ACCURATE ROVIBRATIONAL ENERGIES FOR THE FIRST EXCITED TORSIONAL STATE OF METHYLAMINE

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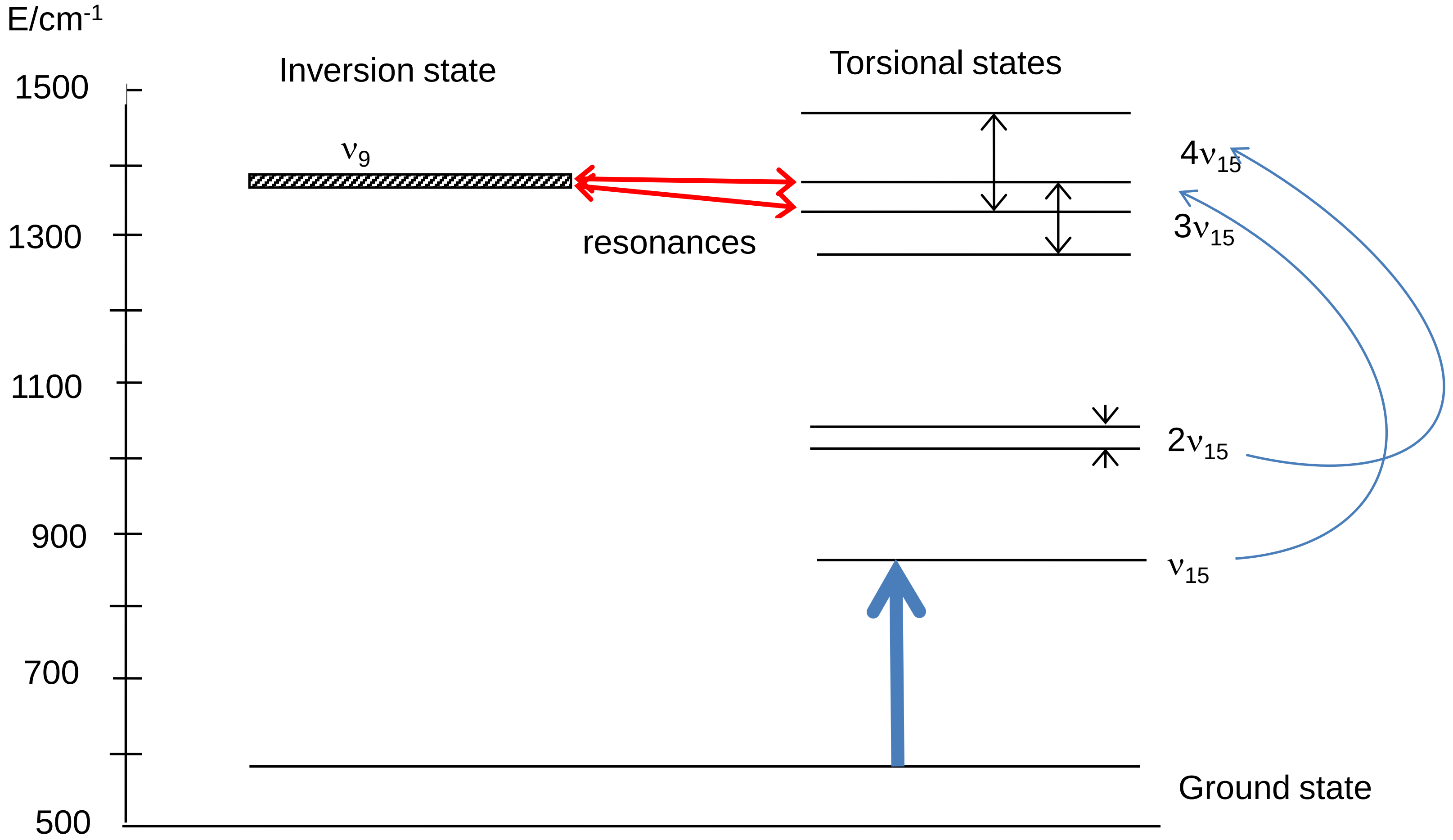
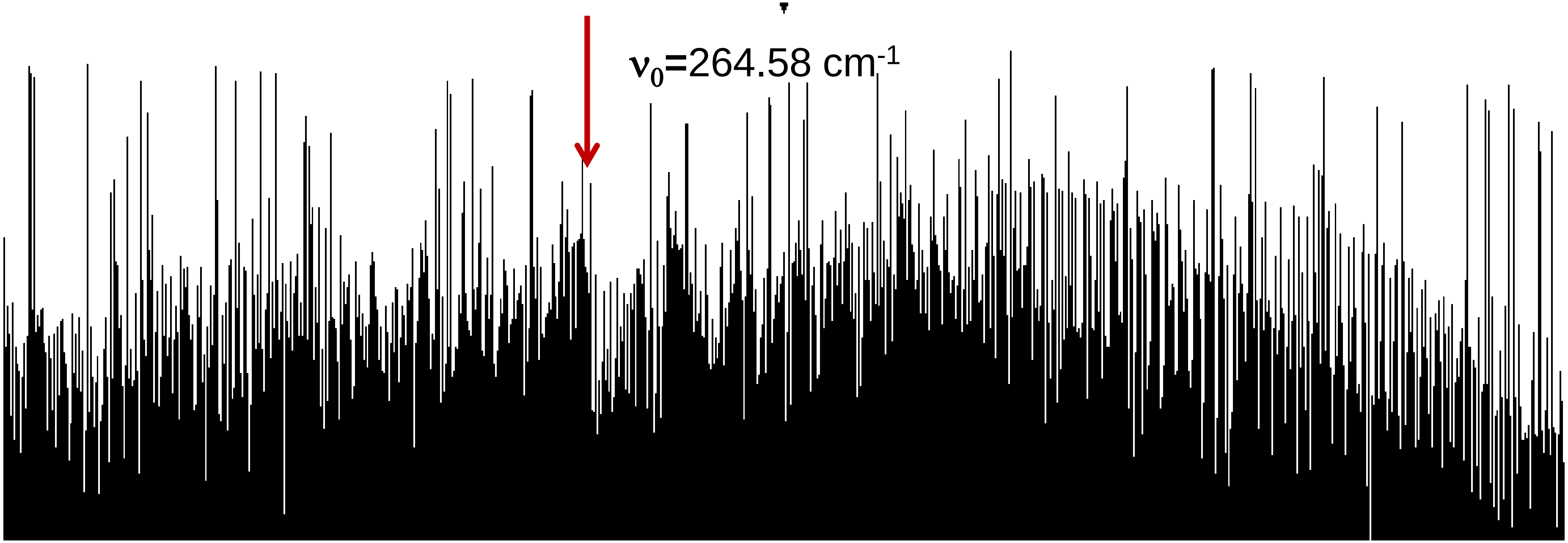
Energies of the inversion-torsional states of CH_3NH_2



Goal of the study

- Assignment and analysis of the hot bands $\nu_{15}\rightarrow 2\nu_{15}$, $\nu_{15}\rightarrow 3\nu_{15}$, $\nu_{15}\rightarrow 4\nu_{15}$ on the basis of the energies of the first excited torsional state (ν_{15})
- Accurate rovibrational energies for the second and third torsional states ($2\nu_{15}$, $3\nu_{15}$)
- Resonances between inversion (ν_9) and the third and fourth excited torsional states ($3\nu_{15}$, $4\nu_{15}$)

The torsional band spectrum of methylamine

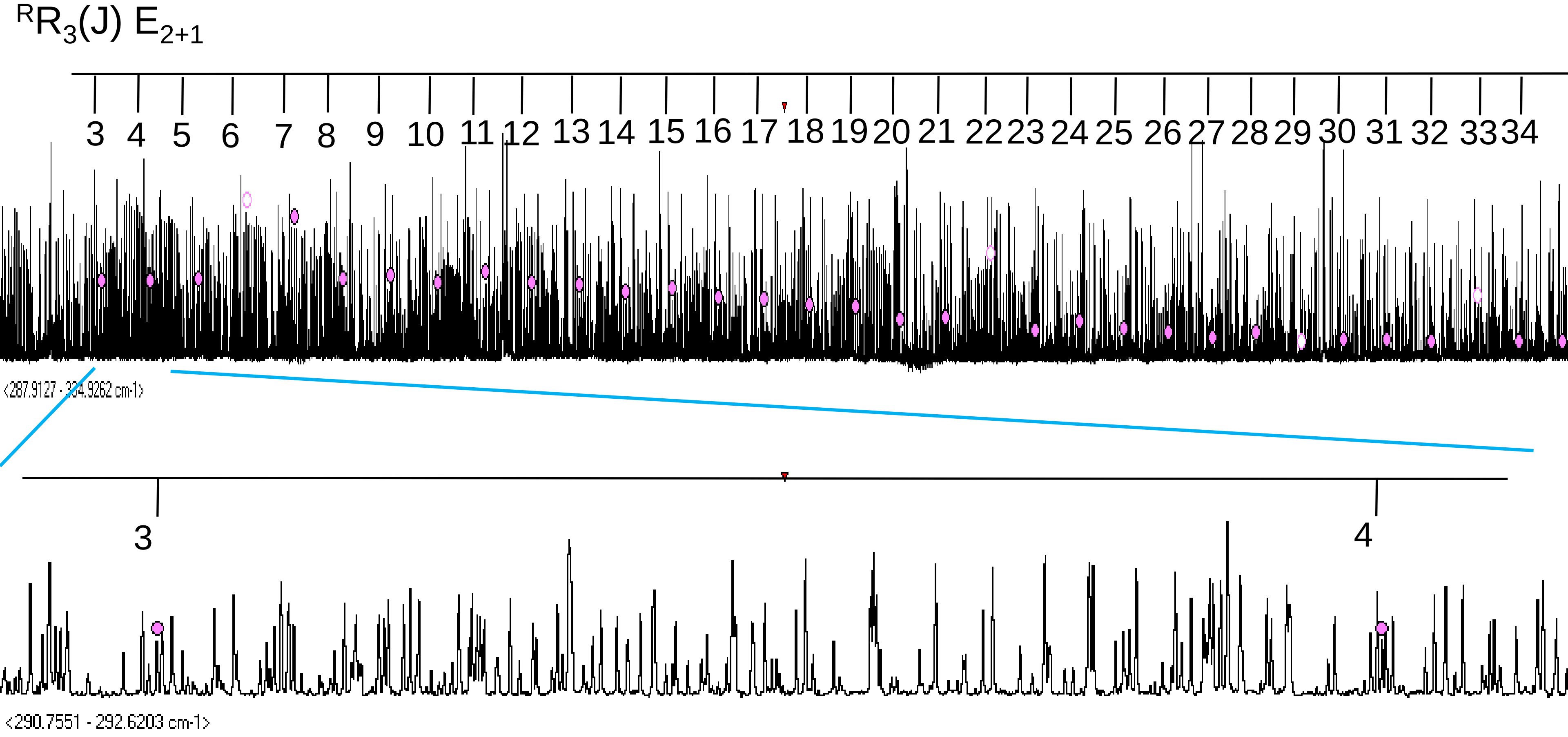


Spectrum: Veli-Matti Horneman, University of Oulu
Bruker IFS-120HR
Range 40 cm^{-1} to 360 cm^{-1}
Number of peaks = 67522

0.36 Torr, 3.2 m
The operating temperature of the bolometer 1.4 -2 K
Resolution due to MOPD = 0.00125
Registration time 37.9 h.

Fragment of the IR ν_{15} band

The structure of the $^RR_3(E_{2+1})$ branch



The first torsional band of methylamine (ν_{15})

1) A near prolate asymmetric rotor
2) Internal rotation and inversion splittings in the ground state: ≤0.3 cm^{-1} and ≤0.2 cm^{-1}, respectively.
3) B-type band (selection rules: $\Delta K = \pm 1$, $\Delta J = 0, \pm 1$).
4) At higher K each symmetric rotor transition split into 6 components: one $A_1 \leftrightarrow A_2$, one $B_1 \leftrightarrow B_2$, two $E_1 \leftarrow E_1$, two $E_2 \leftarrow E_2$ with statistical weights of 2, 6, 3, 1, respectively.
5) At lower K doubled splittings for A and B components (asymmetric rotor effects).
6) The high-frequency side dominated by strong resolved Q branches and ^{r}R-branch series.
7) Near the band center - 264.5825(60) cm^{-1}, the Q branches spread over a large spectrum region make many weak lines obscure.

Analysis of the first excited torsional band (ν_{15}) of methylamine

1) The LWW for LAV molecules software [1] used extensively for assignment, which is confirmed through the ground state combination differences (Loomis – Wood schemes).
2) The global fit carried out using a Hougen-Ohashi effective Hamiltonian [2] (the ν_{15} state-an isolated state split into several sublevels of A, B, E_1 and E_2 symmetry) including infrared (over 11000 transitions assigned), pure rotational and microwave data (from literature)

$$\hat{H} = \sum_{v} \left\{ \begin{array}{l} h_v + h_{vj} J^2 + h_{vk} J_z^2 + \left(f_{v+}^2 J_+^2 + f_{v-}^2 J_-^2 \right) + q_v J_z + \\ + \frac{1}{2} \left[s_{v+} \left(J_+ J_z + J_z J_+ \right) + s_{v-} \left(J_- J_z + J_z J_- \right) \right] + \\ + \left(r_{v+} J_+ + r_{v-} J_- \right) + higher \quad order \quad terms \end{array} \right\}$$

[1] W.Łodyga, M.Kręglewski, P.Pracna, Š. Urban, *J.Mol.Spectrosc.* **243**, 182-188 (2007)
[2] N. Ohashi and J. T. Hougen, *J.Mol.Spectrosc.* **121**, 474-501 (1987)

Analysis of the first excited torsional band (ν_{15}) of methylamine

3) Ground state constants were fixed to the values determined by Ilyushin et al. [3].
4) Over 11000 lines of the first torsional state with $0 \le K \le 16$ and $K \le J \le 40$ were fit to 58 molecular parameters.
5) Weighting inversely proportionate to the square of precision: IR data (precision 0.0004 cm^{-1}) and MW (precision 0.1 MHz), the number of IR data much higher than that of MW data – the weighting of IR data artificially lowered
6) Results of global fitting for the first torsional state:

   - IR data: σ=0.0039 cm^{-1}, number of transitions=11300
   - IR of pure rotational data: σ= 0.0038 cm^{-1}, number of transitions=88
   - MW data: σ= 0.69 MHz, number of transitions=218

[3] V.V. Ilyushin, E. A.Alekseev, S.F.Dyubko, R.A.Motiyenko, J.T.Hougen, *J.Mol.Spectrosc.* **229**, 170-187 (2005)

Present versus previous analyses

Present work (J ≤ 40):

- MW lines from earlier measurements [4,5]
- Complete assignment of over 11000 IR lines for all symmetry species
- Standard deviation 0.0039 cm^{-1}

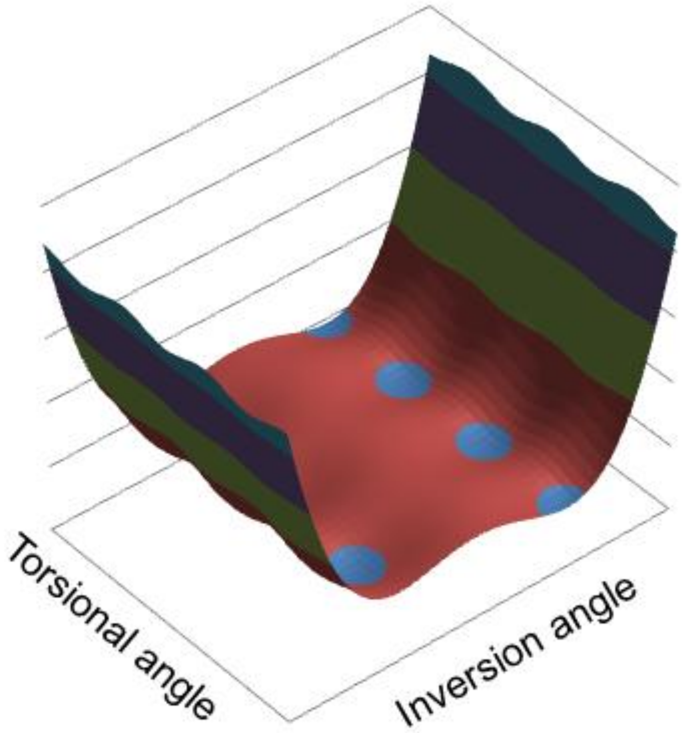
Previous works (J≤30) [4,5]:

- Assignment of IR transitions of B and E_{1+1} symmetry
- Incomplete assignment for IR lines of A and E_{1-1} symmetry
- Lack of IR lines of E_2 symmetry
- Standard deviations for over 700 IR and MW transitions: 0.00095 cm^{-1}

[4] N.Ohashi, K.Takagi, J.T.Hougen, W.B.Olson, and W.J.Lafferty, *J.Mol.Spectrosc.* **132**, 242-260 (1988)

[5] N.Ohashi, S.Tsunekawa, K.Takagi and J.T.Hougen, *J.Mol.Spectrosc*. **137**, 33-46 (1989)

The group theoretical effective Hamiltonian



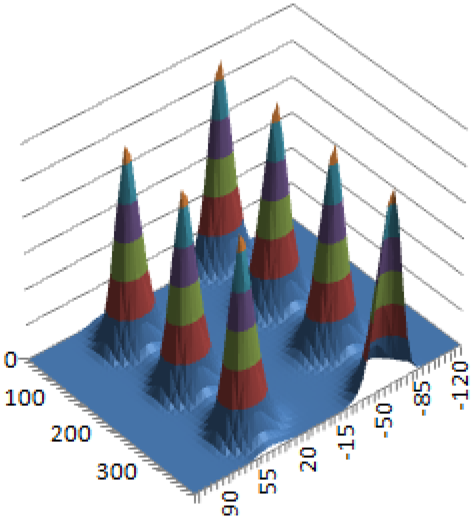
Inversion-torsion potential function of methylamine

Basic assumptions of the model:

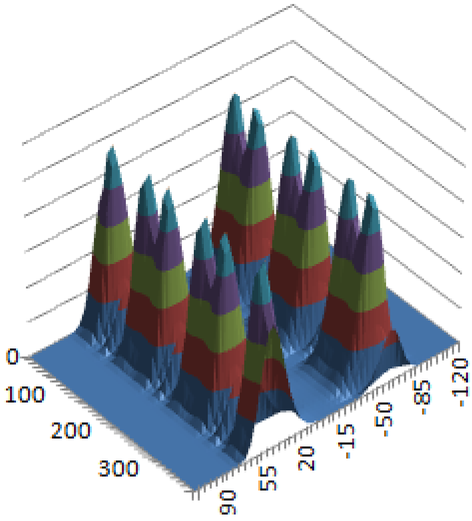
1) Equivalent minima occur in the potential surface separated by inversion and torsional barriers
2) In each minimum a rotation-inversion-torsion function is localized which is attributed to a single configuration
3) The barriers are low enough to allow tunneling between minima, thus, splittings are produced.

The probability density of the inversion-torsion functions from explicit Hamiltonian

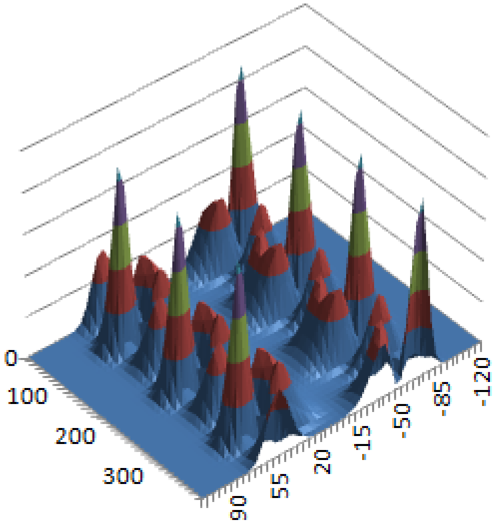
The probability density of the inversion torsion functions for J=K=0 rotational states of A_1 symmetry in different torsional states of methylamine



the ground torsional state



the first excited torsional state



the second excited torsional state

Convergence of the effective Hamiltonian

Ground state

Number of molecular parameters: 55

Number of IR lines (including upper state combination differences): 14544

Number of MW lines: 673

σ_{IR}: 0.0003 cm^{-1}

σ_{MW}: 0.21 MHz

First excited torsional state

Number of molecular parameters: 58

Number of IR lines: 11388

Number of MW lines: 218

σ_{IR}: 0.0039 cm^{-1}

σ_{MW}: 0.69 MHz

Summary and prospects

1) Available list of rotational frequencies for the first excited torsional state of methylamine up to J=40 and K=20 for all symmetry species.

2) Although the precision of the energies of the excited torsional state is not satisfactory, the energies can be used as references and source for further assignments of hot bands $\nu_{15} \rightarrow 2\nu_{15}$, $\nu_{15} \rightarrow 3\nu_{15}$, $\nu_{15} \rightarrow 4\nu_{15}$, which are quite intense in the spectrum recorded at room temperature.

3) The formalism appeared to be less successful in the first excited torsional state comparing to the ground state.