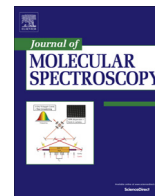




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Accurate rovibrational energies for the first excited torsional state of methylamine

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ABSTRACT

The torsional fundamental band of methylamine has been reassigned in a high resolution IR spectrum in the region from 40 to 360 cm^{-1} . Over 11,700 transitions with a resolution of 0.00125 cm^{-1} for $0 \leq K \leq 17$ and $K \leq J \leq 40$ have been assigned. A global fit of the infrared, and previously assigned pure rotational and microwave data has been carried out and the band centre was determined at 264.583143(12) cm^{-1} . The combined data were fit to a single state model based on the group theoretical formalism of Hougen and Ohashi what resulted in the total standard deviation of 0.00079 cm^{-1} (0.31 MHz for the microwave spectrum). The set of 88 parameters allows for a reliable calculation of rovibrational levels for the first excited torsional state which will subsequently facilitate the analysis of numerous hot bands observed for methylamine.

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1. Introduction

Methylamine, CH_3NH_2 , is the simplest primary amine performing two large amplitude motions: hindered internal rotation of the methyl group about the C–N bond (torsional vibration) and inversion of the hydrogen atoms of the amino group (wagging vibration). These two large amplitude motions are strongly coupled and, due to tunneling splitting, give rise to a fine structure in the vibrational states. As a result, the assignment of methylamine spectrum is rather tedious and challenging.

A lot of experimental work on different regions of methylamine rovibrational spectra has been carried out. The first microwave spectrum of the molecule was reported by Hershberger and Turkevich in 1947 [1]. It was followed by a number of other microwave studies [2–9] in the ground and torsional excited states. The infrared studies began in 1966 with a work of Tsuboi et al. [10] on the amino wagging band in the infrared spectrum of methylamine. The first infrared spectrum of the torsional band under medium resolution was presented by Möller and coworkers in 1982 [11]. They studied the spectrum range from 80 to 300 cm^{-1} and the Q-branch heads in the torsional fundamental band and also in its

associated hot bands were presented. Moreover, a number of pure rotational transitions were assigned.

A study by Ohashi et al. [12] of the pure rotational spectrum of the vibrational ground state of methylamine was reported in 1987 in which far infrared pure rotational data along with microwave data and ground state combination differences from the torsional band were combined and fitted to a group theoretical formalism [13]. With the ground state constants obtained from that fit the complete set of rotational levels for all six symmetry species in the ground vibrational state could be calculated. Thus, in the assignment and analysis of the high resolution IR spectrum of the torsional band the Ground State Combination Differences (GSCD) could be successfully used. A global fit was based on assignments of the pure rotational spectrum in the first excited torsional state, the torsional band and on microwave data from literature [2,4,14,15] resulted in a standard deviation of 0.00094 cm^{-1} . Over 650 transitions with $0 \leq K \leq 14$ and $K \leq J \leq 25$ were fit to 41 molecular parameters [16].

In 1989 Ohashi et al. published a paper [17] based on previous data [16] and new analysis of the microwave spectrum of methylamine in the range from 7 to 90 GHz. The goal of that work was to improve the understanding of the avoided crossings between $K = 0$ and 1 levels of the first torsional state. The global fit was carried out to 714 transitions involving tunneling-rotational levels. The standard deviation was 0.00095 cm^{-1} , for $J \leq 30$ and $K \leq 14$.

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The analysis of the earlier results shows that the data used in Ref. [17] were not complete. The information on E_2 symmetry levels was available only from few microwave data for the lowest values of $K = 0$ and 1. For other symmetry levels the high J transitions ($J > 17$) were observed for lowest K values, only.

It is important to acquire the accurate knowledge on rovibrational energies of the first torsional state because several hot bands originating from this state are observed in the IR spectrum [18,19]. Without this information the Lower State Combination Differences cannot be used in the assignments of hot bands.

In this paper a restudy of the torsional fundamental band, ν_{15} , of methylamine is presented. The combined infrared data, pure rotational IR data and microwave data [17] were fit to a single state Hougen-Ohashi model with 88 parameters for the excited state, for $0 \leq K \leq 17$ and $K \leq J \leq 40$, and with the standard deviation of 0.00079 cm^{-1} . Simultaneously, the GSCD calculated from the assigned lines in the torsional band were used to check the analysis of the ground vibrational state presented by Ilyushin et al. [20]. This analysis, where over 20,000 new combination differences of all symmetry species were included in the fit, confirmed the results of Ilyushin. Since the new data covered higher values of J and K , 55 parameters were used compared to 53 in Ilyushin's paper [20]. The energies of rovibrational levels in the ground state were calculated with the new parameters and used to calculate the GSCD to confirm the assignments in the first excited torsional state.

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 40 to 360 cm^{-1} at a pressure of 0.036 Torr with the path length of 3.2 m in the optimized White cell. The operating temperature of the bolometer was $1.4\text{--}2 \text{ K}$ with the registration time of $37 \text{ h } 9 \text{ min}$.

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 number of peaks is $67,522$.

3. Assignment and analysis of the spectrum

3.1. Theoretical model

The single state group theoretical Hamiltonian used in the present study of the first excited torsional state of methylamine was originally developed by Ohashi and Hougen [13]. It was then subject to a couple of modifications. First of all, $\Delta K = \pm 1$ interaction was included [17] and later the term $\Delta K = \pm 4$ had to be added [20].

The definition of the Hamiltonian operator is the following

$$\begin{aligned} \hat{H} = & h_v + h_j J^2 + h_k J_z^2 + (f_+ J_+^2 + f_- J_-^2) + q J_z + \frac{1}{2} [s_+ (J_+ J_z + J_z J_+) \\ & + s_- (J_- J_z + J_z J_-)] + (r_+ J_+ + r_- J_-) + (f_+^{(2)} J_+^4 + f_-^{(2)} J_-^4) \\ & + \text{higher order terms} \end{aligned} \quad (1)$$

where *higher order terms* stand for expansion of terms in $J(J+1)$ and/or K^2 as it is in a standard expression for the asymmetric top molecule. The Hamiltonian contains effective terms which include $\Delta K = 0, \pm 1, \pm 2, \pm 4$ operators. The coefficients $h, f, s, r, f^{(2)}$ depend on vibrational coordinates and are multiplied by rotational operators.

Applying the group theoretical effective Hamiltonian, a few basic assumptions have been made. Firstly, it is assumed that equivalent minima occurring in the potential surface are separated

by inversion and torsional barriers (Fig. 1). In each minimum a rotation-inversion-torsion function is well localized and may be attributed to a single framework. Still, the barriers to inversion and to torsion are low enough to allow a tunneling between minima, which leads to splittings of energy levels.

Hamiltonian matrix elements of the operators are expanded in Fourier series with the n -th term representing a tunneling from framework 1 to framework n and the respective parameters are defined as h_n, f_n, q_n , etc. Definition of the frameworks is given in Ref. [13].

The nontunneling parameter h_1 is equivalent to vibrational energy whereas the parameters h_n ($n > 1$) correspond to the tunneling splittings in a non-rotating molecule. The parameters of h_{1j}, h_{1k} and f_1 are the standard asymmetric top rotational constants $\frac{1}{2}(B+C), A - \frac{1}{2}(B+C), \frac{1}{4}(B-C)$, respectively. The corrections to rotational energies due to tunneling are denoted as h_{nj}, h_{nk} and f_n ($n > 1$). The terms q, r and s are responsible for interactions of components of the total angular momentum with any angular momentum generated by the two large amplitude motions. The effective Hamiltonian does not give any direct information about the barriers to tunneling, instead it describes splittings due to tunneling.

3.2. Assignment and analysis

The torsional vibration, ν_{15} , is the lowest frequency vibration in the methylamine molecule, and the first excited torsional state is well isolated from other vibrational states (Fig. 2). Therefore, no vibrational perturbations are expected to occur.

The torsional fundamental band follows the b -type selection rules with $\Delta K = \pm 1$ and $\Delta J = 0, \pm 1$. As a result the respective IR transitions are labeled as P, Q or R. At higher K values each symmetric rotor transition splits into 6 components: one $A_1 \leftrightarrow A_2$, one $B_1 \leftrightarrow B_2$, two $E_1 \leftrightarrow E_1$, two $E_2 \leftrightarrow E_2$ with statistical weights of 2, 6, 3, 1, respectively. At lower K each A or B component is further split by the asymmetric rotor effects.

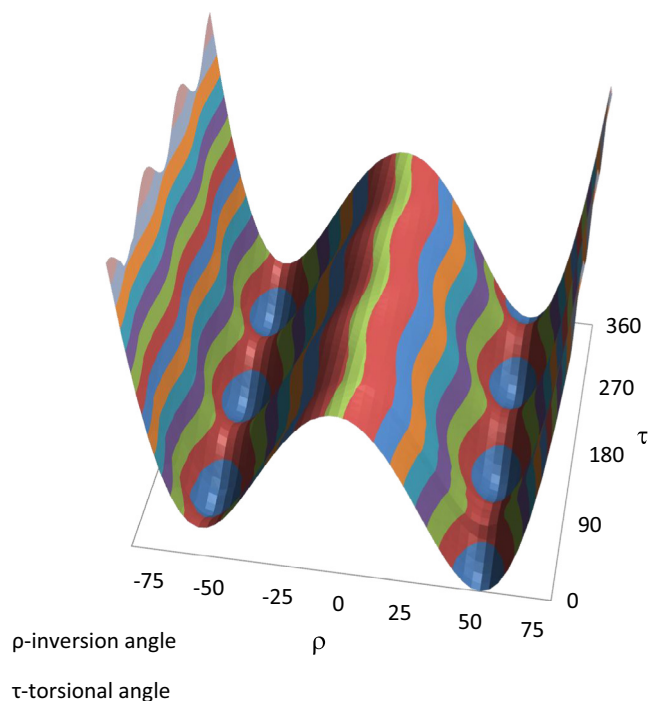


Fig. 1. Inversion-torsion potential function of methylamine where ρ and τ are inversion and torsional angles, respectively, given in [deg].

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