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Vibrational and electronic spectra of tetrahedral molecules $(Me_3M)_4M'$ ($M = Si, Sn$; $M' = Si, Ge$) with heteronuclear M–M′ bonds

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Abstract

Raman, infrared and UV spectra of tetrahedral molecules $(Me_3Si)_4Ge$ (**I**), $(Me_3Sn)_4Ge$ (**II**), and $(Me_3Sn)_4Si$ (**III**) were obtained. To assign and analyze vibrational modes, model normal coordinate calculations for $(C_3M)_4M'$ moieties were carried out. Stretching vibrations of heteronuclear tetrahedra M_4M' were studied comparatively. Solid substances **I**–**III** were found to undergo an order–disorder phase transition between an ordered crystalline phase and a plastic mesophase (**II** and **III** on heating to ca. 65°C while **I** on cooling to ca. −45°C). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silyl- and stannyl-substituted silanes and germanes; Raman, IR, UV spectra; Tetrahedral symmetry; Phase transition

1. Introduction

Compounds of the type $(R_3M)_4M'$ ($M, M' = Si, Ge, Sn$) are of great interest because of their unique structure and synthetic applications as well as implications for Group 14 element-based electronic materials. The compounds of the type $(Me_3Si)_4M$ ($M = Si, Ge, Sn$) with trimethylsilyl outer shells were first synthesized in the late 1960s [1,2]; the syntheses of silanes $(Me_3Sn)_4Si$ and $(Me_3Ge)_4Si$ were reported in Refs. [3–5]. Of these organometallics, the sterically overcrowded molecule $(Me_3Si)_4Si$ is the most studied from the point of view of its chemical and physico-chemical properties as well as potential applications in novel synthesis and material chemistry [1,6–11]. Probable conformations of $(Me_3Si)_4Si$ were computed in Ref. [12] on the basis of empirical force field. Molecular structures of $(Me_3M)_4M'$ have been intensively studied (mostly using $(Me_3Si)_4Si$ as an example) by means of ^{13}C- [13,14] and ^{29}Si- [14] NMR, photoelectron [15] and electron transmission [16] spectroscopy as well as by electron diffraction [17] and X-ray crystallography [18–20]. The molecules of $(Me_3Si)_4Si$ and $(Me_3Si)_4Ge$ appear to be almost ideal spheres with a high tetrahedral symmetry of the heavy skeleton and a gearwheel arrangement of methyl groups.

Important information concerning the molecular structure of $(Me_3Si)_4M'$ ($M' = C, Si, Ge, Sn$) was obtained from the study of their vibrational spectra [21–23]. However, vibrational spectra of $(Me_3M)_4M'$ with M other then Si are not published with the exception of $(Me_3Sn)_4Si$ whose IR spectrum was briefly reported [4]. Electron diffraction and vibrational spectroscopic data of a related compound $(H_3Si)_4Ge$ have been reported [24], and the Si–Ge bond stretching frequency and force constant for H_3Si–GeH_3 are also available [25].

We now report a detailed study of the vibrational (IR, Raman) and electronic spectra of $(Me_3Si)_4Ge$ (**I**), $(Me_3Sn)_4Ge$ (**II**), and $(Me_3Sn)_4Si$ (**III**), the compound **II** being synthesized for the first time.

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2. Results and discussion

2.1. Vibrational spectra

Our investigation of the vibrational spectra of **I**–**III** concentrated upon two areas:

1. Since the molecules studied are highly symmetric and also include metal atoms with high polarizability, a pseudo-Jahn–Teller effect [26] may be anticipated, which could lead to effective symmetry lowering. Hence, it is interesting to elucidate the molecular symmetry in condensed phases by determining the selection rules operating in vibrational spectra.
2. Compounds **I**–**III** can be considered as ‘globular’ molecules, using Timmermans criterion [27], therefore the substances can form plastic (or ‘rotatory’) mesophases with reorientational disorder and exhibit solid-state phase transitions of an order–disorder type. Such a phase transition has been determined for $(Me_3Si)_4Si$ at 238–241 K by differential scanning calorimetry (DSC) [28] and solid-state NMR [14]. With this in mind, we have undertaken variable-temperature Raman investigation of compounds **I**–**III**, the latter method being a very informative in this respect, as described previously [29].

The Raman spectra of the solid samples were recorded at various temperatures in the range 10–3700 cm^{-1}. Depolarization ratios (ρ) of the Raman lines were estimated qualitatively for solutions of **I**–**III** in benzene. IR spectra of solid samples were obtained in the range 80–3700 cm^{-1}. To analyze the normal modes, some model normal coordinate calculations were carried out for the heavy atom skeletons $(C_3M)_4M'$. The results are given in Tables 1–3.

Ignoring C–H bonds and their vibrations, the $(C_3M)_4M'$ moiety possesses $3 \times 17 - 6 = 45$ fundamentals. Assuming a T_d symmetry point group, these fundamentals are broken down into the following symmetry species:

$$\Gamma = 3A_1 + A_2 + 4E + 4F_1 + 7F_2$$

Table 1
Distribution of internal coordinates of $(C_3M)_4M'$ moiety among the symmetry species of the T_d group

Internal coordinate	Designation	Symmetry species				
		A_1	A_2	E	F_1	F_2
$\nu_{MM'}$	Q	1	–	–	–	1
$\delta_{MM'M}$	α	–	–	1	–	1
ν_{MC}	q	1	–	1	1	2
$\delta_{M'MC}$	β	–	–	1	1	1
δ_{CMC}	γ	1	–	1	1	2
MC_3 tors	τ	–	1	–	1	–

The A_1 and E species are only Raman-active, giving rise to polarized and depolarized lines, respectively, while the F_2 species are active both in the IR and Raman spectra, giving rise to depolarized Raman lines. The A_2 and F_1 species are silent. From these, the A_2 and one of the F_1 modes are low-frequency torsions of the MC_3 groups. Internal coordinates are depicted in Fig. 1, and the distribution of internal coordinates among the symmetry species is given in Table 1. In particular, the stretching vibrations of the heteronuclear tetrahedron M_4M' ($\nu MM'$) belong to the A_1 and F_2 species, only the latter being IR-active, while skeleton deformations $\delta MM'M$ belong to the E and F_2 species.

Model normal coordinate analyses (NCA) for $(C_3M)_4M'$ skeletons were performed with variation of the force constants within reasonable limits. Initial force fields were built up on the basis of corresponding data for related molecules of the types $(R_3Si)_4M'$ [23,24], $R_3M–M'R_3$ [25,30], and Me_3MX [31,32] The calculations were not intended to determine exact force constant values. The aim was to analyze mode eigenvectors and their dependence on the force constant variation and also to predict mutual disposition of vibrational frequencies of different symmetry species. In particular, NCA results have shown that the frequencies of the $\delta MM'M$ modes should lie below 100 cm^{-1}. Also, these calculations predict that the νMC stretching vibrations which participate in the A_1, E, F_1 and $2F_2$ species should exhibit only two real spectral bands, because the frequencies of the A_1 and one of the F_2 modes nearly coincide as well as do those of the E, F_1 and the second F_2 modes.

With respect to the methyl groups attached to metal atoms, one may expect, in accordance with the vast experience of vibrational spectroscopy of organometallics, that their internal vibrations would obey their local C_{3v} symmetry.

2.1.1. $(Me_3Si)_4Ge$ (*I*)

The spectra obtained are given in Fig. 2 and Table 2 along with some published data [23], the latter being in good agreement with our solid-state results. The polarization data for the solution Raman spectra are presented for the first time.

Band assignment is based on the band activities and intensities, on the depolarization ratio values, as well as on NCA results and comparison with the well-assigned spectra of related molecules containing Me_3Si group [23,30–32] and Si–Ge bond [24,25]. The spectral features with frequencies above 700 cm^{-1} belong to the methyl group vibrations, and their assignment is straightforward.

As expected, only two spectral features corresponding to the νSiC modes are observed. One of them, at 625 cm^{-1}, manifests itself as a very intense polarized Raman band but also having an IR counterpart. It is

Table 2
Vibrational spectrum of $(Me_3Si)_4Ge$

Raman			IR			Assignment		PED (%)
[23]	Solid, room temp.	Solution in benz.	[23]	Solid	Solution in benz. [a]			
68 m	73 m b			72 w?		E	δSiGeSi	90 α
	83 sh		89 w			F_2		88 α
170 vs	173 vvs	171 vs p	170 w sh	–	–	A_1	δCSiC	44 γ, 34 β,20 Q
202 w	206 w	204 sh dp	213 vs	206 s	208 s	F_2		47 γ, 48 β
	224 w	226 w dp	–	–	–	E		96 γ
243 w	239 w	241 w dp	240 m	241 w	–	F_2		92 γ
319 vs	325 s	324 s p	–	–	–	A_1	νGeSi	61 Q, 18 γ
357 m	357 m	355 m dp	360 vs	356 s	355 s	F_2		79 Q
626 vs	629 vs	627 m p	622 s	620 s		A_1 F_2	νSiC	89 q
	647 sh					2×325		
685 s	688 s	687 m dp	690 m	688 s		E,F_2	νSiC	97 q
744 w	746 w	746 w dp	748 m	746 m			ρCH_3	
835 w b	840 w b	841 wdp	839 vvs	837 vs b				
875 w	877 w	877 w p						
1241 w	1244 w	1244 w dp	1248 vs	1246 s			$\delta^s CH_3$	
1260 vw	1264 w	1264 w p	1259 m	1257 m				
				1304w		620+688		
1402 w	1408 w b		1398 m	1394 mw			$\delta^{as} CH_3$	
1439 vw	1442 vw b		1443 w	1440 w				
2892 vs	2898 m		2899 m	2896 m			$\nu^s CH_3$	
2949 vs	2953 m b		2953 m	2950 ms			$\nu^{as} CH_3$	

[a] Only the region 100–400 cm^{-1} was investigated.

evident that this feature is formed by the A_1 and F_2 modes with close frequencies. Another νSiC band at 688 cm^{-1} (depolarized Raman line, also active in IR) is due to coinciding modes of the E and F_2 species. The deformational δCSiC modes are situated in the region 170–250 cm^{-1} and are easily assigned on the basis of their activity and polarization (A_1 171, F_2 205, E 225, F_2 240 cm^{-1}; see Table 2). This assignment agrees well with the NCA predictions.

The stretching vibrations of the Si_4Ge backbone, νSiGe, manifest themselves as a strong polarized Raman band at 325 cm^{-1} having no IR counterpart (A_1) and a depolarized band at 355 cm^{-1} which is intense both in IR and Raman (F_2). Thus, the selection rules of the T_d symmetry group in the spectrum of **I** are strictly obeyed, which indicates a non-distorted tetrahedral skeleton of the molecule in the solid state at room temperature. The X-ray data for this molecule [19] also showed ideal T_d symmetry in the solid state; however, the latter data were obtained at 153 K and not for a pure substance but for its THF solvate. Electron diffraction data for a related molecule $(H_3Si)_4Ge$ also pointed to T_d symmetry with free rotation of the H_3Si groups in the gas phase [24].

NCA results show that in the A_1 modes at 325 and 171 cm^{-1}, the νSiGe and the δCSiC coordinates are mixed to some extent, the degree of mixing varying noticeably with the force constants used. However, the

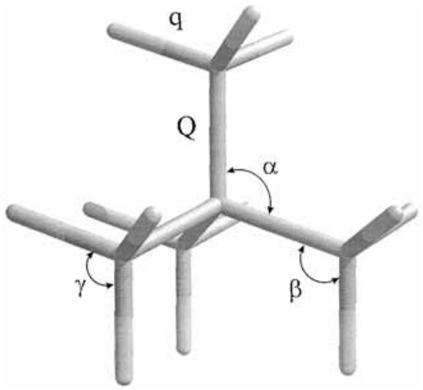


Fig. 1. Designation of internal vibrational coordinates of $(C_3M)_4M'$ moiety.

Table 3
Vibrational spectra of $(Me_3Sn)_4Ge$ and $(Me_3Sn)_4Si$ [a]

$(Me_3Sn)_4Ge$					$(Me_3Sn)_4Si$					Band assignment	PED,%
Raman			IR		Raman			IR			
Solid		Solution in benz.	Solid	Solution in benz. [b]	Solid		Solution in benz.	Solid	Solution in benz.		
Room temp.	+70°C				Room temp.	+70°C					
18 vw?										Lattice mode?	
35 vw					34 vw						
55 m	44 m b				56 m	46 m b		59?		E,F$_2$ δSnM′Sn	96 α
65 sh					66 sh						93 α
			115 vw	116 vvw	117 sh			118 w	118 vw	E, F$_2$ δM′SnC?	80 β
			120 vw	–				125 vw		F?	
122 s	118 m			–	125 s	117 s	117 p		–	A$_1$ νM′Sn	65 Q, γ, β
150 mw	148 m		146 m	145 m	153 w	150 m	149 dp	147 m	148 m	E, F$_2$ δCSnC	95 γ
168 w b	–				171 w	–				A$_1$?	
247 m	246 m b	246 dp	245 m		369 m	367 m	368 dp	367 m		F$_2$ νM′Sn	85 Q
505 vs	504 vs	507 p	498 s		505 vs	507 vs	507 p	498 s		A$_1$, F$_2$ νSnC	99 γ
519 vs	518 s	520 dp	517 vs		518 s	518 s	519 dp	517 vs		E, F$_2$	99 γ
770 vw b			752 vs b		770 vvw b			757 vvs b		ρCH_3	
1177 sh			1180 m		1177 sh			1179 m			
1185 sh			1188 w		1184 sh		1182 p	1186 sh		$\delta^{s}CH_3$	
1190 m		1189 p	–		1190 ms						
1418 vw b			1423 vw b		1420 vw b					$\delta^{as}CH_3$	
2911 m			2908 m		2910 s		2909 p	2913 s		$\nu^{s}CH_3$	
2982 m			2978 m		2982 m b		2978 dp	2983 ms		$\nu^{as}CH_3$	

[a] s, Strong; m, medium; w, weak; b, broad; sh, shoulder.

[b] Only the region 80–200 cm^{-1} was measured.

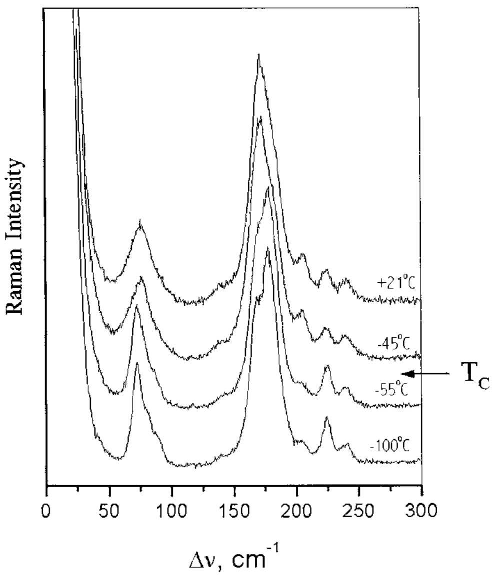


Fig. 2. Variable-temperature Raman spectra of solid $(Me_3Si)_4Ge$. Note slight changes between −45 and −55°C.

contribution from the νSiGe coordinates to the mode at 325 cm^{-1} is always predominant. The mainly stretching character of the mode at 325 cm^{-1}, and mainly deformational character of the mode at 171 cm^{-1}, is evidenced by the polarization data for the corresponding Raman lines, which are $\rho \approx 0.01$ and 0.5, respectively. The remaining modes of the $(C_3Si)_4Ge$ moiety are well localized (see Table 2, where PED data are presented).

The νSiGe frequencies found for **I** lie in the same region as that reported for $H_3Si–GeH_3$ (312 cm^{-1}) [25].

At room temperature we succeeded in observing only one low-frequency feature corresponding to the deformational mode of the Si_4Ge tetrahedron, namely, a broad Raman band at 73 cm^{-1}. However, in the spectrum obtained at lower temperature (see Fig. 2), due to band narrowing, a shoulder at ca. 85 cm^{-1} becomes noticeable whose frequency is close to that of the IR band at 89 cm^{-1} reported in [23]. A similar frequency (84 cm^{-1}) was mentioned for $(H_3Si)_4Ge$ in [24]. Unfortunately, we were unable to obtain unambiguous data for the weak IR bands below 100 cm^{-1}, the value 72 cm^{-1} given in Table 2 being approximate. Thus, we cannot choose between the E and F_2 δSiGeSi modes.

The only feature not identified experimentally is the degenerate δGeSiC mode, predicted by NCA to lie in the region 145 cm^{-1}.

2.1.2. $(Me_3Sn)_4Ge$ (II) and $(Me_3Sn)_4Si$ (III)

Vibrational spectra of **II** and **III** are reported for the first time (Figs. 3(a and b); Table 3). As expected, the two spectra are very much alike, because in both molecules the central atom is surrounded by four Me_3Sn groups. The vibrations of the latter are readily assigned on the basis of comparison with the well-interpreted spectra of $Me_3Sn–SnMe_3$ [30] and Me_3SnX, X = Cl, Br [32]. As for **I**, only two spectral features corresponding to the stretching vibrations of the M–C bonds (νSnC in this case) are observed, those at ca. 505 and 520 cm^{-1} with the same frequencies for both molecules. All the degenerate δCSnC modes seem to merge into one feature at ca. 150 cm^{-1}, which is observed in both Raman and IR spectra.

The only significant difference between the vibrational spectra of **II** and **III** is the frequency of a depolarized Raman line of medium intensity to which a strong IR band corresponds (245 cm^{-1} for **II**, 366 cm^{-1} for **III**). This feature evidently corresponds to the

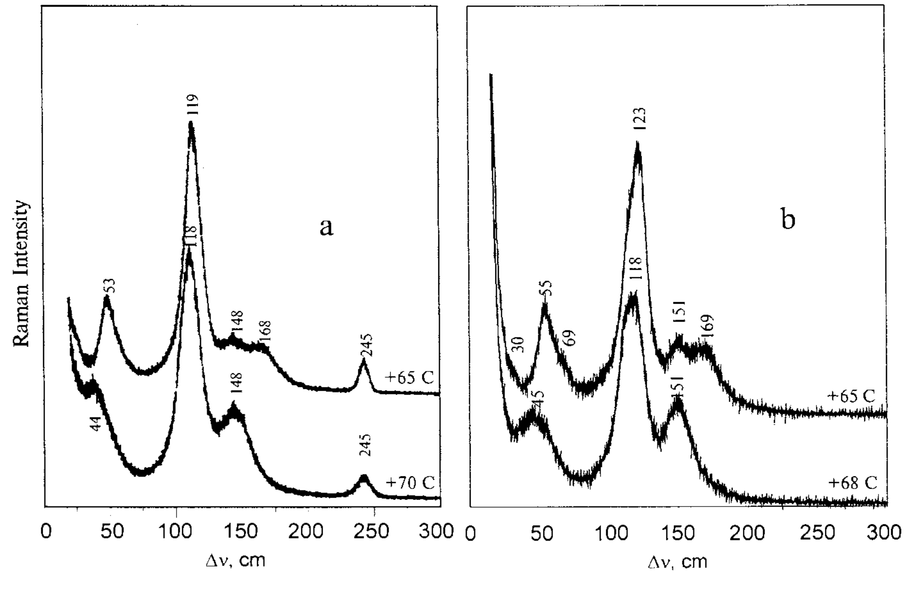


Fig. 3. Manifestation of order–disorder phase transitions in the Raman spectra of solid $(Me_3Sn)_4Ge$ (a) and $(Me_3Sn)_4Si$ (b).

triply degenerate F_2 $\nu SnM'$ mode. The totally symmetric A_1 $\nu SnM'$ mode manifests itself as a very intense polarized Raman line with nearly the same frequencies for both molecules (122 cm^{-1} for **II**, 125 cm^{-1} for **III**; NCA predicts 125 cm^{-1} for **II** and 128 cm^{-1} for **III**.). This vibration is somewhat mixed with deformations of the angles around the SnC_3 groups, but the contribution from the $\nu SnM'$ coordinates is predominant (not less than 60% in PED). It is notable that this band has no IR counterpart in the spectra of solutions, indicating a tetrahedral symmetry of the Sn_4M' skeleton. However, in the IR spectra of solid **II** and **III** a very weak band at ca. 120 cm^{-1} could be seen, pointing to a slight symmetry lowering in the crystal field. If this weak feature were the IR counterpart of the A_1 $\nu SnM'$ Raman line, this would mean that the site symmetry of the molecules in the crystal field is significantly lowered compared to the tetrahedral symmetry in solution (probably, to S_4, or C_{3v}). However, if this were the case, we should also observe a splitting of the band corresponding to the F_2 $\nu SnM'$ mode in the spectra of crystalline samples, but this is not seen. The more probable explanation of this very weak IR band at ca. 120 cm^{-1} present in the spectra of ordered crystals seems to be a symmetry lowering from T_d to T group (Section 2.1.4) which leads to transformation of the silent F_1 species into active F species. The frequency of the F_1 $\delta M'SnC$ mode was computed by NCA to be just in this region. In accord, weak IR bands at ca. 115 cm^{-1} observed for **II** and **III** in both solution and solid state could be assigned to the degenerate F_2 $\delta M'SnC$ mode.

Deformations of the Sn_4M' tetrahedra should be situated below 100 cm^{-1}; NCA predicts them at ca. 30 cm^{-1} (E) and ca. 40 cm^{-1} (F_2). Weak Raman bands at 35 and 55 cm^{-1} are observed for both compounds. However, the line at ca. 30 cm^{-1} could also belong to a lattice vibration.

The Raman spectra of compounds **II** and **III** differ dramatically from that of **I**. Unlike compound **I**, only one (instead of two) intense polarized Raman band is seen in the low-frequency region which presents somewhat of a puzzlement. The second A_1 mode of **II** and **III**, involving mainly $\delta CSnC$ and $\delta M'SnC$ deformations, was computed to lie at ca. 170 cm^{-1}. Indeed, there is a weak Raman band in this region (at 168 cm^{-1} for **III** and 171 cm^{-1} for **II**), not active in IR, but this band disappears when the substances transform to plastic mesophases (see below).

2.1.3. Comparison of the stretching vibrations of the skeletons M_4M'

Our results coupled with published data [23] allow us to examine the spectra of four tetrahedral molecules of the type $(Me_3M)_4M'$ with heteronuclear M–M′ bonds as a group. The frequencies of the stretching vibrations of the M_4M' skeletons are compared below:

	Si_4Ge (**I**)	Si_4Sn (**IV**) [23]	Sn_4Si (**III**)	Sn_4Ge (**II**)
A_1	324	311	125	120
F_2	356	328	368	246

The central atom M′ does not move during the totally symmetric A_1 stretching vibration, and hence the frequency of the latter does not depend on the mass of M′, but only on the mass of M. Thus, these frequencies are close for **I** and **IV** (M = Si) and for **II** and **III** (M = Sn). However, in the molecules **I** and **IV** the central atom M′ is heavier than the outers, while in the molecules **II** and **III** it is lighter, therefore the mechanism of the F_2 vibration is different for these two pairs of molecules. For the second pair, it is the more light central atom which mainly moves inside the tetrahedron formed by the heavier Sn atoms. Thus, the frequency of the F_2 mode in case of **II** and **III**, in contrast to **I** and **IV**, is strongly affected by the mass of M′ and strongly differs from that of the A_1 mode.

A most entertaining result of our study concerns the two tetrahedra Si_4Sn and Sn_4Si, both containing Si–Sn bonds but exhibiting quite different frequencies for the A_1 stretching mode. This is a spectacular illustration of how misleading it can sometimes be to speculate about the given bond nature from its vibrational frequency.

2.1.4. Phase transitions in **I–III**

As mentioned above, the molecules studied are typical representatives of the so-called ‘globular molecules’ [27], which usually form plastic mesophases whose characteristic feature is dynamic orientational disorder [33,34]. For a related molecule $(Me_3Si)_4Si$, a phase transition of an order–disorder type from a plastic mesophase to an ordered crystal on cooling the sample to ca. −35°C was first found by DSC [28] and later confirmed by solid-state ^{13}C- and ^{29}Si-NMR [14].

In contrast, we have found that the substances **II** and **III** undergo a phase transition on heating; namely, at 63–65°C for **II** and at 65–68°C for **III**. The transition manifests itself in the Raman spectra of both substances quite similarly (see Figs. 3(a and b). Abrupt changes in frequency values and band broadening are clearly seen. Especially noticeable is a broadening of the line at 369 cm^{-1} for **III** (from 7 to 17 cm^{-1}; Fig. 4 shows an expanded view of this region).

Such an effect is typical for depolarized Raman lines and is due to dynamic orientational disorder in the plastic mesophase. Quite unexpected was the disappearance of the band at about 170 cm^{-1} in the spectra of both **II** and **III** in going to a plastic state (Fig. 3). We have no definite explanation yet for this fact, but since the region 150–170 cm^{-1} is characteristic of the $\delta CSnC$ vibrations, it is reasonable to assume that the

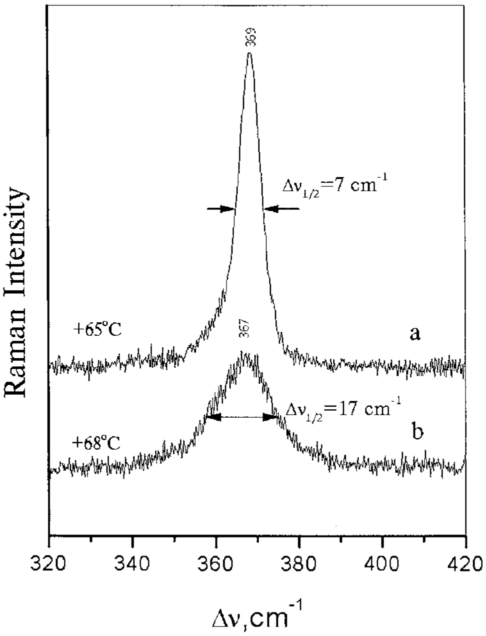


Fig. 4. Band broadening of the F_2 νSi–Sn mode in the Raman spectrum of solid $(Me_3Sn)_4Si$ in going to a plastic state. (a) 65°C; (b) 68°C; $\Delta\nu_{1/2}$, full width at half height, cm^{-1}.

phase transition found involves not only 'defreezing' of orientational degrees of freedom, but also some changes in SnC_3 conformations. Analogous phase transition involving simultaneous 'defreezing' of orientational and conformational degrees of freedom in going to a plastic state was found previously for dodecamethylcyclohexasilane $(Me_2Si)_6$ [35]. It cannot be excluded that at room temperature the methyl groups in the molecules **II** and **III** are disposed in a gearwheel fashion (in analogy with the X-ray data for crystalline $(Me_3Si)_4Si$ [18] and **I** [19]), the overall molecular symmetry group being *T*, whereas in the plastic state large-amplitude torsions or free rotation of these groups occur, in analogy with electron diffraction data for gaseous $(Me_3Si)_4Si$ [17] and $(H_3Si)_4Ge$ [24], thus leading to a higher effective symmetry T_d.

The close values of the phase transition temperatures for **II** and **III**, whose molecules have similar outer shells, suggest that the phase transition for **I** should be observed near that for $(Me_3Si)_4Si$, namely, on cooling to ca. −40°C. Indeed, we have observed some changes in the Raman spectrum of **I** at ca. −50°C (see Fig. 2), similar to those for **II** and **III,** related also to the skeleton and C_3M group deformational modes. In particular, an abrupt small frequency shift and narrowing of the low-frequency band at 73 cm^{-1} are observed, and a shoulder at 83 cm^{-1} becomes more pronounced. An intensity redistribution between the weak bands at 206 and 224 cm^{-1} is also seen. However, these changes are not as spectacular as for **II** and **III**. That is why we have confirmed the phase transition of **I,** using the DSC method, which exhibited an endotherm at ca. −45°C.

Thus, at room temperature the solid substances $(Me_3Si)_4Si$ and **I** exist as plastic mesophases while **II** and **III** as ordered crystals. The latter substances transform to a plastically crystalline state on heating. The nature of inter- and intra-molecular dynamics of **I–III** calls for more detailed investigation and will be the subject of a future paper [36].

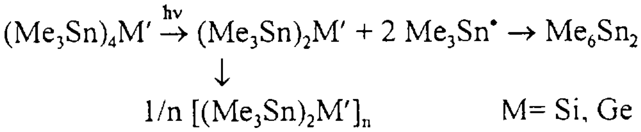
2.2. Electronic spectra

As early as 1966, one of us (O.M.N.) with P.P. Shorygin et al. published the electronic spectra of simple saturated compounds containing one or several atoms of Group 14, such as MR_4, $R_3M–MR_3$, $R[MR_2]_nR$ with *n* from 3 to 6–8 [37]. The authors noted a red shift of the UV band corresponding to the first electronic transition in the series of compounds MR_4 where M = C, Si, Ge, Sn; R = Alk. These bands were assigned to excitation of valence electrons of σ-bonds. For compounds with several adjacent M atoms, the lowest-energy transition showed a red shift with increasing chain length. This effect became more and more pronounced in the series Si < Ge < Sn and was explained by interaction of adjacent M–M σ-bonds. The authors found an analogy between the UV spectra of the compounds with $[M–M]_n$ chains and of the π-conjugated polyenes. Similar results, obtained in 1964 by Gilman et al. [38] for permethylated oligosilanes and later by other authors for polygermanes and polystannanes [39], prompted formation of the σ–σ conjugation concept that is now generally accepted. As the molecules **I–III** contain a skeleton of metal–metal bonds, and thus are, in principle, capable of σ–σ conjugation, it is of interest to measure their electronic spectra.

The results obtained for the lowest-energy transition along with literature data for $(Me_3Sn)_4Sn$ [40] are given below:

	$(Me_3Si)_4Ge$	$(Me_3Sn)_4Si$	$(Me_3Sn)_4Ge$	$(Me_3Sn)_4Sn$ [40]
λ_{max} (nm)	<200	222	238	277
(ε)		(72 000)	(63 000)	(79 000)

Compound **I** does not exhibit UV absorption above 200 nm. In the series $(Me_3Sn)_4M'$, an expected red shift is observed with increase in polarizability of the M′ atom. These data are in accord with photosensitivity of these compounds towards UV irradiation. Thus, **I** does not photolyze upon irradiation with the light of a high-pressure Hg lamp (in cyclohexane solution), whereas compounds **II** and **III** easily decompose under the same conditions to produce Me_6Sn_2 and polymeric materials according to the following scheme:



$$\begin{tikzcd}(Me_3Sn)_4M' \arrow[r, "h\nu"] & (Me_3Sn)_2M' \arrow[d] + 2\ Me_3Sn^{\bullet} \arrow[r] & Me_6Sn_2 \\ & 1/n\ [(Me_3Sn)_2M']_n & M = Si, Ge\end{tikzcd}$$

3. Experimental

All reactions were carried out under Ar atmospheres in flame-dried glassware using Schlenk techniques. The solvents were purified according to conventional methods: THF was distilled from sodium benzophenone-ketyl immediately prior to use, hexane was distilled from $LiAlH_4$. Me_3SiCl, Me_3SnCl, $SiCl_4$ and $GeCl_4$ were freshly distilled under an Ar atmosphere before using. $(Me_3Si)_4Ge$ was obtained by the reaction of $GeCl_4$ with Li in the presence of Me_3SiCl in THF according to [2]. Elemental analyses were performed by the Analytical Laboratory of N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

3.1. Synthesis of tetrakis(trimethylstannyl)germane $(Me_3Sn)_4Ge$ (III)

A solution of 20 g (100 mmol) Me_3SnCl in 50 ml of dry THF was added dropwise with stirring at 0°C to a mixture of 2.8 g (400 mmol) Li in 75 ml of dry THF. After the addition was completed the reaction mixture was stirred for additional 3 h at 0°C and then filtered off. A dark-green filtrate was added dropwise with stirring at −50°C to a solution of 5.36 g (25 mmol) $GeCl_4$ in 10 ml of dry THF. Reaction mixture was stirred for 1 h at −50°C and for 1 h at room temperature. After hydrolysis with 10% HCl, the organic layer was separated, and the water layer was extracted with ether. The combined organic phases were dried over $MgSO_4$ and evaporated almost completely. The product was separated from this residue after treatment with 10 ml of 96% EtOH and finally purified by vacuum sublimation giving **III** as white crystals (5.4 g, 30%). ^{1}H-NMR (C_6D_6): δ 0.39 (s, 36H, CH_3; $J_{^1H-^{119}Sn} = 49.42$ Hz, $J_{^1H-^{117}Sn} = 47.55$ Hz, $J_{^1H-^{13}C} = 127.58$ Hz). ^{13}C-NMR (C_6D_6): $\delta - 5.98$ (s, $J_{^{13}C-^{119}Sn}$ and $J_{^{13}C-^{117}Sn} = 256.65$ Hz). ^{119}Sn-NMR (C_6D_6): δ -28.40 (s, $J_{^{119}Sn-^{13}C} = 257.91$ Hz, $J_{^{119}Sn-^{119}Sn} = 42.43$ Hz). MS (*m*/*e*): 733 [M^+], 568 [M^+–Me_3Sn]. Anal. Calc. for $C_{12}H_{36}GeSn_4$: C, 19.87; H, 5.14; Ge, 10.04; Sn, 65.65. Found: C, 19.87; H, 4.97; Ge, 10.02; Sn, 65.14.

3.2. Synthesis of tetrakis(trimethylstannyl)silane $(Me_3Sn)_4Si$ (III)

Compound **III** was obtained according to a similar procedure from 20 g (100 mmol) Me_3SnCl in 50 ml THF, 2.8 g (400 mmol) Li in 75 ml THF and 25 g (146 mmol) $SiCl_4$ in 10 ml of dry THF. The product obtained was purified by vacuum sublimation giving **III** as white crystals (3.9 g, 23%). ^{1}H-NMR (C_6D_6): δ 0.36 (s, 36H, CH_3, $J_{^1H-^{119}Sn} = 49.45$ Hz, $J_{^1H-^{117}Sn} = 47.41$ Hz, $J_{^1H-^{13}C} = 128.08$ Hz). ^{13}C-NMR (C_6D_6): δ -6.77 (s, $J_{^{13}C-^{119}Sn} = 264.55$ Hz, $J_{^{13}C-^{117}Sn} = 252.92$ Hz). ^{119}Sn-NMR (C_6D_6): δ -37.35 (s, $J_{^{119}Sn-^{13}C} = 264.97$ Hz, $J_{^{119}Sn-^{119}Sn} = 33.69$ Hz). MS (*m*/*e*): 688 [M^+], 523 [M^+–Me_3Sn]. Anal. Calc. for $C_{12}H_{36}SiSn_4$: C, 21.25; H, 5.33; Si, 4.12; Sn, 69.58. Found: C, 21.18; H, 5.29; Si, 4.12; Sn, 69.41.

3.3. Spectroscopy

Mass spectra were recorded on a Varian MAT CH6 instrument with electron impact ionization at 70 eV.

^{1}H-NMR spectra were recorded on Jeol FX90Q (90 MHz), Bruker AC200 (200 MHz) and Bruker AM300 (300 MHz) spectrometers; ^{13}C-NMR spectra on Bruker WM250 (62.90 MHz) and Bruker AM300 (75.47 MHz); ^{119}Sn-NMR spectra on Bruker AM300 (111.87 MHz) spectrometers.

Raman spectra were obtained for solid samples and for saturated solutions in benzene in the region 10–3600 cm^{-1} using a Ramanor HG-2S, a U-1000 and a T64000 Jobin–Yvon laser Raman spectrometers with 514.5 nm excitation (an Ar^+ laser, Spectra Physics 2020). IR spectra were recorded using a Bruker IFS-113v and Carl Zeiss M-82 spectrophotometers in the region 80–3600 cm^{-1}.

UV spectra of hexane solutions of compounds **I**–**III** were recorded with a Carl Zeiss M-40 spectrophotometer.

Normal coordinate calculations were performed using a set of computer programs elaborated by Gribov and Dement'ev and described in Ref. [41].

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