27. *Infra-red Spectra of Compounds of High Molecular Weight. Part IV. Silicones and Related Compounds.*

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The vibrational spectra of some silicones and related substances have been measured between 2 and 20 μ. The compounds included a series of open-chain methylpolysiloxanes, the corresponding cyclic methylpolysiloxanes, some alkoxysilanes, some phenylsilanols and condensates, phenylsiloxanes, and chlorosilanes. The spectra have been correlated and several plausible vibrational assignments have been made. The results have also been discussed in terms of the nature and strength of the Si–O and Si–C bonds.

In previous papers measurements on the infra-red spectra of several classes of compounds with high molecular weight have been described (Thompson and Torkington, Part I, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3; Part II, *ibid.*, p. 21; Part III, *Trans. Faraday Soc.*, 1945, **41**, 246). The present paper deals with some substances containing silicon, such as the open-chain and cyclic alkyl- and aryl-polysiloxanes, together with some simpler related compounds, namely the alkoxysilanes. The spectra were measured several years ago and some of the results were summarised in an earlier discussion (Thompson, *J.*, 1947, 289). Recently, Wright and Hunter (*J. Amer. Chem. Soc.*, 1947, **69**, 803) have published results for some methylpolysiloxanes. While our own results and interpretations are in full agreement with theirs, we have measured a rather wider spectral range, and our additional measurements with the alkoxy-compounds serve to strengthen some of the vibrational assignments.

EXPERIMENTAL.

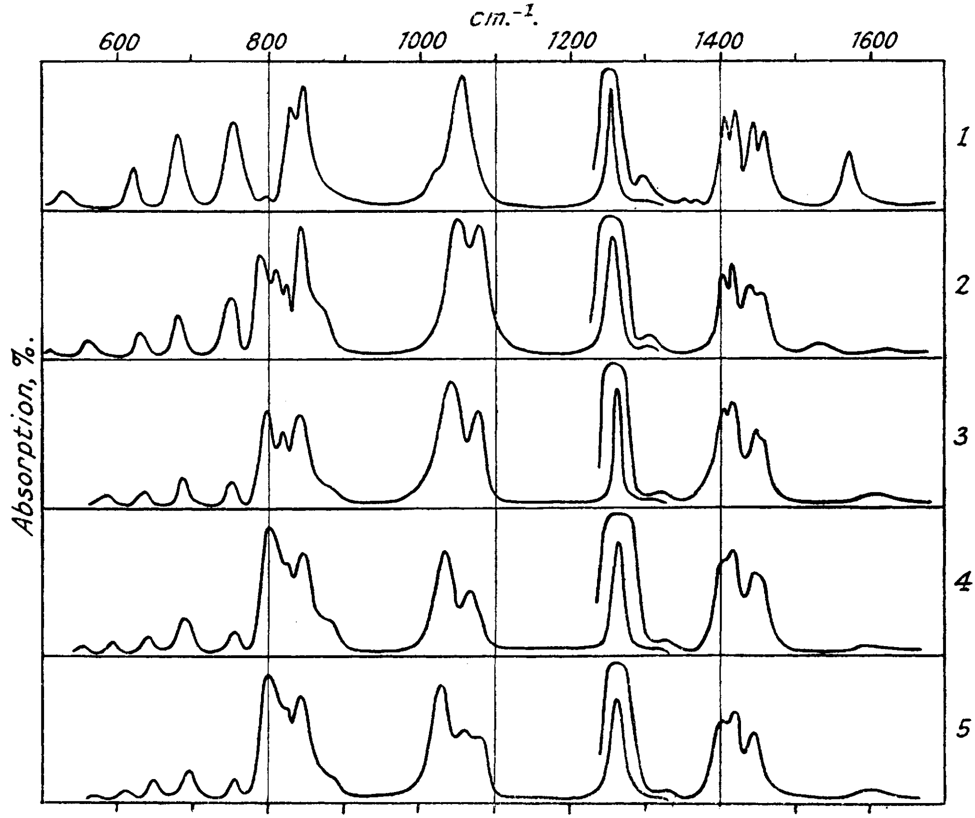
The single-beam and double-beam spectrometers used have been described previously (Whiffen and Thompson, *J.*, 1945, 268; Thompson, Whiffen, Richards, and Temple, Hydrocarb. Res. Group. Inst. Petrol. Rep. No. 17, 1947; Richards and Thompson, *J.*, 1947, 1248). The effective slit widths were approximately 7 cm.$^{-1}$ at 6 μ, 5 cm.$^{-1}$ at 10 μ, and 4 cm.$^{-1}$ at 14 μ. In the region of 3 μ with the fluorite prism the resolving power was about 15 cm.$^{-1}$, and the other experimental conditions were as given in the papers just quoted. Samples of many of the compounds were obtained from the collection of Professor Kipping through the kindness of Mr. Hackford, several were supplied by Professor H. J. Emeléus, and others by the Chemical Research Laboratory, Teddington. We are also particularly grateful to the research laboratory of the General Electric Company, Schenectady, for the gift of many samples of the polymers and alkoxy-compounds. Most of the compounds were of guaranteed high purity, except for some of the alkoxysilanes which tend to hydrolyse easily and may have contained a few per cent. of impurity. However, the identity of the spectra of samples of different origin was a good indication of purity in many cases, and in no case could any of the important strong bands have been attributed to impurity.

The substances were examined as liquids in very thin layers (*ca.* 0·01—0·02 mm.), as solid powders in a paste with paraffin, or in dilute solution in carbon tetrachloride or carbon disulphide. The curves of Figs. 1—6 relate to liquids in a cell about 0·015 mm. in thickness, except for the cyclic tri-polymer in Fig. 2, which is a solid. The curves of Fig. 6 relate to thin layers of the solid powders of indeterminable but comparable thickness.

RESULTS AND DISCUSSION.

The spectra are shown in Figs. 1—6. Some regions masked by possible absorption of "Nujol" are marked. The high intensity of many of the absorption bands is striking, particularly those between 800 and 1300 cm.$^{-1}$. Wright and Hunter have already drawn attention to this in the methylpolysiloxanes, and have attempted to correlate it with the ionic character of silicon–oxygen bonds. In order to reduce the absorption, these authors used dilute solutions in carbon disulphide or carbon tetrachloride. Most of our determinations were made with thin liquid layers, but the spectra of some of the compounds were also measured in the above solvents for comparison. In nearly all cases the positional shifts of the main bands were inappreciable unless special phenomena such as hydrogen-bridge formation were concerned, as explained below.

FIG. 1.



(1) $SiMe_3{\cdot}O{\cdot}SiMe_3$.
(2) $SiMe_3{\cdot}O{\cdot}SiMe_2{\cdot}O{\cdot}SiMe_3$.
(3) $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_2{\cdot}SiMe_3$.
(4) $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_3.SiMe_3$.
(5) $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_4{\cdot}SiMe_3$.

Some tentative assignments of bands to particular types of vibration can be made. As regards the methylpolysiloxanes (Figs. 1 and 2, Tables I and II) perhaps the most striking feature is a sharp intense band near 1265 cm.$^{-1}$ which is found in both the cyclic compounds $[{\cdot}SiMe_2{\cdot}O{\cdot}]_n$ and in the open-chain compounds, $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$. The same band occurs with the alkoxysilanes (Figs. 3, 4, 5, Tables III and IV) provided at least one methyl group is directly attached to a silicon atom, and it therefore seems certain that the band is

TABLE I.

Methylpolysiloxanes, $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$: *Positions of absorption bands (in cm.*$^{-1}$*).*

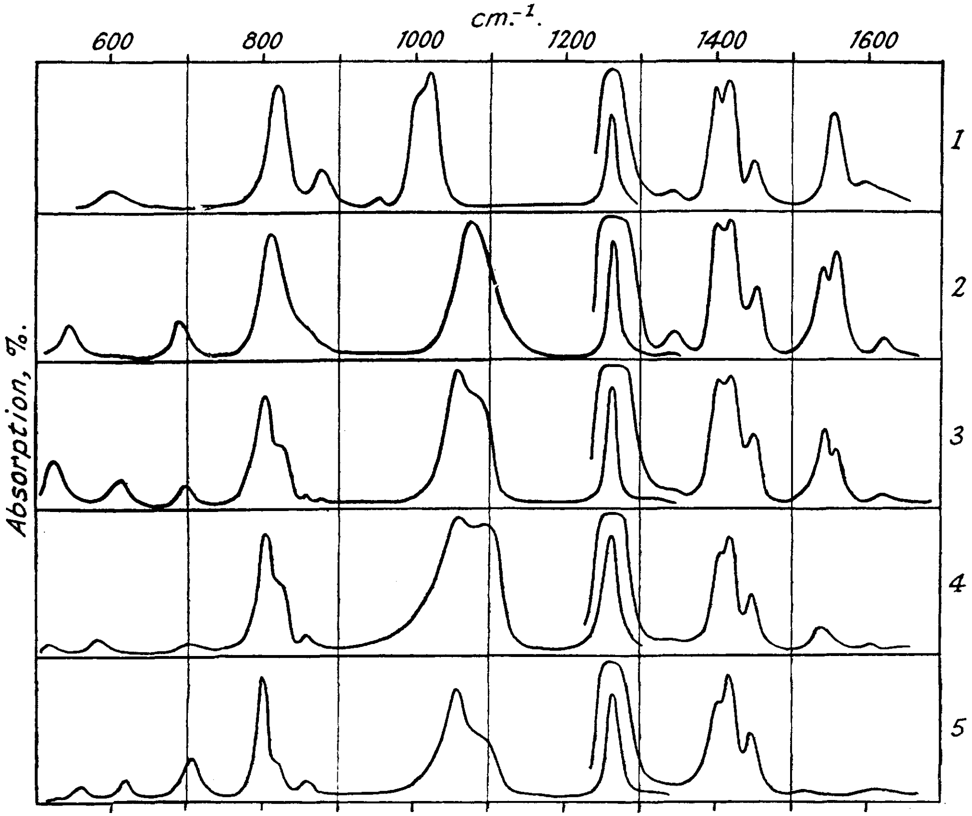
n = 0.		1.		2.		3.		4.	
522	1300	505	1083 s	585	1076 s	536	1034 s	570	1030 s
620	1357	562	1264 s	635	1264 s	596	1066	607	1057
689	1370	631	1317	689	1322	643	1265 s	646	1085
755	1405	692	1405	753	1405	690	1327	698	1264 s
798	1417	755	1417	799 s	1417	755	1405	755	1328
825	1445	794	1445	821	1445	799 s	1417	799 s	1405
843 s	1455	807	1455	842 s	1455	821	1447	821	1417
1013	1577	821	1546	881	1600	842	1590	842 s	1447
1057 s	1720	843 s	1640	1039 s		881		880	1597
1260 s	1735	883	1647						
		1050 s	1740						

TABLE II.

Cyclic methylpolysiloxanes, $[SiMe_2{\cdot}O]_n$: *Positions of absorption bands (in cm.*$^{-1}$*).*

n = 3.		4.		5.		6.		7.	
598	1400	545	1416	522	1265 s	516	1102 s	563	1090
817 s	1417	696	1450	613	1405	584	1264 s	622	1265 s
876	1450	809 s	1545	702	1416	700	1405	707	1405
953	1560	862	1560	804 s	1450	804 s	1416	801 s	1416
1003	1597	880	1620	822	1545	822	1447	821	1448
1020 s	1617	1080 s	1634	859	1560	858	1542	857	1510
1265 s	1638	1265 s	1647	879	1620	1062 s	1604	1060 s	1617
1345		1347	1700	1063 s	1700				
		1403		1090					

FIG. 2.



(1) $[SiMe_2{\cdot}O]_3$.
(2) $[SiMe_2{\cdot}O]_4$.
(3) $[SiMe_2{\cdot}O]_5$.
(4) $[SiMe_2{\cdot}O]_6$.
(5) $[SiMe_2{\cdot}O]_7$.

TABLE III.

Alkoxysilanes : Positions of bands in (cm.$^{-1}$)

(1) $SiMe_2(OEt)_2$.	
798	1368
841	1395
846	1445
953	1485
1078	——
1105	2746
1166	2890
1260	2907
1295	2933
	2973

(2) $SiMe(OEt)_3$.	
732	1266
780	1293
806	1368
820	1390
831	1445
960	1485
1078	——
1100	2747
1120	2892
1166	2940
	2973
	——

(3) $SiEt_2(OMe)_2$	
585	1189
744	1239
768	1405
796	1450
942	——
957	2745
965	2890
1009	2940
1093	2970
	——

(4) $SiEt(OMe)_3$.	
612	1100
675	1192
766	1250
806	——
894	2745
960	2890
1010	2950
1090	2970
	——

(5) $SiEt(OEt)_3$.	
755	1241
789	1300
810	1395
962	1420
1015	——
1080	2750
1109	2890
1170	2940
	2970

(6) Allyltriethoxysilane.	
784	1173
790	1295
814	——
894	2740
930	2885
964	2920
1085	2960
1106	2980

associated with the group Si–Me. In hydrocarbons the symmetrical deformation of a methyl group usually has a frequency around 1380 cm.$^{-1}$, but it is not very intense in the infra-red spectrum. On this ground alone it seems improbable that the band at 1265 cm.$^{-1}$ in the silicones is to be interpreted in this way. Also, with hydrocarbons in which two methyl groups are attached to the same carbon atom, the symmetrical deformation usually splits into two components 20—30 cm.$^{-1}$ apart. No such splitting occurs with the band at 1265 cm.$^{-1}$ in the silicones. Its value is too high for a stretching vibration of the Si–C bond, and there remains as plausible interpretation only the rocking mode of the Me group with respect to the Si–C bond, as also suggested by Wright and Hunter (*loc. cit.*).

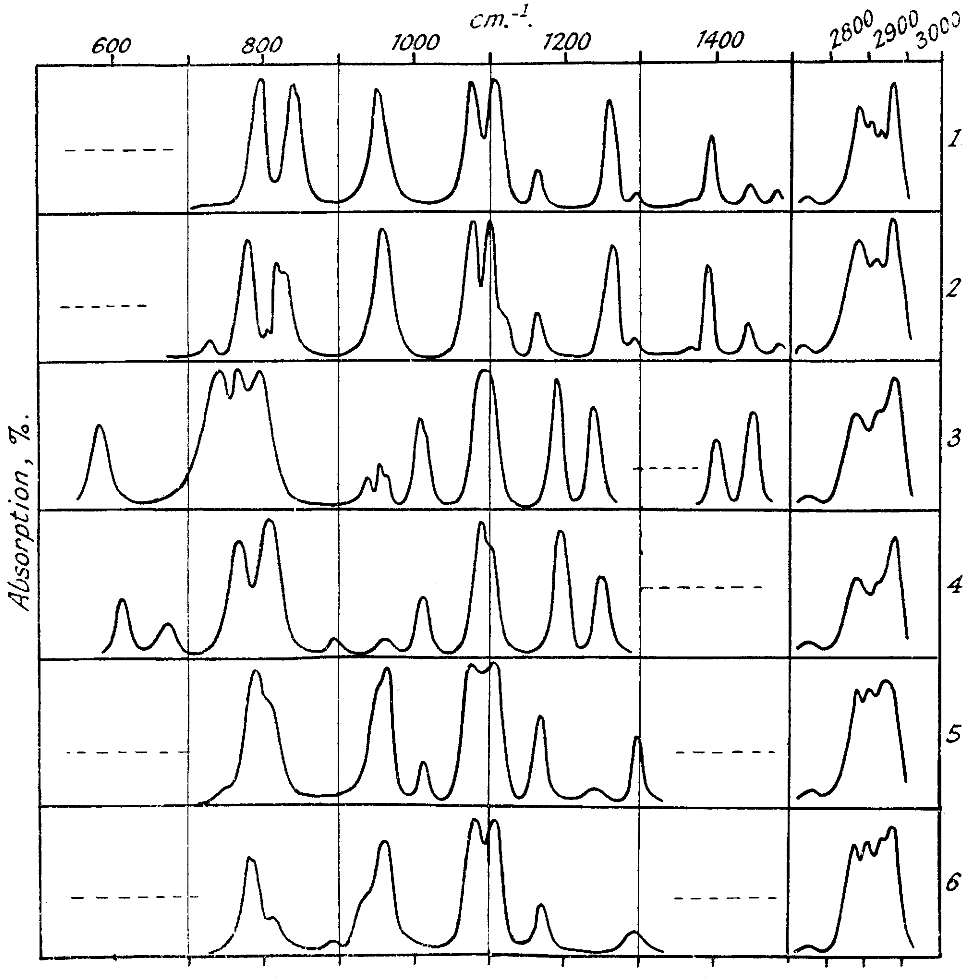
The other intense bands of the methylpolysiloxanes lie near 800 cm.$^{-1}$ and 1050 cm.$^{-1}$, and these must be connected with vibrations of the Si–C and Si–O linkages. Fig. 1 shows that along the series $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$, n being 0, 1, 2, 3, 4, the band near 840 cm.$^{-1}$ falls in intensity and another band near 800 cm.$^{-1}$ gradually increases in strength. This suggests that the former band is connected with the group $\cdot SiMe_3$, and the latter with $\cdot SiMe_2\cdot$, in both cases the controlling factor being the stretching of Si–C bonds. In the methyl*cyclo*polysiloxanes $[SiMe_2{\cdot}O]_n$, n being 3, 4, 5, 6, 7, there is an analogous band near 805 cm.$^{-1}$, attributable in the same way to the $\cdot SiMe_2\cdot$ group. Also in all the alkoxysilanes which we have measured of the type $SiMe_2R_2$, R being *n*-butoxy, *iso*butoxy, ethoxy, *n*-propoxy, and *iso*propoxy, there is a similar intense band close to 800 cm.$^{-1}$, which could be assigned to the group $\cdot SiMe_2\cdot$. With alkoxy-compounds of the type $SiMeR_1R_2R_3$, too, there is a band near 800 cm.$^{-1}$ which may be connected with the group Si–Me, but it seems to vary in position according to the nature of R_1, R_2, and R_3, more than the former band of compounds in which two or more methyl groups are present.

Other Si–C stretching modes will be expected in compounds containing the groups $SiMe_2$ or $SiMe_3$, and it is noteworthy that in all the open-chain methylpolysiloxanes a band appears near 755 cm.$^{-1}$ which is absent from the corresponding *cyclo*polysiloxanes, while another band near 700 cm.$^{-1}$ occurs both in the open-chain and in the cyclic series. We could then assign the former (755) to the $SiMe_3$ group, and the latter (700) to the $SiMe_2$ group. The group $SiMe_3$ would then have a pair of Si–C stretching vibrations with values 840, 755 cm.$^{-1}$, and the group $SiMe_2$ a corresponding pair with values 800, 700 cm.$^{-1}$. In hydrocarbons and many other compounds, the *tert.*-butyl group CMe_3 is characterised by a pair of frequencies near 1200, 1250 cm.$^{-1}$ determined by the stretching of C–C bonds. The change in reduced mass on passing to the Si–C bond would suggest a value of about 900 cm.$^{-1}$ in this case, which after allowing for a small change in the binding force constants would agree well with the values found around 800 cm.$^{-1}$. Although, however, this interpretation seems reasonable, the splitting of the bands near 840 and 800 cm.$^{-1}$ remains unaccounted for, and it is possible that this might arise from the different pairs of Si–C modes.

Two other bands of the open-chain methylpolysiloxanes deserve mention. One has a value 522 cm.$^{-1}$ in $SiMe_3{\cdot}O{\cdot}SiMe_3$, and appears to increase uniformly and slowly along the series $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$ as follows: 562, 585, 596, 607 cm.$^{-1}$. The other lies at 620 cm.$^{-1}$ in the first member, and increases steadily along the series as follows: 631, 635, 643, 646 cm.$^{-1}$. These two bands are presumably associated with vibrations of the whole skeleton, or to bending or rocking modes controlled essentially by the methyl groups.

The strong bands of the methylpolysiloxanes in the region 1000—1100 cm.$^{-1}$ are probably connected with stretching vibrations of the –Si–O– bonds, corresponding to those found around 1100 cm.$^{-1}$ with the ether linkage –C–O–. In the open-chain compounds the band lies near 1050 cm.$^{-1}$ but splits into two or more components as the chain lengthens. In the cyclic compounds the band lies near 1080 cm.$^{-1}$, except for $[SiMe_2{\cdot}O]_3$, where it is near 1020 cm.$^{-1}$; here, too, the band appears to split as the ring increases in size. In the alkoxy-compounds there are intense bands between 950 and 1200 cm.$^{-1}$ attributable to stretching vibrations of Si–O and C–O linkages, which are roughly parallel to those found in esters containing the –O–R linkage (Thomspon and Torkington, *J.*, 1945, 640). The main point therefore is that stretching of the Si–O bond gives rise to a frequency around 1050—1100 cm.$^{-1}$, little different from the corresponding mode in ethers and esters. Wright and Hunter have discussed the high intensity

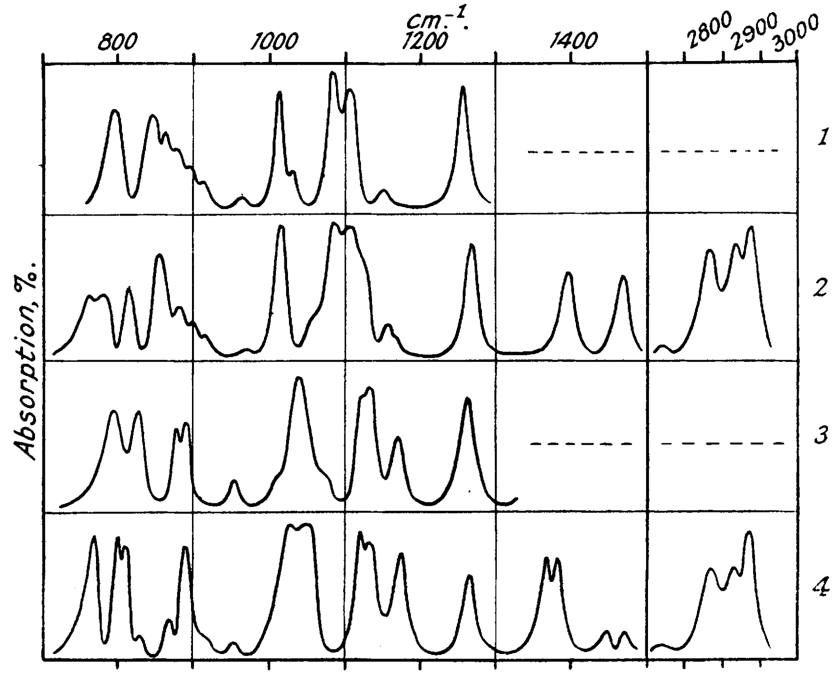
FIG. 3.



(1) $SiMe_2(OEt)_2$.
(2) $SiMe(OEt)_3$.
(3) $SiEt_2(OMe)_2$.
(4) $SiEt(OMe)_3$.
(5) $SiEt(OEt)_3$.
(6) $CH_2{:}CH{\cdot}CH_2{\cdot}Si(OEt)_3$.

of the Si–O vibration. Another point arises, however, namely, that although there is an appreciable change in the reduced mass, the frequencies are hardly altered. This must occur because of an increase in the force constant of the Si–O bonds compared with C–O bonds.

FIG. 4.



(1) $SiMe_2(OPr^n)_2$.
(2) $SiMe(OPr^n)_3$.
(3) $SiMe_2(OPr^i)_2$.
(4) $SiMe(OPr^i)_3$.

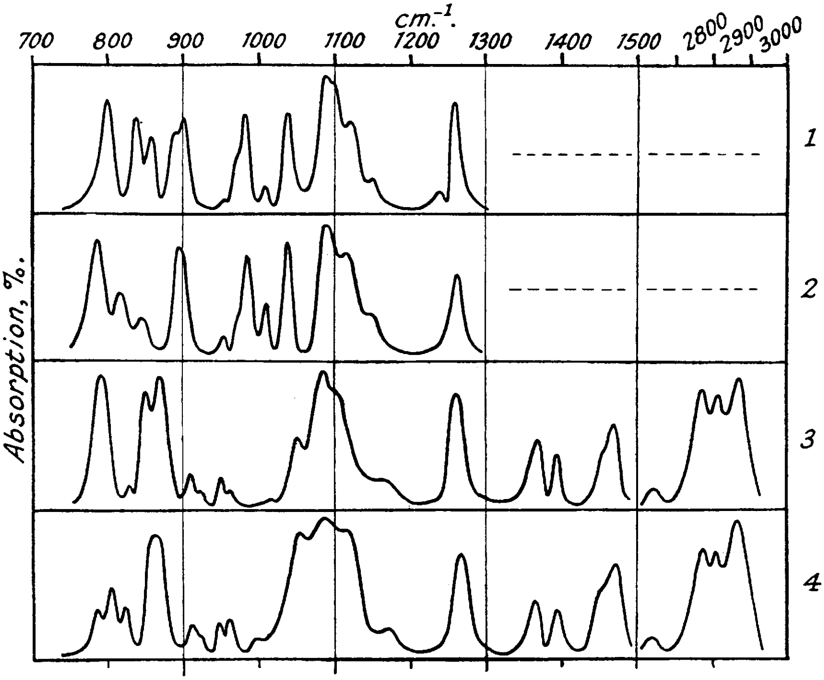
TABLE IV.

Alkoxysilanes : Positions of bands (in cm.$^{-1}$).

(1) $SiMe_2(OPr^n)_2$.		(2) $SiMe(OPr^n)_3$.		(3) $SiMe_2(OPr^i)_2$.		(4) $SiMe(OPr^i)_3$.	
799	1011	761	1104	798	1036	769	1134
849	1030	781	1157	829	1070	801	1175
863	1083	814	1172	881	1123	810	1268
882	1104	855	1269	890	1131	829	1370
897	1150	881	1395	955	1173	874	1382
914	1256	900	1470	1011	1264	890	1450
965		915	——		——	920	1470
		970	2745			935	——
		1016	2888			1030	2740
		1058	2942			1054	2888
		1087	2970			1123	2934
							2970

(5) $SiMe_2(OBu^n)_2$.		(6) $SiMe(OBu^n)_3$.		(7) $SiMe_2(OBu^i)_2$.		(8) $SiMe(OBu^i)_3$.	
800	1007	789	1007	795	1100	789	1118
838	1039	818	1038	827	1166	807	1166
859	1090	845	1089	854	1262	824	1265
889	1099	899	1118	874	1370	863	1370
900	1118	954	1150	914	1397	914	1396
955	1149	973	1264	924	1470	923	1468
975	1237	985		951	——	950	——
983	1260			961	2745	960	2745
				1016	2880	998	2880
				1051	2911	1054	2915
				1085	2968	1089	2965

FIG. 5.



(1) $SiMe_2(OBu^n)_2$.
(2) $SiMe(OBu^n)_3$.
(3) $SiMe_2(OBu^i)_2$.
(4) $SiMe(OBu^i)_3$.

TABLE V.

Phenyl-substituted silanols and cyclic phenylpolysiloxanes : Positions of bands (in cm.⁻¹).

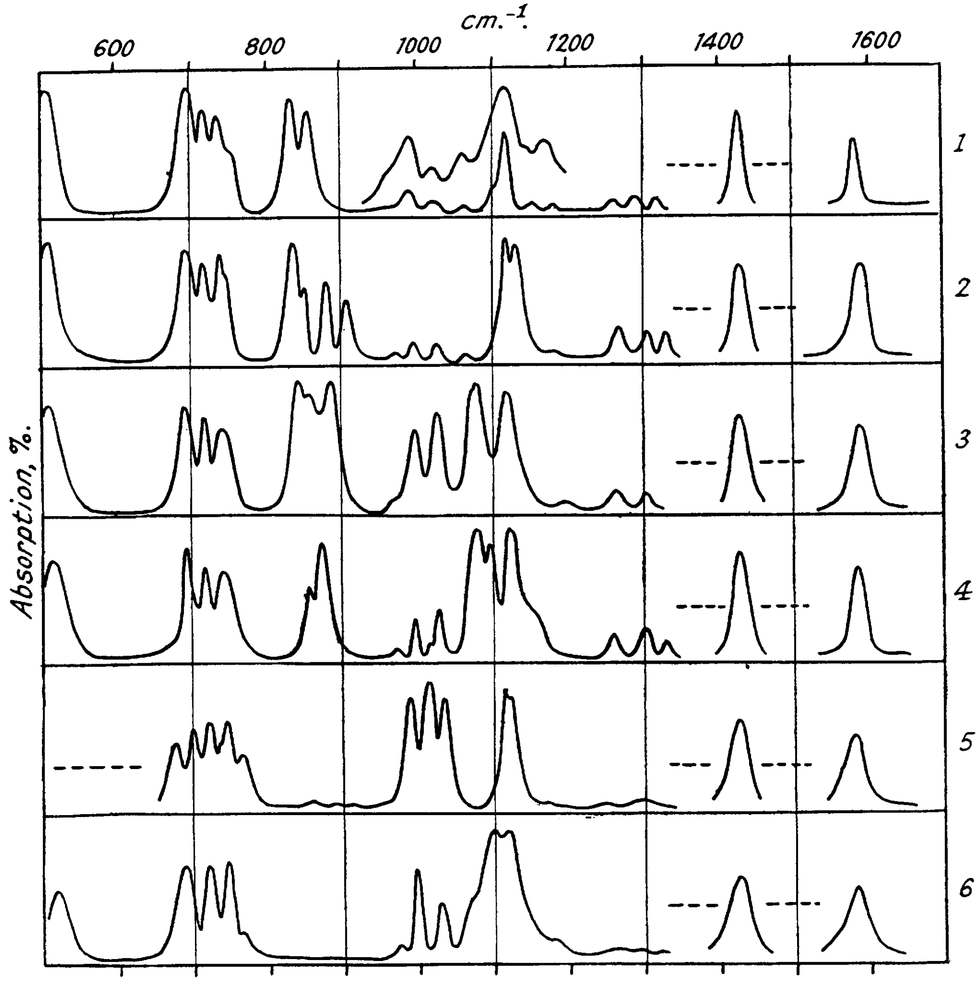
(1) $SiPh_3{\cdot}OH$.		(2) $SiPh_2(OH)_2$.		(3) $(HO{\cdot}SiPh_2)_2O$.	
511	1107	510	1028	510	998
697	1118	696	1068	698	1026
722	1157	720	1120	720	1078
738	1187	741	1129	740	1120
751	1265	749	1184	848	1190
835	1295	839	1172	860	1268
998	1325	852	1306	887	1305
1028	1425	883	1334	972	1430
1070	1585	907	1427		1590
		975	1592		
		998			

(4) $SiPh_2(O{\cdot}SiPh_2{\cdot}OH)_2$.		(5) $[SiPh_2{\cdot}O]_3$.		(6) $[SiPh_2{\cdot}O]_4$.	
518	1076	678	1015	692	1100
697	1096	697	1032	720	1115
720	1123	720	1117	742	1177
742	1157	737	1121	762	1250
856	1262	744	1175	975	1295
867	1304	766	1250	995	1425
975	1328	859	1295	1027	1590
996	1425	892	1430	1070	
1017	1586	918	1585		
1028		992			

Between 1350 and 1500 cm.⁻¹ bands are found due to vibrations of the methyl groups. In the cyclic or open-chain methylpolysiloxanes these occur between 1410 and 1450 cm.⁻¹, and as a rule there are two pairs of close bands. These are presumably analogous to the bands of the methyl groups in hydrocarbons near 1375 cm.⁻¹ and 1460 cm.⁻¹, split by the presence of two or three methyl groups on the same silicon atom. With the alkoxy-compounds, other bands appear below 1400 cm.$^{-1}$, since here methyl groups are attached to carbon or to oxygen atoms as well. The exact position of these bands varies somewhat, much as in the case of esters.

In the region of 3·4 μ, the methylpolysiloxanes and the alkoxysilanes show bands associated with stretching vibrations of C–H links. Four bands are usually found, near 2740, 2890, 2940, 2970 cm.$^{-1}$. The first of these is much weaker than the others, and is almost certainly a combination or overtone of deformational vibrations. The last three are due to stretching vibrations, and the results show that an increase in content of methyl groups strengthens the band at 2970 cm.$^{-1}$, whereas the bands at 2890, 2940 cm.$^{-1}$ are associated with the methylene groups. These values are closely parallel to those found with hydrocarbons (Fox and Martin, *Proc. Roy. Soc.*, 1940, *A*, **175**, 208). It is obvious, however, that before these bands near 3·4 μ can be considered in detail, measurements with higher resolving power will be required.

FIG. 6.



(1) $SiPh_3{\cdot}OH$.
(2) $SiPh_2(OH)_2$.
(3) $(HO{\cdot}SiPh_2)_2O$.
(4) $SiPh_2(O{\cdot}SiPh_2{\cdot}OH)_2$.
(5) $[SiPh_2{\cdot}O]_3$.
(6) $[SiPh_2{\cdot}O]_4$.

The spectra of the compounds containing phenyl substituent groups (Fig. 6) are less easy to interpret in terms of specific molecular vibrations. In all the hydroxy-compounds there are strong bands in the region 830—880 cm.$^{-1}$, which are absent in the case of the cyclic diphenylpolysiloxanes, although an assignment to deformational vibrations of the hydroxyl groups would be speculative. All the compounds show intense absorption between 700 and 750 cm.$^{-1}$ and near 1100 cm.$^{-1}$. We should expect the intense bending vibration of the C–H bonds in the substituted aromatic nuclei near 750 cm.$^{-1}$, and the stretching vibrations of Si–O bonds near 1100 cm.$^{-1}$, but again it is impossible to make unambiguous assignments. The two bands usually found near 1420, 1585 cm.$^{-1}$ probably correspond to the pair of bands near 1500 and 1600 cm.$^{-1}$ which normally occur with aromatic hydrocarbons and simple substituted benzenes and which are associated with vibrations of the aromatic nucleus.

The hydroxy-compounds show hydrogen-bridge formation in the solid state. There are bands between 3020 and 3060 cm.$^{-1}$ connected with stretching modes of aromatic C–H bonds. The solids also show, however, a broad band centred around 3250 cm.$^{-1}$ which gives way in dilute solution in carbon tetrachloride to a sharper band near 3690 cm.$^{-1}$. The latter is due to the stretching vibration of free hydroxyl groups, and the former to bonded hydroxyl groups. The shift of about 450 cm.$^{-1}$ indicates fairly strong hydrogen bonding. It is interesting to notice that the vibrational frequency of the free hydroxyl group is almost exactly equal to that found in methyl alcohol.

Some chlorinated silanes have also been measured in the vapour state, such as trichlorosilane, ethyldichlorosilane, and diethylchlorosilane. These compounds showed several highly intense absorption bands which reached almost complete extinction with a path length of 21 cm. at 1—2 mm. pressure. The stretching vibration of Si–H links was found close to 2200 cm.$^{-1}$. The most intense band seems to lie near 810 cm.$^{-1}$ and may be connected with a vibration of the Si–Cl bond.

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