ROTATIONAL ANALYSIS OF THE INVERSION-VIBRATIONAL SPECTRA OF THE $^{15}NHD_2$ MOLECULE: ν_6 FUNDAMENTAL BAND

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ВРАЩАТЕЛЬНЫЙ АНАЛИЗ ИНВЕРСИОННО-КОЛЕБАТЕЛЬНОГО СПЕКТРА МОЛЕКУЛЫ $^{15}NHD_2$: ФУНДАМЕНТАЛЬНАЯ ПОЛОСА ν_6

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Аннотация. *В настоящей работе было впервые проведено исследование Фурье-спектра высокого разрешения молекулы $^{15}NHD_2$ в районе фундаментальной полосы ν_6. Анализ выполнен на основе метода комбинационных разностей основного состояния. В результате анализа двух инверсионно-колебательных состояний ($\nu_6 = 1, s$) и ($\nu_6 = 1, a$) было найдено более 550 колебательно-вращательных переходов и определены значения около 140 верхних колебательных уровней энергии.*

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. As the result of solution of the inverse spectroscopic problem based on that model, one can determine many spectroscopic constants, which contain information about the structure and properties of the molecule. The first and the most important step in solving the inverse spectroscopic problem is the accurate assignment of the transitions. 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, particular to transitions assignment. 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 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. At present, there are already data on studies of the ammonia molecule and its isotopologues (for example, [5-7]), some of which are presented in the HITRAN database. However, the studied region was analyzed for the first time.

Theoretical background. To provide the assignment of spectra the usual for such purposes method of combination differences was used. Such an efficient method requires some theoretical calculations. First, one needs to know the ground state of the studied molecule with high accuracy. The data concerning the ground state were taken from the work [8]. 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, [9]), the possibility of the transition from the quantum state | φ> to another quantum state | ϕ> 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 | ϕ>. 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: ν_6 (s←s) and ν_6 (a←a) with a-type transitions. So selection rules are $\Delta J=0,\pm1$; ΔK_a=even; ΔK_c=odd.

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 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

Assignment of the transitions. To solve the inverse spectroscopic problem and obtain spectroscopic parameters, one needs to provide assignment of the inversion-vibrational-rotational transitions. The assignment was done using the usual for such purposes method of combination differences. As a result of assignment, more than 550 vibrational-rotational transitions were obtained. In the Figure 2, one can see the fragment of assigned high-resolution transitions.

As it could be noticed in the Figure 2 Q-branches of both states have a specific structure atypical for asymmetric top molecules which the studied molecule belongs to. The standard model expects the strong correspondence between quantum number J and the wavenumber of the transition (with an increase / decrease of quantum number J, the wavenumber of the transition increases / decreases, respectively). Nevertheless, in real spectra this dependency is not satisfied. It could be explained by the interaction between several states located close to each other. Band centers of (v_6 = 1, s) and (v_6 = 1, a) states are 1458.87 and 1458.67 cm^{-1}, respectively. This fact leads to the appearance of the Coriolis resonance and complication of the spectrum structure.

Conclusion. As a result more than 550 vibrational-rotational transitions belonging to (v_6 = 1, s) and (v_6 = 1, a) inversion-vibration states were obtained and values of about 140 upper vibrational energy levels with the maximum values of quantum numbers J^{max}=11, K_a^{max}=6 were determined. This data will be used as input data 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.

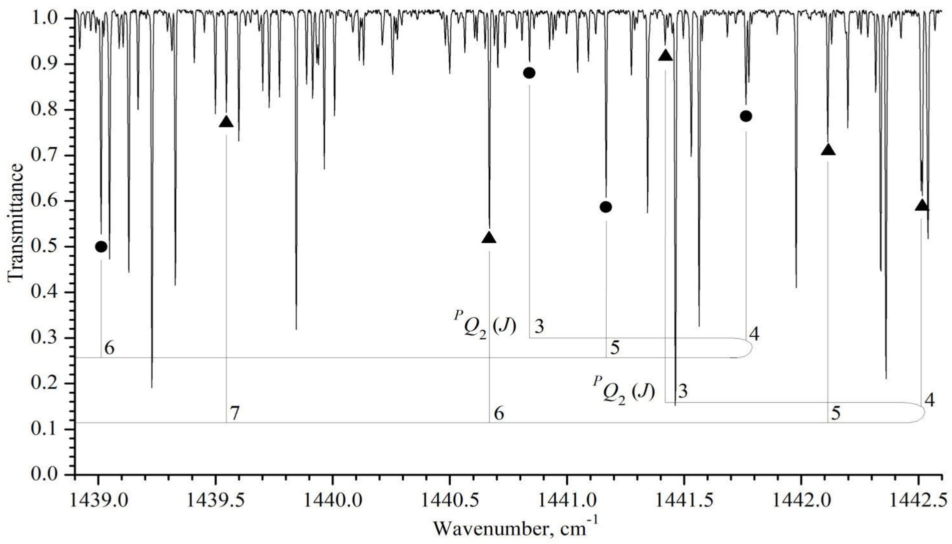

Fig. 1. The fragment of assigned transitions of the high-resolution spectrum of $^{15}NHD_2$ in the Q-branch region. Triangles correspond to ν_6^a band and circles are connected with ν_6^s band

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