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Second torsional state of methylamine from high resolution IR spectra

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ABSTRACT

The high resolution infrared spectrum of methylamine has been analyzed in the 40–720 cm⁻¹ region (the $\nu_{15} = 2 \leftarrow 1$ hot and $\nu_{15} = 2 \leftarrow 0$ overtone bands) with a resolution of 0.00125 cm⁻¹. More than 14,400 rovibrational transitions (out of 133,000 spectral lines) for $0 \leq K \leq 13$ and $K \leq J \leq 40$ have been assigned using an original Loomis–Wood program dedicated to methylamine. A global fit of the torsional hot and overtone transitions has been carried out. The assigned transitions were fit to a single state model based on the group theoretical formalism of Hougen and Ohashi, which for the second torsional state seems to be at the limit of applicability. The standard deviation of the fit with $K \leq 11$ and $J \leq 40$ to 94 parameters was 0.006 cm⁻¹.

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1. Introduction

Methylamine CH₃NH₂, the simplest primary amine, was first detected in the interstellar medium in 1974 [1,2], then in 2011 in a spiral galaxy [3] and observed in cometary samples of the Stardust mission [4]. Apart from astrophysical importance, methylamine plays also significant roles in gas phase chemistry [5].

From a spectroscopic point of view, the molecule has been of great interest for many years, since its internal dynamics are determined by two large amplitude internal motions: hindered internal rotation of the methyl group about the C–N bond (torsional vibration) and inversion of the amino group NH₂ (wagging vibration). These two large amplitude motions are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states. The tunnelling splittings are considerable and lead to very complex and dense spectra. The assignment and interpretation of such spectra is rather challenging. In the present study, high resolution FTIR spectra of the torsional overtone band $\nu_{15} = 2 \leftarrow 0$ were investigated together with the hot torsional band $\nu_{15} = 2 \leftarrow 1$.

The rovibrational spectra of the methylamine molecule have been examined extensively over the years. In 1989 Oda and Ohashi assigned transitions in the second excited torsional state for the first time [6]. Line assignment included the $\nu_{15} = 2 \leftarrow 1$ torsional

hot band (87 transitions) and the pure rotational spectrum (35 pure rotational transitions) of the second torsional state. Both, the $\nu_{15} = 2 \leftarrow 1$ band and the rotational transitions in the second torsional state were strongly overlapped with very intense $\nu_{15} = 0 \leftarrow 0$, $1 \leftarrow 1$ and $1 \leftarrow 0$ transitions (the region of 40–350 cm⁻¹). A least-squares fit was carried out and a couple of the second torsional state molecular parameters were obtained using the group theoretical formalism [7]. Because of the insufficient number of spectral data the results were not satisfactory. The assigned transitions were only of B and E₁ symmetry (the B symmetry of pure rotational transitions and B and E₁ of $\nu_{15} = 2 \leftarrow 1$ torsional band transitions). Thus, the inversion tunnelling splitting parameters were not determined. These problems were expected to be solved from the study of the $\nu_{15} = 2 \leftarrow 0$ torsional band, which was supposed to be free from serious overlapping with other bands.

A few years later, the far-infrared FT spectrum of methylamine was recorded in the region 340–640 cm⁻¹ with a resolution of 0.006 cm⁻¹ [8]. The study was carried out in order to obtain more detailed information on the second torsional band from the analysis of the $\nu_{15} = 2 \leftarrow 0$ overtone spectrum. Although the assignment of the $2\nu_{15}$ band seemed to be straightforward, only 450 transitions could be assigned to 13 sub-bands in the second torsional band, to 8 sub-bands in the $\nu_{15} = 3 \leftarrow 1$ band and to 1 in the $\nu_{15} = 4 \leftarrow 1$. For some transitions ($K = 0 \leftarrow 1$, $1 \leftarrow 0$ etc.) no lower state combination differences were available, thus their assignments were confirmed by the combination differences involving $\nu_{15} = 2 \leftarrow 1$ transitions from the previous study [6]. The same

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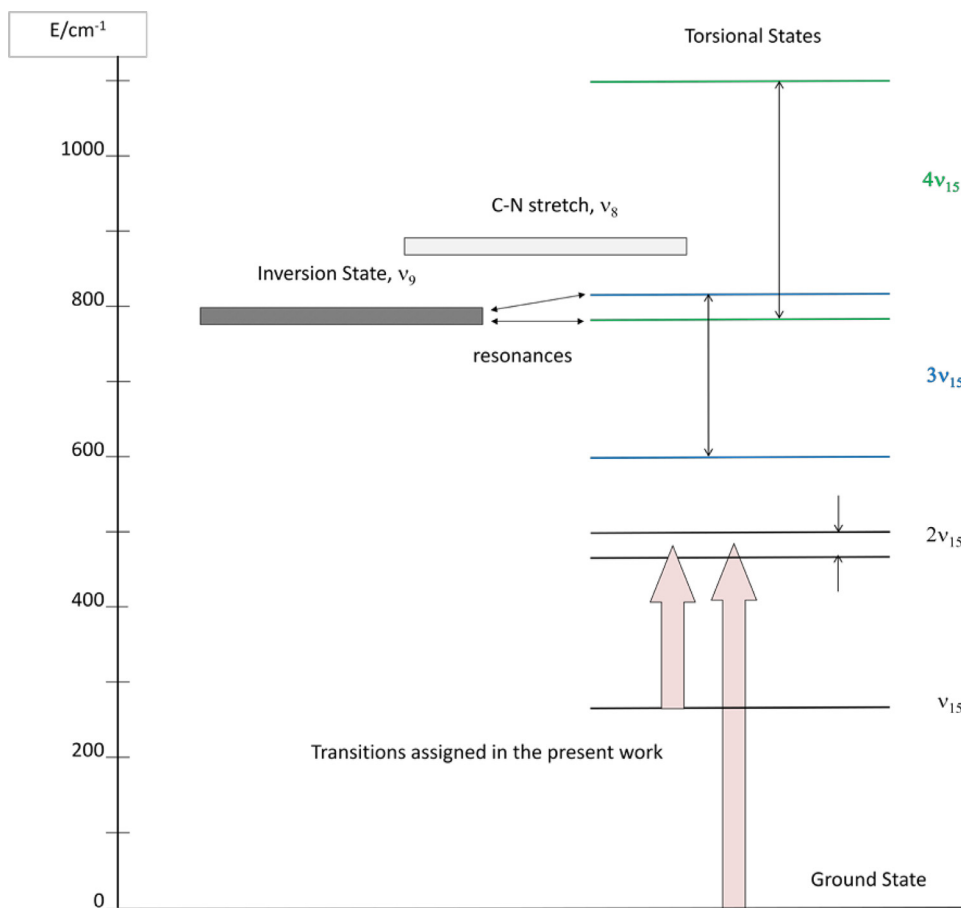


Fig. 1. An energy level diagram of the inversion-torsional states of CH_3NH_2 .

method was used in the present work, where on the basis of the assigned hot transitions, many overtone transitions were successfully assigned. The procedure will be described in more detail in following parts of this paper. In the work from 1992 [8], a global fit of the $\nu_{15} = 2 \leftarrow 0$ band was not satisfactory. Instead, only single sub-bands were fitted individually to polynomials.

The present work reports the complete structure of the second torsional state on the basis of the analysis of the $\nu_{15} = 2 \leftarrow 0$ overtone band and $\nu_{15} = 2 \leftarrow 1$ hot torsional band. The overall number of transitions of the overtone and hot torsional bands exceeds 14,400. A global fit was carried out including these transitions, which resulted in a standard deviation of 0.006 cm^{-1} . Such a complete analysis of the second torsional state was possible thanks to the very precise knowledge of the ground [9] and first torsional [10] states, which could be used simultaneously in a Lower State Combination Differences method (LSCD).

The precise structure of the excited torsional states is crucial for the understanding of resonances observed in the rovibrational spectrum of methylamine. The analyses of infrared bands such as the inversion of the amino group or C–N stretch revealed significant perturbations from highly excited torsional states [11–13]. In Fig. 1 one can see the energy level structure for the ground state, four lowest excited torsional states $\nu_{15} = 1, 2, 3, 4$, the first excited wagging state ν_9 , and the C–N stretching state ν_8 . The first and second excited states are isolated from other states, so there are no significant perturbations in that region. The energy region of the inversion state overlaps with excited torsional states, i.e., the upper component of the third excited torsional state $3\nu_{15}$ and the lower component of the fourth excited torsional state $4\nu_{15}$.

The available theoretical models [14] do not allow for precise calculation of rotational structure of highly excited torsional states. We believe that this information can be extracted from experimental spectra. The region where $\nu_{15} = 3 \leftarrow 1$ and $\nu_{15} = 4 \leftarrow 1$ can be observed covers the range of the overtone band $\nu_{15} = 2 \leftarrow 0$. However, the spectrum is so congested (Fig. 2) that it is necessary to assign the stronger $\nu_{15} = 2 \leftarrow 0$ band first and then to look for weaker bands. This procedure should deliver energies of $\nu_{15} = 3$ and 4 excited torsional states and consequently untangle the perturbation problem in the inversion state.

2. Experimental data

The high-resolution spectra of methylamine have been recorded at the University of Oulu in Finland using a Bruker IFS-120HR Fourier Transform spectrometer in the range from 40 to 360 cm^{-1} (hot band) and from 260 to 720 cm^{-1} (overtone band) at a pressure of 0.036 Torr with the path length of 3.2 m in the optimized White cell (Fig. 2). The operating temperature of the bolometer was 1.4–2 K.

The resolution due to MOPD is 0.00125 cm^{-1} and the relative wavenumber precision is almost one order of magnitude better than the respective resolution due to careful calibration of the spectrum. The registered total number of peaks is 133,000.

Since the aim of this work was to assign both the hot band $\nu_{15} = 2 \leftarrow 1$ and the second overtone band $\nu_{15} = 2 \leftarrow 0$, in a single analysis and these two bands do not appear in the same range, two spectra were merged into a single spectrum from 40 to 720 cm^{-1} . The overlapping region between 260 and 360 cm^{-1} was used to test the consistency of the spectra. Differences in the positions of

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