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VIBRATIONAL SPECTRA OF COMPOUNDS CONTAINING ELEMENTS OF THE CARBON SUBGROUP

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I. INTRODUCTION

This review surveys the experimental results which have accumulated on the vibrational spectra both of organic compounds containing Si, Ge, Sn, and Pb and of inorganic compounds of these elements such as, for example, SiH_4, $HGeCl_3$, etc.

The survey is divided according to the individual bonds and groups representing substitution on silicon, germanium, tin, and lead.

II. COMPOUNDS CONTAINING AN E–H BOND (E = Si, Ge, Sn)

1. Compounds of the Type EH_4 (E = C, Si, Ge)

The molecules CH_4, SiH_4, and GeH_4 belong to the symmetry point group T_d. In conformity with this, they will be expected to have four vibrational frequencies in the Raman spectrum (R), and only the frequencies of the triply degenerate vibrations in the infrared absorption spectrum (i.r.). We shall not consider the methane molecule[1,2] in detail, and say a little only about SiH_4 and GeH_4.

Various workers have described the vibrational spectra of silane and germanium tetrahydride (germane) in several papers, among which must be noted the work of Stitt and Yost[3] on the Raman spectrum of SiH_4, and that of Schäfer and Gonzales-Barredo[4] on the Raman spectrum of GeH_4. The infrared absorption spectra of these compounds have been investigated by Tindal *et al.*[5-7]. Data on the vibrational spectra of SiH_4 and GeH_4 are also available[8-12]. The data in Table 1 and Fig. 1 are based mainly on these papers.

The vibrational spectra of deuterated silanes have been described by Meal and Wilson[13] and Polo and Wilson[14], the first of these papers dealing with the infrared absorption spectra of SiD_4, $SiHD_3$, and SiH_2D_2, and the second with that of SiH_3D. Calculations have also been made on the vibrational spectra of methane[2] and silane[15]. It follows from the calculations that, for compounds of the type EH_4, the force constant of the E–H bond decreases in the sequence E = C, Si, Ge, Sn (calculation of completely symmetrical vibration) (see Fig. 2).

E	$k_{q(E-H)}$, cm^{-2}	r_{E-H}, Å	Refs.
C	$8.34 \cdot 10^6$	1.09	2
Si	$4.67 \cdot 10^6$	1.4798	14,15,17
Ge	$4.3 \cdot 10^6$	1.54	5,16
Sn	$\sim 3.8 \cdot 10^6$	—	16

TABLE 1. Vibration frequencies of molecules of the type EH_4 (symmetry T_d).

ν, cm^{-1}	CH_4	SiH_4		GeH_4	
	(R and i.r.)[1]	(R)[10]	(i.r.)[5,6]	(R)[a,4]	(i.r.)[5,7]
ν_1 (a)	2914 (R)	2180	—	2089 (10)	—
ν_2 (e)	1526	970	975[c]	920[b] (3)	932[c]
ν_3 (f_2)	3020 (i.r.)(R)	2183	2191	2106 (2)	2114
ν_4 (f_2)	1306 (i.r.)	910	910	816[b] (0)	818

[a] Spectrum of GeH_4 determined at -100°.

[b] The assignment given in Ref. 4 is that $\nu_2(e)$ = 816 cm^{-1} and $\nu_4(f_2)$ = 920 cm^{-1}. From the intensity ratio for these lines and from the infrared spectroscopic data[6,7], a more correct assignment is that shown in Table 1.

[c] The authors of the paper give an explanation for the appearance of the frequency $\nu_2(e)$, which is forbidden in the infrared spectrum.

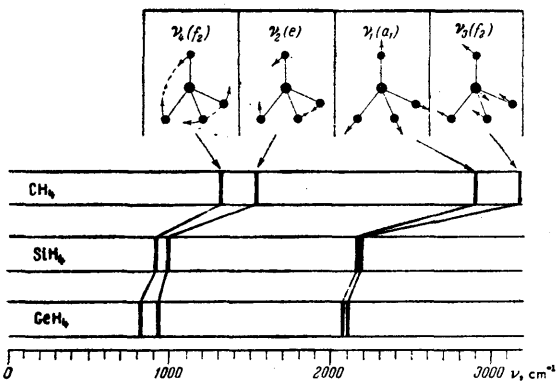


Fig. 1. Molecules of the type EH_4 (symmetry T_d).

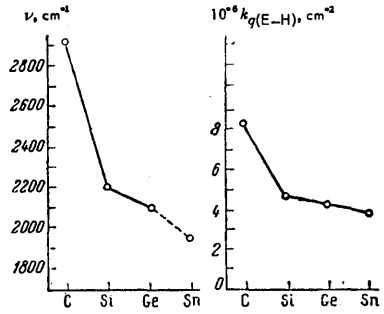


Fig. 2. Vibration frequencies and force constants of E–H bonds in molecules of the type EH_4 (E = C, Si, Ge, Sn).

2. The E–H bond in Halogeno-Derivatives (E = C, Si, Ge)

The chief results for the E–H vibrations in the mono-halogeno-derivatives of methane, silane, and germane are given in Table 2 and also in Fig. 3. Andersen and Bak[22] have examined the infrared absorption spectra of SiD_3Cl, SiH_3F, and SiD_3F. The vibrational–rotational spectrum of monochlorosilane has been studied[23] over the range 650–2200 cm^{-1}. Mayo *et al.*[24] investigated the infrared absorption spectra of SiH_3Br and SiH_2Br_2, the Raman spectra of these compounds having been examined earlier[25].

Results are given for CH_2X_2 and SiH_2X_2 molecules, as examples of dihalogeno-derivatives (Table 3 and Fig. 4).

In the case of the trihalogeno-derivatives the frequencies of the E–H vibrations lie within the ranges indicated in Table 4; the variation in frequency for molecules of type EHX_3 can be judged from Fig. 6.

3. Alkyl, Alkenyl, and Alkenylalkyl Derivatives Containing an E–H Bond (E = Si, Ge, Sn)

Alkylsilanes have been investigated by several workers. Westermark[35] showed that $\geqslant$Si–H groups have intense infrared bands in the region of 2109 cm^{-1}, $>SiH_2$ near 2132–2136 cm^{-1}, and $-SiH_3$ near 2164 cm^{-1}. The values of ν_{Si-H} for $(C_6H_5)_2SiH_2$ and $(C_6H_5)_3SiH$ are 2155 and 2136 cm^{-1} respectively†. Other investigations have been made of the infrared spectra of alkylsilanes containing these same groups[36]. The infrared spectra of triphenylsilane (ν_{Si-H} = 2135 cm^{-1}, δ_{Si-H} = 805 cm^{-1}) and of tripropylsilane (2108 and 820 cm^{-1}) have been investigated by Kaplan[37]. Dialkylsilanes ($RR'SiH_2$) have been investigated by West and Rochow[38], the values of ν_{Si-H} being 2083–2096 cm^{-1} for compounds in which R is an aliphatic radical, and 2096–2118 cm^{-1} where R is aromatic. Studies have also been made[39,40] of the Raman spectra of a series of compounds containing $\geqslant$SiH, $>SiH_2$, and $-SiH_3$ groups, from

TABLE 2. Vibration frequencies of EH_3 groups in molecules of the type EH_3X (E = C, Si, Ge; X = F, Cl, Br, I) (symmetry C_{3v})*

	CH_3F[1]	SiH_3F[18]		CH_3Br[1]	SiH_3Br[18]
$\nu_s(a_1)$	2964	2196		2972	2196
$\nu_{as}(e)$	2982	2206		3056	2200
$\delta_s(a_1)$	1475	990		1305	930
$\delta_{as}(e)$	1471	943		1445	950
	CH_3Cl[1]	SiH_3Cl[18]	GeH_3Cl[19]	CH_3I[1]	SiH_3I[20,21]
$\nu_s(a_1)$	2966	2185	2121	2970	2192
$\nu_{as}(e)$	3042	2201	2129	3060	2205
$\delta_s(a_1)$	1355	949	848	1251	903
$\delta_{as}(e)$	1454	954	874	1440	941

* The types of vibrations and assignment of frequencies are given also in Fig. 3.

† In this paper the infrared spectra of 28 compounds are given (over the range 2–15 μ).

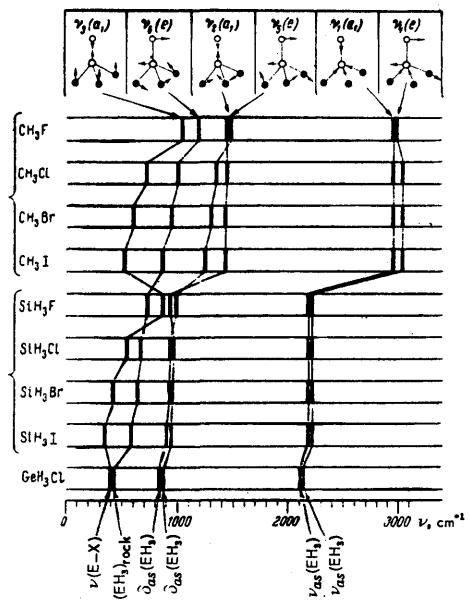


Fig. 3. Molecules of the type EH_3X (symmetry C_{3v}).

TABLE 3. Vibration frequencies of EH_2 groups in molecules of the type EH_2X_2 (symmetry C_{2v}). X = F, Cl, Br, I.

	CH_2F_2(R)[26]		CH_2Br_2(R)[26]	(i.r.)[26]	SiH_2Br_2(R)
$\nu_s(a_1)$	2963		2988	2200	2206
$\nu_{as}(b_1)$	3030		3061	—	2232
$\delta(a_1)$	1509		1388	942	925
$\delta(b_2)$	1509		1133	843	828
	CH_2Cl_2[1]	SiH_2Cl_2(i.r.)[27]	CH_2I_2[28]		
$\nu_s(a_1)$	2984	2200	2968		
$\nu_{as}(b_1)$	3048	2200	3048		
$\delta(a_1)$	1429	953	1348		
$\delta(b_2)$	1255	877	1103		

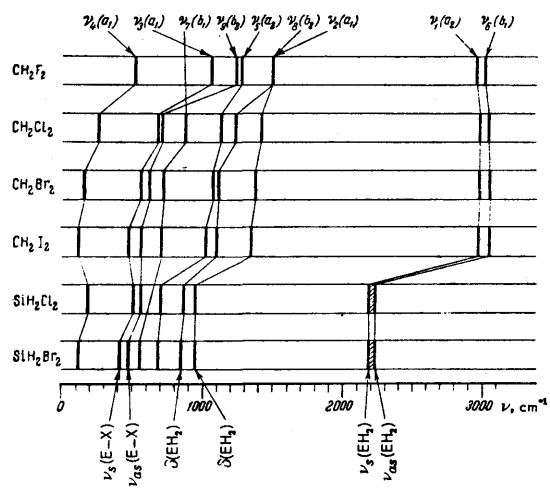


Fig. 4. Molecules of the type EH_2X_2 (symmetry C_{2v}).

TABLE 4. E–H vibration frequencies in molecules of the type EHX_3* (E = C, Si, Ge; X = F, Cl, Br) (symmetry C_{3v}).

	CHF_3(R)[26]	$SiHF_3$(l.s.)[28]	(l.s.)[1] CH_3Cl_3(R)		(l.s.)[29] $SiHCl_3$(R)[30,31]		$GeHCl_3$(R)[32]
ν	3062	2315	3033	3019	2262	2258	2159
δ	1376	851	1205	1215	802	799	699
	$CHBr_3$(R)[26]	$SiHBr_3$(R)[26]	$GeHBr_3$(R)[32]				
ν	3022	2236	2116				
δ	1143	770	674				

* Unfortunately, results[33,34] for the Raman spectra of $SnHX_3$ cannot be used, since the papers do not give frequencies for the Sn–H bond.

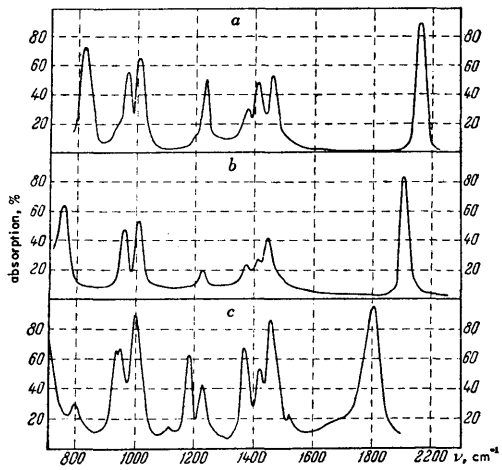


Fig. 5. Infrared absorption spectra of compounds of the type $(C_2H_5)_3EH$: *a*) $(C_2H_5)_3SiH$; *b*) $(C_2H_5)_3GeH$; *c*) $(C_2H_5)_3SnH$.

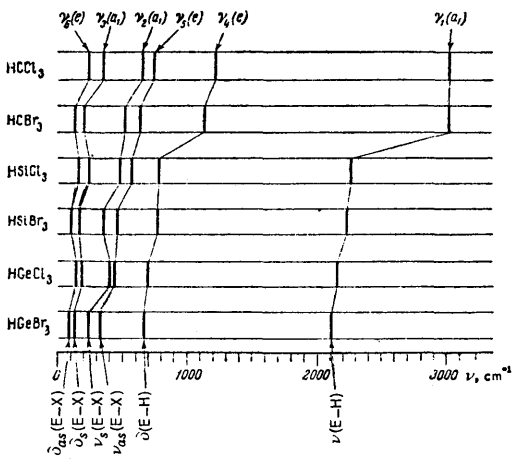
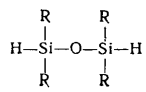


Fig. 6. Molecules of the type EHX_3 (symmetry C_{3v}).

which it follows that the corresponding values of ν_{Si-H} are ~2120, ~2135, and 2155 cm^{-1}. The results of Harvey *et al.*[41] for the infrared absorption spectra of dialkylsilanes of the type $RR'SiH_2$ agree with those of previous work[38].

The values of ν_{Si-H} for alkenylalkylsilanes containing an Si–H bond lie in almost the same regions as those for alkylsilanes[29].

The same relations are observed also with tetrasubstituted disiloxanes having the structure



(where R = CH_3, C_2H_5, $CH:CH_2$, C_6H_5) and with a large number of polymers resulting from their interaction with dienes[29,42,43].

Noteworthy calculations have been made by Kovalev[44-46], showing that the Si–H bond is less stable in alkylsilanes than in SiH_4. With the series $(CH_3)_nSiH_{4-n}$ (n = 0–4) as an example, it has been shown[46] that the strength of the Si–H bond decreases with increasing number of methyl groups on the silicon atom, the corresponding force constant $k_{q(Si-H)}$ becoming smaller (this explains the shift in ν_{Si-H} to lower frequencies).

The halogenosilanes show the reverse relationship, the ν_{Si-H} frequencies becoming higher with increase in the number of halogen atoms attached to the Si in SiH_4 [$k_{q(Si-H)}$ also becomes rather higher]. Information on the Si–H vibrations is also to be found in several other papers, in particular those of Kriegsmann[47,48].

Relatively little work has been done on compounds containing Ge–H and Sn–H bonds. Thus, for example, West[49] gives ν_{Ge-H} = 2040 cm^{-1} in triphenylgermane, and 2060 cm^{-1} in $(CH_3)_2GeH_2$. The infrared absorption spectra of several alkylgermanes[50] of the types R_3GeH, R_2GeH_2, and $RGeH_3$ have been examined (where R represents ethyl and propyl; ethyl, butyl, hexyl, heptyl, and octyl; and pentyl, hexyl, heptyl, and octyl respectively), values of ν_{Ge-H} for the $\rangle$GeH, $\rangle$$GeH_2$, and $-GeH_3$ groups being respectively 2010, 2035, and 2065 cm^{-1}.

The Ge–H and Sn–H stretching frequencies are lower than the Si–H vibration frequencies, this being clearly shown in the series of compounds[16,51] $(C_2H_5)_3EH$ (E = Si, Ge, Sn) (see Fig. 5).

The frequency of the E–H vibration falls regularly from Si to Sn (the same occurs also with δ_{E-H}, from ~810 to ~700 cm^{-1}).

Mention must be made also of work on compounds of the type H_3E-EH_3, disilane and digermane. In the former, investigated by Gutowsky and Stejskal[52], ν_{Si-H} lies in the range 2154–2181 cm^{-1}, and δ_{Si-H} in the range 843–910 cm^{-1}. In the case of digermane[53] ν_{Ge-H} lies between 2078 and 2114 cm^{-1}. It is noted that the vibrational frequencies fall steadily on passing from ethane to disilane and digermane.

A calculation made by Kovalev[54] shows that $k_{q(Si-H)}$ for disilane is 4.51×10^6 cm^{-2}, which is very close to the value in silane. Results for ν_{Si-H} in disilylacetylene[55] are close to those in disilane[52].

Trisilylamine has been investigated by Ebsworth *et al.*[56], and a value of 2168 cm^{-1} has been found[47] for ν_{Si-H} in this compound.

Smith and Angelotti[57] have attempted to correlate the Si–H vibration frequencies with molecular structure, and from their work it follows that the shift in ν_{Si-H} depends on the electronegativity of the substituents attached to the silicon atom, and is almost proportional to the change in electronegativity.

Finally, it is interesting that the E–H vibration bands (E = Si, Ge, Sn) are separated from the rest of the spectrum and are fairly intense. They lie in a frequency range which is separated both from the C–H stretching vibrations and from vibrations involving other functional groups (bonds). Such isolation considerably facilitates the task of identifying compounds containing these bonds (groups). The region of E–H vibrations includes only the C≡C and C≡N stretching vibrations.

It follows from the results given in the present section that in general the bands due to Si–H stretching vibrations lie within the frequency range 2100–2300 cm^{-1}, those due to Ge–H at about 2000–2200 cm^{-1}, and those due to Sn–H at about 1800–2000 cm^{-1}.

The regular decrease in frequency of the E–H vibrations in the sequence C, Si, Ge, Sn is noteworthy. The greatest changes in frequency occur on passing from C to Si, those in the series Si, Ge, Sn being less marked. The chief reason for the change in frequency is a change in the force constants of the E–H bonds. The latter also show the most marked change from C to Si, the value of $k_{q(C-H)}$ being almost double that of $k_{q(Si-H)}$.

The E–H vibration frequencies are somewhat higher in the halogeno-derivatives than in the alkyl and alkenylalkyl derivatives (mainly of silanes, since very extensive data are available for them). This is associated with a rather higher value of the force constants of the E–H bond in the halogenosilanes.

The alkyl and alkenylalkyl derivatives of silicon show little difference in frequency, which indicates fairly convincingly that the Si–H vibrations are quite characteristic of these classes of compounds. The same applies also to the Ge–H vibrations.

III. COMPOUNDS CONTAINING E–Alk AND E–C_6H_5 GROUPS (E = Si, Ge, Sn, Pb; Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9)

Let us consider the frequency range 1150–1270 cm^{-1}, which shows the most specific influence of the central atom (E = Si, Ge, Sn, Pb) on the frequencies of C–H deformation vibrations in the alkyl groups attached to E.

Reference must first be made to work on molecules of the type $E(Alk)_4$. Among the early experimental investigations are those of Kettering and Sleator[58] [although they have only recorded the infrared absorption spectra of $Sn(CH_3)_4$, $Pb(CH_3)_4$, and $Ge(C_2H_5)_4$, without any assignment of the frequencies or interpretation of the results], Rank[59,60] [the first paper on the Raman spectrum of $C(CH_3)_4$, the second on $Si(CH_3)_4$], Duncan and Murray[61] on the Raman spectrum of $Pb(CH_3)_4$, and Anderson[62], who examined the Raman spectra of $C(CH_3)_4$, $Si(CH_3)_4$, $Si(C_2H_5)_4$, $Sn(CH_3)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$. More recent investigations include those of Young *et al.*[63] [who examined the infrared absorption spectra of $C(CH_3)_4$, $Si(CH_3)_4$, and $Ge[CH_3)_4]$, and Rank *et al.*[64] on the vibrational spectra of $C(CH_3)_4$, $Si(CH_3)_4$, and their monodeuterated derivatives. Sheline and Pitzer[65] give results on the infrared absorption spectrum of $Pb(CH_3)_4$.

Lippincott and Tobbin[66] investigated the infrared and Raman spectra of $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Pb(CH_3)_4$, and calculated the thermodynamic functions of these molecules. Data on compounds of the type $E(CH_3)_4$ are given also in several other papers[67-71].

A great deal of work has been done on compounds containing E–Alk groupings, among which must be mentioned investigations[72] on Si–CH_3 and on the infrared spectra of cyclic siloxanes[73] having the structure

$$-[-Si(Alk)_2-O-]_n- ,$$

where Alk = CH_3, C_2H_5, C_6H_5. Compounds containing Si–CH_3 groupings have been investigated also by Richards and Thompson[74], Rank *et al.*[64], Frisch *et al.*[75], Tatlock and Rochow[76], Horak *et al.*[77], Egorov and Bazhulin[78], and the reviewer[42]. Compounds containing the Si–CH_2–R (R = H, CH_3, C_2H_5, n-C_3H_7) grouping have been investigated by the reviewer[29], Kaye and Tannenbaum[36], Harvey *et al.*[41], Plate *et al.*[79], and also Durgar'yan *et al.*[80] Compounds containing Si–CH_3, Ge–CH_3, Sn–CH_3, Pb–CH_3, Si–C_6H_5, Ge–C_6H_5, Sn–C_6H_5, and Pb–C_6H_5 groupings have been investigated[81], and also[16] those containing Sn–CH_3 and Sn–C_2H_5. The above papers show good agreement among themselves in the sense that data on the frequencies of the E–Alk groupings coincide. Thus Si–CH_3 is characterised by the presence of absorption bands and Raman lines within the range 1250–1258 cm^{-1} (in the case of methylchlorosilanes[29] the frequency rises to 1265–1267 cm^{-1}), with Ge–CH_3 the frequency, in the case of alkyl- and alkenylalkyl-germanes, lies at about 1240–1242 cm^{-1} (also rising slightly in the methylchlorogermanes)[51], with Sn–CH_3 at 1190–1195 cm^{-1}, and with Pb–CH_3 at 1170 cm^{-1}.

TABLE 5. Vibration frequencies of E–Alk and E–C_6H_5 groupings[16,29,51].

Grouping	ν, cm^{-1}	Grouping	ν, cm^{-1}
Si–CH_3	1250–1258	Si–n-C_3H_7	1205, 1215 doublet
Ge–CH_3	1238–1242		
Sn–CH_3	1190–1195	Si–n-C_4H_9	1180, 1190 doublet
Pb–CH_3	1170		
Si–C_6H_5	1235–1240	Si–C_6H_5	1110–1120 (1103)*
Ge–C_6H_5	1230–1235	Ge–C_6H_5	1080 (1084)*
Sn–C_6H_5	1183–1190	Sn–C_6H_5	— (1068)*
Pb–C_6H_5	1158	Pb–C_6H_5	— (1055)*

* According to Noltes *et al.*[81]

Table 5 gives the E–Alk and E–C_6H_5 vibration frequencies, where E = Si, Ge, Sn, Pb, and Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9. The following generalisations can be made for the absorption bands and Raman lines due to E–Alk groupings: frequencies decrease (1) in the sequence E = Si, Ge, Sn, Pb, and (2) in the sequence CH_3, C_2H_5, n-C_3H_7, n-C_4H_9.

In contrast, in the assignment of the vibrations having the above frequencies, there is no unity of the sort shown by the agreement between the frequencies. Several workers give different interpretations of the results, but many investigators are inclined to regard the above frequencies as due to symmetrical C–H deformation vibrations. This question can be completely cleared up only by sufficiently careful calculations. *

It should be noted[29] that the intensity of the infrared absorption bands due to Si–Alk groupings (the reviewer has made measurements of the integral intensities of the bands for organosilicon compounds) may serve as a measure of the number of alkyl groups attached to the silicon atom.

IV. GROUPS CONTAINING MULTIPLE BONDS

1. Compounds Containing E–CH=CH_2 and E–CH_2–CH=CH_2 Groupings (E = Si, Ge, Sn). The C=C Bond and Terminal Methylene (=CH_2) Groups

A large proportion of the work on alkenyl derivatives of Si, Ge, Sn has been done by Soviet investigators, among which must be mentioned the work of Egorov *et al.*[78,82–85] on the Raman spectra. The infrared absorption spectra of several alkenyl derivatives have also been examined[16,29,43,51,86,87]. Some allyl derivatives of silicon had been investigated earlier by Scott[75,88] (i.r.).

The Raman spectrum of methyltriallylsilane has been examined by Malkovich and Kolesova[89]. Tetravinyltin has been investigated[90]. The principal C=C vibration frequencies are given in Table 6.

The variation in intensity of C=C vibrational bands is extremely interesting. In the sequence C → Sn the vinyl derivatives show a decrease in intensity of these absorption bands, and the allyl derivatives, on the other hand, an increase. Several workers[83–87] have made detailed studies of the laws governing the changes in intensity and frequency of the C=C vibrations.

TABLE 6. C=C vibration frequencies in vinyl and allyl derivatives* of C, Si, Ge, Sn.

Compound	ν, cm^{-1}	Compound	ν, cm^{-1}
$(CH_3)_3C$–CH=CH_2	1645	$(CH_3)_3C$–CH_2–CH=CH_2	1648
$(CH_3)_3Si$–CH=CH_2	1595	$(CH_3)_3Si$–CH_2–CH=CH_2	1633
$(CH_3)_3Ge$–CH=CH_2	1590	$(CH_3)_3Ge$–CH_2–CH=CH_2	1633
$(CH_3)_3Sn$–CH=CH_2	1583	$(CH_3)_3Sn$–CH_2–CH=CH_2	1628

* In the case of olefins[91] infrared absorption bands in the range 1620–1680 cm^{-1} correspond to an isolated double bond.

Perfluorovinyl derivatives of Si, Ge, Sn have been investigated by Stafford and Stone[92]. Fluorine atoms adjacent to a C=C bond increase $\nu_{C=C}$ appreciably, right up to 1700–1800 cm^{-1}.

With regard to methylene (=CH_2) groups, the C–H stretching vibrations (ν_{as}) for E–CH=CH_2 groupings lie within the range 3040–3050 cm^{-1} in the cases of Si, Ge, Sn. With E–CH_2–CH=CH_2, $\nu_{as(C-H)}$ = 3070–3080 cm^{-1}.

Data on frequencies and intensities of infrared absorption bands and Raman lines due to vibrations of C=C and =CH_2 groups may provide a valuable criterion of the presence of a particular alkenyl group in the compound.

2. Acetylenic Derivatives. The C≡C Bond

The following compounds containing an acetylenic bond have been investigated:

$SiH_3C{\equiv}CSiH_3$ (I) (infrared and Raman),[55]
$Si(CH_3)_3CH_2CH_2C{\equiv}CH$ (II),[93]
$C_2H_5Si(CH_3)_2C{\equiv}CH$ (III),[29]
$Si(CH_3)_3C{\equiv}CSi(CH_3)_3$ (IV),[29]
$C_2H_5SiH(CH_3)C{\equiv}CSiH(CH_3)C_2H_5$ (V) (infrared).[29]

Values of $\nu_{C\equiv C}$ for I–III are 2132, 2116, and 2050 cm^{-1} respectively. In the cases of IV and V, the C≡C vibration frequencies did not appear in the infrared absorption spectra owing to the symmetry of the molecules. We may note that $\nu_{C\equiv C}$ has the values 1974 cm^{-1} (R) for HC≡CH, 2100–2150 cm^{-1} for monosubstituted acetylenic derivatives of the type AlkC≡CH, and 2200–2250 cm^{-1} for disubstituted derivatives RC≡CR. For the terminal ≡C–H bonds $\nu_{\equiv C-H}$ has the values 3305 cm^{-1} (II) (R) and 3280 cm^{-1} (III) (i.r.).

Especially noteworthy is the curious fact that the frequencies and intensities of C=C and C≡C vibrations located α to Si, Ge, and Sn undergo the most significant changes, which indicates that the specific effect of these elements on the above bonds in the molecule is qualitatively different from that found with olefins.

The vibration frequencies of terminal methylene groups also undergo some change compared with olefins, this being especially noticeable in the case of vinyl derivatives.

V. THE E–C BOND (E = Si, Ge, Sn, Pb)

Of the papers on alkyl derivatives of Si, Ge, Sn, Pb noted in Section III, a considerable number are concerned with the compounds $E(CH_3)_4$.[58,60–65,67,94,95] The most complete data on vibrations of this type of molecule are given by Young *et al.*[63]‡ The frequencies of skeletal vibrations of these molecules, taken from this paper, are listed in Table 7.

A considerable number of calculations have been made on $E(CH_3)_4$ molecules, among them being the papers by Wall and Eddy[96] and Silver[97,98] [though these workers determined the frequencies of the $Si(CH_3)_4$ skeleton by regarding the methyl groups as atoms of atomic weight 15], and also by others[65,67,69,99]. The most complete calculation is that of the $Si(CH_3)_4$ molecule made by Kovalev[100].

‡ Data on Raman spectra from other papers are used in this work[63].

TABLE 7. Frequencies of the skeletal vibrations of molecules of the type[63] $E(CH_3)_4$ (E = C, Si, Ge, Sn, Pb).

ν, cm^{-1}	$C(CH_3)_4$	$Si(CH_3)_4$	$Ge(CH_3)_4$	$Sn(CH_3)_4$	$Pb(CH_3)_4$
$\nu(a_1)$	733	598	540	506	460
$\nu(e)$	335	202	110	100	100
$\nu(f_2)$	925	696	590	526	473
$\nu(f_2)$	414	239	200	152	130

Force constants for the Si–C bonds in $Si(CH_3)_4$ from different sources are given in Table 8. Values of k_{E-C} for the $E(CH_3)_4$ series given by Siebert[99] are reproduced in Table 9. Data are available on the infrared absorption spectra[101] and on the Raman spectra[102]. Some results for methylsilicon derivatives are given in Table 10.

In compounds containing $Si-CH_3$ groupings ν_{Si-C} lies within the range 700–760 cm^{-1}.

Thus the frequency range for stretching vibrations of the Si–C bond in methyl derivatives is 600–800 cm^{-1}. In the case of methylgermanium compounds ν_{Ge-C} lie within the ranges[51] ν_s = 570–600 cm^{-1} and ν_{as} = 610–650 cm^{-1}. The Sn–C vibration frequencies in methyltin derivatives[16] are still lower: $\nu_s \simeq$ 510–525 cm^{-1} and ν_{as} = 520–550 cm^{-1}.

Estimated E–C vibration frequencies (for $E-CH_3$ groupings) are compared in Table 11. Information on regularities in the variation of E–C vibration frequencies in ethyl derivatives $E(C_2H_5)_4$ is provided by the data in Table 12. Japanese workers[105] assign the frequency 736 (3) cm^{-1} to $\nu(f_2)$, but Malkovich and Kolesova[89] and Batuev *et al.*[106] have adopted the frequencies 640 (3 w) and 630 (3 w) cm^{-1}§ respectively. The correctness of the assignment[62] is evident from a comparison of the frequency differences $\nu(f_2)-\nu(a_1)$ for molecules of types $E(CH_3)_4$ and $E(C_2H_5)_4$ (see Table 13)

TABLE 8. Force constant k_{Si-C} for $Si(CH_3)_4$.

	$10^{-5}k_s$, dyn cm^{-1}	$10^{-5}k_{s,s'}$, cm^{-2}	References
k_{Si-C}	3.31	5.20	96
k_{Si-C}	3.31	5.20	98
k_{Si-C}	2.93	4.60	99
k_{Si-C}	2.92	4.62	100

TABLE 9. k_{E-C} for compounds of the type $E(CH_3)_4$ according to Siebert[99].

Compound	$10^{-5}k_s$, dyn cm^{-1}
$C(CH_3)_4$	4.22
$Si(CH_3)_4$	2.93
$Ge(CH_3)_4$	2.72
$Sn(CH_3)_4$	2.24
$Pb(CH_3)_4$	1.90

§ w = wide.

TABLE 10. Frequencies of Si–C stretching vibrations* in $Si(CH_3)_4$ groups.

	ν_s(Si–C)	ν_{as}(Si–C)	References
$(CH_3)_3SiH$	623	718	103
$(CH_3)_3Si-Cl$	640	700	104
$(CH_3)_3SiCH=CH_2$	—**	696	
$(CH_3)_3SiCH_2-CH=CH_2$	627	702	
$(CH_3)_2SiCH_2CH_2CH=CH_2$	626	697	
$(CH_3)_3SiCH_2CH_2CH_2CH=CH_2$	—**	700	

* See also Ref. 48.

** It is difficult to make a definite assignment of the lines.

The infrared absorption spectra of $Si(C_2H_5)_4$ have been examined[29,35], though within the range 2–15 μ, and information on the infrared spectrum of $Ge(C_2H_5)_4$ is available[107].

The Raman spectra of some alkyltrichlorosilanes[108] indicate that the Si–C vibration frequency in Si–Alk groupings decreases in the sequence CH_3, C_2H_5, n-C_3H_7, n-C_4H_9 (see Table 14).

Since the E–C vibration frequencies have the lowest value in the case of allyl groups (see Table 11), the Si–C stretching vibrations can be assumed to lie within the range 550–800 cm^{-1}, Ge–C at 500–650 cm^{-1}, Sn–C at 450–550 cm^{-1}, and Pb–C at 420–480 cm^{-1}.

The authors of some papers on the infrared absorption spectra of organosilicon compounds[72,74,91] assume that the Si–C stretching vibrations lie within the range 800–900 cm^{-1}: this is incorrect. This range contains the

TABLE 11. Frequencies of E–C stretching vibrations (E = Si, Ge, Sn) from infrared spectra.

Type of vibrations	$(CH_3)_3SiCH_2CH=CH_2$	$(CH_3)_3GeCH_2CH=CH_2$	$(CH_3)_3SnCH_2CH=CH_2$
A	555	524	480
A	635	573	512 ν_s $E(CH_3)_3$
E	701	602	527 ν_{as} $E(CH_3)_3$

TABLE 12. Frequencies of the skeletal vibrations of $E(C_2H_5)_4$ molecules.

Type of vibrations	$Si(C_2H_5)_4$[62]	$Ge(C_2H_5)_4$*	$Sn(C_2H_5)_4$[16]*	$Pb(C_2H_5)_4$[16]*
A	553 (10)	530 (80) (R)	475 (125) (R)	443 (320) (R)
F	625 (3)	577 (40) (R and i.r.)	500 (84) (R and i.r.)	458 (200) (R and i.r.)

* Intensities (numbers in parentheses) were measured relative to the CCl_4 line at 458 cm^{-1}, the intensity of which was taken as 100.

TABLE 13. $\Delta\nu = \nu(f_2) - \nu(a_1)$ for compounds of the types $E(CH_3)_4$ and $E(C_2H_5)_4$.

Type of compound	Si $\Delta\nu$	Ge $\Delta\nu$	Sn $\Delta\nu$	Pb $\Delta\nu$
$E(CH_3)_4$	98	50	20	13
$E(C_2H_5)_4$	72	47	25	15

TABLE 14. Si–C vibration frequencies[108].

Compound	ν_{Si-C} (I)
CH_3SiCl_3	757 (5)
$C_2H_5SiCl_3$	712 (3d)
n-$C_3H_7SiCl_3$	698 (0d)
n-$C_4H_9SiCl_3$	705 (0s)
n-$C_6H_{13}SiCl_3$	695 (0)

rocking vibrations of CH_3 groups in Si–CH_3, etc. groupings. Experiment shows that definite assignment of E–C vibration frequencies requires data on both infrared and Raman spectra. The frequencies of the E–C deformation vibrations lie within the range 100–300 cm^{-1}, falling regularly in the sequence[109] Si, Ge, Sn, Pb.

The problem of the E–C vibrations is the most important in the identification of organosilicon, organogermanium, and organotin compounds, for the E–C bond characterises the above as definite classes of heteroorganic ("organoelemental") compounds. The E–C bonds are more polar than the C–C bond, and as a result the task of finding and assigning E–C vibrations in the spectra is somewhat easier than the analogous problem in the case of hydrocarbons.

Nevertheless, as already noted, several different views exist concerning the frequency range of E–C vibrations. Several recent papers on the vibrational–rotational spectra of the simplest methyl derivatives of silicon again indicate that the frequency range 800–900 cm^{-1} is that of CH_3 rocking vibrations. Incidentally, the frequencies of these vibrations are very close for both Si–CH_3 and Ge–CH_3, around 800 cm^{-1}. However, the difference in Si–C and Ge–C vibration frequencies in the ranges 550–800 and 500–600 cm^{-1} is ~100 cm^{-1}. For example, the values of ν_{Si-C} and $\nu_{(CH_3)rock}$ for CH_3SiCl_3 are 760 and 800 cm^{-1}, while the corresponding values of ν_{Ge-C} and $\nu_{(CH_3)rock}$ for CH_3GeCl_3 are 633 and 824 cm^{-1}.

VI. THE E–X BOND (E = Si, Ge; X = F, Cl, Br, I)

Table 15 gives the frequencies of Si–X stretching vibrations for the groups SiX, SiX_2, and SiX_3, together with references to the original papers. Table 16 gives corresponding data for compounds containing GeX, GeX_2, and GeX_3 groups. For the spectra of $HSiCl_3$, see Refs. 118 and 119; trimethylchlorosilane has been investigated by Duchesne[120] (for monochlorosilane, see Ref. 121). Methylchlorosilanes have been investigated by Goubeau *et al.*[122], Simanouti *et al.*[102], Smith[104], and Ignat'eva *et al.*[101] Murata and Hayashi[112] have investigated the methylbromosilanes. Data on trichlorosilane are given by Collins and Nielsen[123]. The Raman spectra of ethylchlorosilanes have been investigated by Batuev *et al.*[106], and also by Murata *et al.*[105] The Sn–X stretching vibrations (X = Cl, Br) should be sought[33,34,118] within the range 300–400 cm^{-1}.

Several calculations have been made by various workers: for example, Simanouti[124] determined k_{Si-X} for molecules of the type SiX_4 (X = F, Cl, Br)¶. Shimizu and Murata

¶ In this section we shall not discuss the tetrahalides (for which see Ref. 26).

TABLE 15. Si–X stretching vibration frequencies.

Si–X			SiX_2				SiX_3			
compound	ν, cm^{-1}	Ref.	compound	ν_s	ν_{as}	Ref.	compound	ν_s	ν_{as}	Ref.
H_3SiF	874	22	—	—	—	—	—	—	—	—
D_3SiF	885	22	—	—	—	—	—	—	—	—
$(CH_3)_3SiF$	912	110	$(CH_3)_2SiF_2$	818	899	114	—	—	—	—
$(C_6H_5)_3SiF$	852	111	$(C_6H_5)_2SiF_2$	681	918	111	$(C_6H_5)SiF_3$ (soln.)	862	970	114
H_3SiCl	551	18	H_2SiCl_2	531	592	115	$HSiCl_3$	493	589	29
$(CH_3)_3SiCl$ (gas)	487	104	—	—	—	—	$DSiCl_3$	489	555	48
$(CH_3)_3SiCl$ (liq.)	467	102	$(CH_3)_2SiCl_2$	469	538	29	CH_3SiCl_3	450	572	29
$(C_2H_5)_3SiCl$	464	106	$(C_2H_5)_2SiCl_2$	458	?	105	$C_2H_5SiCl_3$	447	580	105
							n-$C_3H_7SiCl_3$	448	588	108
$(CH_3)_2$ n-C_4H_9SiCl	481	29	$(CH_3)C_2H_5SiCl_2$	467	540	29	iso-$C_3H_7SiCl_3$	458	586	29
$(C_2H_5)_2$ n-C_3H_7SiCl	484	29	—	—	—	—	n-$C_4H_9SiCl_3$	448	588	108
$(CH_3)_2(CH_2{=}CH)SiCl$	477	86	$CH_3(CH_2{=}CH)SiCl_2$	462	562	86	$CH_2{=}CHSiCl_3$	453	599	86
$(CH_3)_2(CH_2{=}CH{-}CH_2)SiCl$	476	86	$CH_3(CH_2{=}CH{-}CH_2)SiCl_2$	470	548	86	$CH_2{=}CH{-}CH_2SiCl_3$	455	590	86
$(C_6H_5)_3SiCl$ (soln.)	550	111	$(C_6H_5)_2SiCl_2$	472	553	104	$C_6H_5SiCl_3$ (soln.)	518	593	111
H_3SiBr	430	18	H_2SiBr_2	393	456	115	$HSiBr_3$	360	468	26
$(CH_3)_3SiBr$	374	112	$(CH_3)_2SiBr_2$	355	426	112	CH_3SiBr_3	314	453	112
H_3SiI	355	20								
D_3SiI	351	113								
$(CH_3)_3SiI$	331	116								

TABLE 16. Frequencies of Ge–X stretching vibrations.

GeX		Ref.	GeX_2			Ref.	GeX_3			Ref.
compound	ν, cm^{-1}		compound	ν_s	ν_{as}		compound	ν_s	ν_{as}	
H_3GeCl	423	19	$BrHGeCl_2$	350	432	32	$HGeCl_3$	409	438	32
$(CH_3)_3GeCl$	360–70	117	$(CH_3)_2GeCl_2$	385	428	51	$(CH_3)GeCl_3$	393	427	51
Br_2HGeCl	419	32	$(C_2H_5)_2GeCl_2$	380	420	51	$(C_2H_5)GeCl_3$	397	423	51
Cl_2HGeBr	309	32	$ClHGeBr_2$	290	320	32	$HGeBr_3$	235	325	32
—	—	—	$(CH_3)_2GeBr_2$	272	297	117	CH_3GeBr_3	263	314	117

have made calculations on CH_3SiCl_3,[125] $(CH_3)_2SiCl_2$,[126] and $(CH_3)_3SiCl$.[127] Goubeau *et al.*[122] determined the force constants of Si–Cl bonds for the series $(CH_3)_nSiCl_{4-n}$ (n = = 0–4). Kovalev's calculation[128] is also concerned with this series of compounds. Table 17 gives values of the force constants of Si–Cl bonds in methylchlorosilanes taken from various sources.

Force constants of Si–X bonds for the series $(CH_3)_nSiF_{4-n}$ and $(CH_3)_nSiBr_{4-n}$ are given by Murata[129] and also in Ref. 48. The values of k_{Si-X} are approximately, in 10^5 dyn cm^{-1}, 5.8–6.4 for Si–F, 2.5–3.2 for Si–Cl, and 2.0–2.5 for Si–Br (according to the results of different workers for various compounds).

A series of papers recently published by Kovalev[130-134] gives a fairly detailed numerical analysis of the vibrational spectra of methylchlorosilanes and methylbromosilanes of the structure $(CH_3)_nSiX_{4-n}$ (X = Cl, Br; n = 1–4).

The infrared absorption spectra and the Raman spectra of the complete series of methylchlorostannanes $(CH_3)_nSnCl_{4-n}$ (n = 0–4) have been examined by Edgell and Ward[135], from whose work it follows that for $(CH_3)_3SnCl$ the stretching vibration frequency is ν_{Sn-Cl} = 318 cm^{-1}, for $(CH_3)_2SnCl_2$ $\nu_{s\ and\ as(Sn-Cl)}$ = 344 cm^{-1}, and for CH_3SnCl_3 $\nu_{s\ and\ as(Sn-Cl)}$ = = 363 cm^{-1}.

Among alkylchlorosilanes and alkylchlorogermanes which have the greatest practical application, alkenylalkylchlorosilanes containing one Si–Cl bond usually have infrared absorption bands and Raman lines lying within the range 465–485 cm^{-1}, which can be detected fairly easily. Compounds containing two Si–Cl bonds ($SiCl_2$ groups) are characterised by two fairly intense absorption bands, ν_s in the range 460–470 cm^{-1} and ν_{as} in the range 540–565 cm^{-1}. Compounds containing $SiCl_3$ groups also have two absorption bands due to Si–Cl stretching vibrations, ν_s in the range 445–460 cm^{-1} and ν_{as} at 580–600 cm^{-1}. The difference in the infrared absorption bands of $SiCl_2$ and $SiCl_3$ groups is quite appreciable. This difference is evident primarily in the value of $\Delta\nu = \nu_{as} - \nu_s$, which is greater for $SiCl_3$ than for $SiCl_2$, 140 cm^{-1} compared with 80 – 100 cm^{-1}. Moreover, in the Raman spectra $\nu_{as(Si-Cl)}$ is somewhat more clearly developed with $SiCl_3$ than with $SiCl_2$. In the case of compounds containing $GeCl_2$ groups $\nu_{s(Ge-Cl)}$ = 380 cm^{-1} and $\nu_{as(Ge-Cl)}$ = 420–430 cm^{-1}, while for compounds containing $GeCl_3$ groups $\nu_{s(Ge-Cl)}$ = = 390 cm^{-1} and above, and $\nu_{as(Ge-Cl)}$ = 420–430 cm^{-1} (nearer to 430 cm^{-1}). In the Raman spectra ν_{as} is also more clearly developed with $GeCl_3$ than with $GeCl_2$ groups.

TABLE 17.

Compound	$10^{-5}k_{Si-Cl}$, dyn cm^{-1}		
	Ref. 116	Refs. 125–127	Ref. 128
$(CH_3)_3SiCl$	2.4	2.59	2.54
$(CH_3)_2SiCl_2$	3.7	2.59	2.69
CH_3SiCl_3	3.8	2.59	2.87

TABLE 18. Lengths of E–X bonds, Å.

Compound	r_{E-X}, Å (X = F, Cl)	References
H_3SiF	1.593±0.002	136
H_3SiCl	2.050±0.001	136
D_3SiCl	2.0486	136
$(CH_3)_3SiCl$	2.03	137
$HSiCl_3$	2.021±0.002	137
CH_3SiCl_3	2.021	137
$HGeCl_3$	2.1139±0.0010	138

The variation in the E–X vibration frequencies for molecules of the types EH_3X and EH_2X_2 is quite well seen from Figs. 3 and 4. For molecules of type EHX_3 this dependence is shown in Fig. 6 (the forms of the vibrations for molecules of symmetry C_{3v} are given in Fig. 3).

Table 18 lists the lengths of Si–X and Ge–X bonds in several molecules, these data having been taken from papers on microwave spectra[136-138].

VII. THE E–O BOND (E = Si, Ge)

A large proportion of papers on compounds containing E–O bonds are devoted to disiloxanes and alkoxysilanes, both monomers and polymers. Among the early investigations reference must be made to the work of Wright and Hunter[72] and Young *et al.*[73] The former workers noted that in the methylpolysiloxanes the Si–O stretching vibration frequencies lie in the neighbourhood of 1052 cm^{-1}.

In disubstituted cyclic siloxanes of the type

$$[-Si(Alk)_2-O-]_n,$$

ν_{Si-O} = 1020 cm^{-1} in the case of trimers (n = 3), the value for tetramers being 1081 cm^{-1}. The infrared absorption spectra of several alkylsiloxanes have been examined by McMahon[95], who gives the frequency $\nu_{Si-O-Si}$ = 1075 cm^{-1} for the Si–O–Si grouping. Lord *et al.*[139] investigated the vibrational spectra and the structure of disiloxane (I) and hexadeuterodisiloxane (II), and found that $\nu_{Si-O-Si}$ lie near 606 and 1107 cm^{-1} in the case of (I), and at 555 and 1094 cm^{-1} in the case of (II). They conclude that the SiOSi angle is either equal or close to 180°. McKean, however, considers[140] that this angle lies between 135° and 155°. It has been estimated[141] as 155°. Electron diffraction examination of the structure of $(CH_3)_3SiOSi(CH_3)_3$ suggests[142] that the SiOSi angle is 130° ± 10°.

A considerable number of papers on this question are due to Kriegsmann, who investigated the vibrational spectra of cyclic siloxanes[143] of the type $[(CH_3)_2SiO]_n$ ($n = 4-6$) and compounds of the type $(CH_3)_3SiXSi(CH_3)_3$ (X = O, NH, CH_2, S)[144]. Kriegsmann and Licht[145] examined alkoxy--compounds of the types $Si(OAlk)_4$ and $Ti(OAlk)_4$, where Alk = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9. Compounds of the structure $(CH_3)_2XSiOSiX(CH_3)_2$ (X = OH, Cl, C_6H_5) have been investigated[146]. Data are available[147] on the infrared absorption spectra and Raman spectra of $[(CH_3)_3SiO]_3$ and $[(CH_3)_3SiNH]_3$. It follows from the above work of Kriegsmann that in different compounds $\nu_{s(SiOSi)}$ lies within the range 500–550 cm^{-1}, and $\nu_{as(SiOSi)}$ in the region of 1070–1080 cm^{-1}.

The same result follows from the work of Kirei and Lisitsa[148] on the infrared absorption spectrum of hexaethyldisiloxane, and also that of Lazarev *et al.*[149] The general conclusion from work on organosilicon compounds containing an Si–O bond is that $\nu_{s(SiOSi)}$ = 500–550 cm^{-1}, $\nu_{as(SiOSi)}$ = 1060–1080 cm^{-1} (the frequencies being rather lower for cyclic polysiloxanes), δ_{SiOSi} = 250 cm^{-1}, and $\angle$ SiOSi $\neq$ 180°.

Goubeau and Hiersemann[154] examined the Raman spectra of

$(CH_3)_3SiSH$, Cl_3SiSH, $(CH_3)_3SiSSi(CH_3)_3$,
$Cl_3SiSSiCl_3$, $(CH_3)_2SiS_2Si(CH_3)_2$, and $Cl_2SiS_2SiCl_2$.

Kriegsmann and Clauss[155] investigated $[(CH_3)_2SiS]_2$ and $[(CH_3)_2SiS]_3$. Disilyl sulphide and bistrideuterosilyl sulphide have been investigated by Linton and Nixon[156]. From these papers it follows that $\nu_{s(SiSSi)} \simeq 400-450$ cm^{-1}, $\nu_{as(SiSSi)} = 480-520$ cm^{-1}, $\delta_{Si-S} \simeq 175$ cm^{-1}, and the angle SiSSi is close to 100°. The silicon cyanates $(CH_3)_nSi(NCO)_{4-n}$, where n = 0–4, have been investigated by Goubeau *et al.*[157] Simon and Arnold[158] investigated $(CH_3)_3SiOOSi(CH_3)_3$ and $(C_2H_5)_3SiOOSi(C_2H_5)_3$. Table 19 compares the Si–O vibration frequencies[158] for $(CH_3)_3SiOSi(CH_3)_3$ and $(CH_3)_3SiOOSi(CH_3)_3$.

Extremely interesting data on the angles and force constants of the Si–X bonds in SiXSi groups (X = O, NH, CH_2, S) have been obtained by Kriegsmann[144] (see Table 20).

Among the work on germanium derivatives mention must be made of that of Johnson and Fritz[159], who investigated the infrared absorption spectra of several alkoxygermanes $Ge(OAlk)_4$ (Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}) as well as tetracyclohexyloxygermane. These compounds are characterised by strong absorption bands at 1040 and 680 cm^{-1}, which are attributed to the group



In compounds containing Si–O–C groupings (for example tetraethoxysilane) $\nu_{(Si-O-C)}$ = 1090–1100 cm^{-1}.[29] The

TABLE 19.

Compound	$\nu_{s(Si-O)}$, cm^{-1}	$\nu_{as(Si-O)}$, cm^{-1}	$\nu_{s(SiC_3)}$, cm^{-1}
$(CH_3)_3SiOSi(CH_3)_3$	522	1055	660
$(CH_3)_3SiOOSi(CH_3)_3$	768	1254	614

TABLE 20. Force constants and angles[144] of Si–X–Si groupings (X = O, NH, CH_2, S).

Compound	$10^{-5}k$, dyn cm^{-1}	$\angle$SiXSi
$(CH_3)_3SiOSi(CH_3)_3$	4.65	150°
$(CH_3)_3SiNHSi(CH_3)_3$	3.84	131°
$(CH_3)_3SiCH_2Si(CH_3)_3$	2.77	120°
$(CH_3)_3SiSSi(CH_3)_3$	2.20	104°

frequency 1040 cm^{-1} can most probably also be assigned to the grouping Ge–O–C in the formula denoted by the asterisk. For example, in the case of $(C_6H_5)_3GeOGe(C_6H_5)_3$,[51] $\nu_{Ge-O-Ge}$ = 855 cm^{-1}.

Thus it can be seen that the infrared absorption spectra of the siloxanes contain intense bands in the range 1020–1100 cm^{-1}, which a great many facts show to be due to antisymmetric (ν_{as}) Si–O–Si vibrations. The $\nu_{Si-O-Si}$ frequency is lowest in the case of trimeric cyclic siloxanes, when its value is close to 1020 cm^{-1}. In all other cases — cyclic siloxanes containing more than three Si–O–Si units, and also linear siloxanes and polysiloxanes — this frequency is close to 1060–1070 cm^{-1} and is quite constant, being independent of substituents (alkyl, alkenyl, aryl) on the silicon atoms.

An extremely interesting and important fact is that a large proportion of investigators have reached the conclusion that the Si–O–Si angle is not 180°, its most probable value being 150°.

Little information is as yet available on Ge–O–Ge vibrations, and further data must be accumulated.

VIII. COMPOUNDS CONTAINING AN E–E BOND

Relatively little work has been done on compounds containing an E–E bond. Disilane[52], digermane[53], and hexamethyldisilane[152,153,160] has been investigated. Data on hexachlorodisilane are given by Morino[161], Katayama *et al.*[162], and Stitt and Yost[163]. The work by Brown *et al.*[109] on compounds of the type $(CH_3)_3E-E(CH_3)_3$ (E = Si, Ge, Sn), which has been mentioned before, merits special attention. The principal results on the E–E vibration frequencies and the force constants of E–E bonds are given in Table 21. Kovalev[54] has made a calculation on disilane, and found $k_{Si-Si} = 1.75 \times 10^5$ dyn cm^{-1}.

Of the work on organosilicon compounds which has not been mentioned in the previous sections we would like to enumerate briefly the following. Clark *et al.*[164] investigated the infrared absorption spectra of substituted arylmethylsilanes, Gelkey and Tyler[165] give data on those of 1- and 2-naphthyltrichlorosilanes. The question of hydrogen bonds in silanols has been discussed[166]. Spectroscopic characteristics of individual groups have been given[167] for the range 2–10 μ on the basis of an investigation of the infrared absorption spectra of various classes of organosilicon compounds. Curry[168] notes that $SiCH_2CH_2Si$ groups can be detected from absorption bands at 8.85 and 9.50 μ. The question of the configurations of 1,2-disilylethylenes

TABLE 21.

Compound	$\nu_{E-E'}$, cm^{-1}	$10^{-5} k_{E-E'}$, dyn cm^{-1}	$r_{E-E'}$, Å	References
$H_3Si—SiH_3$	434.5	1.7	2.32	52
$H_3Ge—GeH_3$	—	1.3	2.41	53
$(CH_3)_3Si—Si(CH_3)_3$	404	1.3	—	109
$(CH_3)_3Ge—Ge(CH_3)_3$	273	1.34	—	109
$(CH_3)_3Sn—Sn(CH_3)_3$	190	1.01	—	109

has been cleared up by Egorov *et al.*[169] According to Goubeau and Reyhing[170], $\nu_{C\equiv N}$ in $(CH_3)_3SiC\equiv N$ is 2187 cm^{-1}; these workers have also examined[171] silicon thiocyanates. Grenoble and Launer[172] have made qualitative and quantitative analyses of phenylchlorosilanes over the range covered by the CsBr prism (up to 40 μ). Egorov[173] has devoted a paper to the effect of the nature of substituents attached to the silicon atom on the frequency of the completely symmetrical Si−C stretching vibration. Rao *et al.*[174] have investigated the absorption spectra in the infrared (and also in the near ultraviolet) of polyphenyl derivatives of elements of Groups IV and Vb. The vibration frequencies of various groups in organosilicon compounds have been noted[175], and a spectroscopic examination has been made[176] of the influence of the silicon atom on multiple bonds in organosilicon compounds. Further information on the silanes can be obtained also in a review paper by Janz and Mikawa[177].

Two papers which could be included in Section III deal respectively with compounds containing multiple bonds (C≡C and C=C)[178] and compounds of the type $R_3M-C\equiv C-R$ (M = Si, Sn)[179].

Yakovleva *et al.*[180] have examined the vibrational spectra of alkenynyltin derivatives of the type $Alk_3SnC\equiv C-CH\equiv CH_2$, where Alk = CH_3, C_2H_5, particularly with regard to the vibration frequencies and intensities of the multiple bonds.

The dependence of the vibration frequencies of the Ge−C bond in the spectra of alkylgermanes on the nature of the substituents has been discussed[181], the paper resembling to some extent that noted earlier[173].

Harran *et al.*[182] have examined the question of identifying phenyl derivatives of elements in Groups IVb and Vb from the infrared absorption spectra in the range 2−35 μ.

Investigations of the vibrational−rotational spectra of compounds containing elements of the carbon subgroup are of some interest. Thus Randić[183] has examined the vibrational−rotational spectrum of CH_3SiH_3 in the gaseous state, and Ebsworth *et al.*[184] that of H_3SiNCS. From the structure of the vibrational−rotational bands, it was concluded[184] that the heavy atoms in the H_3SiNCS molecule are arranged linearly, from which it follows that the molecule has the symmetry C_{3v} and is a symmetrical top.

In conclusion, we may mention a recent paper by Kriegsmann[185], on the problem of measuring the intensities of the Si−O−Si bands in siloxanes, which contains a complete list of papers by this author on the vibrational spectra of organosilicon compounds.

Furthermore, extremely interesting and important results have been obtained by Wilson and Rhee[186] on compounds of the type GeH_3X and GeD_3X (X = F, Cl, Br, I), and also by Goldfarb and Sujushi[187], who investigated the infrared absorption spectra of $(H_3Ge)_2O$, $(H_3Ge)_2S$, $(D_3Ge)_2O$, and $(D_3Ge)_2S$. From an analysis of the rotational structure of a series of bands, the latter workers concluded that in $(H_3Ge)_2O$ the GeOGe angle is 108° ± 12°, and in $(H_3Ge)_2S$ the GeSGe angle is 112° ± 10°. A useful paper has also been published by Smith[188].

Summarising what has been said above, we must note the following points.

The E−H vibrations (E = Si, Ge, ...) are very characteristic, as shown by the constancy of their frequencies in the case of alkyl and alkenylalkyl derivatives containing the same number of E−H bonds.

Differences in the E−H vibration frequencies (E = C, Si, Ge, Sn) are to be attributed mainly to variation in the force constants of the E−H bonds; the change in mass of the elements E will make a very small contribution.

It is interesting that, whereas for SiH_4 $k_{q(Si-H)} = 4.67 \times 10^6$ cm^{-2}, it is rather higher for halogenosilanes and rather lower for alkylsilanes, the same generalisation applying to the variation in the ν_{Si-H} frequencies. This is valid also for derivatives of germane GeH_4.

The effect of the central atom (E = Si, Ge, Sn, Pb) on the various vibrations in the spectra of organosilicon, organogermanium, organotin, and organolead compounds is most specific in the frequency range below 1270 cm^{-1}. In the first place we must note how extremely characteristic are the vibration frequencies in the range 1150−1270 cm^{-1} due to E−Alk groups (E = C, Si, Ge, Sn, Pb; Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9). The presence of $E-CH_3$ groups can be further confirmed by the occurrence in the infrared spectrum of bands in the range 800−850 cm^{-1}, due to rocking vibrations of the CH_3 groups. The presence of C_2H_5 groups is characterised by absorption bands at about 735−740 cm^{-1}.

The absorption bands and Raman lines due to E−C vibrations have, of course, the greatest analytical value. As has been seen (Section V), many papers have been published on molecules of the type $E(CH_3)_4$. Quite a lot of work has been done also on methyl derivatives of organosilicon compounds, less on other alkyl derivatives of silicon. In the case of organogermanium and organotin compounds considerably less research has been published on the E−C vibrations than with organosilicon compounds. Nevertheless, available data on E−C bonds enable the frequency ranges of their stretching vibrations to be quite clearly isolated: $\nu_{Si-C} \simeq 550-800$ cm^{-1}; $\nu_{Ge-C} \simeq 500-650$ cm^{-1}; $\nu_{Sn-C} \simeq 450-550$ cm^{-1}; and ν_{Pb-C} lies within 420−480 cm^{-1}. The E−C vibration frequencies are seen to fall regularly on passing from Si to Pb, this being associated with a decrease in the force constants of the E−C bonds.

The intensity of the Raman lines of the E−C stretching vibrations increases on passing from Si to Pb, which may be due to the greater polarisability of the Pb−C bond compared with Si−C, Ge−C, and Sn−C.

Published results on E−X vibrations (E = Si, Ge, Sn; X = F, Cl, Br) are most comprehensive for the chlorosilanes.

Considerably less information is available on the chlorogermanes. This can be inferred, say, from the number of mathematical papers, which are always based on the experimental vibrational spectra of the molecules. Whereas for the chlorosilanes (and also fluoro- and bromo-silanes)

quite a large number of calculations have been made on the molecular vibrations, hardly any have been made on the chlorogermanes (or organogermanium compounds in general): *i.e.* a few years ago insufficient experimental data were available.

The frequency ranges of the E–Cl stretching vibrations (E = Si, Ge, Sn) are: ν_{Si-Cl} = 450–600 cm^{-1}; ν_{Ge-Cl} = = 360–440 cm^{-1}; and ν_{Sn-Cl} = 315–370 cm^{-1}.

Quite a large number of papers have dealt with compounds containing an Si–O bond, from which it follows that no difficulty is involved in identifying compounds containing Si–O–Si and Si–O–C groupings. A very important fact is that, according to the results in most of these papers, the Si–O–Si angle in siloxanes can be accepted as ~150°.

It must be noted that most of the work has been done on organosilicon compounds, and considerably less on derivatives of germanium and tin.

The present survey by no means claims to give a completely exhaustive account of the work which has been done. No doubt several communications may have been omitted, but it seems to the reviewer that the survey may prove a real help to those who are working on organosilicon, organogermanium, and organotin compounds.

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