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The vibrational spectra of germane and silane derivatives—XII. A reassignment of the dimethylhalosilanes

ALLAN J. F. CLARK,* JOHN E. DRAKE, RAYMOND T. HEMMINGS† and QUANG SHEN‡

Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

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Abstract—The i.r. and Raman spectra of the dimethylhalosilanes, Me_2SiHZ and Me_2SiDX (X = F, Cl, Br, I) have been recorded and the fundamental vibrations assigned. Analysis of the spectra of the deuterated compounds indicate that existing assignments for Me_2SiHX are in error.

INTRODUCTION

A report on the vibrational assignments of halogen derivatives of dimethylsilane has appeared in the literature[1]. This naturally included the monohalodimethylsilanes, and the authors recognized the difficulty in assigning the SiH bends and methyl rocks, and suggested that a study of isotopic species would be useful. This report responds to the suggestion and in light of the added information, concludes that the original assignments are questionable.

EXPERIMENTAL

The dimethylsilanes Me_2SiH_2 and Me_2SiD_2 were prepared by the reduction of Me_2SiHCl and Me_2SiCl_2 by $LiAlH_4$ and $LiAlD_4$, respectively, in dibutyl ether. They were separated from unreacted and partially reduced starting material by passage of the volatile products through a trap at −95°C, which retained any chloromethylsilanes and allowed for collection of dimethylsilane in a −196°C following trap. Purity was checked by ^1H NMR, i.r.[2] and Raman spectroscopy, for the detection of unreacted Si–Cl. Preparation of the iodo- and bromo- species was (i) by the reaction of the parent silane with HI (at 0°C) and HBr (at −78°C) for 1 h in the presence of the corresponding aluminum halide[3] and (ii) by the cleavage of $(Me_2SiH)_2NH$ with excess HX, in a clean and facile reaction[4] which only produces the monohalogenated species and an involatile co-product. Salt exchange reactions of the iodo- or bromo- species with $HgCl_2$[4] and SbF_3[5] afforded the chloro- and fluoro- derivatives, whose purity was checked by ^1H NMR spectroscopy[6].

Infrared spectra were recorded on a Beckman IR-12 instrument, using a 9 cm gas cell fitted with KBr windows and, for some less volatile derivatives, a liquid cell fitted with CsI plates. Raman spectra were recorded on the neat liquid in capillary tubes (o.d. *ca.* 2 mm) on a Spectra-Physics 700 spectrometer, using the argon ion line at 488.0 mm. Strong, sharp lines are estimated to $\pm 1\ cm^{-1}$, and weaker features to $\pm 4\ cm^{-1}$. ^1H NMR spectra were recorded on a JEOL C60-HL spectrometer on the neat liquid in sealed capillary tubes.

CALCULATIONS

The normal co-ordinate analyses were performed using an IBM S/360-50 series computer with a program written by Dr J. L. HENCHER of this department, in which the force constants are adjusted to fit the frequencies from the normal and deuterated molecules simultaneously. The following dimensions, taken from related molecules[7] were assumed; C–H 110, Si–C 185, Si–H 148 and Si–X 160(F), 203(Cl), 224(Br) and 246 pm(I). All angles were assumed to be tetrahedral. The methyl groups were defined such that all bonds were staggered when sighted along each C–Si bond.

VIBRATIONAL SPECTRA

The numbering and description of the modes are shown in Table 1 and typical Raman and i.r. spectra in Figs. 1 and 2. For the chloride, bromide and iodide, tthe expected band contours are A and/or C for the *a'* modes and B for the *a"* modes. Me_2SiHF is almost an accidental symmetric top and although A-type bands are predicted for *a'* modes, hybrid band shapes might be anticipated.

Table 1. Fundamental modes and approximate descriptions for $(CH_3)_2SiHX$ molecules

Description	a'	a"
CH_3 str. (asym)	ν_1 ν_2	ν_{16} ν_{17}
CH_3 str. (sym)	ν_3	ν_{18}
SiH str.	ν_4	
CH_3 def. (asym)	ν_5 ν_6	ν_{19} ν_{20}
CH_3 def. (sym)	ν_7	ν_{21}
CH_3 rock	ν_8 ν_9	ν_{22} ν_{23}
SiC_2 str.	ν_{10}	ν_{24}
SiH def.	ν_{11}	ν_{25}
SiX str.	ν_{12}	
SiC_2 def.	ν_{13}	
CSiX def.	ν_{14}	ν_{26}
torsion	ν_{15}	ν_{27}

Present addresses:

*Department of Chemistry, McGill University, Montreal, Quebec, Canada.

†Department of Chemistry, Scarborough College, University of Toronto, West Hill, Ontario, Canada.

‡Department of Chemistry, Colgate University, Hamilton, New York, U.S.A.

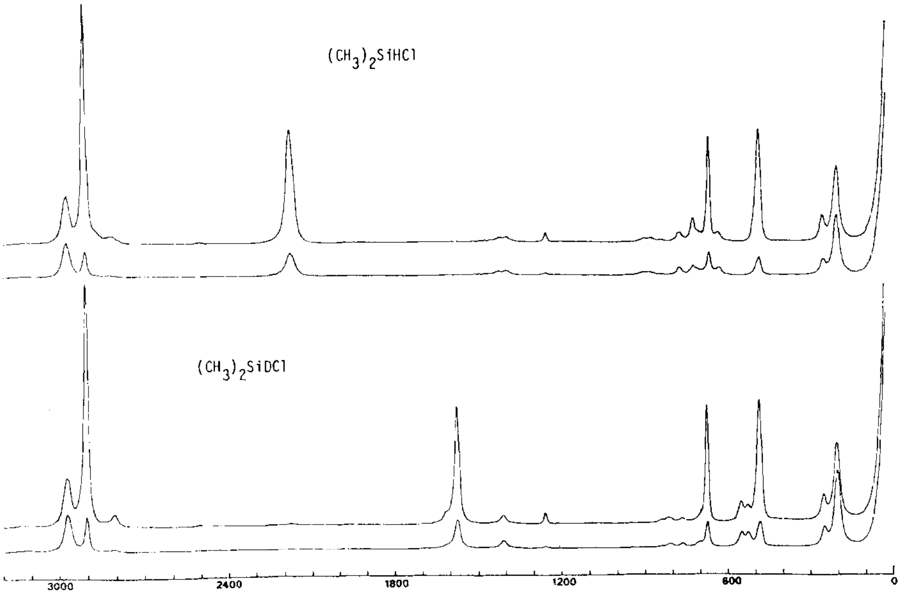

Fig. 1. The Raman spectrum of chlorodimethylsilane.

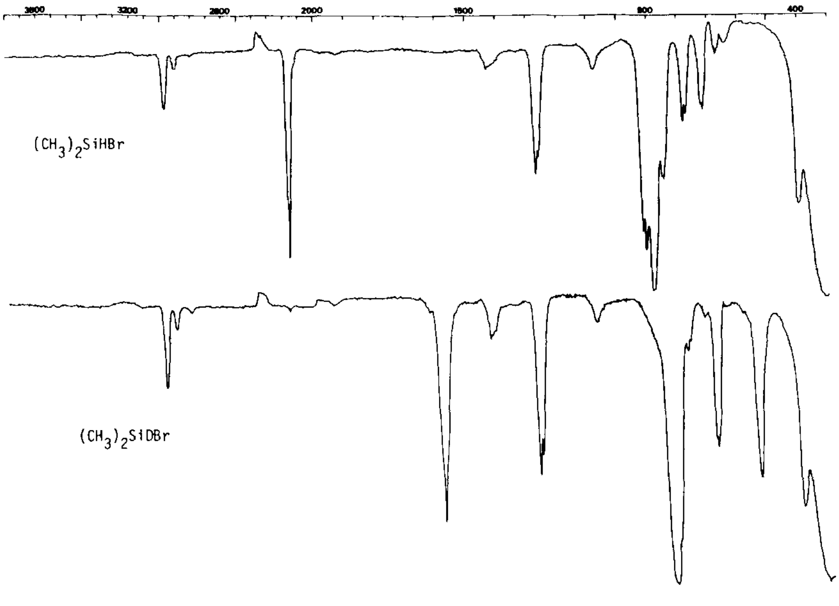

Fig. 2. The gas i.r. spectrum of bromodimethylsilane.

(i) *The region* 3000–1000 *cm*$^{-1}$

The CH_3 stretching regions in both spectra are almost identical for both homologues, with the asymmetric CH_3 stretches resolved into two bands in the Raman spectra. They appear as featureless weak to medium intensity bands in the i.r. spectra.

The Si–H and Si–D stretches are strong bands in both effects, those in the fluoride having the expected A-type contours. A weak shoulder is observed to the high wavenumber side of the Si–D band in both spectra, but not for the Si–H band. It is thus probably an overtone or combination band enhanced by Fermi resonance with ν_4. The highest rock is at *ca.* 820 cm^{-1}, and this fundamental, ν_q, is moderately strong (for a rock) in the Raman spectra and is intense in the i.r. spectra.

The asymmetric deformations appear as two depolarized bands in the Raman spectra, with a C-type maximum to the high frequency side of the i.r. envelope. The *a'* and *a''* symmetric deformations are both observed in the Raman spectra, where they are clearly distinguished in the polarized scan.

(ii) *The region* 1000–350 *cm*$^{-1}$

This region is interpreted mainly from the Raman spectra (Fig. 3–6) and the liquid i.r. spectra (e.g. Fig. 7). The Si–X stretches (X = Cl, Br, I) are

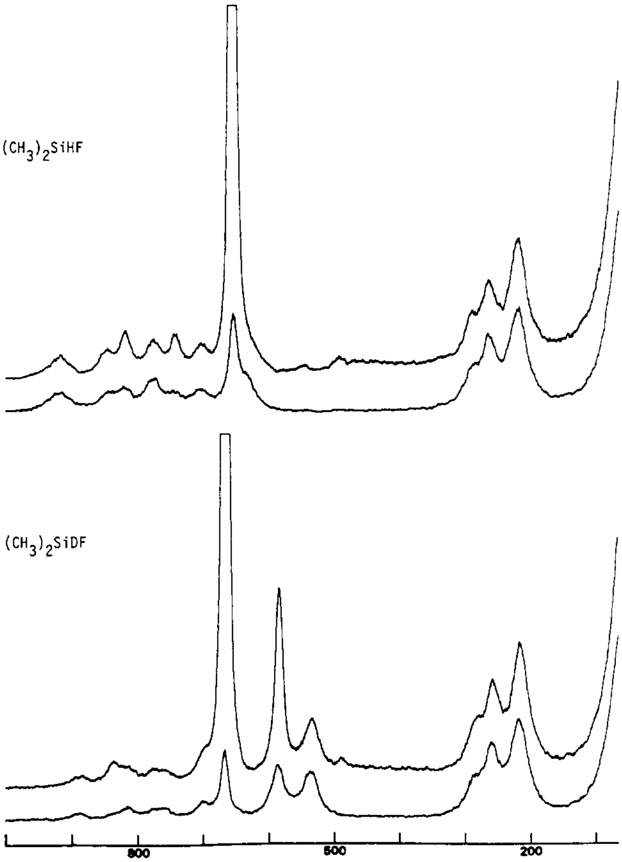

Fig. 3. Partial Raman spectrum of fluorodimethylsilane.

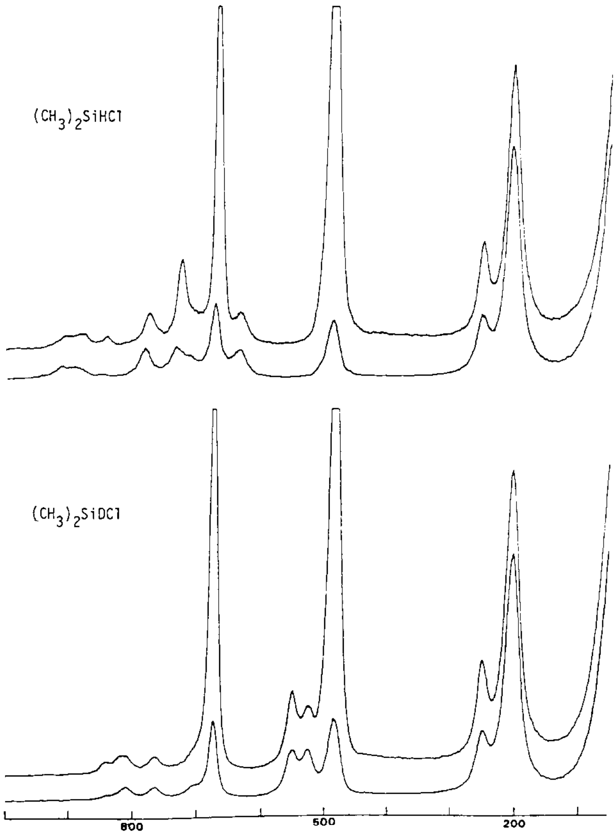

Fig. 4. Partial Raman spectrum of chlorodimethylsilane.

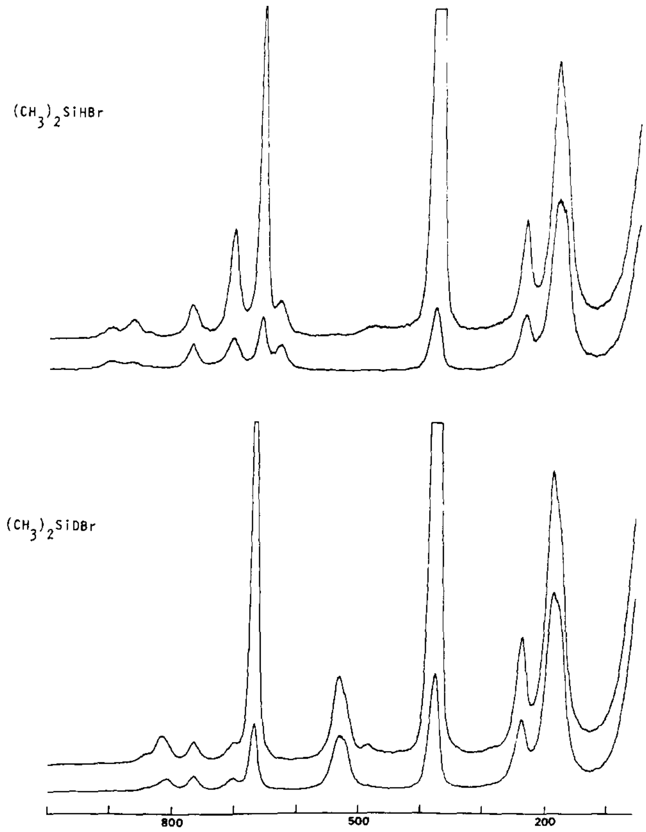

Fig. 5. Partial Raman spectrum of bromodimethylsilane.

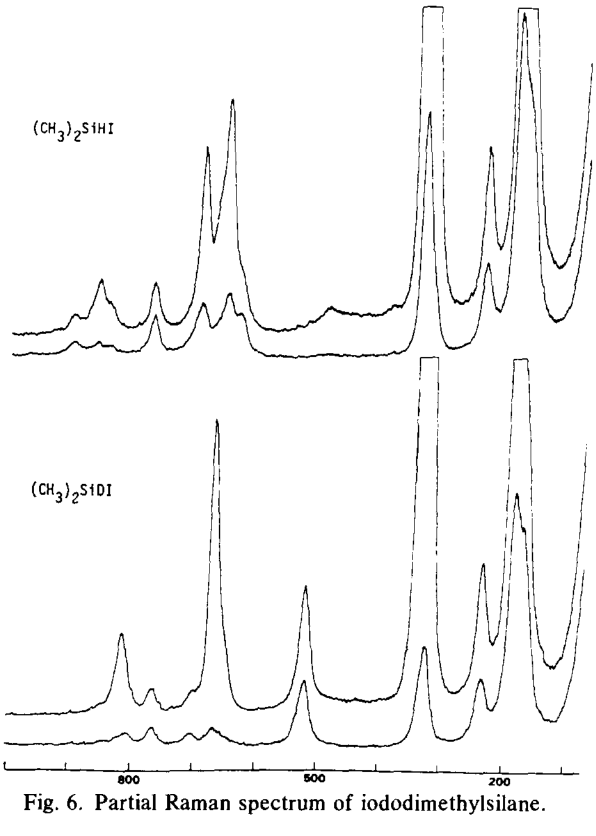

Fig. 6. Partial Raman spectrum of iododimethylsilane.

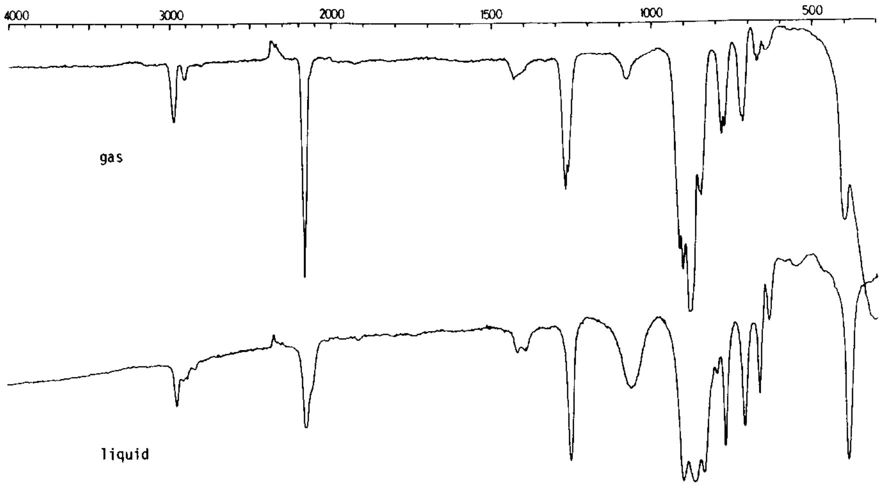

Fig. 7. Gas and liquid phase i.r. spectra of bromodimethylsilane.

intense, polarized bands at characteristic frequencies. The rest of the Raman spectrum is typical of the $\mathrm{Me_2SiH}$-group, and is almost identical to the pattern observed in the $\mathrm{(Me_2SiH)_2E}$ series (E = S, Se, Te)[8]. The bands between 500–600 cm^{-1} in the Raman spectrum of the 'heavy' molecule are without doubt the two Si–D bands, with a decreasing separation as the halogen becomes heavier; the two appearing exactly overlapped in the iodide. This suggests that the depolarized Raman band at *ca.* 634 cm^{-1} in all four compounds is ν_{25}, the a'' SiH band. The strongest remaining Raman band in the spectra of both isotopic species at about 665 cm^{-1} is presumably the symmetric Si–C stretch. The rest of the assignment is less immediately obvious, although the intense envelope at *ca.* 850 cm^{-1} in the i.r. spectra must involve methyl rocking modes.

These methyl rocking modes (ν_8, ν_9, ν_{22} and ν_{23}), the a' SiH deformation, ν_{11}, and the a'' SiC stretch, ν_{24}, can give rise to three apparently reasonable, yet different sets of assignments, depending on the method of approach. These possibilities, together with the data from Durig and Hawley[1] are presented in Table 2, where frequencies for the chloride have been used. It is difficult to see how the intense, polarized band at about 670 cm^{-1} can be assigned to anything but the a' SiC stretch, as is done here and in an earlier study of $\mathrm{Me_2SiHCl}$[9]. This is especially true because the methyl rocking modes, which have been suggested as an alternative, are notoriously weak in the Raman effect. Further, the assignment of methyl rocks to a region 632–667 cm^{-1} places them only a little higher than the $\mathrm{CD_3}$ rocking modes observed for $\mathrm{CD_3Si}$-compounds[10, 11] or $\mathrm{(CD_3)_3SiCl}$[12]. The position of the two Si–D deformations suggests a lower value for the a' SiH deformation than that arrived at by Durig and Hawley[1] and the polarized band at 726 cm^{-1}, with corresponding bands at 742(F) 710(Br) and 694 cm^{-1} (I), appears a more reasonable assignment for this mode. This steady decrease with increasing mass of halogen is to be expected as the a' SiH deformation is mainly

Table 2. Possible assignments within the region 550–910 cm^{-1} for chlorodimethylsilane

		Ref [1]	A		B		C	
		H	H	D	H	D	H	D
ν_{10}	SiC stretch	724	670	676	670	676	670	676
ν_{24}		777	776	705	776	765	705	705
ν_{22}	$\mathrm{CH_3}$ rocks	904	905	812	905	844	905	844
ν_8		879	883	844	883	822	883	822
ν_9		667	843	822	843	812	843	812
ν_{23}		667	843	765	705	705	776	765
ν_{11}	SiH def.	842	726	553	726	553	726	553
ν_{25}		639	633	530	633	530	633	530

dependent on fHSiX, whereas the a'' band depends mainly on fCSiH, and is thus relatively unchanged with the changing mass of the halogen.

Assignment A in Table 2 is arrived at by treating both isotopic series independently. In both the Raman and liquid i.r. spectra there are three bands above 840 and 810 cm^{-1} for the light and heavy molecules, respectively, which contain three (possibly all four) methyl rocking modes. Despite the weakness of the Raman spectra, two of these bands appear to be polarized, leaving the remaining rocking mode (if not coincident with one of the other three) to be assigned to a depolarized band. It will be noticed that ν_{24}, the a''SiC stretch, is assigned to widely different frequencies, and that the weak band at 705 cm^{-1} in the light compound is ignored. This band appears more distinctly in the fluoride, but not in the bromide or iodide where, if it is real, it is almost certainly overlapped by ν_{11}. However, the band is evident in the $(Me_2SiH)_2E$ compounds (E = S, Se, Te). An assignment that ignores this feature is unlikely to be valid, since it cannot be explained as a combination or overtone band, even with the proposed torsional modes[1].

The large difference between the a' and a'' SiC stretching modes is not compatible with calculated product rule ratios, which require, for good agreement, similar values for both the a'' stretches in the isotopic series. It was also impossible to duplicate these splitting patterns (100 and 30 cm^{-1} for H and D, respectively) with NCA calculations Assignment A is therefore rejected as a possibility.

This requirement from the product rule ratio satisfies both assignments B and C, where ν_{24} is now similar for both series of compounds. If we assume that the band at *ca.* 705 cm^{-1} does correspond to a fundamental mode in the spectra of all of the compounds, then it is either the remaining methyl rock (B) or ν_{24}, the a''SiC stretch (C). Both assignments do produce acceptable product rule ratios (Table 3). Little reliable data exist for Me_2SiX_2 compounds except for that of DURIG and HAWLEY [1], where for Me_2SiI_2 depolarized bands

Table 3. Product rule ratios for Me_2SiHX

		calc.	obs. Ra	obs. i.r.
Me_2SiDF	a'	0.517	0.521	0.519
Me_2SiHF	a"	0.725	0.721	0.705
Me_2SiDCl	a'	0.512	0.501	0.502
Me_2SiHCl	a"	0.726	0.727	0.752
Me_2SiDBr	a'	0.509	0.508	0.492
Me_2SiHBr	a"	0.726	0.723	0.709
Me_2SiDI	a'	0.508	0.509	0.511
Me_2SiHI	a"	0.726	0.741	0.742

Table 4. The vibrational spectra of the fluorodimethylsilanes

Me_2SiHF			assignment	Me_2SiDF		
i.r. (gas)	Raman (liq.)	calc.		i.r. (gas)	Raman (liq.)	calc.
2981 mw	2974 mw dp	2978	ν_1, ν_{16}	2981 mw	2975 mw dp	2978
2974 mw		2977	ν_2, ν_{17}	2974 mw		2977
A 2927 2917 w 2909	2912 s p	2911	ν_3, ν_{18}	2914 w	2910 s p	2911
2824 vw			$2\delta_{Me}$	2821 vw	2805 vw p 2505 vw	
A 2184 2169 s 2156	2166 s p	2177	ν_4	A 1594 1582 s 1568	1578 s p	1571
1436 w	1430 vw dp	1419	ν_5, ν_{19}	1430 w	1415 vw dp	1419
1422 w	1404 vw dp	1410	ν_6, ν_{20}	1422 w	1409 vw dp	1410
A 1274 1266 ms 1257	1262 vw p	1266	ν_7	A 1272 1264 s 1257	1262 vw p	1256
		1261	ν_{21}			1254
929 vs	917 vw dp	912	ν_{12}	902 vs	889 vw dp	896
921 vs		911	ν_{22}	821 vs	817 vw dp	841
844 m	848 vw dp	866	ν_8	840 msh	837 vw p	839
B 828 821	819 vw p	770	ν_9	769 w	776 vw p?	770
A/C 786 777 ms 772	775 vw dp	793	ν_{23}	759 w	757 vw dp	793
C? 742 m	742 vw p	756	ν_{11}	584 m	586 mw p	578
	703 vw dp	714	ν_{24}	680 mw	698 vw dp	690
C? 651 vwsh	653 vs p	659	ν_{10}	C 667 mw	668 vs p	659
638 mw	634 vwsh dp	635	ν_{25}	530 m	536 w dp	523
505 w			$\nu_{14}+\nu_{13}$			
A 287	288 w p?	288	ν_{13}		286 w p?	286
270	262 mw dp?	261	ν_{26}		259 mw dp?	260
	218 mw dp?	218	ν_{14}		217 mw dp?	217

appear at 790, 750 and 705 cm^{-1}; presenting the same problem of identification as in this paper. More extensive data exist for Me_3SiX compounds [12–14] much of it accompanied by NCA [12, 13] and the consensus points to methyl rocks being assigned to bands observed at *ca.* 760 cm^{-1} and *a*″SiC stretches to bands around 710–690 cm^{-1}. The report on Me_3SiCl, which included data on $(CD_3)_3SiCl$ [12], studied the most likely assignments and concluded that the *a*″SiC stretches were at 695 and 705 cm^{-1} for the light and heavy molecules, respectively. This comparative data slightly favours assignment C and this is further supported by the fact that NCA calculations cannot calculate the large spread of frequencies (*ca.* 200 cm^{-1}) required for the methyl rocks in assignment B. Thus, it must be concluded that C represents the most likely set of assignments and this is used in Tables 4–7 for all the halides.

(iii) *The region below* 350 *cm*$^{-1}$

Each compound has three bands in this region, the CSiC deformation and the *a*′ and *a*″CSiX deformations. In Me_2SiH_2 the CSiC deformation has a value of 223 cm^{-1} [2], and the CSiX deformations in $MeSiH_2X$, where these are the only skeletal deformations possible, occur at frequencies of 176(I), 192(Br), 213(Cl) and 263 cm^{-1}(F) [10]. The lowest two bands in the Me_2SiHX compounds increase in wavenumber along the series I–Br–Cl more rapidly than does the highest, suggesting that motion of the halogen is involved. Conversely, ν_{13}, which is expected to be less sensitive to a change in substituent, is assigned to the band at *ca.* 250 cm^{-1} in the iodide, bromide and chloride. Further, on the basis of mass, it seems unlikely that in the iodide and bromide the two CSiX deformations should be at a higher wavenumber than the CSiC deformation and moreover, from the point of view of intensity, the *a*′CSiX deformation might also be expected to give rise to a stronger band than the CSiC band in the Raman effect. In the fluoride, the polarization data give no firm clues. The *a*″CSiX deformation increases in wavenumber more rapidly with lighter halogen substituent, than does its *a*′ mode so that they are nearly coincident in the chloride. Thus, the order of these two modes may be expected to be reversed in the fluoride. The assignment is made on the basis of the NCA, where for the preferred assignment, i.e. with the CSiC deformation at highest frequency, the force constants

Table 5. The vibrational spectra of the chlorodimethylsilanes

Me_2SiHCl			assignment	Me_2SiDCl		
i.r. (gas)	Raman (liq.)	calc.		i.r. (gas)	Raman (liq.)	calc.
2983 m	2977 mw dp	2975	ν_1, ν_{16}	2984 mw	2979 mw dp	2975
2974 m	2971 mw dp	2974	ν_2, ν_{17}	2974 mw	2970 mw dp	2974
2916 w	2909 vs p	2909	ν_3, ν_{18}	A? 2916 w	2908 vs p	2909
2821 vw			$2\times\delta_{Me}$		2842 vw p 2807 w p	
2519 vw					2502 vw p	
2176 vs	2173 s p	2181	ν_4	A/C 1591 1581 s 1572	1579 s p	1573
2041 vw			$\nu_{7,21}+\nu_{23}$			
1934 vw			$\nu_{7,21}+\nu_{10}$			
1815 vw 1765 vw			$2\times\rho_{Me}$	1624 vw		
1435 w	1427 w dp	1418	ν_5, ν_{19}	1429 w	1414 w dp	1418
1420 w	1402 w dp	1410	ν_6, ν_{20}	1419 w		1410
C 1267 s	1263 w p	1271	ν_7	C 1268 s	1263 w p	1254
B 1262 s	1258 vw dp	1257	ν_{21}	B 1263 s	1253 vw dp	1251
B 913 905? mssh	905 vw dp	909	ν_{22}	808 s	812 w dp	847
A 894? 885 vs 878	883 vw p?	873	ν_8	∿840 msh	844 vw p	839
C 845 s	843 vw p	817	ν_9	825 vsbr	822 w p	813
B 781 772 ms	776 w dp	792	ν_{23}	B 771 762 w	765 w dp	787
A 734 726 m 718	726 w p	729	ν_{11}	554 m	553 mw p?	554
	∿698 vw dp	707	ν_{24}	715 vw	705 vw dp	694
A 679 671 mw 663	670 s p	672	ν_{10}	A 688 680 ms 672	676 s p	676
636 w	633 w dp	644	ν_{25}	547 m	530 mw dp	522
507 s	489 s p	492	ν_{12}	505 ms	486 s p	484
	258 mw dp	255	ν_{13}		252 mw p	254
	209 m dp	208	ν_{14}		207 m dp	208
	207 m dp	205	ν_{26}		202 m dp	204

Table 6. The vibrational spectra of the bromodimethylsilanes

Me_2SiHBr				assign-ment	Me_2SiDBr		
i.r. (gas)	i.r. (liq.)	Raman (liq.)	calc.		i.r. (gas)	Raman (liq.)	calc.
2980 m	2978 msh	2977 mw dp	2973	ν_1,ν_{16}	2980 m	2977 mw dp	2973
2974 m	2968 m	2967 mw dp	2972	ν_2,ν_{17}	2974 m	2969 mw dp	2973
2914 w	2905 w	2906 vs p	2906	ν_3,ν_{18}	2913 w	2906 mw dp	2906
2814 vw				$2\times\delta Me$	2819 vw	2802 w p	
2176 s	2170 s	2173 s p	2182	ν_4	1581 s	1580 s p	1573
2036 vw				$+\nu_{23}$			
1971 vw				$\delta_s Me+\nu_{11}$			
1928 vw				$+\nu_{10}$	1938 vw		
1816 vw				$2\times\rho Me$	1624 vwsh	1618 wsh p	
1432 w	1428 w	1425 w dp	1417	ν_5,ν_{19}	1428 mw	1414 w dp	1417
∿1417 wbr	1398 w	1401 w dp	1410	ν_6,ν_{20}	∿1418 mw		1410
C 1266 ms	1257 vs	1260 w p	1283	ν_7	C 1266 s	1262 w p	1268
B 1261 ms		1252 vwshdp	1270	ν_{21}	B 1262	1252 vwshdp	1265
B 913 903 s	906 vs	905 w dp	861	ν_{22}	807 s sh	811 w dp	837
880 vs	872 vs	870 w p	900	ν_8	∿843 sh	847 vwsh p	826
852 A 846 ms 842	843 vs	842 vw dp?	778	ν_9	818 vsbr	821 w p	794
B 780 770 m	775 s	775 w dp	801	ν_{23}	B 772 764 w	767 w dp	770
718 A 711 m	711 s	710 mw p	706	ν_{11}	537 s	536 mw dp?	535
706			707	ν_{24}	710 w	706 w dp	699
671 A/B 665 mw 661	665 s	665 s p	668	ν_{10}	680 A/B 674 s 668	672 s p	672
637 w	635 m	635 w dp	624	ν_{25}	519 mwsh	524 m dp	505
		572 vw p		$\nu_{12}+\nu_{13}$			
402 m	389 vs	385 vs p	386	ν_{12}	397 m	382 vs p	380
	242 w	244 m dp	242	ν_{13}		240 mw dp	241
		194 ms dp?	194	ν_{14}		191 ms dp	194
		186 ms dp?	183	ν_{26}		183 ms dp	183

Table 7. The vibrational spectra of the iododimethylsilanes

Me_2SiHI				assign-	Me_2SiDI			
i.r. (gas)	i.r. (liq)*	Raman (liq)	calc.	ment	i.r. (gas)	i.r. (liq)	Raman (liq)	calc.
3136 w				$\nu_{1,16}+\nu_{13}$	3138 vw			
2987 msh	2977 m	2978 mw dp	2973	ν_1, ν_{16}	2988 wsh	*2976 m	2981 mw dp	2973
2974 m	2964 m	2965 mw dp	2972	ν_2, ν_{17}	2975 mw	*2964 mw	2967 mw dp	2972
2913 mw	2903 w	2903 s p	2903	ν_3, ν_{18}	2913 w	*2901 w	2902 s p	2903
2860 vw		2849 vw p						
2813 w	2793 vw	2796 vw p		$2\delta_a$Me	2814 vw		2799 w p	
2512 vw		2503 vw p		$2\delta_s$Me				
1811 w	1801 vw			2ρMe	1617 vw	†*1611 w	1612 wsh p	
2172 vs	2167 vs	2170 m p	2180	ν_4	1579 s	*1574 vs	1578 m p	1571
2136 wsh				$\nu_8+\nu_{22}$				
2034 vw	2030 vw			δ_sMe+ν_{23}	2028 vw			
1962 vw	1956 vw			ν_{11}				
1923 vw	1910 vw			ν_{10}	1929 vw	*1920 vw		
1430 w	1425 m	1424 w dp	1413	ν_5, ν_{19}	1417 wbr	*1420 ms	1411 w dp	1413
~1401 wbr	1397 m	1396 w dp	1408	ν_6, ν_{20}		*1405		1408
1356 vw				$\nu_{10}+\nu_{24}$		†1365 w		
1320 vw				$2\nu_{10}$		*1328 vw		
C 1264 s	1255 vs	1258 w p	1261	ν_7	C 1265 ms	*1254 vs	1257 w p	1254
B 1259		1253 wsh dp	1257	ν_{21}	B 1261		1253 wsh dp	1253
B 909 899 s	900 vs	902 vw dp	893	ν_{22}	806 s sh	†806 vs	808 vwshdp	840
872 vsbr	862 vs	862 w p	848	ν_8	845 s sh	†*843 vs		827
846 s sh	843 vs	843 vwsh	817	ν_9	822 vsbr	†819 vs	817 mw p	800
B 777 768 m	772 m	773 w dp	783	ν_{23}	B 772 763 w	*767 m	767 w dp	772
697 s	694 s	694 mw p	700	ν_{24}	708 wsh	*705 mw	706 vw dp	699
			711	ν_{11}	526 s	*522 ms	522 mw p	524
~710 wsh		668 wsh		$2\nu_{12}$	682 mwsh	†659 m	653 vwsh p?	
656 mw	655 m	656 mw p	652	ν_{10}	667 m	*671 s	662 m p	675
637 mw	634 m	634 wsh dp	643	ν_{25}	526 s	*522 ms	522 mw p	507
486 vw	~490 vwbr	490 vw p		$\nu_{12}+\nu_{26}$			488 vw p?	
		392 vvw		$\nu_{13}+\nu_{26}$				
~350 sh	335 s	337 vs p	336	ν_{12}	342	*329 m	327 vs p	327
	238 w	237 mw p	237	ν_{13}			236 mw p	236
		185 m p	184	ν_{14}			183 ms p	184
		167 sh dp	168	ν_{26}			166 msh dp	168

*Neat liquid.
†Cyclohexane solution.

Table 8. Force constant values for the series Me_2SiHX

		Me_2SiHF	Me_2SiHCl	Me_2SiHBr	Me_2SiHI	
1	f CH	477.30	476.35	475.76	475.31	f CH
2	f SiH	271.37	272.46	272.67	272.02	f SiH
3	f SiC	277.96	272.51	278.39	273.57	f SiC
4	f SiX	482.00	241.54	183.19	129.28	f SiX
5	f HCH	47.90	49.46	50.46	49.68	f HCH
6	f HCSi$^{\perp}$	34.19	35.00	34.88	39.76	f HCSi
7	f HCSi$^{\parallel}$	54.35	51.22	48.84	47.23	f HCSi
8	f CSiH	57.50	56.32	54.49	52.68	f CSiH
9	f HSiX	59.67	56.10	53.90	44.43	f HSiX
10	f CSiC	90.66	69.37	61.61	57.81	f CSiC
11	f CSiX	46.62	57.95	61.65	72.36	f CSiX
12	f CH/CH	5.56	5.63	5.48	5.13	f CH/CH
13	f SiC/SiC	25.02	15.13	15.50	19.85	f SiC/SiC
14	f HCH/HCH	-3.98	-2.44	-1.27	-1.80	f HCH/HCH
15	f HCSi$^{\parallel}$/HCSi$^{\perp}$	-1.97	-3.13	-1.99	-0.33	f HCSi /HCSi
16	f HCSi$^{\parallel}$/HCSi$^{\parallel}$	11.19	9.50	9.50	7.75	f HCSi /HCSi
17	f CSiH/CSiH	2.60	0.90	1.45	3.42	f CSiH/CSiH
18	f CSiX/CSiX	-15.30	-3.83	2.86	14.70	f CSiX/CSiX
19	f c-HCSi/CSiH	-11.61	-13.36	-13.57	-10.69	f c-HCSi/CSiH
20	f t-HCSi/CSiH	-0.80	-2.60	-1.20	-0.07	f t-HCSi/CSiH
21	f CSiH/HSiX	3.26	2.70	3.01	0.85	f CSiH/HSiX
22	f SiC/CSiH	26.33	21.79	20.37	3.29	f SiC/CSiH
23	f SiX/HSiX	9.66	12.90	12.34	5.19	f SiX/HSiX
24	f SiX/CSiX	-	-	4.68	4.91	f SiX/CSiX
25	f SiC/SiX	12.70	-	-	-	f SiC/SiX
26	f SiC/HCSi	17.00*	17.00*	17.00*	17.00*	f SiC/HCSi

*Fixed. Units: Nm^{-1} for stretching and $Nm\,rad^{-2}$ for bending force constants.

Table 9. Frequencies (cm^{-1}) and approximate description of the fundamental modes for halodimethylsilanes

		$Me_2SiH'F$		$Me_2SiH'Cl$		$Me_2SiH'Br$		$Me_2SiH'I$	
H' =		H	D	H	D	H	D	H	D
CH_3 str.	a	2974	2975	2977	2979	2977	2977	2978	2981
	a	2974	2975	2971	2970	2967	2969	2965	2967
	s	2912	2910	2909	2908	2906	2906	2903	2902
SiH' str.		2166	1578	2173	1579	2173	1580	2170	1578
CH_3 def.	a	1430	1415	1427	1414	1425	1414	1424	1411
	a	1404	1409	1402	1414	1401	1414	1396	1411
	s	1262	1262	1263	1263	1260	1262	1258	1257
	s	1262	1262	1258	1253	1252	1252	1253	1253
CH_3 rock	a	917	817	905	812	905	811	902	808
	s	848	837	883	844	870	847	862	843
	s	819	776	843	822	842	821	843	817
	a	775	757	776	765	775	767	773	767
SiC_2 str.	a	703	698	698	705	~ 710	706	694	706
	s	653	668	670	676	665	672	656	662
SiH' def.	s	742	586	726	553	710	536	694	522
	a	634	536	633	530	635	524	634	522
SiX str.		917	889	489	486	385	382	337	327
CSiC def.		288	286	258	252	244	240	237	236
CSiX def.	s	218	217	209	207	194	191	185	183
	a	262	259	207	202	186	183	167	166

*f*CSiC, *f*CSiF and *f*CSiF/CSiF all continue general trends found for the other compounds (Table 8). The value of *f*CSiF is found to be only a little lower than that in CH_3SiH_2F[10] and CH_3SiF_3 [15] and like the value of *f*CSiF/CSiF in the latter compound, the interaction term is large (approximately 1/3 of *f*CSiF) and negative. If the observation of an A-type band in the i.r. spectrum of Me_2SiHF in the CsI region is taken as proof that the highest frequency in this region is an *a'* mode, then placing the two CSiF deformations above the CSiC mode, as did DURIG and HAWLEY [1], calls for a reversal of the expected ordering of the two CSiF modes, and changes in the force constant values which then deviate significantly from those in the other compounds.

The frequencies for the preferred assignments are listed in Table 9*, where it can be seen that the frequencies follow smooth trends, except for some of the methyl rocks in the fluoride which are lower than might be expected. Thus, ν_{25}, the asymmetric SiH bend, dependent on a CSiH angle deformation, remains fairly constant, while ν_{11}, the *a'*SiH bend, reflecting changes in both CSiH and HSiX angles, increases with lighter halogen substituent. Thus, we believe that, given the possible alternative assignments, we have identified the most likely set.

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*Compare with Table 7 in Ref. [1].