Journal of Quantitative Spectroscopy & Radiative Transfer 152 (2015) 28–36

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

A theoretical room-temperature line list for $^{15}NH_3$

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ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form
27 October 2014
Accepted 30 October 2014
Available online 7 November 2014

Keywords:
Ammonia
IR
Linelist
ab initio
HITRAN
Absorption

ABSTRACT

A new room temperature line list for $^{15}NH_3$ is presented. This line list comprised of transition frequencies and Einstein coefficients has been generated using the 'spectroscopic' potential energy surface NH3-Y2010 and an *ab initio* dipole moment surface. The $^{15}NH_3$ line list is based on the same computational procedure used for the line list for $^{14}NH_3$ BYTe reported recently and should be as accurate. Comparisons with experimental frequencies and intensities are presented. The synthetic spectra show excellent agreement with experimental spectra.

1. Introduction

Although the abundance of ^{15}N is 450 times lower than that of ^{14}N [1], $^{15}NH_3$ is an important astrophysical molecule. It is a maser source detected in interstellar molecular clouds [2] and is also a tracer of the $^{15}N/^{14}N$ isotopic ratio in interstellar medium [3–5], planetary [6,7] and Earth [8] atmospheres, meteorites [9], comets [10], important as a probe of chemical processes in the astrophysical environment, of planetary atmospheric and formation processes etc. Very recently Fletcher et al. [11] used the $^{14}NH_3$ and $^{15}NH_3$ spectral features to study the $^{15}N/^{14}N$ ratio for Jupiter and Saturn.

Experimentally the ro-vibrational spectra of $^{15}NH_3$ have been studied in a large number of works, including rotation-inversion spectra [12–17], fundamental bands [18–27], overtone bands [28–33], hot bands [34–37], and intensity measurements [38–41]. Some of these data are now collected in the HITRAN database [42]. The electric dipole moment was experimentally studied by Orr and Oka [43] and Dilonardo et al. [44] using the Stark spectroscopy. The ground state energies were reported by Urban et al. [22]. Very recently a VECSEL laser source study of the 2.3 μm region of $^{15}NH_3$ was presented by Čermák et al. [45] and a tentative assignment of new $^{15}NH_3$ lines in the 1.51 μm region was suggested by Földes et al. [46].

Huang et al. [47] presented theoretical ro-vibrational energies of $^{15}NH_3$ computed variationally using an empirical PES HSL-2 for $J = 0 \ldots 6$. These energies helped them to reassign and correct a number of transitions in HITRAN. An extensive hot line list BYTe for $^{14}NH_3$ was recently generated [48] using the TROVE approach [49]. Containing 1.1 billion transitions BYTe was designed to be applicable for temperatures up to 1500 K. It has proven to be useful for astrophysical and spectroscopic applications (see, for example, Refs. [45,50,51]). In this work we build a room temperature line list for the ^{15}N isotopologue of ammonia using the same computational approach based on the 'spectroscopic' potential energy surface (PES) NH3-Y2010 [52] and the *ab initio* dipole moment surface (DMS) from Ref. [53]. The highest J considered in this work is 18 defining the temperature limit of the current line list to be 300 K. It should be noted that TROVE was also used in

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http://dx.doi.org/10.1016/j.jqsrt.2014.10.023
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Table 1
Comparison of the theoretical term values (cm^{-1}) of $^{15}\mathrm{NH}_3$ before EBSC replacement and experimental ones used in the EBSC approach. See Table 7 for the description of the notations.

Γ_{vib}	v_1	v_2	v_3	v_4	L_3	L_4	L_4	Obs.	Calc.	Obs.-Calc.	Ref.
A_2''	0	0	0	0	0	0	0	0.761	0.758	0.003	[35]
A_1'	0	1	0	0	0	0	0	928.509	928.457	0.052	[35]
A_2''	0	1	0	0	0	0	0	962.912	962.894	0.018	[35]
A_1'	0	2	0	0	0	0	0	1591.236	1591.185	0.051	[28][a]
E'	0	0	0	0	1	1	1	1623.130	1623.149	−0.020	[28][b]
E''	0	0	0	0	1	1	1	1624.190	1624.202	−0.012	[28][b]
A_2''	0	2	0	0	0	0	0	1870.823	1870.853	−0.030	[30]
A_1'	0	3	0	0	0	0	0	2369.274	2369.314	−0.041	[28]
E'	0	1	0	0	1	1	1	2533.382	2533.380	0.002	[28][b]
E''	0	1	0	0	1	1	1	2577.571	2577.590	−0.020	[28][b]
A_2''	0	3	0	0	0	0	0	2876.144	2876.130	0.014	[28][a]
A_1'	0	0	0	0	2	0	0	3210.614	3210.430	0.184	[27]
A_2''	0	0	0	0	2	0	0	3212.335	3212.120	0.215	[27]
E'	0	0	0	0	2	2	2	3234.107	3233.925	0.182	[27]
E''	0	0	0	0	2	2	2	3235.504	3235.338	0.165	[27]
A_1'	1	0	0	0	0	0	0	3333.306	3333.220	0.086	[27]
A_2''	1	0	0	0	0	0	0	3334.252	3334.160	0.092	[27]
E'	0	0	1	1	0	0	1	3435.167	3435.143	0.024	[27]
E''	0	0	1	1	0	0	1	3435.540	3435.475	0.065	[27]
A_1'	1	1	0	0	0	0	0	4288.186	4288.024	0.162	[22]
A_2''	1	1	0	0	0	0	0	4312.345	4312.304	0.041	[22]
E'	1	0	0	0	2	2	2	6546.951	6546.987	−0.036	[60]
E''	1	0	0	0	2	2	2	6548.560	6548.449	0.111	[60]
E'	1	0	1	1	0	0	1	6596.569	6596.605	−0.036	[32]
E''	1	0	1	1	0	0	1	6597.607	6597.498	0.109	[32]
E'	1	0	1	1	0	0	1	6664.486	6664.627	−0.141	[33]
E''	1	0	1	1	0	0	1	6665.480	6665.303	0.177	[33]

[a] Estimated from the $a \to s$ band centers.

[b] Estimated from the corresponding ${}^{p}P(J=1, k=1)$ transition frequencies.

the study of the thermal averaging properties of the spin–spin coupling constants of $^{15}\mathrm{NH}_3$ by Yachmenev et al. [54] and a high-temperature partition function for $^{14}\mathrm{NH}_3$ [55].

The paper is structured as follows. In Section 2 we outline the theoretical approach used for the line list production. In Section 3 the structure of the line list and the description of the quantum numbers are presented, where some comparisons with experimental data are also given and the accuracy of the line list is discussed.

2. Theoretical approach

We use the same computational procedure and the associated program TROVE [49] as was employed to generate the hot ammonia line list BYTe [48], therefore the reader should refer to this paper for a detailed description. Here we present only a short outline of this approach.

In order to obtain energies and associated wavefunctions required for building the line list of $^{15}\mathrm{NH}_3$ we solve the Schrödinger equation for the nuclear motion variationally. Both the kinetic and potential energy terms of the Hamiltonian were expanded to 6th and 8th orders, respectively, in terms of five linearized coordinates around the reference geometry, defined as a non-rigid reference configuration associated with the inversion motion characterized by a relatively low barrier to the planarity. The linearized coordinates are chosen to be close to the three stretching modes associated with the N–H vibrations and two asymmetric bending modes combined from the three bending vibrations of the interbond angles H–N–H. Our vibrational basis set is a product of six one-dimensional (1D) basis functions. The stretching, bending, and inversion 1D basis sets are obtained by solving the corresponding reduced 1D Schrödinger equations using the Numerov–Cooley approach [56,57] for each degree of freedom independently. This so-called primitive basis set is then improved through a number of pre-diagonalizations and consecutive contractions. The latter is controlled by the polyad number:

$$P = 2(v_1 + v_2 + v_3) + v_4 + v_5 + v_6/2, \tag{1}$$

where v_1, v_2, v_3 are the quantum numbers associated with the three stretching modes, v_4, v_5 are associated with the asymmetric bending modes, and v_6 counts the inversion mode functions. As in Ref. [48], we define the size of the basis set using the condition $P \leq 14$. We use the so-called $J=0$ representation, where the final contracted ro-vibrational basis functions are represented by direct symmetrized products of the vibrational $J=0$ eigenfunctions and the rigid rotor wavefunctions $|J, K, \tau_{\mathrm{rot}}\rangle$, where J is the rotational angular momentum, K is the projection of the