The v1 and v3 band system of 15NH3

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The ν_1 and ν_3 band system of $^{15}\text{NH}_3$

Luciano Fusina^{a*}, Giandomenico Nivellini^a, Silvia Spezzano^b

^a *Dipartimento di Chimica Fisica e Inorganica, Facoltà di Chimica Industriale, Università di Bologna, Viale del Risorgimento 4, 40136, Bologna, Italy*

^b *I. Physikalisches Institute, Universität zu Köln, 50937 Cologne, Germany*

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Address for proofs and correspondence:

Prof. Luciano Fusina

Dipartimento di Chimica Fisica e Inorganica

Viale del Risorgimento 4

40136 Bologna

ITALY

tel : +39 051 209 3707

FAX : +39 051 209 3690

E-mail : fusina.luciano@unibo.it

Abstract

The infrared spectrum of $^{15}\text{NH}_3$ has been investigated by high-resolution Fourier transform infrared spectroscopy in the region of the stretching fundamentals. A large number of ro-vibration transitions in the $3050 - 3650 \text{ cm}^{-1}$ spectral range has been recorded and assigned to the fundamentals ν_1 and ν_3 , and to the $2\nu_4$ overtone bands. In total, 1606 transitions involving the (*s*) and (*a*) inversion-rotation-vibration levels have been identified and assigned. They include 256 perturbation allowed transitions with selection rules $\Delta K = \pm 2$, $\Delta l = -1$ in ν_3 , and $\Delta l = +2$ in $2\nu_4^{\pm 2}$, and $\Delta K = \pm 3$, $\Delta l = 0$ in ν_1 and $2\nu_4^0$. All the assigned transitions have been fitted simultaneously to a model Hamiltonian which includes all symmetry allowed interactions between and within the excited state levels in order to obtain accurate sets of spectroscopic parameters for both inversion states. The standard deviation of the fit, 0.034 cm^{-1} , is about seventy times larger than the estimated measurement precision. This results is similar to that reported for the same band system in $^{14}\text{NH}_3$ by I. Kleiner *et al.* (J. Mol. Spectrosc. **193**, 46 (1999)) and is a consequence of the neglect of vibration and ro-vibration interactions between the analysed states and vibrationally excited states with close energies.

Keywords: $^{15}\text{NH}_3$, high resolution infrared spectra, stretching vibrations, rovibrational analysis, rovibrational perturbations, spectroscopic parameters.

1. Introduction

Ammonia is one of the most extensively studied molecules since it collects the interest of experimental, theoretical and astrophysical scientists. It is the prototype molecule for the study of inversion doubling in C_{3v} molecules. The interpretation of its spectroscopic behaviour still poses a difficult challenge to both experimental and theoretical approaches. Ammonia has been detected in the interstellar medium, in remote stars [1], and in the atmospheres of the giant planets of the solar system and of their moons, i.e. the $^{14}\text{N}/^{15}\text{N}$ isotopic ratio in Jupiter's atmosphere from observation of NH_3 transitions has been recently reported [2]. Most of the spectroscopic investigations, based on spectra recorded at high resolution and with different spectroscopic techniques, have concerned $^{14}\text{NH}_3$ and comparatively a few high resolution studies have been performed on its isotopologues, $^{15}\text{NH}_3$, $^{14}\text{ND}_3$ and $^{15}\text{ND}_3$. In the last ten years there has been a revival of interest in the computation of the energies of vibration and ro-vibration levels up to high excitation, fostered by the improvement of the computational methodologies [3–11]. Accurate reproduction of the observed transitions supports the reliability of predictions for unobserved ones and can help the interpretation of data collected by the recent or programmed astronomical missions [12–14]. Experimental studies have been devoted to the enlargement of the spectroscopic data-bases of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ [15–23]. The need for spectroscopic data of ammonia isotopologues has been evidenced in the latest vibrational energy calculation [11]. In fact, these data are essential to test the ability of the calculated potential energy surfaces to predict, with the same precision achieved for $^{14}\text{NH}_3$, the energy pattern of the other isotopologues. Up to now the spectroscopic investigations have been mainly devoted to the ground state or to the

low energy bending states of ammonia, since the stretching levels are strongly perturbed by nearby $v_2 = 4$, $v_4 = 2$, or $v_2 = 2$, $v_4 = 1$ levels [24].

Precise values for the ground state parameters of $^{15}\text{NH}_3$ have been determined by the simultaneous analysis of inversion and inversion–rotation transitions measured in the microwave [25] and far infrared [26–28] regions, and of combination differences (GSCD) from forbidden transitions to the $v_4 = 1$ and $v_2 = 2$ states [29]. The $v_2 = 1, 2, 3$ (A' and A'' symmetry), $v_4 = 1$ and $v_2 = v_4 = 1$ (E' and E'' symmetry) bending states have been characterised by means of Fourier transform spectra [29–31], laser Stark [32,33], diode laser [34] and two-photon [35,36] spectra of the v_2 band, and of inversion spectra in the $v_4 = 1$ state [37], measured in the microwave region. Far–infrared laser emissions have also been observed by optically pumping $^{15}\text{NH}_3$ samples with a tunable CO_2 –laser [38,39]. Contrary, the $v_1 = 1$ (A' and A'' symmetry) and $v_3 = 1$ (E' and E'' symmetry) stretching states are less characterized. In fact, only the Q branch of v_1 recorded with the coherent anti–Stokes Raman technique has been measured and assigned [40]. At higher energies, the $v_1 = v_2 = 1$ [41], $v_1 = v_3 = 1$ [19], $v_1 = 1$, $v_4 = 2$ [20], and $v_1 = 3$, $v_4 = 2$ [22] states have been reported.

Aim of the present study is to improve the understanding of the fundamental stretching vibrations in $^{15}\text{NH}_3$, thus contributing to determine the complete anharmonic potential surface for ammonia. We report for the first time the analysis of the high resolution infrared spectra recorded in the region of the v_1 and v_3 band system of $^{15}\text{NH}_3$. All the transitions between levels with the same or the opposite inversion symmetry assigned in the spectra will be analysed simultaneously, taking into account all the symmetry–allowed interactions between vibration–inversion–rotation levels in the theoretical model [42 and refs. therein].

The paper is structured as follows. The experimental details are given in section 2; the description of the spectra and the procedure adopted for the assignments are given in section

3; the theoretical model used in the analyses and the results of the fits are described in section 4 which concludes the manuscript.

2. Experimental details

The spectra of $^{15}\text{NH}_3$ were recorded in the region between 3050 and 3650 cm^{-1} on a BOMEM DA3.002 Fourier transform spectrometer capable of a resolution of 0.004 cm^{-1} . The achieved unapodized resolution was about 0.010 cm^{-1} . The Doppler width of $^{15}\text{NH}_3$ at room temperature is 0.0095 cm^{-1} at 3300 cm^{-1} . Spectra were recorded using a 0.18 m long glass cell with NaCl windows, with sample pressure of 2.0 mbar, or using a multipass cell with an optical path length of 5.0 m and 8.0 m, at pressures of 2.0 and 10.0 mbar, respectively. An isotopically pure (99%) sample of $^{15}\text{NH}_3$ was purchased from Stohler Isotope Chemicals. Absorption lines of residual H_2O in the spectrometer were used for calibration [43]. Both the wavenumber precision and accuracy of the spectra are estimated to be about $0.5 \times 10^{-3} \text{ cm}^{-1}$.

3. Description of the spectrum and assignments

The ν_1 parallel band of $^{15}\text{NH}_3$ consists of a crowded Q -branch region, which extends for about 6 cm^{-1} around 3331 cm^{-1} , due to the proximity of the origins of $s \leftarrow a$ and $a \leftarrow s$ bands, at 3332.4 and 3334.1 cm^{-1} , respectively. The P and R branches appear as groups of lines separated by about 20 cm^{-1} ($\approx 2B$) with resolved, blue-degraded, K structures for both $a \leftarrow s$ and $s \leftarrow a$ components up to $J' = 5$ or 7, respectively. Transitions with the same J'' and

K'' values are ca. 1.7 cm^{-1} apart, a value which corresponds to the sum of the inversion splittings in the ground and in the vibration excited states, owing to the $a \leftarrow s$ and $s \leftarrow a$ selection rule. Transitions are easily identified up to $P(7)$ and $R(6)$. For higher J'' the K branch structures seem to be perturbed, particularly at high K . In fact, with increasing K the lines are red-degraded at low K , form a branch head and reverse their trend. In addition, the spacing between the lines and their intensity become irregular, see Fig. 1. As a consequence, transitions for $K > 6$ have been identified only with the assistance of precise GSCD calculated with the parameters in [28].

[insert figure 1 about here]

The spectrum of the ν_3 perpendicular band is characterised by strong $^pP_K(J)$ branches which are red-degraded and by $^rR_K(J)$ branches which are blue-degraded, for increasing J . Intense $^pQ_K(J)$ and $^rQ_K(J)$ transitions are also observed towards higher and lower wavenumbers with respect to the band centres at about 3435 cm^{-1} . Lines are red-degraded for increasing J in both rQ and pQ sub-branches. Transitions belonging to the ν_3 band are easily identified since they always appear as close doublets, corresponding to the two components, $s \leftarrow s$ and $a \leftarrow a$, of the inversion splitting. The separation of the s and a doublet components is ca. 0.40 cm^{-1} and, due to the selection rule of the transitions, corresponds to the difference of the inversion splitting in the ground and $\nu_3 = 1$ states. In fact, the energy differences between the a and s levels for $J = K = 0$ in the ground and in $\nu_3 = 1$ are 0.758 cm^{-1} and 0.332 cm^{-1} , respectively. Fig. 2 illustrates portions of the spectrum where $^pQ_K(J)$ and $^rQ_K(J)$ transitions are present. For the $^pQ_4(J)$ and $^rQ_2(J)$ lines the separation between s and a components decreases slowly with increasing J , with the s component at higher wavenumbers, because of the larger inversion splitting in the ground state compared to that in the excited state. A more irregular pattern was observed for the s and a separation within the

doublets of the ${}^PQ_3(J)$ sub-branch, see Fig. 3. The separation is alternatively large and small for odd and even J , up to $J = 6$, but for $J = 7$ is larger than expected, the s component being in all cases at higher wavenumbers. For $J = 8$, corresponding to the last observed ${}^PQ_3(J)$ doublet, the separation becomes anomalously small and the a component appears at higher wavenumbers. The ${}^PP_3(J)$ and ${}^PR_3(J)$ sub-branches exhibit anomalies analogous to those observed in the ${}^PQ_3(J)$ sub-branch.

[insert figures 2 and 3 about here]

These anomalies could not be rationalised in terms of vibration-rotation-inversion interactions between the $\nu_1 = 1$ and $\nu_3 = 1$ levels only, and should be attributed also to interactions with other nearby vibration excited states. A similar behaviour was observed in the spectra of the stretching fundamentals for ${}^{14}\text{NH}_3$, and was in part rationalized taking into account the interactions with the $\nu_4 = 2$, $l = 0, \pm 2$ states [24]. Transitions involving these excited states were in fact observed in the spectra. Other interactions with $\nu_2 = 2$, $\nu_4 = 1$ (s and a) and $\nu_2 = 4$ (s) were suggested, but only a limited number of transitions to the latter state were identified. The overtones and combination states present in the region between 3000 and 3600 cm^{-1} for ${}^{15}\text{NH}_3$ are listed in Table 1.

Lines which have not been assigned either to ν_1 or ν_3 transitions are scattered all over the investigated spectral region, the most intense being located in the lower wavenumber range. The feature observed between 3210 and 3230 cm^{-1} , in good agreement with the theoretical predictions for $2\nu_4^0$ [11], was assigned to the Q branch transitions. A series of doublets separated by about 1 cm^{-1} , from about 3238 cm^{-1} towards higher wavenumbers, was observed. They were assigned to ${}^PQ_1(J)$ transitions and represented the starting point for the analysis of the whole $2\nu_4^{\pm 2}$ band. Fortunately, both the parallel $2\nu_4^0$ and perpendicular $2\nu_4^{\pm 2}$ bands are located in a spectral region where only lines of ν_1 already assigned are present, so

their identification was easier. In the high wavenumber region lines without a recognizable pattern are present: they probably belong to the $4\nu_2$ s band but could not be assigned with certainty.

Extensive use of GSCD, calculated from the parameters in [28], has been made to check the correctness of the assignments, or to predict the wavenumbers of weak P , Q , or R lines from the corresponding assigned R , Q , or P partners. An important aid for the initial assignments was the relative intensity of the lines, which is governed by the nuclear spin–statistical weights, and by the absence of $K'' = 0$ lines for even J'' (s) or odd J'' (a) in the various sub–branches. Finally, toward the end of the analysis, a large number of perturbation allowed transitions were identified in all bands, once their positions could be calculated with reliable precision from improved values of the parameters. However, only 256 lines were contained in the data set, i.e. those pertaining to series of at least 3 perturbation allowed transitions. In total, 1606 transitions have been assigned, 243 of which to the ν_1 band with $J'_{\max}/K'_{\max}$ values up to 9/8, 666 to the ν_3 band, with $J'_{\max}/K'_{\max}$ up to 13/13, 222 to the $2\nu_4^0$ band, with $J'_{\max}/K'_{\max}$ up to 9/6, and 425 to the $2\nu_4^{\pm 2}$ band, with $J'_{\max}/K'_{\max}$ up to 12/11. The maximum values of J' and K' of the transitions were due essentially to the decreasing line intensity for high quantum numbers, and to the effect of the interactions.

4. Discussion

4.1 Details of the analysis

The anomalies observed in the spectral features of $^{15}\text{NH}_3$ are similar to those reported in a previous investigation of the same spectral range for $^{14}\text{NH}_3$ [24]. That study evidenced the necessity of analysing simultaneously the experimental data adopting a theoretical model

which explicitly takes into account all the symmetry-allowed interactions between and within the vibrationally excited states [42 and ref. therein]. Fermi-type resonances are effective between $v_1 = 1$ and $v_4 = 2^0$ and between $v_3 = 1$ and $v_4 = 2^{\pm 2}$, Coriolis interactions between $v_1 = 1$ and $v_3 = 1$, $v_1 = 1$ and $v_4 = 2^{\pm 2}$, $v_3 = 1$ and $v_4 = 2^0$, l -type resonances within $v_3 = 1$ and $v_4 = 2^{\pm 2}$ and k -type resonances within all vibration states.

All the assigned transitions were analysed on the basis of a model similar to that adopted for the same system of bands in $^{14}\text{NH}_3$ [24] using an upgraded version of the program described in details in Ref. [44]. For each value of J the program constructs two Hamiltonian matrices of dimensions $4 \times (2J+1)$: one is set up for levels of A_1' , A_2' and A_1'' , A_2'' symmetry, and the other corresponds to one of the two (degenerate) blocks of E' and E'' symmetry. The two blocks are numerically diagonalised to obtain the energy levels. The diagonal matrix elements, containing the usual contributions up to the 6th power in the angular momentum operators, were given by

$$\begin{aligned}
 {}^{(i)}E_v(J, K, l) = & {}^{(i)}E_v^0 + {}^{(i)}B_v[J(J+1) - k^2] + {}^{(i)}C_vk^2 - 2{}^{(i)}(C\zeta)_vkl - {}^{(i)}D_{vJ}[J(J+1)]^2 \\
 & - {}^{(i)}D_{vJK}[J(J+1)]k^2 - {}^{(i)}D_{vK}k^4 + {}^{(i)}\eta_{vJ}[J(J+1)]kl + {}^{(i)}\eta_{vK}k^3l + {}^{(i)}H_{vJ}[J(J+1)]^3 \\
 & + {}^{(i)}H_{vJK}[J(J+1)]^2k^2 + {}^{(i)}H_{vKJ}[J(J+1)]k^4 + {}^{(i)}H_{vK}k^6 \quad (1)
 \end{aligned}$$

where (i) refers to the parity of the level with respect to the inversion, s or a ; $k = \pm K$; $v = 1, 3$ or 4 ; $l = l_3$ or l_4 and all terms containing l vanish for the $v_1 = 1$ and $v_4 = 2^0$ levels. The off-diagonal matrix elements are reported in the Appendix, where H_{mn} represents a group of terms in the Hamiltonian containing m vibrational operators q_r and/or p_r , and n rotational operators J_α [45]. We remind that, except the Fermi constants, the subscript of a constant represents the Δk and Δl selection rules for the levels connected by the interaction term in the Hamiltonian. Moreover, a constant without the left superscript (i) corresponds to an $s \leftrightarrow a$

resonance, while an (s) or (a) superscript represents interaction between levels of the same parity, i.e. $^{(s)}q_{22}$, $^{(s)}q_{22}^J$, $^{(s)}q_{22}^K$, $^{(s)}C_{21}^2$, etc.. For the Coriolis constants C_{11}^1 , C_{11}^2 , C_{11}^{3a} , and C_{11}^{3b} we adopted the same constant for both the $\langle (a); v_1 = 1; v_3 = 0^0; J k | H_{21}/hc | (s); v_1 = 0; v_3 = 1^{\pm 1}; J k \pm 1 \rangle$ and $\langle (s); v_1 = 1; v_3 = 0^0; J k | H_{21}/hc | (a); v_1 = 0; v_3 = 1^{\pm 1}; J k \pm 1 \rangle$ matrix elements. Our model included interaction terms only up to the fourth-order of approximation, but the $\Delta k = \pm 3$ and $\Delta k = \pm 6$ interaction terms containing the coefficients α , β and η_3 , were neglected since no A_1/A_2 splitting for $K = 3n$ was observed.

A weighted least-squares analysis was performed simultaneously on all the assigned transitions to derive the parameters of the excited states. In the least-squares fits a unitary statistical weight has been attributed to each transition that corresponds to an isolated line, while the weight has been reduced to $1/n$ if n transitions are assigned to the same wavenumber. Finally, all the transition wavenumbers that differed from their corresponding calculated values by more than 0.1 cm^{-1} were excluded from the data set in the final cycle of the fitting procedure.

The parameters obtained from a polynomial fit reported in Table II of [28] were used to derive the energy of the ground state levels necessary to calculate the wavenumbers of the transitions.

4.2 Spectroscopic parameters

The analysis was accomplished in an iterative process, which consists in improving the values of the excited state parameters by means of the assigned lines, predicting the wavenumbers of higher J and K unassigned transitions to be searched in the spectra, enlarging the data set, and so on. Once all the transitions that could be unambiguously assigned were

identified, a systematic investigation to derive the set of parameters that best reproduces the experimental data was carried out. All the constants up to the third order of approximation, E^0 , B , C , $C\zeta$, C_{11}^1 , C_{11}^2 , C_{21}^2 , q_{22} , q_{12} , C_{11}^{3a} , C_{11}^{3b} , C_{21}^3 , η_J , and η_K were refined. The other parameters, for instance the distortion constants D and H , were constrained to their ground state values or to zero. In the following steps, higher order parameters were included in the model according to some selective criteria. For example, both the J and K dependences of a lower order constant already determined, i.e. q_{tt}^J and q_{tt}^K , were added simultaneously and, if present, both the s and a constants. The significant fourth order interaction parameters were determined together with the distortion constants D while the sextic distortion constants H were kept constrained. At the end of each fit we checked that the newly, as well as the previously determined parameters, were statistically determined, that they improved the standard deviation of the fit and that anomalous correlations between the parameters were not present. The parameters not fulfilling these requirements were constrained either to zero or to their corresponding ground state values in the following fits. Empirical damping factors were introduced to approach the convergence region in cases of severe correlations. They were set equal to zero in the final cycles of the refinement procedure.

Table 2 lists the parameters derived from the analysis of 1514 transitions contained in the final fit, 20 of $v_1=1$, 26 of $v_3=1$, 20 of $v_4=2^0$, 25 of $v_4=2^{\pm 2}$ and 9 interaction constants, including the H 's which were not refined. All the parameters in Eq. (1) and in the Appendix which are not reported in Table 2 were set equal to zero and constrained in the refinement procedure. The number of transitions rejected in the final fit was equal to 92, ca. 6% of the assigned transitions. The chosen rejection limit, 0.1 cm^{-1} , is much larger than the estimated experimental precision, 0.0005 cm^{-1} , to discard only poorly measured blended lines or transitions perturbed by interactions with levels other than those considered in our model. The exclusion of lines corresponding to high J or K values in a given sub-branch, which could be

better reproduced by the refinement of further constants, was carefully avoided. The standard deviation of the fit, 0.034 cm^{-1} , is about 70 times larger than the estimated experimental precision, 0.0005 cm^{-1} . This result clearly suggests that the other bands present in the investigated region should be analysed and the interaction model adopted in the analysis should be enlarged to include the $v_2 = 2 / v_4 = 1$ and $v_2 = 4$ excited bending states.

The values of the refined s and a rotation parameters are very similar in all the vibration states and close to the corresponding ones in the ground state. However, all the parameters should be considered as effective, including the contributions due to interactions with neighbouring levels not considered in our model. With the exception of the values for $v_3 = 1$, large differences are observed between the centrifugal distortion constants D for the s and a states, and between corresponding parameters of the ground and excited states.

Parameters in Table 2 can be compared to those for $^{14}\text{NH}_3$ (see Table 7 in [24]). The unperturbed vibration term values follow the expected decreasing trend due to the ^{15}N isotopic substitution. The K dependent parameters C and $C\zeta$ have nearly identical values. Contrary, with few exceptions, the distortion constants D differ substantially. Different choices of refined interaction parameters prevent a meaningful comparison. However, it is worth noting that the $v_1 = 1 / v_4 = 2^0$ Fermi interaction constants of the two isotopologues differ by only about 3%. Finally, the vibration energies of the analysed states, including the values for $v_1 = 1$, $3333.22 (s)$ and $3334.16 (a) \text{ cm}^{-1}$, and $v_4 = 2^0$, $3210.43 (s)$ and $3212.12 (a) \text{ cm}^{-1}$, perturbed by the Fermi interaction, are in excellent agreement with those calculated from the potential energy surface, see Table 1, thus supporting its reliability. It should be pointed out that while the differences between calculated and experimental term values are about 0.02 cm^{-1} for the E states, equal to the standard deviation in Ref. [11], they are larger for the A states affected by the Fermi resonance, $0.04\text{--}0.09 \text{ cm}^{-1}$. Since the values calculated from the potential energy surface are expected to have the same precision, the differences for

the A levels could be ascribed to several factors. These could be the high correlation between the Fermi constants and the deperturbed term values and the impossibility to determine the J and K dependences affecting the Fermi constant value, leading to a worse reproduction by the model of the transitions assigned to the A states with respect to the E states. The statistics for the fitted line positions of the separate bands listed in Table 3 seem to support the last suggestion. Our results confirm the difficulties encountered in the analysis of the stretching region for ammonia and reaffirm the need for further experimental work to identify and characterise all the vibrational states present in the studied spectral range.

A table with a list of the transition wavenumbers, assignments and residuals from the simultaneous fit associated with all the analysed bands is available from the Bologna authors.

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References

- [1] T.L. Wilson, C. Henkel and S. Hüttemeister, *Astron. Astrophys.* **460**, 533 (2006).
- [2] M.M. Abbas, A. LeClair, T. Owen, B.J. Conrath, F.M. Flasar, V.G. Kunde, C.A. Nixon, R.K. Achterberg, G. Bjoraker, D.J. Jennings, G. Orton and P.N. Roman, *Astrophys. J.* **602**, 1063 (2004).
- [3] C. Léonard, N.C. Handy, S. Carter and J.M. Bowman, *Spectrochim. Acta, Part A* **58**, 825 (2002).
- [4] H. Lin, W. Thiel, S.N. Yurchenko, M. Carvajal and P. Jensen, *J. Chem. Phys.* **117**, 11265 (2002).
- [5] T. Rajamäki, M. Kallay, J. Noga, P. Valiron and L. Halonen, *Mol. Phys.* **102**, 2297 (2004).
- [6] S.N. Yurchenko, J. Zheng, H. Lin, P. Jensen and W. Thiel, *J. Chem. Phys.* **123**, 134308 (2005).
- [7] R. Marquardt, K. Sagui, W. Klopper and M. Quack, *J. Phys. Chem.* **109**, 8439 (2005).
- [8] X. Huang, D.W. Schwenke and T.J. Lee, *J. Chem. Phys.* **129**, 214304 (2008).
- [9] S.N. Yurchenko, R.J. Barber, A. Yachmenev, W. Thiel, P. Jensen and J. Tennison, *J. Phys. Chem.* **113**, 11845 (2009).
- [10] X. Huang, D.W. Schwenke and T.J. Lee, *J. Chem. Phys.* **134**, 044320/1-15 (2011).
- [11] X. Huang, D.W. Schwenke and T.J. Lee, *J. Chem. Phys.* **134**, 044321/1-18 (2011).
- [12] A. Wotten, *Proc. SPIE* **4837**, 110 (2003).
- [13] E.E. Becklin, A.G.G.M. Tielens, R.D. Gehrz and H.H.S. Callis, *Proc. SPIE* **6678**, 66780A (2007).
- [14] G.L. Pilbratt, *Proc. SPIE* **7010**, 701002 (2008).

- [15] Š. Urban, F. Herlemont, M. Khelkhal, H. Fichoux and J. Legrand, *J. Mol. Spectrosc.* **200**, 280 (2000).
- [16] C. Cottaz, I. Kleiner, G. Tarrago, L.R. Brown, J.S. Margolis, R.L. Poynter, H.M. Pickett, T. Fouchet, P. Drossart and E. Lellouch, *J. Mol. Spectrosc.* **203**, 285 (2000).
- [17] I. Kleiner, G. Tarrago, C. Cottaz, L. Sagui, L.R. Brown, R.L. Poynter, H.M. Pickett, P. Chen, J.C. Pearson, R.L. Sams, G.A. Blake, S. Matsuura, V. Nemtchinov, P. Varaanasi, L. Fusina and G. Di Lonardo, *J. Quant. Spectrosc. Radiat. Transf.* **82**, 293 (2003).
- [18] P. Chen, J.C. Pearson, H.M. Pickett, S. Matsuura, G.A. Blake, *J. Mol. Spectrosc.* **236**, 116 (2006).
- [19] R.M. Lees, L. Li, Z. Liu, Li-H. Xu, *J. Mol. Struct.* **795**, 134 (2006).
- [20] L. Li, R.M. Lees, Li-H. Xu, *J. Mol. Spectrosc.* **243**, 219 (2007).
- [21] R. Vasudev, *Appl. Phys. B* **87**, 163 (2007).
- [22] R.M. Lees, L. Li, Li-H. Xu, *J. Mol. Spectrosc.* **251**, 241 (2008).
- [23] S. Yu, J.C. Pearson, B.J. Drouin, K. Sung, O. Pirali, M. Vervloet, M.-A. Martin-Drumel, C.P. Endres, T. Shiraishi, K. Kobayashi and F. Matsushima, *J. Chem. Phys.* **133**, 174317 (2010).
- [24] I. Kleiner, L.R. Brown, G. Tarrago, Q-L. Kou, N. Picqué, G. Guelachvili, V. Dana and J-Y. Mandin, *J. Mol. Spectrosc.* **193**, 46 (1999).
- [25] H. Sasada, *J. Mol. Spectrosc.* **83**, 15 (1980).
- [26] M. Carlotti, A. Trombetti, B. Velino and J. Vrbancich, *J. Mol. Spectrosc.* **83**, 401 (1980).
- [27] Š. Urban, D. Papoušek, S.P. Belov, A.F. Krupnov, M.Y. Tretyakov, K. Yamada and G. Winnewisser, *J. Mol. Spectrosc.* **101**, 16 (1983).
- [28] Š. Urban, S. Klee and K. Yamada, *J. Mol. Spectrosc.* **168**, 384 (1994).

- [29] Š. Urban, R. D'Cunha, K. Narahari Rao and D. Papoušek, *J. Mol. Spectrosc.* **111**, 361 (1985).
- [30] F.O. Shimizu and T. Shimizu, *J. Mol. Spectrosc.* **36**, 94 (1970). Nu2
- [31] G. Di Lonardo, L. Fusina, A. Trombetti and I.M. Mills, *J. Mol. Spectrosc.* **92**, 298 (1982).
- [32] F. Shimizu, *J. Chem. Phys.* **53**, 1149 (1970).
- [33] K. Shimoda, Y. Ueda and J. Iwahori, *Appl. Phys.* **21**, 181 (1980).
- [34] V. A. Job, N.D. Patel, R. D'Cunha and V.B. Kartha, *J. Mol. Spectrosc.* **101**, 48 (1983).
- [35] S.M. Freund and T. Oka, *Phys. Rev A* **13**, 2178 (1976).
- [36] H. Jones, *J. Mol. Spectrosc.* **70**, 279 (1978).
- [37] E.A. Cohen, *J. Mol. Spectrosc.* **79**, 496 (1980).
- [38] W. Schatz, K.F. Renk, L. Fusina and J.R. Izatt, *Appl. Phys. B* **59**, 453 (1994).
- [39] S. Marchetti, *Int. J. of Infrared and Millimeter Waves* **24**, 761 (2003).
- [40] S. Anders, J. Jonuscheit, U. Lehner, K. Sarka and H.W. Schrötter, *J. Raman. Spectrosc.* **31**, 711 (2000).
- [41] Š. Urban, P. Misra and K. Narahari Rao, *J. Mol. Spectrosc.* **114**, 377 (1985).
- [42] K. Sarka and H.W. Schrötter, *J. Mol. Spectrosc.* **179**, 195 (1996).
- [43] R.A. Toth, *J. Opt. Soc. Am. B* **10**, 2006 (1993).
- [44] L. Fusina, G. Di Lonardo and J.W.C. Johns, *J. Mol. Spectrosc.* **118**, 397 (1986).
- [45] M.R. Aliev and J.K.G. Watson, *J. Mol. Spectrosc.* **61**, 29 (1976).

Figure captions

Figure 1. Details of the ν_1 fundamental of $^{15}\text{NH}_3$ illustrating the K progression of a few $^qR_K(J)$ and $^qP_K(J)$ sub-branches. The J sub-branches at lower wavenumbers are $s \leftarrow a$ transitions, those at higher wavenumbers $a \leftarrow s$ transitions. The K assignment is given. Lines identified by an asterisk are $^rR_3(3)$ transitions of ν_3 . Note also that the $K = 0$ lines are observed depending on even/odd and a/s symmetry. Experimental conditions: pressure, 2.0 mbar; path length, 5.0 m.

Figure 2. Details of the ν_3 fundamental of $^{15}\text{NH}_3$ illustrating the K progression of a few $^pQ_K(J)$ and $^rQ_K(J)$ sub-branches. The J assignment and the a/s symmetry are given. Experimental conditions: pressure, 2.0 mbar; path length, 5.0 m.

Figure 3. Details of the ν_3 fundamental of $^{15}\text{NH}_3$ illustrating the K progression of the $^pQ_3(J)$ sub-branch. The J assignment and the a/s symmetry are given. Note also the anomalous splitting of the $J = 7$ and 8 lines. The intense lines between 3447 and 3451 cm^{-1} are $^qR_5(J)$ transitions of ν_1 . Experimental conditions: pressure, 2.0 mbar; path length, 5.0 m.

Table 1

Vibrational states in the region between 3000 and 3600 cm^{-1} for $^{15}\text{NH}_3$

Vibrational state	Calculated / cm^{-1} [11]	This work
$\nu_2 = 1, \nu_4 = 1^{\pm 1} (s) (E)$	3179.54	
$\nu_2 = 1, \nu_4 = 1^{\pm 1} (a) (E)$	3487.77	
$\nu_4 = 2^0 (s) (A)$	3210.51	3210.43
$\nu_4 = 2^0 (a) (A)$	3212.08	3212.12
$\nu_4 = 2^{\pm 2} (s) (E)$	3233.94	3233.92533(631)
$\nu_4 = 2^{\pm 2} (a) (E)$	3235.32	3235.33849(707)
$\nu_1 = 1 (s) (A)$	3333.27	3333.22
$\nu_1 = 1 (a) (A)$	3334.25	3334.16
$\nu_3 = 1 (s) (E)$	3435.12	3435.14291(547)
$\nu_3 = 1 (a) (E)$	3435.45	3435.47468(542)
$\nu_2 = 4 (s) (A)$	3438.70	

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Table 2. Spectroscopic parameters (in cm⁻¹) for the $\nu_1/\nu_3/2\nu_4$ system of $^{15}\text{NH}_3^a$

	$\nu_1=1$ (s)	$\nu_1=1$ (a)	$\nu_4=2$ (s) $l_4=0$	$\nu_4=2$ (a) $l_4=0$	$\nu_3=1$ (s) $l_3=\pm 1$	$\nu_3=1$ (a) $l_3=\pm 1$	$\nu_4=2$ (s) $l_4=\pm 2$	$\nu_4=2$ (a) $l_4=\pm 2$
E^0	3322.0611(303)	3324.9220(183)	3221.5849(304)	3221.3628(178)	3435.14291(547)	3435.47468(542)	3233.92533(631)	3235.33849(707)
B	9.766364(675)	9.775467(628)	10.424236(721)	10.533122(795)	9.741241(194)	9.739151(204)	10.388892(384)	10.444103(493)
C	6.19105(106)	6.19575(102)	6.122431(685)	6.1196(159)	6.231238(241)	6.231178(248)	6.099094(472)	6.10018(482)
$D_J \times 10^3$	1.15877(869)	1.30522(860)	0.91025(965)	1.4123(113)	0.76176(149)	0.75031(161)	1.33922(533)	1.56778(704)
$D_{JK} \times 10^3$	-2.1627(256)	-1.5440(234)	-0.7912(250)	-6.0748(418)	-1.50792(369)	-1.45749(403)	-2.3410(144)	-3.0300(174)
$D_K \times 10^3$	1.2028(257)	0.6968(212)	0.4111(209)	2.6813(557)	0.93412(321)	0.89996(309)	1.0374(104)	1.7333(141)
$H_J \times 10^6$	0.25542	0.2206	0.25542	0.2206	0.25542	0.2206	0.25542	0.2206
$H_{JK} \times 10^6$	-0.9125	-0.7709	-0.9125	-0.7709	-0.9125	-0.7709	-0.9125	-0.7709
$H_{KJ} \times 10^6$	1.102	0.9092	1.102	0.9092	1.102	0.9092	1.102	0.9092
$H_K \times 10^6$	-0.434	-0.346	-0.434	-0.346	-0.434	-0.346	-0.434	-0.3460
$C\zeta$					0.244526(559)	0.239202(599)	-1.342214(636)	-1.369016(651)
$\eta_J \times 10^3$					-1.0181(176)	-1.0694(194)	0.1558(232)	2.5598(303)
$\eta_K \times 10^3$					112236(205)	1.2882(183)		-3.6553(399)
Interaction	$C_{21}^2 \times 10^2$	3.9413(219)	$W_{144}(s)$	35.2866(409)	$^{(s)}q_{22}^4$	0.1143097(830)		
Parameters	R_{144E}^B	0.17745(856)	$W_{144}(a)$	32.2790(224)	$^{(a)}q_{22}^4$	0.1365641(640)		
			R_{344E}^A	-0.2250(124)	$^{(s)}q_{22}^{4J} \times 10^4$	-0.5650(132)		
					$^{(a)}q_{22}^{4K} \times 10^4$	-0.5512(179)		

^a The uncertainties as 1σ given in parentheses refer to the last significant digits. Parameters without uncertainty have been constrained to the corresponding ground state values.
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Table 3
Statistics for fitted line positions ^a

Band	Number of fitted / assigned lines	rms (cm ⁻¹)
ν_1	275 / 293	0.037
s $\leftarrow$ a,s	135 / 148	0.030
a $\leftarrow$ s,a	140 / 145	0.042
$2\nu_4^0$	213 / 222	0.042
s $\leftarrow$ a,s	125 / 127	0.045
a $\leftarrow$ s,a	88 / 95	0.037
ν_3	642 / 666	0.029
s $\leftarrow$ a,s	321 / 326	0.027
a $\leftarrow$ s,a	321 / 340	0.030
$2\nu_4^{\pm 2}$	384 / 425	0.036
s $\leftarrow$ a,s	212 / 228	0.040
a $\leftarrow$ s,a	172 / 197	0.030
Global fit	1514 / 1606	0.034

^a The two inversion parities of the lower state indicate symmetry allowed and perturbation allowed transitions, respectively

Figure 1

Figure 2

Figure 3

Appendix

Off-diagonal matrix elements of the vibration-rotation-inversion Hamiltonian^a

The basis functions are ${}_a^s | \nu_s \nu_t l_t \nu_t l_t, J, K \rangle = {}_a^s | \nu_1 \nu_3 l_3 \nu_4 l_4, J, K \rangle$

Coriolis type resonances

$${}_a^s \langle \nu_1, J, K | (H_{21} + H_{23}) / hc | \nu_3, J, K \pm 1, l \pm 1 \rangle_s^a = \pm \left\{ \sqrt{2} [C_{11}^1 + C_{11}^{3a} J(J+1) + C_{11}^{3b} (2K \pm 1)^2] \right\} F_{\pm 1}$$

$${}_a^s \langle \nu_1, J, K | H_{22} / hc | \nu_3, J, K \pm 1, l \pm 1 \rangle_s^a = \sqrt{2} C_{11}^2 (2K+1) F_{\pm 1}$$

$${}_a^s \langle \nu_1, J, K | H_{22} / hc | \nu_3, J, K + 2, l \mp 1 \rangle_s^a = \sqrt{2} C_{21}^2 F_{\pm 2}$$

$${}_a^s \langle \nu_1, J, K | H_{31} / hc | 2\nu_4^{\mp 2}, J, K + 1, l \pm 2 \rangle_s^a = \pm \frac{1}{2} R_{144E}^B F_{\pm 1}$$

$${}_a^s \langle 2\nu_4^0, J, K | H_{31} / hc | \nu_3, J, K + 1, l \pm 1 \rangle_a^s = \mp R_{344A}^B F_{\pm 1}$$

$${}_a^s \langle 2\nu_4^{\pm 2}, J, K | H_{31} / hc | \nu_3, J, K + 1, l \mp 1 \rangle_s^a = \pm R_{344A}^B F_{\pm 1}$$

Fermi type resonances

$${}_a^s \langle \nu_1, J, K | (H_{30} + H_{32}) / hc | 2\nu_4^0, J, K \rangle_a^s = [W_{144} + W_{144}^K K^2 + W_{144}^J J(J+1)]_a^s$$

$${}_a^s \langle \nu_3^{\pm 1}, J, K | (H_{30} + H_{31} + H_{32}) / hc | 2\nu_4^{\mp 2}, J, K \rangle_s^a = W_{344} \mp \sqrt{2} R_{344E}^A K$$

Essential resonances

$${}_s^a \langle \nu_3, l_3, J, K | (H_{22} + H_{24}) / hc | \nu_3, l_3 \pm 2, J, K \pm 2 \rangle_s^a = -\frac{1}{2} [q_{22}^3 + q_{22}^{3J} (J(J+1) + q_{22}^{3K} (2K \pm 2)^2)] F_{\pm 2}$$

$${}_s^a \langle \nu_4, l_4, J, K | (H_{22} + H_{24}) / hc | \nu_4, l_4 \pm 2, J, K \pm 2 \rangle_s^a = 2[q_{22}^4 + q_{22}^{4J} (J(J+1) + q_{22}^{4K} (2K \pm 2)^2)] F_{\pm 2}$$

$${}_s^a \langle \nu_4, l_4, J, K | (H_{22} + H_{24}) / hc | \nu_4, l_4 \pm 2, J, K \pm 1 \rangle_s^a = 2(2K \pm 1)[q_{12}^4 + q_{12}^{4J} (J(J+1) + q_{12}^{4K} (2K \pm 1)^2)] F_{\pm 1}$$

$${}_s^a \langle \nu_4, l_4, J, K | (H_{22} + H_{24}) / hc | \nu_4, l_4 \pm 2, J, K \pm 1 \rangle_s^a = 2(2K \pm 1)[q_{12}^4 + q_{12}^{4J} (J(J+1) + q_{12}^{4K} (2K \pm 1)^2)] F_{\pm 1}$$

$$^a F_{\pm n} = [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \dots \{J(J+1) - [K \pm (n-1)](K \pm n)\}^{1/2}$$