Journal of Quantitative Spectroscopy & Radiative Transfer ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Infrared absorption spectra of hot ammonia

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ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form
21 February 2017
Accepted 21 February 2017

Keywords:
Fourier transform spectroscopy
Infrared absorption
Hot ammonia
Brown dwarfs
Line lists

ABSTRACT

Infrared absorption spectra of NH_3 have been obtained at high resolution (0.02 cm^{-1}) at seven temperatures between 296 and 973 K. The spectra were recorded using a Bruker IFS 125 infrared Fourier transform spectrometer in the 2400–5500 cm^{-1} region and empirical lower state energies have been obtained by comparison of line strengths at different temperatures. Using two reference line lists, quantum number assignments have been made for each temperature for between 1660 and 3020 transitions, with J up to 22. The line lists obtained provide accurate line positions as well as intensities and experimental lower state energies at temperatures relevant for modeling the atmospheres of brown dwarfs and exoplanets.

1. Introduction

Ammonia (NH_3) is a widely studied molecule in atmospheric science. In the Earth's atmosphere, where sources include animal waste and fertilizers [1], it acts as a precursor in the production of aerosols [2] and particulate matter [3]. Deposition of atmospheric NH_3 can lead to fertilization, a side effect of which may be decreased biodiversity [4].

NH_3 has also been observed in a number of astrophysical environments. In the solar system, it has been detected in the atmospheres of Jupiter [5,6], Saturn [7] and Titan [8] as well as on comets [9,10]. The pure rotational transitions and inversion transitions of NH_3 have been detected in molecular clouds [11,12] making it one of the first extraterrestrial polyatomic molecules discovered. The atmospheres of cool astronomical objects, such as brown dwarfs and exoplanets, are of low enough temperatures to allow small molecules such as NH_3 to form and maintain large enough concentrations to be detected.

Sub-stellar objects with sufficiently low mass (<0.08 solar masses) are known as brown dwarfs and cannot fuse hydrogen within their cores [13]. The first such object discovered was Gliese 229B [14] and since then a large number of brown dwarfs have been detected with atmospheres cool enough (500 – 2400 K) for a number of molecular species to exist. Indeed, brown dwarfs, similar to stars, are classified by the presence or absence of particular atomic and molecular features. The hottest such objects, the L dwarfs, contain features from electronic transitions of metal hydrides such as FeH [15] and CrH [16,17]. T dwarfs are distinguished by hot H_2O and CH_4 transitions [18,19]. NH_3 is observed in late T dwarfs, with increasing concentrations as the objects cool [19,20]. As such, NH_3 is expected to characterize a yet cooler class, the Y dwarfs that have an approximate maximum temperature of $\sim$700 K. Y-dwarfs have now been observed and NH_3 appears as a shoulder on an emission feature at 1.58 μm [21,22].

Since the discovery of the first exoplanet in 1995 [23] more than 3500 have been discovered (http://exoplanet.eu/). If the planet passes in front of the star it orbits, then it may be detected by observation of periodic decreases in light intensity of the parent star. This technique is known as the transit method and was first used successfully to detect the planet HD 209458b [24] and has since been used by the Kepler mission to observe large numbers of exoplanet candidates [25]. This technique also allows the spectrum of the exoplanet atmosphere to be obtained by recording the transit dips as a function of wavelength [26] and use of the method has resulted in the detection of a number of molecules such as H_2O [27,28], CH_4 [29], CO [30] and CO_2 [31]. As yet, NH_3 has not been observed in the atmosphere of an exoplanet, however a number of modelling studies have predicted its presence in hydrogen-rich hot-Jupiters [32–34].

NH_3 is a polyatomic molecule having four atoms arranged in a trigonal pyramid structure with C_{3v} symmetry [35]. Ammonia has

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http://dx.doi.org/10.1016/j.jqsrt.2017.02.012
0022-4073/

a complex infrared spectrum with 6 fundamental vibrational modes, two of which are doubly degenerate. The four fundamental vibrational frequencies are: the symmetric stretch at 3336.2 cm^{-1} (ν_1, a_1), the symmetric bend at 932.5 cm^{-1} (ν_2, a_1), the antisymmetric stretch at 3443.6 cm^{-1} (ν_3, e) and the antisymmetric bend at 1626.1 cm^{-1} (ν_4, e).

There has been extensive work on the spectroscopy of ammonia in the infrared; for example experimental line lists have been obtained in the 2 μm [36] and 3 μm [37] regions. The most complete line assignments for NH_3 in the infrared are compiled in the HITRAN 2012 database [38]; however HITRAN is intended for applications near room temperature and lacks complete hot band coverage in this region. The hot bands are essential when comparisons are made to high temperature atmospheres. Down *et al.* [39] provide a re-analysis of the HITRAN 2012 NH_3 line list which was used for comparison to HITRAN in this paper; where the original HITRAN 2012 data has been used, the text will mention HITRAN specifically. A comprehensive theoretical line list, BYTe, has been calculated for NH_3 that can be used at temperatures up to 1500 K and contains approximately 1.1 billion transitions [40]. The ro-vibrational calculations from Huang *et al.*, [41,42] and references therein, provide an additional line list for ammonia in this region. High temperature experimental line lists have been obtained using emission spectroscopy at high resolution (0.01 cm^{-1}) from 740–2100 cm^{-1} [43] and 1650–4000 cm^{-1} [44]. Absorption spectra at moderate resolution (0.09 cm^{-1}) of hot samples at atmospheric pressure have also been recorded in the 500–2100 cm^{-1} [45] and 2100–5500 cm^{-1} [46] spectral regions. Existing experimental line lists have been used in an energy level analysis (MARVEL) to predict a large number of unmeasured lines [47]. Our work reported below details an extension of these experimental line lists, in the 2400–5500 cm^{-1} region using an improved cell design and technique [48] to record transmission spectra of hot samples. We provide empirical lower state energies, intensities and line positions (± 0.002 cm^{-1}) which can be used in atmospheric models for brown dwarfs and exoplanets.

2. Experimental

Transmission spectra were recorded at seven different temperatures, 23 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C, using a sealed quartz cell, tube furnace and Fourier transform spectrometer. This range includes the effective temperatures of the mid and late T dwarfs [19] and Y dwarfs [22] as well as the coolest observed hot Jupiters [32]. Above 700 °C thermal decomposition of the sample gas reduces the signal to such an extent that reliable spectra could not be obtained.

The transmission spectrum for each temperature is obtained from four individual spectra that, when combined, correct for NH_3 and cell emission; this method has been used previously to record spectra for methane [48]. An absorption spectrum (A_{ab}) is recorded with NH_3 in the cell at temperature with an external emission source (200 W tungsten halogen broadband lamp). A background reference spectrum for the absorption (A_{ref}) is recorded without the NH_3 in the cell. The emission spectrum (B_{em}) is recorded with NH_3 in the cell at temperature without the lamp. The background reference spectrum for emission (B_{ref}) is recorded without the sample in the cell and with the lamp turned off. These spectra are combined to calculate the transmission spectrum for each temperature as

$$\tau = \frac{A_{ab} - B_{em}}{A_{ref} - B_{ref}}.$$

Spectra were recorded in the 2400–5500 cm^{-1} region, providing overlap with previous experimental work [44]. This previous work includes spectral regions that cover $3\nu_2/\nu_2+\nu_4$ and $\nu_1/\nu_3/2\nu_4$ bands and the work provided here extends this coverage to include spectral regions that contain the $\nu_1+\nu_2/\nu_2+\nu_3$ and $\nu_1+\nu_4/\nu_3+\nu_4$ bands as well as associated hot bands.

Table 1
Experimental conditions.

Parameter	Value
Spectral region (cm^{-1})	2400–5500
Detector	InSb
Beamsplitter	CaF_2
Spectrometer Windows	CaF_2
Lens	CaF_2
Filter	Ge
Scans	300
Resolution (cm^{-1})	0.01
NH_3 Pressure (Torr)	40
Zerofilling factor	x 16

The 50 cm quartz tube sample cell was used under static conditions to contain the NH_3 sample. The cell is contained within the tube furnace which is heated to the appropriate temperature, which is accurate to within ± 10 °C. The cell was aligned with the entrance aperture of a Bruker IFS 125HR Fourier transform spectrometer and radiation was focused into the spectrometer using a CaF_2 lens. The spectrometer used a CaF_2 beamsplitter and an indium antimonide (InSb) detector. Experimental parameters are summarized in Table 1.

The resulting transmittance spectra contained a number of H_2O lines which were removed manually using the Bruker OPUS software. After combining the spectra at each temperature to calculate a transmission spectrum, peaks were picked using WSpectra [49] to measure their position and intensity. Lines were calibrated for line position and intensity by matching strong and isolated lines that are also found in the HITRAN 2012 database. The number of lines found for each temperature is given in Table 2.

The line intensity equation gives the line intensity as a function of temperature,

$$S' = \frac{2\pi^2\nu_{10}S_{J'J''}}{2\varepsilon_0 hcQ}\exp\left(-\frac{E''}{kT}\right)\left[1-\exp\left(\frac{h\nu_{10}}{kT}\right)\right]$$

where ν_{10} is the line frequency, $S_{J'J''}$ is the line strength, ε_0 is the permittivity of free space, h is the Planck constant, c is the speed of light, Q is the internal partition function, E'' is the lower state energy, k is the Boltzmann constant and T is the temperature [35]. If a line is measured at different temperatures, the intensity of the line at each temperature may be compared to the intensity at a reference temperature by taking a ratio of the line intensity equation

$$\frac{S'}{S'_0} = \frac{Q_0}{Q}\exp\left(\frac{E''}{kT_0}-\frac{E''}{kT}\right)\left[\frac{1-\exp\left(-\frac{h\nu_{10}}{kT}\right)}{1-\exp\left(-\frac{h\nu_{10}}{kT_0}\right)}\right]$$

where S'_0 and T_0 refer to the line intensity and temperature of the reference measurement. For these results 400 °C was used as the reference as this temperature contained the most lines with which to compare the line intensities of other temperatures. If there was no line measured at 400 °C then the reference used was the temperature with the next greatest number of lines. The partition function used for NH_3 was obtained from Yurchenko *et al.* [40], which for our temperature range is essentially the same as the more recent values of Sousa-Silva et al. [50].

The lower state energy can be obtained from a rearranged version of the line intensity equation

Please cite this article as: Beale CA, et al. Infrared absorption spectra of hot ammonia. J Quant Spectrosc Radiat Transfer (2017), http://dx.doi.org/10.1016/j.jqsrt.2017.02.012