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Vibrational spectra and structure of some silicon containing compounds—IV* Normal vibrations and free rotation in phenylsilane

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Abstract—The i.r. spectra of liquid and gaseous phenylsilane and gaseous phenylsilane-d_3 have been recorded from 3500 to 33 cm^{-1}. The Raman spectra of the liquids have also been recorded and depolarization values have been measured. The vapor-phase spectra show that the silyl group is "freely" rotating in these molecules. Thus, the local symmetry of the phenyl group is C_{2v}, and the vibrations have been assigned according to this symmetry. The effective symmetry of the SiH_3 group is essentially C_{3v}. These spectra have been interpreted in detail, and the 39 fundamental vibrations have been assigned by consideration of previous assignments for the phenyl moiety, depolarization ratios and vapor-phase i.r. band contours. The "free rotation" of the silyl group shows that the sixfold barrier to internal rotation around the Si—C bond is quite small. The vibrations of silyl and silyl-d_3 group have also been identified in spectra obtained by the matrix (argon and krypton) isolation technique.

INTRODUCTION

RECENTLY, we reported the vibrational spectra of phenylgermane with assignments to the normal modes [1]. This study showed that the sixfold barrier to internal rotation about the C—Ge bond is so small that the germyl group rotates freely. In continuing our studies of the phenyl substituted group IV *A* hydrides, we have investigated the vibrational spectra of phenylsilane and phenylsilane-d_3 in order to determine (1) the frequencies of the six substituent-sensitive phenyl modes [2–4], (2) the frequencies of the normal modes of the silyl group when it is attached to the phenyl ring, and, particularly, (3) the order of magnitude of the sixfold barrier to internal rotation about the Si—C bond. The band contours and possible degeneracy of the antisymmetric stretching, deformational and rocking modes of the silyl group provide qualitative information concerning hindered internal rotation. For a barrier small as compared to thermal energy, essentially free internal rotation should be unmistakably discernible in the infrared spectra of the vapors. Therefore, the vibrational spectra of these molecules have been analyzed in detail. Portions of the i.r. and Raman spectra of these compounds have been reported previously [5–8].

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* For Part III, see *J. Mol. Struct.* **6**, 315 (1970).

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[1] J. R. DURIG, C. W. SINK and J. B. TURNER, *J. Chem. Phys.* **49**, 3422 (1968).

[2] C. V. STEPHENSON, W. C. COBURN, JR. and W. S. WILCOX, *Spectrochim. Acta* **17**, 933 (1961).

[3] D. H. WIFFEN, *J. Chem. Soc.* 1350 (1956).

[4] R. R. RANDLE and D. H. WHIFFEN, *Molecular Spectroscopy* (Edited by G. SELL), p. 111. The Institute of Petroleum, London (1955).

[5] A. L. SMITH, *Spectrochim. Acta* **24A**, 695 (1968).

[6] J. KNÍŽEK, V. CHVALOSKÝ and M. HORÁK, *Coll. Czech. Chem. Commun.* **29**, 2935 (1964).

[7] R. N. KNISELEY, V. A. FASSEL and E. E. CONRAD, *Spectrochim. Acta* **15**, 651 (1959).

[8] H. KRIEGSMANN and K. H. SCHOWTA, *Z. Phys. Chem. Leipzig* **209**, 261 (1958).

Experimental

The samples of phenylsilane and phenylsilane-d_3 were prepared by adding a solution of phenyltrichlorosilane in anhydrous ether to a suspension of lithium aluminum hydride (or deuteride) also in anhydrous ether. The solutions were made under an atmosphere of nitrogen in order to prevent hydrolysis of either of the reactants. The phenyltrichlorosilane was added dropwise during a period of about one hour to the suspension which was stirred continuously and kept at 0°C. When addition had been completed, the mixture was refluxed, with continuous stirring for another hour, and then the ether and phenylsilane (or phenylsilane-d_3) were fractionally distilled from the reaction flask under reduced pressure. The product was finally separated completely from the ether by distillation at atmospheric pressure.

After distillation, the phenylsilane was found to be pure as indicated by its NMR spectrum. Although gas phase chromatography (20 ft column packed with UCON 50 HB 2000 polar on chrom W, operated at 120°C) permitted separation of a very minor impurity (less than 1 per cent), the i.r. spectrum of the chromatographically pure sample was identical to that of the original sample. In the same manner, the phenylsilane-d_3 sample was shown to be spectroscopically pure except for a small amount of hydrogen bonded to silicon as shown by the very weak band in the Si—H stretching region of the i.r. spectrum; the corresponding Raman band was scarcely observable. Since the extinction coefficient for this i.r. band is apparently much larger than that for any other band in the spectrum of phenylsilane, it is not surprising that the impurity was not otherwise in evidence.

The i.r. spectrum of each compound was measured from 3500 to 250 cm^{-1} with a Perkin–Elmer Model 621 spectrophotometer. The instrument housing was purged with nitrogen to remove atmospheric water vapor and carbon dioxide. Calibration was performed by using standard gases for the higher frequency region [9] and atmospheric water vapor for the lower frequency region [10]. The spectra of gaseous samples of the substituted silanes were recorded at pressures varying between approx. 2 and 10 torr; a 10-cm cell with CsI windows was used. In addition, the spectrum of a contact film of phenylsilane between CsI discs was recorded. Also, the i.r. spectra of both isotopic species isolated in argon and krypton matrices at 20°K were recorded. An Air Products Corporation cryostat described by White and Mann [11] was used for refrigeration at 20°K. The Cryo-Tip delivers approximately 2 W of refrigeration at 20°K. Mole ratios (matrix to absorber) of 500:1 and 1000:1 were employed.

The far-i.r. spectral region (320–33 cm^{-1}) was recorded by using a Beckman IR-11 spectrophotometer. The housing of the spectrophotometer was continuously purged with dry air while gaseous, liquid, and solution samples of the two compounds were being studied. However, no absorptions attributable to either phenylsilane or phenylsilane-d_3 were observed.

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[9] IUPAC, *Tables of Wavenumbers for the Calibration of Infrared Spectrometers* Butterworth, Washington, D.C. (1961).

[10] H. M. Randall, D. M. Dennison, N. Ginsburg and L. R. Weber, *Phys. Rev.* **52**, 160 (1937).

[11] D. White and D. E. Mann, *Rev. Sci. Instr.* **34**, 1370 (1963).

The Raman spectra of the liquids were recorded on a Cary Model 81 spectrophotometer equipped with a Spectra Physics Model 125 helium–neon laser.* The samples were contained in Pyrex capillary tubes. Spectra were also obtained with the same spectrophotometer by using a Toronto arc source with a circulating filter solution for isolating the 4358 Å exciting line. The filter solution was made of 125 ml of *o*-nitrotoluene and 1.75 g of ethyl violet in 3 liters of isopropyl alcohol. Samples for use with this source were contained in standard Cary 2-mm-o.d. cells which have a volume of 0.6 ml. Depolarization ratios were measured by using cylindrical polaroid filters in the usual manner [12]. Measurements of the relative intensities of the Raman bands were also made from the spectra obtained by the arc excitation. The instrument was calibrated over the spectral range by using emission lines from a neon lamp.

VIBRATIONAL ASSIGNMENTS

A striking aspect of the gas-phase spectra of phenylsilane and phenylsilane-d_3 is the fine structure which appears on certain bands arising from vibrations of the silyl or silyl-d_3 group. This spectral feature indicates free internal rotation about the Si—C bond as explained in the following section of this paper. Thus, the effective symmetry of the phenyl group is C_{2v}. The 30 fundamental vibrations of the substituted benzene ring factor into $11A_1$, $3A_2$, $10B_1$ and $6B_2$ symmetry species. These fundamentals are designated by an adaptation of HERZBERG's notation for benzene [13], primed and unprimed numbers are used to distinguish between components of vibrations degenerate in benzene but non-degenerate in substituted benzenes. Other notations have been used repeatedly to designate the fundamental modes of substituted benzenes, but STEPHENSON *et al.* [2] have provided a table correlating the three frequently used nomenclatures.

Assignment of the fundamental modes of the phenyl group is facilitated since all but six of them are fairly insensitive to the nature of the substituent group in monosubstituted benzenes [2–4]. Many of the insensitive modes are observed at approximately the same frequency as they are for unsubstituted benzene. Monosubstitution of benzene usually leaves the frequency of one component of each of the degenerate vibrations almost unchanged and causes the other component to shift to lower frequency. A tabulation [2] of the average values of wavenumbers of monosubstituted benzenes according to the data and assignments of RANDLE and WHIFFEN [4] provides a reliable guide for assigning the fundamental modes of the phenyl group in phenylsilane and phenylsilane-d_3. Comparison of the data and assignments for closely related compounds [1, 14–18] to this tabulation increases one's confidence in its reliability for use in assigning the fundamental modes of phenylsilane and phenylsilane-d_3.

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[12] B. L. CRAWFORD, JR. and W. HORWITZ, *J. Chem. Phys.* **15**, 246 (1947).

[13] G. HERZBERG, *Infrared and Raman Spectra of Polyatomic Molecules*, p. 118. Van Nostrand, Princeton, N.J. (1945).

[14] J. R. DURIG, B. M. GIBSON and C. W. SINK, *J. Mol. Struct.* **2**, 1 (1968).

[15] J. R. DURIG, C. W. SINK and S. F. BUSH, *J. Chem. Phys.* **45**, 66 (1966).

[16] C. V. STEPHENSON, *J. Chem. Phys.* **42**, 35 (1965).

[17] J. K. WILMHURST and H. J. BERNSTEIN, *Can. J. Chem.* **35**, 911 (1957).

[18] N. A. NARASIMHAM, J. R. NIELSEN and ROSE THEIMER, *J. Chem. Phys.* **27**, 740 (1957).

Band contours derived from the i.r. spectra of the gases together with the polarization data of the Raman spectra further facilitate assignments. The symmetry species of practically all of the fundamental modes giving rise to i.r. bands are immediately apparent since the A_1 modes result in A-type bands and the B_1 and B_2 modes produce B- and C-type bands, respectively, each type being clearly distinguishable in most cases. The A_2 modes are i.r. inactive whereas all fundamentals are Raman active.

Thus, with few exceptions, reliable assignments to the fundamentals are easily made; for, if the assignments to the substituent insensitive modes are made first then there is little choice for assigning each of the substituent sensitive modes. Essentially complete assignments are presented together with the i.r. and Raman data in Tables 1 and 2. In Table 3, wherein frequencies are listed according to the

Table 1. Infrared and Raman spectra of phenylsilane*

Infrared				Raman			Assignments
Liquid $\bar{\nu}$	Gas $\bar{\nu}$	Band type	Rel. int.	$\Delta\bar{\nu}$	Rel. int.	Depol. ratio	
3138	3146 ctr	?	vw				$\nu SiH_3 + \delta_{as}SiH_3$
				3116	1	?	$A_1 2\nu_{16}$
	3101		sh				Overtone or combination
3088	3086 *R* ~3080 ctr ~3076 *P*	*B*	s				$B_1\nu_{12}'$
3071	3072 *R* 3067 *Q* 3062 *P*	*A*	s				$A_1\nu_5$
3055				3052	16	0.33	$A_1\nu_1$
	3037 *R* 3033 ctr 3028 *P*, *R*	*B*	m				$B_1\nu_{15}$
3023	3023 *Q* — *P*	*A*	m				$A_1\nu_{15}'$
3015	3014		sh	3018	1	dp?	$\nu SiH_3 + \nu_{11}$
2959			vw	2960	1	p	$A_1 2\nu_{13}$
2931	2942 *R* ~2936 ctr 2931 *P*	*B*?	vvw				$B_1\nu_9 + \nu_{16}'$†
2917	2927 *R* ~2920 ctr 2916 *P*	*B*?	vvw				$\begin{cases} B_1\nu_{13} + \nu_{13}' \\ \nu SiH_3 + \nu_4 \end{cases}$
2893			vvw				$\begin{cases} A_1\nu_9 + \nu_{16} \\ B_1\nu_3 + \nu_{16} \end{cases}$
2855			vvw				$\begin{cases} A_1 2\nu_{13}' \\ \nu SiH_3 + \nu_8 \\ \nu SiH_3 + \nu_2 \end{cases}$
2706			vvw				$A_1\nu_{12} + \nu_{16}'$
2617			vvw				$\begin{cases} A_1\nu_{14} + \nu_{16}' \\ A_1\nu_{12} + \nu_{13} \\ B_1\nu_{17} + \nu_{13}' \end{cases}$
2587			vvw				Combination of overtone‡
2397							$\begin{cases} \delta_{as}SiH_3 + \nu_{13}' \\ A_1\nu_{10} + \nu_9 \end{cases}$
2348	2358 *R* 2353 ctr 2348 *P*	*B*	vvw				$\begin{cases} B_1\nu_9 + \nu_{14} \\ B_1\nu_{17} + \nu_{17}' \end{cases}$
2319	2324 *R* 2320 *Q* 2315 *P*	*A*	vvw				$\begin{cases} \nu_s SiH_3 + \nu_{20}' \\ A_1 2\nu_{17} \end{cases}$
2158	2174 *R* 2169 *Q* 2164 *P*	*A*	vs	2157	29	0.21	$\begin{cases} \nu_{as}SiH_3§ \\ \nu_s SiH_3 \end{cases}$

Table 1 (*cont.*)

Infrared				Raman			
Liquid $\tilde{\nu}$	Gas $\tilde{\nu}$	Band type	Rel. int.	$\Delta\tilde{\nu}$	Rel. int.	Depol. ratio	Assignments
2015			vvvw				$B_1\nu_2 + \nu_9$ $B_2\nu_{16}' + \nu_{19}'$ $B_2\nu_{17} + \nu_{11}$ $B_2\nu_7 + \nu_{14}$
1969	1976 *R* 1973 *Q* 1967 *P*	*A*	w				$A_1 2\nu_6$ $A_1 2\nu_7$ $\rho SiH_3 + \nu_9$ $\delta_{as}SiH_3 + \nu_6$
1953	1960 *R* 1956 ctr 1951 *P*	*B*	w				$B_1\nu_{15} + \nu_{18}'$ $\rho SiH_3 + \nu_8$ $\delta_s SiH_3 + \nu_{14}$ $\delta_{as}SiH_3 + \nu_7$
1896	1903 *R* 1898 *Q* ~1894 *P*	*A*	w				$A_1\nu_7 + \nu_{11}'\|$ $\delta_{as}SiH_3 + \nu_{11}'$
1880	~1889 *R* 1883 ctr 1877 *P*	*B*	mw				$B_1\nu_8 + \nu_{17}'$ $\delta_{as}SiH_3 + \nu_{11}'$
1831			vvvw				$A_1 2\nu_{11}'$ $B_2\nu_7 + \nu_{11}$ $\rho_{ip}SiH_3 + \nu_{17}'$ $2\delta_s SiH_3$
1814	1820 *R* 1816 *Q* 1810 *P*	*A*	mw				$A_1\nu_2 + \nu_{12}$ $A_1 2\nu_{11}'$ $\rho SiH_3 + \nu_{17}$ $\delta_{as}SiH_3 + \nu_{11}$
1775			vvw				$A_1\nu_{14}' + \nu_{16}$ $A_1\nu_{17} + \nu_{15}$ $A_1\nu_{11} + \nu_{19}\|$ $\rho_{ip}SiH_3 + \nu_{12}$ $\delta_s SiH_3 + \nu_{11}$
1762	1767 *R* 1761 ctr 1756 *P*	*B*	vw				$B_1\nu_2 + \nu_{10}$ $B_1\nu_{11} + \nu_{11}'\|$ $\rho_{ip}SiH_3 + \nu_{12}$
1665	1667 ctr	*C*?	vw				$A_1\nu_4 + \nu_{11}'\|$ $A_1 2\nu_{11}{}^*$ $\delta_{as}SiH_3 + \nu_2$ $\delta_{as}SiH_3 + \nu_8$
1645			vvvw				$B_1\nu_{14} + \nu_{18}$ $B_2\nu_{13} + \nu_{20}'$ $\rho_{ip}SiH_3 + \nu_8$
	1617 *R* 1612 *Q* ~1606 *P*	*A*?	vw				$B_1\nu_6 + \nu_{18}\|$ $B_2\nu_{17}' + \nu_{19}'$ $B_2\nu_2 + \nu_{11}'$
1590	~1602 *R* 1596 *Q* 1590 *P*	*A*?	w	1591	5	0.70	$A_1\nu_{16}'$
				1567	2	dp	$B_1\nu_{16}$
1550			vw				$A_1\nu_{17} + \nu_{20}$ $B_1\nu_{17} + \nu_{18}'$ $B_2\nu_{18} + \nu_{19}$ $B_2\nu_8 + \nu_{11}\|$ $\delta_s SiH_3 + \nu_{18}$ $B_2\nu_{13} + \nu_{19}'$
1483	1492 *R* 1487 *Q* 1482 *P*	*A*	w	1484	<1	?	$A_1\nu_{13}$
1428	1437 *R* 1432 ctr 1427 *P*	*B*	m				$B_1\nu_{12}'$
1373	1375 *R* 1371 ctr 1365 *P*	*B*	vvw				$B_1\nu_7 + \nu_{20}\|$

Table 1 (*cont.*)

Infrared				Raman			
Liquid $\tilde{\nu}$	Gas $\tilde{\nu}$	Band type	Rel. int.	$\Delta\tilde{\nu}$	Rel. int.	Depol. ratio	Assignments
1330	1336 *R* 1331 ctr 1326 *P*	*B*	w	1330	<1	?	$B_1\nu_9$
1299	1303 *R* 1298 ctr ~1292 *P*	*B*	vw				$B_1\nu_3$
1280	~1283 *R* 1278 ctr 1273 *P*	*B*	vw				$\begin{cases}\rho_{ip}\mathrm{SiH}_3 + \nu_{18} \\ 2\rho_{ip}\mathrm{SiH}_3\end{cases}$
1253			vvw				?
1188	1195 *R* 1190 *Q* 1184 *P*	*A*	vvw	1187	3	0.41	$A_1\nu_{17}'$
1157	1165	?	vw	1156	2	dp	$B_1\nu_{17}$
1122	1127 *R* 1123 *Q* 1119 *P*	*A*	s	1117	4	0.15	$A_1\nu_{12}$
1118	1116 *Q*?	?	ms				$\begin{cases}B_2\nu_3 + \nu_{19}' \\ A_1\nu_8 + \nu_{19}'\Vert\end{cases}$
1096			vvvw				$\begin{cases}B_1\nu_{19} + \nu_{20}' \\ \delta_s\mathrm{SiH}_3 + \nu_{20}'\end{cases}$
1075	1080 *R* 1076 *Q* 1071 *P*	*A*	vw				$\begin{cases}A_1\nu_{11}' + \nu_{20}' \\ A_1\nu_2 + \nu_{18}'\Vert \\ \rho_{ip}\mathrm{SiH}_3 + \nu_{19}'\end{cases}$
1068			vvw	1064	<1	?	$B_1\nu_{10}$
				1027	13	0.24	$A_1\nu_{14}$
997			vvw	998	100	0.13	$A_1\nu_6$
				985	3	?	$B_2\nu_7$
	952 ctr (calculated)		m				$\delta_{as}\mathrm{SiH}_3$
				936			$A_2\nu_{19}$
					5¶	dp¶	
928	933 *R* 929 *Q* 925 *P*	*A*	s	930			$\delta_s\mathrm{SiH}_3$
920				920			$B_2\nu_{11}'$
852			vvw	847	<1	?	$A_2\nu_{11}$
766			vvw				$\begin{cases}A_1 2\nu_{18}' \\ A_1 2\nu_{20}\end{cases}$
750	~759 *R* 752 *Q* ~745 *P*	*C*	w				$B_2\nu_4$
	706 *Q*	*C*?	s				?
698	699 *Q*	*C*	vs				$B_2\nu_8$
	~690	?	sh	692	28	0.12	$A_1\nu_2$
678				674	<1	?	$\rho_{op}\mathrm{SiH}_3$
645	655 ctr	?	s	648	1	dp	$\rho_{ip}\mathrm{SiH}_3$
618				619	4	dp	$B_1\nu_{18}$
421	420 ctr	?	vvw	420	<1	?	$B_2\nu_{19}'$
390	392 *R* 388 *Q* 382 *P*	*A*	m	388	31	0.31	$A_1\nu_{18}'$
				(386)			$A_2\nu_{20}$
				203	1	?	$B_1\nu_{14}'$
				159	16	dp	$B_2\nu_{20}'$

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* Abbreviations are as follows: ctr means center; dp, depolarized; m, moderate; p, polarized; s, strong; sh, shoulder; v, very; w, weak.

† No combination or overtone gives a value within the limits imposed for other combination and overtone bands.

‡ Possible combinations or overtones involve ν_3, ν_6, ν_7, ν_{12}, ν_{14}, ν_{16}, ν_{16}', ν_{17}, ν_{19} and $\nu\mathrm{SiH}_3$.

§ The calculated band center for the asymmetric stretching mode is 2169.0 cm^{-1}.

‖ This assignment is common to Whiffen's list (see text).

¶ Composite intensity and depolarization measurement.

( ) This value is inferred from the combination band at 1371 cm^{-1}.

Table 2. Infrared and Raman spectra of phenylsilane-d_3*

Infrared			Raman			
Gas $\bar{\nu}$	Band type	Rel. int.	$\Delta\bar{\nu}$	Rel. int.	Depol. ratio	Assignments
			3179	3	dp?	$A_1 2\nu_{16}'$ $\nu_{as}\mathrm{SiD}_3 + \nu_{16}'$ $B_2\nu_{20}' + \nu_{15}$
3146 ctr	?	vw	3139	4	dp?	$\nu_s\mathrm{SiD}_3 + \nu_{16}'$ $\nu_s\mathrm{SiD}_3 + \nu_{as}\mathrm{SiD}_3$ $\nu_{as}\mathrm{SiD}_3 + \nu_{16}$ $2\nu_{as}\mathrm{SiD}_3$
3087 *R*						
~3081 ctr	*B*	ms				$B_1\nu_{12}'$
~3076 *P*						
3072 *R*						
3067 *Q*	*A*	s				$A_1\nu_5$
3062 *P*						
			3053	60	0.57	$A_1\nu_1$
3036 *R*						
~3032 ctr	*B*	ms				$B_1\nu_{13}$
~3028 *P*, *R*						
3024 *Q*	*A*	ms	3024	4	dp?	$A_1\nu_{15}'$
3020 *P*						
3010	?	sh				$\nu_{as}\mathrm{SiD}_3 + \nu_{13}$
2955 bd	?	vvw				$A_1 2\nu_{13}$
			2981	4	dp?	$\nu_s\mathrm{SiD}_3 + \nu_{13}'$
			2959	4	dp?	$A_1 2\nu_{13}$
2895 bd		vvw				$A_1\nu_9 + \nu_{16}$ $B_1\nu_3 + \nu_{16}'$
2855 dp		vvw				$A_1 2\nu_{13}'$
2174 *R*						
2169 *Q*		vw	2157	<1	?	Impurity (Si—H stretching) $\delta_{as}\mathrm{SiD}_3 + \nu_{13}$
2164 *P*						
2146	*C*?	vvw				$A_1\nu_3 + \nu_{13}$ $A_1\nu_{14} + \nu_{12}$ $B_2\nu_{11} + \nu_3$ $\delta_s\mathrm{SiD}_3 + \nu_{13}'$
~1972 ctr	?	w				Overtone or combination**
1960 *R*						
~1955 ctr	*B*	w				$B_1\nu_2 + \nu_3$ $\nu_{as}\mathrm{SiD}_3 + \nu_{18}'$
1949 *P*						
1903 *R*						
1899 *Q*	*A*?	w				$A_1\nu_7 + \nu_{11}'$†
~1893 *P*						
~1887 *R*						
~1881 ctr	*B*	w				$B_1\nu_8 + \nu_{17}'$ $\delta_s\mathrm{SiD}_3 + \nu_{17}$
1876 *P*						
1820 *R*						
1816 *Q*	*A*	w				$A_1 2\nu_{11}'$
1810 *P*						
1659 *R*						
1654 *Q*	*A*	vw				$A_1\nu_3 + \nu_6$ $A_1\nu_4 + \nu_{11}'$ $\rho_{op}\mathrm{SiD}_3 + \nu_{12}$ $\delta_s\mathrm{SiD}_3 + \nu_{19}$
1648 *P*						
			1590	29	0.78	$A_1\nu_{16}'$
1584 ctr		s				$\nu_{as}\mathrm{SiD}_3$
			~1568	~10	?	$B_1\nu_{16}$
1563 *R*						
1558 *Q*	*A*	vs	1551	100	0.42	$\nu_s\mathrm{SiD}_3$
1553 *P*						
1485 ctr	*A*?	vw	1483	1	?	$A_1\nu_{13}$
1436 *R*						
1431 ctr	*B*	m	1430	1	?	$B_1\nu_{13}'$
1426 *P*						
1376 *R*						
1370 ctr	*B*	vw				$B_1\nu_{20}\| + \nu_7$† $\delta_{as}\mathrm{SiD}_3 + \nu_8$
1364 *P*						

Table 2 (*cont.*)

Infrared			Raman			
Gas $\tilde{\nu}$	Band type	Rel. int.	$\Delta\tilde{\nu}$	Rel. int.	Depol. ratio	Assignments
1334 *R*						
1329 ctr	*B*	w	1329	1	?	$B_1\nu_9$
1324 *P*						
1303 *R*						
1298 ctr	*B*	vw				$B_1\nu_3$
1292 *P*						
1273 *R*						
1266 *Q*	*A*?	vw				$\begin{cases} B_2\nu_{12} + \nu_{20}' \\ \rho_{\text{op}}\text{SiD}_3 + \delta_s\text{SiD}_2§ \end{cases}$
1262 *P*						
1193 *R*						
1188 *Q*	*A*	w	1187	4	0.74	$A_1\nu_{17}'$
1183 *P*						
			1156	4	dp	$B_1\nu_{17}$
1134	?	sh				$\begin{cases} A_1\nu_7 + \nu_{20}'† \\ B_2\nu_{14}'‖ + \nu_{19} \end{cases}$
1124 *R*						
1119 *Q*	*A*	ms	1117	4	0.39	$A_1\nu_{12}$
1114 *P*						
1083 ctr	*C*?	w	1084	1	?	$\begin{cases} B_2\nu_8 + \nu_{20}‖† \\ 2\rho_{\text{op}}\text{SiD}_3 \end{cases}$
1060 ctr	?	vw	1064	<1	?	$B_1\nu_{10}$
1033 *R*						
1028 *Q*	*A*	vw	1027	11	0.39	$A_1\nu_{14}$
1022 *P*						
1004 *R*						
999 *Q*	*A*	w	998	74	0.36	$A_1\nu_6$
993 *P*						
			986	vw	?	$B_2\nu_7$
			940	<1	?	$A_2\nu_{19}$
			914	<1	?	$B_2\nu_{11}'$
868 *R*						
863 *Q*	*A*	vw				$\begin{cases} \delta_{as}\text{SiD}_3 + \nu_{14}'‖¶ \\ \delta_s\text{SiD}_3 + \nu_{20}'¶ \end{cases}$
857 *P*						
			846	1	?	$A_2\nu_{11}$
831 ctr	*A* or *C*	m				$\delta_{as}\text{SiD}_3 + \nu_{20}'$
740 *Q*	*C*	ms	744	<1	?	$B_2\nu_4$
723 *R*						
718 *Q*	*A*	vs	713	9	0.43	$A_1\delta_s\text{SiD}_3$, ν_2
713 *P*						
697 *Q*	*C*	s	697	2	?	$B_2\nu_8$
688		sh				$\rho_{\text{op}}\text{SiD}_3 + \nu_{20}'$
			671	4	dp?	$\delta_{as}\text{SiD}_3$
667 *R*						
662 *Q*	*A*	vs	657	11	0.53	$A_1\delta_s\text{SiD}_3$, ν_2
658 *P*						
			618	7	dp	$B_1\nu_{18}$
540 *Q*	*C*	s	533	<1	?	$\rho_{\text{op}}\text{SiD}_3$
510 *R*						
507 ctr	*B*	ms	505	1	dp	$\rho_{\text{ip}}\text{SiD}_3$
503 *P*						
381 *R*						
376 *Q*	*A*	mw	376	21	0.58	$A_1\nu_{18}'$
371 *P*						
			154	15	?	$B_2\nu_{20}'$

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* Abbreviations are as in Table 1.

† This assignment is common to Whiffen's list (see text).

§ An exceptionally wide range is allowed because the position of a *Q* branch of the $\rho_{\text{op}}\text{SiD}_3$ mode, rather than the band center, is reported.

‖ The value of this fundamental was estimated by consideration of the spectra of phenylsilane.

¶ For this band, no combinations or overtones give values within the error limits imposed in making assignments to other combination and overtone bands.

** There are numerous possible assignments involving ν_3, ν_6, ν_7, ν_{10}, ν_{11}, ν_{11}', ν_{12}, ν_{13}', ν_{14}, ν_{16}', ν_{18}', ν_{19}, ν_{19}', ν_{20}, $\delta_{as}\text{SiD}_3$, $\rho_{\text{op}}\text{SiD}_3$ and $\nu_{as}\text{SiD}_3$.

Table 3. Vibrational fundamentals for phenylsilane and phenylsilane-d_3 (Raman data except as noted)

C_{2v} Species	$C_6H_5SiH_3$ (cm^{-1})	$C_6H_5SiD_3$ (cm^{-1})	Assignment	
			HERZBERG designation [13]	Approximate description
A_1	388	376	ν_{18}'	Ring deformation
	692	657, 713*	ν_2	Ring breathing
	998	998	ν_6	Ring deformation
	1027	1027	ν_{14}	C—H parallel bending
	1117	1117	ν_{12}	C—Si stretching
	1187	1187	ν_{17}'	C—H parallel bending
	1484	1483†	ν_{13}	C—C stretching
	1591	1590	ν_{16}'	C—C stretching
	3023†	3024	ν_{15}'	C—H stretching
	3052	3053	ν_1	C—H stretching
	3067†	3067†	ν_5	C—H stretching
A_2	(386)	—	ν_{20}	Perpendicular ring deformation
	847	846	ν_{11}	C—H perpendicular bending
	936	940	ν_{19}	C—H perpendicular bending
B_1	203	—	ν_{14}'	C—Si parallel bending
	619	618	ν_{18}	Ring deformation
	1064	1064	ν_{10}	C—H parallel bending
	1156	1156	ν_{17}	C—H parallel bending
	1298†	1298†	ν_3	C—H parallel bending
	1330	1329	ν_9	C—C stretching
	1432†	1430	ν_{13}'	C—C stretching
	1567	1568	ν_{16}	C—C stretching
	3033†	3032†	ν_{15}	C—H stretching
	3080†	3081†	ν_{12}'	C—H stretching
B_2	159	154	ν_{20}'	C—Si perpendicular bending
	420	—	ν_{19}'	C—H perpendicular bending
	699	697	ν_8	Perpendicular ring deformation
	752†	744	ν_4	C—H perpendicular bending
	920	914	ν_{11}'	C—H perpendicular bending
	985	986	ν_7	C—H perpendicular bending
SiH_3, SiD_3 Vibrations				
	648	505	In-plane SiX_3 rocking	
	674	533	Out-of-plane SiX_3 rocking	
	930	657, 713*		Symmetric SiX_3 deformation
	930	671		Asymmetric SiX_3 deformation
	2157	1551		Symmetric SiX_3 stretching
	2157	1584†		Asymmetric SiX_3 stretching

* ν_2 and $\delta_s SiD_3$ are in Fermi resonance.

† Infrared frequencies.

( ) This value is inferred from combination bands.

symmetry species of the vibrations, descriptions of the fundamental modes are given.

The assignments which are not perfectly straightforward involve ν_1, ν_2, ν_5, ν_{14}', ν_{20}, ν_{20}' and the symmetric SiD_3 deformational mode. The difficulty in assigning ν_1 and ν_5 arises because both modes are of the A_1 species and lie close together; it is simply necessary either to assume that ν_1 will have the higher frequency or else that the in-phase stretching of the carbon–hydrogen bonds in the course of the ν_1 vibration will result in a greater change of the polarizability ellipsoid than the out-of-phase motion of ν_5, the effect being that ν_1 will produce the more intense Raman line. The latter choice is made here.

The frequencies of both ν_{14}' and ν_{20}' are variable and their frequency ranges overlap. Since neither ν_{14}' nor ν_{20}' was observed in the i.r. spectra and their Raman shifts cannot be distinguished on the basis of their different symmetry types—B_1

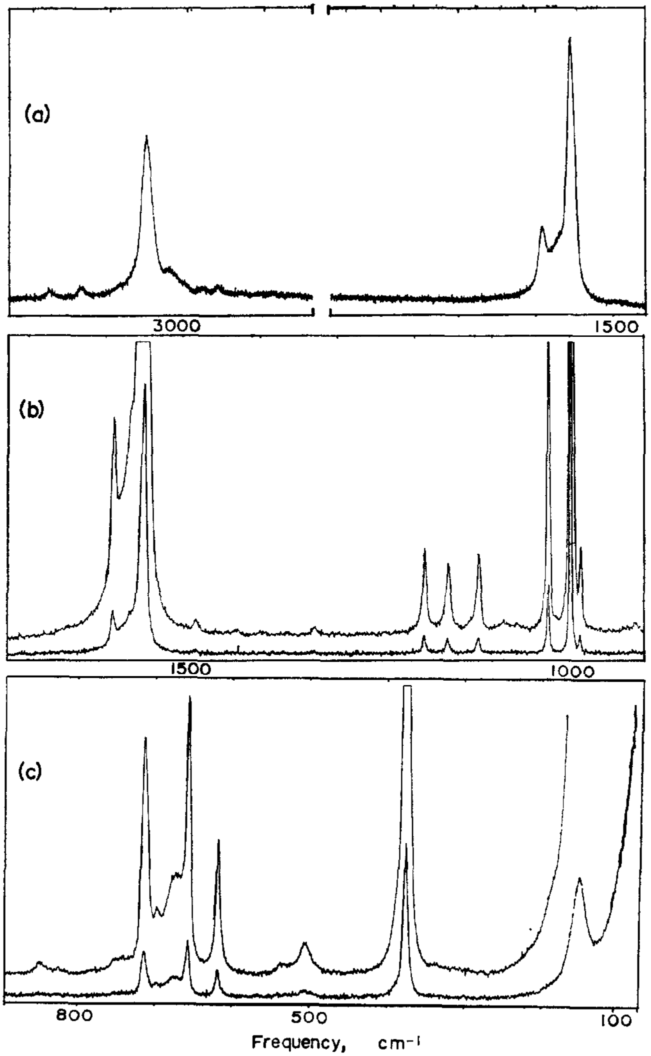

Fig. 1. Raman spectrum of liquid phenylsilane-d_3. Arc excitation was used to obtain the high frequency region (a); laser excitation allowed somewhat better resolution at lower frequencies (b and c).

and B_2 respectively—it is simply assumed that the frequency of ν_{20}' is lower than that of ν_{14}' in phenylsilane and that ν_{14}' is unobserved in the spectra of phenylsilane-d_3.

The SiH_3 symmetric deformational mode and ν_2, both A_1 modes, are confidently assigned to the bands near 930 and 692 cm^{-1}, respectively, in the spectra of phenylsilane. A maximum isotopic shift would place the corresponding modes of phenylsilane-d_3 at 658 and 662 cm^{-1} respectively. A single A-type band and a strongly polarized Raman band are indeed observed near 660 cm^{-1}, but a similar band (both i.r. and Raman active) which must be attributed to one of these two modes lies near 716 cm^{-1}. Evidently, these modes are in Fermi resonance such that they give rise to this pair of bands at 662 and 718 cm^{-1} (see Figs. 1 and 2). The one fundamental which was not observed in the spectra of at least one of the two compounds is ν_{20} which is often weak or unobservable [1, 13–17].

Although the rocking and deformational vibrations of the silyl or silyl-d_3 group fall among vibrations of the phenyl group, there is, in general, no difficulty in identifying them; for, either they are distinguishable by the rotational structure evident on the i.r. bands arising from the antisymmetric modes or else their band contours and/or depolarization ratios set them apart. Thus, assignments to these vibrations can be made even without recourse to a knowledge of their frequencies. If rotation about the Si—C bond were entirely free, the gas-phase spectra would show adherence to the selection rules of C_{3v} symmetry for the silyl and the silyl-d_3 groups. That is, there would appear a single band arising from a degenerate rocking mode, two from the deformational modes (one degenerate), and two from the stretching modes (one degenerate). However, the rocking modes of the silyl group appearing at 674 and 648 cm^{-1} in the Raman spectrum are split by 26 cm^{-1}. The 620–680 cm^{-1} region of the gas-phase i.r. spectrum shows numerous Q-branches spread over a broad absorption which must be attributed to both components of the rocking mode; however, the breadth of this band allows the argument for exclusion of the degeneracy of the rocking modes (see Fig. 3). On the other hand, the spectra give little indication that the antisymmetric deformational and stretching modes are non-degenerate. This situation is not at all surprising because the rocking modes should be more sensitive to interactions between the phenyl and silyl groups. The degenerate rocking mode of the silyl-d_3 group is similarly split by 33 cm^{-1} but no fine structure is discernible on these two i.r. bands at 507 and 540 cm^{-1} (see Fig. 2). The Raman counterparts of these bands appear at 505 and 533 cm^{-1}. Since the band at 507 cm^{-1} has a B-type contour and that at 540 cm^{-1} has a C-type contour, these bands are attributed to the in-plane and the out-of-plane rocking modes, respectively. On the basis of this

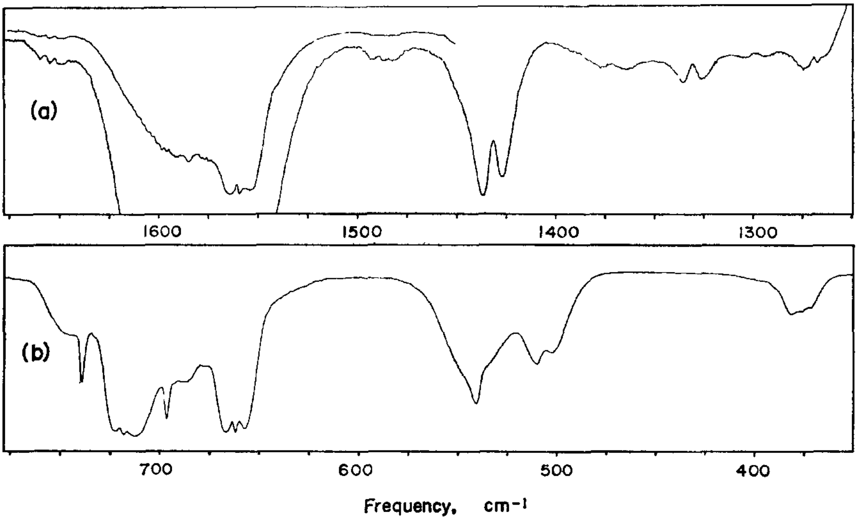

Fig. 2. Selected portions of the i.r. spectrum of gaseous phenylsilane-d_3.

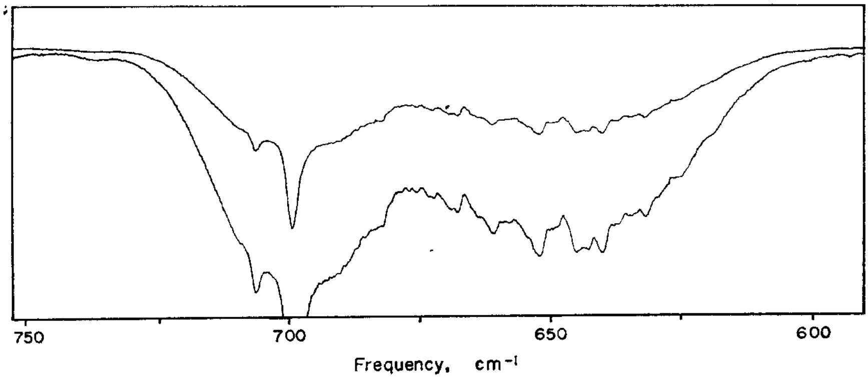

Fig. 3. Region of the i.r. vapor-phase spectrum of phenylsilane showing the SiH_3 rocking modes.

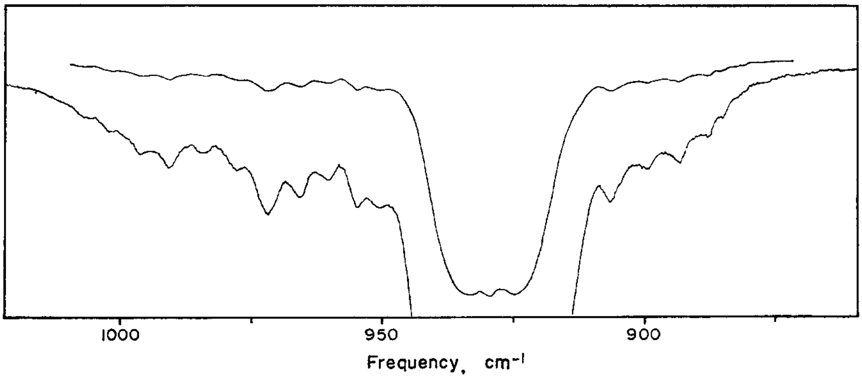

Fig. 4. Infrared vapor-phase spectrum of the SiH_3 deformational modes of phenylsilane.

distinction, the out-of-plane rocking mode of the SiH_3 group is expected likewise to lie above the corresponding in-plane mode.

The i.r. bands at 929 and 952 cm^{-1} in the i.r. spectrum of phenylsilane are attributed respectively to the symmetric and the degenerate deformational modes of the silyl group. Only the symmetric mode is manifested in the Raman spectrum by an incompletely resolved band at 930 cm^{-1}. The i.r. band at 952 cm^{-1}which is attributed to the antisymmetric deformational mode shows pronounced, well resolved fine structures (see Fig. 4). This vibrational–rotational structure clearly indicates nearly free rotation about the Si—C bond. (Detailed discussion is presented in the following section.) No such structure can be observed in the spectrum of phenylsilane-d_3 because the antisymmetric deformational frequency of the silyl-d_3 group, 671 cm^{-1} as indicated by the Raman spectrum, falls within a region of the i.r. spectrum so densely occupied by other strong bands that absorption due to this mode is completely obscured (see Fig. 2). The symmetric deformational mode gives rise to a strong A-type band at 662 cm^{-1} in the i.r. spectrum and a strongly polarized Raman line (657 cm^{-1}) for the d_3 molecule.

Numerous Q-branches are also observed on the i.r. band arising from the antisymmetric stretching mode of the silyl group (Fig. 5). This mode is accidentally degenerate with the symmetric stretching vibration which gives rise to the A-type band at 2169 cm^{-1} and the strongly polarized Raman band at 2157 cm^{-1}. The center of the band arising from the antisymmetric mode is calculated (see following section) to be 2169.0 cm^{-1}. The i.r. band at 1584 cm^{-1} in the spectrum of phenylsilane-d_3 also exhibits a number of Q-branches (Fig. 2), providing further indication of free rotation about the Si—C bond. In contrast to the stretching modes of the silyl group, the corresponding modes of the silyl-d_3 group are clearly seperated; the i.r. band assigned to the antisymmetric mode appears at 1584 cm^{-1} whereas that attributed to the symmetric stretching is at 1558 cm^{-1}. The latter A-type band has an intense strongly polarized Raman counterpart at 1551 cm^{-1}.

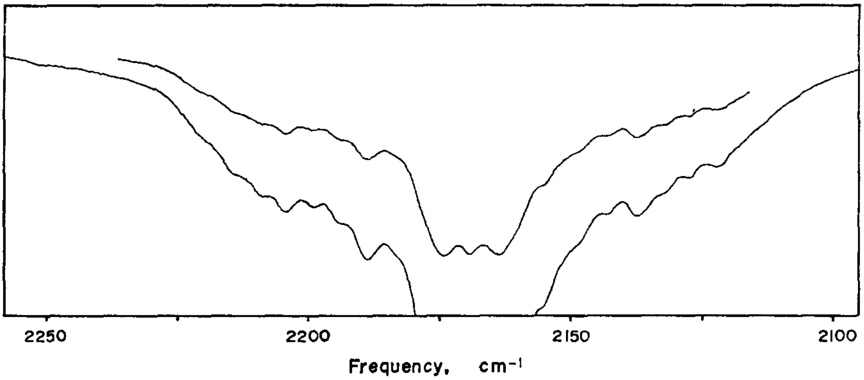

Fig. 5. Infrared vapor-phase spectrum of the SiH_3 stretching modes of phenylsilane.

Numerous overtones and combinations were observed. Assignments to these bands, as indicated in Tables 1 and 2, were made from computer-prepared lists for each band not assigned to a fundamental mode. Each list consisted of all possible binary sums within 8 cm^{-1} of the frequency of the band to be assigned and all possible overtones for which twice the fundamental frequency was not more than 40 cm^{-1} greater than the frequency of the band being assigned nor more than 6 cm^{-1} smaller. The assignments indicated in Tables 1 and 2 were chosen from these lists by using the following criteria: (1) the symmetry species of the combination or overtone must be as required by band contours and/or polarization data; (2) observed combination bands must fall within 6 cm^{-1} of the calculated value if the frequency values of the observed fundamentals and that of the unassigned band were all obtained from spectra of samples of the same phase. All overtones contained in the lists for unassigned bands requiring totally symmetric species are indicated in Tables 1 and 2 if twice the fundamental is no more than 30 cm^{-1} greater than the band to be assigned. Difference bands were not considered except for those bands for which no overtone or combination satisfying the above requirements could be found. In these cases, however, no difference combinations were found which satisfied the criteria imposed for the sum bands and the additional requirement that if a difference band is observed, the corresponding sum band should also be observed.

These assignments were compared to those made by WHIFFEN [3] for the series of monohalobenzenes. WHIFFEN's list contains assignments for 26 overtones and combination bands. Of these 26 assignments 9 are included as possible assignments to overtone and combination bands in the spectra of phenylsilane; three of these and one additional assignment common to WHIFFEN's list are included as possibilities in the spectra of phenylsilane-d_3. These assignments are indicated by asterisks in Tables 1 and 2.

ANALYSIS OF VIBRATIONAL–ROTATIONAL STRUCTURE

The rotational constants of phenylsilane and phenylsilane-d_3 were calculated from the bond distances derived from an electron diffraction analysis [19] of phenylsilane and from results of microwave spectra of other compounds containing Si—H bonds [20, 21]. The valence angles about the silicon atom were assumed to be tetrahedral and all other valence angles, 120°. The values obtained for phenylsilane are $A = 0.179$, $B = 0.0512$ and $C = 0.0403$ cm^{-1}. These rotational constants are so small that no fine structure arising from molecular rotation can be expected in the spectra of the vapors.

However, as indicated in the previous section, all of the i.r. bands attributed to the antisymmetric modes of the silyl group exhibit clearly resolved fine structure. The sub-bands of the antisymmetric stretching and deformational bands showed an alternation of intensity—strong, weak, weak—characteristic of perpendicular vibrations of molecules having a threefold symmetry axis. The band arising from the rocking modes also shows fine structure, but there appears to be no regular pattern of intensity alteration, presumably because the in-plane and the out-of-plane rocking modes—each with its fine structure—overlap as pointed out in the previous section. This structure must be the result of free rotation of the silyl group about the Si—C axis since the spacing between successive sub-bands is more than an order of magnitude greater than that required for rotation of the molecule about the axis of its smallest moment.

The frequencies of the Q-branches of the stretching and deformational modes are listed in Tables 4 and 5 with assignments based on the pattern of relative intensities The $K = 0$ sub-band is expected to appear at the center of the band and the sub-bands corresponding to K equal zero and multiples of three must be relatively strong. Further, the member of a pair of "weak" bands closer to the band center should be slightly stronger than its companion.*† Figures 4 and 5 show that these criteria are met by the assignments in Tables 4 and 5 with the exception of the four sub-bands at the low frequency edge of the deformational band (Fig. 4, Table 4). An additional

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* See Ref. [13] 424 ff.

† See Ref. [13], 428 ff.

[19] F. A. KEIDEL and S. H. BAUER, *J. Chem. Phys.* **25**, 1218 (1956).

[20] J. M. O'REILLY and L. PIERCE, *J. Chem. Phys.* **34**, 1176 (1961).

[21] J. R. DURIG, unpublished results from the microwave spectra of sila*cyclo*pentane and sila*cyclo*pentane-d_2.

Table 4. Wavenumbers of sub-bands of the degenerate SiH_3 deformation of phenylsilane

K	Relative intensity	^RQ_K	^PQ_K
0	s	954.9	
1	w	960.3	950.4
2	w	965.9	—
3	s	971.7	—
4	w	977.9	—
5	w	984.5	—
6	s	990.7	—
7	w	996.1	—
8	w	1001.8	906.5
9	s	1006.7	899.5
10	w		893.2
11	w		880.0

Table 5. Wavenumbers of sub-bands of the degenerate SiH_3 stretching of phenylsilane

K	Relative intensity	^RQ_K	^PQ_K
0	—	—	
1	—	—	—
2	w	2183.3	—
3	s	2188.8	2155.1
4	w	2194.0	2148.9
5	w	2199.1	2142.9
6	s	2204.4	2137.3
7	w	2208.8	2133.5
8	w	2213.5	2127.6
9	s	—	2122.1

feature is the fact that the sub-bands of the ^PQ_K branch of this band extend to slightly higher K values than do the sub-bands of the ^RQ_K branch.

The frequencies of the Q-branches of these two bands were found, by the least square method, to fit the following equations:

$$\nu_0^{\text{sub}} = 2171.8 \pm 5.46K - 0.0158K^2 \text{ (for the stretching mode) and}$$

$$\nu_0^{\text{sub}} = 954.8 \pm 5.95K - 0.0152K^2 \text{ (for the deformational mode).}$$

The band centers are calculated to be 2169·0 and 952·0 for the antisymmetric stretching and deformational modes, respectively. This value for the center of the antisymmetric stretching mode is the same as the value recorded for the A-type band at 2169 cm^{-1} so that the stretching modes of the silyl group, unlike the deformational modes, are accidentally degenerate.

Since the average spacing of the Q-branches of each of these bands is equal to

$[2A_1(1 - \zeta) - (B' + C')]$ [1], the Coriolis coupling constants (ζ) for these antisymmetric modes can be calculated. For the antisymmetric stretching mode, ζ is 0.0658 and for the antisymmetric deformation mode it is −0.0197. For comparison, these values are presented with the ζ values for the degenerate vibrations of the silyl halides in Table 6.

Table 6. Comparison of Coriolis coupling constants

Degenerate vibration	SiH_3F*	SiH_3Cl*	SiH_3Br*	SiH_3I†	ΦSiH_3	ΦSiD_3	SiD_3I†
Stretching	0.0260	0.00724	0.0108	0.015	0.0658	0.143	0.145
Deformation	−0.145	−0.178	−0.185	−0.196	−0.0197	—	−0.197
Rocking	0.206	0.215	0.200	0.199	—	—	0.085

* Calculated from the data of CAROLYN NEWMAN, J. K. O'LOANE, S. R. POLO and M. K. WILSON, *J. Chem. Phys.* **25,** 855 (1956).

† H. R. LINTON and E. R. NIXON, *Spectrochim. Acta* **12,** 41 (1958).

The vapor-phase i.r. spectrum of phenylsilane-d_3 exhibits rotational fine structure only on the antisymmetric SiD stretching band. Since the relative intensities of the strong and weak sub-bands are 11:8 (as compared to 2:1 for the silyl group), no assignments to the sub-bands can be made on this basis with any certainty. The average spacing of these sub-bands is 2.37 cm^{-1}, resulting in a calculated ζ value equal to 0.143 for the antisymmetric stretching mode of the silyl-d_3 group. The antisymmetric deformational mode of the silyl-d_3 group was observed in the Raman spectrum only. The degenerate rocking mode was observed to be split into two components, neither showing any fine structure.

Since the completion of this work, a theoretical treatment of the rotational–vibrational interactions in phenylsilane, phenylgermane, and their "d_3" derivatives has appeared. FLEMING and BANWELL [22] locate the centers of the components of the perpendicular stretching vibration of the silyl group at 2167 and 2170 cm^{-1}, corresponding to our value of 2169.0 cm^{-1} for each component. Similarly, these investigators indicate 944 and 953 cm^{-1} for the frequencies of the two components of the antisymmetric deformational mode, whereas we interpret this mode to be degenerate, giving rise to a band centered at 952.0 cm^{-1}. However, we would like to point out that our work is a first order approximation while their work is more complete by taking into account the rotational–vibrational interaction.

SPECTRA OF MATRIX ISOLATED PHENYLSILANE AND PHENYLSILANE-d_3

In order to confirm the locations of the centers of the bands which arise from the perpendicular vibrations of the silyl group, we investigated the i.r. spectrum of phenylsilane isolated in both argon and krypton matrices (see Fig. 6). At the initiation of this part of the study, it was generally thought that the frequency data from matrix isolated materials would compare within a few wavenumbers of that obtained from molecules in the gaseous state. However, a comparison of the frequencies for the SiH_3 rocking mode shows approximately a three wavenumber difference between bands observed for the two host materials. Furthermore a correlation between the

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[22] J. W. FLEMING and C. N. BANWELL, *J. Mol. Spectry* **31,** 318 (1969).

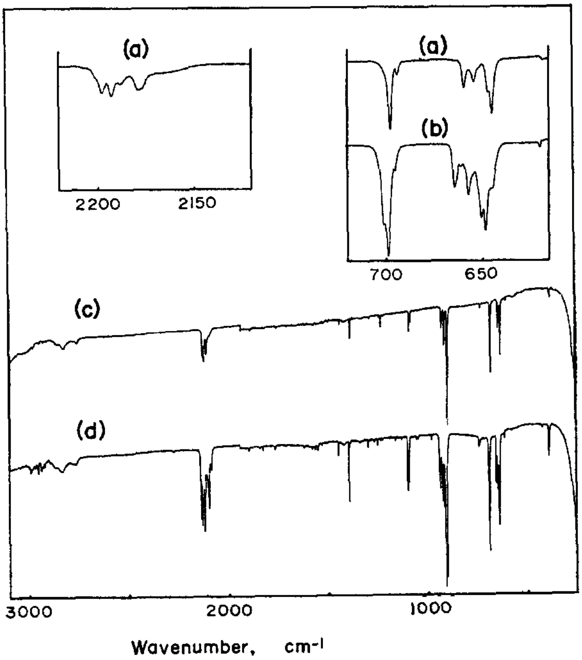

Fig. 6. Selected portions of the infrared spectrum of matrix isolated phenylsilane. Traces A and C were obtained by isolation in Kr matrices and traces B and D, in Ar matrices.

spectra in the SiH_3 stretching region is quite difficult. Of the two spectra, that obtained from the argon matrix is considerably more complex; definite splitting was observed for some of the bands which were not split in the spectrum from the krypton matrix. These differences are consistent with the recent investigations of HALLAM *et al.* [23–28] who have found significant dependences upon the nature of the solute and host.

In each of the spectra obtained from the argon and the krypton media, there appear four bands between 644.8 and 664.0 cm^{-1}. All four bands must be attributed to the rocking modes of the silyl group since only these vibrations have frequencies near this range. Thus, the matrix apparently splits both the in-plane and the out-of-plane rocking modes. The lower frequency doublets which are attributed to the in-plane motion are split by 2 cm^{-1} (644.8 and 646.8 cm^{-1} in the krypton medium and 648 and 650 cm^{-1} in the argon medium). The higher frequency doublets (out-of-plane motions) are more widely separated: 654.3 and 659.5 in the krypton matrix and 656.8 and 664.0 in the argon matrix. Thus, the matrix frequency of the in-plane

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[23] A. J. BARNES, J. B. DAVIES, H. E. HALLAM and G. F. SCRIMSHAW, *Chem. Commun.* 1089 (1969).
[24] A. J. BARNES, H. E. HALLAM and G. F. SCRIMSHAW, *Trans. Faraday Soc.* **65**, 3150 (1969).
[25] A. J. BARNES, H. E. HALLAM and G. F. SCRIMSHAW, *Trans. Faraday Soc.* **65**, 3159 (1969).
[26] A. J. BARNES, H. E. HALLAM and G. F. SCRIMSHAW, *Trans. Faraday Soc.* **65**, 3172 (1969).
[27] A. J. BARNES and H. E. HALLAM, *Trans. Faraday Soc.* **66**, 1920 (1970).
[28] A. J. BARNES and H. E. HALLAM, *Trans. Faraday Soc.* **66**, 1932 (1970).

mode nearly coincides with the liquid phase frequency (648 cm^{-1}) whereas the matrix (Ar and Kr) frequencies for the out-of-plane motion are about 20 cm^{-1} lower than that of the liquid phase. It should be noted that the gas phase frequency of the in-plane mode nearly coincides with the matrix frequencies of the out-of-plane motion.

In the region between 850 and 985 cm^{-1} fall several bands arising from phenyl group motions as well as the symmetric and the antisymmetric deformation of the silyl group. Only the deformational modes are observed in the gas phase infrared spectrum; therefore, the bands observed in this region in the spectrum from the matrix are assumed to arise from the deformational motions. The symmetric deformation is manifested by a strong band centered at 929 cm^{-1} in the gas phase i.r. spectrum. The spectrum from the krypton matrix shows the corresponding strong (slightly asymmetric) band at 923.1 cm^{-1}. Bands appearing at 938.4 and 953.2 cm^{-1}, each of which has a shoulder on the low frequency side (934.0 and 950.4 cm^{-1}) apparently represent the components of the antisymmetric deformational mode. This splitting is quite comparable to that of the two components of the rocking modes as indicated by the matrix spectra. These frequencies 938.4 and 953.2 agree reasonably well with the proposed assignments of 944 and 953 given by FLEMING and BANWELL [22] and confirm the non-degeneracy of the deformation mode.

The stretching modes in the matrix give rise to bands that are not so readily interpreted. Whereas these modes are accidentally degenerate in the liquid phase (2158 cm^{-1}) and in the gas phase (2169 cm^{-1}), the spectrum from the argon matrix shows a series of five intense bands plus six shoulders or less intense bands. These range in frequency from 2148 to 2202 cm^{-1}. The spectrum from the krypton matrix shows fewer bands, but their exact origin is by no means obvious.

The rocking modes of the silyl-d_3 group give rise to bands at 508.0 and 538.0 cm^{-1}, the higher frequency band showing a shoulder at 534.0 cm^{-1}. These frequencies differ little from the liquid phase frequencies of the in-plane and out-of-plane rocking modes (505 and 533 cm^{-1}, respectively).

The symmetric deformational mode of the silyl-d_3 group is in Fermi resonance with ν_2 (see VIBRATIONAL ASSIGNMENTS). The strong bands of equal intensity arising from these modes in the matrix appear at 659.6 and 715.7 cm^{-1} as compared to 657 and 713 cm^{-1} in the Raman spectrum and 662 and 718 cm^{-1} in the gas phase i.r. spectrum. Falling between these two easily identified bands are absorptions attributed to the antisymmetric deformation of the silyl-d_3 group (675.3 cm^{-1} with shoulders at 672.0 and 669.2 cm^{-1}), to a combination band (687.6 and 684.8 cm^{-1}), and to ν_8 (696.0 cm^{-1} with shoulders at 698.7 and 700.7 cm^{-1}).

The symmetric stretching mode apparently undergoes a large frequency shift upon matrix isolation, giving rise to a band at 1569.0 cm^{-1}. This band has shoulders at 1567.6, 1571.3 and 1575.0 cm^{-1}. Although all these components possibly arise from this stretching mode, the frequency of ν_{16} (1568 cm^{-1} in the Raman spectrum) falls in this region; however, ν_{16} was not observed in the gas phase i.r. spectrum. The antisymmetric stretching mode gives rise to bands at 1589.0, 1592.0 and 1598.8 cm^{-1} with a shoulder at 1586.7 cm^{-1}. Within this range is the frequency of $\nu_{16'}$ (1590 cm^{-1} in the Raman spectrum) which, like ν_{16} was not observed in the gas phase i.r. spectrum.

HALLAM *et al.* [25] have made the tentative deduction that when the site size of a matrix is about 2.0 times the effective diameter of a rotating hydrogen halide, then rotation of the hydrogen halide within the matrix cavity can occur unhindered. These workers indicate that the cavity diameters for argon and krypton matrices are 3.761 and 3.998 Å at 20°K. Our calculations indicate that the distance between a pair of hydrogen nuclei in the silyl group is 1.40 Å. This value together with 1.2 Å for the van der Waals radius of hydrogen [29] gives 5.2 Å for the diameter of the circle swept out by the hydrogen atoms of a silyl group rotating about its unique axis. Thus, the silyl group fits tightly in the matrix cavities so that free rotation is not to be expected. Because of these results and because there is no significant decrease in the intensity of bands progressively farther removed from the central band of any given set of absorption attributed to the perpendicular vibrations of the silyl group, we do not interpret the multiplicity of bands to arise from rotational–vibrational interactions.

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[29] L. PAULING, *The Nature of the Chemical Bond*, 3rd Edition, p. 260. Cornell University Press (1960).