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#### ADVERTISEMENT



# Effect of the internal rotation of the $CHD_2$ group on the aliphatic CH stretching mode of the toluenes $C_6H_5CHD_2$ and $C_6D_5CHD_2$ in solid crystalline phases

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The infrared and Raman spectra of the toluenes  $C_6H_5CHD_2$  and  $C_6D_5CHD_2$  in the aliphatic CH stretching mode range have been recorded in a large temperature range (17 to 165 K) for both crystalline phases  $\alpha$  and  $\beta$ . At very low temperature, the  $\beta$  form spectra show three bands; each of them is assigned to the vibration of a CH oscillator localized in a different site. Three groups of bands are also observed in the  $\alpha$  phase spectra: a single band at higher frequency and two doublets at lower frequency. This splitting is assigned to the existence of two types of molecules in the unit cell, involving six different CH vibrators. A quantum theory of these spectra is carried out, assuming an anharmonic coupling of the CH stretching mode with the CHD<sub>2</sub> torsion. As a consequence of this coupling, in the adiabatic approximation, the vibrational energy depends on the conformation and can be considered as an additional torsional potential. This latter has no ternary symmetry so that the total torsional potential has three principal unequal wells that correspond to three different locations of the CH oscillator. Therefore, no tunneling effect appears, which 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 that, at very low temperature, the isotopic system gets ordered. At higher temperature, a strong relaxation of the  $v_{CH}$  vibration bands is observed. This relaxation is much stronger than that of the aromatic ring modes... Thus the relaxation process is essentially due to the influence of the anharmonic coupling between the CH stretching mode and the  $\tau_{\rm CHD_2}$  mode. Two mechanisms are considered: the first one involves Markovian jumps of the system from an equilibrium position to another one, the second one involves fluctuations of the CH vibration around each of these equilibrium positions. NMR and neutron scattering data have already been analyzed on the basis of the first process. Starting from the residence times so determined, the computations show that this mechanism is an efficient relaxation process, but indicate that it is not sufficient to fit the experimental profiles. This fit is obtained rather by using the second model with parameters of reasonable physical values; thus, the second process is also efficient. A better treatment of the relaxation process would be to elaborate; it would have to include both mechanisms and to take into account motions of the methyl group with different amplitudes.

#### I. INTRODUCTION

Several investigations on the  $Z-CH_3$  molecules, where Z has no ternary symmetry, have shown, mainly from the isotopic substitution of a CH<sub>3</sub> group by a CHD<sub>2</sub> group, 1-6 that the force constant of the CH bond depends on its conformation. Several CH stretching bands are thus expected in the infrared and Raman spectra. However, when the height of the barrier to the internal rotation is low, such a splitting is expected only at low temperature. Indeed, at higher temperature, the internal rotation of the methyl group should affect the spectrum; if the rotation is slow, the CH oscillator modulation should be slow and several more or less broad bands should be observed; on the contrary, if the motion is fast, at higher temperature only a single band is expected because of the fast oscillator modulation. This collapsing phenomenon by fast exchange is well known in NMR.

The toluene molecules provide a good model to study this effect. The barrier to internal rotation of the methyl group is very low in the gas phase  $(14 \text{ cal mol}^{-1})^{6,9}$ and increases to approximately 200 to 600 cal mol<sup>-1</sup> in the solid state because of the intermolecular forces. <sup>10-15</sup> A previous study on the  $C_6H_5CHD_2$  compound in different physical states and at different temperatures<sup>16</sup> has given results in agreement with the ideas outlined above. At low temperature, in the solid crystalline state, three aliphatic CH stretching bands are observed and assigned to three different conformations of the methyl group. In the liquid phase, infrared and Raman spectra exhibit only one nearly symmetrical band. Furthermore, the bands of the other vibrations of the CHD<sub>2</sub> group are also very much affected by the temperature and by the physical state while the aromatic ring modes are much less affected.<sup>17</sup>

These results have encouraged us to carry on a careful study of the CH stretching vibration of this type of molecules, the CH oscillator being considered as a probe to analyze the structure and the reorientational motion of the CHD<sub>2</sub> methyl group. In this paper, the solid crystalline state has more particularly attracted our interest; the toluene is known to exist under several solid forms, 18, 19 a vitreous phase, and two crystalline phases: a stable one  $\alpha$  that melts at 178 K and an unstable one  $\beta$  that melts at 154 K. The  $\beta$  phase structure, determined at 110 K, is orthorhombic Pbcn with eight molecules per unit cell in a general position.<sup>20</sup> The  $\alpha$  phase, determined at 165 K, is monoclinic  $P2_1/c$ with eight molecules per unit cell in a general position, grouped in two categories of molecules.<sup>21</sup> The  $\alpha$  form density is slightly higher than the  $\beta$  form ( $\rho_{\alpha} = 1.052$ ,  $\rho_{\rm B} = 1.047 \text{ g cm}^{-3}$ ). Furthermore, a structural transformation of the  $\alpha$  form is postulated between 80 and 40 K; in fact upon cooling, a band at 24 cm<sup>-1</sup> disappears in the phonons Raman spectra<sup>22</sup> while this does not happen in the  $\beta$  phase.<sup>23</sup>

#### II. EXPERIMENTAL CONDITIONS AND RESULTS

First, the synthesis of the toluene deuterated derivatives is briefly recalled. Then the method to obtain the crystalline samples and the spectrometers used are described. At last, the different infrared and Raman spectra are presented.

### A. Preparation of the isotopic derivatives $C_6H_5CHD_2$ and $C_6D_5CHD_2$

The synthesis requires three stages: from the methyl benzoate, the  $\alpha - \alpha$  dideuterated benzyl alcohol and the benzyl chloride are successively prepared<sup>24,25</sup>

$$C_{\delta}X_{5}COOCH_{3} \xrightarrow{\text{4 Al Li } D_{4}}_{\text{then hydrolysis}} C_{\delta}X_{5}CD_{2}OH ,$$

$$(X = H \text{ or } D) ,$$

$$C_{\delta}X_{5}CD_{2}OH \xrightarrow{\text{ZnCl}_{2}}_{\text{HCl}} C_{\delta}X_{5}CD_{2}Cl .$$

The benzyl chloride can then undergo either a classic organomagnesian reaction followed by an  $H_2O$  hydrolysis or a reduction with  $Bu_9SnH$ .<sup>28</sup> The advantage of this last method is to give products that are very easily

isolated by distillation. The isotopic purity as obtained by the mass spectrometry is higher than 98% for  $C_8H_5CHD_2$  and higher than 96% for  $C_8D_5CHD_2$ .

#### **B. Samples preparation**

The samples crystallization is rigorously performed in order to get a very well determined crystalline phase:

(a) At first, a very small amount of the compound is trapped around 110 K on a copper surface for the Raman work or on a CsI window for the infrared work.

(b) The thin film so obtained of the amorphous compound is then warmed up to 160 K in order to get the  $\alpha$  phase or to 130 K to obtain the  $\beta$  phase. The amorphous and crystalline  $\alpha$  and  $\beta$  forms are easily distinguished from their low frequency Raman bands and from their  $\delta_{C-X}$  aromatic bands in the infrared spectra  $(X = H \text{ or } D) (\nu_{18\alpha}, \nu_{18b}).^{14,22,23}$ 

(c) In the  $\alpha$  form case, the trapping is very slowly continued at 160 K until a sufficient layer is deposited. Then, the sample is very slowly cooled down to 17 K to avoid unsticking or crackling of the film.

(d) In the  $\beta$  form case, as soon as the crystallization is finished and without increasing the layer thickness, the sample is cooled down to 17 K. This cooling is faster than for the  $\alpha$  phase, because (i) since the film is thinner, there are fewer risks of damaging it, and (ii) the irreversible transition from the  $\beta$  to the  $\alpha$  form, which occurs very easily in the 100 to 130 K temperature range, is so avoided.

#### C. The spectrometers

The infrared spectra were recorded on a PE180 spectrometer while the Raman spectra were obtained on a Coderg T 800 and on a Jobin *et* Yvon "Ramanor" spectrometer, equipped with a Spectra Physics Argon ion laser. All the Raman spectra were obtained with the 488 nm line at a power of 200 mW. The observation direction was perpendicular to the incident beam direction. In both cases, the spectral slit width was approximately 1 cm<sup>-1</sup>. A cryodine 20 instrument equipped with the appropriate accessories allowed us to do a low temperature study.

#### D. Experimental results

The aliphatic CH stretching infrared and Raman spectra of the toluenes  $C_6H_5CHD_2$  and  $C_6D_5CHD_2$  at different temperatures were recorded in both  $\alpha$  and  $\beta$  crystalline forms.

Figure 1 shows the infrared and Raman spectra of the two crystalline isotopic derivatives in the  $\alpha$  phase at 17 K. The following figures present the infrared and Raman spectra of the toluene C<sub>6</sub>D<sub>5</sub>CHD<sub>2</sub> crystallized in the  $\alpha$  and  $\beta$  phases at 17 K (Fig. 2) and the spectra of the same compound isotopically diluted in the toluene C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> crystallized in the  $\alpha$  phase at 17 K (Fig. 3).

Figure 4 compares the CH stretching infrared and Raman spectra of the toluene  $C_6D_5CH_3$  crystallized in the  $\alpha$  and  $\beta$  phases. Finally, Figs. 6 and 8 illustrate the temperature effect on the CH stretching infrared and Raman spectra of the toluene  $C_8D_5CHD_2$  crystallized in the  $\beta$  and  $\alpha$  phases, respectively.

#### III. DISCUSSION

#### A. The low temperature spectra (17 to 100 K)

### 1. Qualitative assignment of the spectral bands at 17 K $\,$

As is clearly shown in Fig. 1, several bands are observed in the aliphatic CH stretching range of the  $\alpha$ phase spectra: two bands at 2930 and 2925 cm<sup>-1</sup>, each one being seen to split in two components, if their Raman spectra are carefully looked on and a third one at higher frequency (2950 cm<sup>-1</sup>) (Table I). The infrared and Raman spectra of the  $\beta$  phase (Fig. 2), which are almost identical, are different from those of the  $\alpha$ phase but nevertheless show three bands in the same spectral range.

Fermi resonance occuring between a  $\nu_{CH}$  excited level and overtone or combination vibrational levels could justify several bands in the CH stretching spectra of the CHD<sub>2</sub> group. However this first hypothesis is wrong; indeed the spectra of both compounds  $C_{6}H_{5}CHD_{2}$  and  $C_{6}D_{5}CHD_{2}$  are exactly the same in the 2900–2980 cm<sup>-1</sup> range (Fig. 1), even though the frequencies of the aromatic rings  $C_{6}H_{5}$ - and  $C_{6}D_{5}$ -normal modes are all different.<sup>17</sup> Furthermore the overtone vibrations  $2\delta_{CH}$ (2550 cm<sup>-1</sup>) and  $2\delta_{CD_{2}}(2092 \text{ cm}^{-1})$  are not found in this spectral range.<sup>17</sup>

A correlation effect could also occur between the  $\nu_{CR}$ 



FIG. 1. The CH aliphatic stretching infrared and Raman spectra of the pure toluenes  $C_6H_5CHD_2$  and  $C_6D_5CHD_2$  crystallized in the  $\alpha$ phase at 17 K.

vibrations of the different molecules in the crystal and explain some splittings. However no important modification of the  $\nu_{CH}$  spectra is observed by isotopic dilution of  $C_6D_5CHD_2$  in  $C_6D_5CD_3$ ; even the splitting of the two lowest frequency Raman bands of the  $\alpha$  phase is observed with a better resolution in the isotopic dilution than in the pure compound (Fig. 3). Therefore the second hypothesis must also be excluded.

Thus, we are led to assign each of the observed bands to a CH stretching vibration of a CH oscillator in a different site. Actually if the methyl group is located in a site without symmetry element, three CH stretching bands of the CHD<sub>2</sub> group are expected in the infrared as well as in the Raman spectra. This is observed for the  $\beta$  phase spectra, where there is only one type of molecule in a general position in the unit cell<sup>20</sup> (Fig. 2). In the  $\alpha$  phase, the splitting of the two lowest frequency bands has to be explained. However, at 165 K, the xray study has shown that there are two types of molecules per unit cell in this phase.<sup>21</sup> If we suppose that it is still the same thing at 20 K, although a phase transition



FIG. 2. The CH stretching infrared and Raman spectra of the pure toluene  $C_6D_5CHD_2$  crystallized in two  $\alpha$  and  $\beta$  phases at 17 K.



FIG. 3. The CH stretching infrared and Raman spectra of the pure toluene  $C_6D_5CHD_2$  and of the toluene  $C_6D_5CHD_2$  diluted at 20% in the toluene  $C_6D_5CD_3$  and crystallized in the  $\alpha$  phase at 17 K.

is likely to occur,  $^{22}$  these splittings are easily explained: two families of methyl group per unit cell generating six different sites for the hydrogen atom of the CHD<sub>2</sub> group. In a first analysis, we will hold this interpretation.

Then, for force constants, uncorrected for the anharmonicity, can be evaluated for each CH vibrator; for that purpose, the approximation of an isolated  $CHD_2$ group is made and the HD interaction constant is neglected. This leads to the results given in Table II. For the isolated molecule, because of its symmetry, the  $k_{CH}$  force constant follows a general law such as:

$$k_{\rm CH} = k_0 + \sum_{n=1}^{\infty} \Delta k_n \cos(2n\theta) , \qquad (1)$$

where  $\theta$  is the dihedral angle between the C-C-H plane

and the aromatic ring plane. McKean *et al.*<sup>5,6</sup> have often used Eq. (1) with only the first terms of this expansion:

$$k_{\rm CH} = k_0 + \Delta k \cos(2\theta) \ . \tag{2}$$

Furthermore, it can be assumed that  $\Delta k$  is positive, as there are hyperconjugation effects in toluene, the  $k_{\rm CH}$  force constant is minimum for  $\theta = \pi/2$  and  $\theta = 3\pi/2$ .  $2.^{27,26}$  In the solid state, as well as in the  $\alpha$  phase and the  $\beta$  phase, the toluene molecule is in a general position in the unit cell and looses all symmetry elements, so that it is possible to write:

$$k_{\rm CH} = k_0 + \sum_{n=1}^{\infty} A_n \exp(in\theta) + \sum_{n=1}^{\infty} A_n^* \exp(-in\theta) . \qquad (3)$$

We can however ask ourselves about the relative im-



FIG. 4. The CH stretching infrared and Raman spectra of the pure toluene  $C_6D_5CH_3$  crystallized in the two  $\alpha$  and  $\beta$  phases at 17 K (the arrows drawn on the infrared spectra show the calculated frequencies.)

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TABLE I. The experimental frequencies of the CH aliphatic stretching bands in the spectra of the toluenes  $C_6H_5CHD_2$ ,  $C_6D_5CHD_2$ ,  $C_6D_5CHD_2$ ,  $C_6D_5CHD_3$ , and  $C_6D_5CH_3$  crystallized in the  $\alpha$  and  $\beta$  phases at 17 K.

	Structure $\alpha$		Structure $\beta$	
	<i>ν</i> <sub>IR</sub> (cm <sup>-1</sup> )	$\overline{\nu}_{Raman}$ (cm <sup>-1</sup> )	<i>ν</i> <sub>IR</sub> (cm <sup>-1</sup> )	$\overline{\nu}_{Raman}$ (cm <sup>-1</sup> )
	2925, 0	2925.0		
C <sub>6</sub> D <sub>5</sub> CHD <sub>2</sub>	2927.0	2927.5	2911.5	2911.0
or	2932.5	2932.0 2934.5	2918.5	2918.5
C <sub>6</sub> H <sub>5</sub> CHD <sub>2</sub>	2947.5	2948.5	2953.5	2954.0
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2917.0 2950.5	2918.0 2953.0	2912.0 2941.0	2912.5 2943.5
	2971.0	2973.0	2974.5	2974.5
C <sub>6</sub> D <sub>5</sub> CH <sub>3</sub>	2921.5 2951.5 2971.0	2922. 0 2950. 0 2973. 0	2916. 0 2942. 0 2976. 0	2916.0 2943.0 2976.0

portance of the intramolecular and intermolecular effects. So far as the intermolecular effects on the force constant  $k_{CH}$  are small, Eq. (2) is a first approximation. For example, we have collected in Table II the  $k_0$ ,  $\Delta k$ , and  $\theta$  values found with Eq. (2). For comparison purposes, the crystallographically determined angles at 165 K are also given<sup>21</sup> for the  $\alpha$  form.

One sees that the  $\Delta k$  and  $k_0$  values that we have calculated from the frequencies for the  $\alpha$  and  $\beta$  forms (Table II), are not the same, which is a good indication of the existence of some intermolecular effects.

From the so determined force constants, the spectrum of the  $\nu_{CH}$  vibrations of the methyl group of the toluenes  $C_6H_5CH_3$  and  $C_6D_5CH_3$  can be calculated, with the introduction of an interaction constant  $f_{H-H}$ , in the  $\alpha$  and  $\beta$  phases ( $f_{HH\alpha} = 0.051 \times 10^5$  dyn cm<sup>-1</sup>;  $f_{HH\beta} = 0.039 \times 10^5$  dyn cm<sup>-1</sup>). These results are indicated by means of arrows on Fig. 4. The frequencies so calculated do not coincide with the experimental ones, because, as is often mentioned, Fermi resonance occurs between the  $2\delta_{CH_3}$  harmonic and the CH stretching levels<sup>27,26</sup>; this

resonance affects all three vibrations by the absence of symmetry.

Finally, it can be noticed that the intensity of the  $\nu_{\rm CH}$  bands is very different. Since the polycrystalline samples are certainly slightly orientated when deposing, a pleochroic effect certainly exists. However, this orientation effect is not sufficient to explain completely the difference of the band intensities. The transition moments and the transition polarizabilities are probably dependent upon the conformation, as are the force constants.

#### 2. Quantum theory of these spectra

The previous considerations suggest that the existence of several bands due to the CH aliphatic stretching modes in the infrared and Raman spectra of the toluenes  $C_{\theta}H_{5}CHD_{2}$  and  $C_{\theta}D_{5}CHD_{2}$  in both crystalline phases is due to three or six CH oscillators located in different environments. Nevertheless, it is worthy to discuss the possibility of tunneling effects. Is it not the origin of the splitting of the two low frequency lines observed in the  $\alpha$  phase? Consequently the problem must be considered from a quantum point of view.

It is supposed that in the R-CHD<sub>2</sub> molecule, the aromatic ring R is fixed and rigid and that the CHD<sub>2</sub> group rotates around the C-R axis. As suggested by the vibrational analysis of the whole spectrum of the  $C_{6}H_{5}CHD_{2}$  and  $C_{6}D_{5}CHD_{2}$  molecules crystallized in the  $\alpha$  phase at different temperatures,<sup>7</sup> some vibrational modes of the CHD<sub>2</sub> group (stretching, bending and rocking) are assumed to be dependent upon the conformation, especially the CH stretching mode, whereas the aromatic ring modes do not vary. Finally, the intermolecular coupling of the methyl group modes in the crystal are neglected, as indicated by the isotopic dilution results. So the total Hamiltonian H, describing the vibrations of the CHD<sub>2</sub> group and the torsion mode is written:

$$\hat{H} = \hat{H}_{\mathbf{y}} + \hat{H}_{\mathbf{T}} + \hat{H}_{\mathbf{yT}} , \qquad (4)$$

with:

	<sup>k</sup> сн (×10 <sup>5</sup> dyn cm <sup>-i</sup> )	From relation (2)			$\theta$ from
		$k_0$ (×10 <sup>5</sup> dyn cm <sup>-1</sup> )	$\frac{\Delta k}{(\times 10^5 \text{ dyn cm}^{-1})}$	ذ	crystallographical data
	4.767933			4°7	
β	4.653718	4.684069	0.084977	124°7	
	4.631359			244°7	
	4.750147			4°	7°8
	4.696989	4,709912	0,043214	124°	141°
	4.682543			244°	258°
α	4,748532			12°5	26°
	4.705 024	4.709912	0.043214	132°5	146°
	4.674527			252° 5	264°5

TABLE II. The values of the force constants of the calculated angles and of the x-ray angles at 165 K.

$$\hat{H}_{V} = \sum_{i} - \frac{\hbar^{2}}{2} \frac{\partial^{2}}{\partial q_{i}^{2}} + V_{i}(q_{i}) ,$$
$$\hat{H}_{T} = -\frac{\hbar^{2}}{2I} \frac{\partial^{2}}{\partial \theta^{2}} + V(\theta) ,$$
$$\hat{H}_{VT} = \sum_{i} V_{i}(q_{i}, \theta) .$$

 $\hat{H}_{V}$ ,  $\hat{H}_{T}$ , and  $\hat{H}_{VT}$  are, respectively, the Hamiltonians of the vibrational modes, of the torsional mode and of their interaction. *I* is the moment of inertia of the CHD<sub>2</sub> group, and  $q_i$  the vibrational normal coordinates. Each potential  $V_i(q_i)$  can be written, in the harmonic approximation:

$$V_{i}(q_{i}) = \frac{1}{2} \omega_{0i}^{2} \cdot q_{i}^{2} .$$
 (5)

 $V(\theta)$  is the potential part depending only on the torsional coordinates, the methyl group internal coordinates having their equilibrium values. Even though the methyl group is located in an asymmetrical site in the crystal, this potential has a ternary symmetry as a first approximation. Indeed, the circular permutation of a proton and deuterons does not alter this potential, and it is equivalent to a  $2\pi/3$  or a  $4\pi/3$  rotation, if the little distortions of the methyl group equilibrium configuration are neglected, in other words, if all the bond lengths and all the angles between these bonds are supposed equal. As the previous authors who have studied the dynamics of the methyl group in the solid state, <sup>14,15,29</sup> we can write:

$$V(\theta) = \sum_{n} B_{3n} \exp(i3n\theta) + B_{3n}^* \exp(-i3n\theta) .$$
 (6)

Finally, the  $V_i(q_i, \theta)$  potentials, assuming  $\omega_i = \omega_{0i} + \Delta \omega_i(\theta)$ , with  $\Delta \omega_i(\theta)$  little in front of  $\omega_{0i}$  can be written:

$$V_i(q_i, \theta) = \omega_{0i} \cdot \Delta \omega_i(\theta) \cdot q_i^2 .$$
<sup>(7)</sup>

These potentials have not ternary symmetry. Indeed, if a proton is exchanged for a deuteron in a determined configuration, the force constants F matrix is not modified but any nonequivalent terms are exchanged in the G matrix which alters at the same time the frequency and the shape of each mode. In opposition to this, a proton change in the CH<sub>3</sub> group involves no modification in the G matrix and in this case,  $V_i(q_i, \theta)$  keeps a ternary symmetry. For the various modes of the CHD<sub>2</sub> group,  $\Delta \omega_i(\theta)$  can be written:

$$\Delta \omega_i(\theta) = \sum_n C_n \exp(in\theta) + C_n^* \exp(-in\theta) . \qquad (8)$$

Since the frequency of the torsional mode is very low, approximately 50 cm<sup>-1</sup>,<sup>14,15</sup> and that of the conformation dependent modes of the CHD<sub>2</sub> group is higher than 800 cm<sup>-1</sup>,<sup>17</sup> the adiabatic approximation is justified. Hence, the total wave function can be written as a product of two functions  $\chi(q_1, q_2 \cdots q_i, \theta) \varphi(\theta)$  such as

$$[\hat{H}_{V} + \hat{H}_{VT}]\chi(q_1, q_2 \cdots q_i, \theta) = \epsilon_i(\theta)\chi(q_1, q_2 \cdots q_i, \theta),$$
(9)

$$[\hat{H}_T + \epsilon_t(\theta)]\varphi(\theta) = E\varphi(\theta) , \qquad (10)$$

where  $\chi(q_1, q_2 \cdots q_i, \theta)$  describes the rapid motions and depends slowly on  $\theta$ , and where  $\epsilon_i(\theta)$  is ascribed to a torsional potential in Eq. (10). The  $\epsilon_i(\theta)$  are easily computed since the potentials are harmonic in  $q_i$  in Eq. (9):

$$\epsilon_{i}(\theta) = \sum_{i} \bar{n}(v_{i} + \frac{1}{2}) \left[ \omega_{0i} + \Delta \omega_{i}(\theta) \right] .$$
(11)

Since we are essentially interested in the spectrum of the CH stretching mode, we will consider only in  $\epsilon_i(\theta)$ the terms with a quantum number  $v_i = 0$ , except for the stretching vibration term, whose frequency is  $\omega_0$  $+ \Delta \omega(\theta)$ . So:

$$\epsilon(\theta) = \hbar(v + \frac{1}{2}) \omega_0 + \sum_{i \neq v_{CH}} \frac{\hbar}{2} \omega_{0i} + \hbar(v + \frac{1}{2}) \Delta \omega(\theta) + \sum_{i \neq v_{CH}} \frac{\hbar}{2} \Delta \omega_i(\theta) .$$
(12)

Unfortunately, the  $\Delta \omega_i(\theta)$  cannot be evaluated for each mode. However, we can reasonably suppose that the effects of the conformation on the frequency is smaller for the various *i* modes than for the CH stretching mode, as it is suggested by the analysis of the spectra,<sup>17</sup> and that the frequency extrema occur at the same values of  $\theta$  for every mode. Thus, as a simplifying hypothesis, we can write that  $\Delta \omega_i(\theta) = k_i \Delta \omega(\theta)$ ,  $k_i$  being a positive or a negative constant with an absolute value lower than one. Under these conditions,  $\epsilon(\theta)$  is such that:

$$\epsilon(\theta) = \hbar(v + \frac{1}{2}) \omega_0 + \sum_{i \neq v_{CH}} \frac{1}{2} \hbar \cdot \omega_{0i} + \hbar\left(v + \frac{\lambda}{2}\right) \Delta \omega(\theta) , \qquad (13)$$

where

$$\lambda = 1 + \sum_{i \neq v_{\rm CH}} k_i$$

It is important to emphasize that, because of the shape of the potentials  $V_i(q_i, \theta)$ ,  $\epsilon(\theta)$  has no ternary symmetry. Furthermore, the extreme values of  $V(\theta)$ are known to be very much greater than those of  $\epsilon(\theta)$ . Thus, to the three equal minima of the potential  $V(\theta)$ that represent three equivalent equilibrium configurations, correspond three potential wells with different depths for  $V'(\theta) = V(\theta) + \epsilon(\theta)$ . If the depth difference between the  $V'(\theta)$  wells is appreciably higher than the splitting between the two levels A and E in the torsional ground state of the  $V(\theta)$  potential, a strong localization of the wave functions and, as it will be seen afterwards, a great simplification of the spectra consequently occur. The tunneling frequency of the toluene  $C_8D_5CH_3$  methyl group is not known, <sup>14,15</sup> but for some structurally analogous molecules<sup>30</sup> it is known to be much lower than 1 cm<sup>-1</sup>. In opposition, the  $\Delta \omega(\theta)$  frequency variations can reach more than 20 cm<sup>-1</sup>, so that the previously described situation is very probable.

To illustrate these considerations, several computations of the torsional energy levels and wave functions have been performed by diagonalization of the Hamiltonian representation on the basis of the free rotation wave functions with a suitable size. We have used successively a ternary potential  $V(\theta)$ :

$$V(\theta) = \frac{V_3}{2} \left[ 1 - \cos 3(\theta - \theta_0) \right], \qquad (14)$$



FIG. 5. The plots of the potential barrier  $V'(\theta)$  of the CHD<sub>2</sub> group internal rotation in the vibrational ground state (v = 0) and in the first vibrational excited state (v = 1).

 $V(\theta) = \frac{V_3}{2} [1 - \cos 3(\theta - \theta_0)], \text{ with } V_3 = 100 \text{ cm}^{-1}, \theta_0 = 4^\circ,$  $V(\theta, q) = \frac{1}{2} \Delta k \cdot \cos 2\theta \cdot q^2, \text{ with } \Delta k = 0.043214 \times 10^5 \text{ dyn cm}^{-1}.$ 

The broken lines materialize the presence probabilities of the functions  $\varphi(\theta)$  (-----); the arrows (---) materialize the most probable transitions.  $(|0,1\rangle \rightarrow |1,1\rangle \ \overline{\nu} = 2927.4 \text{ cm}^{-1}; \ |0,2\rangle \rightarrow |1,2\rangle \ \overline{\nu} = 2930.2 \text{ cm}^{-1}; \ |0,3\rangle \rightarrow |1,3\rangle \ \overline{\nu} = 2948.6 \text{ cm}^{-1}).$ 

where  $\theta_0$  defines the position of the first bond in the equilibrium configuration with respect to the aromatic ring plane and the two potentials proposed by Schüler *et al.*:<sup>14,15</sup>

$$V(\theta) = \frac{V_3}{2} \left[ 1 + (-1)^k \cos 3(\theta - \theta_0) \right] + \frac{V_6}{2} \left[ 1 + (-1)^k \cos 6(\theta - \theta_0) \right]$$
(15)

with k = 0 or 1.

The  $V_3$  and  $V_6$  used values were consistent with a torsional frequency of about 50  $cm^{-1}$  for the CH<sub>3</sub> group. Concerning  $\Delta \omega(\theta)$ , it would be reasonable to use an expansion of Eq. (8) until n = 3, if the potential  $V(\theta)$ [Eq. (14)] is chosen, and until n=6 with Eq. (15). Unfortunately, it is beyond our power to evaluate the terms of this expansion; so, some laws with  $\Delta \omega(\theta)$ =  $(\Delta k \cos \theta)/2(M \cdot k_0)^{1/2}$  and  $\Delta \omega(\theta) = (\Delta k' \cdot \cos 2\theta)/2(M \cdot k_0)^{1/2}$  $2(M \cdot k_0)^{1/2}$  are used [compare Eq. (2)]. (M is the reduced mass of the oscillator CH). The  $\Delta k$ ,  $\Delta k'$ ,  $k_0$ , and  $\theta_0$  values are fitted, so that the relations give the observed frequencies of the  $\nu_{\rm CH}$  bands for the toluene  $\alpha$ and  $\beta$  forms. Finally, two values of the coefficient  $\lambda$ are successively used: 1 and  $(1-1/\sqrt{2}) \approx 0.3$ . The first value assumes a compensation of the effects of all the modes except for the  $\nu_{\rm CH}$  mode. The second value implies that the  $\nu_{\rm CD}$  frequencies are considered and that the oscillators CD and CH have the same apparent force constants. The results obtained in all these computations are fundamentally the same and are illustrated by Fig. 5. The difference of the depth of the wells of the function  $V'(\theta)$ , as well in the  $\nu_{CH}$  fundamental vibrational state as in the first excited state, is sufficient for the wave functions of the three first torsional levels to be strongly localized in each well. Therefore whatever  $\theta$  dependent expression of the operator that controls the transitions, the intense transitions for the  $v_{\rm CH}$  mode at  $\Delta v = +1$  occur only between the levels localized in the same well:  $|0,1\rangle - |1,1\rangle$ ,  $|0,2\rangle - |1,2\rangle$ , and  $|0, 3\rangle + |1, 3\rangle$ . This phenomenon is very similar to that described by Somerjai and Hornig for systems connected together by a hydrogen bond in the case of a two dissymmetrical wells potential.<sup>31</sup> Furthermore, the transition frequencies are approximately equal to the classical ones,  $\omega_0 + \Delta \omega(\theta_0)$ ,  $\omega_0 + \Delta \omega(\theta_0 + 2\pi/3)$ , and  $\omega_0 + \Delta \omega (4\pi/3 + \theta_0)$ . Thus, from the quantum theory, the classical results are found again, and the occurrence of a tunneling effect in the  $\nu_{\rm CH}$  mode spectra seems improbable. This justifies our interpretation of the  $\alpha$ form spectrum by two nonequivalent methyl groups.

Furthermore the splittings of the first three torsional levels in the vibrational ground state are found to be approximately equal to:

$$E_{01} - E_{02} \simeq \frac{\lambda}{2} \left[ (E_{11} - E_{01}) - (E_{12} - E_{02}) \right],$$



FIG. 6. The CH stretching infrared and Raman spectra of the pure toluene  $C_6D_5CHD_2$  crystallized in the  $\beta$  phase at different temperatures. By comparison, the infrared band  $(\nu_{19a} + \nu_{9a})$  evolution is shown in the same temperature range.

$$E_{01} - E_{03} \simeq \frac{\lambda}{2} \left[ (E_{11} - E_{01}) - (E_{13} - E_{03}) \right],$$
 (16)

and essentially depend on the zero energies of the vibrational modes.

#### 3. Temperature effect on the band intensities

This model predicts a temperature effect on the intensity of the  $\nu_{CH}$  transitions, due to the population of the different torsional levels (Fig. 5). According to Eq. (16) the following expression is found:

$$\frac{I_b}{I_a} = C \exp\left[-\lambda \cdot \frac{\overline{\nu}_b - \overline{\nu}_a}{2} \cdot \frac{hc}{kT}\right].$$
(17)

For the  $\beta$  form, we have plotted the logarithm of the intensity ratio for two bands,  $-v_b$  the higher frequency and  $\overline{\nu_a}$  the lower frequency of the infrared and Raman spectra (Fig. 6) against the inverse of the temperature (Fig. 7); a straight line was obtained, whose slope leads, using Eq. (17), to a  $\lambda$  value of about 1(0.88). This result is a little surprising, because it suggests a compensation of the influence of the modes other than the  $\nu_{CH}$  mode in the zero energy [Eq. (12)]. We are not in a position to give a clear explanation of this result. We can only note that it is not fortuitous since an analogous result has been found in a study presently in progress on the nitromethane NO<sub>2</sub>CHD<sub>2</sub>.<sup>32</sup> Nevertheless, this result suggests the complete disappearance of the highest frequency  $\nu_{CH}$  band at very low temperature (4 K) as a result of the decrease of the population of the torsional level that corresponds to the state in which the CH vibrator is localized in the less deep well. In other words, the isotopic system can get ordered by a temperature effect. New experiments at very low temperature are worth being performed to verify this conclusion.

For the  $\alpha$  phase, an increase of the relative intensity of the highest frequency band is found again when the temperature is increased (Fig. 8) which can be explained as for the  $\beta$  form case. A quantitative analysis is however difficult because the shape of the infrared and Raman spectra changes between 40 and 80 K (Fig. 8). The appearance of hot bands could explain this change;



FIG. 7. The plot of the logarithm of the ratio of the band intensities vs the inverse of the temperature in the case of the toluene  $C_6D_5CHD_2$ :  $\beta$  phase (+) ( $\overline{\nu}_b = 2953.5 \text{ cm}^{-1}$  and  $\overline{\nu}_a = 2911.5 \text{ cm}^{-1}$ ),  $\alpha$  phase (0) ( $\overline{\nu}_b = 2948.0 \text{ cm}^{-1}$  and  $\overline{\nu}_a = 2925.0 \text{ cm}^{-1}$ ).



FIG. 8. The CH stretching infrared and Raman spectra of the pure toluene  $C_6D_5CHD_2$  crystallized in the  $\alpha$  phase at different temperatures. By comparison, the infrared band  $\nu_{18a}$  evolution is shown in the same temperature range.

but, since it occurs neither in the  $\beta$  form spectra (Fig. 6), nor in the nitromethane NO<sub>2</sub>CHD<sub>2</sub> spectra, <sup>32</sup> it seems specific to the  $\alpha$  crystalline phase. This phenomenon must undoubtedly be related to the modification of the Raman spectrum of the lattice modes in the same temperature range, which has suggested a crystalline structure transformation.<sup>22</sup> This transformation seems therefore to affect the methyl group.

## B. High temperature spectra (from 100 to 160 K). Relaxation study

When the temperature is raised, the CH aliphatic stretching bands broaden clearly in both crystalline phases spectra, while the bands of the C<sub>6</sub>D<sub>5</sub> group vibrational modes are very slightly affected, (Figs. 6 and 8). Thus, some relaxation processes peculiar to the CHD<sub>2</sub> group must be considered to explain this broadening. The CH stretching mode is probably a very much localized mode in the crystal; so it seems possible to discuss the relaxation processes of this mode using terms similar to those of liquids. Recently, Laubereau has enumerated the principal mechanisms that cause the vibrational relaxation in liquids<sup>34</sup>: (a) The "direct" dephasing by interaction with the nearest molecules; (b) The "indirect" dephasing by an anharmonic coupling to the low frequency vibrational modes; (c) The resonant exchange of vibrational quanta between identical oscillators; (d) The vibrational energy transfer in the thermic bath.

The three first processes can be said to be "pure dephasing" processes. On the contrary, the last one is relative to the temporal evolution of the excited state population. Now, in the condensed phases, it is usually known as a process very much slower than the phase relaxation ones.<sup>35</sup> So it probably does not contribute significantly to the band broadening in the present case. The third process can also be neglected because the isotopic dilution in the fully deuterated toluene has no marked effect on the spectra at any temperature. On the contrary, it seems reasonable to suppose that the fastest relaxation processes are, in some way, in connection with the anharmonic coupling that appears between the CH stretching mode and the CHD<sub>2</sub> group torsional motion. However, this coupling effect cannot be reduced to the simple appearance of hot bands, with a torsional potential assumed independent of the temperature. Indeed, as has been already underlined, this potential is essentially due to the molecular interactions in the crystal. So it must fluctuate under the effect of the thermal activation of the phonon reservoir. Unfortunately, a quantum theory that is general enough and that takes into consideration such fluctuations does not exist. Therefore, we will restrict ourselves to semiclassical approaches and especially to band profiles at relatively high temperature (T > 100 K).

One of the very well known results of the potential barrier fluctuations is the appearance of jumps of the system from an equilibrium position to another one. This phenomenon has been studied by NMR<sup>14,15,29</sup> and by elastic neutron scattering<sup>15,33</sup> in the case of the  $\alpha$ crystallized toluene CH<sub>3</sub> methyl group. These data were fitted by a model of  $2\pi/3$  jumps around the C-C bond with residence times that vary from 2.12 ps at 100 K to 1.30 ps at 155 K.<sup>33</sup> Thus we have tried to determine the influence of this process on the spectral profiles. For this purpose, the NMR theories of the oscillator exchange,<sup>7,36</sup> already adapted to the vibrational spectroscopy in particular by Gordon,<sup>37</sup> are used.

Another possible mechanism will also be examined; under the potential  $V(\theta)$  fluctuations influence, even in the absence of jump, the torsional motion is strongly relaxed, when the temperature is raised, as show the inelastic neutron scattering spectra of the toluene  $C_{\theta}D_{5}CH_{3}$  and of similar molecules.<sup>14,15,30,33</sup> Consequently, each component of the  $\nu_{CH}$  band must broaden. This mechanism is similar to the one that seems generally accepted for the stretching bands of the X-H oscillators involved in hydrogen bonding in the liquid state.<sup>36</sup> A semiclassical theory of this process has been proposed by Robertson,<sup>39</sup> theory that can be easily suited to our problem.

## 1. Model of the vibrational phase relaxation by markovian jumps

A spectral profile can be written:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(-i\omega t) \langle A(0) \cdot A(t) \rangle dt , \qquad (18)$$

where  $\langle A(0) \cdot A(t) \rangle$  is the autocorrelation function of the Heisenberg operator that corresponds to the studied type of spectroscopy.

If we define  $H_0$  as the Hamiltonian of the torsionvibration nonperturbed system and  $|v, n\rangle$  the torsion levels *n* in the vibration state *v*, the effect of a fluctuating potential can be represented by adding to the Hamiltonian  $H_0$  a time dependent Hamiltonian H'(t) such as:

$$H(t) = H_0 + H'(t) . (19)$$

The evolution operator, U(t, 0), associated with the Hamiltonian H(t) can be written as a function of the operator  $U_0(t, 0)$ :

$$U(t, 0) = U_0(t, 0) \cdot U'(t, 0) , \qquad (20)$$

such as:

$$\frac{\partial U'(t, 0)}{\partial t} = \frac{-i}{\hbar} U_0^{-1}(t, 0) \cdot H'(t) \cdot U_0(t, 0) \cdot U'(t, 0) .$$

The operator A(t) is given by:

$$A(t) = U^{*}(t, 0) \cdot A(0) \cdot U(t, 0) . \qquad (21)$$

Thus, from Eqs. (18) and (21), the autocorrelation function of the operator A is:

$$G(t) = \langle A(0) \cdot A(t) \rangle$$
  
=  $\sum_{i, j, k, i} \rho_i \cdot A_{ij}(0) \cdot U_{jk}^*(t, 0) \cdot A_{kl}(0) \cdot U_{li}(t, 0) ; (22)$ 

*i*, *j*, *k*, and *l* correspond to the different states  $|v, n\rangle$  and  $\rho_i$  is the initial level population.

In the following calculations, several hypotheses are put forward.

(a) In this theory, only the first three torsional levels are considered in the ground and in the first excited vibrational state (Fig. 5). As has already been shown, each of these levels corresponds to a CH vibrator location in each potential well. (b) In the absence of the perturbation H'(t), only the transitions between the states  $|v, n\rangle \rightarrow |v', n'\rangle$  such as  $v \neq v'$ , n=n' are allowed by the operator A. (cf. §A).

(c) The vibrational energy relaxation that corresponds to the nonradiative transitions  $|1, n\rangle + |0, n'\rangle$ , is neglected.

(d) The relaxation process is markovian and obeys Smoluchoski's equation<sup>7</sup>

$$\frac{d\hat{P}(t)}{dt} = -\hat{P} \cdot \hat{\pi} , \quad \hat{P}(t) = 1 \exp(-\hat{\pi} \cdot |t|) , \qquad (23)$$

where the elements  $P_{n'n}(t)$  of the matrix  $\hat{P}(t)$  are the probabilities to found the system in the state n' after a time t when it was in the state n at the time t=0 and where the elements  $\pi_{n'n}$  of the matrix  $\hat{\pi}$  are the transition probabilities by unit time from the state n to the state n'.

If *i* is the state  $|0, n\rangle$ , the hypotheses (b) and (c) lead to  $l = |0, n'\rangle$ ,  $k = |1, n'\rangle$  and  $j = |1, n\rangle$  with  $n \neq n'$ . The properties of the evolution operator [Eq. (20)] allow us to write Eq. (22) as

$$G(t) = \sum_{nn'} \rho_{0n,0n'} \cdot A_{0n,1n}(0) \cdot A_{1n',0n'}(0) \cdot a_{1n,1n'}(t) \cdot a_{0n',0n}(t) \cdot \exp(i\omega_{1n,0n}t) , \qquad (24)$$

where  $a_{0n',0n}(t) = \langle 0, n' | U'(t, 0) | 0, n \rangle$ .

Knowing that  $a_{1n,1n}$ , $(t) \cdot a_{0n',0n}(t) = P_{n'n}(t)$  and having defined a diagonal matrix  $\hat{\rho}$  with the elements  $\rho_{0n,0n}$ , a diagonal matrix  $\hat{\Omega}$  whose elements  $\omega_{1n,0n}$  are the frequencies of the three considered transitions and a matrix  $\hat{D}$  with the elements  $[A_{0n,1n}(0) \cdot A_{1n',0n'}(0)]$ . Equation (24) can be written:

$$G(t) = \sum_{nn'} (\hat{\rho})_{nn} \cdot (\hat{D})_{nn'} \cdot [\exp(i\hat{\Omega}t - \hat{\pi}|t|)]_{n'n}$$
(25)

and by a Fourier transform<sup>37</sup>

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \operatorname{Tr} \hat{\rho} \cdot \hat{D} \cdot \frac{1}{i(\omega - \hat{\Omega}) + \hat{\pi}} \quad .$$
 (26)

If  $v_{\mu}(\omega)$  are the elements of the matrix  $1/[i(\omega - \hat{\Omega}) + \hat{\pi}]$  and if the dipole moment of the vibrational transition, with a modulus  $\mu$ , is supposed collinear with the C-H bond, whose direction is defined by the unit vector **u**, the infrared profile can be given by:

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \sum_{ij} \rho_i \cdot |\mu_i^*(0)| \cdot |\mu_j(0)| \cdot (\mathbf{u}_i \cdot \mathbf{u}_j) \cdot v_{ji}(\omega) .$$
(27)

Equation (26) could also be made explicit for the Raman scattering case but its application is difficult to powder spectra for which the isotropic and anisotropic contributions are not separated.

An analogous process is used by Zatsepin<sup>45</sup> to treat the effect of the rotational isomerism on the contours of the bands of the vibrational spectrum of molecules in liquids. But this author does not take into account the different orientations of the oscillator and the different values of the transition dipole moment which are expressed by  $|\mu_i^*(0)| \cdot |\mu_j(0)| \cdot (\mathbf{u}_i \cdot \mathbf{u}_j)$  in Eq. (27).

There is also a formal analogy between this theory and that proposed by Harris *et al.*,  $^{40-42}$  about the origin of the vibrational phase relaxation in solids. However, the physical meaning of the two theories is different. These authors suppose a coupling between a CH stretching mode and a low frequency mode which gives rise to two or several hot bands which are modulated by the population fluctuations of the low frequency states, as we do; nevertheless, for Harris *et al.*, the jumps between the different low frequency states do not correspond to some jumps between different conformations.

## 2. Model of the vibrational phase relaxation by the methyl group fluctuations around an equilibrium configuration

While the methyl group torsional mode is very clearly distinguished in the inelastic neutron scattering spectrum at very low temperature, it is completely embedded into the phonon spectral density at 100 K. We are thus justified in considering it as an overdamped mode and to classify it as a vibrational mode that follows a Langevin type equation. Therefore, the influence of this motion on a harmonical quantum oscillator, with which it is weakly coupled, is analyzed. For this purpose, the procedure proposed by Robertson in his theory of the hydrogen bonding profiles<sup>39</sup> is followed. We consider that our spectra are constituted of three bands associated with three CH oscillators in three different environments. The profile of each oscillator vibration is separately studied.

In the following theoretical analysis, the reaction of the  $\nu_{CH}$  motion back on the torsion mode is ignored, the anharmonicity of the two modes  $\nu_{CH}$  and  $\tau_{CHD_2}$  is neglected and we will work under the adiabatic approximation. Finally, the torsional oscillation, considered as an Ornstein-Uhlenbeck process, is classically treated.<sup>39,43</sup> This approximation is nevertheless opened to criticism, because this motion is studied from 100 to 160 K, and its frequency is approximately 43 cm<sup>-1</sup>.

So the torsional motion equation is written:

$$\Delta \ddot{\theta} + \gamma \Delta \dot{\theta} + \omega_T^2 \Delta \theta = I^{-1} \cdot F(t) , \qquad (28)$$

where  $\Delta\theta$  is the torsional angle displacement,  $\gamma$  the damping parameter, *I* the moment of inertia of the CHD<sub>2</sub> group,  $\omega_T$  the torsional frequency and F(t) the gaussian random force with a zero mean and an infinitesimal correlation time. The Hamiltonian, which governs the  $\nu_{\rm CH}$  motion is now a stochastic operator

$$H_{\boldsymbol{V}}(t) = \frac{P^2}{2M} + \frac{1}{2} M \cdot \omega_{\boldsymbol{V}}^2 \cdot q^2 + K_{\boldsymbol{V}\boldsymbol{V}\boldsymbol{T}} \cdot \Delta\theta(t) \cdot q^2 . \tag{29}$$

*M* is the CH oscillator reduced mass, *q* the C-H bond normal coordinate, and  $\omega_v$  the CH stretching frequency. The coupling parameter  $K_{vvr}$  is connected to  $\Delta \omega(\theta)$ [Eq. (8)]:

$$K_{VVT} = \left(\frac{d\Delta\omega(\theta)}{d\theta}\right)_{\theta_0} = i \sum_n n \left[C_n \exp(in\theta_0) - C_n^* \exp(-in\theta_0)\right] .$$

In Eq. (29), the potential function can be regarded as the result of a linear expansion of the function  $\Delta\omega(\theta)$  for small amplitude oscillations  $\Delta \theta(t)$  around the position  $\theta_0$ . Equation (29) can also be written:

$$H_{v}(t) = \frac{P^{2}}{2M} + \frac{1}{2} M \cdot \omega^{2}(t) \cdot q^{2} , \qquad (30)$$

with

$$\omega(t) = \omega_v \left[ 1 + \left( 2K_{VVT} / M \cdot \omega_v^2 \right) \Delta \theta(t) \right]^{1/2} . \tag{31}$$

Suppose that the Heisenberg operator A corresponds to the studied spectroscopic method; its correlation function can now be written, after a linear expansion of the relation (31):

$$\langle A(0)A(t)\rangle = |A_0(0)|^2 \cdot \exp(-i\omega_v t) \cdot \phi(t) , \qquad (32)$$

with

$$\phi(t) = \left\langle \exp\left[-ia \int_0^t \Delta\theta(t') dt'\right] \right\rangle$$

and

$$a = K_{VVT} / (M \cdot \omega_v).$$

Since  $\Delta \theta(t)$  is supposed to have a gaussian nature [Eq. (28)], the classical theory for the brownian motion in the overdamped case  $(\gamma > 2\omega_T)$  gives, for t > 0, a correlation function such as<sup>39</sup>:

$$\phi(t) = \exp\left[-a^2 \cdot \langle \Delta \theta^2 \rangle \cdot \omega_T^2 \{\gamma t + \omega_T^{-2} \\ \times \left[(\gamma^2 - \omega_T^2) \left[\exp(-\frac{1}{2}\gamma t) \cdot \cosh(\hat{\omega}t) - 1\right] \\ + (\gamma/2\,\bar{\omega})(\gamma^2 - 3\,\omega_T^2) \exp(-\frac{1}{2}\gamma t) \cdot \sinh(\tilde{\omega}t)\right] \}, \quad (33)$$

with  $\tilde{\omega}^2 = \gamma^2/4 - \omega_T^2$  and  $\langle \Delta \theta^2 \rangle = k T / \omega_T^2 \cdot I$ .

So, after a Fourier transformation, the profile of each band is given by:

$$I(\omega) = \frac{|A_0(0)|^2}{2\pi} \int_{-\infty}^{+\infty} \exp[-i(\omega - \omega_0)t] \cdot \phi(t) dt .$$
 (34)

The  $\nu_{CH}$  oscillator autocorrelation function [Eq. (33)] is monotonically decreasing, so that the Kubo's general theory can be applied directly.<sup>7</sup> We define:

(i) the amplitude modulation  $\Delta = a \cdot \langle \Delta \theta^2 \rangle^{1/2}$ 

(ii) the modulation correlation time  $\tau_c = \gamma/\omega_T^2$ .

Thus there is a *slow modulation if*  $\Delta \cdot \tau_c \gg 1$ : and the correlation function  $\phi(t)$  leads to a limiting expression:

$$\phi(t) \approx \exp\left(-\frac{1}{2}\Delta^2 \cdot t^2\right)$$
.

The bandshape is gaussian and the theory leads to an inhomogeneous broadening. On the contrary, there is a fast modulation if  $\Delta \cdot \tau_c \ll 1$  and  $\phi(t)$  has the asymptotic form:

$$\phi(t) \approx C \exp(-\Delta^2 \cdot \tau_c \cdot t) \ .$$

The bandshape is lorentzian.

#### 3. Comparison with the experimental results

Figure 9 presents the comparison between the  $\alpha$  and  $\beta$  phases experimental infrared profiles observed at relatively high temperatures and the profiles calculated in the hypothesis of the CHD<sub>2</sub> group jumps between three conformations. In the case of the  $\alpha$  phase, the residence



FIG. 9. The CHD<sub>2</sub> group CH stretching spectra calculated by means of the  $2\pi/3$  jumps model (----). By comparison, the infrared experimental spectra are shown in each case ( $\infty$ ).

(a) the $\alpha$ phase at 100 K	$\tau = 2.12 \text{ ps.}$
(b) the $\alpha$ phase at 145 K	$\tau = 1.30$ ps.
(c) the $\beta$ phase at 110 K	$\tau = 0.76 \text{ ps}.$

time values determined by NMR and by elastic neutron scattering for the toluene  $C_8D_5CH_3$  methyl group are used.<sup>14,15,29,33</sup> These values can perhaps be affected by the deuteration. Nevertheless, in this first analysis, the order of magnitude is supposed the same. In the  $\beta$  phase case, no dynamical measure has been performed either by NMR, or by elastic neutron scattering and we



The above presented second mechanism could bring a significant contribution to the spectral shapes. Indeed, Fig. 10 allows the comparison of the experimental profiles ( $\beta$  phase at 110 K) with a profile calculated by means of this model. The agreement does not seem significant in itself, in consideration of the number of introduced parameters. The only important fact is that all these parameters have an order of magnitude suitable from the physical point of view. They correspond to some ( $\Delta \cdot \tau_c$ ) values nearly equal to one. This suggests a middle modulation between the fast and the slow ones.

This analysis outlines that, in the solid crystalline state at the temperatures higher than 100 K, the toluene methyl group motion cannot be described only by a model of instantaneous jumps from an equilibrium position to another one. A fluctuation motion around each of these equilibrium positions seems to constitute a nonnegligible complementary relaxation process. These small amplitude fluctuations can moreover cause a broadening intermediate between the inhomogeneous and homogeneous ones.

#### **IV. CONCLUSIONS**

The presence of several  $\nu_{CH}$  aliphatic stretching bands in the spectra of the  $\alpha$  and  $\beta$  crystalline toluenes  $C_{\theta}H_5CHD_2$  and  $C_{\theta}D_5CHD_2$  at low temperature can be essentially interpreted by the existence of several sites which correspond to the different conformations of the CH vibrator in the molecule. Even at very low temperature (17 K) and despite of the low height of the potential barrier to the internal rotation of the methyl



FIG. 10. The CHD<sub>2</sub> group CH stretching spectrum calculated by means of the frequency fluctuation model in the  $\beta$  phase case at 110 K (----) ( $\gamma/2\pi c = 250 \text{ cm}^{-1}$ ;  $v_1$ = 2914 cm<sup>-1</sup>;  $v_2 = 2927 \text{ cm}^{-1}$ ;  $v_3$ = 2948 cm<sup>-1</sup>.  $a_1/2\pi c = 14.5 \text{ cm}^{-1}$ ;  $a_2/2\pi c = 22.0 \text{ cm}^{-1}$ ;  $a_3/2\pi c = 33.0 \text{ cm}^{-1}$ ). By comparison, the experimental spectrum is also shown ( $\infty$ ).

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group, no tunneling effect appears in these spectra. A quantum theory of these spectra is nevertheless interesting, because it gives an explanation to the temperature effect observed on the relative intensity of the bands. Furthermore it suggests that, at very low temperature (4 K), the isotopic system becomes ordered.

When the temperature is raised, a very important relaxation phenomenon appears. Probably its origin is essentially due to the coupling between the CH stretching mode and the  $\tau_{\rm CHD_2}$  mode. However, although it contributes significantly to the spectrum shape, the jumps mechanism is clearly insufficient to reproduce entirely the experimental profiles. So, the time residence values would be underestimated when determined from the width of the infrared and Raman spectra. The presence of other complementary relaxation processes must thus be considered; the most probable one is the CH oscillator fluctuation around each equilibrium position. A more complete analysis of this relaxation would consist of introducing the two processes together into the same theory. Besides, these two processes are only two aspects of the same phenomenon whether the large or the small amplitude motions of the methyl group are considered. With such an extended theoretical basis, the spectroscopic method that we present here could lead, with other physico-chemical methods (NMR, neutron scattering,...) to a more elaborate analysis of the methyl group motion in solids.

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