Rotational analysis of the inversion-vibrational spectra of the $^{15}NHD_2$ molecule: ν_6 fundamental band

A L Fomchenko, A S Belova and A V Kuznetsov

Research School of High-Energy Physics, National Research Tomsk Polytechnic University, Tomsk, 30 Lenin av., 634050, Russia

E-mail: fomchenko@tpu.ru

Abstract. This paper considers an assignment of the high-resolution Fourier spectra of $^{15}NHD_2$ molecule in the region of ν_6 band. The analysis is based on the combination differences method. As a result of the analysis, the energy structure of inversion-vibrational states ($\nu_6=1$, s) and ($\nu_6=1$, a) was obtained. More than 550 vibration-rotation transitions were found and values of about 140 upper vibrational energy levels were determined in total.

1. Introduction

High-resolution infrared and microwave spectra of molecules are a source of important information about the internal structure and physical properties of molecules. One of the most common methods for analyzing experimental rotational spectra is based on using the effective Hamiltonian model. The use of such a model makes it possible to determine many spectroscopic constants, primarily rotational constants, which contain information about the structure of the molecule. In addition, solving an inverse spectroscopic problem with an effective Hamiltonian makes it possible to obtain centrifugal distortion parameters. A complete analysis of the rotational spectrum of the ground and lower excited vibrational states gives accurate information about the energies of the interacting vibrational states, as well as more detailed information about the corresponding intramolecular interactions occurred because of the resonances.

Present study is devoted to the high resolution study of di-deuterated ^{15}N-ammonia species. During the decades, gaseous ammonia is known to have played a key role in atmospheric chemical processes and in the bio-, geo-chemical processes that occur in sensitive ecosystems (forests, soils, streams, and coastal waters) after the deposition. Astrophysical monitoring of ammonia allows one to recognize both main mother molecule and its isotopically substituted species as an important gas tracers for characterizing different evolutionary stages before and after the formation of stars [1-4]. Thus, high resolution study of ammonia and its isotopologues gives possibility to supplement the line lists needed and used for astrophysical applications. From the theoretical point of view, the inversion at the pyramidal nitrogen atom is among the most interesting theoretical problems in intramolecular dynamics and, in particular, tunneling dynamics, including the possibility of molecular chirality with appropriate substitution [5].

At present, there are already data on studies of the ammonia molecule and its isotopologues (for example, [6-9]), some of which are presented in the HITRAN database. However, for a complete and correct description of the intramolecular structure of ammonia, it is necessary to have data on all its isotopologues. In this article, we continue the analysis of the ammonia molecule.

2. Experimental part

The high-resolution absorption spectra of the $^{15}NHD_2$ molecule were recorded using the Bruker IFS 125HR Fourier transform spectrometer at LISA in Créteil (France). Experimental setup one can see in Table 1 for both spectra. Due to the rapid exchange of H / D, spectra have a significant number of lines belonging to the isotopologues of $^{15}NH_2D$, $^{15}NHD_2$, $^{15}NH_3$ and $^{15}ND_3$. The spectra were recorded at a stabilized room temperature of (297 ±1) K and calibrated with CO_2 and H_2O lines. The resulting accuracy of recorded spectra is ±0.0003 cm^{-1} for well isolated lines.

Table 1. Experimental setup for the spectral region 1000 – 1800 cm^{-1}.

Spectrum	Resolution, cm^{-1}	Optical path length, m	Pressure, Pa	Temperature, K	Measuring time, h	No of scans	Calibration gas
I	0.004	5.649	237.5	297	8	320	CO_2, H_2O
II	0.004	5.649	52.1	297	10.5	420	CO_2, H_2O

3. Theoretical part

The $^{15}NHD_2$ molecule is an asymmetric top with values of the three rotational parameters close to 7.45, 5.37, and 3.80 cm^{-1}. $^{15}NHD_2$ is the deuterated isotopologue of the NH_3 molecule, which is very well studied in ro-vibrational spectroscopy. For that reason, the most of the effects and features, which are peculiar to the NH_3 molecule, can also be found in the $^{15}NHD_2$ one. It is, first of all, inversion motion in the ammonia molecule which, in combination with the isotopically substituted configuration of $^{15}NHD_2$, leads to a very complicated picture of the ro-vibrational spectra.

Figure 1 shows equilibrium configuration of mother molecule NH_3 and isotopologue $^{15}NHD_2$. Taking into account the numbering of nuclei and orientation of axes in the $^{15}NH_2D$ molecule one can easily estimate the values of the equilibrium inertia momenta of the $^{15}NH_2D$ molecule and to show that the following relation is fulfilled: $I_{zz}^e > I_{xx}^e > I_{yy}^e$.
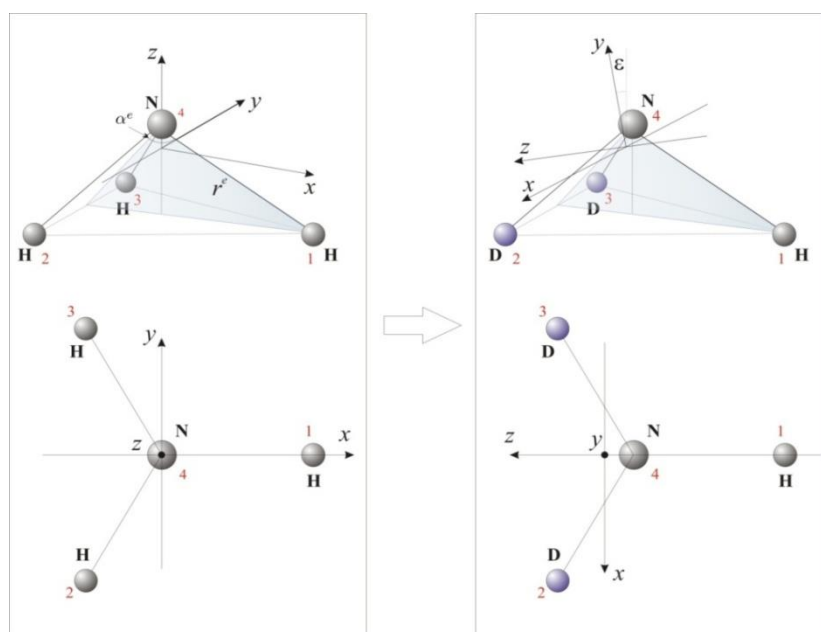

Figure 1. Equilibrium structure of ammonia molecule NH_3 and isotopologue $^{15}NHD_2$.

At the same time, the mostly efficient and the widely used model of the Hamiltonian of asymmetric top molecule (the *A*-reduction and *I^r*-representation) assumes that for the rotational parameters the following relations are fulfilled: $I_{yy}^e > I_{xx}^e > I_{zz}^e$. To satisfy these conditions in our case, it is necessary to replace the coordinate axis of the molecular fixed coordinate system: z axis by the y axis, and y axis by the z one.

To provide the assignment of spectra method of combination differences was used. Such an efficient method requires some theoretical calculations. First, one needs to know the energy structure of ground state of the studied molecule with high accuracy. As there is inversion motion in ammonia molecule, the ground state of $^{15}NHD_2$ consists of two sub-states, (GS, *s*) and (GS, *a*). The parameters of ground state were taken from [10].

Secondly, it is important to know the selection rules specific to the studied band. In accordance with the general principles of quantum mechanics (see, for example, [11]), the possibility of the transition from the quantum state | φ> to another quantum state | ф> is determined by the inequality to zero of the square of the matrix element of the dipole moment P_Z (here P_Z is the component dipole moment operator in the laboratory coordinate system) on the functions | φ> and | ф>. Due to the symmetric properties of the molecule and considering that operator of the dipole moment P_Z of a molecule is transformed in accordance with the irreducible representation A_2 of the C_{2v} group one can show that the ν_6 band consists of two sub-bands of the *b*-type: ν_6 (*s←s*) and ν_6 (*a←a*). So selection rules are: $\Delta J=0,\pm1$; ΔK_a=odd; ΔK_c=odd (*s←s*) or (*a←a*).
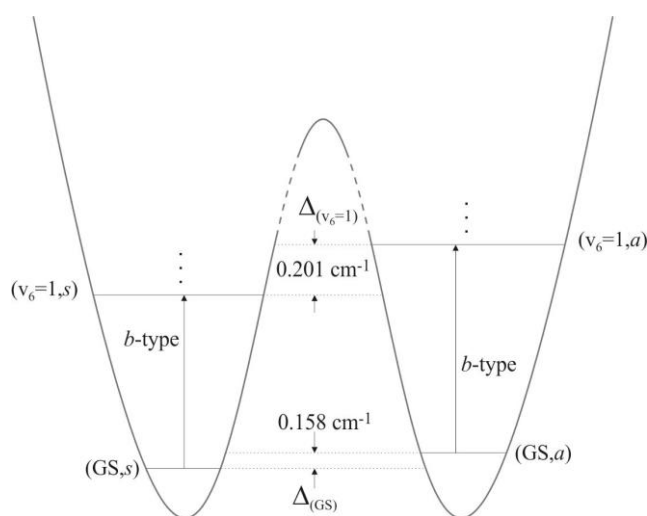

Figure 2. Scheme of possible transitions in the ν_6 band of the $^{15}NH_2D$ molecule. Types of possible rotation-inversion-vibration transitions are marked.

4. Results of analysis

To solve the inverse spectroscopic problem and obtain spectroscopic parameters, one needs to provide assignment of the inversion-vibrational-rotational transitions. In the part (a) of Figure 3 one can see the central part (Q-branch) of the ν_6 inversion–vibration band of the $^{15}NHD_2$ molecule. The presence of two strongly interacting sub-bands ν_6 (*s←s*) and ν_6 (*a←a*) leads to complicated picture of the spectrum with the absence of regular structure of transitions. One can see two closely located sub-band centres near 1459 cm^{-1}. A small part of the high-resolution spectrum is presented in the part (b) of Figure 3. The assignment is also complicated by the fact that the sample is consists of mixture of different ammonia isotopologues ($^{15}NH_3$, $^{15}ND_3$, $^{15}NH_2D$, $^{15}NHD_2$).

As the result of analysis, more than 550 transitions belonging to the two sub-bands ν_6 (*s←s*) and ν_6 (*a←a*) were assigned in the experimental spectrum. Correctness of assignment was confirmed by the presence of numerous combination differences. Small part of assigned transitions and energies of upper state is presented in Table 2. We obtained the values of about 140 upper energy levels of (ν_6=1, *s*) and (ν_6=1, *a*) states with the values of quantum numbers $J^{max.}$ / $K_a^{max.}$ equal to 11/6.

The obtained data will be used as an input in a weighted least square fit with the aim to determine rotational, centrifugal distortion, and resonance interaction parameters of the effective Hamiltonian. As an outcome the set of spectroscopic parameters will be obtained.
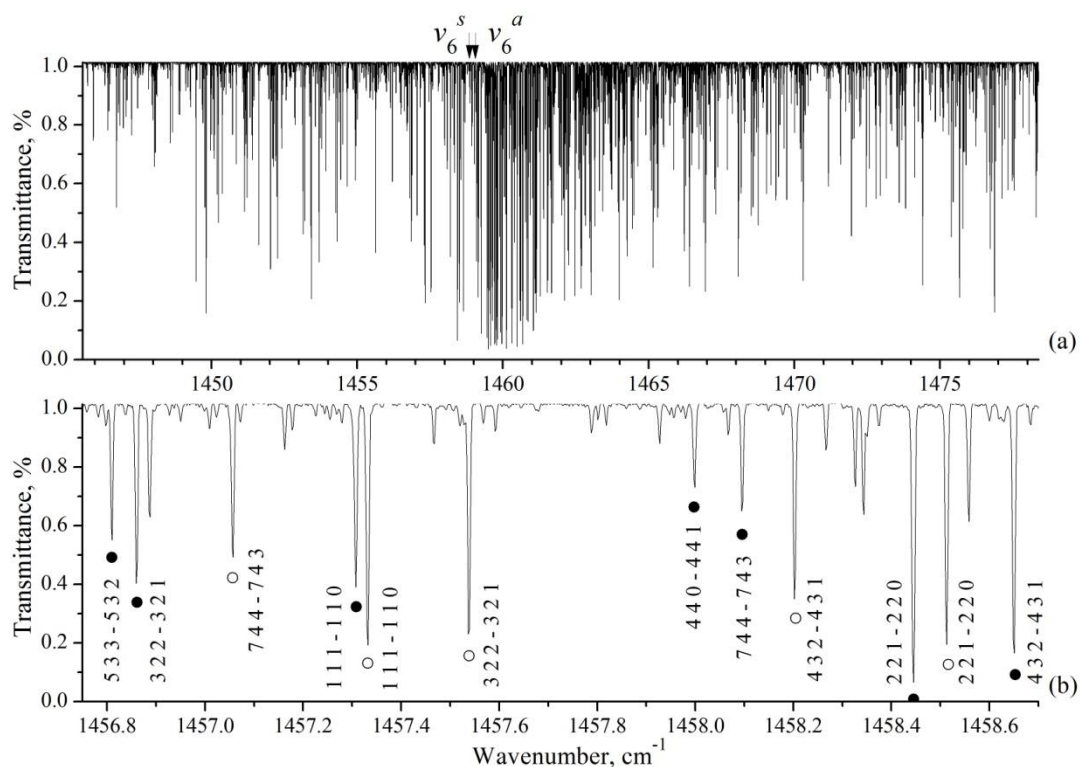

Figure 3. The central part (Q-branch) of the ν_6 inversion-vibration band of the $^{15}NHD_2$ molecule of the spectrum II (part a). Fragment of the high-resolution spectrum II in the 1456.75–1458.70 cm^{-1} region (part b). Lines belonging to the ν_6^s and ν_6^a bands are marked by dark and open circles, respectively. Quantum numbers $J\,K_a\,K_c$ of upper and lower states are indicated.

Table 2. Small part of assigned transitions and energies of (ν_6=1, s) and (ν_6=1, a) states.

Quantum numbers of upper state			Quantum numbers of groung state			Wavenumber	Transmittance	Energy	Spectrum	State
J	K_a	K_c	J	K_a	K_c	cm^{-1}	%	cm^{-1}		
			2	2	0	1458.4450	6.2			
2	2	1	2	0	2	1471.1693	57.9	1497.7789	II	(ν_6=1, s)
			3	2	2	1431.8411	19.7			
			2	2	1	1486.7880	46.6			
3	2	2	3	2	1	1456.8601	38.9	1525.4895	II	(ν_6=1, s)
			3	0	3	1473.7093	86.6			
			4	2	3	1423.7597	23.7			
			3	2	2	1495.9239	12.2			
4	3	2	4	2	2	1453.6901	33.2	1561.8615	II	(ν_6=1, s)
			4	0	4	1477.5766	73.8			
			5	2	4	1416.1519	8.6			
			4	2	3	1504.1970	29.9			
5	2	4	5	2	3	1448.5886	73.5	1605.9269	II	(ν_6=1, s)
			5	0	5	1481.7664	90.3			
			6	2	5	1408.3765	29.7			

			5	2	4	1512.7898	9.3			
6	2	5	6	2	4	1443.3029	56.0	1658.4992	II	$(v_6=1, s)$
			6	0	6	1487.0378	81.8			
			7	2	6	1401.4713	9.6			
			6	2	5	1520.9864	31.1			
7	2	6	7	2	5	1437.8203	78.6	1718.5367	II	$(v_6=1, s)$
			7	0	7	1492.3315	93.7			
			8	2	7	1394.5185	34.4			
			3	3	0	1459.2608	8.9			
3	3	1	3	1	2	1478.3809	94.6	1540.1487	II	$(v_6=1, a)$
			4	3	2	1422.2266	47.3			
			3	3	1	1496.4982	54.6			
4	3	2	4	3	1	1458.2028	34.2	1577.1957	II	$(v_6=1, a)$
			4	1	3	1477.7535	94.7			
			5	3	3	1412.9429	37.6			
			4	3	2	1505.4160	18.7			
5	3	3	5	3	2	1455.6316	36.4	1623.3382	II	$(v_6=1, a)$
			5	1	4	1478.5716	84.1			
			6	3	4	1403.9847	18.9			
			5	3	3	1514.1296	40.6			
6	3	4	6	3	3	1451.3903	76.5	1678.3826	II	$(v_6=1, a)$
			6	1	5	1481.0923	87.9			
			7	3	5	1395.5711	47.4			
			6	3	4	1522.7468	20.7			
7	3	5	7	3	4	1445.9450	73.1	1742.1002	II	$(v_6=1, a)$
			7	1	6	1485.0609	80.0			
			8	3	6	1387.8546	29.3			

5. Conclusion

We performed the first analysis of the high resolution IR spectra of the $^{15}NHD_2$ molecule in the region of $1000 - 1800$ cm^{-1}, where the fundamental v_6 band is located. More than 550 transitions belonging to this band were assigned in the experimental spectra with the maximum values of quantum numbers $J^{max.}/K_a^{max.}$ equal to 11/6. Information obtained from the experimental data will be used as initial data in the weighted fit procedure for determination of spectroscopic parameters of $(v_6=1, s)$ and $(v_6=1, a)$ states.

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