Reinvestigation of the inversion band of methylamine

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Motivation

Two large amplitude motions of methylamine, inversion/wagging and internal rotation, are strongly coupled. The band centers of fundamental bands for internal rotation (ν_{15}) and wagging (ν_9) occur at 264.6 cm^{-1} and 779.6 cm^{-1}, respectively.

Earlier analyses [1,2] left a number of series in the ν_9 band unassigned (Table 1). This problem could result from strong local perturbations between the **wagging** and **third** and **fourth excited torsional** states (Fig.1 based on Ref.[3]) and inadequate tools for searching weak lines in a congested spectrum of a LAV molecule.

The aim of this work was to extend the assignment to perturbed series of the wagging band in a new high resolution spectrum of methylamine in the region from 640 to 960 cm^{-1} using extensively the LWW software for the LAV molecule.

The LWW software for symmetric and asymmetric top molecules was subject of earlier reports (http://www.lww.amu.edu.pl) . Here a new version specific for LAV molecules is applied.

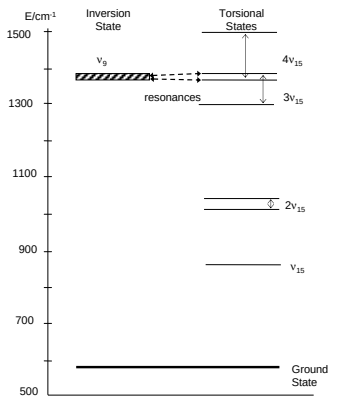

Fig. 1. Energies of the inversion-torsional states of CH_3NH_2

Experimental data

The high-resolution spectrum of methylamine has been recorded at the University of Oulu in Finland using Bruker IFS-120HR Fourier transform spectrometer in the range from 640 cm^{-1} to 960 cm^{-1} at a pressure of 0.039 Torr with the path length of 3.2 m in the optimized White cell at a temperature of 20ºC. Total registration time was 69 h 36 min.

The resolution due to MOPL = 0.0012 cm^{-1}. The resolution due to APT = 0.0011, 0.0013, 0.0014, 0.0016 cm^{-1} and Doppler broadening = 0.0013, 0.0015, 0.0017 and 0.0019 cm^{-1} at 700, 800, 900, and 1000 cm^{-1}, respectively..

The relative wavenumber precision is one order of magnitude better than the respective resolution.

Fig. 2. Part of the methylamine spectrum showing the structure of the $^{P}Q_1$(B) branch and two LW diagrams with the $^{P}Q_1$(B) and $^{Q}P_0$ (B) branches.

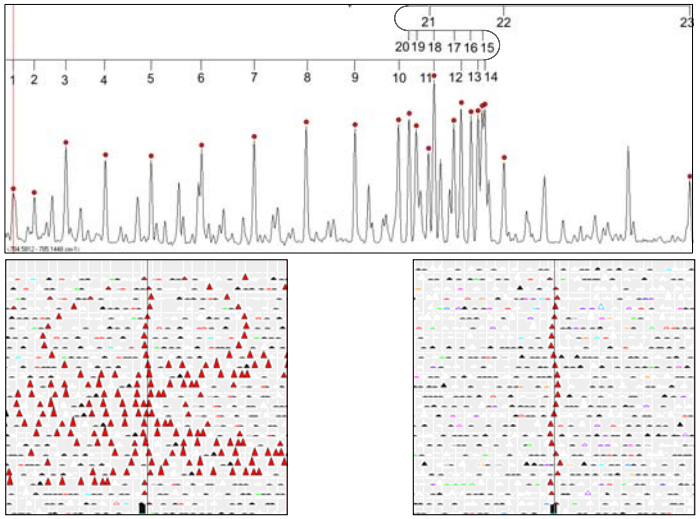

Table 1. The summary of the results of the previous and present analyses.

Symmetry species	Earlier analyses [1, 2]		Present analysis	
	Max K' assigned	Missing series	Max K' assigned	Missing series
A	13	K'=0, 1, 2, 3, 4	13	K'=0
B	17	K'=0	18	
E_{1+1}	12	K'=3	13	
E_{1-1}	10	K'=0, 1, 2	15	K'=11
E_{2+1}	9	K'=0,1,2,3,4,5	9	K'=3
E_{2-1}	9	K'=0, 1, 2, 3, 4, 5	10	

LWW program for LAV molecules

The LWW software has been developed to be used for molecules with large amplitude motions such as methylamine or hydrazine and its role in the present analysis was crucial.

In the methylamine spectrum it was possible to assign successfully very weak lines since the LWW making use of the energy file could predict the lines positions.

Great advantage for the series identification is the automatic use of the GSCD.

The LW diagrams can be displayed simultaneously with the spectra, which helps a lot in the assignment.

The LWW software for LAVs includes a window for adding either a specified branch or a set of the appropriated type of branches for a chosen range of K quantum number (Fig.3).

The search of strongly perturbed series was greatly facilitated by simultaneous display of Q-type branches together with P and R branches in the LW diagrams (see Fig. 2).

Other features of the LWW software are presented in a separated poster.

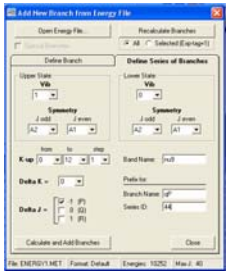

Fig. 3. Adding new branches in the LWW software

Each rotational transition in a branch is labeled with the vibrational number, J and K rotational numbers, and symmetry species.

Table 2. The perturbed series in the inversion band.

The series	Shift [cm^{-1}]
K'=0 (B)	4.0
K'=6 (E_{1-1})	1.5
K'=13(E_{1-1})	1.0
K'=14 (B)	0.8
K'=14 (E_{1-1})	0.4
K'=3 (E_{1-1})	0.2
K'=11 (A)	0.2
K'=12 (E_{1+1})	0.2
K'=3 (E_{1+1})	0.2
K'=2 (E_{2-1})	0.1

New assignment of the first excited inversion band (ν_9) of methylamine

1. Newly identified series

- The summary of newly assigned branches is given in Table 1.
- The K'=0 series of B symmetry species have been identified, which is the most important result. They are strongly perturbed and thus shifted from the predicted frequencies as far as 4 cm^{-1} (Fig. 2).
- From the low K' series of substantial intensity unassigned in earlier papers, the K'=0, 1, 2 set of series of the E_{1-1} symmetry and the K'=3 set of series of the E_{1+1} symmetry have also been found. They are slightly perturbed as shown in Table 2.
- The entire set of weak or very weak series of A, E_{2+1} and E_{2-1} symmetry species has been identified.
- Each set of intensive series (of B, E_{1+1} and E_{1-1} symmetry) has been completed with the series ^{P}R and ^{R}P. Some weak series of low K values have been completed with the PR and RP transitions.
- For low K values (K'=0 and 1) transitions of mixed types have been also observed: $E_{1+1} \leftrightarrow E_{1-1}$.
- Most series extend as far as J=40 comparing to 30 in earlier papers.
- In total, the present number of assigned lines in the inversion band is about 13000 (see Fig.4) whereas earlier there were about 5000 lines identified [1].

2. Still unassigned lines

There are still problems with finding three sets of series: K'=0 for A symmetry, K'=11 for E_{1-1} and K'=3 for E_{2+1} (Table 1). The series of A and E_{2+1} symmetries are of low intensities and if they are shifted (probably are), it is difficult to identify them. For the K'=11 series of the E_{1-1} symmetry, it is possible that the lines are perturbed since the series for higher K' values have been identified.

Plans

1) All assigned experimental data will be fit globally using a new model for two interacting states, ν_9=1 and ν_{15}=3 or 4 [3].
2) Other bands belonging to the methylamine spectrum will be analyzed in a systematic way.

References

[1] M. Kręglewski, F. Winther, J.Mol.Spectrosc. 156, (1992) 261-291

[2] L. Sztraka, S. Alanko., M. Koivusaari, J. Mol. Structure 410-411 (1997) 391-395

[3] I. Gulaczyk, M. Kręglewski, J. Mol. Spectrosc. 256 (2009) 86-90

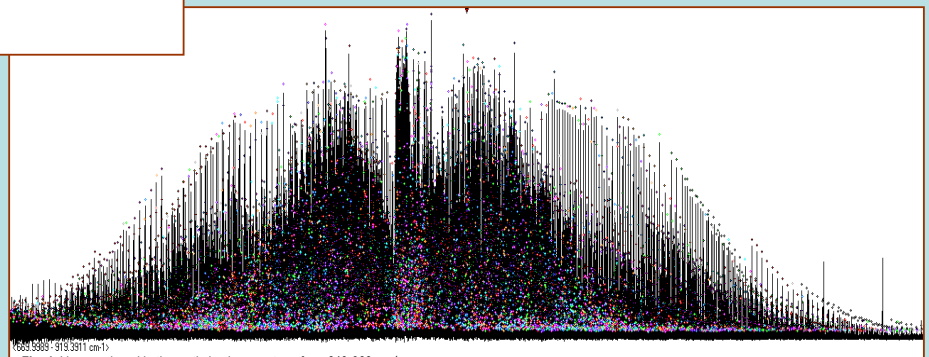

Fig. 4. Lines assigned in the methylamine spectrum from 640-960 cm^{-1}.