104. *Raman Spectra of the Hexamethyl Compounds of Silicon, Germanium, and Tin.*

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Raman frequencies for hexamethyl compounds of silicon, germanium and tin are reported, and those for hexamethyldisilane are compared with previous values. Eight-atomic, ethane-like structures are assumed, with each methyl group acting as a single particle, and the strongly polarised Raman bands occurring in the region of skeletal vibrations are assigned to the A_1 modes. Results of simple valence force field calculations, and comparison with similar calculations for corresponding tetramethyl compounds, indicate that this approach is useful for hexamethyl compounds of germanium and tin, but is not applicable to hexamethyldisilane. Bond stretching force constants of $1{\cdot}3 \pm 0{\cdot}1$ and $1{\cdot}0 \pm 0{\cdot}1 \times 10^5$ dynes/cm. are obtained for the Ge–Ge and Sn–Sn bonds respectively.

THE hexamethyl compounds [1] are the simplest, and therefore the most convenient, organometallic compounds of the type R_6M_2 (where M = silicon, germanium, or tin) for spectroscopic study. Only the spectra of hexamethyldisilane have previously been published; Murata and Kumada [2] report the Raman spectrum; Cerato, Lauer, and Beachell [3] report both Raman and infrared spectra; and an assignment and calculation of skeletal vibrational frequencies is reported by Murata and Shimizu.[4]

If we assume that the interaction between C–H and skeletal vibrations is negligible, we can treat methyl groups as single particles, and consider the molecules as eight-atomic, ethane-like structures of D_{3d} (staggered), D_{3h} (eclipsed), or $D_{3h'}$ (free rotation) symmetry types. In each case there are three symmetrical vibrational modes of type A_1 (on the notation of the $D_{3h'}$ model) associated with polarised Raman bands, and these are the only polarised Raman bands predicted for molecules of this symmetry.[5] We observe three polarised bands in the region of skeletal frequencies ($\nu < 700$ cm.$^{-1}$) in the spectrum of each of the three hexamethyl compounds, and we assign the observed frequencies to the A_1 skeletal modes of vibration.

Force constants have been calculated, by assuming a simple valence bond force field of the type used by Howard [6] for ethane; the M–CH_3 stretching (K_1), M–CH_3 bending (K_2), and M–M (K_3) stretching force constants can be obtained from an equation involving the A_1 vibration frequencies and the masses of M and of the CH_3 group. The validity of this

[1] Brown and Fowles, *J.*, 1958, 2811.

[2] Murata and Kumada, *J. Chem. Phys.*, 1953, **21**, 945.

[3] Cerato, Lauer, and Beachell, *J. Chem. Phys.*, 1954, **22**, 1.

[4] Murata and Shimizu, *J. Chem. Phys.*, 1955, **23**, 1968.

[5] Mizushima, " Structure of Molecules and Internal Rotation," Academic Press Inc., New York, 1954, p. 95.

[6] Howard, *J. Chem. Phys.*, 1937, **5**, 442.

simplified treatment has been tested by comparing the M–CH_3 stretching constants, K_1, for the hexamethyl compounds with corresponding constants for the tetramethyl compounds, obtained by using the same assumptions, *viz.*, methyl groups acting as single particles, and a simple valence force field. These stretching force constants for the tetramethyl compounds have already been calculated by several workers;[7,8] the results, however, are not very consistent, and we have repeated the calculations using the most recently accepted values of the vibration frequencies. We have also compared the K_1 force constants with stretching force constants calculated by Siebert[8] and by Waters and Woodward;[9] these authors used a simple valence force field applied to a 17-atomic system.

EXPERIMENTAL

Materials.—The hexamethyl compounds of silicon, germanium, and tin were prepared,[1] and their purity established by analysis,[10] as previously described, and by gas chromatography (Griffin and George equipment).

Raman Spectra.—These were recorded by means of a two-prism glass spectrograph, designed for us by Professor A. M. Taylor and constructed in his Department. The camera lens (Kodak Aero Ektar) has an aperture F/2·5, and the dispersion is approximately 36 Å per mm. at 4500 Å. The light source consisted of four vertical mercury-arc lamps (G.E.C. type MA/V, 400 w), under-run at 2 amp. to reduce the intensity of continuous radiation, and surrounded by a reflector coated with magnesium oxide.

The hexamethyl compounds were distilled *in vacuo* into Pyrex Raman tubes of 6 mm. internal diameter. Scattered light emerging from the base of the tube was directed on to the slit of the spectrograph by a reflecting prism and a condensing lens arranged to satisfy the Nielsen conditions.[11] The Raman tube was surrounded by two concentric cylindrical jackets: one contained a sodium nitrite filter solution, and the other was used for water-cooling. Good spectra were obtained from 1·5—3·0-ml. samples with a slit width of 0·030 mm. and 30—60-minute exposures on Kodak Oa-O plates.

Raman frequencies were obtained by interpolation, with iron-arc spectra recorded on each plate. Sharp lines were measured on a travelling microscope, weak lines on a Hilger non-recording microphotometer; the estimated limits of error are ±2 cm.$^{-1}$ for most of the lines. The value quoted for each band is the mean of at least four separate measurements from different plates. The state of polarisation was determined by the method of polarised incident light, with Polaroid cylinders round the Raman tube. Only those bands which are *clearly* polarised are so reported; no definite conclusion is drawn about the polarisation states of the other bands.

RESULTS

Hexamethyldisilane (Table 1).—Our measurements agree well with those by Murata and Kumada, with the exception of two lines (1259w and 1417m cm.$^{-1}$) which we find and they do not, and two (1317m and 1373 cm.$^{-1}$) which they observe and we do not. It is possible that the latter pair represents frequency shifts excited by Hg 4078 Å (see Table 2). Cerato, Lauer, and Beachell find a further 15 lines of weak or medium intensity, but we suggest that eight of these (we observe six ourselves) are not true Raman displacements from Hg 4358 Å. Table 2 shows that in every case the frequency displacement of these weak lines from mercury lines other than 4358 Å coincides with an existing high-intensity Raman frequency. These suggestions are supported by the observation that the lines we suppose to originate from excitation by Hg 4047 Å appear with much greater intensity when the sodium nitrite filter is removed. Further, we find bands excited by the 4047, 4339, and 4348 Å mercury lines in the spectra of other hexamethyl compounds; thus, two apparent Raman displacements of 411(vw) and 455(vw) cm.$^{-1}$ from Hg 4358 Å in the spectrum of the tin compound are excitations of the intense 512 cm.$^{-1}$ Raman line by Hg 4339 and 4348 Å. The remaining seven bands reported by Cerato, Lauer, and Beachell are presumably too weak for us to observe. The very intense broad band

[7] See, *e.g.*, Wall and Eddy, *J. Chem. Phys.*, 1938, **6**, 107; Sheline and Pitzer, *ibid.*, 1950, **18**, 595.
[8] Siebert, *Z. anorg. Chem.*, 1952, **268**, 177.
[9] Waters and Woodward, *Proc. Roy. Soc.*, 1958, *A*, **246**, 119.
[10] Brown and Fowles, *Analyt. Chem.*, 1958, **30**, 1689.
[11] Nielsen, *J. Opt. Soc. Amer.*, 1930, **20**, 701.

TABLE 1. *Raman frequencies (in cm.$^{-1}$) of hexamethyldisilane.*

This work	C.L.B.^{3}	M.K.^{2}	This work	C.L.B.^{3}	M.K.^{2}	This work	C.L.B.^{3}	M.K.^{2}
	87vw			(578w,d)		1247m	1241d	1245
	(124vw) *			598vw,b		1259w,p	1256p	
184vs,b,p	180p	178	638vs,p	638p	638		1283w,p	
	216w,d		688s	686d	689		(1315m,p)	1317
249m	251d	250	755w	753d	754		(1372w,d)	1373
	(305w,p)		834w	830d	833	1417m,b	1415d	
	(346w,p)		887m,p	883p	883		1443w,p	
	373vw			(1130w,d)		2900vs,p	2898p	2893
404vs,p	404p	403		(1190w,d)		2958vs	2957d	2955
	510							

Intensities and polarisation states indicated as follows: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, p = polarised, d = depolarised.

* It is suggested that frequencies enclosed in parentheses are not true Raman shifts from Hg 4358 Å (see Table 2).

TABLE 2. *Suggested re-interpretation of some Raman frequencies (in cm.$^{-1}$) reported for hexamethyldisilane.*

Reported shift from Hg 4358 Å	Suggested shift	Excited by Hg line Å	Known strong line excited by Hg 4358 Å	Reported shift from Hg 4358 Å	Suggested shift	Excited by Hg line Å	Known strong line excited by Hg 4358 Å
124vw	181	4348	184	1130w	2897	4047	2900
305w	406	4339	404	1190w	2957	4047	2958
346w	403	4348	404	1315m	2893	4078	2900
578w	635	4348	638	1372w	2950	4078	2958

with peak intensity at 184 cm.$^{-1}$ has a complex structure which we were unable to resolve either visually or with the aid of the microphotometer; Cerato *et al.* were able to resolve this band, and they report, among other lines, one at 200 cm.$^{-1}$ which is polarised.

Assignment of frequencies (Table 5). The previous workers [3,4] conclude that hexamethyldisilane has the D_{3h} (eclipsed) or $D_{3h'}$ (free rotation) rather than the D_{3d} (staggered) structure. There are nine Raman-active normal vibrations for molecules of D_{3h} or $D_{3h'}$ symmetry type: three A_1 vibrations (ν_1, ν_2, and ν_3) giving polarised lines, three E vibrations (ν_7, ν_8, and ν_9) which are also infrared-active, and three $\bar{E}$ vibrations (ν_{10}, ν_{11}, and ν_{12}). The two A_2 vibrations ν_5 and ν_6 are active only in the infrared region, and ν_4 (the torsional mode) is inactive in both infrared and Raman spectra.

The A_1 vibrations are readily identified: 404 cm.$^{-1}$ is assigned to ν_2, the Si–Si stretching vibration, and 638 cm.$^{-1}$ to ν_1, an Si–C stretching vibration. The polarised component of the intense low-frequency band is assigned to ν_3, an Si–C bending vibration. Although this low-frequency band has been resolved, and the polarised component identified,[3] we take 184 cm.$^{-1}$, the frequency at peak intensity, as ν_3, in order to be consistent with the ν_3 values for the germanium and the tin compound whose intense low-frequency bands we are again unable to resolve.

Murata and Shimizu [4] assign 688 cm.$^{-1}$, the remaining strong band in the skeletal frequency range, to ν_7 (E), a Si–C stretching vibration, and 249 cm.$^{-1}$ to ν_8 (E), a Si–C bending vibration; both these bands are active, and observed, in the infrared spectrum. These are all the assignments considered in this paper, the purpose of which is a comparative study of the three hexamethyl compounds, rather than a detailed study of any one compound.

Hexamethyldigermane and Hexamethyldistannane (Tables 3 and 4).—The complexity of the Raman spectra increases in the order Me_6Sn_2, Me_6Ge_2, and Me_6Si_2; hexamethyldistannane gives a very intense Raman spectrum, but long exposures failed to reveal any lines other than those reported in Table 4. Frequency assignments are summarised in Table 5. The strong, broad low-frequency band (or, more strictly, the polarised component of this band) is assigned to ν_3 (A_1); as explained above, we take the frequency at peak intensity (164 cm.$^{-1}$ for Me_6Ge_2 and 126 cm.$^{-1}$ for Me_6Sn_2) since we are unable to resolve the band. The sharp, strongly polarised bands at 273 cm.$^{-1}$ for Me_6Ge_2 and 190 cm.$^{-1}$ for Me_6Sn_2 are assigned to ν_2, the M–M stretching vibration, and the very strong bands at 572 cm.$^{-1}$ (Me_6Ge_2) and 512 cm.$^{-1}$ (Me_6Sn_2) to ν_1, the M–CH$_3$ stretching vibration. By comparison with the spectrum of Me_6Si_2, the strong band at 589 cm.$^{-1}$ in Me_6Ge_2 is assigned as ν_7 (E). The separation of ν_7 from ν_1 is only 17 cm.$^{-1}$ for Me_6Ge_2, compared with a corresponding separation of 50 cm.$^{-1}$ in Me_6Si_2; it is therefore not surprising that ν_7 and ν_1 are indistinguishable in the spectrum of Me_6Sn_2, and we assign 512 cm.$^{-1}$ to both ν_7 and ν_1. The band of medium intensity at 195 cm.$^{-1}$ in Me_6Ge_2 is assigned to ν_8 (E); it is just distinguishable from the broad low-frequency band at 164 cm.$^{-1}$, but ν_8 for the tin compound merges into the low-frequency band and cannot be separately identified.

It is noteworthy that the spectra of these two compounds in the higher frequency region ($\nu > 1000$ cm.$^{-1}$) strongly resemble the spectrum of Me_6Si_2 in this region. In each case there is a pair of C–H stretching vibrations at about 2900 cm.$^{-1}$, and a pair of C–H deformation vibrations at about 1200 cm.$^{-1}$.

TABLE 3. *Raman frequencies (cm.$^{-1}$) of hexamethyldigermane.*

164	195	273	572	589	1229	1243	1407	2801 *	2904	2970
vs,b,p	m,b	s,p	vs,p	s	m	m,p	w,b	w	s,p	m,b

* This band was only observed as a Hg 4047 Å excitation.

TABLE 4. *Raman frequencies (cm.$^{-1}$) of hexamethyldistannane.*

126	190	512	1183	1193	2910	2978
vs,b,p	m,p,	vs,p	m	m,p	s,p	m,b

TABLE 5. *Assignment of certain Raman bands.*

Description	Assignment	Frequencies (cm.$^{-1}$)			Description	Frequencies (cm.$^{-1}$		
		Me_6Si_2	Me_6Ge_2	Me_6Sn_2		Me_6Si_2	Me_6Ge_2	Me_6Sn_2
δ(M–CH$_3$)	$\nu_3(A_1)$	184p	164p	126p	δ(C–H)	1247	1229	1183
δ(M–CH$_3$)	$\nu_8(E)$	249d	195	126	δ(C–H)	1259p	1243p	1193p
ν(M–M)	$\nu_2(A_1)$	404p	273p	190p	ν(C–H)	2900p	2904p	2910p
ν(M–CH$_3$)	$\nu_1(A_1)$	638p	572p	512p	ν(C–H)	2958	2970	2978
ν(M–CH$_3$)	$\nu_7(E)$	689d	589	512				

CALCULATION OF FORCE CONSTANTS

Hexamethyl Compounds.—It is assumed that: (*a*) all bond angles are tetrahedral (this is justified at least for hexamethyldisilane, where Brockway and Davidson [12] showed by electron diffraction that the Si–Si–C bond angle is 109° ± 4°); and (*b*) the "active" mass of the methyl group is 15·0. The simple valence bond force field does not distinguish between D_{3d}, D_{3h}, and $D_{3h'}$ structures, and so, for these calculations, it does not matter whether the structures of these molecules are D_{3h} or $D_{3h'}$, as concluded by previous workers, or D_{3d}.

The equation developed by Howard [6] for the A_1 frequencies was used to determine values of the force constants K_1 (M–C stretching), K_2 (M–C bending), and K_3 (M–M stretching) that give the best agreement between calculated and observed A_1 frequencies. Stretching force constants for the Si–Si, Ge–Ge, and Sn–Sn bonds of 1·30, 1·34, and 1·01 × 10^5 dynes/cm. respectively were obtained, and the calculated frequencies agree reasonably well with those observed experimentally (see Table 6).

TABLE 6. *Results of the* A_1 *frequency calculations.*

Hexamethyldisilane

$K_1 = 2·39$, $K_2 = 0·23$, and $K_3 = 1·30 \times 10^5$ dynes/cm.

	Frequencies (cm.$^{-1}$)		
Observed	184	404	638
Calculated	179	421	628

Hexamethyldigermane

$K_1 = 2·57$, $K_2 = 0·16$, and $K_3 = 1·34 \times 10^5$ dynes/cm.

	Frequencies (cm.$^{-1}$)		
Observed	164	273	572
Calculated	153	296	563

Hexamethyldistannane

$K_1 = 2·18$, $K_2 = 0·09$, and $K_3 = 1·01 \times 10^5$ dynes/cm.

	Frequencies (cm.$^{-1}$)		
Observed	126	190	512
Calculated	119	203	509

Tetramethyl Compounds.—The tetramethyl compounds are assumed to have five-atomic tetrahedral structures of T_d symmetry type; four normal vibrations are expected, one A_1 (ν_1), one E (ν_2), and two F vibrations (ν_3 and ν_4). Equations for the determination of force

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[12] Brockway and Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287.

constants, on the assumption of a simple valence bond force field, are given by Herzberg;[13] these involve K, the M–CH$_3$ stretching force constant, and K_δ, the M–CH$_3$ bending force constant. The value of 15·0 is again chosen for the mass of the methyl group. The force constants are obtained by inserting observed values of ν_1 and ν_2 in the equations, and the values of these force constants may be checked by using them to calculate ν_3 and ν_4 frequencies.

The experimentally observed skeletal vibration frequencies, and the results of the force-constant and frequency calculations are summarised in Table 7. Some slight disagreement about the exact values of ν_2 and ν_4 exists, and since K is determined directly from ν_2 it is important to select reliable values for these frequencies. We select Siebert's[8] values for Me$_4$Si and those of Lippincott and Tobin[14] for Me$_4$Ge; the latter authors succeeded in resolving the low-frequency band into its two components at 175 (ν_2) and 195 cm.$^{-1}$ (ν_4). The ν_1 and ν_3 values for Me$_4$Sn are those of Edgell and Ward;[15] we ourselves re-examined the low-frequency band containing the ν_2 and ν_4 frequencies, and obtained a value of 150 cm.$^{-1}$ for the frequency at peak intensity. This value is used for both ν_2 and ν_4, since, like other workers, we could not resolve the band into its two components.

TABLE 7. *Frequency calculations for the tetramethyl compounds (force constants in dynes/cm.).*

	Force constants		Frequencies (cm.$^{-1}$)					
			ν_1	ν_2	ν_3		ν_4	
Comp.	$10^{-5}K$	$10^{-5}K_\delta$	Obs.	Obs.	Obs.	Calc.	Obs.	Calc.
Me$_4$Si	3·17	0·12	598	202	696	794	239	220
Me$_4$Ge	2·76	0·09	558	175	599	632	195	171
Me$_4$Sn	2·28	0·07	507	150	530	549	150	139

The results of the calculations (Table 7) show that the observed and the calculated values of ν_3 and ν_4 are in rough agreement, and that the agreement tends to improve with an increase in the atomic weight of the metal.

The stretching force constants, F_{CX}, for the tetramethyl compounds, calculated by Siebert[8] and Waters and Woodward,[9] are reported in Table 8; F_{CX} represents Siebert's $f_{\text{CX}} + 3f'_{\text{CX}}$, and Waters and Woodward's f_{33}. These authors use a simple valence force field applied to a 17-atomic system, and they obtain calculated frequencies in excellent agreement with those observed.

DISCUSSION

The M–M stretching, M–C stretching, and M–C bending force constants are collected in Table 8.

M–C *Stretching Force Constants.*—The values of 2·18, 2·28, and 2·39 × 10^5 dynes/cm. for the Sn–C bond are considered to be in reasonable agreement; K_1 and K differ only by 0·1 × 10^5 dynes/cm., and the largest difference, between K_1 and F_{CX} is 0·2 × 10^5 dynes/cm. The agreement between the values for the Ge–C bond is also reasonably good; here, K_1 and K differ by 0·2 × 10^5 dynes/cm., and K_1 and F_{CX} by 0·4 × 10^5 dynes/cm. There is, however, a considerable difference, 0·78 × 10^5 dynes/cm., between K_1 and K for the Si–C bond.

TABLE 8. *Force constants (dynes/cm.).*

M–M stretching, K_3. Si–Si = 1·30, Ge–Ge = 1·34, and Sn–Sn = 1·01 × 10^5.

	M–C Stretching			M–C Bending	
	Me$_6$M$_2$	Me$_4$M	Me$_4$M	Me$_6$M$_2$	Me$_4$M
	$10^{-5}K_1$	$10^{-5}K$	$10^{-5}F_{\text{CX}}$*	$10^{-5}K_2$	$10^{-5}K_\delta$
M = Si	2·39	3·17	3·41	0·23	0·12
M = Ge	2·57	2·76	2·96	0·16	0·09
M = Sn	2·18	2·28	2·39	0·09	0·07

* Siebert's values, see ref. 8.

M–CH$_3$ *Bending Force Constants.*—The different values for the bending force constants

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[13] Herzberg, "Infra-red and Raman Spectra," Van Nostrand, New York, 1945, p. 182.

[14] Lippincott and Tobin, *J. Amer. Chem. Soc.*, 1953, **75**, 4141.

[15] Edgell and Ward, *J. Amer. Chem. Soc.*, 1955, **77**, 6486.

are of the same order of magnitude for a given compound; close agreement is not expected, since these constants will be affected much more than stretching force constants by changes in the force field. It must also be noted that the bending force constants for the hexamethyl compounds involve changes in the $M-M-CH_3$ angles as well as in the CH_3-M-CH_3 angles.

We therefore conclude, on the limited basis of comparisons between $M-CH_3$ stretching force constants, that our treatment of the hexamethyldigermane and hexamethyldistannane molecules is reasonably valid, but that a similar method applied to hexamethyldisilane gives results which may be considerably in error. This is perhaps not surprising, since silicon (atomic weight 28·09) is so very much lighter than germanium and tin (atomic weights 72·60 and 118·7 respectively); we should expect far more interaction between skeletal and C–H vibrations in hexamethyldisilane than in either of the other two compounds.

These results indicate that the stretching force constants for the Sn–Sn and Ge–Ge bonds in Me_6Sn_2 and Me_6Ge_2 are $1{\cdot}0 \pm 0{\cdot}1$ and $1{\cdot}3 \pm 0{\cdot}1 \times 10^5$ dynes/cm. respectively: the value of $1{\cdot}3 \times 10^5$ dynes/cm. for the Si–Si force constant in Me_6Si_2 is probably in error. Additional confirmation of these conclusions is obtained by comparisons with force constants reported for Si–Si and Ge–Ge bonds in the hydrides H_6Si_2 and H_6Ge_2; the Si–Si value [16] of $1{\cdot}7 \times 10^5$ dynes/cm. differs considerably from our value of $1{\cdot}3 \times 10^5$, but that of $1{\cdot}29 \times 10^5$ for the Ge–Ge bond [17] is close to our value of $1{\cdot}34 \times 10^5$ dynes/cm.

Finally it should be noted that we have not compared our force constants for the hexamethyldisilane molecule with those of Murata and Shimizu,[4] since these authors assume a Urey–Bradley type of force field, which is known to give force constants often differing widely from those obtained by using valence bond force fields.

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[16] Stitt and Yost, *J. Chem. Phys.*, 1937, **5**, 90.
[17] Dows and Hexter, *J. Chem. Phys.*, 1956, **24**, 1029.