

# Eigenstate resolved infrared and millimeter-wave–infrared double resonance spectroscopy of methylamine in the N–H stretch first overtone region

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Received 13th January 1999, Accepted 22nd March 1999

The eigenstate resolved, near-infrared spectrum of methylamine,  $\text{CH}_3\text{NH}_2$ , has been measured at 5 MHz resolution in the region near  $6615\text{ cm}^{-1}$  using a molecular-beam laser spectrometer with optothermal detection. Part of the spectrum of the NH  $2\nu_1$  (symmetric stretch first overtone) has been assigned by applying a millimeter-wave–infrared double resonance technique. The spectra are very fractionated by intramolecular vibrational energy redistribution with an observed density of states between 20 and 30 states per  $\text{cm}^{-1}$  which is about four times the density of vibrational states calculated in the harmonic approximation. The coupling between the bright states and the bath is found to be rather strong ( $0.1\text{ cm}^{-1}$ ), and the lifetime for the redistribution is determined to be 3 ps for the  $2\nu_1$  vibration.

## I. Introduction

One of the central goals of chemical physics is the understanding, and eventual manipulation, of vibrational energy flow in molecules. Energy initially deposited in an infrared active vibrational mode of a polyatomic molecule will redistribute to other modes on time scales that span a relatively wide range, from a few picoseconds to a few nanoseconds. Intramolecular vibrational energy redistribution (IVR) results in the fragmentation of a zeroth-order transition into a multiplet of transitions: transitions to the molecular eigenstates. The frequencies and intensities of the multiplet contain information on the dynamics of the IVR process. The use of high resolution, infrared, molecular-beam spectroscopy to obtain detailed information about the rates and mechanisms of IVR has been recently reviewed by Lehmann *et al.*<sup>1</sup> and by Nesbitt and Field.<sup>2</sup>

In studying the structural dependence of the IVR process, much attention has been paid to the role played by large amplitude motions. Large amplitude motions, such as the internal rotation of methyl groups or skeletal torsions are highly anharmonic and are usually the lowest frequency vibrations. Evidence has been obtained that these motions enhance the IVR rates.<sup>3,4</sup> Walters *et al.*<sup>5</sup> have found indications of increased IVR rates in carbonyl compounds with methyl rotors. Parmenter and coworkers<sup>6–8</sup> have shown that the IVR rate of *para*-difluorobenzene is enhanced by nearly two orders of magnitude after substituting a fluorine atom with a methyl group. Martens and Reinhardt<sup>9</sup> have explained this enhancement by a coupling between the methyl rotation and the low-frequency ring modes. However, a successful theoretical treatment of IVR in molecules containing rotor groups treats the torsional modes as harmonic oscillators, thus without internal rotation at all.<sup>10,11</sup>

Perry *et al.*<sup>3,4</sup> have reviewed IVR in molecules with methyl rotors or skeletal torsions. They have found an empirical correlation between the IVR rate and the proximity of a pre-

pared vibration to a center of flexibility (COF). A COF is defined as a bond about which hindered internal rotation can occur. Molecules with large amplitude motions show faster IVR than rigid molecules. The closer the excited vibration is to a COF, the more rapidly it relaxes. Furthermore, Perry *et al.* have concluded that for systems in which the prepared vibration is adjacent to the COF the rate of IVR decreases with increasing height of the barrier to internal rotation. More data are needed to confirm and clarify this empirical correlation and there are other questions that are still open, for example about the dependence of IVR on the nature of the chromophore.<sup>1</sup>

The goal of the present work is to investigate the IVR mechanism in methylamine, a prototypical molecule with large amplitude motions. Methylamine,  $\text{CH}_3\text{NH}_2$ , has been chosen because it has two large amplitude motions which are strongly coupled (the torsion of the methyl top and the inversion of the amine group<sup>12</sup>) and because the molecule has been extensively studied in the microwave, millimeter-wave and far-infrared spectral regions.<sup>13,14</sup> However, no rotationally resolved near-infrared spectra have been published so far. Most of the theoretical work has been centered on the torsional–wagging–rotational problem.<sup>12,15,16</sup> The barriers for the torsion and the inversion were calculated to be  $718\text{ cm}^{-1}$  and  $1943\text{ cm}^{-1}$ , respectively.<sup>12</sup>

The overtone of the NH stretch has been studied at low resolution ( $0.5\text{ cm}^{-1}$ ) by Wolff and Wolff.<sup>17</sup> The band centers of the symmetric ( $2\nu_1$ ) and asymmetric ( $2\nu_{10}$ ) overtone stretch were determined to be at  $6595\text{ cm}^{-1}$  and  $6791\text{ cm}^{-1}$  respectively. The combination band of symmetric and antisymmetric NH stretch ( $\nu_1 + \nu_{10}$ ) has been observed at  $6619\text{ cm}^{-1}$ . Since the band contours of  $2\nu_1$  and  $\nu_1 + \nu_{10}$  were found to overlap in these static gas cell measurements, the values given for these bands are not precise.

In this paper we report the eigenstate-resolved, molecular-beam spectrum of methylamine in the region of the first overtone of the symmetric NH stretch at  $6615\text{ cm}^{-1}$ . The spectrum was found to be highly perturbed and millimeter-wave–infrared double resonance was used to assign three of its clumps.

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## II. Experimental

The experiment has been carried out using an optothermal molecular-beam laser spectrometer which has been described in detail in a previous paper.<sup>18</sup> Briefly, a 1% mixture of methylamine in helium is expanded through a 50  $\mu\text{m}$  nozzle at a backing pressure of 400 kPa. A molecular beam, formed by collimating the expansion with a 0.5 mm conical skimmer, impinges on a liquid helium cooled bolometer which detects the changes in the energy content of the beam. The laser is a stabilized 1.5  $\mu\text{m}$  F-Center laser (Burleigh FCL-130) which is tuned in 1 MHz steps. The laser frequency is monitored with a wavemeter and two scanning etalons of 8 GHz and 150 MHz free spectral range, respectively. The 150 MHz etalon is temperature stabilized and serves as a frequency reference. For calibration purposes, the absorption spectrum of acetylene<sup>19</sup> is collected in a White-type gas cell simultaneously with the methylamine spectrum. The estimated absolute and relative accuracy of the calibrated spectra is 10 MHz.

The interaction between the laser and the molecular beam takes place in a resonant build-up cavity<sup>20</sup> which is located perpendicularly across the molecular beam and enhances the laser power by a factor of  $\sim 600$ . The instrumental resolution is about 5 MHz FWHM. For single resonance spectra, the laser is chopped at about 280 Hz and the output of the bolometer detector is monitored using a phase-sensitive amplifier. Eigenstate resolved spectra obtained in the energy region 6609–6620  $\text{cm}^{-1}$  could not be assigned because of excessive spectral congestion ( $\sim 10^3$  lines per  $\text{cm}^{-1}$ ).

A millimeter-wave source was then introduced in the spectrometer for millimeter-wave-infrared double resonance studies. Two BWO source modules driven by a KVARTZ synthesizer are used to obtain about 20 mW of power in the spectral region between 53 and 118 GHz. The millimeter-wave radiation is coupled into the molecular-beam a few centimeters downstream of the skimmer by a K-band waveguide. Amplitude modulation of the millimeter-wave radiation at 284 Hz is achieved by a mechanical chopper blade mounted in a 10 mm gap of the waveguide outside the molecular beam chamber.

For a double resonance scan, the millimeter-wave frequency is amplitude modulated and fixed to a ground state transition of methylamine<sup>21</sup> while the unmodulated IR-laser frequency is scanned. Bolometric signals are obtained when the laser is tuned to an IR transition that originates from either of the two levels belonging to the rotational ground state whose populations are modulated by the millimeter-wave. These two signals can be distinguished by their relative phase of 180°. Rotational assignment to one of the two ground states was achieved by comparison of the phase of the signals with the phase of a known double resonance transition in the CH overtone stretch of propyne.<sup>22</sup>

## III. Results

### A. The information content of eigenstate-resolved spectra

In the standard analysis of frequency-domain studies of IVR the molecular Hamiltonian  $\hat{H}$  is expanded into a zeroth-order Hamiltonian  $\hat{H}_0$  (which is the standard Hamiltonian used in the analysis of rovibrational spectra at lower energies) and a perturbation term  $W$ .<sup>1</sup> The eigenstates of  $\hat{H}_0$  are the anharmonic normal-mode rovibrational states.<sup>23</sup> Higher-order rovibrational interactions (anharmonic, Coriolis, and centrifugal couplings) are grouped together in the term  $W$ . A rovibrational eigenstate of  $\hat{H}_0$  which carries oscillator strength from the ground vibrational state is called a bright state. The bright state is immersed in a bath of other zeroth-order rovibrational states that are not optically accessible from the ground state. These dark states are comprised of overtone and combination

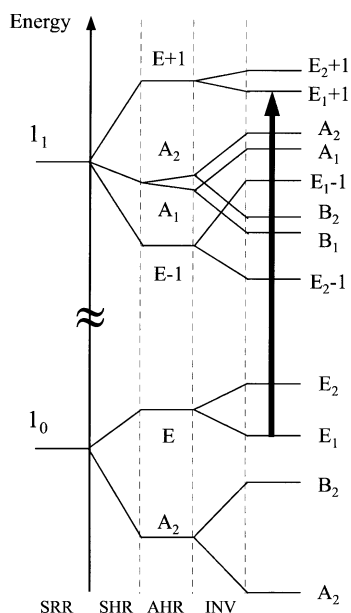
bands of lower lying normal modes. The interaction term  $W$  couples the bright state to a bath of near-resonant dark states inducing intramolecular vibrational energy redistribution. In frequency-resolved experiments, the IVR process is observed *via* the fragmentation of a single expected transition to the bright state, into transitions of a multiplet of molecular eigenstates. (If the density of coupled bath states is high, a “continuous” broadening of the spectroscopic transition is observed.) The center-of-gravity of the IVR multiplet or Lorentzian line is given by the position of the bright state, and the sum of intensities is equal to the bright state transition strength.<sup>1</sup> The time evolution of the bright state population can be calculated using the fluorescence theorem.<sup>24</sup> Since the radiative lifetime of infrared transitions is sufficiently long, the time evolution of the excited state population is given by the Fourier transformation of the autocorrelation function of the multiplet spectrum.<sup>25</sup> The strength of the coupling between the bright state and the dark states can be determined by the Lawrence–Knight deconvolution.<sup>26,27</sup> Although in highly fragmented spectra an assignment of the coupled dark states is often not possible, useful information can be obtained using statistical methods. For instance, the fraction of the bath states that couple to the bright state can be obtained. Moreover energy level spacing statistics<sup>28</sup> can be used to study the nature of the vibrational dynamics—that is to find whether the classical motion is regular or chaotic. Most of the methods assume that only a single bright state exists. In strongly perturbed spectra, where the components of a multiplet are intercalated among the components of other clumps, double resonance techniques are often the only way to obtain accurate assignment of transitions to a single IVR multiplet.<sup>1</sup>

### B. The energy levels of methylamine

For the assignment of the double resonance spectrum an understanding of the energy levels of methylamine and their symmetry is essential. A group theoretical treatment of the torsion-inversion-rotation problem in methylamine has been given by Ohashi and Hougen.<sup>15</sup> Methylamine is a nearly prolate symmetric rotor with the following ground state rotational constants:<sup>29</sup>

$$A - \bar{B} \approx 2.70 \text{ cm}^{-1}, \quad \bar{B} \approx 0.74 \text{ cm}^{-1}, \quad \text{and} \\ B - C \approx 0.03 \text{ cm}^{-1}.$$

The rotational energy levels associated with  $J_K$  in the symmetric top notation are split by the effect of the methyl group internal rotation and the inversion of the amine group.<sup>21</sup> In Fig. 1 the splittings of the energy levels as they change from those of a symmetric rigid rotor (SRR) to those of an asymmetric hindered rotor with inversion (INV) are schematically shown. Level symmetries which refer to the permutation-inversion group  $G_{1,2}$ <sup>15</sup> and the relative positions of the methylamine energy levels on the right side of the diagram are taken from ref. 30. When torsion of the methyl group becomes possible, the symmetric rotor state  $1_0$  is split into two levels of, respectively, E and A symmetry. Both levels are split further by the inversion of the amine group. For the  $1_1$  level, the torsional sublevel of E-symmetry is split further into two E-levels by coupling of the torsion with the rotation about the symmetry axis. To distinguish between these two E-levels with the same  $J$  and  $K > 0$ , the notations E + 1 and E – 1 have been introduced by Ohashi *et al.*<sup>29</sup> Basically, the +1 and –1 labels indicate the different sign of the product of the torsional-wagging and the rotational quantum numbers. For  $K = 0$ , these labels have no meaning. The degeneracy of the A-level is removed by asymmetric rotor  $K$ -type doubling effects. For  $K = 1$ , the E + 1 and E – 1 levels are strongly mixed by these asymmetric rotor effects.<sup>29,31</sup> Since with higher  $K$  the torsional splitting increases relative to the asymmetric rotor doubling, the +1 and –1 labels behave approximately like

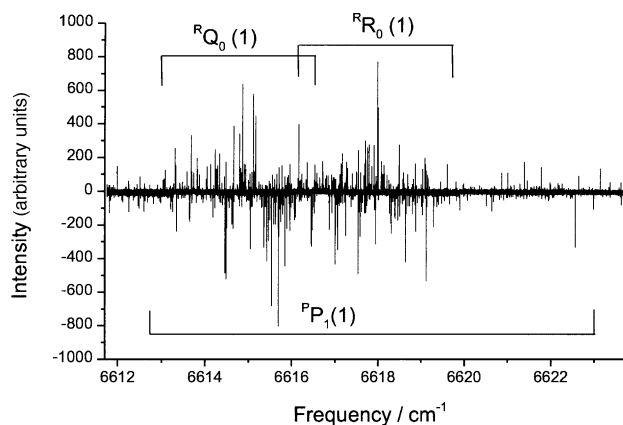


**Fig. 1**  $J_{K_a} = 1_0$  and  $J_{K_a} = 1_1$  rotational energy levels of methylamine in the vibrational ground state. The diagram shows schematically the transition from a rigid rotor mode (left side) to an asymmetric hindered rotor with inversion (right side). (SRR = symmetric rigid rotor, SHR = symmetric hindered rotor, AHR = asymmetric hindered rotor, INV = asymmetric hindered rotor with inversion) (adapted from ref. 21). The bold arrow marks the millimeter-wave transition used for the double resonance experiment.

good quantum numbers for  $K \geq 2$  and allowed transitions obey the selection rules  $+1 \leftrightarrow +1$  and  $-1 \leftrightarrow -1$ .<sup>29</sup>

### C. Double resonance spectrum

Some of the low  $J$  millimeter-wave transitions of methylamine in the vibrational ground state, given in ref. 21, have been tested with respect to their suitability in the double resonance experiments. The best signal to noise was observed for the transition  $E_1 + 1: J_{K_a} = 1_1 \leftarrow E_1: J_{K_a} = 1_0$  ( $F = 2 \leftarrow F = 2$ ) where  $F$  denotes the spin of the hyperfine component. This transition is marked with an arrow in Fig. 1. The optimized frequency of 84 305.136 MHz was found to be slightly off the value of 84 305.39(10) MHz given in ref. 21. In Fig. 2 the double resonance spectrum obtained in the energy region 6612–6623  $\text{cm}^{-1}$  is shown. Positive signals have been assigned to transitions originating from the ground state level  $J_{K_a} = 1_0$ , negative signals to those originating from  $J_{K_a} = 1_1$ . Even though double resonance was used in the measurement, the recorded spectrum is still too congested to be assigned by



**Fig. 2** Double resonance spectrum of methylamine. The three IVR multiplets that have been assigned are shown.

visual inspection. Indeed, more than 450 transitions have been observed with a maximum signal to noise ratio of about 40.

### D. Rotational assignment

A traditional method for the assignment of spectra makes use of ground state combination differences.<sup>32</sup> IVR-multiplets of transitions originating from different rotational ground state levels but going to the same bright state will show the same pattern of fractionation. As mentioned before, the application of this method to the single resonance spectrum failed. The measured density of lines of about 1000 per  $\text{cm}^{-1}$  in combination with an estimated precision of 10 MHz resulted in too many line position accidental agreements. Therefore, the method of ground state combination differences was applied simultaneously to both the double resonance and the single resonance spectrum. Line positions of the double resonance spectrum were shifted by ground state combination differences,<sup>30</sup> and the resulting spectra were compared with the single resonance spectrum. A ground state combination difference was verified when a multiplet of lines of the frequency shifted spectrum coincided with lines in the single resonance spectrum. In this way, accidental agreement played a minor role since the double resonance spectrum contains only a few IVR multiplets, each having a relatively high number of lines, and a ground state combination difference must hold for any line of a multiplet.

For the transitions of the double resonance spectrum originating from the  $J_{K_a} = 1_0$  state with  $E_1$  symmetry (positive signals in Fig. 2), two multiplets were found: One of these multiplets is centered at 6614.6  $\text{cm}^{-1}$  and was identified by a ground state combination difference with the state  $J_K = 0_0$  of  $E_1$ -symmetry. This multiplet consists of 92 lines and is assigned to a  ${}^R Q_0(1): 1_1 \leftarrow 1_0$  transition. For the other multiplet centered at 6617.8  $\text{cm}^{-1}$ , a ground state combination difference with the  $E_1$ -level  $J_K = 2_0$  was found. Two different assignments, a  ${}^R Q_0(1): 1_1 \leftarrow 1_0$  or a  ${}^R R_0(1): 2_1 \leftarrow 1_0$  transition, are possible for this ground state combination difference. However, since the center of the multiplet is blue shifted with respect to the center of the other multiplet, the 115 observed lines of the second multiplet have been assigned to a  ${}^R R_0(1): 2_1 \leftarrow 1_0$  transition. The two IVR-multiplets are identified in Fig. 2. Line positions and relative intensities are available as supplementary information.† In each of the excited states  $J_K = 1_1$  and  $J_K = 2_1$ , there are torsional sublevels of  $E_1 + 1$  and  $E_1 - 1$  symmetry. Transitions to both these states are allowed from the  $J_K = 1_0$  ground state according to the selection rules of the permutation-inversion group  $G_{12}$  ( $E_1 \pm 1 \leftrightarrow E_1 \pm 1$  for low  $K$ ,  $E_1 + 1 \leftrightarrow E_1 + 1$  and  $E_1 - 1 \leftrightarrow E_1 - 1$  for high  $K$ ).<sup>29</sup> Therefore, it must be considered that the two observed multiplets are not pure multiplets, but that they might arise from two different bright states each. However, in case the mixing of the  $E_1 + 1$  and  $E_1 - 1$  levels by asymmetric rotor effects, as pointed out in Section B, is sufficiently strong, only one of these states will carry oscillator strength from the vibrational ground state. This bright state is mixed with the other rovibrational state by diagonal Coriolis interaction in the zeroth-order vibrational state and each of these states can be coupled to background states.

As for the negative signals of Fig. 2, no combinations differences, either to ground states having  $E_1 + 1$  symmetry or to those having  $E_1 - 1$  symmetry, could be found for the double resonance transitions originating from the  $J_{K_a} = 1_1$  state with  $E_1 + 1$  symmetry. The finding of combination differences in the spectra is expected if the selection rules of the

† Available as supplementary material (SUP 57525, 6pp.) deposited with the British Library. Details are available from the Editorial Office. For direct electronic access see <http://www.rsc.org/suppdata/cp/1999/2427>.

**Table 1** Fundamental frequencies of methylamine<sup>a</sup>

Sym. <sup>b</sup>	Mode <sup>c</sup>	Energy/cm <sup>-1</sup>	Sym. <sup>b</sup>	Mode <sup>c</sup>	Energy/cm <sup>-1</sup>
A'	$\nu_1$ NH <sub>2</sub> s-str.	3360	A''	$\nu_{10}$ NH <sub>2</sub> a-str.	3424
A'	$\nu_2$ CH <sub>3</sub> d-str.	2962	A''	$\nu_{11}$ CH <sub>3</sub> d-str.	2985
A'	$\nu_3$ CH <sub>3</sub> s-str.	2820	A''	$\nu_{12}$ CH <sub>3</sub> d-def.	1485
A'	$\nu_4$ NH <sub>2</sub> sci.	1623	A''	$\nu_{13}$ NH <sub>2</sub> twist.	1485 <sup>d</sup>
A'	$\nu_5$ CH <sub>3</sub> d-def.	1474	A''	$\nu_{14}$ CH <sub>3</sub> d-rock.	1057 <sup>d</sup>
A'	$\nu_6$ CH <sub>3</sub> s-def.	1430	A''	$\nu_{15}$ Torsion	264
A'	$\nu_7$ CH <sub>3</sub> d-rock.	1130			
A'	$\nu_8$ CN str.	1044			
A'	$\nu_9$ NH <sub>2</sub> wag.	780			

<sup>a</sup> From ref. 35. <sup>b</sup> Symmetry of modes in C<sub>s</sub>. <sup>c</sup> a-, antisymmetric; s-, symmetric; d-, degenerate; str., stretching; sci., scissoring; def., deformation; wag., wagging; twist., twisting; rock., rocking. <sup>d</sup> Calculated values.

permutation-inversion group G<sub>12</sub> are not restricted by asymmetric rotor effects. Therefore, it is more appropriate to use asymmetric rotor notation to assign the observed negative double resonance transitions. The  $J_{K_a} = 1_1$  level with E<sub>1</sub> + 1 symmetry can be identified with the asymmetric rotor state  $J_{K_a K_c} = 1_{10}$  with E<sub>1</sub>-symmetry since it is higher in energy than the  $J_{K_a} = 1_1$  level with E<sub>1</sub> - 1 symmetry.<sup>30</sup> The only transitions originating from  $J_{K_a K_c} = 1_{10}$  (E<sub>1</sub>-symmetry) for which no combination differences can be found are c-type transitions to 0<sub>00</sub> and 2<sub>20</sub> (both E<sub>1</sub>-symmetry). A transition to 2<sub>20</sub> can be discarded since the torsional splitting dominates the asymmetric rotor effects at K<sub>a</sub> = 2 and the selection rules of G<sub>12</sub> should not be restricted, *i.e.* a transition to 2<sub>20</sub> should also be observed from the 2<sub>11</sub> ground state. As a result of this analysis, all 251 observed negative lines are attributed to the <sup>P</sup>P<sub>1</sub>(1) transition to the IVR-multiplet of the bright state  $J_{K_a} = 0_0$  with E<sub>1</sub>-symmetry (using symmetric rotor notation for comparison with the other assigned transitions). All the transition frequencies and relative intensities are available as supplementary information.

Therefore, the analysis of the spectra points out that the <sup>P</sup>P<sub>1</sub>(1) transition is more affected by asymmetry through the mixing of E states than the <sup>R</sup>Q<sub>0</sub>(1) and <sup>R</sup>R<sub>0</sub>(1) transitions. Since this mixing decreases with increased torsional splitting the above described behaviour would be expected when the torsional splitting is much larger in the vibrational excited state than in the ground state. While for the <sup>R</sup>Q<sub>0</sub>(1) and <sup>R</sup>R<sub>0</sub>(1) transitions E-states are mixed in the excited state, this mixing occurs for the <sup>P</sup>P<sub>1</sub>(1) transition in the ground state. Since torsional splittings can get quite large when a strong coupling to a torsionally excited vibrational state is present (as observed in the spectrum of the carbonyl overtone stretch of acetaldehyde<sup>33</sup>) the observed behaviour can be justified.

## E. Vibrational assignment

In the energy region analysed, the overtone of the symmetric NH stretch, 2 $\nu_1$ , and the combination band of symmetric and antisymmetric NH stretch,  $\nu_1 + \nu_{10}$ , have been observed previously.<sup>17</sup> For 2 $\nu_1$ , the transition dipole moment lies in the symmetry plane  $\sigma_{ac}$  and in general, a- and c-type transitions are expected. While b-type transitions are forbidden in this case, they are allowed for the  $\nu_1 + \nu_{10}$  vibration. Therefore, the pure c-type transitions observed for the negative double resonance signals are assigned to 2 $\nu_1$ . The positive transitions of the double resonance spectrum can be attributed to this vibration, too, if the torsional splitting in the excited state is of the order of a few cm<sup>-1</sup>. Equal tunneling splittings in both excited and ground state would imply that the perpendicular transitions <sup>R</sup>Q<sub>0</sub>(1) and <sup>P</sup>P<sub>1</sub>(1) are well separated by about 7 cm<sup>-1</sup>. However, since the tunneling splittings were not determined in this experiment and the band origins of 2 $\nu_1$  and  $\nu_1 + \nu_{10}$  are not precisely known, we cannot rule out the possibility that the positive signals originate from b-type tran-

sitions of the  $\nu_1 + \nu_{10}$  vibration. Both vibrational assignments seem to imply that in methylamine the  $\nu_1 + \nu_{10}$  mode be lower in energy than the 2 $\nu_1$  mode, in contradiction to the results of the low resolution work of Wolff and Wolff.<sup>17</sup>

## F. IVR analysis

**1. Density of states (DOS).** Information on the coupling between the bright state and the dark states can be obtained by determining the fraction of available dark states that are coupled to the bright state. The available DOS has been calculated from a harmonic oscillator model by a direct count algorithm<sup>34</sup> which gives the number of vibrational combination bands in a certain energy interval. The fundamental frequencies of methylamine have been taken from ref. 35 and are listed in Table 1. The torsion has been treated as a hindered rotor with three-fold symmetry<sup>36</sup> in order not to underestimate the DOS by too much when using a harmonic oscillator model. The calculated DOS has to be multiplied by a factor of two to take the inversion splitting into account. This resulted in a total vibrational density of states of 36 per cm<sup>-1</sup> within a 20 cm<sup>-1</sup> energy window centered at 6615 cm<sup>-1</sup>. In the permutation-inversion group G<sub>12</sub>, this total density breaks down to 3 per cm<sup>-1</sup> of A<sub>1,2</sub> or B<sub>1,2</sub> symmetry and 6 per cm<sup>-1</sup> of E<sub>1,2</sub> symmetry. The degeneracy of those E<sub>1,2</sub> levels that are carrying angular momentum can be lifted by Coriolis interactions, resulting in an observed DOS which is twice as high as calculated. In our double resonance spectrum only E<sub>1</sub> states can be observed because of the selection rule E<sub>1</sub> ↔ E<sub>1</sub> of the G<sub>12</sub> group. The observed DOS  $\rho$  is calculated from the spectrum by

$$\rho = (N - 1)/\Delta E$$

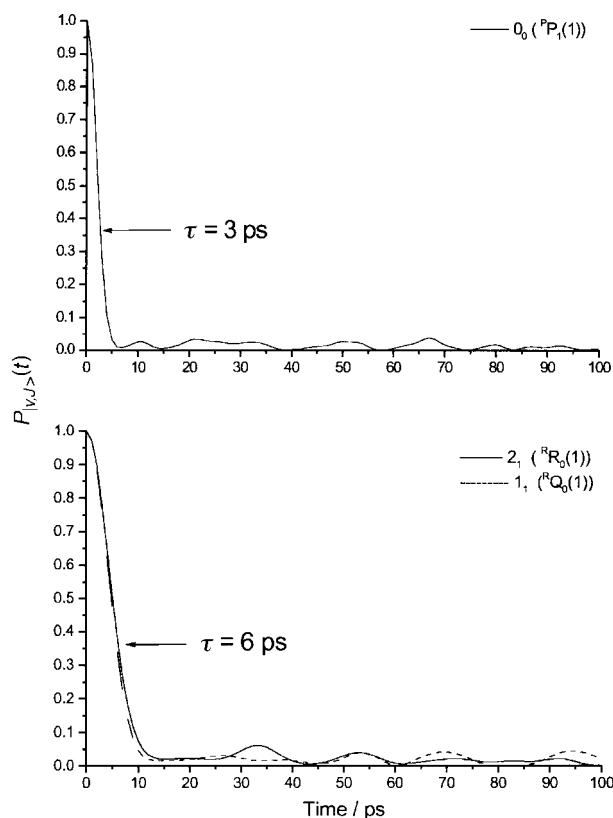
where  $N$  is the total number of eigenstates in each IVR-multiplet and  $\Delta E$  the energy window in which the multiplet appears.<sup>22</sup> The observed DOS for each multiplet listed in Table 2, is about 20–30 states per cm<sup>-1</sup>.

For the <sup>P</sup>P<sub>1</sub>(1) transition of 2 $\nu_1$ , the observed DOS is a factor of four larger than the calculated DOS. Coriolis interactions are able to lift the degeneracy of E levels and to increase the DOS by an additional factor of 2 $J$  + 1 by coupling of rotational levels.<sup>37</sup> However, since the excited state of

**Table 2** Calculated and observed density of states

Mode	Transition	Bright state	Calculated DOS/per cm <sup>-1</sup>	Observed DOS/per cm <sup>-1</sup>
$\nu_1 + \nu_{10}$	<sup>R</sup> R <sub>0</sub> (1)	2 <sub>1</sub>	6 (12) <sup>a</sup>	28
$\nu_1 + \nu_{10}$	<sup>R</sup> Q <sub>0</sub> (1)	1 <sub>1</sub>	6 (12) <sup>a</sup>	22
2 $\nu_1$	<sup>P</sup> P <sub>1</sub> (1)	0 <sub>0</sub>	6	25

<sup>a</sup> Values in parentheses refer to lifted degeneracy of E levels by Coriolis interaction.



**Fig. 3** Time evolution of the bright states for the  ${}^{\text{P}}\text{P}_1(1)$ -,  ${}^{\text{R}}\text{R}_0(1)$ - and  ${}^{\text{R}}\text{Q}_0(1)$ -transitions calculated from the Fourier transform of the spectrum autocorrelation function. The lifetimes  $\tau$  are given by the times when the survival probability  $P_{|v,j>}(t)$  has decayed to  $1/e$  of its initial value.

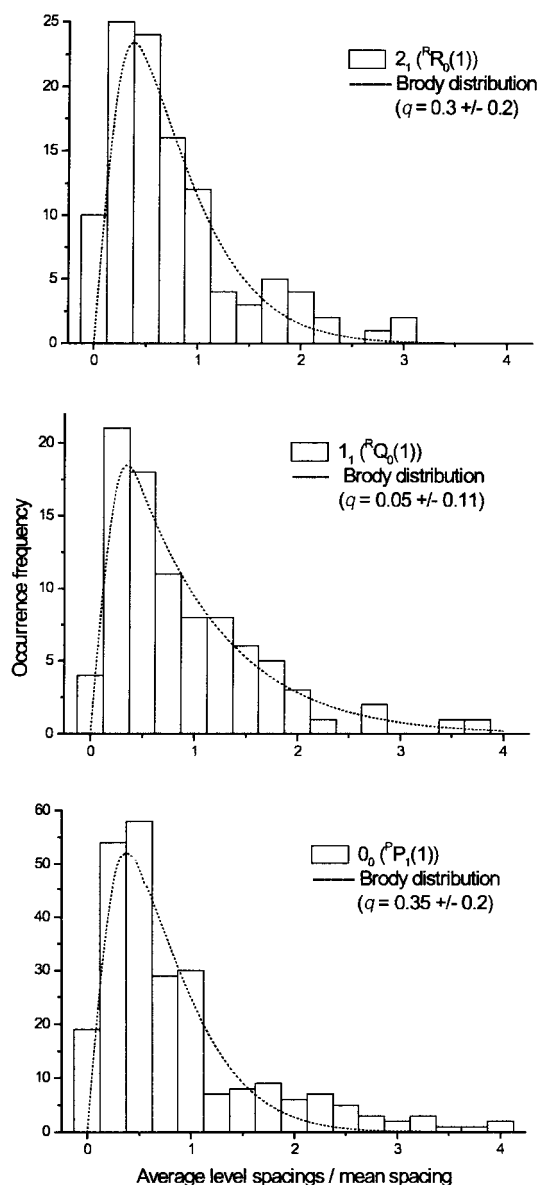
${}^{\text{P}}\text{P}_1(1)$  does not carry angular momentum ( $J = 0$ ), Coriolis interactions cannot be responsible for the discrepancy between observed and calculated DOS. The underestimation of the DOS is most probably due to the harmonic oscillator approximation, especially for the inversion mode. Moreover, the strong coupling between the torsion and the inversion has been neglected. In fact, deviations between calculated and observed DOS by a factor of two or more are not surprising and have been reported previously.<sup>37</sup> Therefore, to a good approximation the  $J = 0_0$  state of  $2\nu_1$  couples to all dark states with the same symmetry and quantum numbers.

For the multiplets of the  ${}^{\text{R}}\text{Q}_0(1)$  and  ${}^{\text{R}}\text{R}_0(1)$  transitions we have pointed out that two bright states might contribute if asymmetric rotor effects play only a minor role. But the similarities in the observed DOS between the  $0_0$  multiplet and the  $1_1$  and  $2_1$  multiplets lead to the assumption that the transitions of those two multiplets can be attributed to a single bright state as well. Therefore in the further analysis we will regard all observed IVR-multiplets as pure.

**2. Time evolution of the bright state.** Information about the intramolecular dynamics is obtained from the time evolution of the bright state. While the energy of the bright state is given by the center-of-gravity of its IVR multiplet,<sup>1</sup> the probability  $P_{|v,j>}$  of finding the molecule in the bright state excited at a time equal to zero is calculated from the relative positions of the eigenstates by

$$P_{|v,j>}(t) = \sum_i |c_i|^4 \times \exp(-\gamma_r t) + 2 \sum_{i>j} |c_i|^2 |c_j|^2 \times \cos[(E_i - E_j)t/\hbar] \times \exp(-\gamma_r t)$$

(ref. 24), where  $|c_i|^2$  are the normalized intensities of the eigenstates in an IVR multiplet,  $E_i$  are the transition frequencies and  $1/\gamma_r$  is the radiative lifetime of the excited vibrational state

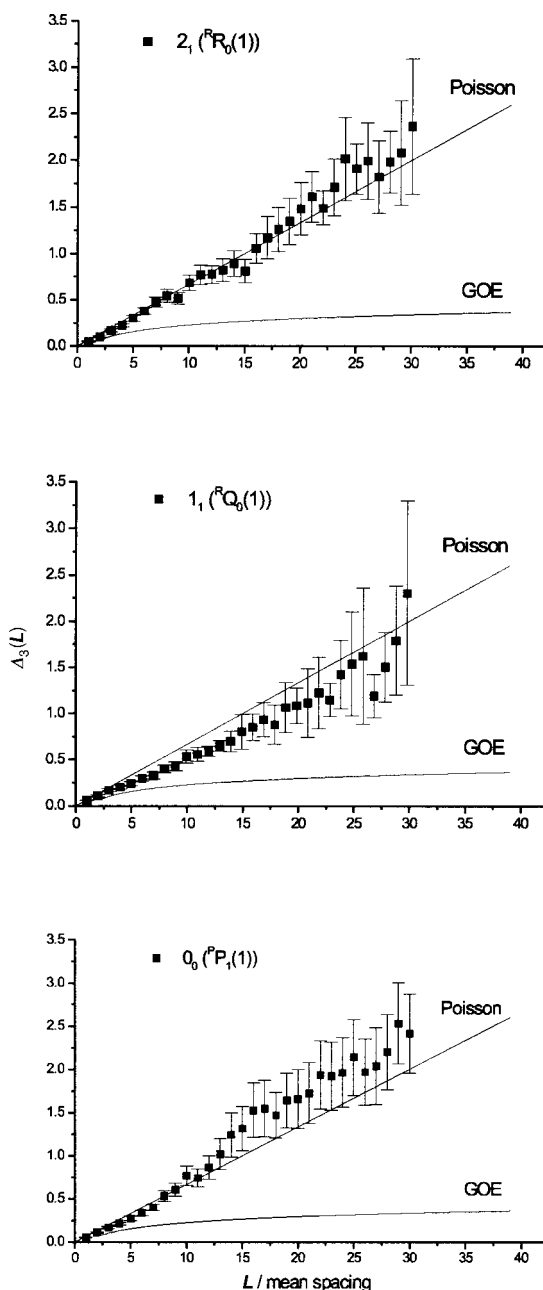


**Fig. 4** Observed nearest neighbour level spacing histogram for the three observed IVR multiplets using 0.2 bins. The histograms are compared by the Brody distribution  $P(S) = \alpha S^q \exp(-\beta S^{1+q})$  that allows for a continuous transition from a Poisson ( $q = 0$ ) to a Wigner ( $q = 1$ ) distribution of level spacings.

which is sufficiently long for infrared transitions to neglect the exponentially decaying term. Calculating  $P_{|v,j>}$  using this formula corresponds to taking the Fourier transform of the autocorrelation of the IVR multiplet.<sup>25</sup>

In Fig. 3 the evolution of each bright state is estimated from the time that needs to elapse before the intensity has decayed to  $1/e$  of its initial value. For the  $0_0$  multiplet, the lifetime is about 3 ps, while it is 6 ps for the  $2_1$  and  $1_1$  multiplet. After the initial decay, only weak quantum beats are present. The energy in the bright state is rapidly redistributed in the molecule. These lifetimes are among the shortest ever determined from a fully eigenstate resolved spectrum.<sup>1</sup> The reason for the larger lifetime of the  $2_1$  and  $1_1$  multiplets might be an insufficient experimental sensitivity leading to missing transitions in the wings of these multiplets. However, as pointed out before, it is also possible that these transition arise from the  $\nu_1 + \nu_{10}$  mode of methylamine which may have a different IVR lifetime.

**3. Energy level spacing statistics.** At a high level of fragmentation, a well resolved spectrum is well suited for a statistical analysis of energy level spacings. Spectra which have



**Fig. 5**  $\Delta_3$  statistics for the three observed IVR multiplets.  $L$  is normalized to the mean level spacing in each multiplet. The limiting cases  $\Delta_3(L) = L/15$  and  $\Delta_3(L) = (\ln L - 0.0687)/\pi^2$  for a Poisson and a GOE level distribution, respectively, are plotted for comparison.

regular classical dynamics are expected to show a Poisson's distribution of spacings<sup>38</sup> while chaotic spectra resemble the Gaussian orthogonal ensemble (GOE) spectrum, due to level repulsion of each level with its neighbours.<sup>39</sup>

In Fig. 4 the observed nearest neighbour level spacing distribution is shown for the three different bright states. The distributions were fit to the function

$$P(S) = \alpha S^q \exp(-\beta S^{1+q})$$

suggested by Brody *et al.*<sup>28</sup> The parameter  $q$  allows for a continuous transition from a Poisson ( $q = 0$ ) to a Wigner ( $q = 1$ ) distribution of nearest neighbour level spacings. For all three distributions only weak level repulsion ( $q < 0.3$ ) is observed. These observations are confirmed by  $\Delta_3$  statistics<sup>40</sup> which mainly reflect long-range level correlations. Fig. 5 shows that the level distributions are close to a Poisson distribution. Thus level spacing statistics point out that the IVR occurs through regular classical dynamics.

**4. Coupling strengths.** At the high level of fragmentation observed in the spectrum of methylamine the identification of the perturbers is not possible. In order to determine the strengths of the couplings between the bright states and the dark states a modified version<sup>27</sup> of the Lawrence–Knight deconvolution<sup>26</sup> was performed. In the Lawrence–Knight deconvolution a single bright state and a lack of direct coupling between the bath states is assumed. As supported by the assignment and the energy level spacing statistics, both assumptions are met in our spectrum to a good approximation. The root mean square coupling strength determined in this way is about  $0.1 \text{ cm}^{-1}$  for all three bright states.

## IV. Discussion

In the spectra of  $2\nu_1$  of methylamine, the bright states of  $E_1$  symmetry are strongly coupled to the bath states of same symmetry and rotational quantum numbers, resulting in a high level of fragmentation at a relatively small vibrational density of states. Energy level spacing statistics indicate regular classical dynamics. For the  ${}^{\text{P}}\text{P}_1(1)$  transition of  $2\nu_1$ , intramolecular energy redistribution can only be mediated by anharmonic coupling because of the lack of angular momentum of the excited state. The density of state analysis indicates that the same holds for the  ${}^{\text{R}}\text{R}_0(1)$  and the  ${}^{\text{R}}\text{Q}_0(1)$  transitions. Since the measured relaxation time of a few ps is of the same order as the time constant for molecular rotation, it is not surprising that Coriolis couplings do not play a dominant role in the relaxation process.

Coupling strengths between bright and dark states observed in IVR processes are typically of the order of  $0.01 \text{ cm}^{-1}$ .<sup>1</sup> The average coupling strength of about  $0.1 \text{ cm}^{-1}$  observed in methylamine is one order of magnitude larger. The high coupling strength and fast IVR can be considered as evidence for a low-order resonance coupling of the  $2\nu_1$  mode to other vibrational modes. A possible mode is  $\nu_1 + 2\nu_4$  where  $\nu_4$  is  $\text{NH}_2$  scissoring mode. Hamada *et al.*<sup>35</sup> have found in an *ab initio* force field calculation relatively high positive force constants for the coupling of  $\nu_1$  and  $\nu_4$  in methylamine. This means that the instability caused by the N–H elongation is compensated by bringing the H atoms closer to one another.<sup>35</sup> Furthermore, it was observed in the NH stretch overtone region of  $\text{NH}_3$  that anharmonic resonances between the NH stretching modes with two quanta of the asymmetric NH bending mode result in a rapid energy relaxation.<sup>41</sup> Thus  $\nu_1 + 2\nu_4$  is likely to be a doorway state for the relaxation of  $2\nu_1$  in methylamine. In a following step of relaxation the second  $\nu_1$  quantum of  $2\nu_1$  could relax in  $2\nu_4$ , as well, though the energy mismatch would be by about  $100 \text{ cm}^{-1}$  larger.

A central question remaining is whether the two large amplitude motions increase the IVR rate in methylamine. There is no doubt that the methyl group torsion and the inversion of the amine group strongly participate in the IVR dynamics: In our DOS calculation it has turned out that, on average, a dark state contains two quanta of the inversion mode and six torsional quanta. But according to the empirical correlation of Perry *et al.*<sup>4</sup> between the barrier height in flexible molecules and the IVR lifetime, the IVR lifetime in methylamine is about two orders of magnitude shorter than expected. Thus the fast IVR dynamics in methylamine are probably mainly due to the low-order resonances between the amine group modes discussed above. The strong coupling between the two large amplitude motions (the amine inversion and the methyl top torsion) might help to redistribute the energy that relaxes on a fast time scale in the amine group, over the whole molecule.

## V. Conclusions

In the present work, the overtone spectrum of the symmetric

NH stretch ( $2\nu_1$ ) has been measured with eigenstate resolution. A millimeter-wave-infrared double resonance technique has been applied to assign the highly fractionated IVR multiplets to the  ${}^R R_0(1)$ ,  ${}^R Q_0(1)$  and  ${}^P P_1(1)$  transitions between  $E_1$  symmetry states. The IVR-lifetime has been determined to be 3 ps. This lifetime is one of the shortest lifetimes that has ever been found for a fully eigenstate resolved spectrum. Although the two large amplitude motions do strongly participate in the IVR process, the short lifetime and a high average coupling strength of about  $0.1 \text{ cm}^{-1}$  indicate that the relaxation is enhanced by low-order resonances. Most probably, in a first step anharmonic coupling to the scissoring mode  $\nu_4$  results in a fast redistribution of the energy within the amine group and in a second step, this energy is further relaxed into the molecule by a strong coupling between the two large amplitude motions. IVR studies on overtone excitation of the CH stretching modes in methylamine would help in further elucidating the energy relaxation process. Finally, this work points out that interpreting short IVR lifetimes as a direct consequence of molecular flexibility may not always be justified.

### Acknowledgements

This work was supported by the National Science Foundation under grant CHEM-9703604. We gratefully acknowledge the financial support by the German academic exchange program (DAAD-Doktorandenstipendium aus Mitteln des zweiten Hochschulsonderprogramms) granted to U.M. The authors would also like to thank G. T. Fraser at NIST, Gaithersburg, for the loan of millimeter-wave equipment.

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Paper 9/00370C