

INTERNAL ROTATION IN CH₃CD₃: RAMAN SPECTROSCOPY OF TORSIONAL OVERTONES

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Received 7 April 1986; in final form 23 May 1986

CH₃CD₃ torsional overtones have been observed by spontaneous Raman scattering in a laser intracavity apparatus. $\Delta\nu = 2$ multiplet transitions up to the sixth torsional level have been measured. The new data were combined with $\Delta\nu = 0$ transitions from microwave and molecular-beam avoided crossing experiments and with $\Delta\nu = 1$ IR measurements. The barrier parameters $V_3 = 997.72 \pm 0.32 \text{ cm}^{-1}$ and $V_6 = 8.45 \pm 0.37 \text{ cm}^{-1}$ have been determined.

1. Introduction

The problem of internal rotation in ethane has recently been reconsidered [1,2]; torsional overtones up to the fifth excited torsional state have been observed in Raman spectra of C₂H₆ [1]. New barrier parameters were determined, $V_3 = 1009.1 \pm 0.7 \text{ cm}^{-1}$ and $V_6 = 11.0 \pm 0.7 \text{ cm}^{-1}$, by fitting $\Delta\nu = 2$ transitions up to the third torsional level. The failure in reproducing the position of some of the fourth torsional levels was attributed mainly to perturbations due to the nearby ν_3 vibrational mode. It could not be excluded that the discrepancies between the observed and predicted positions of those levels were due to the fact that the fourth torsional state is close to the top of the barrier. Although unambiguous conclusions could not be drawn about the fifth torsional state, located well above the barrier, the results for these levels seem to indicate that their positions are quite well predicted.

A further investigation on deuterated substituents was therefore undertaken to give more information on the physical meaning of the barrier parameters as well as on the levels near and above the barrier top. From a spectroscopic point of view, CH₃CD₃ is the simplest deuterated derivative of CH₃CH₃. It is still a symmetric top; the lowering of symmetry results in all its vi-

brational modes being infrared and Raman active, except the torsion [3]. The $\Delta\nu = 2$ torsional overtones are expected to be Raman active as in CH₃CH₃, with the same selection rule [1]. From low-resolution far-IR measurements on weakly allowed CH₃CD₃ transitions, the torsion frequency ν_4^* , its hot band $2\nu_4 - \nu_4$ and its first overtone $2\nu_4$ are available [4].

The ground state of CH₃CD₃ has been studied [2] by the anticrossing technique in an electric-resonance molecular-beam experiment. The limited data set only allowed the determination of the height, $V_3 = 1004.13 \text{ cm}^{-1}$, of a single-parameter barrier. Lower symmetry deuterated species were studied by microwave absorption experiments [5].

In the present work we have combined our new $\Delta\nu = 2$ torsional overtone transitions of CH₃CD₃ with the $\Delta\nu = 1$ IR data and the results of the microwave and anticrossing experiments. A fit of all these data allows us to determine independently the two lowest-order coefficients in the Fourier expansion of the barrier potential V_3 and V_6 .

* In the present paper all the CH₃CD₃ vibrations are labelled according to ref. [3], in order to facilitate the comparison with the data of ref. [4] and with results of ref. [1] on CH₃CH₃.

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2. Theory

The normal vibrations of CH_3CD_3 are usually assigned in the C_{3v} symmetry point group [3], considering the molecule to be semirigid. Dealing with the torsional mode this approach is no longer valid; in that case three equivalent equilibrium configurations, which are defined by the relative positions of the hydrogen atoms on one methyl group with respect to the deuterium atoms on the other, are coupled. A high barrier ($V_3 = 1004.13 \text{ cm}^{-1}$ [2]) impedes the free rotation of each group about the C–C axis. If torsional tunnelling is included the CH_3CD_3 molecule belongs to the G_{18} point group whose table of characters is given in ref. [6] (table A-18). Under this symmetry group the 11 vibrational modes of the molecule, apart from the torsion, are grouped in the representation

$$\Gamma_{\text{vib}} = 5A_1 + 6E_1.$$

The symmetry of the components of the polarizability given in ref. [6] indicates that all 11 modes are Raman active, and that only A_1 vibrations generate Q branches; the torsion belongs to A_2 symmetry, thus only its even overtones will appear in Raman spectra as Q branches.

The usual treatment for molecules undergoing an internal rotation starts from an adiabatic approximation for the Hamiltonian [6]. Vibrational, rotational and torsional terms constitute three distinct parts of this Hamiltonian, the latter two relevant to the present problem of torsional overtone transitions. The rotational–torsional Hamiltonian for CH_3CD_3 is written using the internal-axis method [2]; a complete treatment can be found in ref. [7]. The zeroth- and first-order terms relevant to the present work are

$$H_{\text{R}}^{(0)} = BJ^2 + (A - B)J_z^2, \quad (1)$$

$$H_{\text{T}}^{(0)} = Fp^2 + \frac{1}{2}V_3(1 - \cos 3\alpha) + \frac{1}{2}V_6(1 - \cos 6\alpha) + \dots, \quad (2)$$

$$H_{\text{TR}}^{(1)} = \frac{1}{2}F_3J(1 - \cos 3\alpha) + \frac{1}{2}F_3K(1 - \cos 3\alpha) + \dots, \quad (3)$$

where J and J_z are the total angular momentum and its projection on the symmetry axis of the molecule, with the corresponding quantum numbers J and K ; p is the torsional angular momentum. In eq. (2) F is

the reduced rotational constant, $F = A/\rho(1 - \rho)$, with $\rho = I_\alpha/(I_\alpha + I_F)$ the ratio of moments of inertia about the symmetry axis (I_α stands for the CH_3 -top group and I_F for the CD_3 -frame group). Rotational distortion constants [2] are neglected in eq. (3). The terms depending on the torsional angle α arise from a Fourier expansion of the potential. It is generally assumed that this series is rapidly converging.

The three-fold symmetry of the torsion–rotation problem for $K \neq 0$ generates six torsional sublevels for each value of v_4 . For $K = 0$ there are only three levels; two of them ($\sigma = \pm 1$) are two-fold degenerate (E_4), while the non-degenerate ($\sigma = 0$) level is of A_1 or A_2 symmetry for even or odd numbers of torsional quanta (v_4), respectively. Here σ labels the torsional states [7,8]. If $K \neq 0$ the six torsion–rotation levels consist of three pairs of doubly degenerate states labelled by $K\sigma = 0$, $K\sigma > 0$ and $K\sigma < 0$. The quantum number J (even or odd) defines the symmetry of rotational wavefunctions in the $K = 0$ case, A_1 for J even, A_2 for J odd. For $K \neq 3n$ the symmetry of rotational wavefunctions is E_1 ; for $K = 3n$ it is $A_1 + A_2$ independent of J . The nuclear spin functions for CH_3CD_3 under G_{18} are reduced according to ref. [8] to

$$44A + 32E_1 + 22E_2 + 16E_3 + 16E_4. \quad (4)$$

Here A indicates A_1 and A_2 , where it is not necessary to distinguish between them, since the total torsion–rotation-spin function must be of either A_1 or A_2 symmetry. The spin statistical weight can be deduced from eq. (4).

The torsion–rotation energy solutions to the Hamiltonian from eq. (1) through eq. (3) are labelled by the quantum numbers (v_4, J, K, σ). The eigenvalues of the zeroth-order Hamiltonian $H_{\text{T}}^{(0)}$ can be expanded in a Fourier series [9] as

$$\langle H_{\text{T}}^{(0)} \rangle = \sum a_n^{(v_4)} \cos[\frac{2}{3}\pi n(\rho K - \sigma)]. \quad (5)$$

First we investigate the K -periodicity with K of eq. (5). From well-known geometric relations it follows that $\langle H_{\text{T}}^{(0)} \rangle_{v_4 K \sigma} = \langle H_{\text{T}}^{(0)} \rangle_{v_4 (K+l) \sigma}$ for $l\rho = 3$. Since l must be an integer and ρ is in general not a rational number, this relation cannot be fulfilled exactly. However, we can define a rational number ρ_0 such that $l\rho_0 = 3$, $\rho = \rho_0 + \delta$ and $\delta/\rho \ll 1$. If $\delta \neq 0$ the energies of the state (K, σ) are no longer exactly equal to that of the state $(K + l, \sigma)$. Relevant for the $\Delta v = 2$ Q-

branch spectrum is the quantity

$$R = |(\langle H_{\text{T}}^{(0)} \rangle_{\nu_4 K \sigma} - \langle H_{\text{T}}^{(0)} \rangle_{\nu_4 (K+1) \sigma}) / a_1^{\nu_4}| \\ \approx (2\pi/\rho) \delta |\sin[\frac{2}{3}\pi(\rho K - \sigma)]| \ll (2\pi/\rho) \delta. \quad (6)$$

In eq. (6) R describes the relative torsional splittings of IR or Raman transitions. It is assumed here that $a_1^{\nu_4}$ dominates the torsional splitting. The values of $a_1^{\nu_4}$ are $a_1^0 = 0.0015$, $a_1^1 = -0.078$, $a_1^2 = 1.650$, $a_1^3 = -3.180$, $a_1^4 = 74.131$, $a_1^5 = -221.37$ and $a_1^6 = 271.48$, all in cm^{-1} . For CH_3CD_3 $\rho = 0.339792 \pm 0.000022$ [2], this results in an approximate $K \bmod 9$ periodicity of eq. (5). The value of R is such that within the present resolution of the Raman spectra the assumption of a periodicity of 9 in K is valid.

Because ρ is so close to $\frac{1}{3}$ in CH_3CD_3 there exist other accidental or near degeneracies in the torsional energies. From eq. (5) it can easily be verified that for a given ν_4 state only 5 distinct energy levels can be distinguished, corresponding to $E_n^{\nu_4} = a_1^{\nu_4} \cos[\frac{2}{3}\pi(\rho K - \sigma)] = a_1^{\nu_4} \cos(\frac{2}{3}n\pi)$, where $n = 0$ through 4. It should be noted that the order of the energy levels is determined by the sign of $a_1^{\nu_4}$, which is alternating with ν_4 .

It is for this reason that the Raman spectrum ($\Delta\nu_4 = 2$, $\Delta J = 0$, $\Delta K = 0$) consists of quintuplets. The relative intensities within a quintuplet are found by summing the individual contributions of the "degenerate" levels multiplied by the spin statistical weight factors and the Boltzmann distribution function. Because there is an almost equal distribution of the five "non-degenerate" energy levels over the various K -states, the Boltzmann weighted intensity ratio is quite close to the unweighted ratio. The latter is 64 : 140 : 140 : 128 : 140, where the order is the same as given above for the energy levels.

The resolution of the Raman spectrometer only allows us to observe the piled-up intensities of the Q branches. The width of each Q branch is dominated by the contribution of the parameters F_{3J} and F_{3K} in $H_{\text{TR}}^{(1)}$ (eq. (3)).

3. Experimental

The apparatus used for Raman spectroscopy has been described in ref. [1]. The excitation radiation was provided by an Ar^+ laser (Spectra Physics 170). In order to maximize the available power an intracavity

apparatus has been built by removing the original laser output mirror and replacing it by two convex reflectors (radius of curvature 10 and 5 cm respectively) which are mounted inside the sample cell and supplied with fine adjusting systems. Measurements have been performed by using the two intense Ar^+ laser lines at $\lambda = 488.0$ nm and $\lambda = 514.5$ nm. A beam waist of 50 μm diameter is obtained in the focus. The scattered Raman light is collected by a reflector ($R = 5$ cm) and a lens ($f = 8$ cm) and focused on the entrance slit of a double monochromator (Ramanor HG2S, Jobin-Yvon). The adjustable slit allows us to increase the resolution at the cost of signal intensity. Typically a resolution of 1.2 cm^{-1} at 400 cm^{-1} is obtained with 100 μm slits. At the monochromator exit the Raman signal is detected by a cooled photomultiplier with a red sensitive GaAs photocathode (Hamamatsu R943). A microprocessor (Apple IIc) controls the monochromator scans and processes the data from the photon-counting system (Brookdeal 5C1). After each scan the frequency scale of the monochromator is calibrated against some hundreds of plasma lines present in our discharge tube. The accuracy achieved in this way is better than 0.5 cm^{-1} .

The same gas sample of CH_3CD_3 was used as in ref. [2]; the intracavity cell was filled to 1 atm pressure. The isotopic purity was checked on the strong ν_3 fundamentals of the various deuterated species. At 945 cm^{-1} a peak was found, corresponding to the ν_3 mode of the 1,1-D₂ species ($\text{CH}_3\text{CD}_2\text{H}$) which was also observed in ref. [3]. From its intensity ratio relative to the ν_3 signal of CH_3CD_3 and using the results of ref. [10] we estimate that 1.2% of the sample consisted of $\text{CH}_3\text{CD}_2\text{H}$. Only about 0.1% of C_2H_6 could be traced. No evidence for other deuterated species was found.

4. Results and discussion

The complete Raman spectrum from 250 to 500 cm^{-1} measured with a slit corresponding to a width of 2.15 cm^{-1} is shown in fig. 1. The $2\nu_4$ multiplet appears unresolved in the present experiment, the $3\nu_4 - \nu_4$ is partially resolved, while all the higher overtones are distinct and widely spread over the spectrum. Hot band transitions between torsional sublevels have been identified up to $6\nu_4 - 4\nu_4$; no evidence for $7\nu_4 - 5\nu_4$

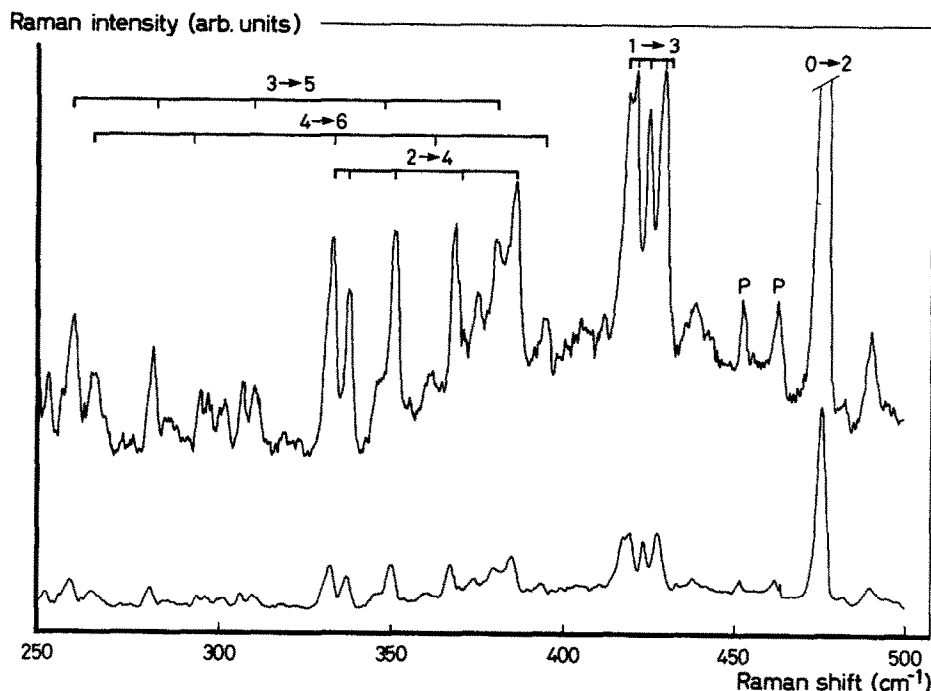


Fig. 1. CH_3CD_3 : measured Raman spectrum in the range $250\text{--}500\text{ cm}^{-1}$, experimental resolution 2.15 cm^{-1} ($\lambda = 514.5\text{ nm}$). The upper curve has been expanded by a factor of 5 on the y axis. The assignments of torsional transitions are marked, Plasma lines are labelled with P,

was found. Minor unassigned impurities have been detected in the same frequency range. The extra peak found on the blue of the $2\nu_4$ overtone at 494.8 cm^{-1} is assigned to the $0 \rightarrow 2$ Raman excitation in the $\text{CH}_3\text{CD}_2\text{H}$ impurity [10,11]. A few plasma lines, marked with a P in the figure, have been identified.

The $3\nu_4 - \nu_4$ band has been investigated in detail with better resolution ($\text{fwhm}_{\text{exp}} = 1.2\text{ cm}^{-1}$). Fig. 2 shows the deconvolution of the transitions in five Gaussian-shaped peaks. The intensity ratios among the components of this multiplet are in agreement with the theoretical prediction. The profile of the five peaks is symmetric and the best fit yields a width of 2.1 cm^{-1} . The remaining width of 1.7 cm^{-1} , after subtracting the experimental width, stems from distortions due to the torsion-rotation Hamiltonian; the expected leading terms are given in eq. (3). If the spread of the Q-branch transitions were affected solely by $F_{3J} = -134\text{ MHz}$ [2] we found that it cannot account for the observed width. Unfortunately the

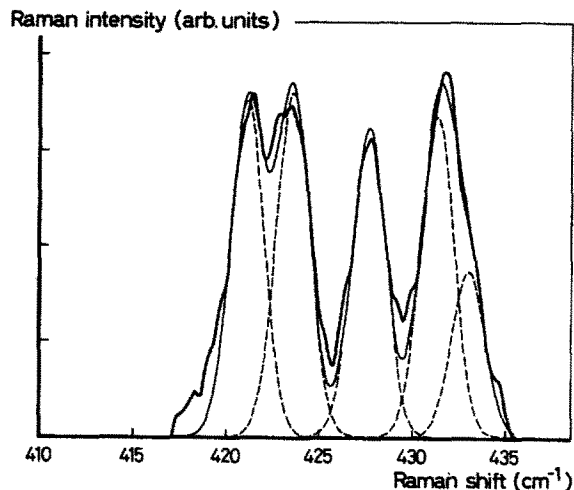


Fig. 2. $3\nu_4 - \nu_4$ multiplet measured with 1.2 cm^{-1} resolution (thick solid line) compared with the best fit curve (thin solid line); each Gaussian used in the deconvolution is also shown (dashed lines).

Table 1
Observed and calculated Raman torsional transitions in cm^{-1} and their relative intensities

Transitions ($\nu'' \rightarrow \nu'$)	Observed	Error	n	Obs. - calc.	Relative intensity	
					obs.	calc.
(0 → 2) ^{a)}	480.1	1.0	0	1.1		105
	480.1	1.0	1	0.9		228
	480.1	1.0	2	0.6	1000	228
	480.1	1.0	3	0.2		211
	480.1	1.0	4	0.0		228
(1 → 3)	421.4	0.7	4	0.3	161	194
	422.8	0.7	3	-0.7	165	177
	427.7	0.7	2	0.3	148	193
	431.7	0.7	1	0.6	154	193
	433.0	0.7	0	0.3	80	88
(2 → 4)	334.7 ^{b)}	1.0	0	0.1	-	45
	339.7	0.5	1	0.4	115	98
	352.9	0.5	2	0.6	138	101
	371.3	0.5	3	0.4	137	93
	389.2	0.5	4	-0.1	154	109
(3 → 5)	259.6 ^{c)}	0.5	4	1.0	144	71
	282.2	0.5	3	-0.3	69	51
	313.3	0.5	2	-0.2	52	45
	347.8	0.5	1	-0.7	36	37
	383.5	0.5	0	-0.5	154	20
(4 → 6)	265.9	0.5	0	0.3	93	15
	298.6 ^{c)}	0.5	1	-1.9	36	22
	332.2 ^{b,c)}	1.0	2	-2.1	-	25
	363.8	0.5	3	-0.6	28	21
	398.1	0.5	4	0.8	38	22

a) Not resolved. b) Overlapped. c) Not included in the fit.

total line width is determined by a combination of F_{3J} , F_{3K} , D_{Jm} and D_{Km} and by the approximation of $\rho = 1/3$ in eq. (6). The two distortion constants D_{Jm} and D_{Km} are defined in ref. [2]. Information on F_{3K} and D_{Km} is absent at the moment; we must conclude that the present low-resolution measurements do not allow an independent determination of these parameters.

The experimental frequencies for the $\Delta\nu_4 = 2$ hot bands are summarized in table 1. A combined fit was made for these data and those from avoided crossing measurements [2], microwave [5,12] and IR [4] experiments. The latter spectra yield the forbidden lines, ν_4 at 253 cm^{-1} and $2\nu_4 - \nu_4$ at 228 cm^{-1} ; we as-

sumed an uncertainty of 1 cm^{-1} in these numbers. From the present fit we discarded the overlapping transitions around 333 cm^{-1} , and the transitions at 259.6 cm^{-1} and 298.6 cm^{-1} which will be discussed below. The uncertainties of present Raman data are listed in table 1 and are typically $\pm 0.5 \text{ cm}^{-1}$; the uncertainties in microwave results are much smaller [2]. With the exception of V_3 and V_6 , the set of parameters and their values are the same as those used in ref. [2]. The best fit results are $V_3 = 997.72 \pm 0.32 \text{ cm}^{-1}$ and $V_6 = 8.45 \pm 0.37 \text{ cm}^{-1}$; they reproduce the properties of the excited torsional states much better than the potential parameter obtained from the microwave measurements alone [2] which contained mainly in-

formation on the torsional ground state.

In spite of the overall agreement between the measured spectrum and the model predictions, a few perturbations have been observed. They can be discussed in terms of Fermi ($\Delta K = 0$) interaction of high- ν_4 levels with other Raman active vibrational modes in CH_3CD_3 . Fermi resonances are allowed with vibrational modes of A_1 symmetry. The energies $E_n^{\nu_4} = E_4^5$ and E_1^6 at 931.4 cm^{-1} and 1119.0 cm^{-1} are perturbed by Fermi resonances with the ν_3 (904.66 cm^{-1}) and ν_6 (1125 cm^{-1}) modes [10,11], respectively. This explains the observed blue-shift of 1.0 cm^{-1} of the $5\nu_4 - 3\nu_4$ transition to the E_4^5 level and the red-shift of 1.9 cm^{-1} of the $6\nu_4 - 4\nu_4$ transition to the E_1^6 level.

The error bars in the present work, as well as in ref. [1], represent one standard deviation. Within three standard deviations the value of V_6 in CH_3CD_3 is identical to that in CH_3CH_3 [1], which agrees with our expectation that within 10% V_6 is independent on isotopic substitution [13]. This result clearly demonstrates the consistency of the data for isotopic substitution and the fact that the barrier to internal rotation in ethane is very well described by the two lowest-order coefficients in the Fourier expansion, V_3 and V_6 .

The calculated Raman spectrum (in the range $250-500 \text{ cm}^{-1}$) for $2\nu_4$ and its hot bands up to $6\nu_4 - 4\nu_4$ is shown in fig. 3. In this simulation rotational fine structure has been neglected and an experimental Gaussian profile has been assumed with a width of 1.2

cm^{-1} . The Boltzmann factor, the nuclear spin statistics and the Raman transition strengths have been included to calculate the relative intensities. In order to calculate the Raman transition linestrengths an expression for the polarizability is required. Due to the (three-fold) symmetry of the problem, the polarizability can be written as a Fourier expansion. In the present calculations only the leading term has been retained, so that the polarizability is proportional to $\frac{1}{2}(1 - \cos 3\alpha)$. The calculated linestrengths were used in the predicted spectrum (fig. 3) and are compared in table 1 with the experimental ones. The uncertainties in the observed intensities are estimated to be 15%. Within these uncertainties the agreement is satisfactory, apart from the few exceptions discussed below.

Coriolis interactions ($\Delta K = \pm 1$) are most likely responsible for some of the anomalous intensity behaviour. These interactions are allowed between the E_1 vibrations and the torsional levels. Only strongly Raman active bands are considered and this restricts the problem to ν_{11} at 1070 cm^{-1} [10,11]. A Coriolis interaction, resulting in a vibrational intensity borrowing, of ν_{11} with the $E_n^{\nu_4} = E_0^5$ level at 1068.4 cm^{-1} and $E_n^{\nu_4} = E_0^6$ level at 1079.3 cm^{-1} could be responsible for the large increase in intensity (see table 1) observed on the $5\nu_4 - 3\nu_4$ and the $6\nu_4 - 4\nu_4$ transitions to E_0^5 and E_0^6 , respectively. The disagreement between the observed and calculated intensity of the $5\nu_4 - 3\nu_4$ transition to the E_4^5 level is probably due to the above-

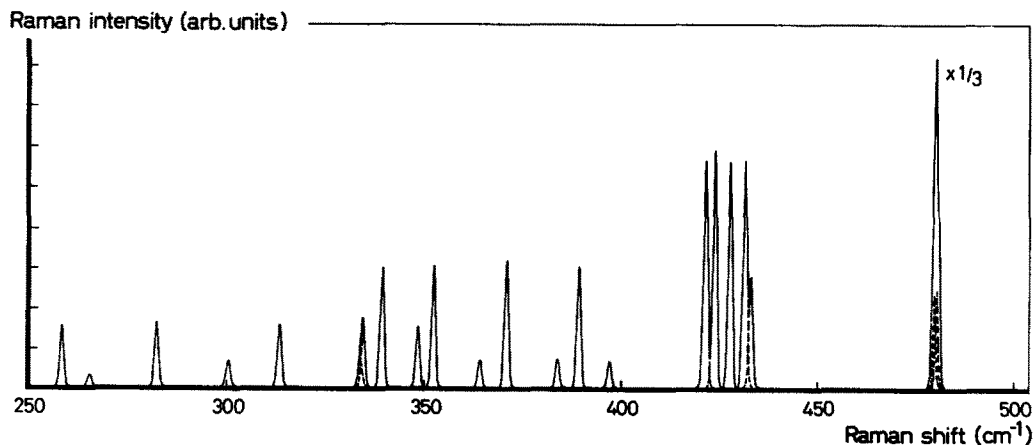


Fig. 3. CH_3CD_3 : calculated spectrum ($V_3 = 997.72 \text{ cm}^{-1}$, $V_6 = 8.45 \text{ cm}^{-1}$) for Raman transitions between torsional overtones. The $0 \rightarrow 2$ peak intensity has been reduced by a factor of $1/3$ with respect to all the others. The experimental resolution ($\text{fwhm} = 1.2 \text{ cm}^{-1}$) fixes the width of the Gaussian peaks.

mentioned Fermi resonance with the ν_3 vibration.

In summary, it can be concluded that the present model gives a satisfactory prediction of the torsional levels deep in the well, and around the barrier top as well as over it. It seems that the remaining disagreements for some of the high torsional overtones in CH_3CD_3 are due to Fermi and Coriolis interactions. This supports the assumption made for CH_3CH_3 that the perturbations of the $4\nu_4$ levels of CH_3CH_3 [1] originate from the same interactions.

Acknowledgement

One of us (RF) would like to thank ZWO (Netherlands Organization for the Advancement of Pure Research) for a fellowship. Dr. J.T. Hougen is acknowledged for suggesting the present study.

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