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The C–N stretching band of methylamine

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For the first time the C–N stretching band of methylamine has been assigned in a high resolution spectrum in the region from 960 to 1200 cm^{-1}. Over 3500 transitions with a resolution of 0.001 cm^{-1} for K from 0 to 12 have been assigned. A global fit has been made and the band center was determined at 1044.8134(33) cm^{-1}. Several branches of the C–N band are strongly perturbed through Fermi and Coriolis type resonances. The sources of the perturbations have been identified – the fourth torsional state $4\nu_{15}$ and the combination state $\nu_9 + \nu_{15}$. An attempt to fit the observed transitions to a single state model based on the group theoretical formalism of Ohashi and Hougen [1] resulted in the standard deviation of 0.04 cm^{-1}.

1. Introduction

Methylamine (CH_3NH_2) is well known as a typical example of a non-rigid molecule possessing two different types of large amplitude motions. These two modes are the wagging of the hydrogen atoms of the amine moiety (wagging vibration), and the torsion of the methyl group around the C–N bond (torsional vibration). These two large amplitude motions are strongly coupled and give rise, due to tunneling, to a fine structure in the vibrational states.

In this paper a new band of methylamine has been studied, the ν_8 C–N stretching band. This analysis is a next step of the systematic study on high resolution spectrum of the CH_3NH_2 in the region from 860 to 1200 cm^{-1}. The first investigation of the high-resolution study in that region was the analysis of the wagging band of methylamine started by Kreglewski and Winther [2]. The inversion band has been recently successfully reanalyzed and completed [3].

The C–N stretching band of methylamine was recorded over 50 years ago at low resolution by Gray and Lord [4]. The center of the band was determined to be at 1044 cm^{-1} and the band clearly had a parallel fine structure displaying the P, Q and R branches. In 1972 and 1973 far-infrared laser (FIRL) emission from CH_3NH_2 was detected by Dyubko et al. [5] and Plant et al. [6], respectively. In 2007 Lees et al. [7] identified far-infrared laser lines for five different transitions systems of CH_3NH_2 optically pumped by a CO_2 laser. The assigned infrared pump transitions were all to the excited C–N stretching state.

In the present paper most of the series in the infrared band have been identified and their assignments were confirmed by the ground state combination differences (GSCD), which are the part of the Loomis–Wood schemes [8,9]. Besides, some lines that do not belong to the ν_8 band have been observed and labeled. These are probably the lines of a "dark" state. It has been proved that the $4\nu_{15}$ and the $\nu_9 + \nu_{15}$ are the states interacting with the C–N stretching. The rather poor result of the global fit achieved using the single state group theoretical effective Hamiltonian [1] confirms that indeed some parts of the C–N band are strongly perturbed.

2. Experimental data

The high-resolution spectrum of methylamine has been recorded at the University of Oulu in Finland using a Bruker IFS-120HR Fourier transform spectrometer in the range from 960 to 1200 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 20 °C. Total registration time was 69 h 36 min.

The estimated resolution due to mean optical path length, aperture and Doppler broadening is 0.0021, 0.0023, 0.0025 and 0.0028 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.

3. Theoretical model

The group-theoretical Hamiltonian model presented originally by Ohashi and Hougen [1] has been applied in this work. The

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Hamiltonian contains effective terms similar to the standard Hamiltonian for the asymmetric top molecule, which include $\Delta K = 0, \pm 1, \pm 2, \pm 4$ operators.

$$\hat{H} = h_v + (f_+^{(2)} J_+^2 + f_-^{(2)} J_-^2) + (f_+^{(4)} J_+^4 + f_-^{(4)} J_-^4) + qJ_z + (r_+ J_+ + r_- J_-) + [s_+(J_+ J_z + J_z J_+) + s_-(J_- J_z + J_z J_-)] + \text{higher order terms} \quad (1)$$

Coefficients h, f, s, r depend on vibrational coordinates and are multiplied by rotational operators. The higher order terms arise when these coefficients are expanded in terms of $J(J+1)$ and/or K^2 as it is in a standard expansion for the asymmetric top molecule. More detailed information about the Ohashi–Hougen model is presented in the paper on the wagging band of methylamine [3]. Since the ν_8 band is perturbed by neighboring bands, the Hougen–Ohashi approach does not seem to work properly any longer.

4. Assignment and analysis

The C–N stretching band of methylamine spreads in the spectrum from about 960 to 1200 cm^{-1}. The C–N stretching vibration is a parallel band with an a-type transition moment. The K-selection rule is $\Delta K = 0$ whereas the J-selection rules are $\Delta J = -1$, 0 or +1. They correspond to IR transitions labeled as P, Q or R, respectively. Since the band is parallel and not very intense, it appears in the spectrum as a very crowded structure and many lines are indeed strongly overlapped. In order to assign K values correctly, a lot of alternative attempts of assignment were made until the unambiguous results based on the GSCD could be reached. All in all, the assignment of the ν_8 band is really hard and tedious.

Table 1 summarizes the results of the C–N stretching band assignment. One can notice that the number of series assigned for B symmetry species is the highest (up to $K' = 12$) in contrast with those of A, E_2 and even E_1 symmetries. This is obviously due to different statistical weights, which result in the following relative intensities of individual lines A_1: A_2: B_1: B_2: E_{1+1}: E_{1-1}: E_{2+1}: E_{2-1} = 1: 1: 3: 3: 3: 3: 1: 1. Starting from $K = 3$ for B symmetry all components of the triads, ^{Q}P, ^{Q}R and ^{Q}Q, are assigned. Additionally, for $K > 4$ the asymmetry splitting in A and B symmetry transitions disappear and the intensities are doubled.

For E_{1+1} and E_{1-1} symmetry species the complete sets of series up to $K' = 11$ and $K' = 9$, respectively, have been identified and assigned. Although the lines of E_1 symmetry posses significant intensities, the assignment was troublesome. This can be explained by two leading effects: (a) the strong congestion of the band which causes many irregularities shown in Figs. 1 and 2 and thus difficulties with the identification and (b) by resonances. Fig. 1 presents a part of the C–N stretching band showing the $J = 4 \leftarrow 5$ manifold of the ^{Q}P branch consisting of lines for $K' = 1$ values and different symmetry species. One can notice that due to incidental overlapping some lines have higher intensities than predicted by the statistical weights. Furthermore, in Fig. 2 a structure of the ^{Q}P branch for $J = 8$ and B symmetry for different K values is shown and one can see that there is no correlation between the position of line and the value of K. That disorder makes the identification process very difficult.

Despite the high density of lines in the C–N band, it was possible to find and identify even the low intensity transitions of A and E_2 symmetry. For A symmetry all series up to $K' = 9$ have been identified whereas for E_{2+1} and E_{2-1} symmetry, series up to $K' = 8$ have been assigned. The only series not found are the $K' = 5$ series of E_{2-1} symmetry (Table 1). All assignments have been confirmed by the GSCD and agree with previously measured laser lines [5–7].

Apart from transitions belonging to the ν_8 band of methylamine, some additional lines have been observed. They have been assigned to the $K' = 4$ series of E_{2-1} symmetry. They probably belong to a "dark" state, which is in resonance with the ν_8 state. In order to

Table 1
Line assignments[a] by symmetry species in the ν_8 C–N stretching band of CH_3NH_2.

K'	A[b]	B[b]	E_{1+1}	E_{1-1}	E_{2+1}	E_{2-1}
0	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R		^{Q}P, ^{Q}R	
1	^{Q}PP, ^{Q}RR	^{Q}PP, ^{Q}RR	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R
2	^{Q}PP, ^{Q}RR	^{Q}PP, ^{Q}RR	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R
3	^{Q}PP, ^{Q}RR	^{Q}PP, ^{Q}RR, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R
4	^{Q}PP, ^{Q}RR	^{Q}PP, ^{Q}RR, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R
5	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}PP, ^{Q}RR, ^{Q}QQ	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R	
6	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q
7	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q
8	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q
9	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q		
10		^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R, ^{Q}Q			
11		^{Q}P, ^{Q}R, ^{Q}Q	^{Q}P, ^{Q}R			
12		^{Q}P, ^{Q}R, ^{Q}Q				

[a] The symbols ^{Q}R, ^{Q}P, ^{Q}Q indicate that lines in the corresponding branches have been identified in the C–N stretching band.
[b] The double letters RR, PP or QQ indicate that the A_1, A_2, B_1, B_2 splitting have been observed.

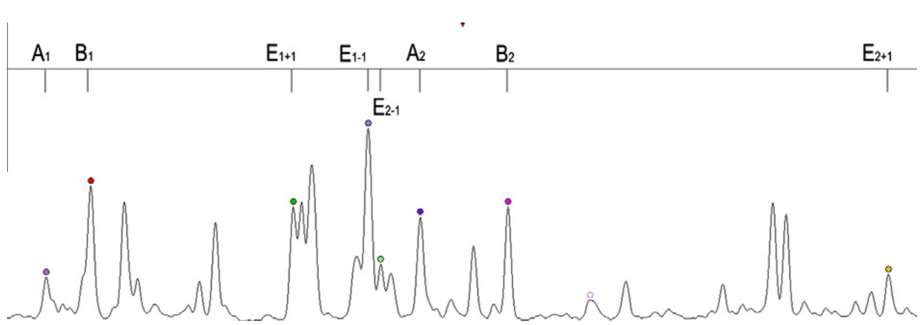

Fig. 1. Part of the C–N stretching band in the 1037.14–1037.52 cm^{-1} range showing the $J = 4 \leftarrow 5$ manifold of the ^{Q}P branch consisting of lines for $K' = 1$ values and different symmetry species.