

Molecular Beam Infrared Spectrum of Nitromethane in the Region of the First C–H Stretching Overtone

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The infrared spectrum of the first C–H stretching overtone of nitromethane (CH_3NO_2) was measured in the wavenumber region 6047–6055 cm^{-1} with a resolution of 5 MHz using a molecular beam laser spectrometer equipped with bolometric optothermal detection and a power build-up cavity. The assignment of the spectrum was made using ground-state combination differences and an asymmetric rotor energy level simulation program. The following parameters were obtained for the $m = 0$ upper state: $\nu_0 = 6050.1378(24) \text{ cm}^{-1}$, $A = 0.55399(84) \text{ cm}^{-1}$, $B = 0.2936(15) \text{ cm}^{-1}$, $C = 0.2567(13) \text{ cm}^{-1}$. The intramolecular vibrational energy redistribution (IVR) rate of the C–H stretch was calculated from the spectrum. The IVR rate of the different $J_{K_a K_c}$ levels in the spectrum ranged from 170 to 300 ps, comparable to the rate measured for methyl C–H stretching overtones in molecules of similar size (CH_3SiH_3 and CH_3CD_3).

Introduction

Nitromethane (CH_3NO_2) is an asymmetric top consisting of a heavy frame (NO_2) and a lighter top (CH_3), the local symmetries of which are C_{2v} and C_{3v} , respectively (Figure 1). It is an almost free rotor with a very low 6-fold torsional barrier in the ground vibrational state (the potential barrier height is 2 cm^{-1}),^{1,2} which makes it an interesting molecule to study from the dynamic point of view. In the ground vibrational state the torsional barrier gives rise to both staggered and eclipsed configurations, which belong to the C_s point group. However, due to low barrier height the full torsional–vibrational molecular symmetry group G_{12} (isomorphic to D_{3h}) should be used to label states.

Earlier spectroscopic works on nitromethane investigated the microwave^{1–6} spectra as well as low-resolution IR and Raman spectra in the region of the fundamentals^{7–10} and the overtones.^{11,12} In this study, the dynamics of nitromethane in the first C–H stretching overtone region (6047–6055 cm^{-1}) was investigated at very high resolution ($\approx 6 \text{ MHz}$) using a molecular beam laser spectrometer. The purpose was 2-fold. First, the aim was to find out whether the low 6-fold torsional barrier of the ground vibrational state turns into a higher 2-fold barrier upon excitation of the C–H bonds with two quanta of stretching vibration, which in turn would imply that the vibrational energy stays localized in one bond for a longer time than the period of the internal rotation. Second, the aim was to measure the intramolecular vibrational energy redistribution (IVR) rate of the C–H stretch and compare it with the IVR rate of the methyl C–H stretch in molecules of similar size.

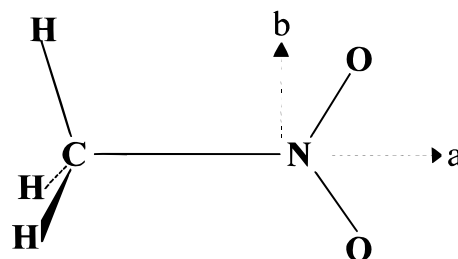


Figure 1. Nitromethane.

Experimental Section

A Fourier transform IR (FTIR) spectrum of nitromethane was measured in the wavenumber region 5600–6200 cm^{-1} with a Bruker 120 IFS interferometer in Helsinki (Figure 2) in a room-temperature cell at 19-mbar pressure with an optical path length of 20 m. At the maximum achievable spectral resolution (0.01 cm^{-1} , which is close to the room-temperature Doppler width of nitromethane), the spectrum shows two strong, broad bands. Therefore, to resolve the rotational fine structure it was necessary to use a molecular beam spectrometer. The spectrometer has been described in a previous paper.¹³ A beam of the molecule of interest is formed by expanding a 0.9% mixture of nitromethane in helium at a stagnation pressure of 0.48 MPa through a 50- μm diameter nozzle into a vacuum chamber pumped by a 5000 L/s oil diffusion pump. Upon collimation by a 0.5-mm diameter skimmer the beam enters a second vacuum chamber where it is probed with a tunable infrared laser. The increased energy gained from the beam upon excitation of a molecular vibrational transition is detected further downstream by means of a cryogenically cooled bolometer on which the beam impinges. The $\text{He}-\text{CH}_3\text{NO}_2$ mixture is obtained by bubbling gaseous helium through a reservoir of liquid ni-

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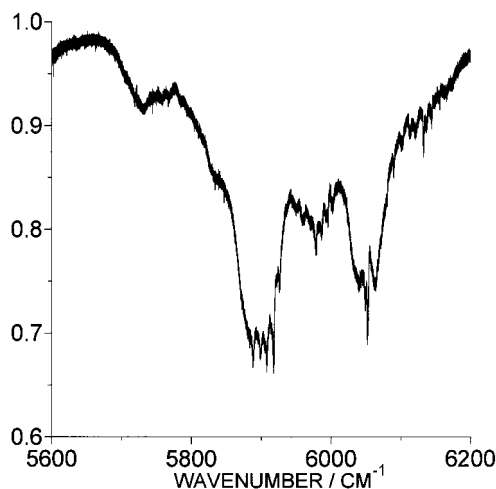


Figure 2. An FTIR spectrum of the first C-H stretching overtone region of nitromethane. The intensity scale is of transmittance.

nitromethane. Nitromethane (99.3% purity) was purchased from Aldrich and was used without further purification.

The laser used is a stabilized 1.5- μ m color-center laser, delivering about 300 mW of power in the region under investigation. The laser is tuned in 1-MHz increments at a rate of about 20 MHz/second, and its wavelength is monitored with a wavemeter and two scanning confocal etalons of 150 and 8000 MHz free spectral ranges, respectively. The 150-MHz etalon is temperature stabilized and serves as a frequency reference. In addition, absolute calibration is achieved by simultaneously collecting the spectrum of methyl iodide (CH₃I) (whose transitions have been precisely measured in this wavelength region¹⁴), which was placed in a White-type gas cell at a pressure of about 1 Torr. The laser excitation occurs inside a resonant power build-up cavity¹⁵ located across the molecular beam. Construction details have been reported previously.¹⁶ About 100 mW of laser power are coupled to the cavity through a single mode fiber. A gradient index lens located between the cavity and the fiber output ensures effective mode matching and thus maximum power coupling. The effective power enhancement is about 100. The highly collimated nature of the beam reduces Doppler broadening significantly, thus enhancing the resolution; an instrumental line width of about 2×10^{-4} cm⁻¹ (6 MHz) is achieved, limited primarily by transit time broadening and residual Doppler broadening, which are estimated to be 2.6 and 2.7 MHz, respectively.¹⁶

Because the effective rotational temperature in the beam is low (about 5 K), most of the spectral congestion is also removed since only a few rotational states are significantly populated. The spectrum also appears in a narrow wavenumber region. Due to the slow effective scanning speed (about 1 cm⁻¹/h) not all the region covered by the FTIR spectrum could be probed. Instead, several trial measurements were made in the wavenumber region of the lower energy band (5886.9–5888.1 cm⁻¹, 5904.8–5908.3 cm⁻¹, and 5915.3–5918.2 cm⁻¹), but no spectrum was observed for reasons not clearly understood at this stage. However, the higher energy band was observed, and the wavenumber range 6047–6055 cm⁻¹ was measured (Figure 3).

FTIR Spectrum and Its Analysis

The spectrum of the C-H stretching fundamentals consists of one a-type band at 2974 cm⁻¹ corresponding to the symmetric stretch ν_1 and two bands, b-type at 3080 cm⁻¹, and c-type at 3044 cm⁻¹, respectively,⁸ corresponding to the doubly degenerate ν_9 asymmetric stretch in the hypothetical symmetric top limit.

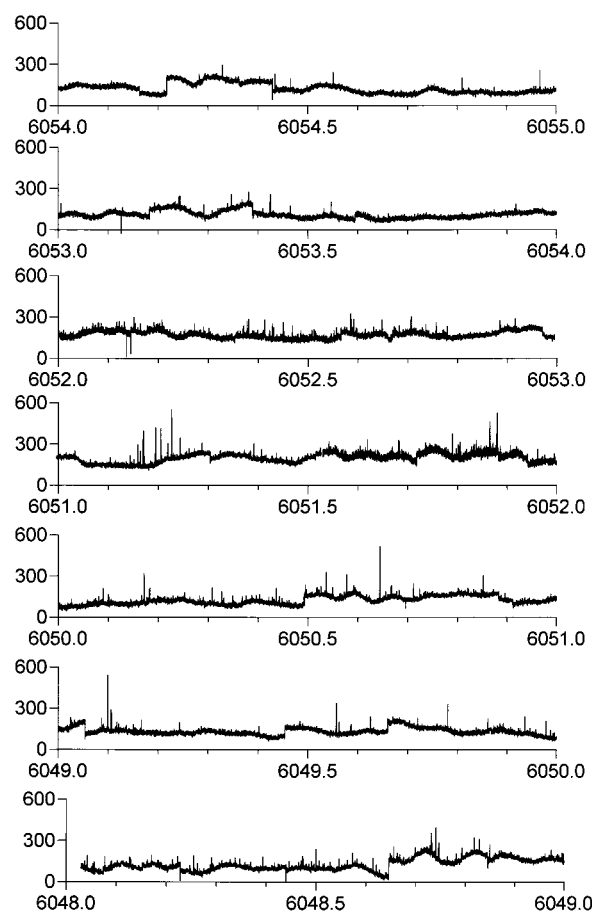


Figure 3. A molecular beam spectrum of the $2\nu_9$ band of nitromethane. In all spectrographs the horizontal axis is given as wavenumbers units, and the vertical axis is given as arbitrary units of bolometer signal.

Assignment of the FTIR spectrum of the first overtone of the C-H stretch (the two broad bands in Figure 2) was done regarding nitromethane as a symmetric top molecule and using a simple local mode model¹⁷ with the following parameter values: harmonic wavenumber $\omega = 3151.4$ cm⁻¹, anharmonicity constant $\omega x = 60$ cm⁻¹, and interbond coupling parameter $\lambda = -28.7$ cm⁻¹. According to this model the higher wavenumber band in the FTIR spectrum is the $2\nu_9$ band, and the lower wavenumber band system consists of the $2\nu_1$ band at 5887.1 cm⁻¹ and the $\nu_1 + \nu_9$ band at 5932.4 cm⁻¹. This assignment agrees with the one obtained by Cavagnat et al.¹²

Molecular Beam Spectrum and Its Analysis

The molecular beam spectrum of the $2\nu_9$ band of nitromethane is shown in Figure 3. Because of the low effective rotational temperature of the beam (5 K), only levels that possess a low total angular momentum quantum number J and where the internal rotation quantum number m is equal to 0 and 1 should be significantly populated. Because of this and the low intensity of the band investigated, only transitions originating from $J'' \leq 4$ were observed. An asymmetric rotor energy level simulation program¹⁸ was used for the prediction of the spectrum. The predicted relationships between the intensities of the transitions having the same upper state are well obeyed, which was useful in assigning the spectrum. The final assignments were made using ground-state combination differences. The observed transitions along with their assignments for the $m = 0$ state are given in Table 1. The deviations of the observed combination differences from their expected values were less than 4.5 MHz.

TABLE 1: Observed Transitions of the First C–H Stretching Overtone of Nitromethane ($2\nu_9$) for $m = 0^a$

wavenumber (cm^{-1})	intensity (arbitrary units)	$J'_{K_a K_c}$	$J''_{K_a K_c}$	wavenumber (cm^{-1})	intensity (arbitrary units)	$J'_{K_a K_c}$	$J''_{K_a K_c}$
6052.17506	87.4	3_{21}	2_{20}	6050.61074	147.1	2_{20}	2_{21}
6052.15562	73.1	3_{21}	2_{20}	6050.56967	152.6	2_{20}	2_{21}
6052.14604	63.8	3_{21}	2_{20}	6050.53893	26.2	2_{20}	2_{21}
6052.10905	49.5	3_{21}	2_{20}	6050.52969	45.7	2_{20}	2_{21}
6051.90287	267.7	3_{03}	2_{02}	6049.19550	81.5	1_{01}	2_{02}
6051.90107	120.8	3_{03}	2_{02}	6049.12813	378.5	1_{01}	2_{02}
6051.89414	64.8	3_{03}	2_{02}	6048.87750	108.6	2_{02}	3_{03}
6051.88772	233.6	3_{03}	2_{02}	6048.86976	24.7	2_{02}	3_{03}
6051.86970	54.0	3_{03}	2_{02}	6048.85595	88.6	2_{02}	3_{03}
6051.85538	80.5	3_{03}	2_{02}	6048.84547	92.1	2_{02}	3_{03}
6051.82403	85.3	3_{03}	2_{02}	6048.82130	73.5	2_{02}	3_{03}
6051.81228	151.9	3_{03}	2_{02}	6048.82032	41.6	2_{02}	3_{03}
6051.26493	318.5	2_{02}	1_{01}	6048.80970	48.7	2_{02}	3_{03}
6051.25716	97.1	2_{02}	1_{01}	6048.74884	123.0	3_{03}	4_{04}
6051.24336	216.9	2_{02}	1_{01}	6048.74729	79.1	3_{03}	4_{04}
6051.23292	248.8	2_{02}	1_{01}	6048.74027	43.7	3_{03}	4_{04}
6051.20868	234.8	2_{02}	1_{01}	6048.73375	139.4	3_{03}	4_{04}
6051.20773	174.8	2_{02}	1_{01}	6048.71584	18.2	3_{03}	4_{04}
6051.19706	145.2	2_{02}	1_{01}	6048.70140	55.8	3_{03}	4_{04}
6050.74505	103.1	1_{01}	0_{00}	6048.67005	37.3	3_{03}	4_{04}
6050.67766	367.1	1_{01}	0_{00}	6048.65829	95.6	3_{03}	4_{04}
6050.62526	53.5	3_{21}	3_{22}	6048.61642	92.6	2_{20}	3_{21}
6050.60583	31.5	3_{21}	3_{22}	6048.57535	89.8	2_{20}	3_{21}
6050.59629	33.9	3_{21}	3_{22}	6048.54464	21.5	2_{20}	3_{21}
6050.55933	21.0	3_{21}	3_{22}	6048.53539	21.6	2_{20}	3_{21}

^a J is the total angular momentum quantum number, and K_a and K_c are asymmetric rotor quantum numbers. Prime refers to the upper state, and double prime to the lower state of the transition.

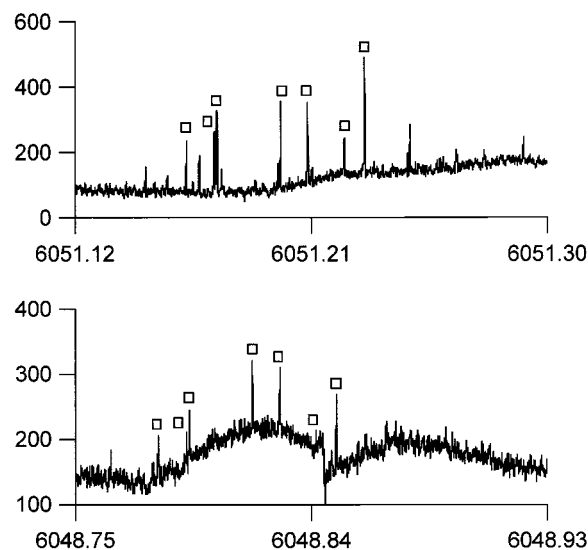


Figure 4. The $R(1)$ and $P(3)$ peak groups of the $2\nu_9$ band of nitromethane for $m = 0$. In both spectrographs the horizontal axis is given as wavenumber units, and the vertical axis is given as arbitrary units of bolometer signal.

except in the transition to the upper state $J'_{K_a K_c} = 3_{03}$ for which the deviation from the calculated value was approximately 10 MHz. One reason might be that because the spectrum was measured in several parts, the calibrations in all the parts were not exactly coincidental.

A group of peaks corresponds to each $J'_{K_a K_c} \leftarrow J''_{K_a K_c}$ transition because the upper state of the transition is split due to IVR, as described below. The splitting pattern is identical for transitions having the same upper state as in Figure 4 where the transitions $J'_{K_a K_c} = 2_{02} \leftarrow 1_{01}$ and $2_{02} \leftarrow 3_{03}$ are shown. The magnitude of the splitting of the whole group ranges from

TABLE 2: Input Data and Fits for $m = 0$ ($2\nu_9$)^a

J'	K'_A	K'_C	J''	K''_A	K''_C	$\nu_{\text{OBS}}/\text{cm}^{-1}$	$(\text{o}-\text{c})/\text{cm}^{-1}$
1	0	1	2	0	2	6049.140	0.002
1	0	1	0	0	0	6050.692	0.004
2	0	2	3	0	3	6048.846	-0.004
2	0	2	1	0	1	6051.233	-0.005
2	2	0	3	2	1	6048.585	0.000
2	2	0	2	2	1	6050.579	-0.001
3	0	3	2	0	2	6051.874	0.002
3	0	3	4	0	4	6048.719	0.001
3	2	1	3	2	2	6050.604	0.002
3	2	1	2	2	0	6052.151	-0.001

^a The standard deviation of the fit is 0.003 cm^{-1} . ν_{OBS} is the wavenumber of the observed transition, and $(\text{o} - \text{c})$ is the observed minus calculated value.

0.07 to 0.09 cm^{-1} depending on the transition, which is fairly typical in IVR for molecules of this size.¹⁹

The positions of the zero-order transition lines were calculated as the “center of mass” of each multiplet, considering the peaks as “mass points” where the intensity of the peak represents the “mass”. These zero-order transitions were used as entries in the least-squares calculation (Table 2). A justification of this procedure is obtained by noticing that the normalized intensity of a line is the fraction of the bright state character in the eigenstate. If the Hamiltonian is averaged for the bright state by expanding the bright state in terms of the eigenstates, the mass point model follows.^{21,22} The asymmetric rotor energy level simulation program¹⁸ was used to obtain with the least-squares method the band center and the upper state rotational constants for $m = 0$. They are given in Table 3. The standard deviation of the fit is 0.003 cm^{-1} . For $m = 1$, the lower state energy levels were calculated using the Hamiltonian in ref 4. Thus, the ground-state combination differences could be used to assign $m = 1$ peaks. Unfortunately, for the $m = 1$ state not

TABLE 3: Parameters of Nitromethane for $m = 0$ Spectrum ($2\nu_9$)^a

parameter/cm ⁻¹	G. S.	$2\nu_9$
ν	0.0	6050.13779(240)
A	0.44503725	0.553988(840)
B	0.35172249	0.29363(150)
C	0.19599426	0.25673(130)
$D_J/10^{-6}$	0.2048	0.2048 ^b
$D_{JK}/10^{-6}$	0.5921	0.5921 ^b
$D_K/10^{-6}$	-0.2515	-0.2515 ^b
$\delta_J/10^{-7}$	0.8229	0.8229 ^b
$\delta_K/10^{-6}$	0.52536	0.52536 ^b

^a G. S. denotes the ground-state parameters. They were obtained from ref 4. We have used the A reduced asymmetric rotor Hamiltonian in the I^R representation for lower and upper states.²⁰ Uncertainties in parentheses represent one standard error in the least significant digit.

^b Constrained value in the least-squares calculation.

enough assignments could be made to determine the band center and the upper state rotational constants.

Discussion

Torsional Dynamics. Rotational constants of the $2\nu_9$ band changed somewhat compared with the ground-state values (Table 3). The A constant increased, $B + C$ did not change significantly, whereas $B - C$ has decreased making the spectrum resemble more that of a prolate symmetric top. From the rotational constants the so-called inertial defect $I_c - I_a - I_b$ can be calculated. A value 0.202 uÅ² was obtained for the ground state.¹ For the $2\nu_9$ band of $m = 0$ it has decreased substantially to -22.2 uÅ², which might be a sign of the potential barrier becoming higher. However, one must bear in mind the limited data set available (Table 2). Cavagnat et al. also measured a low-resolution (1 cm⁻¹) FTIR spectrum of nitromethane in the first C-H stretching overtone region and analyzed it with a model that takes into account the coupling of vibrations of the methyl group with the internal rotation.¹² They obtained the value 8.4 cm⁻¹ for the torsional barrier height of the $2\nu_9$ band.

IVR Dynamics. As mentioned earlier, each ro-vibrational transition is split into several components (hereby termed as an IVR multiplet) as a consequence of coupling of the optically active state, also called “bright state”, (in this case the C-H stretching overtone) with a dense manifold of optically inactive (“dark”) states.^{23,24} As soon as the size of the molecule investigated is larger than 4–5 atoms, it becomes a formidable task (if possible at all) to construct a model Hamiltonian that accounts for the frequency and the intensity of every single transition observed. Instead, statistical properties of the spectrum are analyzed, such as the density of coupled states, the average coupling strength between the bright state and the dark states, the lifetime of the bright state, and are compared with the expected values.

The density of coupled states is estimated from the spectrum as $(N - 1)/\Delta E$, where N is the number of lines in a given multiplet and ΔE is the energy range spanned by the multiplet. A theoretical estimate of the total number of vibrational states (ρ_{tot}) available for coupling is calculated for comparison from a harmonic approximation by an inverse Laplace transformation of the vibrational partition function.²⁵ When the coupling is through anharmonic Hamiltonian terms, only states with the same vibrational symmetry as the bright state can couple to it. It has been shown²⁶ that on average the fraction (f_r) of states of a given symmetry class is equal to the square of the degeneracy of the class (d_r) divided by the order of the molecular symmetry group (g): $f_r = d_r^2/g$. Assuming that the

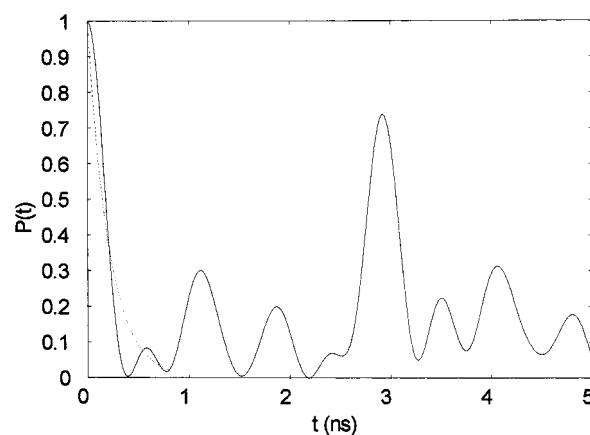


Figure 5. Survival probability calculated from the $2_{02} \leftarrow 3_{03}$ transition of the first C-H stretching overtone spectrum of nitromethane (solid line) and exponential decay fit (dashed curve). See text for details.

degeneracy is not removed, the expected density of levels is: $\rho_e = \rho_{\text{tot}} f_r / d_r$. If nitromethane is considered as a rigid molecule without torsion, then in the conformer belonging to the C_s point group there are two nondegenerate classes, each accounting for 50% of the density of vibrational states. If torsional motion is included, then the contribution to the density of states from torsional modes must be taken into account. Given the very low barrier height (compared with the excitation energy), this is done by treating the methyl group as a free rotor and using the full G_{12} vibrational-torsional group.

The average coupling strength is determined from the spectrum using Lawrance–Knight deconvolution²¹ as implemented by Lehmann.²² Several methods can be used to estimate the lifetime of the bright state from the frequency domain spectrum,^{24,27} which are equally good in principle. In fact the results that they give converge to correct values, when the spectral intensity distribution better approximates a true Lorentzian. For more sparse spectra, different methods give slightly different answers, which reflects the fact that the lifetime is in this case less well defined, because true relaxation can never occur for a system with a finite number of states. This is especially true for spectra composed of a small number of lines, for which the result obtained should be regarded more as a characteristic time scale for the energy redistribution process than a lifetime in the strict statistical sense. The method we used involves computing the survival probability $P(t)$ of the initially prepared state $\Psi(0)$ from the observed normalized spectral intensity $I(\omega)$:²⁸

$$P(t) = |\langle \Psi(t) | \Psi(0) \rangle|^2 = \int e^{i\omega t} d\omega \int I(\omega') I(\omega' - \omega) d\omega' \quad (1)$$

which for a spectrum with narrow, resolved lines, i.e., $I(\omega) \approx \sum_i I_i \delta(\omega - \omega_i)$, becomes

$$P(t) = \sum_{i,j} I_i I_j \cos[(\omega_i - \omega_j)t] \quad (2)$$

The initial decay of the survival probability obtained in this way is then fitted to an exponential decay, as shown in Figure 5 for the 2_{02} state.

Finally, the dependence of the above-mentioned statistical properties on the $J'_{K_a K_c}$ quantum number can be analyzed to study the effect of vibration–rotation coupling on the dynamics. In the state $J'_{K_a K_c} = 1_{01}$, the term “statistical properties” is used somewhat loosely because there is only one state coupled to the bright state. Therefore, the numbers for coupling, lifetime, and density of states should be taken as approximative.

TABLE 4: IVR Lifetimes of the $J_{K_a K_c}$ States of the $2\nu_9$ Band of Nitromethane, Number (N_d) and Density ($\rho_{\text{obs.}}$) of Observed Coupled States and Average Couplings (See Text for Details)^a

$J'_{K_a K_c}$	lifetime/ps	N_d	$\rho_{\text{obs.}}$ (states/cm ⁻¹)	coupling/(10 ⁻³ cm ⁻¹)
1 ₀₁	280 (30)	1	14	26.5 (1)
2 ₀₂	210 (2)	6	88	9.7 (0.1)
2 ₂₀	170 (2)	3	37	16.7 (0.1)
3 ₀₃	173 (2)	7	77	12.7 (0.1)
3 ₂₁	261 (4)	3	45	12.9 (0.2)

^a Numbers in parentheses are estimated uncertainties.

Table 4 shows that the lifetimes range between 170 and 260 ps, which was observed previously for methyl group stretching overtones in molecules of similar size and structure.¹⁹ The observed density of coupled states, instead, is several times larger than expected, ranging from 37 to 88 states/cm⁻¹ versus a calculated value of 5 states/cm⁻¹ with the right symmetry to couple to the bright state. This last number increases to 42/cm⁻¹ if the presence of torsional states is taken into account, which is still up to a factor 2 lower than the observed value. The presence of perpendicular Coriolis coupling with states $J'_{K_a K_c \pm 1}$ (which would further increase the density of available states by a factor of 3) is probably the explanation for the observed values. Coriolis resonance would show up as a $J(J+1)$ dependence in the mean squared coupling matrix element, which is calculated by the deconvolution procedure. If one makes a plot of this matrix element versus $J(J+1)$, the slope gives an estimate of the mean squared perpendicular Coriolis matrix element. Although the limited set of data available does not allow for a quantitative test of its effect in the present case, the observed density of coupled states is consistently larger for the states with $K_c = 2,3$ than it is for those with $K_c = 0,1$. The extensive coupling between vibrational and torsional modes suggests that the torsional barrier has increased from the low 2 cm⁻¹ of the ground state and perhaps has become a 2-fold barrier, but based on the available data, it is not possible to say to what extent each one of these effects contributes to the increased coupling.

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