

Vibrational spectra and structure of trimethylindium and trimethylthallium¹

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Abstract

A detailed vibrational spectrum of trimethylthallium is reported for the first time (Raman spectra of the melt and crystal, IR spectra of crystalline, gaseous and matrix-isolated samples). Analogous data were also obtained for trimethylindium for comparison. In the Raman spectra of both compounds in the liquid state some peculiarities are found which suggest low-barrier hindered rotation of the methyl groups. Some features in the spectra of trimethylthallium and triethylthallium distinguish these compounds from their In and Ga analogues, and could be interpreted as arguments in favour of distortion of the planar TlC_3 skeleton in condensed phases, probably as a result of the pseudo-Jahn–Teller effect. © 1997 Published by Elsevier Science S.A.

Keywords: Thallium; Indium; Trialkylthallium; Trialkylindium; Raman and IR spectroscopy; Selection rules; Methyl group rotation

1. Introduction

According to electron diffraction studies, gaseous Me_3Tl has a planar skeleton [1], as have its Ga [2] and In [3] congeners. Structural data for Et_3Tl are not available.

Meanwhile, in the course of a systematic study of vibrational spectra of alkyl derivatives of Group 13 metals and their complexes [4–8], we have found that the spectrum of liquid Et_3Tl in the region of the $Tl-C$ stretching vibrations (νTlC) does not obey the selection rules for the symmetry of a planar TlC_3 skeleton [8]. In contrast to Et_3Ga and Et_3In , whose totally symmetric νMC vibrations are not observed in the IR absorption, the IR spectrum of Et_3Tl does exhibit a band corresponding to this mode (Fig. 1). Rigorously, owing to hindered rotation of Et groups about the $Tl-C$ bonds, the Et_3Tl molecule could exist as a mixture of conformers belonging to different symmetry groups. Therefore, to solve the problem of the TlC_3 skeleton structure, it seems reasonable to analyse in detail the selection rules operating in the vibrational spectrum of the simplest trialkyl derivative Me_3Tl .

We have investigated in detail the IR and Raman spectra of Me_3Tl in different physical states. The spectra of Me_3In were also re-investigated for comparison. The spectra of Me_3Ga can be found in Refs. [4,9–11], those of R_3Ga ($R = Et, Pr, Bu$) in Ref. [4].

2. Results and discussion

Under an assumption of a planar skeleton and free rotation of methyl groups (the latter was proved only for Me_3B on the basis of comparison of the calculated and experimental entropy values [12,13]), the Me_3M molecule belongs to a non-rigid symmetry group G_{324} . The selection rules for this group were shown to strictly coincide with those for the D_{3h} point group [11], the latter usually being chosen for analysis of the vibrations of such molecules. Vibrations of a non-planar Me_3M model are analyzed in terms of an effective C_{3v} point group. In these two cases, the 30 normal modes are broken down into the following symmetry species: $\Gamma(D_{3h}) = 3A'_1(R, p) + 3A'_2 + 4A''_2(IR, ||) + 7E'(R, dp; IR, \perp) + 3E''(R, dp)$; $\Gamma(C_{3v}) = 7A_1(R, p; IR, ||) + 3A_2 + 10E(R, dp; IR, \perp)$.

If the methyl groups in the planar molecule undergo hindered rotation (from their most symmetric positions with one CH bond in each methyl group lying in the

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¹ Dedicated to the memory of Professor Yu.T. Struchkov.

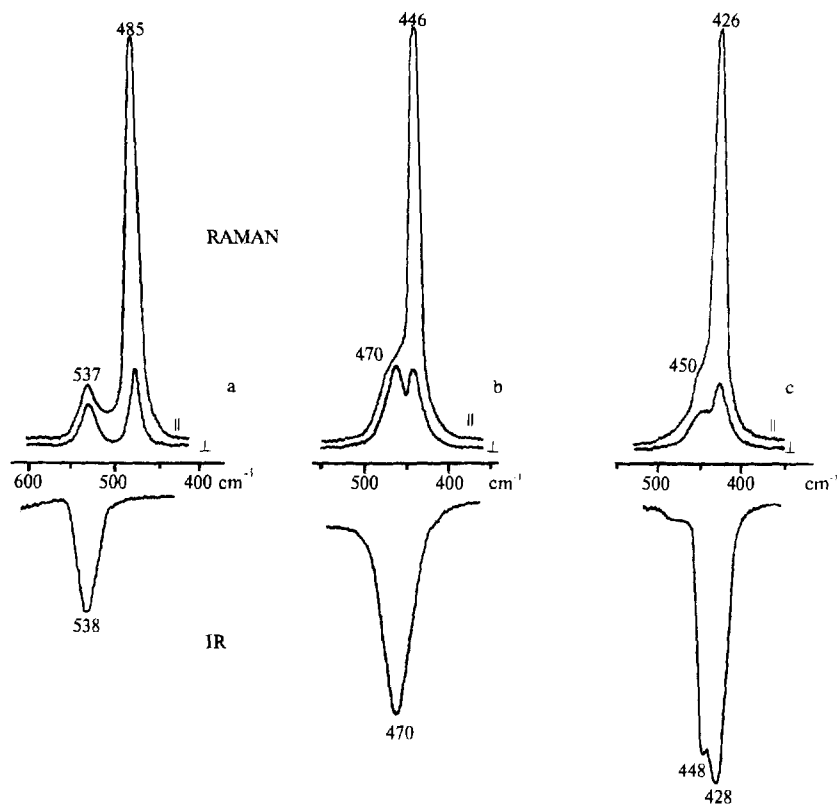


Fig. 1. The Raman and IR spectra of liquid Et_3M in the region of νMC stretching vibrations: (a) $\text{M} = \text{Ga}$; (b) $\text{M} = \text{In}$; (c) $\text{M} = \text{Tl}$.

MC_3 plane, Fig. 2), the molecular vibrations could be treated in terms of C_{3h} symmetry. Then the A'_2 modes, silent under D_{3h} , turn into the A' modes, Raman active under C_{3h} , and one must observe in the Raman spectrum three additional polarized lines, forbidden in the IR absorption: $\Gamma(\text{C}_{3h}) = 6\text{A}'(\text{R}, \parallel) + 4\text{A}''(\text{IR}, \parallel) + 7\text{E}'(\text{R}, \text{dp}; \text{IR}, \perp) + 3\text{E}''(\text{R}, \text{dp})$. Besides, in the latter case, the methyl group torsional modes (of the A'' and E'' species) should appear in the low-frequency spectral region.

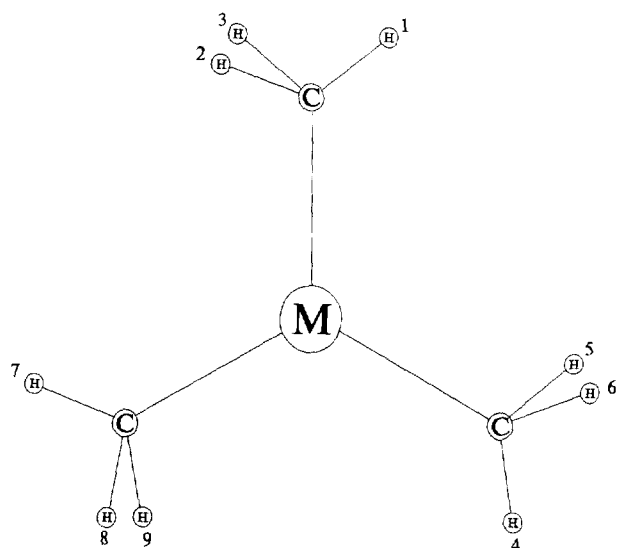


Fig. 2. Me_3M molecule of C_{3h} symmetry point group.

Thus, for the Me_3M molecule with a planar skeleton, one must observe in the Raman spectrum only three polarized lines in the case of methyl group free rotation and six polarized lines if rotation is hindered. If the skeleton is pyramidal, four IR active A''_2 modes turn into A_1 species and become Raman active, increasing the number of polarized lines to seven. For the planar models, A'_1 or A' modes are forbidden in IR, for the non-planar one, seven A_1 modes are active in both IR and Raman.

The distribution of the vibrational coordinates among the symmetry species under various possible point groups is presented in Tables 1 and 2.

We shall discuss the results obtained for Me_3In and Me_3Tl separately, beginning with a more clear case of Me_3In .

2.1. Trimethylindium

The planar skeleton of Me_3In was demonstrated by an electron diffraction study [3] and two X-ray investigations [14–16]. A weak self-association of the molecules in the crystal into ‘loose tetramers’ was found in the latter.

The Raman spectrum of a melt and the gas phase IR spectrum were published in Ref. [9], the Raman spectra of solid samples in Ref. [16], the Raman spectra of gaseous Me_3In and Et_3In in Ref. [17]. Vibrational

Table 1
Distribution of 30 normal modes of Me₃M model with free methyl group rotation among the symmetry species for possible symmetry point groups D_{3h} and C_{3v}

Point group mode description	D _{3h}	C _{3v}
$\nu^s\text{CH}$	A ₁ ' + E'	A ₁ + E
$\nu^{\text{as}}\text{CH}$	A ₂ ' + A ₂ ' + E' + E''	A ₁ + A ₂ + 2E
$\delta^s\text{CH}_3$	A ₁ ' + E'	A ₁ + E
$\delta^{\text{as}}\text{CH}_3$	A ₂ ' + A ₂ ' + E' + E''	A ₁ + A ₂ + 2E
τCH_3	A ₂ ' + A ₂ ' + E' + E''	A ₁ + A ₂ + 2E
νMC	A ₁ ' + E'	A ₁ + E
$\delta^{\text{as}}\text{MC}_3$	E' (in plane)	E
$\delta^s\text{MC}_3$	A ₂ ' (out of plane)	A ₁

ν , δ , τ , τ – stretching, deformation, rocking and torsional vibrations respectively.

spectra of related moieties [Me₄In]⁻ and [Me₂In]⁺ can be found in Refs. [18,19] respectively.

We have obtained the Raman spectra in the region 10–3700 cm⁻¹ for the solid sample and the melt (above 80 °C). Band half-widths $\Delta\nu_{1/2}$ were estimated in both spectra, and depolarization ratios ρ in the spectrum of the melt. The IR spectra were recorded in the region 400–3700 cm⁻¹ for gaseous and crystalline samples, the spectrum of the latter being reported for the first time. The results are presented in Table 3 along with the data [9,16,17] and in Figs. 3–6. In numbering of normal modes we follow previous authors (see, for example, Ref. [9]).

As in Ref. [9], we did not observe in the IR spectrum of the gas the νInC mode of A' species, which manifests itself in the Raman spectrum as a strong polarized line at 478 cm⁻¹ [17]. The IR band corresponding to the degenerate νInC mode in the vapour spectrum consists of P and R branches, the PR separation found is close in value to that calculated according to Ref. [20]. Thus, the planarity of the InC₃ skeleton in the gas phase is doubtless.

Our results for the Raman spectrum of the melt (Table 3) in most respects agree with the data of Ref. [9], but with some meaningful exceptions. Unlike in

Ref. [9], we succeeded in obtaining a weak but distinct depolarized Raman band at 1450 cm⁻¹, which is readily assigned as a degenerate $\delta^{\text{as}}\text{CH}_3$ mode.

The most unexpected and paradoxical finding was that shown in Fig. 3. A very broad band in the $\delta^s\text{CH}_3$ region, that at 1115 cm⁻¹ reported in Ref. [9] as depolarized and assigned to an E' species, appeared to be polarized with $\rho \approx 0.3$. From the viewpoint of spectroscopy, for a Raman band to be 'broad' and 'polarized' simultaneously seems very strange. That is why we did not publish this result for about 20 years, checking it again and again, using various more and more advanced spectrometers and newly synthesized samples. It goes without saying that we repeatedly measured depolarization ratios in the spectra of standard liquids (benzene, CCl₄) under the same conditions as for Me₃In, and obtained the usual standard values within the limits of experimental error (± 0.05).

For comparison, we also present in Fig. 3 polarization data for an analogous $\delta^s\text{CH}_3$ region of the Me₃Sb Raman spectrum obtained previously [6]. The difference in spectral patterns between these two related molecules is striking. Both spectra contain an intense narrow polarized band of the A' $\delta^s\text{CH}_3$ mode. However, in contrast to the Me₃Sb spectrum, where the second, lower-frequency band is clearly depolarized ($\rho \approx 0.85$) and narrow (half-width $\Delta\nu_{1/2} \approx 15$ cm⁻¹), the analogous band of Me₃In is polarized and unusually broad ($\Delta\nu_{1/2} \approx 70$ cm⁻¹).

In the νCH region of the Me₃In Raman spectrum (Fig. 4(a)), along with a polarized band at 2910 cm⁻¹, there is a second polarized feature at 2855 cm⁻¹, also broad ($\Delta\nu_{1/2} \approx 50$ cm⁻¹). If one considers this band as corresponding to a fundamental, then the number of polarized lines in the Raman spectrum of the liquid Me₃In is not less than five. However, there is an alternative: attributing the band at 2855 cm⁻¹ to an overtone of the $\delta^{\text{as}}\text{CH}_3$ mode. The latter shows itself as an extremely weak Raman band at about 1450 cm⁻¹; its overtone could gain intensity due to Fermi resonance. Anyhow, the Raman spectrum observed exhibits more than three polarized bands, which is in accord with C_{3h} rather than D_{3h} symmetry.

Table 2
Distribution of 33 normal modes of Me₃M in the case of planar model with hindered methyl group rotation among the symmetry species of the C_{3h} symmetry point group

Symmetry species	Mode description								
	νCH	νCH_p^a	$\delta^s\text{HCH}_p$	$\delta^s\text{HCH}$	$\delta^{\text{as}}\text{HCH}_p$	τCH_3	νMC	δMC_3	τ
A'	ν_1	ν_4	ν_2	ν_5		ν_6	ν_3		
A''	ν_7				ν_8	ν_9		ν_{10}	ν_{21}
E'	ν_{11}	ν_{12}	ν_{13}	ν_{14}		ν_{15}	ν_{16}	ν_{17}	
E''	ν_{18}				ν_{19}	ν_{20}			ν_{22}

^a Hp – H atoms 1, 4, 7 (Fig. 2) lying in the skeleton plane. In mode numbering we follow that for D_{3h} symmetry, but bearing in mind that the modes of A₂' species (ν_4 – ν_6) transform to A' under C_{3h}.

Table 3
Vibrational spectrum of Me₃In

Gas			Melt		Crystal			Normal mode assignment
Raman	IR		Raman	Raman	IR			
[17]	[9]	(400–3700 cm ⁻¹)	[9]	[16]	(400–3700 cm ⁻¹)			
					12 m (7) 28 m (7) 36 vw sh			} lattice modes
					50 vw 86 m (25) 110 vw		τ E'' ν_{22}	
113 s			132 s dp	128 m dp (45)	125 155	125 m (30) 157 w (25)		δ InC ₃ E' ν_{17}
478 vs	—	—	467 vs	365 vvw dp br 465 vs p (15)	462 vs 480 m	461/463 vs (10) 481 sh	—	ν^{δ} InC A' ν_3
489 s	500 s	497 s } 510 s } P, R	495 s dp	488 s dp (28)	488 s 498 s	491 s (5) 501 s (5)	488 vs 507 s	} ν^{as} InC E' ν_{16}
	687 ms 725 s	695 sh br 735 vs br	635 w dp br 725 w dp br	630 w dp (70) 725 vw dp (> 70) 945 vvw?		655 w (35) 745 vw (75)	735 vs br	
1173 vs	1155 vw	1144 w br	1116 m dp br 1157 s p	1115 m p (70) 1156 sp (15) 1270 vvw?	1094 m 1123 m 1151 s	1096 m (25) 1125 m (15) 1152 s (5)	1092 m 1120 m 1155 m	} δ^{s} HCH A'E' ν_5, ν_{14} A', E' ν_2, ν_{13}
		1390 w		1450 vvw dp (50)		1450 vvw br	1390 vw 1450 vw	
2925 vs	2860 m 2920 s 3000 s	2850 m 2920 s 3000 m	2861 w sh 2910 ms p 2974 mw dp	2855 w p (50) 2910 m p (20) 2970 w dp (70)	2915 m 2975 mw br	2865 w (70) 2913 s (25) 2975 s (40)	2860 vw sh 2915 s br 2970 s	} ν CH A' ν_4 A', E' ν_1, ν_{11} A'', E', E'' $\nu_7, \nu_{12}, \nu_{18}$

* Numbers in brackets – band half-width $\Delta\nu_{1/2}$ (cm⁻¹) estimated with accuracy ± 5 cm⁻¹.

ν stretching, δ deformation, r rocking, τ torsional modes.

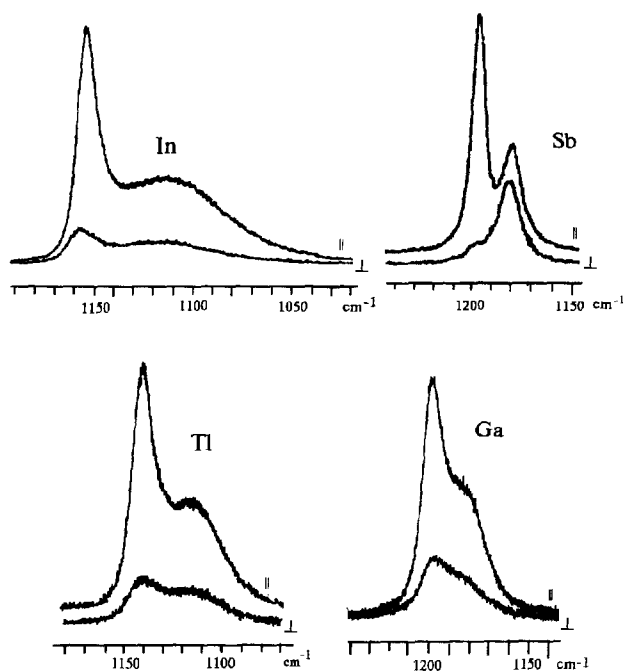


Fig. 3. The Raman spectra of liquid Me_3M ($\text{M} = \text{In}, \text{Sb}, \text{Tl}, \text{Ga}$) in the region of the $\delta^s\text{CH}_3$ modes (polarization data).

Additionally, in the low frequency Raman spectrum we found on the Rayleigh wing a weak and ill-defined but distinct depolarized Raman band at 75 cm^{-1} , not reported in Ref. [9]. It cannot be assigned to a missing out-of-plane skeleton deformation mode because the latter belongs to the A' species permitted only in IR. Moreover, Durig and Chatterjee [10] have demonstrated and proved with the aid of normal coordinate analysis that the two MC_3 skeleton deformations belonging to the A'_2 and E' species under D_{3h} symmetry (or to A' and E' species under C_{3h}) must have similar frequencies. This means that the frequency of the missing out-of-plane skeleton deformation mode of Me_3In should occur near 121 cm^{-1} , that of the E' in-plane skeleton deformation observed in the low-frequency Raman spectrum (Table 3). If so, it only remains for us to conclude that the depolarized Raman line at 75 cm^{-1} corresponds to the E' methyl torsional mode. Its frequency value is quite reasonable, taking into account

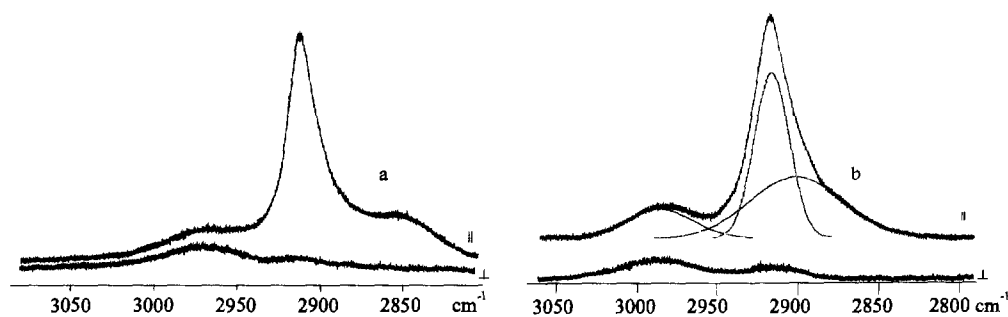


Fig. 4. The Raman spectra of liquid Me_3M [$\text{M} = \text{In}$ (a), Tl (b)] in the region of the νCH (polarization data and computer analysis).

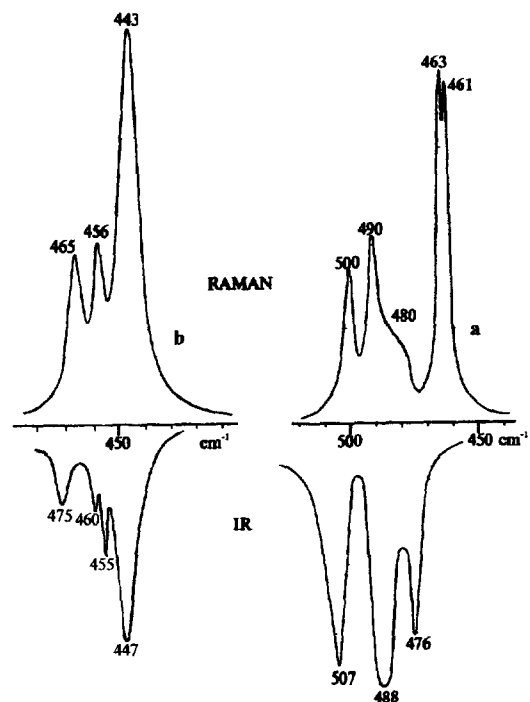


Fig. 5. Comparison of the Raman and IR spectra of polycrystalline Me_3M [$\text{M} = \text{In}$ (a), Tl (b)] in the region of the νMC .

the analogous value of 101 cm^{-1} reported by Durig et al. [21] for Me_4Sn , a compound of a metal of the same row of the Periodic Table. The presence in the spectrum of a methyl torsional mode also speaks in favour of the hindered methyl group rotation, its very low frequency (which seems to be the lowest among all those known for methyl–metal compounds) points to a very low rotational barrier.

An unusual broadness (more than 50 cm^{-1} , see Table 3) in the spectrum of the melt of some Raman bands, corresponding to the methyl group vibrations, especially those of methyl rocking modes, is striking. It can be attributed to the elevated temperature of the experiment (InMe_3 melts at about 80°C) only partly, because some other lines in the same spectrum exhibit ordinary $\Delta\nu_{1/2}$ values ($15\text{--}30\text{ cm}^{-1}$). Analogous broadening of some Raman bands, corresponding to methyl vibrations, was observed for Me_4M ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) in Ref. [22].

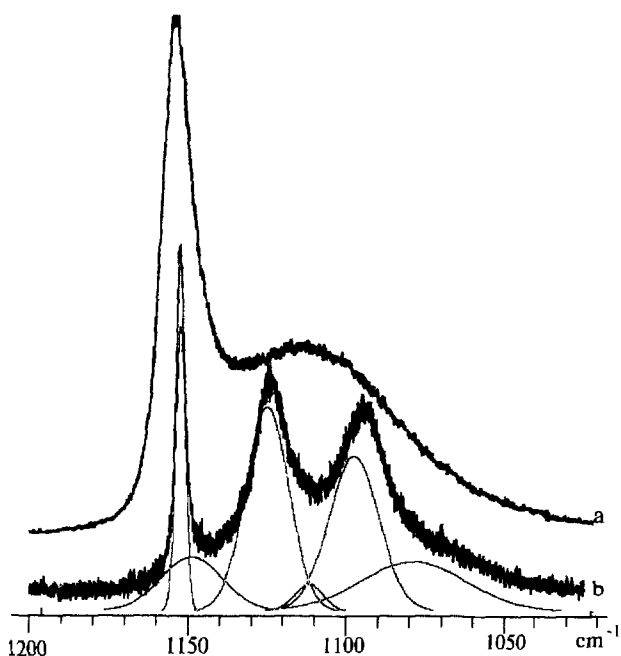


Fig. 6. Comparison of the $\delta^s\text{CH}_3$ region in the Raman spectra of liquid (a) and crystalline (b) Me_3In . The results of computer analysis of the curve b are also presented.

Taking into account the data [23,24], such a broadening is the second evidence of a very low rotational barrier in Me_3In .

Thus, our results for Me_3In in the liquid phase do not agree with the selection rules for the D_{3h} symmetry point group, but rather suggest the C_{3h} group. This fact, along with the presence in the spectrum of a methyl torsional mode, points to not free but hindered rotation of the methyl groups. In the latter case, we can assume the most symmetric molecular configuration, with one of the hydrogen atoms in each methyl group lying in the MC_3 plane. Then the C–H bonds and the HCH angles form not one but two sets of equivalent internal coordinates, those involving and not involving H atoms 1, 4, 7 (Fig. 2) lying in the molecular plane. The distribution of these coordinates among the symmetry species is given in Table 2. Hence, the presence in the spectrum of two polarized lines in both stretching and bending C–H regions becomes understandable. However, we realize that this approach is rather formal, and it is only our will which makes one hydrogen atom in each methyl group differ from the other two. Anyhow, today we see no other explanation of the data obtained.

Both X-ray investigations [14–16] have shown that in the crystal the Me_3In molecules are linked into loose tetramers that form an infinite three-dimensional network, the molecules occupying general positions. It was of interest to follow this change in symmetry by vibrational spectroscopy. As is seen in Table 3, our Raman spectrum of crystalline Me_3In agrees well with that reported in Ref. [16], but we succeeded in obtaining

some more features. The IR spectrum of the crystalline sample (sublimed on a cold window of a vacuum cryostat) is reported for the first time. The crystallinity of the sample is confirmed by the presence in the low-frequency Raman region of several narrow lines corresponding to lattice vibrations (those at 12, 28, 36, 50 and 110 cm^{-1}). The effective symmetry lowering clearly manifests itself in the spectral region of the νInC modes (Fig. 5(a)). Instead of a single band corresponding to the doubly-degenerate mode in the spectrum of the melt, a complicated pattern with three peaks is observed for the crystal which cannot be explained by the loss of the three-fold symmetry axis alone. The reasons for such a complication were adequately discussed in Ref. [16]. However, it is notable that the Raman line corresponding to the totally symmetric νInC mode, split in a Davydov doublet $461/463\text{ cm}^{-1}$ (correlation field splitting due to $Z=8$ [16]), has no IR counterpart, which is in accord with the X-ray data, showing that the InC_3 skeleton also persists as essentially planar in the crystalline state.

An interesting evolution on going from the liquid to the crystalline state is also exhibited by the mysterious region of the $\delta^s\text{CH}_3$ modes. In spite of being polarized, the broad band at 1115 cm^{-1} behaves as if it belongs to a doubly-degenerate vibration, splitting in two main components. This is illustrated in Fig. 6. However, computer analysis of this pattern in the spectrum of the crystal shows (Fig. 6) that it is more complicated and involves six components. This fact can be rationalized if one remembers that four fundamentals are situated in this region under the C_{3h} symmetry (two of A' and two of E' species, Table 2). The splitting of the degenerate E' modes in the crystal leads to further complications.

Comparison of the band width values (Table 3) shows a natural general effect of band narrowing on going to the crystal. Some Raman lines become quite sharp ($\Delta\nu_{1/2}$ $5\text{--}10\text{ cm}^{-1}$). However, some bands corresponding to methyl group vibrations continue to be very broad. This means that low-barrier hindered rotation of the methyl groups also persists in the solid.

Significant broadening of the band at 86 cm^{-1} allowed us to distinguish this feature from the narrow bands corresponding to the lattice modes in the low-frequency Raman region and to assign it to a methyl torsional mode. An increased value of this mode frequency in the crystal suggests an increase in rotational barrier height, which is quite natural taking into account the enhanced intermolecular interactions.

2.2. Trimethylthallium

In the literature, one can find mentions of the experimental Me_3Tl spectrum, but these are references to unpublished results [24–27]. Some features of this spectrum are presented in the dissertation of Lee [28], who

Table 4
Vibrational spectrum of Me_3Tl

Gas		Solution		Matrix	Melt	Crystal				Band assignment			
Raman	IR	Raman	IR	IR	Raman	Raman	IR						
(300-600 cm^{-1})	[28]	in benzene	in ch [*] (300-700 cm^{-1})	in ch [*] (400-900 cm^{-1})	(400-900 cm^{-1})	[28]	[28]	[28]	(400-3700 cm^{-1})				
							28 vw			lattice modes			
	86 sh						33 w			τ	E''	ν_{22}	
	98 m					55 w br dp	70 bd	70 m br		$\delta^s\text{TIC}_3$	A'	ν_{10}	
						103 w br dp		100 m br		$\delta^s\text{TIC}_3$	E'	ν_{17}	
						335 vwvp?							
454 s p		450 s	450 sp	458 s	450m	444 vs p	444 vs	443 vs	445 vs	447 vs	$\nu^s\text{TIC}$	A'	ν_3
	457		458 sh dp			454 dp	457 m	456 s	454 sh	455 m			
465 w dp	465 s									460 sh			
	468						466 m	465 s	475 sh	475 s	$r\text{CH}_3$		
	610 w br									610 vw br?			
	710 sh		720 sh	720 sh	727 s	655 w br dp		670 vw br			A''	ν_9	
	753 vs		755 s	745sbr	750vs	750 w br dp		760 vw br	750 vs	750 s	E'	ν_{15}	
									830 w		$\delta^s\text{HCH}$		
									860 w				
	1100 vw					1117 m br p	1105 s	1102 m	1107 w	1102 m	$\delta^{as}\text{HCH}$		
	1148 m	1146 s				1142 s p	1113 s	1111 m	1137 m	1114 m			
										1144 m	A'	ν_8	
										1445 vwbr?	E''	ν_{19}	
										2171	$2 \times 1102?$		
										2184 w	$2 \times 1112?$		
	2276 m								2247 w	2261 w	$2 \times 1140?$		
	2870 sh					2875 sh p				2854 vw	A'	ν_4	
	2931 s					2918 s p	2914	2914 w br	2902 m	2915 m br	A'	ν_1	
	2960 sh										νCH		
						2985 w dp	2995	2986 w br	2990 m	2986 m	E', E''	$\nu_{11}, \nu_{12}, \nu_{18}$	
	3023 m								2995 m	A'			ν_7

* ch = cyclohexane.

obtained the Raman spectra of the solid and of a concentrated solution in benzene. The spectra were still excited by a mercury lamp. This illumination led to rapid decomposition of the compound, so that only the most intense lines of the spectrum could be registered. No polarization measurements were reported. The most prominent features of the IR spectrum of a polycrystalline film, sprayed on at 77 K, were also given in Ref. [28]. Force field calculations for Me_3Tl and other methylthallium species and references to their vibrational spectra are presented in Ref. [26].

We have obtained the Raman spectra in the region $10\text{--}3700\text{ cm}^{-1}$ of Me_3Tl as a melt (with polarization measurements) and as a polycrystalline solid; the spectral region of the νTIC was also recorded for a solution in cyclohexane and for the gas. The IR spectra of a polycrystalline film ($400\text{--}3700\text{ cm}^{-1}$) and of the gas ($70\text{--}3700\text{ cm}^{-1}$) were registered. The IR spectra for a solution in cyclohexane and for a matrix-isolated sample were recorded only in the region $400\text{--}900\text{ cm}^{-1}$. The results are given in Table 4 (along with the data of Ref. [28]) and in Figs. 3–9.

As is seen from Table 4, the spectrum of Me_3Tl is characterized by the same salient features which made us suggest hindered rotation of the Me groups in the In analogue. In particular, two polarized bands are observed again in the $\delta^s\text{CH}_3$ region of the Raman spectrum of the melt, one of them at 1117 cm^{-1} being rather

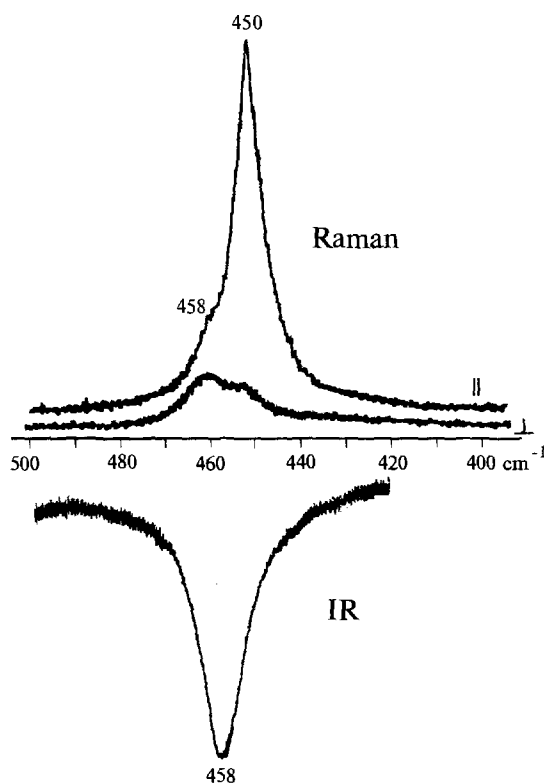


Fig. 7. Comparison of the νTIC region in the Raman and IR spectra of Me_3Tl in dilute solution in cyclohexane.

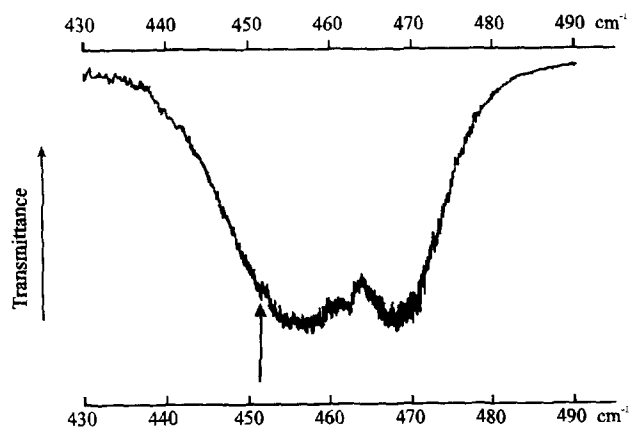


Fig. 8. The IR band corresponding to the degenerate νTIC stretching mode in the spectrum of gaseous Me_3Tl . The point where the band corresponding to the A' $\nu^s\text{TIC}$ mode could appear is marked with an arrow.

broad ($\Delta\nu_{1/2} \approx 40\text{ cm}^{-1}$, Fig. 3), but more narrow compared with the In analogue. As in the case of Me_3In , in spite of being polarized the band at 1117 cm^{-1} splits into two components on going to the crystalline state, as if belonging to an E' mode. Computer analysis of the νCH pattern in the Raman spectrum of the melt reveals the second polarized band at 2875 cm^{-1} in this region as well (Fig. 4(b)). In the case of Me_3Tl , the $\delta^s\text{CH}_3$ vibration at about 1440 cm^{-1} (ν_{19}) is not observed in the Raman spectrum, and could be detected only in the IR spectrum of the crystal as a very weak broad feature (if at all). That is why we are inclined to

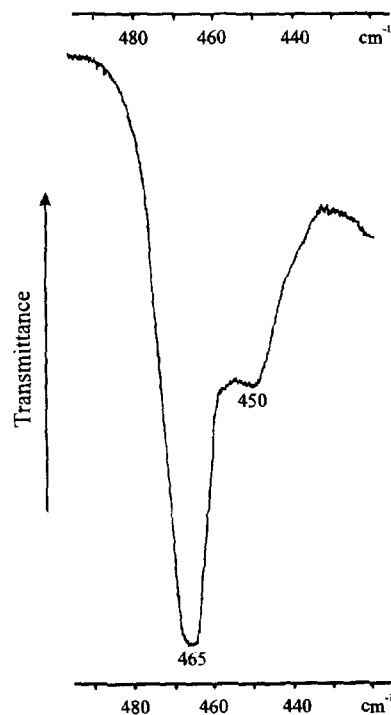


Fig. 9. The IR spectrum of matrix-isolated Me_3Tl in the region of the νTIC .

assign the polarized and broad band at 2875 cm^{-1} not as an overtone $2\nu_{19}$, but as a fundamental A' ν_4 .

In the low-frequency region of the Me_3Tl spectrum, we succeeded in observing both δTIC_3 deformation modes (IR band of the A' ν_{10} mode at 86 cm^{-1} and also the IR and Raman active E' ν_{17} mode at about 100 cm^{-1}). Additionally, as in the case of Me_3In , another low-frequency depolarized broad feature was detected in the Raman spectrum, its frequency being 55 cm^{-1} for the melt and 70 cm^{-1} for the crystal. It is readily assigned to the E'' methyl torsional mode. Its frequency lowering compared with that of Me_3In is in accord with the general trend of a decrease in the frequency of methyl torsional modes on going down in the Periodic Table, found by Durig et al. [21] for methyl compounds of elements of other groups.

However, the spectrum of Me_3Tl shows some properties which distinguish it from that of Me_3In . Primarily this concerns the νTIC region in the spectrum of the crystal. According to the X-ray data [27], the crystalline Me_3In and Me_3Tl are isostructural, both belonging to the space group $P4_2/n$ with $Z = 8$. The IR and Raman spectra of these solid substances in the region of the νMC are compared in Fig. 5. For both compounds, the splitting of the degenerate mode is observed. However, in contrast to Me_3In (see above), the totally symmetric νMC vibration of Me_3Tl shows itself in the IR spectrum as an intense band at 447 cm^{-1} , more intense than the bands corresponding to the components of the degenerate mode. Strictly speaking, in the crystal lattice, both Me_3M molecules in question occupy general positions, i.e. their site symmetry is C_1 , and all the vibrations should be active in both Raman and IR, so that the selection rules of a free molecule should not be obeyed. However, violation of the selection rule, which forbids the totally symmetric vibration of the planar skeleton to be active in the IR spectrum, is observed only for the crystalline Me_3Tl , in spite of the fact that both compounds are isostructural.

With this in mind, it was of interest to investigate the spectral region of the νTIC modes in solution and in the gas phase as well. The Raman spectrum of a diluted Me_3Tl solution in cyclohexane exhibits a very strong line at 450 cm^{-1} (Fig. 7). In the course of polarization measurements, two components can be resolved in this line: that at 450 cm^{-1} (polarized) and that at 458 cm^{-1} (depolarized). In the IR spectrum of this solution only one broad band at 458 cm^{-1} is observed, its profile exhibiting slight unresolvable asymmetry from the low-frequency side. The frequencies of the A' and E' νTIC modes being very close in value, it would be impossible to resolve them in the IR spectrum of the solution if both were present.

The same situation takes place in the spectrum of the gas. In the Raman spectrum of a gaseous TIC_3 sample, a very strong polarized line at 453 cm^{-1} was recorded,

a depolarized shoulder at 465 cm^{-1} is hardly distinguishable on its wing. In the IR spectrum of gaseous Me_3Tl , the band of the degenerate νMC mode consists of P and R branches (as in the case of Me_3In), the P branch having a complicated contour (Fig. 8). The Q branch of the totally symmetric νTIC mode, if present in the IR spectrum, would be superimposed on the P branch of the degenerate mode (in Fig. 8 this point is marked with an arrow). Thus, due to close spacing of the totally symmetric and degenerate νTIC modes, the spectra of the gas and of the solution do not give an unambiguous answer as to whether the totally symmetric νTIC mode is active in the IR absorption.

We also obtained the IR spectrum of Me_3Tl isolated in an argon matrix at 25 K (Fig. 9). Unlike matrix-isolated Me_3Ga [11], two bands at 450 and 465 cm^{-1} are observed in the νTIC region whose frequencies correspond to the A' and E' modes. However, this fact also cannot be regarded as decisive evidence of distortion of the planar TIC_3 skeleton, because we are not aware that our matrix was well-ordered and that the molecules of Me_3Tl were uniformly distributed in it. Both the disorder in the argon matrix itself and the possible association of the Me_3Tl molecules in it could lead to the observed violation of the selection rules [29].

Summing up the results obtained for Me_3Tl in the νTIC spectral region, and taking into account the data obtained previously for Et_3Tl (Fig. 1), we have to conclude that we have no decisive spectroscopic evidence of distortion of the planar TIC_3 skeleton, but the data obtained for the crystalline and matrix-isolated Me_3Tl and for the liquid Et_3Tl suggest such a possibility in condensed phases. This distortion, if it exists, could be explained by a pseudo-Jahn–Teller effect [30]. The absence of such an effect for Me_3Ga and Me_3In is understandable, taking into account that for them the energy difference between the ground and excited electronic levels is larger [31] than for Me_3Tl , polarizability values for Ga and In atoms being smaller than that for Tl. A possibility of distortion of the planar MR_3 skeleton in the case of $M = \text{Tl}$ was also assumed by Gillespie in terms of his VSERP conception [32].

2.3. On the problem of methyl group rotation in the series Me_3M ($M = \text{Ga}, \text{In}, \text{Tl}$)

Bearing in mind the above data on Me_3M ($M = \text{In}, \text{Tl}$) which served as a basis for the assumption of hindered methyl group rotation, we have revisited the Raman spectrum of liquid Me_3Ga , previously published in Ref. [9], then by us [4] and later by Durig and Chatterjee [10]. In the $\delta^s\text{CH}_3$ region, a sharp polarized line at 1198 cm^{-1} with a shoulder at 1180 cm^{-1} was observed, the latter was previously reported as depolarized. As a result of thorough re-investigation of this spectral region at room temperature, using narrow slits,

Table 5

M	ν_2 (cm^{-1})	ρ	$\Delta\nu_{1/2}$ (cm^{-1})	ν_5 (cm^{-1})	ρ	$\Delta\nu_{1/2}$ (cm^{-1})	Temperature
Ga	1198	0.2	10	1180	0.3	30	room
In	1156	0.2	15	1115	0.3	70	85°C
Tl	1140	0.2	20	1117	0.3	40	40°C

slow registration for better resolution and computer band analysis, we have found that the band at 1180 cm^{-1} is distinctly polarized with $\delta \approx 0.3$, as are its analogues in the Raman spectra of In and Tl congeners (Fig. 3). The half-width of this band is $\Delta\nu_{1/2} \approx 30\text{ cm}^{-1}$. Thus, we can now compare the data obtained for the $\delta^5\text{CH}_3$ region of the Raman spectra of the liquid Me_3M in the series $\text{M} = \text{Ga}, \text{In}, \text{Tl}$ (Table 5).

It is seen from Table 5 that the value of the depolarization ratio (estimated with an accuracy of ± 0.5) for ν_5 is the same for all three substances, which means that this is not an experimental error but a regularity. The same is true of band broadening, especially prominent in the case of Me_3In . However, at this point the different temperatures of the experiments should be taken into account.

Computer analysis of a complicated band profile in the νCH region of the Me_3Ga spectrum reveals a second polarized line at 2855 cm^{-1} . These facts suggest that the vibrations of Me_3Ga also obey the selection rules for C_{3h} rather than D_{3h} symmetry.

Thus, strange polarization data for a Raman band in the region of $\delta^5\text{CH}_3$, unusual broadening of some Raman bands corresponding to methyl group vibrations, and the presence in the low-frequency Raman spectra of a band corresponding to a methyl torsional mode made us presume low-barrier hindered methyl group rotation in the liquid and crystalline states.

However, if BMe_3 does exhibit free rotation of methyl groups, the reason for hindered rotation in its Ga, In and Tl congeners seems unclear. This situation calls for further experimental and theoretical refinement. In particular, temperature studies of the band widths are being planned.

3. Experimental

Me_3In and Me_3Tl are extremely unstable in air, that is why special care was taken in order to obtain pure samples and to prevent their decomposition during the process of spectral registration.

Me_3In and Me_3Tl were synthesized according to the methods of Refs. [33,34] respectively in an atmosphere of pure dry argon. The substances were sublimed in high vacuum (10^{-4} mm Hg) just before spectral measurements. To ascertain the purity of the samples during the spectral registration, the processes of slow decom-

position of Me_3In and Me_3Tl under addition of air traces were specially investigated by means of IR spectroscopy. During the process of registration of the IR spectra of gaseous samples, a weak band at 1306 cm^{-1} was found to appear, which corresponds to methane, formed as a result of partial thermodestruction or hydrolysis of Me_3M , in accordance with the data of Refs. [28,35].

The Raman spectra were scanned starting from $10\text{--}30\text{ cm}^{-1}$ (depending on the spectrometer used) using laser Raman spectrometers Coderg PHO, T-800, Ramanor HG-2S and U-1000 excited by different lines in the visible region of Ar^+ (CR-8) and krypton (SP-165) lasers. To obtain the spectra of the melts, the samples sealed in ampoules in vacuo were heated in a special cell slightly above the melting points (about 85°C for Me_3In [14] and 38.5°C for Me_3Tl [34]). The depolarization ratios ρ of the Raman lines were measured in the spectra of the melts. To check the accuracy of ρ values obtained, analogous measurements for standard liquids, benzene and CCl_4 , under the same conditions were performed.

IR spectra were run on Perkin–Elmer 457 and 180 spectrophotometers and a Fourier spectrometer Bruker IFS-113V. The band contours in the IR spectra of an Me_3Tl solution in cyclohexane and of gaseous samples were recorded using a Perkin–Elmer 180 with a resolution of better than 1 cm^{-1} . To obtain the IR spectra of crystalline samples, the compounds were allowed to sublime slowly onto a CsI target cooled to liquid nitrogen temperature in a vacuum cryostat. The solid samples were repeatedly annealed. The IR spectra of gases were obtained using a gas cell of 300 mm length equipped with KRS-5 or polyethylene windows; various vapour pressure values were applied.

The IR spectrum of Me_3Tl isolated in an argon matrix at 25 K (argon: Me_3Tl 100:1) was obtained using a cryosystem Displex 'Air products'.

Computer analysis of complicated band profiles was applied, allowing estimation of ρ and $\Delta\nu_{1/2}$ values of the Raman bands with an accuracy of ± 0.05 and $\pm 5\text{ cm}^{-1}$ respectively.

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