



Analysis of the red and green optical absorption spectrum of gas phase ammonia

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ABSTRACT

Room temperature NH₃ absorption spectra recorded at the Kitt Peak National Solar Observatory in 1980 are analyzed. The spectra cover two regions in the visible: 15,200 – 15,700 cm⁻¹ and 17,950 – 18,250 cm⁻¹. These high overtone rotation-vibration spectra are analyzed using both combination differences and variational line lists. Two variational line lists were computed using the TROVE nuclear motion program: one is based on an *ab initio* potential energy surface (PES) while the other used a semi-empirical PES. *Ab initio* dipole moment surfaces are used in both cases. 95 energy levels with $J = 1 - 7$ are determined from analysis of the experimental spectrum in the 5ν_{NH} (red) region and 46 for 6ν_{NH} (green) region. These levels span four vibrational bands in each of the two regions, associated with stretching overtones.

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1. Introduction

There are a number of reasons why one might attempt to analyse the high resolution optical ro-vibrational spectrum of ammonia. Firstly, the spectrum of ammonia is a textbook example of high resolution molecular spectroscopy. However, for almost 70 years, the vibration-rotation spectrum of ¹⁴NH₃ was only studied in detail at wavelengths longer than 2 μm; these spectra are assembled in comprehensive high resolution molecular spectroscopic databases such as the 2008 edition of HITRAN [1]. Only relatively recently and rather gradually has the absorption spectrum of NH₃ been successfully analyzed in the near infrared region [2–8]; some of these data are included in the recent, 2016, release of HITRAN [9]. The spectrum of ammonia at visible wavelengths remains poorly characterized and, at best, only partially analyzed. A full review of high resolution, vibration-rotation studies of ¹⁴NH₃ was recently provided by Al Derzi et al. [10] as part of their MARVEL (measured active rotation-vibration energy levels) study of the molecule.

Secondly, there is renewed interest in the spectrum of ammonia caused by attempts to analyze spectra of brown dwarfs [11], and in particular the fact that the coldest of these object, Y-dwarfs, should be characterized by strong ammonia features [12,13], but possibly are not. Nonetheless, detailed ammonia spectra have been assigned in brown dwarfs [11]. The discovery of the exoplanets, and especially the use of the transit method to observe molecular spectra [14], has led to discussions on the presence of ammonia in these objects too [15,16]. Water and methane are essential to the characterization of exoplanetary spectra. However, ammonia may be a “mind-marker” as ammonia is the most-manufactured molecule on Earth and is also a major byproduct of intensive agriculture, and hence a possible sign of intelligent life. Ammonia is among a number of molecules being actively discussed as a possible bio-marker [17,18]. Ammonia has recently been detected in the atmosphere of a hot Jupiter exoplanet [19].

Thirdly, the umbrella motion in NH₃ is a classic example of a molecule undergoing a large amplitude motion. The effect of this motion on the energy levels in the system has been the subject of recent careful analysis [20]. However, the corresponding energy levels for higher states remain unknown. The spectrum of ammonia remains hard to calculate accurately and to analyse [21] due to

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Table 1

Calculated vibrational band centers and band intensities using our two different PESs and our most reliable DMS. Units of intensity are $\text{cm}^{-1}/(\text{molecules cm}^{-2})$ and units of frequency are cm^{-1} .

| Symmetry | $(\nu_1 \nu_2 \nu_3 \nu_4 \nu_5 \nu_6 \nu_7 \nu_8 \nu_9 \nu_{10})$ | ν_0^{ai} | I_0^{ai} | ν_0^{rf} | I_0^{rf} |
|----------|--|--------------|-------------------------|--------------|-------------------------|
| A_1^s | 5 0 0 0 0 0 s | 15,463.3924 | 2.412×10^{-22} | 15,445.9471 | 2.686×10^{-22} |
| A_2^a | 5 0 0 0 0 0 a | 15,461.3950 | 1.039×10^{-22} | 15,447.2406 | 2.512×10^{-22} |
| E^a | 4 0 1 1 0 0 a | 15,463.5532 | 6.454×10^{-23} | 15,445.5068 | 6.731×10^{-23} |
| E^s | 4 0 1 1 0 0 s | 15,462.4164 | 7.176×10^{-23} | 15,446.9127 | 5.780×10^{-23} |
| A_1^s | 6 0 0 0 0 0 s | 18,131.8294 | 8.271×10^{-23} | 18,106.5124 | 6.338×10^{-23} |
| A_2^a | 6 0 0 0 0 0 a | 18,144.9957 | 6.855×10^{-23} | 18,118.3103 | 4.262×10^{-23} |
| E^a | 5 0 1 1 0 0 a | 18,132.3858 | 3.907×10^{-23} | 18,106.7462 | 1.568×10^{-23} |
| E^s | 5 0 1 1 0 0 s | 18,145.0979 | 3.540×10^{-23} | 18,118.3656 | 9.478×10^{-24} |

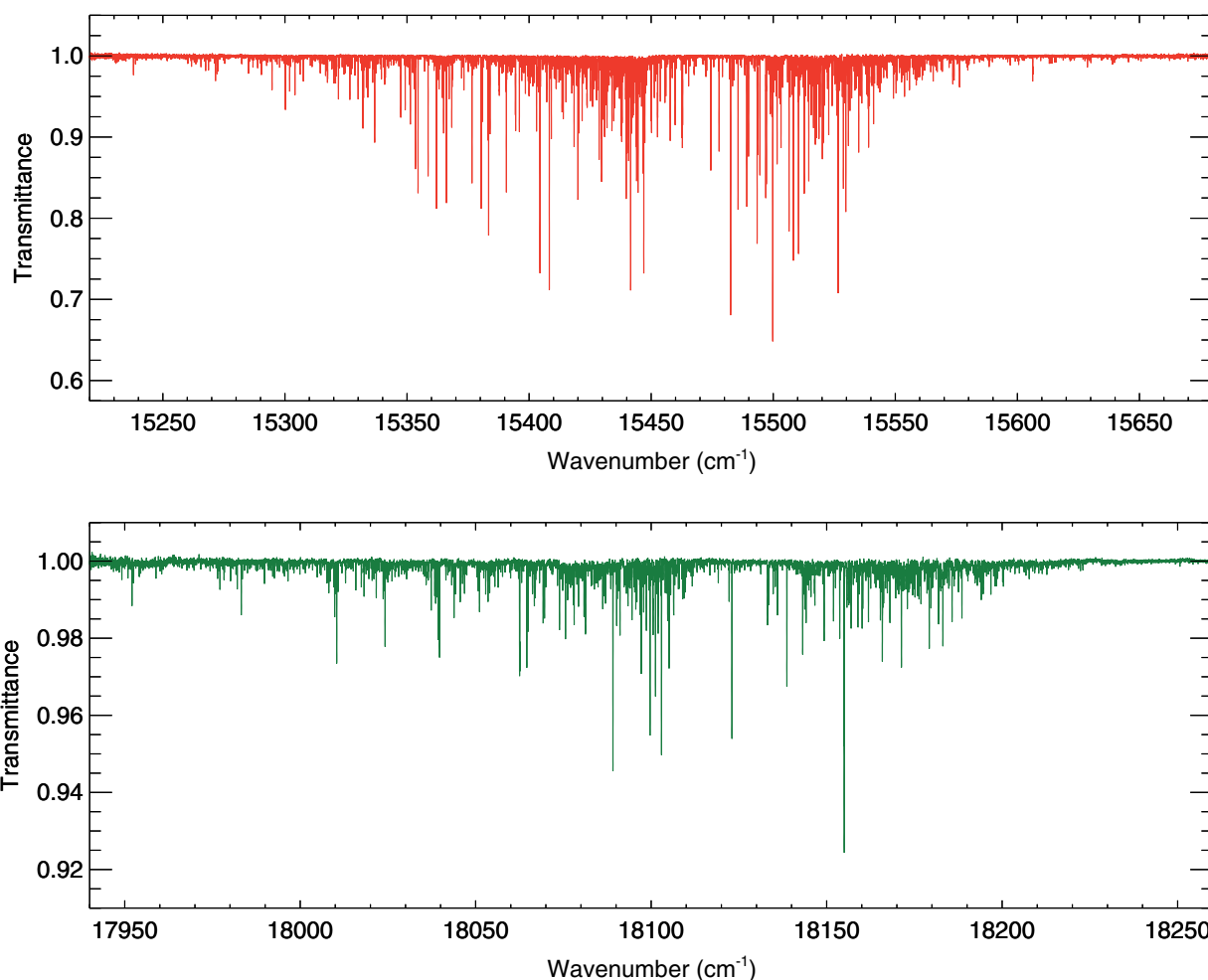


Fig. 1. Overview transmission spectra calculated from the Kitt Peak Fourier transform spectra 800406R0.007 (upper) and 800407R0.001 (lower).

this unusual umbrella motion. This is especially true for states of high vibrational excitation such as those found in its visible spectrum.

Finally, transitions at visible wavelengths provide a pathway to the study of the spectrum of ammonia up to and beyond dissociation. For the isoelectronic water molecule, the use of multiple-resonance visible-wavelength spectra has provided a direct route to dissociation [22] and beyond [23].

In fact, visible wavelength spectra have been available for some time. Ammonia lines in this region were observed at Kitt Peak in 1980, but remained unanalyzed; see next section. This work was directly followed by dye laser experiments by Kuga et al. [24] and microwave-detected microwave-optical double resonance studies by Coy and Lehmann [25–27]. About 1000 ammonia transitions in the $15,260 - 15,590 \text{ cm}^{-1}$ region were measured by Kuga et al.

[24] using Stark modulation with 193 of them being given rotational assignments. Coy and Lehmann [25] recorded visible ammonia spectra around $15,450$ and $18,110 \text{ cm}^{-1}$ with both photoacoustic absorption and microwave-optical double resonance spectra techniques. Again rotational assignments, only, were given for 318 and 105 lines respectively in the two regions. These partial (rotational) assignments do not supply information on the upper vibrational state. It is only very recently, with the advent of high quality *ab initio* studies, that vibrational assignments have begun to emerge e.g. [28].

This paper is organized as follows. Section 2 provides a description of the Kitt Peak observation of ammonia in the optical region. Section 3 presents our analysis of this spectrum and Section 4 compares the results with those of previous studies. Conclusions are made in Section 5.

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