291. *The Infrared Spectra of the Methylsilyl Halides and Related Compounds.*

By E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard.

Infrared spectra have been recorded of the compounds $(CH_3 \cdot SiH_2)_n X$; X is CH_3, F, Cl, Br, I, and NC when $n = 1$; X is O or S when $n = 2$; and X is N when $n = 3$. Particular attention has been paid to the assignment of frequencies to the vibrations of the SiH_2 group and to the Si–X bond-stretching modes. The ranges recorded for the SiH_2 frequencies were 2200—2140 (νSiH); 980—940 (SiH_2 bend. or scissors); 955—875 (SiH_2 wag.); 740—630 (SiH_2 twist.); and 520—460 cm.$^{-1}$ (SiH_2 rock.). The frequencies of the SiH_2 wagging and bending modes increase approximately linearly with the electronegativity of X.

CONSIDERABLE interest has been shown in the characteristic frequencies of vibrations of the SiH_3, SiH_2, and SiH groups as observed in complex molecules.[1-4] Several series of compounds have recently been prepared in this laboratory containing the groupings $CH_3 \cdot SiH_2-$, $(CH_3)_2SiH-$, and $(CH_3)_3Si-$ bound to various atoms, and their infrared spectra have been recorded and compared. The purpose of this paper is to interpret the spectra of the monomethylsilyl compounds in terms of the vibrations of these molecules. In the spectra of the simpler compounds vapour-phase band-contour data often make it possible to classify the absorption frequencies reliably in terms of the symmetry species of the corresponding vibrations.

A second paper will deal with the spectra of derivatives of more highly methylated silyl groups.

[1] West and Rochow, *J. Org. Chem.*, 1953, **18**, 303.
[2] Kaye and Tannenbaum, *ibid.*, p. 1750.
[3] Opitz, Peake, and Nebergall, *J. Amer. Chem. Soc.*, 1956, **78**, 292.
[4] Westermark, *Acta Chem. Scand.*, 1955, **9**, 947.

EXPERIMENTAL

The preparation of the compounds is described elsewhere.[5, 6, 7] The spectra were studied in the region 4000—400 cm.[-1] by use of a Perkin-Elmer model 21 double-beam spectrometer fitted with 60° calcium fluoride, sodium chloride, or potassium bromide prisms. The substances were examined in the vapour phase, and their purities were checked by vapour-pressure measurements. The only impurity detected spectroscopically was the analogous methylsilyl ether $(CH_3 \cdot SiH_2)_2O$; very small concentrations of this substance can be detected because its spectrum contains a band at 1085 cm.[-1], due to the Si–O–Si grouping, which is intrinsically very strong. Because the methylsilyl amines, sulphides, or halides would be expected to be hydrolysed to form this ether [5, 8, 9] even by the minute quantities of water present in tapgrease, and since many of the compounds cannot be separated from it by fractional distillation, it was impossible to avoid slight contamination of this kind. The spectra of the halides and of dimethylsilane are illustrated in the Figures.

As mentioned above, much use has been made of vapour-phase band contours in the assignments that follow. Any vibration that produces a dipole change parallel to the axis of greatest moment of inertia should give rise to a band with type C contour (P, Q, and R branches with a particularly prominent Q branch). A dipole change parallel to the axis of intermediate moment of inertia should give a band of type B contour (a doublet P–R structure without the central Q branch), while a change parallel to the axis of least moment of inertia should give a band with contour of type A (P, Q, and R branches, often of comparable intensity).[10]

Assignments.—(1) *Dimethylsilane*, $CH_3 \cdot SiH_2 \cdot CH_3$. The molecule of dimethylsilane should have one two-fold rotational axis of symmetry, and two planes of symmetry perpendicular to that axis, corresponding to the symmetry group C_{2v}. Being an eleven-atomic molecule, it has 27 possible modes of vibration, but only 22 of them are infrared active. The vibrations, divided into their symmetry classes, are listed in Table 1.

TABLE 1. *Vibrations to be expected of the molecules of methylsilyl fluoride and dimethylsilane, with their symmetry classes and expected infrared band contours.*

		$CH_3 \cdot SiH_2F$ Symmetry class		$CH_3 \cdot SiH_2 \cdot CH_3$ Symmetry class			
Vibration		A'	A''	A_1	A_2	B_1	B_2
Band contour		A–B	C	B	Forbidden	A	C
C–H stretch. (a)		ν_1	ν_{12}	ν_1	ν_{10}	ν_{15}	ν_{22}
C–H stretch. (s)		ν_2	—	ν_2	—	ν_{16}	—
Si–H stretch.		ν_3	ν_{13}	ν_3	—	—	ν_{23}
CH₃ deform. (a)		ν_4	ν_{14}	ν_4	ν_{11}	ν_{17}	ν_{24}
CH₃ deform. (s)		ν_5	—	ν_5	—	ν_{13}	—
SiH₂ bend. (scissors)		ν_6	—	ν_6	—	—	—
SiH₂ wag.		ν_7	—	—	—	ν_{19}	—
Si–F stretch.		ν_8	—	—	—	—	—
CH₃ rock.		ν_9	ν_{15}	ν_7	ν_{12}	ν_{20}	ν_{25}
Si–C stretch.		ν_{10}	—	ν_8	—	ν_{21}	—
SiH₂ twist.		—	ν_{16}	—	ν_{13}	—	—
SiH₂ rock.		—	ν_{17}	—	—	—	ν_{26}
C–Si–X deform.		ν_{11}	—	ν_9	—	—	—
CH₃ torsion		—	ν_{18}	—	ν_{14}	—	ν_{27}

The bonds from the silicon atom are probably directed tetrahedrally, making the C–Si–C bond angle greater than 90°. As the moment of inertia of the molecule as a whole must be largely governed by the relative positions of the heavy atoms, there can be little doubt that the axis of intermediate moment of inertia is parallel to the two-fold rotational axis, while the axis of least moment of inertia is perpendicular to the two-fold axis but lies in the plane of the heavy atoms. The axis of greatest moment of inertia is then perpendicular to this plane. It follows that vibrations of symmetry class A_1 will give bands with type B contours, those of class B_1

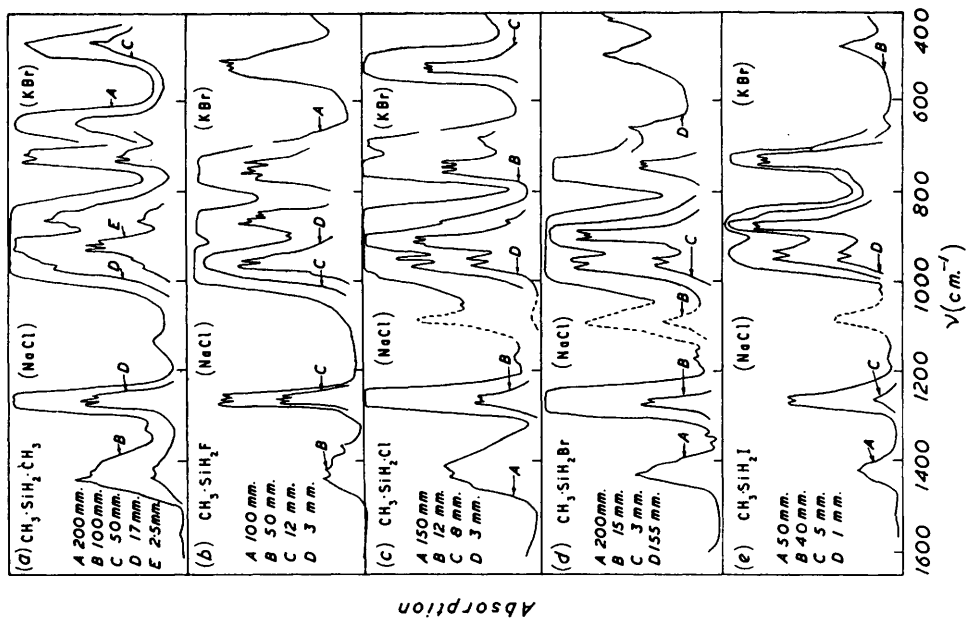[5] Eméleus, Kuchen, and Onyszchuk, *Z. anorg. Chem.*, 1956, **283**, 74.
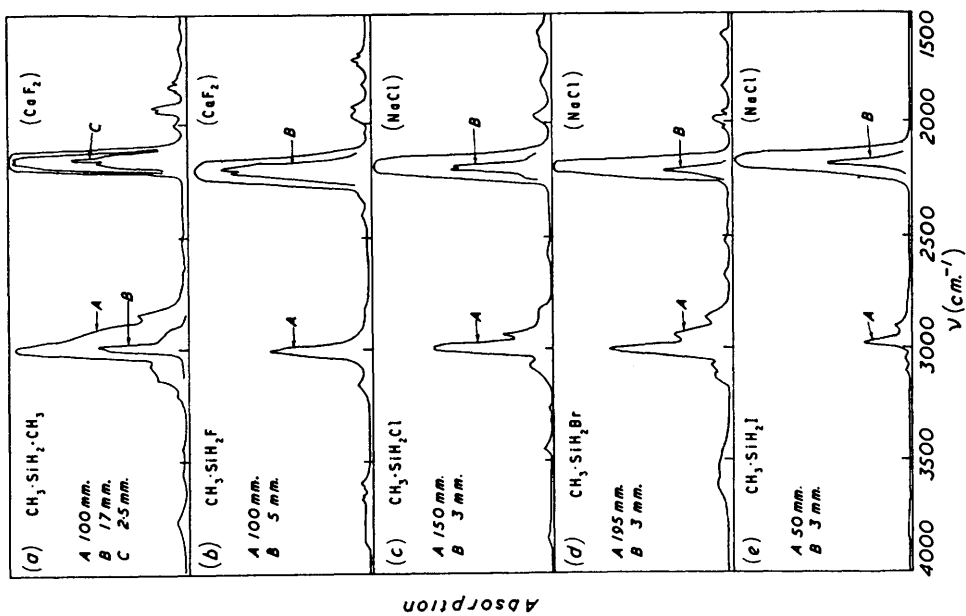[6] Eméleus and Onyszchuk, unpublished work.
[7] Eméleus and Ebsworth, unpublished work.
[8] Eméleus, Macdiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.
[9] Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707.
[10] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

FIG. 2. $\nu = 1600—400$ cm.$^{-1}$.

Absorption

(a) CH₃·SiH₂·CH₃
A 200mm.
B 100mm.
C 50mm.
D 17mm.
E 2·5mm.

(b) CH₃·SiH₂F
A 100mm.
B 50mm.
C 12mm.
D 3mm.

(c) CH₃·SiH₂Cl
A 150mm
B 12mm.
C 8mm.
D 3mm.

(d) CH₃·SiH₂Br
A 200mm.
B 15mm.
C 3mm.
D 155mm.

(e) CH₃·SiH₂I
A 50mm.
B 40mm.
C 5mm.
D 1mm.

ν (cm.$^{-1}$)

FIG. 1. $\nu = 4000—1500$ cm.$^{-1}$.

Absorption

(a) CH₃·SiH₂·CH₃
A 100mm.
B 17mm.
C 2·5mm.

(b) CH₃·SiH₂F
A 100mm.
B 5mm.

(c) CH₃·SiH₂Cl
A 150mm.
B 3mm.

(d) CH₃·SiH₂Br
A 195mm.
B 3mm.

(e) CH₃·SiH₂I
A 50mm.
B 3mm.

ν (cm.$^{-1}$)

Vapour-phase infrared spectra of dimethylsilane and the methylsilyl halides, with the pressure at which each curve was recorded and the prism used (given in parentheses).

will give bands with type A contours, while those of class B_2 will give type C bands. In designating the B_1 and B_2 vibrations, the x axis is chosen to be in the plane of the heavy atoms, perpendicular to the two-fold (z) axis.[11]

In the spectrum recorded, the complex band at 2900—3000 cm.$^{-1}$ must include all the five active CH bond-stretching vibrations. Only one of these, ν_{22}, should give a band with a type C contour, and the sharp peak at 2970 cm.$^{-1}$ can probably be assigned to this mode; the remainder cannot be distinguished from one another. In the same way, the band at 2140—2150 cm.$^{-1}$ is due to both of the two SiH bond-stretching vibrations, but with the help of a calcium fluoride prism it is possible to resolve it into two overlapping components. The one at 2142 cm.$^{-1}$ has a type C contour, and so must correspond to ν_{23}, while the other, with a type B contour centred at about 2145 cm.$^{-1}$, is clearly ν_3. The groups of bands at about 1425 cm.$^{-1}$ and 1260 cm.$^{-1}$ are to be assigned to the three asymmetrical and two symmetrical CH_3 deformation frequencies respectively. The two symmetrical vibrations cannot be experimentally distinguished from one another and give a single band (type A) at 1260 cm.$^{-1}$; the sharp peak at 1430 cm.$^{-1}$ has been attributed specifically to ν_{24} because only this, of all the asymmetrical CH_3 deformation modes, should give rise to a type C band.

At frequencies below 1000 cm.$^{-1}$ the spectrum becomes more complex. The bands at 961 and 919 cm.$^{-1}$ do not have analogies in the spectra of fully methylated derivatives of silane,[12] and so must be due to deformation vibrations of the SiH_2 group. The former, a type B band, has been assigned to the bending (scissors) vibration (ν_6), while the latter, with a type A contour, may be identified with the wagging mode (ν_{19}). In the spectrum of the symmetrical-top molecule methylsilane, a band at 700 cm.$^{-1}$ has a parallel, and another at 873 cm.$^{-1}$ a perpendicular, contour,[13] showing that the dipole changes concerned must be parallel and perpendicular respectively to the C–Si bond. It follows that the former must represent the stretching vibration of that bond, and the latter the methyl rocking mode. In dimethylsilane, the two C–Si bond-stretching vibrations are directly coupled together through the silicon atom, and so may be expected to split into two separate bands with a mean frequency not very different from the value for the corresponding vibration in methylsilane. Hence the bands in the spectrum of dimethylsilane at 730 and 650 cm.$^{-1}$ almost certainly represent the two C–Si bond-stretching modes. Of the two, that at 730 cm.$^{-1}$ has a type A contour, and so is identified with the asymmetrical vibration (ν_{21}), while the other, with a less well-defined shape, is assigned to the symmetrical mode (ν_8). The methyl rocking vibrations in dimethylsilane are coupled together less directly than the bond-stretching modes, and so should lie in a smaller range of frequencies. The group of bands at 875—850 cm.$^{-1}$ lies close to the frequencies of the analogous vibrations of methylsilane [13] and of the more highly methylated derivatives,[12] and has therefore been assigned to the methyl rocking vibrations. The type C peak at 865 cm.$^{-1}$ is identified with the only one of these vibrations that should give a band with a type C contour (ν_{25}); the other two modes are probably hidden under the complex envelope centred at about 855 cm.$^{-1}$.

Since the SiH_2 twisting mode is forbidden, the only remaining band, at 467 cm.$^{-1}$, is assigned to the SiH_2 rocking mode (ν_{26}), in accordance with its C type contour. Of the 22 active modes, only the solitary active CH_3 torsional and the skeletal deformation vibrations remain unaccounted for. The former is likely to give very weak infrared absorption at low frequencies;[14] the frequency of the analogous skeletal deformation vibration of dimethyl sulphide appears at 278 cm.$^{-1}$ in the Raman spectrum,[15] so that its absence from the spectral range studied here is also to be expected. The overall assignments are summarised in Table 2.

(2) *Methylsilyl fluoride*, $CH_3 \cdot SiH_2F$. This molecule can have at most a single plane of symmetry (symmetry group C_s) if the bonds from the silicon atom are directed tetrahedrally, so that all its 18 modes of vibration should be infrared active. Those occurring with a dipole change in the plane of the heavy atoms will have A–B hybrid contours; those producing a dipole change perpendicular to that plane should give type C bands. The assignments at frequencies higher than 1000 cm.$^{-1}$ follow the lines established above, although it is not possible to distinguish all the individual modes of vibration (see Table 2). The band at

[11] Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 359, 360.
[12] Tobin, *J. Amer. Chem. Soc.*, 1953, **75**, 1788.
[13] Randić and Sheppard, unpublished work.
[14] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.
[15] Kohlrausch, " Ramanspektren," Becker and Erler, Leipzig, 1943.

975 cm.$^{-1}$ with a B type contour, and the type A band at 952 cm.$^{-1}$, have been assigned respectively to the bending and the wagging mode of the SiH$_2$ group by analogy with the bands of similar shape in the spectrum of dimethylsilane, for the moments of inertia of the two molecules will probably not differ greatly. Similarly, the C–Si bond-stretching vibration is identified with the absorption band at 760 cm.$^{-1}$. The group of bands at 850 cm.$^{-1}$ is more complex in this spectrum because, judging from the spectra of related compounds,[16, 17] the stretching frequency of the Si–F bond should appear in this region, in addition to the two CH$_3$ rocking modes. The type C contour that may be distinguished at 871 cm.$^{-1}$ is assigned to ν_{15}, the only

TABLE 2. *Analysis of the infrared spectra of methylsilyl fluoride and dimethylsilane.*

CH$_3$·SiH$_2$F				CH$_3$·SiH$_2$·CH$_3$			
Frequency *	Strength	Contour	Vibration	Frequency *	Strength	Contour	Vibration
4225	w	—	$2\nu_3$	No data			
3130	w	—	$\nu_7 + \nu_3$	3060	w	—	$\nu_{19} + \nu_3$
2988	m	C	ν_{12}	2970	m	C	ν_{22}
2970	m	—	ν_1, ν_2	2980 to }	m	—	$\nu_1, \nu_2,$
2910	w	—	—	2920 }	—	—	ν_{15}, ν_{16}
				2860	w	—	$\nu_4 + \nu_{17}$
~2185	s	B	ν_3	2145	s	B	ν_3
2185	s	C	ν_{13}	2142	s	C	ν_{23}
1945	w	—	$2\nu_6$	1912	w	—	$2\nu_6$
1910	w	—	$\nu_6 + \nu_7$				
1710	w	—	$2\nu_8$	1820	w	—	$2\nu_{19}$
1440 }				1430	m	C	ν_{24}
1418 }	m	—	ν_4, ν_{14}	1440 to }	m	—	ν_4, ν_{17}
				1380 }			
1265	s	A	ν_5	1260	s	A	ν_5, ν_{18}
975	vs	B	ν_6	961	vs	B	ν_6
952	vs	A	ν_7	919	vs	A	ν_{19}
871	vs	C	ν_{15}	865	vs	C	ν_{25}
858	vs	B	ν_8				
850	vs	—	ν_9	855	s	—	ν_7, ν_{20}
760	s	—	ν_{10}	730	s	A	ν_{21}
733	s	C	ν_{16}				
				650	s	—	ν_8
522	m	B	$2\nu_{11}$				
510	m	C	ν_{17}	467	m	C	ν_{26}

* The spectra were recorded with a CaF$_2$ prism at frequencies higher than 2000 cm.$^{-1}$.

one of these vibrations that could give rise to such a band; the type B band at 858 cm.$^{-1}$ has been identified with the Si–F stretching frequency, while the remaining CH$_3$ rocking mode probably lies under the complex envelope at about 850 cm.$^{-1}$.

By analogy with dimethylsilane, the band at 510 cm.$^{-1}$ with a type C contour corresponds to the SiH$_2$ rocking mode (ν_{17}), while the overlapping type B band at 520 cm.$^{-1}$ probably represents the overtone of the skeletal deformation frequency ν_{11} (the frequency seems to be too high to be that of the fundamental). There remains a strong band with a type C contour at 733 cm.$^{-1}$, which must be identified with the SiH$_2$ twisting mode (ν_{16}). Of the 18 possible vibrations, only the torsional oscillation of the methyl group remains unaccounted for in this case.

(3) *Compounds* CH$_3$·SiH$_2$X, *where* X = Cl, Br, I, *or* NC. Apart from variations in skeletal frequencies, the spectra of these compounds are very like that of methylsilyl fluoride. The band due to the SiCl bond-stretching vibration appears at 527 cm.$^{-1}$ in the spectrum of the chloride, and the SiBr stretching mode at ~415 cm.$^{-1}$ in the bromide's spectrum. The spectrum of the *iso*cyanide was not recorded in the range 650—400 cm.$^{-1}$; the Si–I frequency was not observed but would be expected to lie outside the range covered by the potassium bromide prism, as the corresponding frequencies of silyl [18] and trimethylsilyl iodide [19] are at ~355 and 331 cm.$^{-1}$, respectively. Otherwise, the spectra can easily be correlated with one another.

[16] Newman, O'Loane, Polo, and Wilson, *J. Chem. Phys.*, 1956, **25**, 855.
[17] Ebsworth, Onyszchuk, and Sheppard, unpublished work.
[18] Dixon and Sheppard, *Trans. Faraday Soc.*, 1957, **53**, 282.
[19] Goubeau and Sommer, *Z. anorg. Chem.*, 1957, **289**, 1.

The frequency of the SiH_2 twisting mode decreases considerably in the series $X = F$ to $X = I$, as does its intensity. The frequency of the wagging vibration also drops in the same way, making it progressively harder to distinguish the bands due to the rocking of the methyl group. The various assignments are summarised in Table 3. The stretching frequency of the NC bond was not observed, but is probably overlaid by the strong ν_{Si-H} absorption band; [17] in methyl *iso*cyanide [15] the corresponding ν_{NC} frequency is 2161 cm.[-1].

(4) *Di(methylsilyl) ether*, $(CH_3 \cdot SiH_2)_2O$, *di(methylsilyl) sulphide*, $(CH_3 \cdot SiH_2)_2S$, *and tri(methyl-silyl)amine*, $(CH_3 \cdot SiH_2)_3N$. The spectra of these compounds are in principle too complicated for detailed analysis; but by assuming that the methylsilyl groups vibrate relatively independently it is possible to pick out the bands due to certain groups of vibrations by using the assignments described above for the simpler spectra. Very satisfactory correlations result from this procedure (see Table 3).

The spectra of both the amine and the ether should contain at least one band in the frequency

TABLE 3. *Assignments of the bands observed in the spectra of molecules of the type* $(CH_3 \cdot SiH_2)_nX.$

	$CH_3 \cdot SiH_2F$	$CH_3 \cdot SiH_2Cl$	$CH_3 \cdot SiH_2Br$	$CH_3 \cdot SiH_2I$	$CH_3 \cdot SiH_2 \cdot NC$
C–H stretch.	2988, 2970 *	2985, 2930	2985, 2915	2985, 2874	2967
Si–H stretch.	2185 *	2200	2198	2190	2198
CH_3 deform. (as)	1440, 1418	1442, 1410	1425	1418	1422
CH_3 deform. (s)	1265	1265	1265	1264	1266
SiH_2 bend. (scissors) ...	975	960	955	947	948
SiH_2 wag.	952	912	898	880	900
CH_3 rock.	{ 871 (C) { 850	873	870	~855	877
		?900	?922	—	—
Si–C stretch.	760	751	740	735	758
SiH_2 twist.	733 (C)	682	656	?631	707 (C)
SiH_2 rock.	510	~510	495	480	No data
Si–X stretch.	858	527	~415	—	—
C–Si–X deform.	(261)	—	—	—	—
	$(CH_3)_2SiH_2$	$(CH_3 \cdot SiH_2)_2O$	$(CH_3 \cdot SiH_2)_3N$	$(CH_3 \cdot SiH_2)_2S$	
C–H stretch.	~2970 *	2970, 2920 *	2967, 2907	2970	
Si–H stretch.	2145 *	2158 *	2146	2160	
CH_3 deform. (as)	1440, 1380	1418, 1375	1453, 1418, 1380	1375	
CH_3 deform. (s)	1260	1264	1260	1260	
SiH_2 bend. (scissors) ...	961	964	955	952 †	
SiH_2 wag.	919	915	907	878	
CH_3 rock.	865	880	~880	?	
Si–C stretch.	730, 650	763	765	740	
SiH_2 twist.	Forbidden	?670	723	?	
SiH_2 rock.	467	520	510	No data	
Si–X stretch.	—	1085	987	—	
C–Si–X deform.	—	—	—	—	

* Recorded by using a CaF_2 prism. † There is another band at 913 cm.[-1] in the spectrum of the sulphide.

range studied due to one of the Si–X bond-stretching vibrations. There is a strong band at 1085 cm.[-1] in the ether's spectrum that cannot be assigned to any other group.

In the spectrum of the amine, once the bands characteristic of the methylsilyl groups have been identified, there remains a strong band at 987 cm.[-1] which has therefore been assigned to the asymmetrical Si–N bond-stretching mode.

DISCUSSION

In all the spectra described above, the stretching vibrations of the CH, SiH, and SiC bonds and the deformation modes of the CH_3 group appear at frequencies close to those observed in the spectra of other compounds which contain these groups. The SiF bond-stretching mode in $CH_3 \cdot SiH_2F$ has been assigned to a band at a frequency (858 cm.[-1]) similar to those of the corresponding vibrations in the spectra of silyl fluoride [16] (872 cm.[-1]) and of trimethylsilyl fluoride [17] (916 cm.[-1]). The SiCl and SiBr bond-stretching frequencies (527 cm.[-1], ~415 cm.[-1]) and the band assigned to the asymmetric Si–O–Si bond-stretching

vibration (1087 cm.$^{-1}$) are also close to the frequencies reported for the analogous vibrations in the spectra of the corresponding silyl derivatives [551 cm.$^{-1}$ (refs. 16, 20), 430 cm.$^{-1}$, (ref. 16) and 1107 cm.$^{-1}$ (ref. 21), respectively]. Only one band that could be assigned to a Si–N bond-stretching mode was observed in the spectrum of tri(methylsilyl)amine (987 cm.$^{-1}$); this may be significant in view of Hedberg's conclusion [22] from electron-diffraction studies that the silicon and nitrogen atoms in the molecule of trisilyl-amine are coplanar. If this were also true of tri(methylsilyl)amine (the two amines are chemically very much alike [7]), the symmetrical Si–N stretching vibration ought to be forbidden or very weak in the infrared spectrum, depending on the overall configuration of the molecule.

TABLE 4. SiH_2 *Deformation frequencies in the molecules* $(CH_3)_2SiH_2$, $CH_3 \cdot SiH_2X$, *and* SiH_2X_2, *where* X *is* F, Cl, Br, *or* I.

Vibration	SiH_2F_2 [17]	$CH_3 \cdot SiH_2F$	$(CH_3)_2SiH_2$	$CH_3 \cdot SiH_2Cl$	SiH_2Cl_2 [24]
Bending	985	975	961	960	953
Wagging	?~975	952	919	912	877
Twisting	—	733	—	682	710
Rocking	?	510	467	~510	610

	SiH_2Br_2 [25] [26]	$CH_3 \cdot SiH_2Br$	$(CH_3)_2SiH_2$	$CH_3 \cdot SiH_2I$	SiH_2I_2 [8, 17]
Bending	942	955	961	947	925
Wagging	843	898	919	880	791
Twisting	688 *	656	—	631	—
Rocking	556	495	467	480	497 †

* Raman data. † In the infrared spectrum of the liquid.

The frequencies of the four SiH_2 deformation modes are now clearly established in the spectra of several compounds of formula $CH_3 \cdot SiH_2X$, and it is interesting to see how they change as the atom X is varied. The frequencies might be influenced either by the mass of X, or by electronic effects connected with that atom's electronegativity—in other words, through induced changes in the force-constants of the bonds concerned. The frequencies of the bending and of the wagging modes have been plotted against the electronegativity of the atom X, and the points in each case lie very close to a straight line. This has previously been shown to be true of one of the CH_3 deformation frequencies.[23] The observation that the values for the bending and wagging modes from the spectra of di(methylsilyl) ether and tri(methylsilyl)amine fall on the appropriate lines shows clearly that the electronegativity of X is the operative factor here, for nitrogen and chlorine have the same electronegativity but probably differ considerably in reduced mass. This relation between the frequencies of the bending and wagging modes and electronegativity influenced the choice made when one of two bands had to be assigned to the SiH_2 wagging vibration in the spectrum of di(methylsilyl) sulphide. The twisting and rocking frequencies do not vary with electronegativity in the same simple fashion.

It is also interesting to compare the deformation frequencies of the SiH_2 group observed in the spectra of the methylsilyl halides with those recorded for dimethylsilane and the silylene halides (see Table 4). The spectra of silylene chloride and bromide had been analysed in detail,[24, 25, 26] and the frequencies obtained in the present work fit in well with these.

Westermark,[4] following West and Rochow,[1] found that in the spectra of a number of more complex dialkylsilanes there were three characteristic absorption bands between

[20] Monfils, *Mem. Acad. roy. Belg. (Classe des Sciences)*, 1956, **29**, 7.
[21] Lord, Robinson, and Schumb, *J. Amer. Chem. Soc.*, 1956, **78**, 1327.
[22] Hedberg, *ibid.*, 1955, **77**, 6491.
[23] Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.
[24] Hawkins and Wilson, *J. Chem. Phys.*, 1953, **21**, 360.
[25] Hawkins, Polo, and Wilson, *ibid.*, p. 1122.
[26] Mayo, Opitz, and Peake, *ibid.*, 1955, **23**, 1344.

660 and 1000 cm.$^{-1}$. The strongest was at about 940 cm.$^{-1}$, while others appeared at about 890 and 715 cm.$^{-1}$. On the basis of the assignments made above for dimethyl-silane, it seems reasonable to associate the first of these bands with the SiH$_2$ bending and the second with the SiH$_2$ wagging modes, while the last band is probably due to one of the Si–C stretching vibrations. The analogous frequencies in the spectrum of the dimethyl compound (see above) are 961, 919, and 730 cm.$^{-1}$, respectively. Similarly, the bands in the spectra of dialkylsilanes at 938—917 and 862—826 cm.$^{-1}$ which Opitz *et al.*[3] have assigned to a deformation and a rocking mode of the SiH$_2$ group, respectively, are more accurately to be described as representing the bending and the wagging modes.

UNIVERSITY CHEMICAL LABORATORY,
    LENSFIELD ROAD, CAMBRIDGE.
[Present address (M. O.): DEPARTMENT OF CHEMISTRY,
    McGILL UNIVERSITY, MONTREAL, CANADA.]