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Analysis of high temperature ammonia spectra from 780 to 2100 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 $v_3 + 2v_4$ bands, with the highest frequency about 7000 cm^{-1}, which is very low for this fundamental stable molecule. The reason for this is that the spectrum around 7000 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 $v_2 = 1$ vibrational states, and J about 15 for other excited vibrational states. Yu et al. [11] extended this to $J = 35$ for the ground and $v_2 = 1$ 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