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# Analysis of high temperature ammonia spectra from 780 to 2100 $\mathrm{cm}^{-1}$

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ABSTRACT

A recently-recorded set [Hargreaves et al., Astrophys. J., in press] of Fourier transform emission spectra of hot ammonia is analyzed using a variational line list. Approximately 3350 lines are newly assigned to mainly hot bands from vibrational states as high as $v_2 = 2$. 431 new energy levels of these states are experimentally determined, considerably extending the range of known rotationally-excited states. Comparisons with a recent study of high $J$ levels in the ground and first vibrational states [Yu et al., J. Chem. Phys., 133 (2010) 174317] suggests that while the line assignments presented in that work are correct, their energy level predictions suffer from problems associated with the use of very high-order perturbation series in the effective Hamiltonian. It is suggested that variational calculations provide a more stable method for analyzing spectra involving highly-excited states of ammonia.

## 1. Introduction

Ammonia is a textbook example in molecular spectroscopy. A symmetric top with a simple rotational spectrum and selection rules, its spectrum becomes complicated due to its low-frequency inversion motion which is caused by tunneling through the barrier to planarity. Observation of the ammonia rotation–inversion spectrum, which was one of the cornerstones in establishing molecular spectroscopy as a branch of science, was an unintended beneficiary of the development of radar electronics during the World War II. Since then considerable work on the rotation–inversion spectrum in mm and submm regions has been published [1–6], as well as work on the vibration–rotation–inversion spectra [7–10].

Interest in the study of ammonia spectra is not only due to inversion motion; its spectrum is important in many astrophysical objects: the interstellar medium, solar system planets, extrasolar planets and brown dwarfs to name a few. The wide interest in ammonia notwithstanding, only a limited spectral range has thus far been observed and analyzed. The spectrum of ammonia is both congested and complicated due to its nonrigidity, lightness and, in particular, the very same inversion motion which makes it so interesting. The range of both vibrational and rotational motions probed spectroscopically remains limited. The highest vibrational overtones observed in conventional spectra of ammonia involve the $\nu_3 + 2\nu_4$ bands, with the highest frequency about 7000 $\mathrm{cm}^{-1}$, which is very low for this fundamental stable molecule. The reason for this is that the spectrum around 7000 $\mathrm{cm}^{-1}$ becomes so congested and perturbed that the analysis using effective Hamiltonians becomes problematic.

In effective Hamiltonians, the nonrigidity of ammonia as a result of the three light hydrogen atoms and the inversion motion leads to a very slow convergence of the perturbation series. For example, analysis by Yu et al. of hot spectra of $NH_3$ [11] used a perturbation theory (PT) series in terms of the total rotational quantum number, $J$, and its projection on the symmetry axis, $K$. Their PT expansion included terms up to the 18th power in $J$ and $K$. This slow convergence limits the highest rotational numbers, both $J$ and $K$, assignable in ammonia spectra. Until recently the limit was $J = 22$ for the ground and $\nu_2 = 1$ vibrational states, and $J$ about 15 for other excited vibrational states. Yu et al. [11] extended this to $J = 35$ for the ground and $\nu_2 = 1$ vibrational states.

A goal of our paper is to expand the range of the assigned $NH_3$ lines. Two major tools are used for this purpose. On the experimental side, two of us have recently used a heated cell to observe ammonia emission spectra for a range of temperatures up to 1370 °C creating a large dataset of ammonia transitions [12]. On the theoretical side, variationally-calculated line lists have recently become available [13,14]; use of these helps to overcome the problems of divergent PT.

Use of a heated cell increases significantly the Boltzmann factor for states with highly-excited rotational and vibrational quantum numbers, which in turn increases the intensity of the associated lines. However, problems with divergence or slow convergence of

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PT hinder the process of assignment, especially for lines involving highly-excited vibrational states. Variational calculations are based on numerical diagonalization of the full Hamiltonian matrix which is based on an exact or approximate kinetic energy operator and an *ab initio* or fitted ("spectroscopically-determined") potential energy surface (PES). The diagonalization produces energy levels and wavefunctions for all states of a given *J*, parity and symmetry. These can then be used to calculate spectral line positions and line intensities, given a dipole moment surface. Since this approach does not use a perturbation expansion, it is in principle possible to obtain almost exact values of the energies within the Born–Oppenheimer approximation provided the PES used is of sufficient accuracy. The combination of very accurate quantum chemical calculations and a fitting procedure for the PES can lead to PESs which reproduces the fitted data with an accuracy better than 0.1 $cm^{-1}$. Since no divergent PT is involved, the extrapolation to higher energies both for vibrations and rotations remains reliable. This accuracy has been demonstrated for other similar molecules [15] and will be shown for ammonia in this work. Thus, the combination of Fourier transform spectroscopy with a high temperature cell and a variational line list is used to significantly increase the known rotational quantum numbers for the vibrational states studied in this work.

In the following sections we summarize the experimental data that we analyze and the BYTe variational line list which is the basis of our analysis. Section 4 gives our assignment procedure and summarizes our results, the majority of which are given as Supplementary data. Section 5 gives our conclusions and discusses the prospects for further progress on this problem.

## 2. Experimental details

Laboratory emission spectra of $NH_3$ were recorded using a Fourier Transform Infrared (FT-IR) spectrometer aligned with a tube furnace capable of maintaining stable temperatures up to 1370 °C. We recorded 12 separate spectra every 100 °C between 300–1300 °C as well as at 1370 °C for two regions of the infrared from 740 to 1690 $cm^{-1}$ (region A) and 1080 to 2200 $cm^{-1}$ (region B). The experimental setup is described in detail by Hargreaves et al. [12] and only important aspects are highlighted here. The tube furnace consisted of a 1.2 m evacuated alumina ($Al_2O_3$) sample tube sealed with calcium fluoride ($CaF_2$) windows for region B (KRS-5 for A), where the central 0.5 m was surrounded by a tube furnace. The sample tube was first evacuated and a small flow of $NH_3$ was maintained using a needle valve with a pressure of 1 Torr for region B (5 Torr for A) for all measurements to avoid the build-up of impurities and loss of sample from the system. The area between the sample tube and the spectrometer was purged with "dry" air ($H_2O$ largely absent) to minimize the intensity of absorption lines due to atmospheric $H_2O$. The radiation exiting the windows of the sample tube was focused by a $CaF_2$ lens for region B (zinc selenide for A), through the aperture of the FT-IR spectrometer where a potassium bromide (KBr) beamsplitter separates and recombines the radiation and reflects it onto a liquid nitrogen-cooled mercury–cadmium-telluride (MCT) detector.

All spectra were recorded at a resolution of 0.01 $cm^{-1}$ and were generated from an average of 240 scans for region A, and 80 scans for region B. The peak picking program Wspectra [16] was used to select all the observed emission peaks and a Voigt line profile was then fitted to each peak to generate a line list of positions (in $cm^{-1}$) and arbitrary line intensities. To account for the contribution of the experimental setup to the relative strength of the lines, a blackbody (graphite rod with a concave cone face) was placed at the centre of the sample tube and a spectrum recorded at low temperature (250–350 °C) to obtain an instrument response curve for both regions. The line lists were then divided by the appropriate instrument response curve to remove the experimental effects on the relative intensity of the lines.

To calibrate the wavenumber scale of each line list, comparisons were made to 20 strong, clear lines present in the HITRAN 2008 database [17]. The calibrations were obtained by dividing the HITRAN line positions by observed line positions to obtain a calibration factor, resulting in an approximate shift of about 0.002 $cm^{-1}$ for each spectrum. The overall accuracy of our line positions after calibration is about ±0.002 $cm^{-1}$. Sample raw spectra have been deposited in the Supplementary data.

Finally, both regions were merged by splicing at 1350 $cm^{-1}$ to make 12 line lists (one for each temperature) in the range 740–2200 $cm^{-1}$. The experimental study gave about 18 500 lines between 740 $cm^{-1}$ and 2200 $cm^{-1}$. The experimental procedure has been based upon that used by Nassar and Bernath [18] to obtain line lists of $CH_4$.

## 3. The BYTe linelist

The theoretical line list used in this study [14], known as BYTe, was computed with a view to modeling the atmospheres of hot astronomical bodies such as extrasolar planets and brown dwarfs. It was computed using the NH3-2010 spectroscopically-determined potential energy surface [19] and the TROVE [20] rovibrational computer program. Intensities were calculated using an *ab initio* dipole moment surface [13].

BYTe is designed to model ammonia spectra at all temperatures below 1500 K and is therefore well matched to the experiment. It comprises 1 138 323 251 transitions in the frequency range from 0 to 12 000 $cm^{-1}$, constructed from 1 373 897 energy levels lying below 18 000 $cm^{-1}$. Rotational levels up to $J = 41$ were considered, although only those up to $J = 36$ contribute directly to the line list as the levels with higher *J* lie too high in energy.

## 4. Assignments

The results of the previous studies of cold $NH_3$ spectra in the region between 780 $cm^{-1}$ and 2100 $cm^{-1}$ are summarized in the HITRAN data base [17]. The total number of assigned lines given there in this range is 2733.

The assignment of 18 500 observed hot lines is probably not possible at the moment, so our aim here is more modest. The majority of the weak lines are associated with hot bands, the upper levels of which belong to vibrational states which have yet to be observed experimentally. The comprehensive assignment of all weak lines is only likely to be feasible in combination with the observation and assignment of higher frequency spectra which probe these higher vibrational states more directly. Previous experience suggests that intercombination transitions between excited vibrational states are likely to be particularly prevalent in hot emission spectra [21]. Here we concentrate on the assignment of the strong lines, whose upper levels belong to vibrational states with band origins within the frequency region of this work; that

**Table 1**
Summary of $NH_3$ lines assigned in the 780–2100 $cm^{-1}$ and the energy levels derived from them.

| | Lines | | New levels |
|---|---|---|---|
| All | 18 370 | | |
| HITRAN | 2733 | Confirmed by | |
| New trivial | 2509 | Comb. diff. | 287 |
| Combination difference | 711 | | |
| Line list | 130 | Line list | 144 |
| Total assigned | 5953 | Total new levels | 431 |

is up to 2100 cm$^{-1}$. Table 1 presents statistics on the numbers of lines assigned and the resultant rotation-vibration energy levels. 612 empirical energy levels could be determined for the vibrational states considered here from the previous experimental studies; our analysis adds a further 431 levels.

As can be seen from Table 1, about 2700 lines observed in the hot spectrum were previously assigned and the assignments given in the HITRAN data base. A further 2509 of the observed lines were easily assigned for the first time. We call these trivial assignments, as these lines can be associated with energy levels already determined by experimental data in HITRAN. These lines can be tentatively assigned using a simple procedure of subtraction of upper and lower state energies and matching the result to the observed line frequency. However, to avoid the generation of false assignments, these trivial assignments were confirmed by comparison with the calculated line intensities from BYTe. At high temperatures, some of the lines designated “trivially assigned” actually became quite strong and easily identified. The assignment of these lines is difficult in cold (room temperature) spectra as these lines are weak and choices must be made between lines with very small signal-to-noise ratios during the assignment procedure; wrong choices can easily lead to misassignments. Observation of spectra at high temperatures facilitates the reassignment of some of these lines. For this reason, Table 1 designates some levels as newly-determined although transitions to them are already given in HITRAN. In such cases the assignments, and hence the levels, in HITRAN are incorrect.

The most interesting part of the assignment consists of 841 lines, which we assigned by direct comparison with the BYTe line list [14]. The majority of these line assignments (711 lines) were confirmed using combination differences. These assignments can be considered secure. This does not mean that we doubt the assignments of the other 130 lines because the observed–calculated differences remain very stable within a given vibrational state, as can be seen from the energy levels tabulated in the Supplementary data. The Supplementary data present energies for levels belonging to the six vibrational states considered in this paper, for which the newly-determined data for are summarized in Table 2.

Table 2 gives the labels of the vibrational states analyzed in this work as well as the values of maximum $J$ rotational quantum number of the associated energy levels known previously and determined here. One can see that the highest increase in $J$ values is for the $v_2 = 2$ (a) inversion state, where previous studies assigned levels with $J$ up to 13 and we present levels up to $J = 22$. The spectrum undoubtedly contains transitions to higher $J$ states, but these lines are too weak and too numerous to be assigned at present.

The energy levels derived from the assigned lines are given in the Supplementary data along with the lines (partially assigned) from the 1300 °C experimental list. These levels were calculated using the lower state energy levels of Yu et al. [11] which correspond closely with those of Chen et al. [22] but extend beyond $J = 22$. Upper state energies were computed using the frequency of the strongest assigned transition to each state. A project to determine all experimental energy levels of ammonia using the MARVEL procedure [23] is currently in progress. The determination of these energy levels is important for comparison of observed and calculated data, and also for the possibility of future trivial assignments. The majority of these levels are confirmed by combination differences, and the smooth variation of the observed minus calculated value with $J$ and $K$ for a given vibrational state can be used as an additional tool for assignment of lines for which no combination difference partner could be found. The smooth extrapolation of the observed minus calculated differences gives us confidence that to within about 0.1 cm$^{-1}$ we can predict the position of a line even though the absolute accuracy of the variational predictions is often only 1 cm$^{-1}$. As the density of lines with approximately similar intensity is, on average, less than 1 line per 1 cm$^{-1}$, an accuracy of 0.1 cm$^{-1}$ is enough for reliable assignments to be made.

This property of variational calculations allows us to consider problems involving energy levels with highly-excited rotational quantum numbers. Recently [11], high powers of $J$ (up to 18th order) were used in an effective Hamiltonian expansion to fit experimentally observed data up very high $J$ (up to 35) and $K$ levels of the ground and the $v_2 = 1$ excited vibrational state. Comparison of energy levels calculated in Ref. [11] with our variationally-calculated energy levels shows an increasing discrepancy with

**Table 2**
Summary of new energy level information obtained by vibrational state.

| $v_1$ | $v_2$ | $v_3$ | $l_3$ | $v_4$ | $l_4$ | | Band origin | $J_{max}$ | | Levels | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calculated (cm$^{-1}$) | Old | New | Old | New |
| 0 | 2 | 0 | 0 | 0 | 0 | s | 1597.487 | 15 | 19 | 87 | 95 |
| 0 | 0 | 0 | 0 | 1 | −1 | s | 1626.280 | 15 | 18 | 107 | 40 |
| 0 | 0 | 0 | 0 | 1 | 1 | s | | 15 | 18 | 124 | 32 |
| 0 | 0 | 0 | 0 | 1 | −1 | a | 1627.376 | 15 | 18 | 104 | 47 |
| 0 | 0 | 0 | 0 | 1 | 1 | a | | 15 | 18 | 104 | 66 |
| 0 | 2 | 0 | 0 | 0 | 0 | a | 1882.183 | 13 | 22 | 86 | 147 |

**Table 3**
Sample energy levels for the vibrational ground state: variationally-calculated energy levels from BYTe [14] and levels obtained by Yu et al. [11] using an effective Hamiltonian.

| $J$ | $K$ | BYTe [14] | Yu et al. [11] | |
|---|---|---|---|---|
| 25 | 25 | 4070.041 | 4065.731570 | −4.31 |
| 25 | 24 | 4255.370 | 4252.189734 | −3.18 |
| 25 | 23 | 4428.832 | 4426.582940 | −2.25 |
| 25 | 22 | 4591.273 | 4589.737285 | −1.54 |
| 25 | 21 | 4743.392 | 4742.367405 | −1.03 |
| 25 | 20 | 4885.780 | 4885.097121 | −0.68 |
| 25 | 19 | 5018.939 | 5018.470866 | −0.47 |
| 25 | 18 | 5143.310 | 5142.963196 | −0.35 |
| 25 | 17 | 5259.273 | 5258.987505 | −0.29 |
| 25 | 16 | 5367.166 | 5366.903977 | −0.26 |
| 25 | 15 | 5467.286 | 5467.026821 | −0.26 |
| 25 | 14 | 5559.898 | 5559.630767 | −0.27 |
| 30 | 30 | 5760.118 | 5748.361947 | −11.76 |
| 30 | 29 | 5985.990 | 5976.289713 | −9.70 |
| 30 | 28 | 6197.567 | 6189.240727 | −8.33 |
| 30 | 27 | 6396.171 | 6389.128148 | −7.04 |
| 30 | 26 | 6582.849 | 6577.107157 | −5.74 |
| 30 | 25 | 6758.452 | 6753.963684 | −4.49 |
| 30 | 24 | 6923.690 | 6920.316896 | −3.37 |
| 30 | 23 | 7079.165 | 7076.710428 | −2.45 |
| 30 | 22 | 7225.396 | 7223.645997 | −1.75 |
| 30 | 21 | 7362.837 | 7361.591060 | −1.25 |
| 30 | 20 | 7491.888 | 7490.977231 | −0.91 |
| 30 | 19 | 7612.897 | 7612.197303 | −0.70 |
| 30 | 18 | 7726.188 | 7725.603916 | −0.58 |
| 30 | 17 | 7832.038 | 7831.510441 | −0.53 |
| 30 | 16 | 7930.701 | 7930.193633 | −0.51 |
| 30 | 15 | 8022.403 | 8021.897286 | −0.51 |
| 30 | 14 | 8107.351 | 8106.836218 | −0.52 |
| 35 | 35 | 7718.808 | 7499.114650 | −219.69 |
| 35 | 34 | 7987.027 | 7879.250599 | −107.78 |
| 35 | 33 | 8237.627 | 8184.624681 | −53.00 |
| 35 | 32 | 8472.709 | 8444.935746 | −27.77 |
| 35 | 31 | 8693.859 | 8677.073865 | −16.79 |
| 35 | 30 | 8902.303 | 8890.271647 | −12.03 |
| 35 | 29 | 9099.019 | 9089.349236 | −9.67 |
| 35 | 28 | 9284.814 | 9276.732443 | −8.08 |
| 35 | 27 | 9460.369 | 9453.650630 | −6.72 |
| 35 | 26 | 9626.269 | 9620.793647 | −5.48 |
| 35 | 25 | 9783.026 | 9778.639236 | −4.39 |
| 35 | 24 | 9931.089 | 9927.597917 | −3.49 |

increasing $K$ starting from about $K = 20$; see Table 3. A fuller comparison is given in the Supplementary data.

Before commenting on this discrepancy, we consider the similar situation in another light molecule, water. Because of its lightness and quasilinearity, the PT series effective Hamiltonians for water converge slowly and start to diverge above $K_a$ about 15 for the ground state [24] and about 10 for the first excited bending state [25]. In Ref. [24], the use of a one-dimensional Pade–Borel approximation was proposed to solve the problem of PT divergence. Use of this approximation allowed the accuracy of the fit to high $K_a$ levels of water to be improved by several orders of magnitude. Very high $K_a$ and $J$ observed in hot water laboratory spectra [26] and in sunspots [27] allowed a comparison of observed and calculated values to be made. Whereas PT series were generally divergent and gave very poor predictive properties, the accuracy of variational calculations does not depend on the value of $K$; these calculations demonstrated smoothness similar to that described here for the rotational energy levels of ammonia.

The situation with water helps us to understand the discrepancy between variationally-calculated [14] and PT [11] energy levels summarized in Table 3. High temperature notwithstanding, the intensities of lines with very high $K$ are weak and cannot be readily assigned. The discrepancy between the PT high $K$ energies and variationally-calculated ones suggests that we should consider assignments to high $K$ levels with caution. However we have checked the assignments of the high $K$ lines given in Ref. [11] and all of them are confirmed by the variational calculations.

At low values of $J$ there is excellent agreement between BYTe and Yu et al. For $J < 12$, the energies of the $J = K$ ground vibrational states agree to better than 0.03 $\text{cm}^{-1}$, and for $J < 21$ the agreement is still better than 0.6 $\text{cm}^{-1}$. However, at higher $K$ values the two sets of levels rapidly diverge, and by $J = K = 33$, the energy in Yu et al. is more than 50 $\text{cm}^{-1}$ below the BYTe value, whilst at $J = K = 35$, the difference is more than 200 $\text{cm}^{-1}$.

Barber et al. [28] demonstrate that computed line lists are self-consistent, and that for ro-vibrational states having the same vibrational quantum numbers and value of $J$–$K$, it is possible to accurately predict the energies of the next highest $J$ state if the energies of lower $J$ states are known, see Eq. (4) of Ref. [28]. In order to ascertain which of the two line lists errors for higher $J$s we used the Barber et al. algorithm (5 terms) to test self-consistency of the BYTe and Yu et al. data by checking which energies for states with $J > 20$ match the values that are predicted by the algorithm. To do this we used the $J = 16$–$20$ energies in each of the two lists as the starting point and included the projected values in the five-term algorithm for subsequent $J$ values. Using this methodology, the accuracy of each subsequent prediction decreases, but despite this limitation, the algorithm is still able to easily identify any inconsistencies in the $J$ levels.

Fig. 1 shows the extent to which BYTe and Yu et al. data for values of $J = K > 24$ differ from those predicted by the algorithm. It can be seen that for BYTe the energy of the $J = K = 35$ state agrees with value derived to better than 2 $\text{cm}^{-1}$. In contrast, Yu et al.'s energies do not agree with the predicted values. Their energies for $J = 23$–$32$ are too high to be consistent with lower $J$ values, whilst the energies for higher $J$s are progressively too low; the $J = K = 35$ state is 160 $\text{cm}^{-1}$ below that predicted from the energies of the lower $J$ states in their own list.

The problem here would appear to arise from the fact that the majority of transitions obey the dominant $\Delta K = 0$ selection rule. This means that in a PT fit to purely experimental data, the $K$-dependent constants are not very well determined. Thus, two possible causes of the discrepancy should be considered, namely indeterminacy of $K$-dependent constants and divergence of perturbation series. If one wants to use a fitted effective Hamiltonians for calculations of high $K$, the methods of summation of divergent series [24] should probably be applied. However, if an accuracy of a few tenths of a $\text{cm}^{-1}$ is sufficient, variationally-calculated energy levels are probably more reliable than those calculated using PT. We note that the first rational Hamiltonian (similar to the Pade Hamiltonian used in [25]) that was applied to sum a divergent series in molecular spectroscopy was a Hamiltonian for the inversion-rotation spectra of ammonia [29].

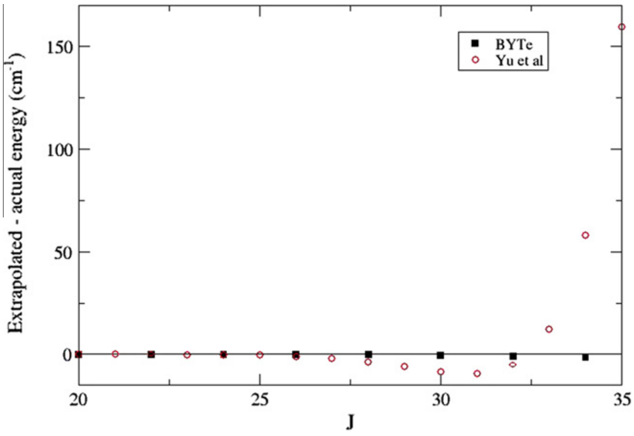

**Fig. 1.** Comparison of BYTe energy levels [14] and those of Yu et al. [11] for states with $J = K$ for the vibrational ground state with predictions of the 5-term formula of Barber et al. [26]; see text for details.

## 5. Conclusions

In this paper we present analysis of hot rovibrational spectra of ammonia in the region between 780 $\text{cm}^{-1}$ and 2100 $\text{cm}^{-1}$. We analyzed the spectra involving nine vibrational states whose band origins fall within this spectral region. Use of the recently calculated BYTe variational line list allowed us to assign about 3400 lines and to demonstrate the smooth dependence of the discrepancies between theory and experiment with increasing rotational quantum numbers. Previously, variational calculations have proved to be very effective for analyzing highly-excited rotational and vibrational spectra of triatomic molecules, including helping to determine the energy levels of water up to its dissociation limit [30]. Here we demonstrated the effectiveness of a variationally-calculated line list for the analysis of the spectrum of the tetraatomic ammonia molecule. We intend to apply this line list to the assignment of higher vibrational states of ammonia which have so far defied conventional analysis due to the complicated nature of the spectra. We note that very recently Huang et al. [31,32] have also presented ammonia frequency calculations. Their calculations are more accurate than the BYTe line list used here but more limited in scope. Huang et al. have also used their energies for spectral analysis [32], in particular making a number of assignments and re-assignments to the HITRAN database [17].

Out of almost 18 500 lines measured at 1300 °C, we have assigned about one-third. The remaining two-thirds are hot lines and can be divided into two categories. Most of these lines are weak, grass-like features in the spectrum. These will probably be partially assigned using trivial assignments once new energy levels are determined from analysis of spectra in other regions. About 1000 unassigned lines could be classified as strong or medium. These are transitions to upper states which were not included in the analysis performed in this work. We intend to analyze them together with experimental data obtained in higher frequency regions.

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## Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2011.05.003.

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