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Neutron and Raman scattering studies of the methyl dynamics in solid toluene and nitromethane

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Résumé. — Le toluène solide a été étudié dans sa phase α à 5 K par diffusion inélastique des neutrons à haute résolution. L'éclatement de l'état fondamental de torsion du méthyle a été trouvé de $0,196 \text{ cm}^{-1}$ ($24,3 \text{ } \mu\text{eV}$) pour $\text{C}_6\text{D}_5\text{CH}_3$ et $0,0088 \text{ cm}^{-1}$ ($1,1 \text{ } \mu\text{eV}$) pour $\text{C}_6\text{D}_5\text{CD}_3$.

On peut rendre compte de cet éclatement par de simples potentiels cosinusoidaux (V_3, V_6) ou carrés, mais les valeurs calculées des premières transitions de torsion ($\sim 56 \text{ cm}^{-1}$) sont alors légèrement plus élevées que celles déduites de l'analyse des spectres Raman et neutroniques de plusieurs dérivés isotopiques étudiés dans une large gamme de température.

Pour expliquer ces observations, on peut supposer que les premiers niveaux excités de torsion se couplent avec des phonons.

Une étude similaire du nitrométhane solide permet de situer la torsion du groupe CH_3 à environ 53 cm^{-1} et conduit à des conclusions analogues.

Abstract. — Solid toluene has been studied in its α phase at 5 K by high resolution Inelastic Neutron Scattering (I.N.S.). The tunnel splitting of the methyl torsion group state has been found to be 0.196 cm^{-1} ($24.3 \text{ } \mu\text{eV}$) for $\text{C}_6\text{D}_5\text{CH}_3$ and 0.0088 cm^{-1} ($1.1 \text{ } \mu\text{eV}$) for $\text{C}_6\text{D}_5\text{CD}_3$.

Simple cosine (V_3, V_6) or square well potentials are able to reproduce this splitting but the calculated first torsional transitions ($\sim 56 \text{ cm}^{-1}$) are then slightly higher than the value of 46.8 cm^{-1} deduced from the analysis of the Raman and I.N.S. spectra obtained for several isotopic derivatives in a large temperature range. The possibility of coupling of the first torsional excited states with some phonons is invoked to explain these observations.

A similar Raman and I.N.S. study of solid nitromethane allows the $-\text{CH}_3$ torsion to be situated at about 53 cm^{-1} and leads to similar conclusions.

1. Introduction.

The hindered rotation of a methyl group about a single covalent bond has been the object of a great number of studies because it provides a relatively simple example of internal motion occurring in many molecular systems and in a wide temperature range [1, 2].

In the gas phase, direct information can be obtained, for example by microwave spectrometry, on the intra-

molecular potential energy function, the external contributions being in general negligible [2, 3].

In the condensed state, the intermolecular forces can play an important rôle in determining the shape and the height of the potential. In this case, and especially when the hindering barrier is low, complementary information obtained by several physical methods is necessary to get a comprehensive picture of the dynamics of the methyl group. The comparison of the results given by different techniques has often proved

to be a difficult task. However, successful studies combining Nuclear Magnetic Resonance (N.M.R.) and Neutron Scattering techniques have recently appeared [4-9]. N.M.R. techniques provide more and more sophisticated and precise methods to analyse the methyl dynamics in the solid state [10-14]. In particular, tunnel splittings can be predicted and activation energies measured, the remaining problems being to assign these energies to a particular relaxation mechanism, as discussed by several theoretical models [7, 10-12]. Inelastic Neutron Scattering (I.N.S.) and Raman (R) and infrared (I.R.) spectroscopies are in principle well adapted to a direct observation of the torsional energy level separations. The first method (I.N.S.) has the advantage to mainly reflect the large amplitude vibrational and librational motions involving the hydrogen atoms, however this advantage is partly destroyed by rather poor resolution, except at very small energy transfers where the tunnel splitting of the torsional ground state has been observed in many instances [5, 15-17]. On the other hand, the infrared and Raman methyl torsional bands, even if they can be well resolved, have only weak intensity relatively to the strong phonon density of states. For low hindering barriers, the torsional excitations fall in the phonon frequency range and undergo strong relaxation effects when the temperature increases.

Toluene and nitromethane are examples of such molecules with low hindering barriers studied by various techniques, including the above discussed ones, but they still present problems of interpretation of the methyl dynamics in the low temperature solid phase [8, 16-20]. The low frequency Raman spectra of the fully hydrogenated and fully deuterated molecules have been recently investigated [18]. For toluene, several weak peaks at 77, 94, 106 and 115 cm^{-1} have been assigned to transitions between torsional levels of the CH_3 group at variance with I.N.S. and N.M.R. results which situate the first torsional excitation at 47 cm^{-1} [8-9]. For nitromethane, the assignment of the Raman line at 148 cm^{-1} to the methyl torsion agrees neither with the I.N.S. results which situate this transition at about 60 cm^{-1} [16], nor with the recent tunnel splitting measurements, from which the first torsional transition is calculated at about 73 cm^{-1} [17].

But it must be pointed out that the Raman experiments were performed at only one relatively high temperature (> 110 K), restricting severely the range of observable phenomena in the solid state and preventing any valid comparison with the low temperature results of the other techniques.

Thus it appears important to re-investigate the low frequency Raman spectra over a wide temperature range. Furthermore, the recent establishment of the crystal structures [21-24] allows a better assignment of the molecular vibrations.

We present here a Raman study performed between 10 and 250 cm^{-1} on several isotopic derivatives of

toluene and nitromethane in the temperature range 17-170 K and an I.N.S. study of toluene between 4×10^{-3} and 250 cm^{-1} in a similar temperature range (5-150 K).

2. Experimental.

The isotopic derivatives NO_2CHD_2 , $\text{C}_6\text{H}_5\text{CHD}_2$, $\text{C}_6\text{D}_5\text{CHD}_2$ and $\text{C}_6\text{D}_5\text{CH}_3$ were synthesized as described in our previous papers [19, 20]. The isotopic purity of these compounds, checked by mass spectrometry, was higher than 98 %. The commercial compounds NO_2CD_3 , $\text{C}_6\text{D}_5\text{CD}_3$, $\text{C}_6\text{H}_5\text{CD}_3$ (C.E.A.) and NO_2CH_3 , $\text{C}_6\text{H}_5\text{CH}_3$ (MERCK) (purity higher than 99 %) were used without further purification.

The sample cooling was carefully controlled in order to get a very well determined crystalline phase, especially in the toluene case, where two crystalline phases α and β can be generated according to the applied temperature cycle [21-23]. The experimental procedure has been described previously [19].

The Raman spectra were recorded with a Coderg T800 spectrometer equipped with a Spectra-Physics argon ion laser. The 488 nm line was used at a power of 200 mW and the spectral slit width was kept at about 1 cm^{-1} for all spectra. Gaseous toluene or nitromethane was condensed on a copper plate adapted to a Cryodine 20 system. The lowest temperature reached by the samples and checked by the Stokes/antistokes intensities ratio was 17 K.

The I.N.S. experiments were carried out at the Laue-Langevin Institute in Grenoble with the IN4, IN13 and IN10 spectrometers.

The IN4 time of flight machine was used with a graphite monochromator at incident energies of 12 meV and 32 meV corresponding respectively to spectral regions 2-10 meV and 2-32 meV which are explored with resolutions ranging respectively from 0.4 meV to 0.6 meV and from 0.7 meV to 1.4 meV. The $\text{C}_6\text{D}_5\text{CH}_3$ and $\text{C}_6\text{H}_5\text{CD}_3$ samples were contained in a 10×2 cm^2 rectangular can; the internal thickness of the cells were such that only 13 % and 9 % of the incident neutrons were scattered by the sample. The sample temperatures were 5 K, 50 K and 150 K.

For the IN13 experiment, the incident energy was 16.2 meV with a resolution of 7 μeV . The $\text{C}_6\text{D}_5\text{CH}_3$ sample was contained in a circular slab aluminium can of 5 cm diameter. For the IN10 experiment, the incident energy was 2.07 meV with a resolution of 0.4 μeV and the $\text{C}_6\text{D}_5\text{CD}_3$ container was an aluminium cylinder of 2.5 cm diameter and 3 cm height. In the last two measurements, the sample temperature was respectively 1.2 K and 5 K.

3. Results and discussion.

3.1 TUNNELLING TRANSITIONS. — The results obtained on $\text{C}_6\text{D}_5\text{CH}_3$ and $\text{C}_6\text{D}_5\text{CD}_3$ respectively with the IN13 and IN10 backscattering spectrometers are reported in figure 1. In both cases, the tunnel splitting

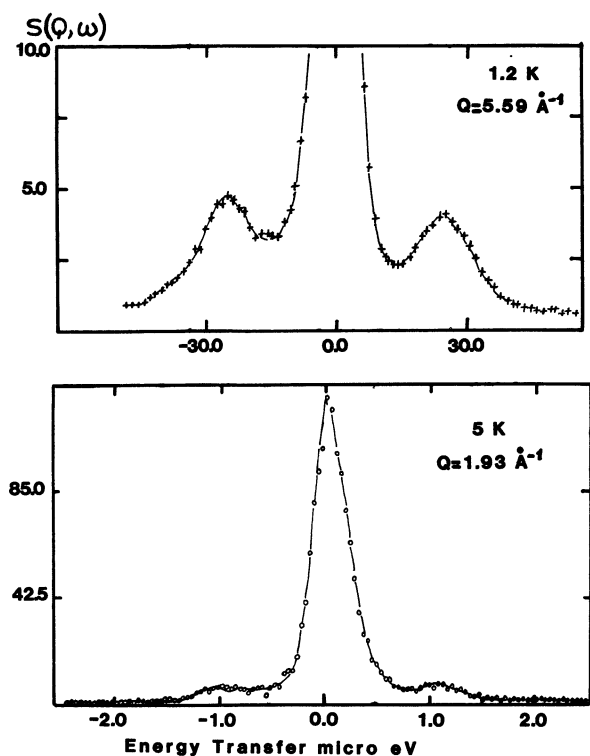


Fig. 1. — I.N.S. spectrum of $C_6D_5CH_3$ obtained with the IN13 spectrometer (upper) and of $C_6D_5CD_3$ obtained with the IN10 spectrometer (lower).

of the torsional ground state is clearly observed. It is of 0.196 cm^{-1} ($24.3 \text{ } \mu\text{eV}$) for $-\text{CH}_3$ and 0.0088 cm^{-1} ($1.1 \text{ } \mu\text{eV}$) for $-\text{CD}_3$.

The inelastic lines are somewhat broader than the resolution of the spectrometer.

These I.N.S. results constitute the first experimental evidence of the tunnel splitting for toluene and confirm nicely the predictions of Clough *et al.* [25] based on N.M.R. data. Indeed, the relationship established by these authors for a large number of methylated

molecules between the tunnel splittings and the spin-lattice relaxation times T_1 predicts a tunnel splitting of $25 \text{ } \mu\text{eV}$ for $C_6D_5CH_3$ from the T_1 value measured by Müller-Warmuth *et al.* [8].

However, with a simple $\cos(3\theta)$ potential rather different V_3 values are calculated for the $-\text{CH}_3$ and $-\text{CD}_3$ groups ($\Delta V_3 = 19 \text{ cm}^{-1}$) and torsional frequencies of about respectively 81 cm^{-1} and 57 cm^{-1} (Table I).

With the more general potential form :

$$V = \frac{V_3}{2}(1 - \cos 3\theta) + \frac{V_6}{2}(1 - \cos 6\theta) \quad (1)$$

a single couple of V_3, V_6 values can be found for the two isotopic derivatives to reproduce the observed tunnel splittings.

Torsional frequencies of 56 and 31 cm^{-1} are then calculated respectively for $-\text{CH}_3$ and $-\text{CD}_3$. A square well potential leads approximatively to similar results (Table I).

Thus, neither of these potential models can reproduce exactly the torsional frequency of 47 cm^{-1} deduced from previous N.M.R. and I.N.S. experiments on $C_6D_5CH_3$ [8].

It must be pointed out that a very similar situation is encountered for nitromethane. The tunnel splittings of NO_2CH_3 and NO_2CD_3 have recently been measured respectively to be 0.283 cm^{-1} ($35 \text{ } \mu\text{eV}$) and 0.0135 cm^{-1} ($1.7 \text{ } \mu\text{eV}$) at 5 K by Alefeld *et al.* [17]. From these values, torsional frequencies for the $-\text{CH}_3$ and CD_3 groups are calculated respectively to be 75 and 54 cm^{-1} with a pure V_3 potential, 60 and 37 cm^{-1} , with a mixed V_3, V_6 potential and 56 and 32 cm^{-1} for a square well potential (Table I). I.N.S. peaks assigned to torsional transitions have been found at 53.5 and 67.5 cm^{-1} for NO_2CH_3 and at 42.8 cm^{-1} for NO_2CD_3 [16].

Thus, although toluene and nitromethane are amongst the most simple methylated systems, it has

Table I. — Ground and first excited state torsional transitions (cm^{-1}) for toluene and nitromethane calculated according to cosine or square well potentials.

	Cosine potential		Square well pot.		$A_0 \rightarrow E_0$		$A_0 \rightarrow E_1$		$A_0 \rightarrow A_1$	
	V_3	V_6	V	θ'_0	$-\text{CH}_3$	$-\text{CD}_3$	$-\text{CH}_3$	$-\text{CD}_3$	$-\text{CH}_3$	$-\text{CD}_3$
Toluene	192.5	0.0			0.1961	0.0054	80.7	60.65	84.7	60.8
$C_6D_5-\text{CH}_3$	173.3	0.0			0.2701	0.0089	75.2	57.1	80.4	57.4
and	258.0	-119.2			0.1961 (*)	0.0089 (*)	56.5	31.3	57.8	31.3
$C_6D_5-\text{CD}_3$			283.0	$19^\circ 5$	0.1961 (*)	0.0089 (*)	54.2	29.7	55.3	29.8
Nitromethane	170.7	0.0			0.2823	0.0095	74.4	56.6	79.8	56.9
CH_3-NO_2	157.3	0.0			0.3558	0.0137	70.4	54.0	76.7	54.4
and	211.0	-77.1			0.2823 (*)	0.0137 (*)	59.6	36.8	62.0	36.9
CD_3-NO_2			212.4	$22^\circ 1$	0.2821 (*)	0.0137 (*)	56.2	31.9	58.1	32.0

(*) Couple of calculated values in agreement with the experimental observation.

not been yet possible to find a potential model which reproduces both the observed ground state splittings and the experimentally deduced torsional transitions.

3.2 TORSIONAL TRANSITIONS. — Owing to the discrepancy between experimental and calculated torsional frequencies, the methyl torsion spectral range has been reinvestigated by I.N.S. as well as by Raman spectroscopy for the two compounds.

3.2.1 Toluene.

3.2.1.1 I.N.S. study. — Two isotopic derivatives have been selected: $C_6D_5CH_3$ already studied by Schüler *et al.* [8, 9] and $C_6H_5CD_3$. In the first compound, the spectrum is expected to be essentially due to the scattering of the three protons of the methyl group and dominated by the torsional mode of this group. In $C_6H_5CD_3$, the scattering of the five protons of the benzene ring is supposed to give the frequency distribution of the lattice modes.

At 5 K, the spectrum of $C_6D_5CH_3$ is characterized by a very intense peak at 46.8 cm^{-1} (5.8 meV) with two shoulders at 32 cm^{-1} (4 meV) and 66 cm^{-1} (8.2 meV) (Fig. 2). The 46.8 cm^{-1} peak was already observed by Schüler *et al.* [8, 9] and assigned to the methyl torsion. This assignment is supported by the momentum transfer dependence presented in figure 2. Indeed, as pointed out in a recent work on the inelastic structure factor of the methyl torsion [26], the mean square amplitude of libration $\langle u^2 \rangle_{\text{lib}}$ is much higher ($\approx 0.06\text{ \AA}^2$ for nitromethane) than the mean square amplitude of vibration of the centre of mass $\langle u^2 \rangle_{\text{vib}}$ ($\approx 0.009\text{ \AA}^2$ for nitromethane). It follows that at small Q values where the intensity is governed by a harmonic $\langle u^2 \rangle Q^2$ law, the methyl torsion is expected to show up clearly in the total density of states. It is what occurs in figure 2a. By comparison, the $C_6H_5CD_3$ spectrum at the same temperature does not show any structure at low Q (Fig. 2b) but presents, at high Q , an intense peak at 32 cm^{-1} (4 meV) with a broad shoulder at 45.2 cm^{-1} (5.6 meV) and a weaker one at 67 cm^{-1} (8.3 meV). This suggests that most of the $C_6H_5CD_3$ spectrum intensity is given by the phonon density of states.

At 50 K, a broadening of the main peak in $C_6D_5CH_3$ spectrum is observed as if the methyl torsion was already noticeably damped. The shoulder at 4 meV becomes more pronounced and one can notice that at the same time the phonon density of states for $C_6H_5CD_3$ becomes more strongly peaked at 4 meV.

The spectra obtained with a higher incident energy (32 meV) are less well resolved. However, the first internal mode of the benzene ring is clearly observable at 219 cm^{-1} (27.2 meV) for $C_6D_5CH_3$ [9] and at 214.5 cm^{-1} (26.6 meV) for $C_6H_5CD_3$ in very good agreement with the Raman results respectively 219 cm^{-1} and 216 cm^{-1} [27]. The more intense peaks remain those already observed at lower incident energy.

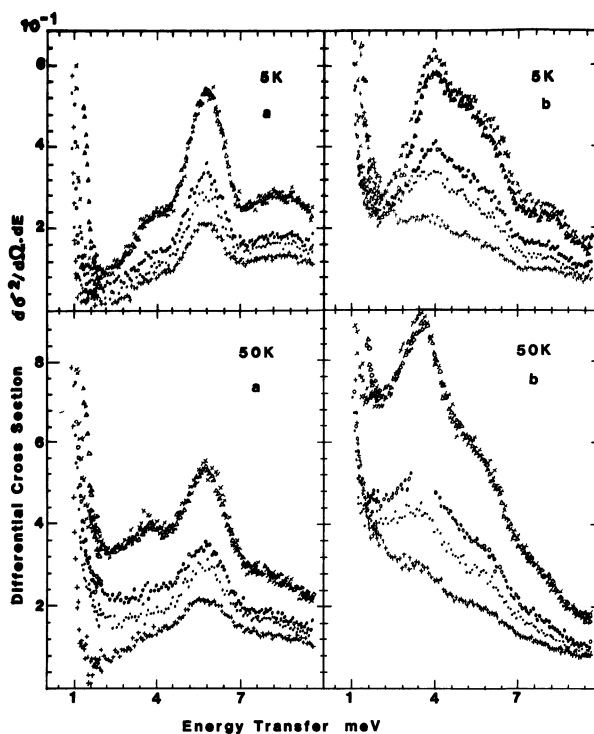


Fig. 2. — I.N.S. spectra of α crystallized toluenes obtained with the IN4 spectrometer ($E_0 = 12\text{ meV}$) at 5 and 50 K for various scattering angles. Left column (a): $C_6D_5CH_3$; right column (b): $C_6H_5CD_3$. The Q values at $\hbar\omega = 0$ are: $+ 0.94\text{ \AA}^{-1}$, $\bullet 1.89\text{ \AA}^{-1}$, $\circ 2.46\text{ \AA}^{-1}$, $\times 3.91\text{ \AA}^{-1}$, $\triangle 4.41\text{ \AA}^{-1}$.

All these observations (strong intensity, temperature and isotopic effect and Q dependence) play in favour of an assignment of the 46.8 cm^{-1} peak to the methyl torsion in the I.N.S. spectra of $C_6D_5CH_3$. However, its temperature dependence is less pronounced than expected for a pure torsional mode with a low hindering barrier and its width (about 12 cm^{-1} FWHH) is more important than that resulting from a splitting of the torsional excited state of 1 to 2 cm^{-1} (Table I) convoluted by the resolution (~ 5 to 6 cm^{-1}). The presence of a high phonon density in this frequency range, as shown in the $C_6H_5CD_3$ spectrum, suggests that some coupling between the torsion and one or several phonons cannot be excluded.

For the CD_3 group, the determination of the torsional mode is made difficult by its small intensity relatively to the phonon density of states.

3.2.1.2 Raman study. — The Raman spectra of six isotopic derivatives of toluene were recorded from 0 to 160 cm^{-1} in the α phase between 17 and 165 K. All the bands observed below 150 cm^{-1} in these spectra are to be assigned either to lattice mode or to the methyl torsion. Indeed, the next lowest internal mode, the bending $\gamma(C-CH_3)$, is situated between 200 and 230 cm^{-1} according to the considered isotopic derivative [28].

The Raman spectra of the β phase have also been recorded and analysed [29]. They are not presented here because they do not bring any information on the methyl torsion and cannot be compared to the I.N.S. spectra.

The α phase of toluene, determined by X-ray diffraction at 156 K, is monoclinic $P2_1/c$ with 8 molecules per unit cell in general position grouped in two families [21]. The group theory predicts 45 external vibrations (12 A_g , 12 B_g , 11 A_g and 10 B_u) of which 21 are infrared active and 24 Raman active. Actually, only 18 Raman lines are observed (Table II, Fig. 3).

Owing to the polycrystalline nature of our samples, these spectra cannot be assigned in terms of vibration symmetry, but the analysis can be guided by the isotopic effects. Indeed, the ratios of the moments of inertia or of the masses of the various isotopic derivatives can give indications on the isotopic effects expected respectively for the rotational-librational motions around the principal axis of inertia and for the translational motions when coupling between the modes can be neglected.

As for the methyl torsional mode, the expected isotopic effect would be given, in the harmonic approximation, by the ratio of the moments of inertia of the methyl group. Nevertheless, this approximation fails for relatively low potential barriers for which

the isotopic effect depends greatly on the potential shape. Therefore, we have tried to find further arguments to assign the torsional modes : absence of isotopic effect by changing C_6H_5- to C_6D_5- and strong damping of these bands when the temperature is increased.

As shown in table II, at 17 K, most of the Raman bands exhibit only weak isotopic effects when deuterating the methyl group and can be assigned to phonon modes. The distinction between rotational and translational modes is achieved by deuterating the benzene ring : the seven lines at 64.5, 70.5, 93.0, 100.0, 106.0, 125.0 and 135.0 cm^{-1} , which undergo isotopic effects lower than 0.97, are assigned to rotations (Table II), the others to translations.

Only a relatively strong frequency shift of the bands at 41.5, 56.0 and 81.0 cm^{-1} is observed when deuterating the methyl group (Table II, Fig. 4). Furthermore, the frequencies of these modes are very little affected by the ring deuteration (Table II), which excludes their assignment to a rotational motion of the whole molecule. In addition, these lines and those situated between 44-56 and 90-100 cm^{-1} undergo a very strong temperature effect (Fig. 4). Therefore, they could well correspond to torsional excitations. Concerning the line at 81.0 cm^{-1} , which undergoes marked isotopic substitution effects (Table II) it could well correspond

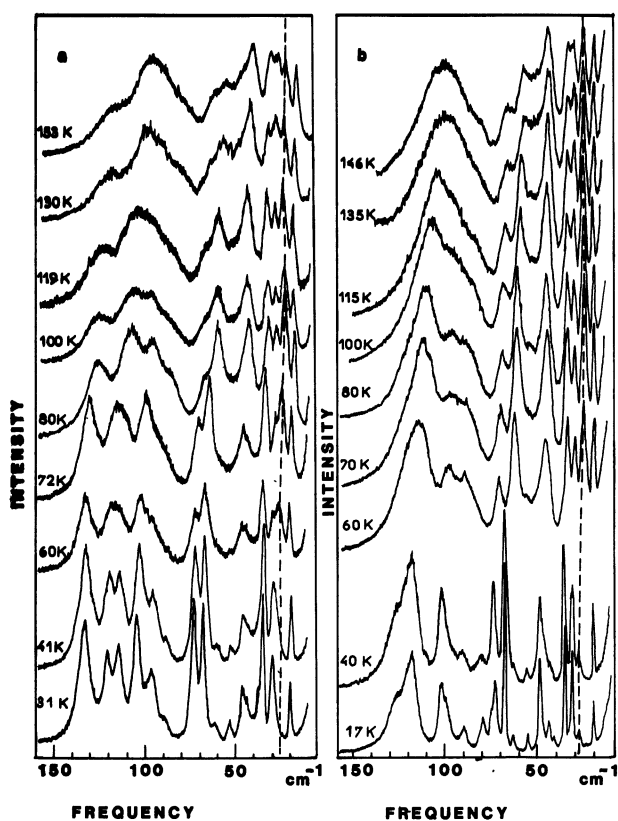


Fig. 3. — Raman spectra of α crystallized toluenes (a) $C_6H_5CD_3$; (b) $C_6D_5CH_3$ at different temperatures. The dashed vertical line follows the position of the particular phonon discussed in the text.

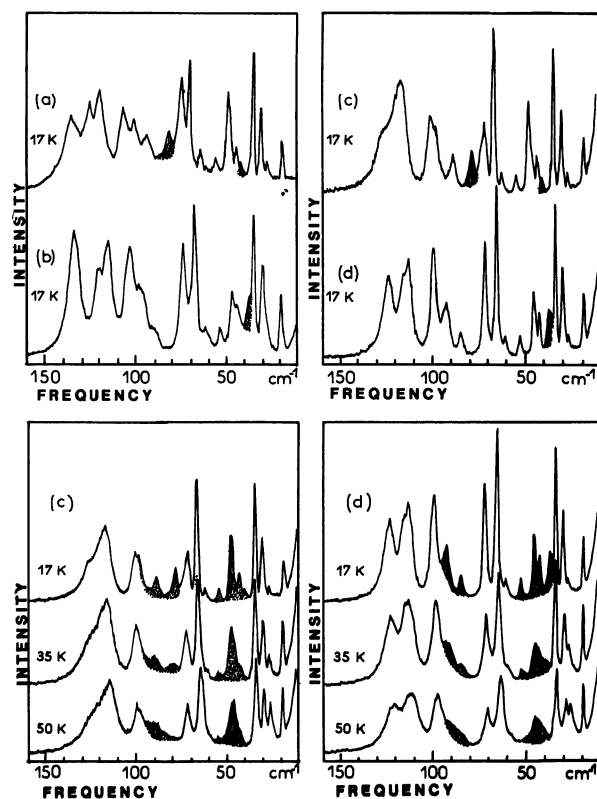


Fig. 4. — Raman spectra of α crystallized toluene $C_6H_5CH_3$ (a); $C_6H_5CD_3$ (b); $C_6D_5CH_3$ (c) and $C_6D_5CD_3$ (d) at 17 K and between 17 and 50 K (c and d). The shaded areas indicate the bands which undergo particular isotopic or temperature effects (see text).

Table II. — The observed Raman frequencies (cm^{-1}) of different deuterated derivatives of α crystallized toluene at 17 K and their proposed assignments ($\tau(\text{CH}_3)$): CH_3 torsion, T: translation, R: rotation). Ratios of the frequencies: (1) $\text{C}_6\text{X}_5\text{CD}_3$ and $\text{C}_6\text{H}_5\text{CH}_3$, (2) $\text{C}_6\text{D}_5\text{CX}_3$ and $\text{C}_6\text{H}_5\text{CH}_3$, (3) $\text{C}_6\text{D}_5\text{CD}_3$ and $\text{C}_6\text{H}_5\text{CH}_3$, (X = H or D).

Tempe- ratures K	C_6H_5-				C_6D_5-				$\frac{\text{C}_6\text{D}_5\text{CH}_3}{\text{C}_6\text{H}_5\text{CH}_3}$ (2)	$\frac{\text{C}_6\text{D}_5\text{CD}_3}{\text{C}_6\text{H}_5\text{CD}_3}$ (2)	$\frac{\text{C}_6\text{D}_5\text{CD}_3}{\text{C}_6\text{H}_5\text{CH}_3}$ (3)	Assignment
	$-\text{CH}_3$	$-\text{CHD}_2$	$-\text{CD}_3$	$\frac{\text{CD}_3}{\text{CH}_3}$ (1)	$-\text{CH}_3$	$-\text{CHD}_2$	$-\text{CD}_3$	$\frac{\text{CD}_3}{\text{CH}_3}$ (1)				
17 K	19.5	19.5	19.5	1.0	19.5	19.5	19.5	1.0	1.0	1.0	1.0	T
	27.5	27.5	27.5	1.0	27.5	27.0	27.5	1.0	1.0	1.0	1.0	T
	31.0	31.0	30.0	0.968	31.0	31.0	30.0	0.968	1.0	1.0	0.968	T
	35.5	35.5	35.0	0.986	35.5	35.0	34.5	0.972	1.0	0.985	0.972	T
	41.5 Sh	38.5	37.5 Sh	0.903	41.0 Sh	38.0	37.0	0.902	0.988	0.987	0.891	R(I_b) or $\tau(\text{CH}_3)$
	44.5	44.5 Sh	44.0	0.989	44.0	44.5	43.0	0.977	0.989	0.977	0.965	T
	48.5	47.5	46.5	0.960	47.5	47.0	46.0	0.968	0.980	0.989	0.948	T
	56.0	55.0	53.5	0.955	55.5	54.0	52.5	0.946	0.991	0.981	0.937	R(I_b) or $\tau(\text{CH}_3)$
	64.5	64.0	62.5	0.969	62.5	62.0	60.5	0.968	0.961	0.968	0.938	R(I_b or I_c)
	70.5	70.5	68.0	0.964	67.5	66.5	65.5	0.970	0.957	0.963	0.929	R(I_c)
	75.0,	75.0	74.0	0.987	73.5	73.5	72.5	0.986	0.980	0.980	0.966	T
	81.0				79.5				0.981			? + $\tau(\text{CH}_3)$
	93.0	90.5	88.5	0.951	89.5	87.5	85.0	0.950	0.962	0.960	0.914	R(I_b) + $\tau(\text{CH}_3)$
	100.0	98.0	96.0	0.960	98.0	95.0	93.0	0.949	0.980	0.969	0.930	R(I_b) + $\tau(\text{CH}_3)$
	106.0	106.0	104.5	0.985	101.0	100.5	99.5	0.985	0.953	0.952	0.938	R(I_b)
	119.5	117.5	115.0	0.962	117.5	115.5	113.5	0.966	0.983	0.987	0.950	T
	125.0	122.5	120.0	0.960	121.0 Sh	118.5 Sh	116.0 Sh	0.959	0.968	0.966	0.928	R(I_b) + R(I_c)
135.0	134.5	134.0	0.995	126.5	125.5	124.0	0.980	0.937	0.925	0.918	R(I_b)	
155 K	18.0	18.0	18.0	1.0	18.0	18.0	18.0	1.0	1.0	1.0	1.0	
	24.5	24.5	24.5	1.0	23.5	23.5	23.5	1.0	0.959	0.959	0.959	
	29.0	28.0	29.0	1.0	28.5	28.0	28.5	1.0	0.983	0.983	0.983	
	32.0	32.5	32.0	1.0	31.5	31.5	31.5	1.0	0.984	0.984	0.984	
	43.5	43.0	42.5	0.977	41.5	41.5	42.0	1.012	0.954	0.988	0.965	
	51.5 Sh	51.0 Sh			55.0	54.5	55.5	1.0	0.940	0.965	0.957	
	58.0	58.0	57.5	0.991	63.0	62.5	62.5	0.995	0.969	0.976	0.961	
	65.0	65.5	64.0 Sh	0.985	79.5 Sh	80.0 Sh	80.0 Sh	1.005	0.975	0.987	0.981	
	81.5 Sh	81.0 Sh	81.0 Sh	0.995	95.0	95.0	95.0	1.0	0.936		0.936	
	101.5	100.0	120.0 Sh		110.0 Sh	110.0 Sh	110.0 Sh	1.0				

to the torsional frequency calculated from tunnel data in the hypothesis of a pure V_3 potential (Table I). But we don't find its equivalent at 60 cm^{-1} in the $-\text{CD}_3$ toluene spectra and in the I.N.S. spectra. On the other hand, the set of very well resolved lines observed at 17 K in the spectral range $36\text{--}60\text{ cm}^{-1}$ merges, already at 35 K, into a broad band centred at about 47 cm^{-1} (Fig. 4), corresponding well to the more intense I.N.S. peak at 46.8 cm^{-1} and to the right spectral region with respect to the calculated torsional frequency in the hypothesis of a V_3, V_6 mixed potential or of a square well potential.

This analysis leads to the conclusion that the first torsional transition occurs between 40 and 60 cm^{-1} . But, owing to the presence of a strong density of phonons in this range, a coupling between the methyl torsion and the phonons cannot be excluded. In this hypothesis, the lines situated between 80 and 100 cm^{-1} which have peculiar temperature and isotopic effect can be either considered as phonons strongly coupled with higher order torsional transitions or as combinations of phonons with this mode. This latter possibility can be particularly invoked for the line at 81 cm^{-1} .

On heating, most of the bands of the spectra broaden and some merge with other lines (Fig. 3), but in addition an unexpected phenomenon occurs : a weak and narrow line (FWHM = 4 cm^{-1}) at about 27 cm^{-1} , grows continuously in intensity till 80 K and then decreases slowly until the melting point is reached while its frequency is slightly shifted to 24.5 cm^{-1} (Fig. 3 and 5). This band undergoes no isotopic effect and cannot be assigned to a transition between torsional levels of the methyl group. Furthermore, several arguments are contrary to the hypothesis of a two phonons hot transition : this type of transition, due to anharmonicity, appears only very rarely in the molecular crystals [30] and gives generally broader

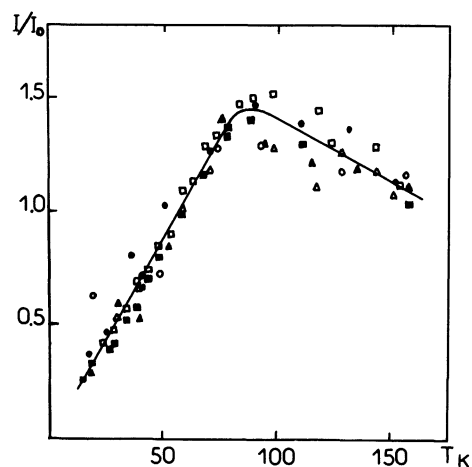


Fig. 5. — Temperature dependence of the intensity of the 24.5 cm^{-1} Raman line of different isotopic derivatives of α crystallized toluene. (I : intensity of the 24.5 cm^{-1} line, I_0 : intensity of the 19.5 cm^{-1} reference line.)

bands than observed here ; finally, the intensity of a band resulting from a negative combination of two phonons should increase continuously above 80 K . Two hypotheses could be still advanced : firstly, a structural transition could appear progressively between 17 and 80 K although no anomaly has been observed in the temperature dependence of the specific heat [31-35] : secondly, the α phase of toluene could be an incommensurable phase in the investigated temperature range (17 K to 178 K). This second idea is based on recent results obtained by Pick *et al.* [36], who have observed a similar phenomenon in the Raman spectra of the crystalline monomer of diacetylene : the intensity of a phonon at 13 cm^{-1} increases and disappears in the temperature range of the incommensurable phase. Only a careful crystallographical study of the α crystallized toluene could destroy or confirm these last hypotheses.

3.2.2 Nitromethane. — In the I.N.S. spectra of NO_2CH_3 , Trevino *et al.* [15] note the presence of two overlapping peaks at 53.5 cm^{-1} (6.6 meV) and 67.5 cm^{-1} (8.4 meV), which they interpret in terms of first torsional excited state splitting. The width of these peaks is thought to result from finite life-time for these excited levels. Only a single peak at 42.5 cm^{-1} (5.3 meV) is observed for NO_2CD_3 .

The Raman spectra of the three compounds NO_2CH_3 , NO_2CHD_2 and NO_2CD_3 were recorded from 0 to 170 cm^{-1} between 17 and 170 K (Table III) (Fig. 6). All the bands observed below 200 cm^{-1} are to be assigned either to external modes or to methyl torsion modes, the next lowest frequency internal mode, the rocking NO_2 , occurring between 480 and

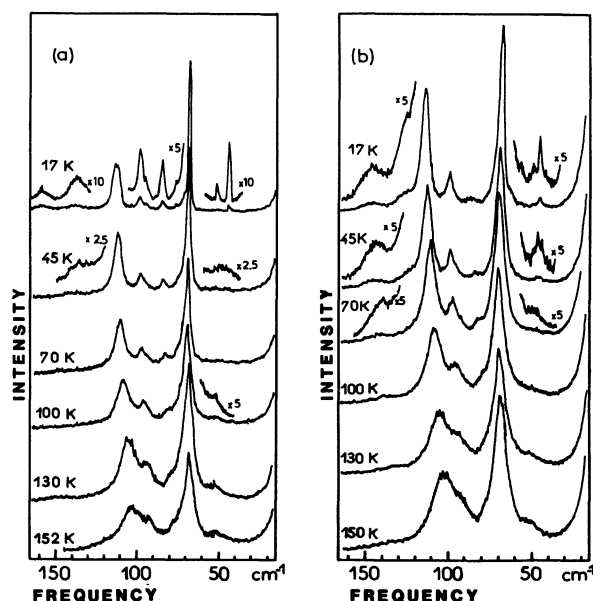


Fig. 6. — Raman spectra of crystalline nitromethane at different temperatures. Left column (a) NO_2CH_3 ; right column (b) NO_2CD_3 .

Table III. — The observed Raman frequencies (cm^{-1}) of different crystallized derivatives of nitromethane at 17 K and their proposed assignment ($\tau(\text{CH}_3)$: CH_3 torsion, T : translation, R : rotation).

CH_3NO_2	CHD_2NO_2	CD_3NO_2	$\frac{\nu(\text{CD}_3)^{(*)}}{\nu(\text{CH}_3)}$	Assignment
45.0	45.0	44.0	0.978	T or $\text{R}(I_a)$
52.5	50.0 Sh	48.0 Sh	0.914	$\text{R}(I_b)$ or $\tau(\text{CH}_3)$
	58.0	56.0		
66.0 Sh	63.5 Sh	62.5 Sh	0.947	$\text{R}(I_c)$
69.0	67.5	67.0	0.971	T or $\text{R}(I_a)$
72.0 Sh	74.0 Sh	70.5 Sh	0.979	T or $\text{R}(I_a)$
77.0 Sh		76.0 Sh	0.987	T
85.5	84.5	85.0	0.994	T
95.5 Sh	95.0 Sh	94.5 Sh	0.989	T
99.5	98.5	98.5	0.990	T
114.0	113.0	113.0	0.991	T
139.0	127.0 Sh	125.0 Sh	0.900	$\text{R}(I_b)$
160.0	150.0	146.0	0.913	$\text{R}(I_b)$

(*) Ratio of the frequencies in NO_2CD_3 and NO_2CH_3 .

430 cm^{-1} according to the considered isotopic derivatives (37).

The crystalline structure of nitromethane, determined at 4 K, is orthorhombic $\text{P2}_1\text{2}_1\text{2}_1$ with 4 molecules per unit cell in a general position [24]. Thus, 21 external vibrations are expected by group theory ($6A$, $5B_1$, $5B_2$ and $5B_3$), 15 infrared active and 21 Raman active, but only 12 Raman lines are observed at 17 K (Table III).

As previously for toluene, we have used several isotopic derivatives of polycrystalline nitromethane and applied the same method of analysis. All the bands, which have an isotopic effect between 0.97 and 1.0 may be assigned to translational modes (9 are expected) or to rotations around the higher symmetry molecular axis (I_a). The four remaining bands at 52.5, 66.0, 139.0 and 160.0 cm^{-1} , which have an isotopic effect of about 0.91 and 0.94 could be assigned in a first approximation to rotations around the axes I_b or I_c respectively. However, the 52.5 cm^{-1} weak line undergoes a strong damping when the temperature is increased (Fig. 6) and corresponds very well to the I.N.S. peak assigned to the methyl torsion. It can be pointed out that the second I.N.S. peak at 68 cm^{-1} occurs at the same frequency as the most intense phonon Raman line (Fig. 6) providing a possible argument for its assignment to a maximum in phonon density of states.

Thus Raman and I.N.S. results suggest that the methyl torsion transition is around 53 cm^{-1} for $-\text{CH}_3$ and around 44 cm^{-1} for $-\text{CD}_3$. The analysis of the nitromethane data leads to a more satisfactory description than for toluene. The relative simplicity of the phonon density of states in the former compound possibly reduces the perturbation of the methyl torsion excited states.

4. Conclusions.

The I.N.S. results at high resolution reported previously by Alefeld *et al.* [17] on nitromethane and those presented here on toluene provide interesting examples of determination of the ground state tunnel splitting in the one dimensional methyl orientational potential for both isotopic species $-\text{CH}_3$ and $-\text{CD}_3$. The values of the $-\text{CH}_3$ tunnel splitting thus obtained agree well with those determined from the N.M.R. T_1 minimum.

To a first approximation, the observed tunnel splitting values for $-\text{CH}_3$ and $-\text{CD}_3$ can rather satisfactorily be fitted with a mixed V_3 , V_6 potential or a square well potential for the two compounds. The first excited torsional transitions are then predicted at about 56 cm^{-1} for toluene and 60 cm^{-1} for nitromethane. These calculated values are a little higher than the methyl torsion frequencies observed in the I.N.S. and Raman spectra (47 cm^{-1} for toluene and 53 cm^{-1} for nitromethane).

Therefore, it is clear that the simple description given above in terms of cosine or square well potentials has to be improved. For systems with such low hindering barriers, the possibility of coupling between some phonons and the first torsional excited state near to the top of the barrier has certainly to be considered. It has already been invoked by Alefeld *et al.* [17] and it is suggested by the present I.N.S. and Raman results.

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