Silanes. Vibrational Assignments and Frequency Correlations

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Silanes have received widespread attention during the last decade and are of continuing current interest[1-4]. As part of a program in this laboratory on the vibrational spectra, molecular structure, and thermodynamic properties of this class of compounds, a review of the widely scattered results was undertaken to assess the status of our information. It became apparent in the course of this review that a need existed for a critical evaluation of the vibrational assignments, and for the interpretation of the normal frequencies on a series of simplified vibrational modes. This communication reports the results thus obtained, together with a useful table of generalized characteristic frequencies and bond distances based on this work.

Status

Information for about one hundred silanes, widely scattered in the published literature, was reviewed relative to the subjects: frequency assignment (FA), infrared spectra (IR), Raman spectra (R) molecular structure (M), thermodynamic properties (T), normal coordinate vibrational analyses (NC) and force constants (FC). For reference and guidance, the status of knowledge is presented in summary form in Table I.

Vibrational Spectra

Relative to the vibrations associated with the silicon atom and the surrounding four atoms attached with tetrahedral angles, all of the silanes considered can be classified into three groups based on the symmetry of molecule; SiX_4, $SiXY_3$ and SiX_2Y_2. The designation of normal vibrations, symmetry class and selection rules for each type of molecules are shown in Table II, where the symbols ν, δ and τ denote stretching, deformation and twisting vibrations, respectively, and the suffixes a, e, f and b denote the class of symmetry group to which the vibration belongs. The simplified vibrational modes for each type of molecule are illustrated in Figs. 1—3. It is recognized that the exact feature of the normal mode differs from molecule to molecule depending on the masses of atoms and the force constants of the bonds, and can be calculated by the normal

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TABLE I. STATUS OF KNOWLEDGE FOR SILANES

Silane	FA	IR	R	M	T	NC	FC	Ref.
SiH_4	×	×	×	×	×	×	×	7—17
H_2SiD_2	×	×			×			17, 18
$HSiD_3$	×	×		×	×			17—20
SiD_4	×	×			×			17—19
$H_3Si(CH_3)$	×	×		×		×	×	3, 21—23
$H_2Si(CH_3)_2$	×	×	×			×	×	21—25
$HSi(CH_3)_3$	×	×	×	×		×	×	21—23
$Si(CH_3)_4$	×	×	×	×	×	×	×	16, 17, 26—40
$H_3SiCH{=}CH_2$	×	×						21
$H_3SiC_2H_5$		×						21
$H_2Si(C_2H_5)_2$		×						21, 41
$HSi(C_2H_5)_3$		×						21
$Si(C_2H_5)_4$	×	×	×					21, 42, 43
$H_nSi(C_3H_7)_{4-n}$*		×						41, 44, 45
$Si(CH_2CH{=}CH_2)_4$		×						46
$H_3Si(C_4H_9)$		×						21, 45
$H_2Si(C_4H_9)_2$		×						41
$H_2Si(C_5H_{11})_2$		×						45
$H_3Si(C_6H_5)$		×						3, 73
$H_2Si(C_6H_5)_2$	×	×	×					41, 73
$HSi(C_6H_5)_3$		×						44, 73
$Si(C_6H_5)_4$				×				47
$D_3Si(C_6H_5)$		×						3
$DSi(C_6H_5)_3$		×						44
$H_3SiC_6H_{11}$		×						45
$H_2Si(C_6H_{11})_2$		×						41
$H_3SiC_{10}H_9$		×						45
$(CH_3)_nSi(C_2H_5)_{4-n}$*			×					35
$(CH_3)_2Si(C_3H_7)_2$		×						21
$(CH_3)_3Si(C_6H_5)$		×	×					48
$Si(OCH_3)_4$	×	×	×				×	49—53
$Si(OC_2H_5)_4$	×	×	×					49, 51, 54
$Si(OC_3H_7)_4$		×	×					49
$R_3Si(OR')$**	×	×	×					55
$R_2Si(OR')_2$**	×	×	×					55, 56, 115
$RSi(OR')_3$**	×	×	×			×		55, 56, 109
SiF_4	×	×	×	×	×	×	×	16, 17, 57—62
H_3SiF	×	×		×	×		×	17, 63—65
H_2SiF_2	×	×			×			17, 66, 67
$HSiF_3$	×	×		×	×			17, 65—68
D_3SiF	×	×		×	×			17, 64, 65, 67, 69
D_2SiF_2	×	×			×			17, 66
$DSiF_3$	×	×			×			17, 66, 67
$(CH_3)_3SiF$	×	×	×	×				70, 71
$(CH_3)_2SiF_2$	×	×	×					25
$(CH_3)SiF_3$	×	×	×	×	×		×	17, 65, 72
CH_3SiH_2F	×	×						24
$(C_6H_5)_nSiF_{4-n}$*	×	×	×					73
$SiCl_4$	×	×	×	×	×	×	×	5, 6, 14, 16, 17, 26—28, 52, 61, 62, 74, 79
H_3SiCl	×	×		×	×			14, 17, 75—78, 111
H_2SiCl_2	×	×	×	×	×			3, 17, 24, 42, 80, 81, 85
$HSiCl_3$	×	×	×	×	×	×	×	17, 19, 82—87
D_3SiCl	×	×		×				67, 69

TABLE I. (Countinued)

Silane	FA	IR	R	M	T	NC	FC	Ref.
$(CH_3)_3SiCl$	×	×	×	×	×	×	×	5, 17, 26—28, 43, 71, 83, 91, 93—95
$(CH_3)_2SiCl_2$	×	×	×	×	×	×	×	5, 17, 25—28, 43, 89, 92
$(CH_3)SiCl_3$	×	×	×	×	×	×	×	5, 17, 26—28, 43, 83, 88—91
$CH_2=CHSiCl_3$	×	×						97
$(C_2H_5)_3SiCl$	×		×					42, 43
$(C_2H_5)_2SiCl_2$	×		×					42, 43
$(C_2H_5)SiCl_3$	×	×	×					42, 43, 51
$(CH_2=CH-CH_2)_nSiCl_{n-4}$*		×						46
$(C_3H_7)SiCl_3$		×						51
$(C_4H_9)SiCl_3$		×						51
$(C_{10}H_7)SiCl_3$		×						96
$(C_6H_5)_nSiCl_{4-n}$*	×	×	×					73
CH_3SiCl_2H	×		×					43
$C_2H_5SiCl_2H$	×		×					43
$(CH_3O)_nSiCl_{4-n}$*	×	×	×					50, 52, 55, 113
$(C_2H_5O)_nSiCl_{4-n}$*	×		×					54, 114
$SiBr_4$	×		×	×	×	×	×	5, 12, 16, 17, 29, 74, 98
H_3SiBr	×		×	×	×	×	×	12, 13, 17, 63, 100, 101
H_2SiBr_2	×	×	×		×	×	×	13, 17, 80, 100, 102
$HSiBr_3$	×		×	×	×	×	×	12, 13, 17, 98, 102, 103
$(CH_3)_3SiBr$	×		×	×				29, 95, 104
$(CH_3)_2SiBr_2$	×	×	×	×				25, 29, 104
$(CH_3)SiBr_3$	×		×	×				29, 104
SiI_4	×		×	×	×	×	×	6, 17, 74, 105
H_3SiI	×	×		×			×	106—108
H_2SiI_2		×						24, 106
D_3SiI	×	×					×	108
$(CH_3)_3SiI$	×		×	×				95, 110
F_3SiCl				×				26, 65
F_3SiBr				×				65
F_2SiBr_2				×				65, 98
Cl_nSiBr_{n-4}*	×	×	×	×	×	×	×	6, 17, 74, 99, 111
Cl_3SiI	×		×		×	×	×	6, 17, 74
Cl_2SiI_2	×		×			×	×	6, 74
$ClSiI_3$	×		×		×	×	×	6, 17, 74
$(CH_3)_3SiOH$	×	×	×					71, 112
$(C_6H_5)_nSi(OH)_{4-n}$*	×	×	×					73
$(CH_3)_3SiSH$	×	×	×					71

* $n=1, 2, 3$ ** R, R′=CH_3 or C_2H_5

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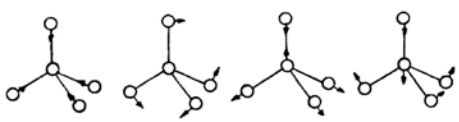
TABLE II. DESIGNATION OF NORMAL VIBRATIONS, SYMMETRY CLASS AND SELECTION RULES

Type of molecule	Symmetry class	Designation	Activity		Interpretation
			Raman	Infrared	
SiX_4	A_1	$\nu_a(SiX_4)$	p*1	i*3	Symmetrical stretching
	E	$\delta_e(SiX_4)$	d*2	i	The 1st kind of deformation
	F_2	$\nu_f(SiX_4)$	d	a*4	Asymmetrical stretching
	F_2	$\delta_f(SiX_4)$	d	a	The 2nd kind of deformation
$SiXY_3$	A	$\nu_a(SiX)$	p	a	Stretching vibration
	A	$\nu_a(SiY_3)$	p	a	Symmetrical stretching
	A	$\delta_a(SiY_3)$	p	a	The 2nd kind of deformation
	E	$\nu_e(SiY_3)$	d	a	Asymmetrical stretching
	E	$\delta_e(SiY_3)$	d	a	The 1st kind of deformation
	E	$\delta_e(SiXY_3)$	d	a	Bending of SiX or wagging of SiY_3
SiX_2Y_2	A_1	$\nu_a(SiX_2)$	p	a	Symmetrical stretching
	A_1	$\nu_a(SiY_2)$	p	a	Symmetrical stretching
	A_1	$\delta_a(SiX_2)$	p	a	The 1st kind of deformation
	A_1	$\delta_a(SiY_2)$	p	a	The 1st kind of deformation
	A_2	$\tau(SiX_2Y_2)$	d	i	Twisting
	B_1	$\nu_b(SiX_2)$	d	a	Asymmetrical stretching
	B_1	$\delta_b(SiX_2Y_2)$	d	a	Rocking of SiX_2 or wagging of SiY_2
	B_2	$\nu_b(SiY_2)$	d	a	Asymmetrical stretching
	B_2	$\delta_b(SiY_2X_2)$	d	a	Rocking of SiY_2 or wagging of SiX_2

*1 polarized *2 depolarized *3 inactive *4 active

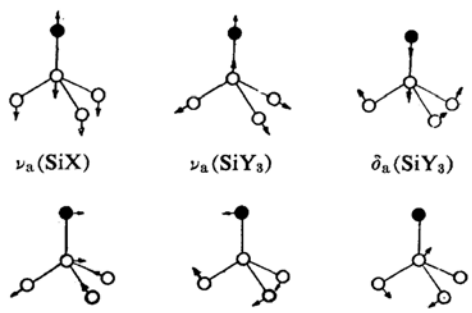
coordinate treatment for the individual molecule.

$\nu_a(SiX_4)$ in SiX_4, $\nu_a(SiX_3)$ in SiX_3Y, $\nu_a(SiX_2)$ in SiX_2Y_2 and $\nu_a(SiX)$ in $SiXY_3$ are interpreted as symmetrical stretching vibrations of Si–X in which X atoms vibrate in phase back and forth in the direction of the bonds. $\nu_f(SiX_4)$ in SiX_4, $\nu_e(SiX_3)$ in SiX_3Y and $\nu_b(SiX_2)$ in SiX_2Y_2 are interpreted as asymmetrical stretching vibrations of Si–X in which X atoms vibrate out of phase in the direction of the bonds. The deformation vibrations $\delta_e(SiX_4)$ in SiX_4, $\delta_e(SiX_3)$ in SiX_3Y and $\delta_a(SiX_2)$ in SiX_2Y_2 make one group called the first kind of deformation vibrations. This kind produces the change in the angle between the two adjacent bonds. The second kind of deformation vibrations which inculdes $\delta_f(SiX_4)$ in SiX_4 and $\delta_a(SiX_3)$ in SiX_3Y is a symmetrical deformation vibration with respect to the threefold axes. As for $\delta_e(SiXY_3)$, two alternative ways for interpretation are possible. If X is a lighter atom than Y, $\delta_e(SiXY_3)$ should be interpreted as a bending of X, whereas, in the opposite case it should be interpreted as a wagging of Y_3. $\delta_b(SiX_2Y_2)$ may be interpreted either as a wagging vibration in which



$\nu_a(SiX_4)$ $\delta_e(SiX_4)$ $\nu_f(SiX_4)$ $\delta_f(SiX_4)$

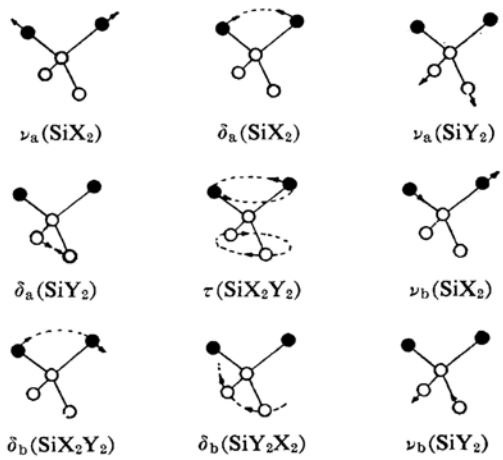
Fig. 1. Normal vibrations of SiX_4.



$\nu_a(SiX)$ $\nu_a(SiY_3)$ $\delta_a(SiY_3)$

$\nu_e(SiY_3)$ $\delta_e(SiXY_3)$ $\delta_e(SiY_3)$

Fig. 2. Normal vibrations of $SiXY_3$.



$\nu_a(SiX_2)$ $\delta_a(SiX_2)$ $\nu_a(SiY_2)$

$\delta_a(SiY_2)$ $\tau(SiX_2Y_2)$ $\nu_b(SiX_2)$

$\delta_b(SiX_2Y_2)$ $\delta_b(SiY_2X_2)$ $\nu_b(SiY_2)$

Fig. 3. Normal vibrations of SiX_2Y_2.

two X atoms swing as a unit in SiX_2 plane or as a rocking vibration in which two Y atoms swing back and forth parallel to the same plane. The situation is the same for $\delta_b(SiY_2X_2)$ if X is replaced by Y and vice versa. $\tau(SiX_2Y_2)$ is interpreted as a twisting vibration of SiX_2 in respect to SiY_2. This vibration depends upon the nature of the X atom as well as of the Y atom.

All of the published data are tabulated in Tables III—V in accordance with the above designations. Some values are from Raman spectra of the liquid state and some from infrared spectra of the liquid or gaseous states. In most instances, the differences in the frequencies reported with the different methods or by various investigators were not sufficiently

TABLE III. NORMAL FREQUENCIES OF SiX_4 TYPE MOLECULES

SiX_4	$\nu_a(SiX_4)$	$\delta_e(SiX_4)$	$\nu_f(SiX_4)$	$\delta_f(SiX_4)$
SiH_4	2187	974.6	2190.6	914.2
SiD_4	(1582)[c]	(689)[c]	1597	681
SiF_4	800	268	1031	391
$SiCl_4$	424	150	610	221
$SiBr_4$	249	90	487	137
SiI_4	168	63	405	94
$Si(CH_3)_4$	598	202	696	239
$Si(C_2H_5)_4$	553	160	736	303
$Si(OCH_3)_4$	640	251	844	308
$Si(OC_2H_5)_4$	654	240	792	305

c: Calculated value

TABLE IV. NORMAL FREQUENCIES OF $SiXY_3$ TYPE MOLECULES

$SiXY_3$	$\nu_a(SiX)$	$\nu_a(SiY_3)$	$\delta_a(SiY_3)$	$\nu_e(SiY_3)$	$\delta_e(SiY_3)$	$\delta_e(SiXY_3)$
$SiHD_3$	2182	1573	683	1598	683	851
$SiHF_3$	2314.5	858.6	425.2	998.6	305.5	844.5
$SiHCl_3$	2274	497	250	600	179	810
$SiHBr_3$	2234	360	168	470	113	767
$SiDF_3$	1688	854	421.9	994.4	302.2	628.5
$SiFH_3$	872.0	2206	989.7	2196	943.4	728.1
$SiFD_3$	888	1577	704	1615	(764)[c]	549
$SiClH_3$	551	2201	949	2195	954.4	664.0
$SiClD_3$	538	1581	702	1616	(734)[c]	488
$SiClBr_3$	583	291	173	489	102	159
$SiClI_3$	557	220	114	411	73	134
$SiH(CH_3)_3$	2118	625	219	718	251	908
$SiF(CH_3)_3$	898	620	206	695	259	290
$SiCl(CH_3)_3$	487	640	242	700	188	330
$SiCl(C_2H_5)_3$	464	592	221	739	160	295
$SiCl(OCH_3)_3$	510	717	264	845	—	357 ?
$SiCl(OC_2H_5)_3$	520	695	290	799	—	—
$SiBrH_3$	430	2200	930	2196	950.4	632.6
$SiIH_3$	362	2192	903	2206	941	592
$SiID_3$	352	1575	664	1607	—	435
$SiBrCl_3$	368	545	191	610	205	135
$SiICl_3$	333	519	169	600	197	123
$SiBr(CH_3)_3$	373	632	238	704	177	214
$SiI(CH_3)_3$	331	627	231	704	164	198
$Si(CH_3)H_3$	700	2167	940	2167	980	540
$Si(CH_3)F_3$	700	900	390	982	332	229
$Si(CH_3)Cl_3$	764	458	229	577	163	229
$Si(CH_3)Br_3$	746	314	153	453	98	186
$Si(C_2H_5)Cl_3$	715	447	187	580	152	224
$Si(OCH_3)Cl_3$	808	450	226	602	170	295
$Si(OC_2H_5)Cl_3$	775	475	215	603	171	249

C: calculated value

great to be of concern relative to the problem of the characteristic frequencies for the molecules. The assignments in the literature were, in large part, without ambiguity for most of the silanes in Tables III—V. Some new assignment are proposed in the light of the correlation rule developed in this work. For $Si(CH_3)_3Cl$, 188 cm^{-1} should be assigned to $\delta_e(SiC_3)$ because the first kind of deformation vibration of Si–C usually appears near 200 cm^{-1}; and $\delta_e(SiC_3)$ should lie at a lower frequency than $\delta_a(SiC_3)$ as in the case of ethyl chlorosilanes. For $Si(CH_3)_2Cl_2$, 241 cm^{-1} should be assigned to $\delta_b(SiC_2Cl_2)$, which belongs to B_1

Table V. Normal frequencies of SiX_2Y_2 type molecules

SiX_2Y_2	$\nu_a(SiX_2)$	$\nu_a(SiY_2)$	$\delta_a(SiX_2)$	$\delta_a(SiY_2)$	$\nu_b(SiX_2)$	$\nu_b(SiY_2)$	$\delta_b(SiX_2Y_2)$	$\delta_b(SiY_2X_2)$	$\tau(SiX_2Y_2)$
SiH_2D_2	2189	1587	944	682.5	2183	1601	743	862	(844)[c]
SiH_2F_2	2245	870	984.8	321.7	2250	(978)[c]	728.2	(905)[c]	(785)[c]
SiH_2Cl_2	2200	531	953	188	2200	592	610	877	710
SiH_2Br_2	2206	393	925	122	2232	456	556	828	688
$SiH_2(CH_3)_2$	2143	954	658	228	2165	732	875	472	703
SiD_2F_2	1614	878.5	708	319	1619	950	579.2	680.2	(563)[c]
$SiCl_2Br_2$	563	326	191	111	605	508	144	182	122
$SiCl_2I_2$	538	276	160	83	589	418	—	149	111
$Si(CH_3)_2F_2$	670	828	213	330	786	952	271	496	213
$Si(CH_3)_2Cl_2$	688	473	232	168	805	553	241	298	177
$Si(C_2H_5)_2Cl_2$	695	458	190	157	746	650 ?	241	299	—
$Si(OCH_3)_2Cl_2$	772	481	250	183	851	590	315	364	—
$Si(OC_2H_5)_2Cl_2$	744	490	240	—	813	598	295	—	—
$Si(CH_3)_2Br_2$	682	355	208	118	797	426	208	208	166

c: Calculated value

Table VI. Characteristic frequencies for silanes

		Number of data
Si–H		
Stretching		
a) symm.	2118~2315 cm^{-1}	16
b) asymm.	2142~2250 cm^{-1}	11
Deformation		
a) 1st kind	925~ 985 cm^{-1}	11
b) 2nd kind	903~ 990 cm^{-1}	6
Si–D		
Stretching		
a) symm.	1573~1688 cm^{-1}	8
b) asymm.	1597~1649 cm^{-1}	7
Deformation		
a) 1st kind	683~ 708 cm^{-1}	6
b) 2nd kind	664~ 704 cm^{-1}	5
Si–C		
Stretching		
a) symm.	553~ 764 cm^{-1}	18
b) asymm.	695~ 805 cm^{-1}	13
Deformation		
a) 1st kind	160~ 232 cm^{-1}	12
b) 2nd kind	221~ 303 cm^{-1}	8
Si–O		
Stretching		
a) symm.	640~ 808 cm^{-1}	8
b) asymm.	782~ 851 cm^{-1}	6
Deformation		
a) 1st kind	240~ 251 cm^{-1}	4
b) 2nd kind	264~ 308 cm^{-1}	4
Si–F		
Stretching		
a) symm.	800~ 900 cm^{-1}	10
b) asymm.	950~1031 cm^{-1}	7
Deformation		
a) 1st kind	268~ 332 cm^{-1}	7
b) 2nd kind	390~ 425 cm^{-1}	4
Si–Cl		
Stretching		
a) symm.	424~ 583 cm^{-1}	23
b) asymm.	577~ 610 cm^{-1}	15
Deformation		
a) 1st kind	150~ 205 cm^{-1}	15
b) 2nd kind	169~ 250 cm^{-1}	8
Si–Br		
Stretching		
a) symm.	249~ 373 cm^{-1}	10
b) asymm.	426~ 507 cm^{-1}	7
Deformation		
a) 1st kind	90~ 118 cm^{-1}	7
b) 2nd kind	137~ 173 cm^{-1}	4
Si–I		
Stretching		
a) symm.	168~ 362 cm^{-1}	7
b) asymm.	405~ 418 cm^{-1}	3
Deformation		
a) 1st kind	63~ 83 cm^{-1}	3
b) 2nd kind	94~ 114 cm^{-1}	2

TABLE VII. BOND LENGTHS

(a) SiX_4

	SiH_4	SiD_4	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4	$Si(CH_3)_4$
Si-X(Å)	1.48	1.48	1.54	2.02	2.15	2.46	1.90

(b) SiX_3Y

	SiH_3F	SiF_3H	SiD_3F	SiF_3D	SiH_3Br	$SiBr_3H$	$SiHCl_3$	$SiCl_3H$
Si-X	1.48	1.56	1.48	1.56	1.48	2.16	1.48	2.02
Si-Y	1.59	1.48	1.59	1.48	2.21	1.48	2.05	1.48
	$SiCl_3Br$	$SiBr_3Cl$	SiD_3H	$SiF_3(CH_3)$	$SiCl_3I$	SiI_3Cl	$Si(CH_3)_3Cl$	$SiCl_3(CH_3)$
Si-X	2.02	2.15	1.48	1.55	2.02	2.46	1.87	2.02
Si-Y	2.15	2.02	1.48	1.88	2.46	2.02	2.03	1.88

(c) SiX_2Y_2

	SiH_2F_2	SiD_2F_2	SiH_2Br_2	SiH_2Cl_2	$SiCl_2Br_2$	SiH_2D_2	$Si(CH_3)_2Cl_2$
Si-X	1.48	1.48	1.48	1.48	2.02	1.48	1.87
Si-Y	1.59	1.59	2.21	2.05	2.15	1.48	2.03

and 298 cm^{-1} to $\delta_b(SiCl_2C_2)$, which belongs to B_2. This assignment is justified from the result of the normal coordinate treatment in which 245 cm^{-1} and 304 cm^{-1} were calculated[5] for $\delta_b(SiC_2Cl_2)$ and $\delta_b(SiCl_2C_2)$, respectively. For the antisymmetrical stretching vibration of Si-I in $SiCl_2I_2$ two Raman lines 418 cm^{-1} and 346 cm^{-1} are reported by Dewaulle[6]. 418 cm^{-1} should be assigned to $\nu_b(SiI_2)$ but 436 cm^{-1} is preferably assigned as a combination, $276+160=436$ cm^{-1}.

Discussion of Characteristic Frequency Assignments

The survey of the normal frequencies listed in Tables III—V shows that symmetrical stretching vibrations, or $\nu_a(SiX_4)$ in SiX_4, $\nu_a(SiX_3)$ in SiX_3Y, $\nu_a(SiX_2)$ in SiX_2Y_2 and $\nu_a(SiX)$ in $SiXY_3$ appear in a narrow frequency range characteristic for the Si-X. In Table VI the characteristic frequencies ranges and the number of the data from which the ranges have been decided are tabulated. The generalized values of the bond lengths, similarly from this review, are listed in Table VII. More detailed inspection shows the correlation: $\nu_a(SiX_4) < \nu_a(SiX_3) < \nu_a(SiX_2) < \nu_a(SiX)$, where X represents C, O, F, Cl, Br and I. Since the Raman line due to this vibration is generally a sharp, strong, and polarized line, this frequecy may be used as a key frequency for the S-X symmetrical stretching mode.

The asymmetrical stretching vibrations: $\nu_f(SiX_4)$ in SiX_4, $\nu_e(SiX_3)$ in SiX_3Y, and $\nu_b(SiX_2)$ in SiX_2Y_2, also occur in a narrow range, characteristic for Si-X. These occur, without exception, in a higher frequency range than the corresponding symmetrical stretching vibrations. Since the infrared band due to this vibration is very strong, this may be used as a key band for Si-X if it lies in a region available for infrared measurements.

If the term "deformation vibration" defines the type of nomal vibration in which some of the atoms vibrate in the direction perpendicular to bands then all the other types of vibrations are included in this category. Among these, the first and the second kind of deformation vibrations may be expected as characteristic frequencies, since these fall in a rather narrow range as defined by the bonds concerned. These are included in Table VI. For Si-H or Si-D, the ranges for the first kind and the second kind of deformation vibrations overlap each other. For the rest, in most of the cases, the second kind of deformation occurs at a higher frequency range than the first kind.

The other types of vibrations such as $\delta_e(SiXY_3)$, $\delta_b(SiX_2Y_2)$ and $\tau(SiX_2Y_2)$ are generally found as broad frequency ranges so that it is difficult to assign a characteristic frequency. However, if one or more hydrogens are present, the modes: $\delta_e(SiHX_3)$, $\delta_e(SiH_3X)$, $\delta_b(SiH_2X_2)$, $\delta_b(SiX_2H_2)$ and $\tau(SiH_2X_2)$ could be characteristic, each for their own structure since the mass of the hydrogen is so very small, relative to the rest of the system.

Generally, as the mass of the atom attached to the silicon atom increases, there is a corresponding decrease in frequency for both the stretching and deformation vibrations. The effect of electronegativity on the frequency of a particular vibration is, however, striking. Thus, for example, the symmetric stretching vibrations of Si-F occcur in a higher frequency range than those of Si-C even though the atomic weight of fluorine is greater than that of carbon.

Si-H.—The symmetrical stretching vibration

of Si–H appears in the range 2118~2315 cm^{-1}. If the molecule has more than two Si–H bonds, the asymmetrical stretching vibration is also observed in the range 2142~2250 cm^{-1} in addition to the symmetrical vibration. The asymmetrical mode falls, as expected, in a higher range than the symmetrical mode. The general correlation: $\nu_a(SiH_3X) < \nu_a(SiH_2X_2) < \nu_a(SiHX_3)$ is true for all of the halogenated silanes. It is striking that in the series of methyl silanes the Si–H symmetric stretching frequencies decrease appreciably as the number of methyl groups increases.

Relative to the deformation vibration, both the first and the second kinds of deformations appear in an almost identical frequency range, 903~990 cm^{-1}. The separation is rather small and, in most of the cases, the higher frequency is assigned to the first kind of deformation.

Since the mass of the hydrogen atom is very small compared with the others, vibrations such as $\delta_e(SiX_3H)$, $\delta_e(SiH_3X)$, $\delta_b(SiH_2X_2)$, $\delta_b(SiX_2H_2)$ and $\tau(SiH_2X_2)$ may be considered as the hydrogen bending or deformation vibrations. Although examples for these modes are very limited at present, it is apparent that these are to be found in the following ranges:

$\delta_e(SiX_3H)$	767~908 cm^{-1}	(5 examples)
$\delta_e(SiH_3X)$	540~728 cm^{-1}	(5 examples)
$\delta_b(SiH_2X_2)$	469~919 cm^{-1}	(5 examples)
$\delta_b(SiX_2H_2)$	828~919 cm^{-1}	(5 examples)
$\tau(SiH_2X_2)$	688~844 cm^{-1}	(5 examples)

Si–D.—Eight deuterated silanes were used in assigning the frequency range of the Si–D vibration. Although deuterium has twice the atomic weight of hydrogen, the Si–D vibration can still be regarded as that of a very light atom vibrating against an atom of infinite mass. Thus many features of this class resemble the case of Si–H.

The symmetrical stretching vibrations occur in the range of 1573~1688 cm^{-1} while the asymmetrical stretching vibrations occur in the region 1597~1649 cm^{-1}. The higher frequencies are always assigned to the non-symmetrical vibrations. It is striking that the stretching vibration of Si–D in $SiDF_3$ has very high frequency (1688 cm^{-1}) compared with the stretching vibration of Si–D in the other compounds. This is the same as in the case of $SiHF_3$, where $\nu_a(SiH)$ was assigned to 2314.5 cm^{-1}, which seems an extraordinarily high value for the stretching vibration of Si–H.

The Si–D deformation vibrations, both the first kind and the second kind, occur in the frequency range 664~708 cm^{-1}, and higher frequencies are assigned to the second kind of deformation.

Si–C.—The Si–C symmetrical stretching vibrations occur in the frequency range of 553~764 cm^{-1} while the asymmetrical stretching vibrations occur in the range of 695~805 cm^{-1}. The tendency of the frequency shift depending on the number of the carbon atoms attached to the silicon atom is apparent, i. e., $\nu_a(SiC_4) < \nu_a(SiC_3) < \nu_a(SiC_2) < \nu_a(SiC)$. For the asymmetrical stretching vibrations, the relation, $\nu_f(SiC_4) < \nu_e(SiC_3) < \nu_e(SiC_2)$ is also true, if a particular series, such as $Si(CH_3)_4-Si(CH_3)_3Cl-Si(CH_3)_2Cl_2$, is considered. The deformation vibrations occur in the frequency range 160~259 cm^{-1} for the first kind, and 206~303 cm^{-1} for the second kind. The latter appaears, without exception, in a higher frequency range than the former.

Si–O–C.—The Si–O symmetrical stretching vibrations in the linkage of Si–O–C occur in the frequency range of 640~808 cm^{-1}, while the asymmetrical stretching vibrations occur in the range of 792~851 cm^{-1}. The frequencies of the symmetrical stretching vibrations decrease as the number of methoxy or ethoxy groups attached to the silicon atom increases, i. e.: $\nu_a(SiO_4) < \nu_a(SiO_3) < \nu_a(SiO_2) < \nu_a(SiO)$. The asymmetric vibration frequencies are concentrated in a rather narrow range, and the correlation $\nu_f(SiO_4) < \nu_e(SiO_3) < \nu_e(SiO_2)$ is true for any series, such as: $Si(OCH_3)_4-Si(OCH_3)_3Cl-Si(OCH_3)_2Cl_2$.

Owing to the very limited data, the frequency range for the deformation vibrations can not be decided with any certainty. From the available information, it appears that the first and second kinds of deformation vibrations occur in the range 240~308 cm^{-1}.

Si–Halogen.—The Si–halogen stretching modes occur in the range of 168~1031 cm^{-1}. The broad frequency range is due to the large variations in atomic weights for the halogen atoms, i. e.: F=19.00 to I=126.9. As the atomic weight of the atom attached to the silicon atom increases, a corresponding decrease in the frequency of the symmetrical and asymmetrical Si–X stretching vibrations is observed. For example, in the SiX_4 series, the Si–X stretching frequency decreases in the order: 800~424–249~168 cm^{-1}, for SiF_4, $SiCl_4$, $SiBr_4$ and SiI_4 respectively. In any series of the type SiX_4–SiX_3Y–SiX_2Y_2–$SiXY_3$, where X is a halogen atom and Y is different or a non-halogen atom, the frequencies of the symmetrical stretching vibration, i. e., $\nu_a(SiX_4)$, $\nu_a(SiX_3)$, $\nu_a(SiX_2)$, $\nu_a(SiX)$, increase as the number of the halogen atoms attached to the silicon atom decreases. By contrast, the frequencies of the asymmetrical stretching vibrations: $\nu_f(SiX_4)$, $\nu_e(SiX_3)$ and $\nu_b(SiX_2)$ do not show this trend. It is apparent that these are limited to narrower ranges than

the symmetrical vibrations. Thus, for Si–Cl, the range of the symmetrical frequencies is 424～583 cm^{-1} whereas the range of the asymmetrical is 577～610 cm^{-1}. It is also seen that the asymmetrical modes always occur in a higher frequency range than the corresponding symmetrical stretching modes. The first kind of deformation vibrations occurs in a definite region for each kind of halogen, e. g.: $\delta_e(SiCl_4)$ in $SiCl_4$, $\delta_e(SiCl_3)$ in $SiCl_3Y$ and $\delta_a(SiCl_2)$ in $SiCl_2Y_2$. All are in the range, 150～205 cm^{-1}. The second kind of deformation vibrations usually occurs in a higher frequency range than the first kind. The other deformation vibrations occur in a range so wide that to list it would be of little significance.

Summary

The status of knowledge relative to the vibrational assignments, molecular structure, and spectral data for a series of about one hundred silanes has been surveyed and is reported in brief tabular form. A scheme of simplified vibrational modes is discussed, and used to develop the assignment of fundamentals for some fifty five silanes. Some new assignments are proposed in the light of a correlation rule which has been developed. Tables of characteristic frequencies, and the best values for bond distances, based on this work, are presented.

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