E-24	2.5	0.10
$\nu_1 + 3\nu_2$ (A ₁ ') s $\leftarrow \nu_2$	4805.4	73	3.89E-23	33	1/8	2.98E-23	67.1	0.33
$2\nu_2 + \nu_3^1 + \nu_4^1$ (E'') a $\leftarrow 2\nu_2$	5355.5	105	3.44E-23	2	5/7	1.92E-24	3.6	-0.10

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Table 2 – Continued from previous page

Vibrational band ^a	C2018			This work			Int. ratio ^h (%)	$\langle \delta \rangle^i$ (cm ⁻¹)
	E_0^b (cm ⁻¹)	Nb^c	Band Int. ^d (cm/molecule)	Nb^e	J_{min}/J_{max}^f	Band Int. ^g (cm/molecule)		
$\nu_1 + 2\nu_4^0 (A_2'') a \leftarrow \nu_4$	4978.4	74	2.73E-23	1	3/3	1.15E-24	3.5	0.09
$\nu_2 + \nu_3^1 (E'') a$	4435.4	33	2.72E-23	13	11/14	2.05E-23	79.6	0.04
$\nu_1 + 3\nu_2 (A_1') s$	5737.9	35	2.59E-23	21	4/8	2.79E-23	89.2	0.42
$6\nu_2 (A_1') s \leftarrow \nu_2$	5110.9	22	2.48E-23	4	8/9	1.87E-23	63.0	0.00
$3\nu_2 + 2\nu_4^2 (E') s$	5622.6	61	2.30E-23	3	1/5	3.16E-24	11.9	0.87
$4\nu_2 + \nu_4^1 (E'') a$	5708.3	51	1.81E-23	1	7/7	2.52E-25	1.3	0.12
$2\nu_2 + \nu_3^1 + \nu_4^1 (E') s \leftarrow \nu_4$	5091.0	84	1.77E-23	1	6/6	6.06E-25	0.6	-0.35
$3\nu_2 + \nu_3^1 (E'') a \leftarrow \nu_2$	5398.9	79	1.72E-23	9	2/7	4.00E-24	21.6	0.11
$\nu_2 + \nu_3^1 (E') s$	4416.9	25	1.54E-23	16	12/15	1.39E-23	90.9	0.12
$3\nu_2 + \nu_3^1 (E') s$	5856.1	35	1.21E-23	5	7/9	5.37E-24	37.6	0.22
$\nu_3^1 + 2\nu_4^2 (A_2'') a \leftarrow 2\nu_2$	5054.6	43	9.89E-24	1	6/6	8.00E-25	7.8	0.18
$3\nu_2 + 2\nu_4^0 (A_2'') a \leftarrow \nu_2$	5201.1	17	9.56E-24	2	9/9	6.11E-24	40.2	0.27
$\nu_1 + 3\nu_2 (A_2'') a \leftarrow \nu_2$	5297.9	35	6.86E-24	2	4/6	8.34E-25	8.7	0.57
$\nu_1 + 2\nu_2 + \nu_4^1 (E') s \leftarrow \nu_4$	4955.9	32	5.71E-24	1	6/6	5.03E-25	9.3	-0.30
$2\nu_2 + \nu_3^1 + \nu_4^1 (E') s \leftarrow \nu_2$	5784.8	19	4.87E-24	1	6/6	4.80E-25	4.2	-0.35
$\nu_1 + \nu_2 (A_1') s$	4294.5	5	2.41E-24	3	12/13	2.10E-24	85.8	0.10
$\nu_2 + 3\nu_4^3 (A_1') s$	5718.7	3	2.26E-24	1	4/4	1.35E-24	43.0	0.50
$\nu_1 + \nu_2 (A_2'') a$	4320.0	8	2.02E-24	4	12/14	1.40E-24	64.5	0.02
$\nu_2 + 2\nu_4^2 (E') s$	4135.8	5	1.89E-24	1	13/13	8.83E-25	40.5	0.42
$\nu_2 + 2\nu_4^2 (E'') a$	4192.9	4	1.62E-24	2	11/13	1.10E-24	78.9	0.29
$\nu_2 + 3\nu_4^3 (A_1') s \leftarrow \nu_2$	4786.3	4	1.54E-24	1	4/4	5.74E-25	32.2	0.49
$\nu_1 + 3\nu_2 (A_2'') a \leftarrow 2\nu_2$	4632.8	4	4.66E-25	1	6/6	1.15E-25	26.8	0.57
$\nu_2 + 2\nu_4^0 (A_2'') a$	4173.1	1	4.13E-25	1	12/12	2.88E-25	100.0	-0.11
Sum ^j		16759	7.38E-19	6562		7.39E-19	98.93	
Others ^k		1182	0.01E-19	2048		0.03E-19		
Total ^l		17941	7.39E-19	8610		7.43E-19		

Notes:

^a Vibrational band labeling: ν_i ($i = 1 - 4$) are the vibrational normal modes corresponding to the ν_1 symmetric stretch, ν_2 symmetric bend, ν_3 the antisymmetric stretch and 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. 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 of given band, larger than 1×10^{-25} cm/molecule. Note that the C2018 intensities are calculated for pure ¹⁴NH₃.

^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 derived from the optical depth, temperature and total pressure of the spectrum for 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.

Continued on next page

Table 2 – Continued from previous page

Vibrational band ^a	C2018			This work			Int. ratio ^h (%)	$\langle \delta \rangle^i$ (cm ⁻¹)
	E_0^b (cm ⁻¹)	Nb^c	Band Int. ^d (cm/molecule)	Nb^e	J_{min}/J_{max}^f	Band Int. ^g (cm/molecule)		

^j Sum of the number of transitions or intensities of the listed bands. Note, that the intensity ratio is calculated with the C2018 intensities. If we compare the sum of experimental intensities (assigned vs. all lines), we obtain a ratio of 99.5 %.

^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.

115 Figure 4 compares the set of unassigned lines to that of the C2018 lines with no experimental counterpart. All unassigned
 116 lines have an intensity smaller than 2.5×10^{-23} cm/molecule. Except for one transition, all the C2018 transitions with intensity
 117 above 2.5×10^{-23} cm/molecule have been found. Overall, the appearance of the two data sets is similar. We nevertheless note that
 118 the unpaired C2018 transitions have a larger intensity than the unassigned lines at the high energy edge near 5600 cm^{-1} while the
 119 situation is opposite near the low energy edge around 4800 cm^{-1} . Extra experimental absorption could be partly due to NH_2D which
 120 has a natural abundance of about 3.4×10^{-4} which leads to transitions with rough estimated intensity of a few 10^{-24} cm/molecule
 121 for the stronger lines. Let us recall that the identified $^{15}\text{NH}_3$ lines have been removed from the experimental panel.

122 5. Upper state energies of $^{14}\text{NH}_3$

123 By adding the lower state energies [9] to the measured experimental line positions, the upper state empirical energies of 2215
 124 $^{14}\text{NH}_3$ rovibrational levels were derived from the assigned transitions. The determined upper levels were reached by up to 11
 125 transitions. 560 levels were derived from a single transition, 496 from two transitions and the remaining (1151) from more than
 126 two transitions. In the last case, the average value and standard deviation were calculated in two ways, for all the transitions and
 127 for a 30% trimmed selection of them. In the last case, the *rms* of the standard deviation over the determined energies was reduced
 128 from $(0.9 \pm 1.8) \times 10^{-3} \text{ cm}^{-1}$ to $(0.3 \pm 0.3) \times 10^{-3} \text{ cm}^{-1}$. The list of derived energy levels is given in Supplementary Materials.

129 The determined $^{14}\text{NH}_3$ energy levels have been highlighted on Figure 5 which presents the overall set of C2018 energy values
 130 for upper states of transitions predicted in the $4705\text{-}5650 \text{ cm}^{-1}$ interval, with intensity larger than 1×10^{-25} cm/molecule. The
 131 average rotational term $[9.7J(J+1) - 3.6K^2]$ have been subtracted for the clarity of the plot. Three groups of energy levels are
 132 observed as upper levels of transitions located in our region of interest. Their reduced energies belong to the $4500\text{-}5500$, 5500-
 133 6100 and $6100\text{-}7000 \text{ cm}^{-1}$ ranges depending if they were determined from cold transitions, hot transitions starting from ν_2 , hot
 134 transitions from $2\nu_2$ and ν_4 , respectively.

135 Among the 2215 upper state energy levels determined in this work, 1939 are new compared to the MARVEL set of levels
 136 of Ref. [9]. Figure 6 presents the differences between upper state energies and the calculated C2018 values, *versus* the quantity
 137 $[J + K/(J + 1)]$. Except for a few outliers, the agreement with MARVEL values [9] is very good (average and *rms* values of
 138 2×10^{-4} and $7 \times 10^{-4} \text{ cm}^{-1}$ for the (MARVEL-exp.) differences, respectively). A small overestimation of the MARVEL values of
 139 $2 \times 10^{-4} \text{ cm}^{-1}$ is noted (right panel). As concerns the C2018 values [11], the deviations remain in a $\pm 0.6 \text{ cm}^{-1}$ range.

140 6. Comparison with the HITRAN line list

141 The overview comparison of our experimental list to the HITRAN2020 list (Fig. 1) illustrates the significant amount of new
 142 information provided by the analysis. Unassigned and assigned $^{14}\text{NH}_3$ lines, as well as minor $^{15}\text{NH}_3$ isotopologue lines can be
 143 distinguished on the plot. Our $^{14}\text{NH}_3$ line list includes about four times more lines than the HITRAN2020 list. As for the 3900-
 144 4700 cm^{-1} range [3], the $^{15}\text{NH}_3$ transitions contribute to about 0.4% of the absorption in the studied range which is consistent
 145 with the natural relative abundance of 0.366% [5]. Note that both our work and HITRAN database do not consider the possible
 146 contribution of weak NH_2D lines.

147 In Fig. 7, a part of the 140.4 Pa spectrum is compared to a simulation based on the HITRAN2020 list around 5290 cm^{-1} .
 148 Transitions with experimental line parameters transferred from HITRAN2016 are distinguished from the transitions newly added
 149 through the MARVEL procedure. In general, the latter show a nice agreement in position and intensity. A number of additional

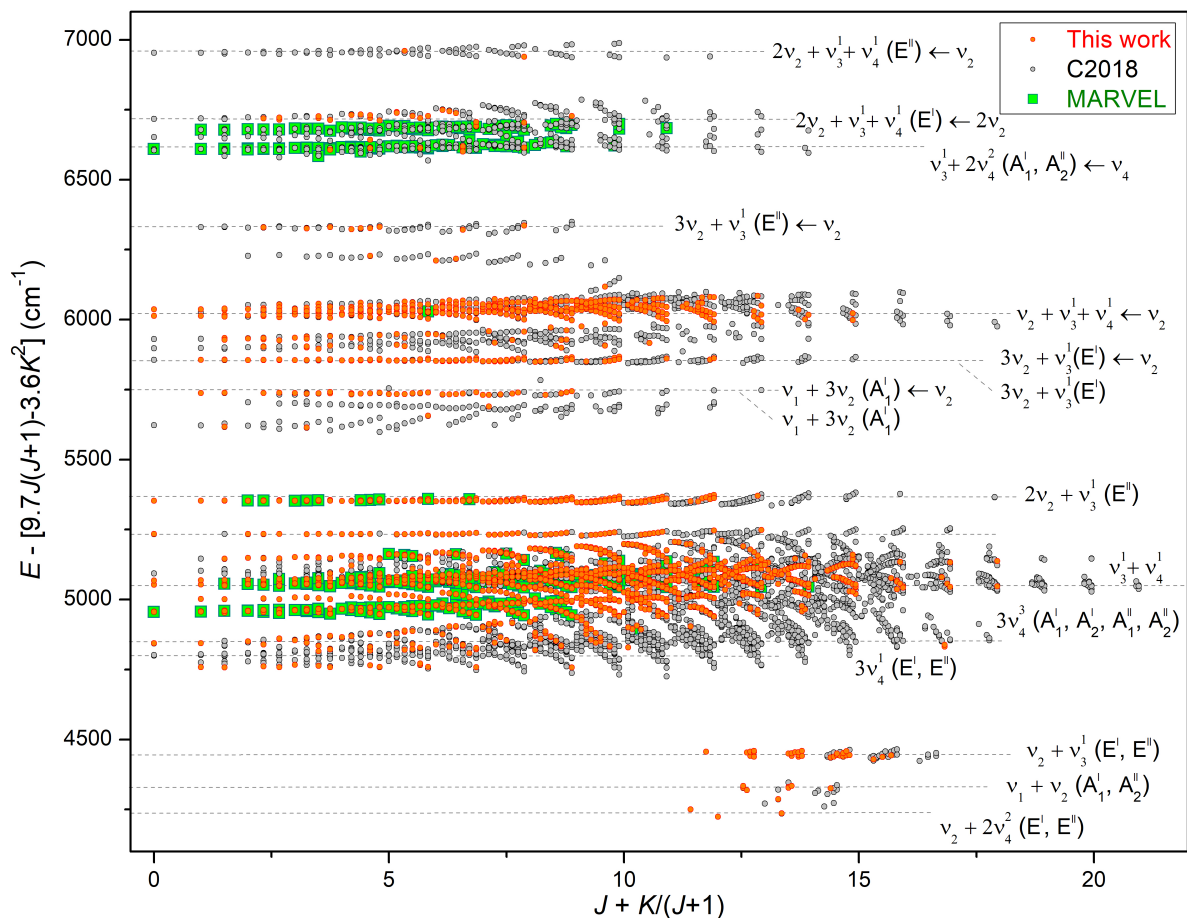


Figure 5: Upper state energies of the $^{14}\text{NH}_3$ transitions of the C2018 list in the $4705\text{--}5650\text{ cm}^{-1}$ interval predicted with intensity larger than 1×10^{-25} cm/molecule (grey dots). The average rotational term $[9.7J(J+1) - 3.6K^2]$ has been subtracted for clarity. The experimental values determined in this work are superimposed (orange dots) together with the existing empirical values provided by the MARVEL procedure (green squares)[9]. Some vibrational hot and cold bands from which the energies have been derived are indicated. Note that in some cases, the same upper levels are reached through both hot and cold bands.

Table 3: Statistics and integrated absorption in various databases for ammonia in the $4703\text{--}5650.3\text{ cm}^{-1}$ spectral range (intensity cut-off of 1×10^{-25} cm/molecule at 296 K).

	HITRAN2008 ^a		HITRAN2016		HITRAN2020		This work		C2018
	$^{14}\text{NH}_3$	$^{15}\text{NH}_3$	$^{14}\text{NH}_3$	$^{15}\text{NH}_3$	$^{14}\text{NH}_3$	$^{15}\text{NH}_3$	$^{14}\text{NH}_3$	$^{15}\text{NH}_3$	$^{14}\text{NH}_3$
Transitions	2001	129	1875	126	2493	126	8632	465	17941
Assignments	771	129	639	126	1255 ^b	126	6562	0	17941
Intensity sum ($\times 10^{-19}$ cm/molecule)	7.66	0.0146	7.65	0.0146	7.66	0.0146	7.42	0.034	7.39

Notes:

^a 140 assignments were lost from the 2008 to 2016 editions of the HITRAN database with no explanation.

^b This number is the sum of the HITRAN2016 transitions (639) and those added using the MARVEL process (616) [9].

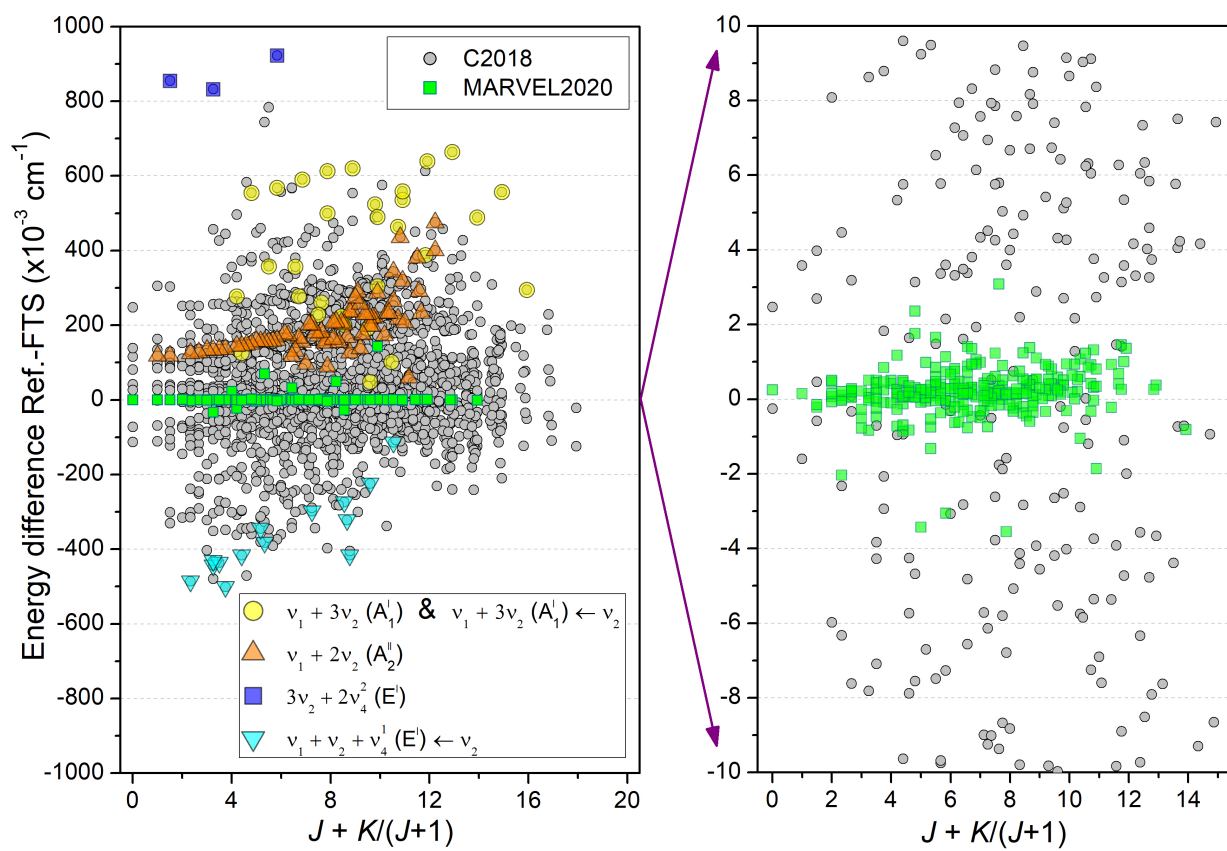


Figure 6: Differences between the C2018 [11] (grey) and MARVEL (green) [9] energies of the upper levels of $^{14}\text{NH}_3$ and the corresponding values derived in the present work. The values corresponding to upper levels derived from four vibrational bands are highlighted.

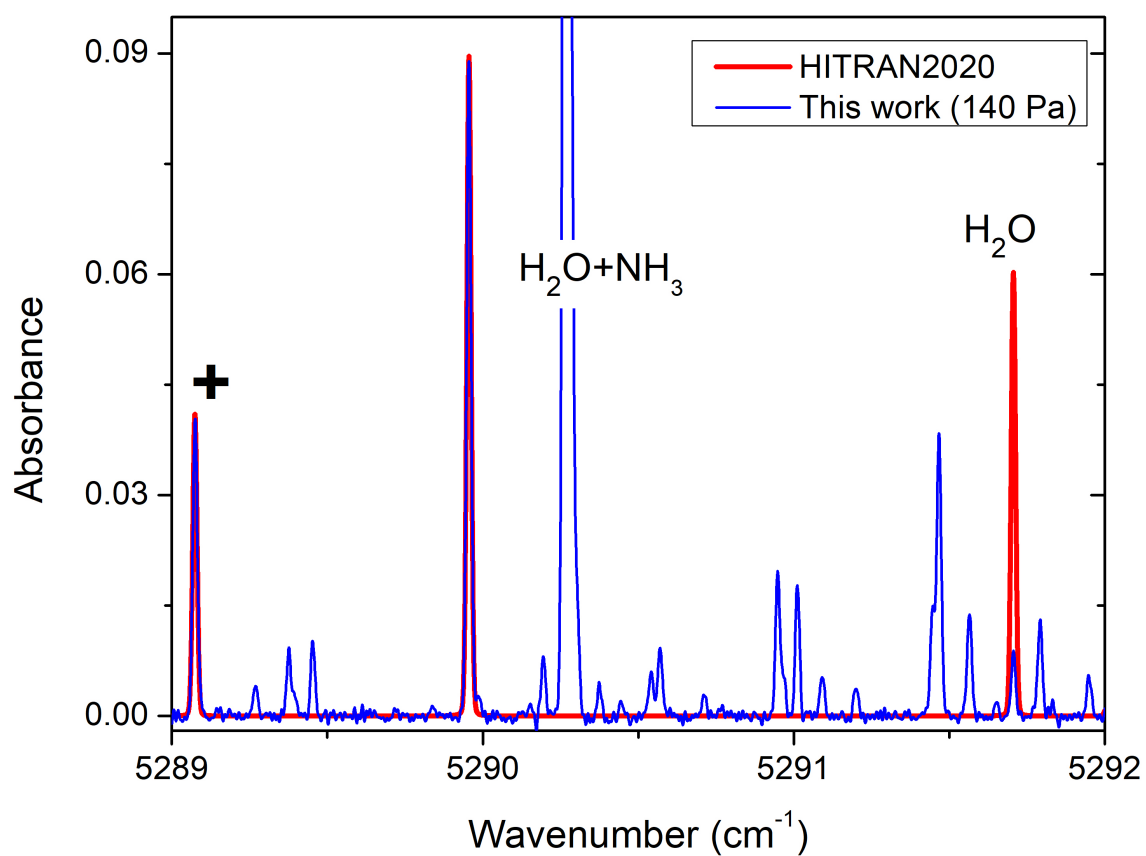


Figure 7: FTS spectrum at 140.4 Pa in the 5289-5292 cm^{-1} range (blue line) compared to HITRAN2020 simulation (red): the two components on the right came from experimentally observed data and were present in HITRAN2016 issue. One of them is a water line at 5291.7064 cm^{-1} present as an impurity. On the left, a line corresponding to a transition added in HITRAN2020 from MARVEL process [8] is visible (indicated by the “+” sign). All the other lines are not present in HITRAN2020.

150 lines are observed in our FTS spectrum illustrating the achieved sensitivity. Note that the water line at 5291.7062 cm^{-1} is present
151 in the HITRAN ammonia line list.

152 We have performed a systematic comparison of our assignments to those attached to the HITRAN2020 transitions. Among the
153 1275 transitions present in HITRAN2020 in our region, only 756 can be found within a 0.005 cm^{-1} interval around the measured
154 position value. Indeed, a significant number of HITRAN transitions missing in our list corresponds to newly added transitions with
155 MARVEL line positions and C2018 intensities which are too weak to be detected in our spectra (see Fig. 1). 70 of the transitions
156 with coincident positions show a large intensity disagreement. Part of these intensity mismatches might be due to accidental
157 position coincidence between a weak HITRAN transitions with MARVEL origin and a strong measured line. Among the 686
158 remaining transitions in common, the assignment fully coincides for 362, is incompatible for 53 as J' value differs and, for the
159 remaining part (271), some differences are observed. For example, J and K are correct but the vibrational assignment is different,
160 mainly interchanged between $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ above $J = 7$.

161 7. Intensity considerations

162 As the assignment process is supported by the intensity matching between the experimental spectrum and the C2018 calcula-
163 tions, it is important to discuss their level of agreement. The corresponding intensity ratios are plotted in Fig. 8 where the values
164 relative to the main vibrational bands - $\nu_3 + \nu_4$ (E), $\nu_1 + \nu_4$ (E) and $\nu_3 + \nu_4$ (A) - are highlighted. These bands represent 63.5 % of
165 the total number of assigned transitions but bring 95.4 % of the total intensity. Overall, the agreement between the experimental
166 and calculated values is excellent. The increase of the dispersion for small line intensities is a usual phenomenon partly due to the
167 larger relative uncertainty of the small experimental intensity values. However, there are some cases of strong transitions showing a
168 large disagreement as for example, the transition measured at 4967.3479 cm^{-1} with intensity of $7.09 \times 10^{-22}\text{ cm/molecule}$, (orange
169 square on Fig. 8) which is predicted to have a ten times smaller C2018 intensity. This particular example is analyzed in details just
170 below.

171 Remember that the first step of the assignment process is to associate C2018 and experimental lines with similar intensities
172 and close line centers. Obviously, in the considered example, the intensity mismatch prevented the association to the C2018
173 transition with closest position. Nevertheless, loosening the intensity criterion, the LSCD search gives a reasonable agreement
174 for the C2018 transition at 4967.2327 cm^{-1} with a smaller intensity of $7.3 \times 10^{-23}\text{ cm/molecule}$. This transition belonging to the
175 $\nu_1 + 2\nu_2$ vibrational band starts from $J = 7, K = 6$ s level and reaches $J = 6, K = 3$ s upper level with an energy of 5389.6889 cm^{-1} .
176 The systematic search for the LSCD partners revealed three hot band transitions assigned in our previous study at lower energy
177 [3] and four matches in the interval presently studied, thus confirming the assignment in spite of a strong underestimation of the
178 C2018 intensity. While the hot transitions show an almost perfect intensity agreement, the FTS/C2018 intensity ratio for the five
179 $\nu_1 + 2\nu_2$ band transitions vary from 1.09 up to 9.7 (Fig.9).

180 Let us recall that the only two good quantum numbers for $^{14}\text{NH}_3$ are J and Γ_{tot} . The other labels given in C2018 list are
181 only approximate. In fact, each wavefunction is found through the diagonalization of the Hamiltonian inside J, Γ_{tot} blocks and is
182 expressed as a linear combination of basis wavefunctions characterized by (J, Γ_{tot}) and completed by quantum labels $\nu_1, \nu_2, \nu_3, \nu_4,$
183 $L_3, L_4, \tau_{inv}, K, \Gamma_{vib}, \Gamma_{rot}$. The labeling is completed by the rank in the block, N_B , which unambiguously designates the N_B^{th} level
184 of the (J, Γ_{tot}) block ordered by increasing value of the energy. The upper state involved in the discussed example corresponds to
185 $N_B = 80$ in the $(6, A_2')$ block and has an experimental energy of $5389.80603\text{ cm}^{-1}$. The experimental value of the energy separation
186 from the next $N_B = 81$ level is only 0.225 cm^{-1} . The $N_B = 81$ upper state is the upper state of strong transitions and we interpret
187 the large intensity of the $\nu_1 + 2\nu_2$ transitions reaching the $N_B = 80$ level as due to an intensity borrowing from those involving the
188 $N_B = 81$ levels. It is interesting to note that the energy separation of the $N_B = 80$ and $N_B = 81$ levels is significantly smaller than its
189 C2018 value of 0.2945 cm^{-1} . This closer energetic resonance might explain the fact that the resulting intensity transfer is much
190 larger than predicted by theory.

191 Table 4 presents the experimental and calculated energies and intensities of the five LSCD pairs of the $\nu_1 + 2\nu_2$ band together
192 with the corresponding intensity ratios. If we sum the experimental intensities of the doublets of transitions reaching the $N_B = 80$
193 and 81 levels (last set of columns in Tab.4), and compare them to the corresponding C2018 sums, an agreement within the
194 experimental error bar (5%) is obtained.

195 The situation observed for the $N_B = 80$ and 81 pair of levels is not isolated and many other cases of intensity transfer were
196 found during the assignment process. This is also the case in other spectral regions. For instance, some examples can be found in
197 our preceding study in the $5650\text{-}6300\text{ cm}^{-1}$ range [1] and, Huang *et al.* [17] pointed out two similar occurrences in their re-analysis
198 of the ammonia spectrum in this region.

199 Let us now try to select systematically the states with possible interaction with their nearby states in our range of interest.
200 In the $4705\text{-}5650\text{ cm}^{-1}$ interval, 1061 doublets of transitions with intensity above $1 \times 10^{-25}\text{ cm/molecule}$ have been found in the
201 C2018 list with upper energy levels separated by less than 2 cm^{-1} (in identical blocks). In addition, 115 triplets, 16 quadruplets
202 and 2 quintuplets fulfill this criterion. Loosening the transition cut-off, the number of possibly interacting transitions groups rises

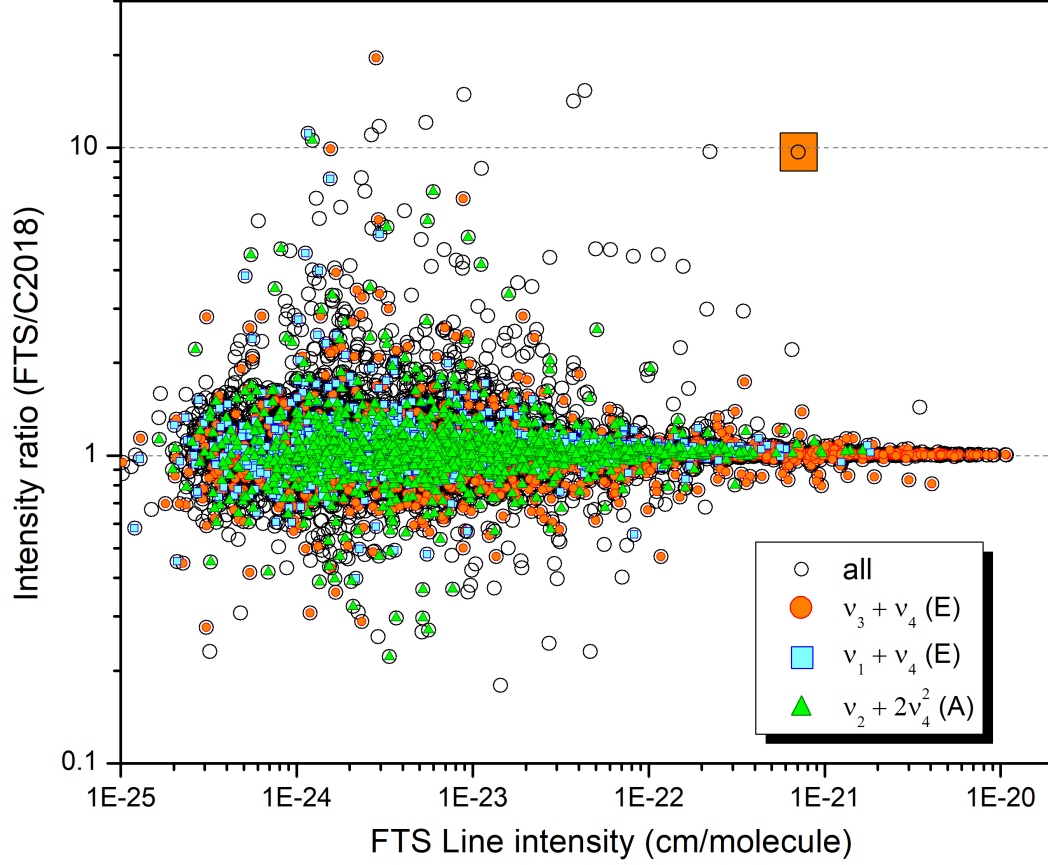


Figure 8: Ratios of the $^{14}\text{NH}_3$ line intensities measured in this work in the $4705\text{-}5650\text{ cm}^{-1}$ spectral region to the corresponding C2018 values [11]. The intensity ratios corresponding to the $\nu_3 + \nu_4$ (E), $\nu_1 + \nu_4$ (E) and $\nu_3 + \nu_4$ (A) strong bands are distinguished (red, blue and green, respectively). The highlighted outlier corresponding to a strongly underestimated C2018 intensity is discussed in the text as an example of intensity transfer.

Table 4: An example of C018 intensity transfer between the transitions arriving into two close upper states of the same J', Γ'_{tot} subspace.

Lower State	Upper state								Sums and ratio		
	$J' = 6, \Gamma'_{tot} = A_2'', N'_B = 80$				$J' = 6, \Gamma'_{tot} = A_2'', N'_B = 81$				Σ_{C2018}	Σ_{TW}	r_Σ
	ν_{TW}	S_{TW}	S_{2018}	$r_{TW/C2018}$	ν_{TW}	S_{TW}	S_{C2018}	$r_{TW/C2018}$			
$J'' \tau''_{inv} N''_B E''_{C2018}$ (cm^{-1})	(cm^{-1})	(cm/mol.)	(cm/mol.)		(cm^{-1})	(cm/mol.)	(cm/mol.)		(cm/mol.)	(cm/mol.)	
7 a 2 522.2222	4867.5832	2.00E-23	1.85E-23	1.09			1.07E-24		1.95E-23	2.00E-23	1.03
7 s 1 422.4562	4967.3479	7.09E-22	7.32E-23	9.68	4967.5729	3.01E-21	3.62E-21	0.83	3.69E-21	3.72E-21	1.01
6 a 2 383.9772	5005.8282	1.55E-23	6.21E-24	2.49	5006.0535	1.25E-23	2.27E-23	0.55	2.89E-23	2.80E-23	0.97
6 s 1 283.5719	5106.2317	2.22E-22	2.29E-23	9.70	5106.4570	9.59E-22	1.20E-21	0.80	1.23E-21	1.18E-21	0.96
5 a 1 265.2263	5124.5797	3.75E-23	1.87E-23	2.00	5124.8042	3.12E-23	5.42E-23	0.58	7.29E-23	6.86E-23	0.94

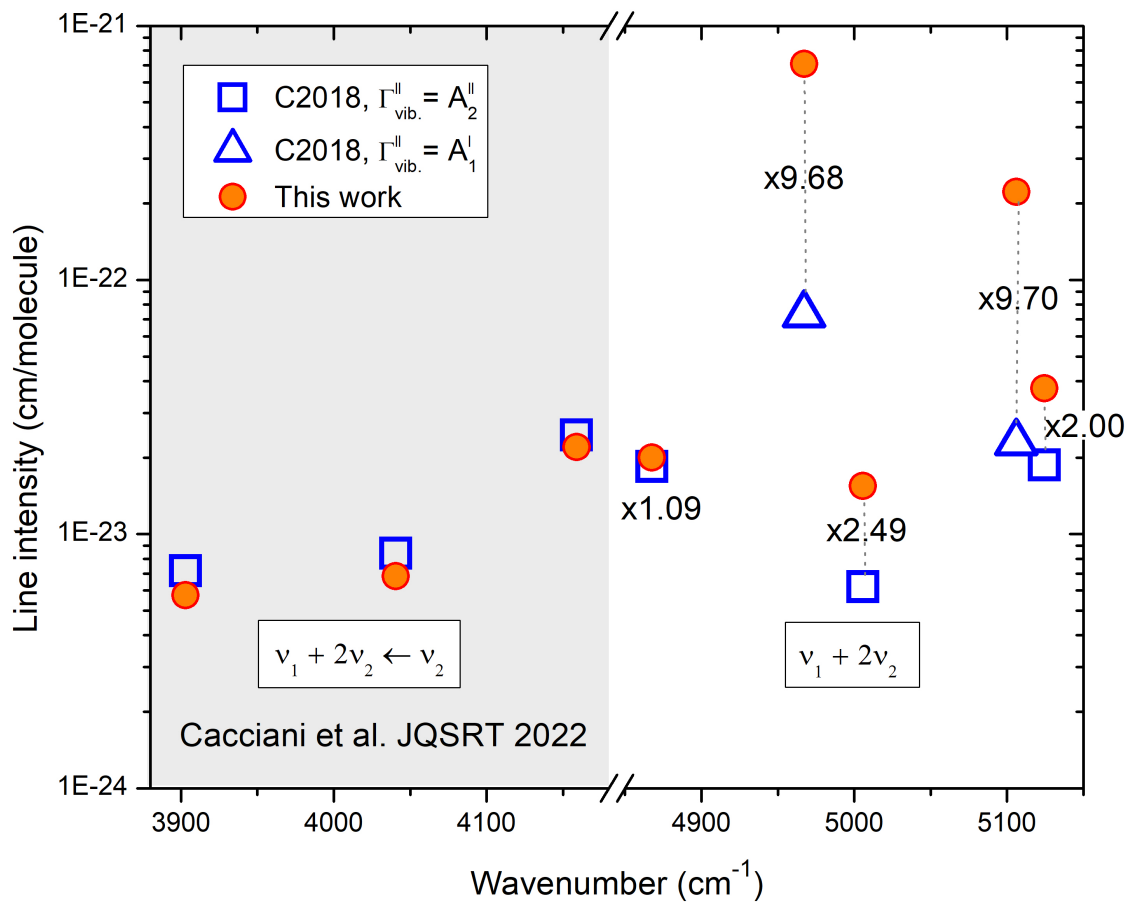


Figure 9: Calculated [11] and experimental transitions reaching the $N_B = 80$ upper level of the block ($J = 6$, $\Gamma_{tot} = A_2''$ at $5389.6889 \text{ cm}^{-1}$). The experimental transitions of the $\nu_1 + 2\nu_2 - \nu_2$ band were reported in Ref. [1] while the $\nu_1 + 2\nu_2$ cold band transitions are observed in the present work. The transition under study is the one at $4967.3479 \text{ cm}^{-1}$ with a C2018 intensity underestimated by a factor of 9.68. The C2018 values are plotted with different symbols (open squares and open triangles) according to the inversion symmetry (a or s , respectively) of the lower state. The corresponding exp./C2018 intensity ratios are indicated for each transition. The experimental counterparts (orange circles) were found in this work and in Ref. [3].

203 up to 1724 from previously mentioned 1194 ones. Comparing this list to our dataset we have found all experimental counterparts
204 for 266 cases (250 doublets, 13 triplets and 3 quadruplets).

205 To test possible intensity transfer within the identified multiplets, we present in the upper panel of Fig. 10 the exp./C2018 inten-
206 sity ratios with different symbols for the transitions reaching the resonant multiplets and the isolated levels. The first observation is
207 that most of the large deviations correspond to resonant levels. In the lower panel of Fig. 10, we plotted the ratios for the intensity
208 sum of the resonant transitions. The obtained result is impressive: while a significant fraction of the individual components show
209 important disagreement between the experimental and C2018 intensities, their intensity sums coincide very well. We believe that
210 the sensitivity of the wavefunctions to small inaccuracies of the potential energy surface could explain the phenomenon: a small
211 variation of the energy separation of the interacting upper levels leads to a large intensity change for the weak component of the
212 resonant doublets but the resulting intensity transfer does not affect the intensity sum of the involved transitions. Note that at higher
213 energy the number of resonances within blocks increases sharply leading to more frequent intensity transfers and might degrade the
214 agreement with C2018 intensity calculations. Let us hope that the results presently obtained will help to improve future theoretical
215 predictions of line intensities at higher energy.

216 8. Conclusion

217 New high resolution and low-pressure FTS recordings have allowed an in depth analysis of the room temperature ammonia
218 spectrum from 4703 to 5650.3 cm^{-1} range. Among the 9110 measured lines, 505 are identified as due to $^{15}\text{NH}_3$ minor isotopologue,
219 and a rovibrational assignment is proposed for 6562 $^{14}\text{NH}_3$ lines. This is a significant improvement compared to the HITRAN2020
220 list [5], which provides 2493 $^{14}\text{NH}_3$ transitions (with 1255 assignments), 626 of them predicted by theory and not experimentally
221 observed. Overall, our assigned transitions belong to 35 cold and 26 hot bands and bring over 98.8% of the integrated absorption
222 in the region. 2215 upper energies were derived with accuracy better than 0.001 cm^{-1} . Among them 1939 are new, compared to
223 those derived in Ref. [9] using the MARVEL procedure. A recommended list of 9110 transitions for ammonia in natural isotopic
224 abundance is provided as Supplementary Material. The $^{14}\text{NH}_3$ line positions were calculated using our best empirical determination
225 of the upper energy levels (estimated accuracy on the order of $5 \times 10^{-4} \text{ cm}^{-1}$). Despite the quality of *ab initio* calculations to
226 accurately predict position and intensity of the $^{14}\text{NH}_3$ transitions [11] and the power of the Lower State Combination Difference
227 technique to assign them, a number of important disagreements between the measured and C2018 intensities was evidenced. Most
228 of the intensity mismatches concern weak transitions reaching an upper level with a close lying neighbour level reached by a
229 stronger transition. As the intensity sum of the two interacting transitions coincides with the C2018 predictions, we conclude that
230 the problematic situations result from intensity transfer between interacting multiplets. In those situations, line intensities provide
231 a sensitive tool to reveal small inaccuracies of the potential energy surface used to generate the C2018 list [11]. As a result, the
232 intensity agreement with C2018 calculations which is in general highly valuable for rovibrational assignment, should be used with
233 caution, in particular at higher energy where the level density increases rapidly making resonance interactions more and more
234 probable. In particular, the rovibrational assignments of the ammonia spectrum in the $1.5 \mu\text{m}$ range ($6300\text{-}7000 \text{ cm}^{-1}$) already
235 studied in Refs. [18, 19] might be extended by a careful consideration of possible intensity transfers.

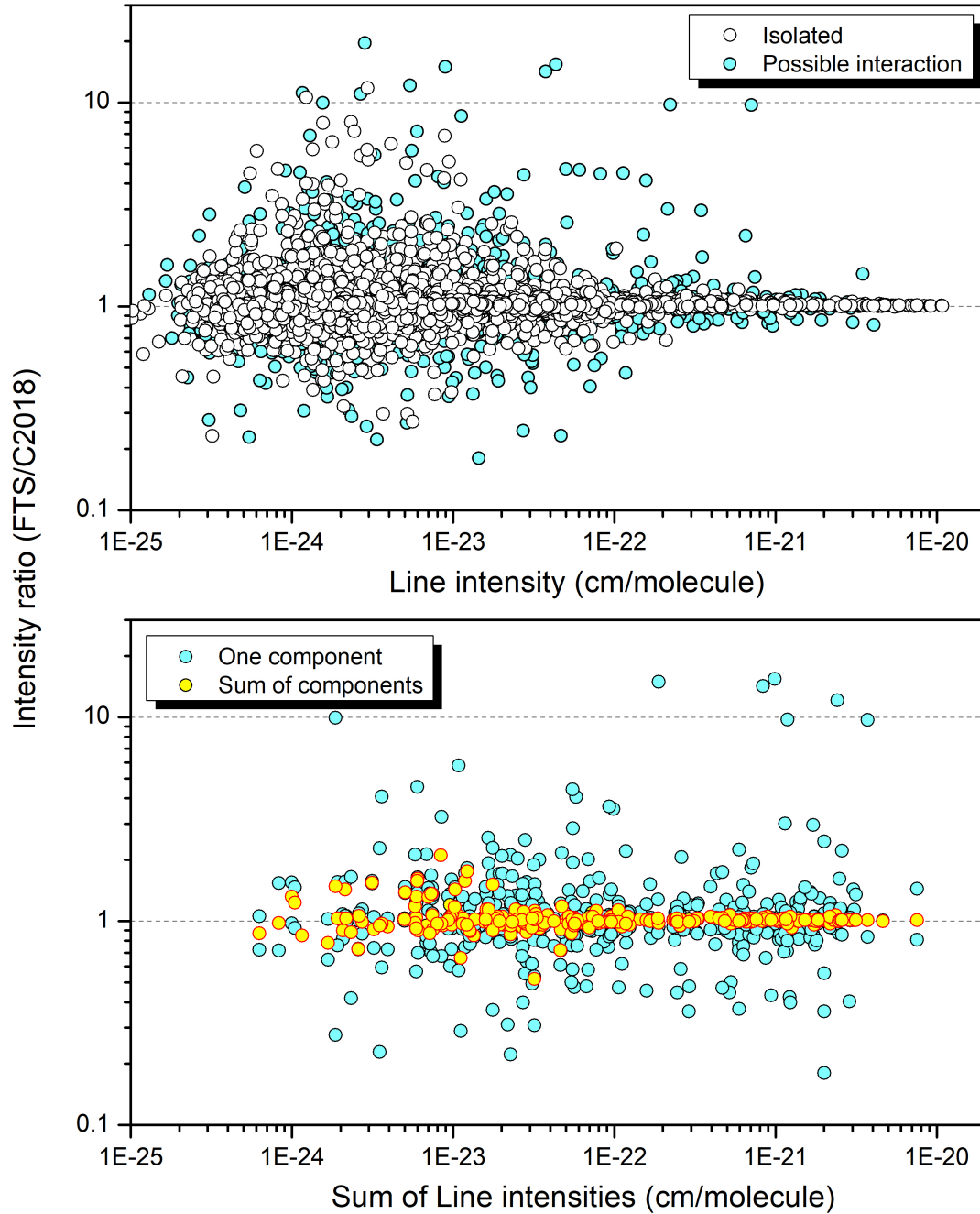


Figure 10: Upper panel: S_{exp}/S_{C2018} intensity ratios for the $^{14}\text{NH}_3$ transitions assigned in the $4705\text{-}5650\text{ cm}^{-1}$ region. According to the energy separation of the upper energy level in a given (J', Γ'_{tot}) subspace, a different symbol is used: black circles and cyan points when the energy separation from the neighbour level is more or less than 2 cm^{-1} , respectively. Lower panel: Intensity ratios for cases when all the possibly interacting components in a given group (belonging to the same J', Γ'_{tot} with $\Delta E < 2\text{ cm}^{-1}$ and sharing the same lower state) were identified experimentally, individual ratio (cyan dots) and ratio of corresponding intensity sums (red /yellow dots).

236 Declaration of competing interest

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

239 CRediT authorship contribution statement

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

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