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Effect of the internal rotation of the CHD₂ group on the CH stretching mode of nitromethane NO₂CHD₂ in crystalline phase

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Résumé. — Les spectres infrarouges et Raman du nitrométhane NO₂CHD₂ cristallisé ont été enregistrés dans la région de la vibration de valence CH dans un grand domaine de températures (17 à 185 K). A très basse température, les spectres présentent trois bandes ; chacune d'elles est attribuée à la vibration d'un oscillateur CH localisé dans un site différent. Une théorie quantique de ces spectres montre qu'aucun effet tunnel n'apparaît, ce qui est en accord avec l'interprétation classique. De plus, cette théorie permet de relier la variation des intensités relatives des bandes v(CH) en fonction de la température à la densité de population des premiers niveaux de torsion dans l'état fondamental de vibration et suggère une mise en ordre très simple du système isotopique CHD₂ à 4 K, le vibrateur CH étant localisé dans le plan perpendiculaire au plan de la molécule. A plus haute température, la forte relaxation observée sur ces bandes v(CH) est due à la réorientation du groupe CHD₂ et peut être décrite, pour sa plus grande partie, par un processus de sauts aléatoires de grande amplitude.

Abstract. — The infrared and Raman spectra of nitromethane NO_2CHD_2 in crystalline state have been recorded in the CH stretching mode range in a large temperature range (17 to 185 K). At very low temperatures, three bands are observed; each of them is assigned to the vibration of a CH oscillator localized in a different site. A quantum theory of these spectra shows that no tunnelling effect appears; this is in agreement with the classical interpretation. Furthermore, this theory ascribes the temperature dependence of the relative intensities of the v(CH) bands to the population density of the first torsional levels in the vibrational ground state and suggests a very simple ordering of the isotopic system CHD_2 at 4 K, the CH vibrator being localized in the plane perpendicular to the molecular plane. At higher temperatures, the strong relaxation observed on these v(CH) bands is due to the CHD_2 group reorientation and can be described, mostly, by a great amplitude random jump process.

1. Introduction. — Most molecular dynamics studies performed in the last decade by various techniques concern small rigid molecules or ions. However, a strong interest is now appearing for the extension of the methods and theories of molecular dynamics to non-rigid systems characterized by low frequency large amplitude internal motions.

Classical examples of such anharmonic motions are the rotation of a specific group in the molecule or the deformation of the entire molecule as in the ringpuckering or the pseudo-rotation of small cycles.

A good starting point for the study of these systems is often provided by the gas phase data obtained by microwaves [1], or infrared and Raman spectroscopies [2-5]. Indeed, in the absence of intermolecular forces, the fine structures observed in the spectra can completely be interpreted and yield very detailed information on the potential energy function which governs the internal motion.

In condensed states, the problem is more complex because the energy levels associated with the internal motion are strongly relaxed by coupling with the thermal bath.

However, in the case of the internal rotation of a methyl group, some results have already been obtained by N.M.R. or Neutron Scattering [6-11].

The infrared (I.R.) and Raman bandshape analysis of the v(CH) stretching vibration of a $-CHD_2$ group substituted in molecules of the type Z-CH₃, where Z is a planar group, has also proved to be a good method of investigation [12, 13]. The presence of a single aliphatic CH vibrator has the advantage of reducing the spectral analysis to the modulation of a diatomic oscillator by the methyl rotation. Moreover, in molecules such as toluene and nitromethane, this internal rotation, which is nearly free in the gas state, remains

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fast in the solid state because the hindering barrier does not increase very much. Consequently, the characteristic times associated with the methyl rotation are well adapted for a study of the v(CH) spectral density since they produce efficient broadening effects.

In previous papers, we have investigated the mechanism of modulation of the v(CH) vibration for gaseous NO₂CHD₂ and C₆D₅CHD₂ molecules [12] and for the α and β crystalline phases of C₆D₅CHD₂ [13].

In the spectra of the latter at low temperatures, several v(CH) excitations were observed and assigned to CH oscillators in various crystallographical sites. These transitions are strongly damped at higher temperature and we showed that an efficient relaxation mechanism was thermally activated reorientational jumps around the C-methyl bond. This mechanism had already been invoked to interpret the N.M.R. and Quasielastic Neutron Scattering (Q.N.S.) spectra. However, it proved to be insufficient for a quantitative interpretation of the observed I.R. and Raman profiles. So, we presented the hypothesis of an additional broadening, either homogeneous or inhomogeneous according to the modulation conditions, due to motions of weaker amplitude inside the potential wells determined by the sites.

One way to verify the validity of our analysis is to perform a comparative study on the nitromethane molecule in the solid state. This study is made easier by the recent work of Trevino *et al.* [10, 11, 14] giving information on the dynamics of the methyl group by Q.N.S. and on the structure of this molecule by X-Ray and Neutron crystallography ($P_{2_{1}2_{1}2_{1}}$ orthorhombic, Z = 4).

2. Experimental conditions and results. — The isotopic derivative NO_2CHD_2 was obtained by reaction

of suitably labelled methyl iodide with solid silver nitrite at room temperature, the more volatile reaction product, methyl nitrite, being removed by fractional condensation. NO₂CHD₂ was then distilled under partial vacuum. Its isotopic purity, as checked by mass spectrometry, was higher than 98 %.

A very small amount of this compound was trapped at about 110 K on a copper surface for the Raman work or on a CsI window for the infrared work. The thin film of amorphous compound thus obtained was then warmed up to 160 K in order to get the crystalline phase. The trapping was slowly continued at this temperature to obtain a layer of sufficient thickness. Finally the sample was slowly cooled down to 17 K to avoid unsticking or cracking of the layer. A liquid helium Cryodine 20 refrigerator was used in these temperature cycles.

The I.R. and Raman spectra of nitromethane NO_2CHD_2 have been recorded in the CH stretching region at different temperatures between 17 K and 185 K. In figure 1, the spectra of the pure crystallized NO_2CHD_2 are compared with those of the same compound diluted in nitromethane NO_2CD_3 at 17 K. Figure 2 presents the I.R. and Raman spectra of nitromethane NO_2CH_3 in the crystalline phase and figure 4 illustrates the temperature effect on the CH stretching transitions observed for the NO_2CHD_2 derivative.

3. **Discussion.** -3.1 THE LOW TEMPERATURE SPECTRA (17 K to 100 K). -3.1.1 Qualitative assignment of the spectra at 17 K. - As clearly shown in figure 1, the infrared and Raman spectra of pure crystallized NO₂CHD₂ exhibit three bands at 17 K in the CH stretching region : a group of two weak bands at



Fig. 1. — The CH stretching infrared and Raman spectra of pure nitromethane NO_2CHD_2 and of a 20 % isotopic dilution of NO_2CHD_2 in NO_2CD_3 at 17 K.



Fig. 2. — The CH stretching infrared and Raman spectra of pure nitromethane NO_2CH_3 crystallized at 17 K. (The calculated frequencies are indicated by arrows.)

3 049 and 3 042 cm⁻¹ and a very intense and narrow one at lower frequency (2 997 cm⁻¹).

The hypothesis of Fermi resonance occurring between av(CH) excited level and overtone or combination vibrational levels cannot explain this splitting. Indeed, as already shown in previous studies [16-18], the binary combinations and overtones of fundamental vibrations are not expected in this spectral range, except the combinations involving the CD₂ stretching vibrations; but, as far as we know, Fermi resonances involving such combinations have never been reported for any molecule. On the other hand, a correlation effect occurring between the v(CH) vibrations of the different molecules in the crystal cannot be invoked either since no important modification of the spectra is observed at any temperature by isotopic dilution of NO₂CHD₂ in NO₂CD₃ (Fig. 1).

Thus, as already inferred for toluene [13], the three observed bands are assigned to CH oscillators located in three different sites. Indeed, the nitromethane molecule is in general position in the crystalline unit cell and the methyl group conformation at 4 K [14] is such that one of the -CH bonds is nearly perpendicular to the molecular plane. We assign the lower frequency band to this perpendicular -CH bond and the doublet at 3 049 and 3 042 cm⁻¹ to the two other -CH bonds which are not quite equivalent because of the absence of a symmetry plane.

Notice that these frequencies follow the law which has been proposed for the isolated molecule [18]:

$$\omega = \omega_0 + C_2 \cos 2\theta \tag{1}$$

where the values of the dihedral angle θ between the NCH plane and the CNO₂ plane are consistent with the crystalline structure (Table I). The comparison

Table I. — Comparison of the v(CH) frequencies observed in the I.R. and Raman spectra of crystalline NO₂CHD₂ at 17 K with the frequencies calculated by means of equation (3) with $\omega_0 = 3.029.3$ cm⁻¹, $C_2 = 33$ cm⁻¹. The values for the gas phase were $\omega_0 = 3.030$ cm⁻¹ and $C_2 = 21$ cm⁻¹ [12].

Experimental frequencies in cm ⁻¹		Calculated frequencies in cm ⁻¹ $\omega = \omega_0 + C_2 \cos 2\theta$	
I.R.	Raman	$\omega \mathrm{cm}^{-1}$	θο
2 997.0 3 042.5 3 049.0	2 997.0 3 042.0 3 049.0	2 996.5 3 042.4 3 049.0	93º 3 213º 3 333º 3

of the values of ω_0 and C_2 in the solid phase and in the gas phase [12] shows that ω_0 is the same in both phases but that C_2 is larger in the crystalline state because of the appearance of non negligible intermolecular effects. In these conditions, the success encountered in the application of equation (1) could be fortuitous; since the environment of the nitromethane molecule does not present any symmetry plane, a rotation of π radians of the -CHD₂ group around the C-C bond leads to an inequivalent structure.

It can be pointed out that our analysis leads to conclusions in agreement with those previously deduced by McKean from more partial results on the same compound [18]. At 78 K, this author observes, as we do (Fig. 4), two I.R. bands at 3 000 and 3 048 cm⁻¹. He assigns the first one to a CH oscillator contained in a plane nearly perpendicular to the CNO₂ plane and the second to CH oscillators in the two other positions.

From the measured values of ω , the force constants, uncorrected for anharmonicity, can be calculated for each CH oscillator. For that purpose, the approximation of an isolated -CHD₂ group is made and the H-D interaction constant is neglected. With these three force constants and an interaction constant f(H-H)it is possible to calculate the frequencies of the v(CH)stretching vibrations of nitromethane NO₂CH₃. Thus, one obtains the frequencies of the -CH₃ group from those of the -CHD₂ group. The results are shown in figure 2, the f(H-H) constant being taken as

$0.035 \times 10^5 \, \text{dynes.cm}^{-1}$,

of the same order of magnitude as in McKean's work [18]. The calculated frequencies are very close to the experimental ones. The agreement could still be improved by introducing, as McKean *et al.* do [18], a dependence of the interaction constant f(H-H) on the conformation. However, one important conclusion to be deduced from figure 2 remains that Fermi resonance effects between the three $v(CH_3)$ stretching



Fig. 3. — Energy of the torsional levels of the -CHD₂ group in the crystallized nitromethane NO₂CHD₂ at 17 K in the ground (v = 0) and in the first excited (v = 1) states of v(CH) vibration ($V_3 = 170 \text{ cm}^{-1}$, $C_2 = 43 \text{ cm}^{-1}$). (A) $\theta_0 = 90^\circ$; (B) $\theta_0 = 92^\circ$ 5. The broken lines (-----) represent $\psi^2(\theta)$, the square of the wave-functions; the arrows (-----) or (-O--) indicate the more probable transitions.

(A) • Scalar or even transition operator (---)

• Odd transition operator $(-- \bigcirc \rightarrow)$

 $|0,0\rangle \rightarrow |1,0\rangle$ $\overline{v} = 2.996.9 \text{ cm}^{-1}$ $|0,1\rangle \rightarrow |1,1\rangle$ $\overline{v} = 3.045.1 \text{ cm}^{-1}$ $|0,2\rangle \rightarrow |1,2\rangle$ $\overline{v} = 3.046.1 \text{ cm}^{-1}$. $\overline{v} = 3.075.3 \text{ cm}^{-1}$ $|0,0\rangle \rightarrow |1,3\rangle$ $|0,1\rangle \rightarrow |1,2\rangle$ $\bar{v} = 3.046.2 \text{ cm}^{-1}$ $|0,2\rangle \rightarrow |1,1\rangle$ $\bar{v} = 3.045.0 \text{ cm}^{-1}$. $|0,0\rangle \rightarrow |1,0\rangle$ $\bar{v} = 2.997.0 \text{ cm}^{-1}$ $|0,1\rangle \rightarrow |1,1\rangle$ $\bar{v} = 3.042.2 \text{ cm}^{-1}$ $|0,2\rangle \rightarrow |1,3\rangle$ $\bar{v} = 3.049.0 \text{ cm}^{-1}$.

B •

IR

 $V_{s}NO_{7}$

17K

45K

75K

110K

50K

1440



Fig. 4. — The CH stretching infrared and Raman spectra of pure crystallized nitromethane NO_2CHD_2 at different temperatures. The evolution of the $v_s(NO_2)$ band in the same temperature range is shown for comparison.

3000

3050

1400 cm¹

110K

1301

150

cmĩ

3050

3000

cmi

vibrations and overtone and combination bands are very weak unlike what happens generally for other methylated molecules [19-24]. This could be due to the fact that the 2 δ_a (CH₃) levels situated at about 2 850 and 2 750 cm⁻¹ are relatively far from the stretching levels. On the other hand, the I.R. bands observed at 2 955 and 2 927 cm⁻¹ (Fig. 2) and assigned by McKean *et al.* [18] to combinations (v_a (NO₂) + v_s (NO₂)) and (v_a (NO₂) + δ_s (CH₃)) correspond to transition moments roughly perpendicular to the transition moment associated with the vibration at 2 969 cm⁻¹ in which the three CH oscillators are approximately in phase. So it can easily be understood that these combination levels interact only weakly with the v_s (CH₃) level in spite of their proximity.

3.1.2 Quantum theory of these spectra. — The preceding considerations suggest that the three v(CH) I.R. and Raman bands observed for crystalline NO₂CHD₂ are due to three CH oscillators located in different environments. Nevertheless, owing to the very low hindering barrier to the methyl internal rotation (< 200 cm⁻¹) [11, 15] and to the relatively low temperature (17 K), it can be objected to this classical interpretation that tunnelling effects can appear and cause band splittings similar to those observed on the high frequency side. This possibility must be discussed and the problem considered from a quantum point of view.

The quantum theory, already applied to toluene [13], is based on an angular dependence of the normal modes of the methyl group. In the approximation of the isolated molecule, justified by the isotopic dilution experiment, the Hamiltonian describing the vibrations of the -CHD₂ group and the torsional mode involves a coupling term.

$$= \hat{H}_{\rm V} + \hat{H}_{\rm T} + \hat{H}_{\rm VT}$$
 (2)

$$\hat{H}_{\mathbf{V}} = \sum_{i} - \frac{\hbar^{2}}{2} \frac{\partial^{2}}{\partial q_{i}^{2}} + \frac{1}{2} \omega_{0i}^{2} \cdot q_{i}^{2}$$
$$\hat{H}_{\mathbf{T}} = -\frac{\hbar^{2}}{2} \frac{\partial^{2}}{I_{\mathbf{r}}} \frac{\partial^{2}}{\partial \theta^{2}} + V(\theta)$$
$$\hat{H}_{\mathbf{VT}} = \sum_{i} \omega_{0i} \cdot \Delta \omega_{i}(\theta) \cdot q_{i}^{2}$$

Ĥ

 I_r is the reduced moment of inertia of the -CHD₂ group, q_i the vibrational normal coordinate, θ the rotational angle. The $\Delta \omega_i(\theta)$ frequency variations are supposed to be small in comparison with the average frequencies ω_{0i} . $V(\theta)$ is the potential part depending only on the torsional coordinates, the methyl group internal coordinates having their equilibrium values. By taking into account the absence of any symmetry plane for the nitromethane molecule in the solid state, the $V(\theta)$ potential takes the form :

$$V(\theta) = \sum_{n} \frac{V_{3n}}{2} (1 - \cos 3 n(\theta - \theta_0))$$

The torsional mode which occurs at about 60 cm⁻¹ [10, 11] is a slow motion compared to the other conformation dependent *i* modes of the -CHD₂ group (the lowest occurs at about 880 cm⁻¹ [18]). Thus, the adiabatic approximation is justified and we follow the same procedure as for toluene by writing first the vibrational energy of the v(CH) mode :

$$\varepsilon(\theta) = \hbar \left(v + 1/2 \right) \omega_0 + \sum_{i \neq v(CH)} \frac{\hbar}{2} \omega_{0i} + \frac{\hbar}{2} \left(v + \frac{\lambda}{2} \right) \Delta \omega(\theta) \quad (3)$$
with

$$\Delta\omega(\theta) = \sum_{n} C_{n} \exp(+in\theta) + C_{n}^{*} \exp(-in\theta)$$
 (4)

where ω_0 is the v(CH) average frequency and $\Delta\omega(\theta)$ its variation versus θ , equation (4) taking again into account the absence of a molecular symmetry plane. The terms $\sum_{i \neq v(CH)} \frac{\hbar}{2} \omega_{0i}$ and λ denote the contribution to the total energy of the modes other than v(CH);

they are all considered in their ground vibrational state and we adopt for them the approximation :

$$\Delta \omega_i(\theta) = k_i \cdot \Delta \omega(\theta), \quad |k_i| < 1$$
$$\lambda = 1 + \sum_{i \neq \nu(CH)} k_i.$$

and

It can again be pointed out that, because of the shape of the expression $\Delta\omega(\theta)$, $\varepsilon(\theta)$ has no ternary symmetry. It follows that the three potential wells of different depths in $V'(\theta) = V(\theta) + \varepsilon(\theta)$ correspond to the three equivalent minima of the $V(\theta)$ potential.

The torsional energy levels and associated wavefunctions have been calculated, as previously [13], by the diagonalization of a Hamiltonian representation $(\hat{H}_T + \varepsilon(\theta))$ with a suitable size on the basis of free rotation wave-functions. A ternary potential $V(\theta)$ has been used :

$$V(\theta) = \frac{V_3}{2} (1 - \cos 3(\theta - \theta_0))$$
 (5)

where θ_0 defines the position of the first bond in the equilibrium configuration with respect to the molecule plane, and with the value V_3 equal to 170 cm⁻¹ determined from the measured splitting of the tunnelling effect [15]. This value is consistent with a torsional frequency of about 70 cm⁻¹ for the -CH₃ group, which is observed in neutron spectroscopy [11]. Concerning $\Delta\omega(\theta)$, as in the toluene case, it is impossible to evaluate all the terms of the expansion (4); we have used the approximate law of table I, although it is questionable, but the important point in the following calculations is not the exact form of this function (4) but the fact that it has not the same symmetry as $V(\theta)$. The λ value is taken as 1. The results are illustrated in figure 3 for two cases :

(i) The CH oscillator is supposed to have two equivalent sites in the $-CHD_2$ group.

This can be simulated in the calculations by taking $\theta_0 = 90^\circ$. Then $V'(\theta)$ shows two symmetrical wells of equal depth at $\theta = -\pi/6$ and $\theta = +7\pi/6$ and a third deeper one at $\theta = +\pi/2$. The wave-function corresponding to the first torsional level is localized in the central well, whereas those relative to the second and third torsional levels remain delocalized between the two other wells (Fig. 3A). Owing to the symmetry properties and to the localization of the wave-functions, if the transition operator is supposed scalar or even in θ , the more intense transitions are those occurring between the levels $|v, n\rangle$ (v vibrational quantum number, n torsional quantum number) of the type :

$$|0, 0\rangle \rightarrow |1, 0\rangle, |0, 1\rangle \rightarrow |1,$$

 $1 \rangle$

and

$$|0,2\rangle \rightarrow |1,2\rangle$$
.

This series of transitions appears in the calculated spectra, in order of increasing frequency, as three bands. The two higher frequency ones are only separated by about 1 cm⁻¹. This splitting corresponds to a tunnelling effect. A comparison with the experimental data where these two bands are separated by about 6.5 cm^{-1} clearly indicates that the observed doublet cannot be explained in terms of tunnelling splitting. If the transition operator is supposed to be odd in θ , the most intense transitions are those occurring between levels of different symmetry : $|0, 1 \rangle \rightarrow |1, 2 \rangle$ and $|0, 2 \rangle \rightarrow |1, 1 \rangle$. The transition between the two even levels $|0, 0 \rangle \rightarrow |1, 0 \rangle$ is now forbidden, but a

transition $|0, 0\rangle \rightarrow |1, 3\rangle$ corresponding to a vibration-torsion combination (Fig. 3A) can appear. The calculated spectrum shows two bands with very little frequency difference ($\Delta \overline{v} = 1.2 \text{ cm}^{-1}$) appearing in the region of the previously described high frequency bands, and a slightly less intense one at higher frequency. This is very different from the observed spectrum.

Thus, this first case, which supposes a symmetrical conformation of the $-CHD_2$ group, must be rejected. Actually it is not in agreement with the crystalline structure, in which the molecule is in general position.

(ii) The three potential sites of the CH oscillator in the $-CHD_2$ group are now supposed to be different.

This is the situation envisaged in the classical interpretation; it can be simulated in the calculations by taking θ_0 slightly different from 90°. Then, V'(θ) loses any symmetry and shows three wells with different depths (Fig. 3B). This depth difference ($\geq 3.5 \text{ cm}^{-1}$) is appreciably higher than the splitting between the two levels A and E in the torsional ground state of $V(\theta)$, measured by Trevino *et al.* as 0.28 cm⁻¹ for the -CH₃ group and 0.013 cm⁻¹ for the -CD₃ group [15]. Thus, a strong localization of the wave-functions of the first torsional levels in each well is observed, in the v = 0 as well as in the v = 1 v(CH) vibrational states. It follows that the intense transitions occur only between the levels whose wave-functions are localized in a same well and have a maximum overlapping : $|0,0\rangle \rightarrow |1,0\rangle, |0,1\rangle \rightarrow |1,1\rangle$ and $[0,2\rangle \rightarrow |1,3\rangle$. The frequency of the three transitions thus calculated are approximately equal to the classical ones :

$$\omega_0 + \Delta\omega(\theta_0), \quad \omega_0 + \Delta\omega(\theta_0 + 2\pi/3),$$
$$\omega_0 + \Delta\omega(\theta_0 + 4\pi/3).$$

Finally, one can conclude that, for nitromethane as well as for toluene, the classical and quantum approaches are equivalent to treat the CH stretching spectra of the -CHD₂ group. Tunnelling effects can be neglected in the interpretation of the spectra.

3.1.3 Temperature effect on band intensities. — If the classical theory is sufficient to explain the observed v(CH) vibrational frequencies, the quantum theory is useful to explain the effect of temperature on the relative intensities (Fig. 4). Indeed, the three v(CH) transitions are shown to come each from a different torsional level in the vibrational ground state. Therefore, their intensity is connected with the variations of the population of these three torsional levels.

The splittings of these levels are approximately equal to the half quantum of vibration in each site. Thus, the intensity ratio of two bands $\overline{\nu}_a$ and $\overline{\nu}_b$ must obey the law (13) :

$$\frac{I_{\rm b}}{I_{\rm a}} = C \exp\left[-\lambda \cdot \frac{\overline{v}_{\rm b} - \overline{v}_{\rm a}}{2} \cdot \frac{hc}{kT}\right]. \tag{6}$$

It is verified for I.R. as well as Raman spectra between 100 and 17 K (Fig. 5) with values of the parameters λ and C close to 1. $\lambda \# 1$ implies a compensation effect of the modes other than v(CH), as already pointed out for toluene where $\lambda = 0.88$ [13]. In this connection, the very close result found for the two molecules may suggest the existence of a general property for this type of methylated molecules. On the other hand, the C constant represents the ratio of the transition moments or transition polarizabilities. A value close to 1 is in good agreement with the theoretical calculations developed in the hypothesis of electrical harmonicity.

Finally, the results reported in figure 5 suggest that by going to very low temperatures the isotopic system can become ordered since the fundamental $|0, 0\rangle$ level is then the only populated one. This order corresponds to a particularly simple situation in nitromethane ; the CH vibrator of the -CHD₂ group would be localized in the plane perpendicular to the molecular plane.

However, this conclusion implies that the evolution rate is fast enough to prevent a freezing of the system at very low temperature [27]. One can simply hope that the very low hindering barrier to methyl rotation in nitromethane allows the isotopic ordering to take place.

3.2 RELAXATION STUDY ON THE HIGH TEMPERATURE SPECTRA (FROM 90 TO 185 K). — When the temperature is raised, the v(CH) stretching bands of nitromethane NO₂CHD₂ clearly broaden (Fig. 4) whereas



Fig. 5. — Temperature dependence of the ratio I_b/I_a where I_b and I_a are respectively the intensities of the nitromethane NO₂CHD₂ bands at

$$\overline{v}_{\rm b} = 3.049.0 \,{\rm cm}^{-1}$$
 and $\overline{v}_{\rm a} = 2.997.0 \,{\rm cm}^{-1}$.

The λ coefficient is 0.83 and C close to one.

the bands due to vibrations of the -NO₂ group are very slightly affected. This specific broadening is similar to that observed for the CH stretching bands of toluene $C_6D_5CH_2$ [13]. It can be ascribed to a relaxation process peculiar to the -CHD₂ group. We will again restrict ourselves to the study of this relaxation at relatively high temperature ($T \ge 90$ K) with semi-classical approaches.

First of all, we have tried to determine the influence of a process involving Markovian jumps around the C-N axis. This model gives, after Fourier transform, the spectral profile :

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \operatorname{Tr} \hat{\rho} \cdot \hat{D} \cdot \frac{1}{i(\omega - \hat{\Omega}) + \hat{\pi}}$$
(7)

with

- $\hat{\rho}$ the diagonal matrix of the populations of each site,
- \hat{D} the square matrix of the intrinsic amplitudes of the transition operator in each site,
- $\hat{\Omega}$ the diagonal matrix of the frequencies in each site,
- $\hat{\pi}$ the matrix of the transition probabilities by unit time from an equilibrium state to another.

As in the toluene case, the isotropic and anisotropic contributions cannot be separated in our powder Raman spectra. We have only tried to calculate the infrared profiles using the same model as previously which supposes instantaneous random 120° jumps with equal residence times in each site [13]. If the dipole moment of the vibrational transition of modulus $\bar{\mu}$ is supposed collinear with the -CH bond directed along the unit vector **u**, the infrared profiles are given by :

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \sum_{ij} \rho_{i*} | \overline{\mu}_{i}(0) | \cdot | \overline{\mu}_{j}(0) | \cdot (\mathbf{u}_{i} \cdot \mathbf{u}_{j}) \cdot v_{ji}(\omega)$$
(8)

where $v_{ij}(\omega)$ are the elements of the matrix

$$\frac{1}{i(\omega-\hat{\Omega})+\hat{\pi}}$$

We used the values of the residence times determined by Trevino et al. from Q.N.S. study [11]. These values, which vary from 1.72 ps at 90 K to 1.02 ps at 150 K, can be affected by the deuteration of the methyl group. Indeed, N.M.R. studies have shown that, in the liquid state, this effect was roughly proportional to the square root of the ratio of the moments of inertia [25, 26]. Thus, the values of the $-CH_3$ residence time have to be multiplied by a factor 1.43 for the -CD₃ group and it would be suitable to multiply them by a factor 1.3 for the -CHD₂ group. But, in the solid state, other problems related to the reorientation mechanism itself can occur. In the absence of more precise information, we have admitted, as a first approximation, that the order of magnitude of these residence times remains the same for the $-CH_3$ and $-CHD_2$ groups.

The infrared profiles observed at four different temperatures above 90 K are compared in figure 6

Fig. 6. — Comparison of the experimental and calculated infrared spectra of the -CHD₂ group of nitromethane in the v(CH) stretching region at different temperatures. Full line : experimental spectra. Dotted line : spectra calculated by means of a 2 $\pi/3$ jump model. τ is the residence time.

with the profiles calculated with the model of instantaneous jumps of the $-CHD_2$ group. The agreement is satisfactory and it can be concluded that this relaxation mechanism takes a great part in the broadening effect.

However, a precise measurement of the residence times for the $-CHD_2$ group, either by N.M.R. or by Q.N.S., would certainly give slightly greater values than those used here which are relative to the $-CH_3$ group. Consequently, the calculated profiles would be narrower and an additional relaxation process, involving small amplitude fluctuations around each of the equilibrium positions could be invoked. Nevertheless, this latter mechanism, which contributes largely to the relaxation in the toluene case [13], is certainly less important for nitromethane.

4. Conclusions. — The study of the v(CH) infrared and Raman spectra of nitromethane NO₂CHD₂ and toluene $C_6D_5CHD_2$ in their crystalline phase leads to closely related results. At low temperatures (17 K), the presence of several v(CH) stretching bands can essentially be interpreted by the existence of several sites which correspond to different conformations of the oscillator CH in the molecule, in good agreement with the equilibrium configuration of the methyl group as determined by crystallographical studies. A quantum treatment shows that, even at low temperatures (17 K) and despite the low hindering barrier to the internal rotation, no tunnelling effect appears in these spectra. Furthermore, this theory explains the temperature effect on the relative intensities of the v(CH)bands and suggests an ordering of the isotopic system CHD_2 at very low temperature (4 K).

At higher temperatures, these spectra are modulated by the internal rotation of the $-CHD_2$ group. Two relaxation processes, involving respectively great amplitude jumps from one equilibrium position to another and small amplitude fluctuations around each equilibrium position, which introduces inhomogeneous broadenings of each v(CH) band, had previously been taken into account to explain the broadenings observed for crystalline toluene. We show in the present work that the first process, large amplitude instantaneous jumps, is sufficient to explain the main spectral features in crystalline nitromethane.

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