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## The NH<sub>2</sub> scissors band of methylamine

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## Abstract

For the first time the  $\nu_4$   $\text{NH}_2$  scissors band has been assigned in a high resolution infrared spectrum. A rotationally resolved spectrum of methylamine was recorded using two infrared spectroscopic techniques. A White-type multipass cell device coupled to the Bruker IFS 125 HR Fourier transform spectrometer was implemented on the AILES beamline at the SOLEIL synchrotron facility and a room temperature spectrum of the whole band in the region of 1540 - 1710  $\text{cm}^{-1}$  was recorded with a resolution of 0.001  $\text{cm}^{-1}$ . Then, a low temperature high resolution spectrum in the 1622.5-1655.6  $\text{cm}^{-1}$  range of Q and R branches of the  $\nu_4$  band was recorded using a quantum cascade laser spectrometer. Preliminary assignment was carried out in the  $\text{NH}_2$  scissors band region, and about 2200 transitions for K from 0 to 6 have been assigned for A, B and  $E_1$  symmetry species.

The simultaneous fit of assigned lines using a group-theoretical effective Hamiltonian was not successful, instead simple polynomial series expansions were used for each symmetry and K value.

Keywords: methylamine;  $\text{NH}_2$  scissors band; high resolution infrared spectrum; laser spectrum; Loomis-Wood for Windows.

## 1. Introduction

Methylamine ( $\text{CH}_3\text{NH}_2$ ) is the simplest primary amine. Its  $\text{CH}_3$  group is connected to the  $\text{NH}_2$  group by the C–N bond. As far as these two groups are concerned, the  $\text{CH}_3$  group undergoes an internal torsional motion while the  $\text{NH}_2$  group an inversion motion, which makes methylamine a prototype in molecular spectroscopy for non-rigid molecules with two coupled large-amplitude internal motions of different types. As the barriers in the potential surface are neither very high nor small and the large amplitude motions are strongly coupled, the spectra of methylamine are complicated.

The methylamine spectrum has been extensively studied both experimentally and theoretically over the past decades, in different spectral regions, by various methods. The system of complex tunneling splittings in the rotational spectrum of the ground state was described in 1956 [1]. However it took more than 30 years to assign successfully the rotational spectrum [2] using a model based on a group theoretical Hamiltonian of Ohashi and Hougen [3]. Later publications presented the extension of the methylamine data set into millimetre- and submillimetre-wave ranges [4,5,6]. The more recent study of the ground state rotational spectrum was realized in a wide frequency range up to 2.6 THz [7]. Detailed studies of tunneling splittings in rotational levels of the first torsional state  $\nu_{15}$  of methylamine have been carried out [8,9,10] as well as of the second torsional state  $2\nu_{15}$  [11,12,13]. Analyses of tunneling-rotational levels of the first excited inversion (wagging) state of methylamine  $\nu_9$  were published [14,15], and also studies on the C-N stretching  $\nu_8$  [16,17] and asymmetric CH stretch  $\nu_{11}$  [18] were achieved.

The systematic analysis of such a high resolution IR spectrum should be continued at higher frequency ranges than the CN stretching band. However the  $1200\text{-}1550\text{ cm}^{-1}$   $\text{CH}_3$  rocking region has no clear features which would facilitate the assignments although three  $\text{CH}_3$  deformation and  $\text{NH}_2$  twist vibrations are expected. The next part of the spectrum is the  $\nu_4$   $\text{NH}_2$  scissors band where strong P, Q and R branches can be clearly identified. Moreover the ab initio calculation of Senent [19] indicates a significant coupling between the  $\nu_4$  scissors and  $\nu_9$  wagging modes which should result in large inversion splitting.

Thus, the present investigation is related to the first high-resolution study of the  $\nu_4$   $\text{NH}_2$  scissors band of methylamine in the  $1540\text{-}1710\text{ cm}^{-1}$  region.

The unresolved band contour of the  $\text{NH}_2$  deformation of methylamine was previously observed around  $1623\text{ cm}^{-1}$  [20]. Using the Loomis-Wood for Windows (LWW) program adjusted for methylamine molecule [21], we were able to identify close to 2200 transitions, mainly of B,  $E_{1+1}$  and  $E_{1-1}$  symmetry species, and only few of A symmetry species. The analysis of the  $\text{NH}_2$  deformation IR band was supported by the laser spectrum: the rovibrational cooling of the supersonic expansion simplifies the congested rovibrational structure observed at room temperature, which makes easier to interpret sharp and well isolated lines. All assignments were confirmed with the Ground State Combination Differences (GSCD).

## 2. Experimental details

Methylamine ( $\text{CH}_3\text{NH}_2$ ) was used for all experiments without further purification. The rovibrational spectrum of  $\nu_4$   $\text{NH}_2$  scissor mode of methylamine has been recorded in very different conditions of temperature using two absorption infrared devices working at room and low temperatures: in a first step, a White-type multipass cell device (150 m optical path from a base length of 2.5 m) coupled to a Bruker IFS 125 HR Fourier Transform InfraRed (FTIR) spectrometer implemented on the AILES beamline at the SOLEIL synchrotron facility. Static absorption spectra were realized in the 1540 -1710  $\text{cm}^{-1}$  range. We injected about 0.05 mbar of  $\text{CH}_3\text{NH}_2$  with the best suitable combination infrared source/ beamsplitter/ detector (Globar/KBr-Ge/HgCdTe) for the mid-infrared region. The acquisition time was 22 hours to obtain 450 coadded scans at the maximal resolution of 0.001  $\text{cm}^{-1}$ . **The precision of line positions is 0.0002  $\text{cm}^{-1}$  for well separated lines but in most cases the lines are overlapped and the precision is close to resolution.**

The strong spectral congestion of methylamine bands at room temperature is caused by the broad rotational distribution and residual hot band but especially, by the presence of torsion-inversion tunneling multiplets due to the coupling between the internal rotation of the methyl group and the inversion motion of the hydrogen atoms of the amine group. Such a spectral complexity requires to work at low temperature to tighten the rotational distribution and to reduce the hot band contribution in order to isolate the cold fundamental band contribution. To reach this objective, we used a jet-cooled laser spectrometer recently developed at the MONARIS laboratory which couples an external-cavity quantum cascade laser (EC-QCL) to a pulsed supersonic jet. The set-up has already been described in detail in recent papers [22, 23]. Only the main characteristics will be presented hereafter.

The light source is a continuous-wave room-temperature mode-hop-free EC-QCL (Daylight Solutions) with a spectral width of 10 MHz, covering the 1620-1690  $\text{cm}^{-1}$  range. About 8% of the total light power is sent through two laser channels for relative and absolute frequency calibrations. The remaining light is sent through a multi pass astigmatic cavity according to a 182-pass pattern which crosses almost perpendicularly the jet expansion. Jet-cooled methylamine is obtained by expanding  $\text{CH}_3\text{NH}_2$ : Ar mixtures (0.7 % in 2 bar Ar) through a pulsed pin hole (1 mm diameter) nozzle from General Valve Series 9 model, controlled by a valve driver (Iota One, Parker Hannifin). At the exit of the pin hole the cylindrical cooled gas mixture flow of the standard configuration is converted into a homogeneous planar expansion thanks to a multichannel interface ended with two modified industrial blades, forming a 30 mm length x 150  $\mu\text{m}$  width slit opening. Rovibrationally cooled  $\text{CH}_3\text{NH}_2$  molecules were probed by the infrared light at small axial distances where the molecular density is still high. Spectra were recorded according a classical rapid scan scheme, by driving the piezo-electric transducer of the EC-QCL diffraction grating with a 100 Hz sine wave [24]. A baseline-free transmittance is obtained by taking the ratio of the corresponding signals recorded with and without the jet. Absolute frequency calibration is achieved by comparing the frequency deviation of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  lines between experimental and well known from the HITRAN 2016 database [25]. The accuracy of the frequency calibration is around 0.0005  $\text{cm}^{-1}$ . Thanks to the narrow line width of the QCL source and the strong reduction of the Doppler broadening at low temperature, experimental widths (full

width at half maximum, FWHM) of isolated rovibrational lines typically equal to 40 MHz were measured in the jet-cooled QCL spectrum of  $\text{CH}_3\text{NH}_2$ .

### 3. Experimental results

Figure 1 displays the long path cell FTIR spectrum of the  $\nu_4$   $\text{NH}_2$  scissors band of  $\text{CH}_3\text{NH}_2$  recorded at maximal resolution ( $0.001\text{ cm}^{-1}$ ) of the spectrometer. Its unresolved band contour was detected around  $1623\text{ cm}^{-1}$ [20].

A highly diluted jet-cooled QCL spectrum of the  $\nu_4$  band of  $\text{CH}_3\text{NH}_2$  was recorded in the  $1622.5\text{-}1655.6\text{ cm}^{-1}$  range and compared to the room temperature cell-FTIR spectrum. The range covered by the jet-cooled QCL set-up corresponds to the Q and R branches of the  $\nu_4$  band. Fig. 2 displays a part the spectrum showing the drastic reduction of the jet-cooled rovibrational distribution (Fig. 2a) with respect to that of the room temperature spectrum (Fig.2b) which evidences the narrow linewidths measured in jet (typically 40 MHz) compared to those measured in cell at 300 K (about 135 MHz). This effect is mainly due to the drop of the temperature by more than one order of magnitude knowing that the FWHM Doppler width at 300 K and  $1620\text{ cm}^{-1}$  for a light molecule as  $\text{CH}_3\text{NH}_2$  is equal to 105 MHz. Such a high experimental resolution combined to a rather good sensitivity of the spectrometer gives the opportunity to proceed to the band contour analysis of the  $\nu_4$  mode of  $\text{CH}_3\text{NH}_2$ .

### 4. The $\text{NH}_2$ scissors band

The molecule  $\text{CH}_3\text{NH}_2$  is treated as a slightly asymmetric prolate top. The  $\text{NH}_2$  scissors band is hybrid of  $A'$  symmetry in the  $C_s$  group which corresponds to  $B_1$  symmetry in the  $G_{12}$  of PI group with components of dipole moment change both parallel and perpendicular to the C-N bond. This is a B type band. The selection rules are the following:  $\Delta K=0,\pm 1$  and  $\Delta J=0,\pm 1$ , and generally result in 9 different rovibrational series for every value of  $K''$  in the ground state.

Further modifications of the hybrid structure by the inversion and torsion of the molecule cause four-, six-, or eightfold splitting of each spectral line. A PI group of methylamine consists of 12 symmetry operations [26] and is isomorphic to the  $C_{6v}$  point group. The tunneling through the barrier to internal rotation produces a splitting between nondegenerate states of A or B symmetry and degenerate of  $E_1$  or  $E_2$  symmetry. Furthermore, the tunneling through the barrier to inversion splits states of A and B symmetry or those of  $E_1$  and  $E_2$  symmetry. According to selection rules each symmetric rotor transition splits into six 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 1, 3, 3, 1, respectively. At higher K the asymmetry splittings for A or B components are below the spectral resolution and the respective lines are twice as intensive. For  $K=0$  each rovibrational transition splits into four sublevels.

As a consequence, a very high number of transitions estimated to more than 11000 lines in the room temperature  $\nu_4$  band spectrum of  $\text{CH}_2\text{NH}_3$  recorded at  $0.001\text{ cm}^{-1}$  resolution from  $1540$  to  $1710\text{ cm}^{-1}$  (Fig. 1). Such a huge spectral congestion fully justifies the benefit of high resolution low temperature infrared spectroscopic methods to untangle the rovibrational analysis.

## 5. Assignment and analysis

First approach to the analysis of the  $\nu_4$  NH<sub>2</sub> scissors band was based on its apparent similarity to the  $\nu_9$  NH<sub>2</sub> wagging band. However, the  $\nu_4$  lies above excited torsional bands, inversion band, C-N stretching band, NH<sub>2</sub> twist and CH<sub>3</sub> rock and deformation bands, and its structure may be strongly perturbed by accidental resonances.

The assignments of the NH<sub>2</sub> scissors band were conducted with the LWW software adapted for methylamine molecule [21]. The LWW project was created on the basis of the peak list and the energy file. The analysis started with the simulation of the  $\nu_4$  band based on the parameters of the wagging band used in the group theoretical effective Hamiltonian [3] where the vibrational frequency of the wagging mode (779.6 cm<sup>-1</sup>) was replaced with the approximate band center for the scissors vibration (1623 cm<sup>-1</sup>). Thus, the energy file with predicted energies levels for the  $\nu_4$  state was introduced into LWW. Once some series of transitions were located and initially assigned to a given quantum set values using trial and error method, their counterparts could be found by the GSCD procedure, which is a built-in part of the LWW program. Since the ground state is known very precisely the series of a given value of K and symmetry in the upper state should look alike in the Loomis-Wood (LW) diagrams. The LWW can simultaneously display 3 LW diagrams and that was the most effective way to assign the observed series. That represented a good start and some levels for B symmetry with K= 5 and 6 were found, and for E<sub>1+1</sub> symmetry with K=4.

Following the relatively easy initial assignments of the NH<sub>2</sub> scissor band the continuation turned out to be more difficult. The parameters in the effective Hamiltonian were modified using first assignments but other series were more perturbed. The tedious analysis made on a basis of the GSCD allowed for identification of B symmetry series for K=1 to 6, E<sub>1+1</sub> series for K=0 to 6, E<sub>1-1</sub> series for K=2, 3 and 5, and for A symmetry for K=5. Until now no E<sub>2</sub> symmetry series could be identified. Figure 3 shows a part of the room temperature FTIR NH<sub>2</sub> scissors band spectrum of methylamine along with a low temperature spectrum representing the structure of the <sup>Q</sup>R<sub>2</sub>(E<sub>1-1</sub>) branch up to J=24 and J=12 in the room temperature and low temperature, respectively.

The group theoretical effective Hamiltonian could not reproduce all assigned series in a single fit. For some values of K the calculated transitions differed from the observed by few wavenumbers. Finally selected parameters of the effective Hamiltonian were used separately for nondegenerate (A and B symmetry) and for degenerate (E<sub>1</sub> and E<sub>2</sub> symmetry) levels. However, the standard deviations of the fits were as large as 0.3 cm<sup>-1</sup> which was helpful for proceeding with new assignments but very far from experimental precision.

Since the effective Hamiltonian could not fit the observed lines with the experimental accuracy, simple polynomial series expansions were used to present the results in a compact form. In a series the energy levels share K and the symmetry index and differ with J. To all available experimental transitions frequencies the energies of the ground state levels were added. For every value of J, K and symmetry the upper state energy level was calculated

several times from different transitions, and then the average energies were used in a polynomial fits in  $J(J+1)$  as it had been done for the wagging band [14],

$$E(q, J) = \sum_m a_m(q) [J(J+1)]^m \pm \frac{1}{2} \frac{(J+1)!}{(J-1)!} \sum_n b_n [J(J+1)]^n \quad (1)$$

In Eq.(1)  $q$  stands for common quantum numbers, i.e.  $K$  and symmetry. For nondegenerate species the symmetry label designates two components of the asymmetry doublet ( $A_1$  and  $A_2$  or  $B_1$  and  $B_2$ ) and their splittings are given by the term including  $b_n$  parameters. For degenerate species the symmetry labels assume such values as  $E_{1+1} : E_{1-1} : E_{2+1} : E_{2-1}$ . In Table 1 the parameters of polynomial series and standard deviations are given. The standard deviations of the polynomial fits are higher than the experimental accuracy of  $0.0002 \text{ cm}^{-1}$  due to many local resonances and line overlapping. An example of such a local resonance is shown in Fig.4., where a part of the  $\text{NH}_2$  scissors spectrum presents a  ${}^Q\text{R}_3$  series of  $E_{1+1}$  symmetry species at the top, along with two LW diagrams underneath with just  ${}^Q\text{R}_3$  series and its counterpart  ${}^Q\text{P}_3$  series. One can notice that at  $J=12$  both series deviate from the LW diagram center in the same way. Thus, a Coriolis-like resonance is present in this series.

In an old paper about the wagging band of methylamine [14] the sinusoidal behavior of  $a_0$  term was used to predict the position of a next branch with higher  $K'$  value. Unfortunately, in the scissors band the local resonances different for almost every  $K'$  value do not allow the application of this strategy and we shall not present the negative results. This approach should be possible if we succeed to assign data for other values of  $K$ . Then the local perturbations of the Fourier expansion will be visible as it has been done by Li-Hong Xu for internal rotation in  $\text{CH}_3\text{SH}$  [27].

A jet-cooled QCL spectrum of the  $\nu_4$  band of  $\text{CH}_3\text{NH}_2$  (Fig. 2b) was recorded in the  $1622.5\text{-}1655.6 \text{ cm}^{-1}$  range and was helpful in assignments of the Q branch series of the  $\text{NH}_2$  scissors range. Due to lower temperature in the jet the series are shorter comparing to the IR spectrum but at the same time much easier to evidence. Thus, in our strategy the series were initially identified in the FTIR spectrum and then unambiguously confirmed by the laser spectrum as illustrated in Figure 2 where comparison of the same Q branch recorded at very different rotational temperatures in both FTIR and laser spectra is presented.

Table 2 summarizes the results of the  $\text{NH}_2$  scissors band assignment. It is preliminary assignment, and one can notice that the number of series found for B and  $E_{1+1}$  symmetry species (up to  $K'=6$ ) is largely higher than of the series of other symmetries. Three series of  $E_{1-1}$  symmetry were also assigned. For A symmetry it was almost accidental that a series with  $K=5$  was found because it was only  $1 \text{ cm}^{-1}$  away from a crude prediction based on positions of B symmetry series. Generally the lines of A symmetry are three times less intense than those of B symmetry. For B and  $E_{1+1}$  symmetry species  ${}^Q\text{P}$ ,  ${}^Q\text{R}$ ,  ${}^Q\text{Q}$ ,  ${}^P\text{P}$ ,  ${}^R\text{R}$ ,  ${}^P\text{Q}$ , and  ${}^R\text{Q}$  seem to be assigned, and in some cases also  ${}^P\text{R}$  and  ${}^R\text{P}$  series. It was not possible to find series for higher  $K$  values than 6, even for B and  $E_1$  symmetry species with significant intensities, and this can be explained by: (a) the strong congestion of the band shown in Figures 1 and 2 and consequently assignment problems, and (b) by resonances with other bands appearing in the  $\text{NH}_2$  band region. In summary the assignment of each group of series with a given value of  $K'$

and symmetry is almost an individual project. Until now no series of  $E_2$  symmetry could be assigned.

The present assignment brings an important information related to the dynamics of the methylamine molecule. The splitting between A and B symmetry species in the scissors state which could be directly observed for  $K'=5$  levels is much larger than in the wagging band. In Table 1 the difference between respective  $a_0$  constants is  $14.2\text{ cm}^{-1}$  comparing to  $6.9\text{ cm}^{-1}$  in the wagging state [14]. This shows that the excitation of the scissors vibration greatly facilitates the inversion of the amino group which agrees well in the prediction from recent ab initio calculations [19].

The identified lines in P-, Q-, and R-type series are collected in a separate table available as supplementary data. Each line of the table contains the assignment, experimental frequency, intensity, and differences between the experimental values and those obtained from the polynomial fits.

## 6. Conclusion

For the first time the  $\text{NH}_2$  scissors band has been assigned in a high resolution infrared spectrum. Although the spectrum of the  $\nu_4$  band of methylamine is very dense and difficult to analyze, we were able to assign a number of transitions. Nevertheless, still a lot of work needs to be done to find more series of lines and identify them properly in this region. As mentioned above, problems with the assignments in the  $\text{NH}_2$  scissors region of the spectrum may arise due to weak line intensities (no transitions were assigned for  $E_2$  symmetry species), perturbations or intense lines overlapping.

In total about 2200 lines have been assigned. The assignment was confirmed through the ground state combination differences (GSCD).

Summarizing, the analysis of the  $\text{NH}_2$  scissors band is tedious and requires a combination of different analytic tools.

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Table 1

Taylor expansion (Eq.1) and K-doubling coefficients (in  $\text{cm}^{-1}$ ) for energy levels of the scissors state of methylamine.  $\sigma$  is a standard deviation of the fit in  $\text{cm}^{-1}$ . Numbers in parentheses are one standard error and apply to the last digits of the parameters.

A symmetry					
K	$a_0$	$a_1$	$a_2*10^5$	$a_3*10^7$	$\sigma$
5	1692.8302(18)	0.740302(27)	-0.068(11)	-0.1239(14)	0.0010
B symmetry					
K	$a_0$	$a_1$	$a_2*10^5$	$a_3*10^7$	$\sigma$
1	1624.3843(37)	0.73521(11)	-1.169(96)	0.146(24)	0.0086
2	1624.9920(12)	0.738844(24)	0.196(14)	-0.4308(25)	0.0016
3	1657.18390(35)	0.7382418(63)	-0.4025(28)	-0.03457(34)	0.0008
4	1668.62530(65)	0.7382554(92)	-0.0504(31)	-0.00825(30)	0.0013
5	1707.05995(57)	0.7363823(66)	-0.1039(21)	-0.00721(20)	0.0007
6	1719.7355(11)	0.7396285(62)	-0.12272(71)		0.0027
K	$b_0$	$b_1$	$b_2$		
1	0.854(16)e-2	-0.208(18)e-4	0.311(46)e-7		
2	0.19524(72)e-4	-0.7997(25)e-7			
3	0.87(12)e-9	0.674(38)e-11	-0.392(31)e-14		
4	0.382(27)e-12	0.351(42)e-15			
5	-0.993(58)e-16				
$E_{1+1}$ symmetry					
K	$a_0$	$a_1$	$a_2*10^5$	$a_3*10^7$	$\sigma$
0	1622.02180(53)	0.738413(26)	-0.669(30)	-0.3276(96)	0.0009
1	1622.02011(37)	0.7386116(99)	-1.1770(47)		0.0007
2	1638.85828(70)	0.737288(10)	-0.1389(35)	0.00790(34)	0.0008
3	1649.2789(12)	0.738395(23)	-0.046(10)	-0.0245(11)	0.0024
4	1668.56540(21)	0.7372633(31)	0.1305(11)	-0.01688(11)	0.0003
5	1689.5054(36)	0.737289(53)	-0.422e-5(22)	0.148e-8(26)	0.0022
6	1719.07922(68)	0.7395503(89)	-0.0800(31)	-0.00299(31)	0.0006
$E_{1-1}$ symmetry					
K	$a_0$	$a_1$	$a_2*10^5$	$a_3*10^7$	$\sigma$
2	1636.00383(31)	0.7389286(86)	0.0650(58)	-0.0372(11)	0.0004
3	1654.84573(43)	0.7382098(63)	0.1557(24)	-0.01810(26)	0.0005
5	1692.58533(77)	0.7396045(91)	-0.1211(29)	-0.01109(26)	0.0008

Table 2. Line assignments<sup>a</sup> by symmetry species in the  $\nu_4$  NH<sub>2</sub> scissors band of CH<sub>3</sub>NH<sub>2</sub>.

K'	A <sup>b</sup>	B <sup>b</sup>	E <sub>1+1</sub>	E <sub>1-1</sub>
0			<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P	
1		<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>R</sup> R	
2		<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ, <sup>R</sup> QQ	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q, <sup>R</sup> P
3		<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>Q</sup> QQ, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ, <sup>R</sup> QQ	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q, <sup>R</sup> P
4		<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>Q</sup> QQ, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ, <sup>R</sup> QQ, <sup>R</sup> PP, <sup>P</sup> RR	<sup>Q</sup> P, <sup>Q</sup> R, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q	
5	<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>Q</sup> QQ, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ, <sup>R</sup> QQ	<sup>Q</sup> PP, <sup>Q</sup> RR, <sup>Q</sup> QQ, <sup>P</sup> PP, <sup>R</sup> RR, <sup>P</sup> QQ, <sup>R</sup> QQ, <sup>R</sup> PP, <sup>P</sup> RR	<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q	<sup>Q</sup> P, <sup>Q</sup> R, <sup>P</sup> P, <sup>R</sup> R, <sup>R</sup> Q,
6		<sup>Q</sup> P, <sup>Q</sup> R, <sup>Q</sup> Q, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q, <sup>R</sup> Q, <sup>R</sup> P, <sup>P</sup> R	<sup>Q</sup> P, <sup>Q</sup> R, <sup>P</sup> P, <sup>R</sup> R, <sup>P</sup> Q,	

<sup>a</sup>The symbols <sup>Q</sup>R, <sup>Q</sup>P, <sup>Q</sup>Q indicate that lines in the corresponding branches have been identified in the NH<sub>2</sub> scissors band.

<sup>b</sup>The double letters RR, PP or QQ indicate that the A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub> splittings have been observed.

Figure captions:

Figure 1. Long path cell-FTIR room temperature spectrum of  $\text{CH}_3\text{NH}_2$  recorded at  $0.001\text{ cm}^{-1}$  resolution in the  $1540\text{-}1710\text{ cm}^{-1}$  region. Intense lines are due to atmospheric absorptions of the bending mode of water centered at  $1594.7\text{ cm}^{-1}$ .

Figure 2. Comparison between the  $\nu_4$   $\text{NH}_2$  deformation mode spectrum in the  ${}^{\text{Q}}\text{Q}_4(\text{B}_1)$  band region ( $1625.25 - 1625.70\text{ cm}^{-1}$ ) of methylamine recorded using our jet-cooled EC-QCL spectrometer (a) and the cell-FTIR room temperature spectrometer (b). The significant reduction of the experimental line widths is visible at low temperature compared to the room temperature line widths broadened by the Doppler contribution.

Figure 3. Part of the IR  $\text{NH}_2$  scissors band of methylamine representing the structure of the  ${}^{\text{Q}}\text{R}_2(\text{E}_{1-1})$  branch in room temperature a) and in jet-cooled b) (filled circles indicate assigned spectral lines whereas empty circles predicted ones).

Figure 4. Coriolis interaction for  $\text{K}=3$  of  $\text{E}_{1+1}$  symmetry species in the  $\text{NH}_2$  scissors band of methylamine.