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The Molecular Vibrations and the Rotational Isomerism of (Chloromethyl)methylsilane

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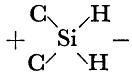
The infrared spectra of (chloromethyl)methylsilane and its deuterated species have been measured in the gaseous, liquid, and crystalline states. The normal vibration calculation has been carried out using a modified Urey-Bradley force field. It has been concluded that, in the gaseous and liquid states, there exist both the *trans* and *gauche* isomers, while only the former persists in the crystalline state. For $ClCH_2SiD_2CH_3$, a different spectral pattern has sometimes been recorded in the crystalline state before the sample has been annealed enough. It has been concluded that the persisting isomer is in the *gauche* form in this metastable crystalline state. The *trans* and *gauche* isomers have been found, from the temperature dependence of the relative intensities of the spectra, to have nearly the same energy in the liquid state. From the solvent effects of the spectra, the *trans* isomer has been found to be more polar than the *gauche* isomer. Therefore, if the C–Cl bond moment is assumed to have the direction of C^{+}–Cl^{-}, the group moment of the C_2SiH_2 part of the molecule must be in the direction of  $+\begin{matrix}C & & H\\ & Si & \\ C & & H\end{matrix}-$ on the bisector of the C–Si–C angle. The vibrational assignments have been worked out taking into account the results of the normal vibration calculations and the reported assignments for chloromethylsilane, dimethylsilane, and ethylmethylsilane.

Recently, we have worked out the vibrational assignments and the rotational isomerism for alkylsilane. The vibrational assignments and the normal vibration calculations for halogenomethylsilane,[1] methylsilane,[2] dimethylsilane,[2] ethylsilane,[2] and ethylmethylsilane[3] have already been reported. In this paper, the vibrational assignments of (chloromethyl)methylsilane will be dealt with in relation to the rotational isomerism around the C–Si bond as an axis.

The normal vibrations of this molecule have been calculated using modified Urey-Bradley force constants transferred from those of chloromethylsilane and dimethylsilane.

The direction of the group moment of the C_2SiH_2 part of the molecule will be discussed using the results of the solvent effects of the spectra.

Experimental

The samples of (chloromethyl)methylsilane and its deuterated species were prepared by the reduction of a commercial product of $ClCH_2SiCl_2CH_3$ (Pierce Chem. Co. U.S.A.) with $LiAlH_4$, $LiAlD_4$, or an equimolar mixture of $LiAlH_4$ and $LiAlD_4$ in *n*-butyl ether.[4] The purities of the samples of $ClCH_2SiH_2CH_3$ and $ClCH_2SiD_2CH_3$ were checked by means of the infrared spectra and gas chromatography.

The infrared spectra in the region from 200 to 4000 cm^{-1} were recorded on a Perkin-Elmer instrument (model 621). For the measurements in the crystalline state, the vapors of the samples were directly condensed on a CsI plate in a cell cooled with liquid nitrogen in a vacuum and were then annealed several times in order to keep the samples from being in a supercooled state. The spectra in the gaseous state were measured with one-meter and 10 cm gas cells with CsI windows.

In order to measure the relative intensity changes in the infrared spectra, the solution spectra were also measured using a sealed KRS-5 cell (0.2 mm thick), with carbon disulfide and acetonitrile as the solvents.

Rotational Isomerism

In this substance, two rotational isomers are expected around the C–Si bond, as is shown in Fig. 1.

The observed infrared spectra of $ClCH_2SiH_2CH_3$ and $ClCH_2SiD_2CH_3$ in the region from 300 to 1000 cm^{-1}

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[1] K. Ohno and H. Murata, This Bulletin, **45**, 3333 (1972).

[2] K. Ohno, M. Hayashi, and H. Murata, *J. Soc. Hiroshima Univ., Ser A.*, **36**, XXX (1972).

[3] M. Hayashi, K. Ohno, and H. Murata, This Bulletin, **45**, 298 (1972); **46**, 684 (1973).

[4] M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.*, **2**, 478 (1964).

TABLE 1. INFRARED SPECTRA OF $ClCH_2SiH_2CH_3$

Gas		Liquid		Crystal		Assignment
cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	
2982 2976 2970	ms	2966	m	2975	m	CH_2 antisym. str. T,G, CH_3 asym. str. (A′, A″) T,G
2948 2942 2936	ms	2942	m	2950	m	CH_2 sym. str. T,G
		2913 b	vw	2912 b	vw	CH_3 sym. str. T,G
		2905 b	vw			
2182 sh	vs					
2174	vs	2156	vs	2155	s	SiH_2 antisym. str. T,G
2154 2148 2142	vs			2130	s	SiH_2 sym. str. T,G
1440 1431 1422	m	1416 b	mw	1421 sh 1416	w m	CH_3 asym. def. (A′,A″) T,G
				1411 sh	w	
1409 1402 1394	ms	1394	m	1400 1388	vw m	CH_2 sci. T,G
				1350	vw	
				1309	vw	
1267 1257	s	1256	s	1249	s	CH_3 sym. def. T,G
1184 1179 1173	m	1179	m	1170	ms	CH_2 wag. T,G
1142 b	w					
1113 1107 1101	m	1109	m	1111	m	CH_2 twist. T,G
				987 981	mw	
952 948 941	vs	940	vs	961 951	vs	SiH_2 sci. T,G
				920 sh	s	
912 905 899	vs	895	vs	908 b 887 b	vs vs	SiH_2 wag. T,G
875	s					
867	s	867	s	867	vs	CH_3 rock. (A″) T,G
				828 sh	m	
816 809	s	809	s	814	s	CH_2 rock. T
772	s					
759 748	s	761	s	766	s	CH_3 rock. (A′) T,G, CH_2 rock. G
740 sh	ms	745	vvw	745	s	C–Si str. T
728	ms	736	ms	—		C–Si str. G
706 701 694	ms	699	s	699	vs	C–Cl str. T
685	m	685	mw	—		C–Cl str. G
620	ms	617 sh	m	—		SiH_2 twist. G
612	ms	607	m	607	s	C–Si str. T
585 579 574	ms	579	m	—		C–Si str. G
490 485 478	s	487	s	492	s	SiH_2 rock. T, G

Int. =intensity; s, m, w=strong, medium, weak;
v=very; sh=shoulder; b=broad;
T=*trans* form; G=*gauche* form.

TABLE 2. INFRARED SPECTRA OF ClCH$_2$SiD$_2$CH$_3$

Gas		Liquid		Crystal A		Crystal B		Assignment
cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	
2975	s			2977	w			CH$_2$ antisym. str.,
2962	s	2967	mw	2967	w	2966	mw	CH$_3$ asym. str. (A′,A″)
2948								
2944	s	2935	mw	2931	w	2944	mw	CH$_2$ sym. str.
2937								
2905	mw	2908	w	2909	vw	2904	w	CH$_3$ sym. str.
1591 sh								
1584	vs			—		1581	s	
1578				1576	vs	—		SiD$_2$ antisym. str.
1571		1573	s	1570				
1566	vs			—		1567	s	
1560						1559		SiD$_2$ sym. str.
1552	vs	1553	s	1555	s	—		
						1427	ms	
1422				1422	w			
1415	ms	1416	m	1416		1420	ms	CH$_3$ asym. def. (A′A″)
1409	ms					—		
				1409	mw	—		
1401		1396	m	1398	m	1396	ms	CH$_2$ sci.
				1388	w			
1346	vw			1333	vw			
1335								
				1274	vw			
1267	s	1253	ms	1250	ms	1250	s	CH$_3$ sym. def.
1257				1246				
1182								
1177	w	1175	w	1178	w	1168	mw	CH$_2$ wag.
1172								
1110								
1105	w	1103	w	1111	w	1107	w	CH$_2$ twist.
1099								
				887	vw	884	vw	
				879	vw	876	vw	
				856	vw	—		
				850	vw	—		
827				826	vs			
824	vs	815	vs	818		819 b	vs	CH$_3$ rock. (A′)
817				813	vs	814	vs	CH$_3$ rock. (A″)
797	vs	783	vs	788	vs	784	w	CH$_2$ rock.
786				780				
749						747	s	C–Si str.
743	s	735	ms	732	ms	—		
734								
728	s	724	ms	—		722 b	s	SiD$_2$ sci.
722								
		689	m	699	ms	—		C–Cl str.
				695				
694				682	s	—		SiD$_2$ sci.
687	vs	681	s	679				
680						675	s	C–Cl str.
651		668 sh	ms					
646	mw	644	w	—		648	w	C–Si str.
640		637	w	637	m	—		
571								
565	s	567	ms	—		570	s	SiD$_2$ wag.
560								
544								
538	s	537	ms	535	s	—		SiD$_2$ wag.
533								
477								
472	w	475	mw	479	mw	—		SiD$_2$ twist.
466								
406								
400	s	401	s	401	s	—		SiD$_2$ rock.
395		389 sh	w	—		392	m	
				240	m	—		Skeletal bend.

Crystal A: The metastable crystalline state, where the *gauche* isomer persists alone.
Crystal B: The stable crystalline state, where the *trans* isomer persists alone.

are shown in Figs. 2 and 3 respectively, where (a) and (b) indicate the spectra in the liquid and in the crystalline states respectively,

TABLE 3. INFRARED SPECTRA OF THE MIXTURE OF $ClCH_2$-$SiHDCH_3$, $ClCH_2SiH_2CH_3(-d)$, AND $ClCH_2SiD_2CH_3(-d_0)$[a]

Liquid		Crystal		Assignment[b]
cm^{-1}	Int.	cm^{-1}	Int.	
803 sh	s	805	vs	CH_2 rock. T
783	s	785	vs	$-d_2$
761	ms	766	m	$-d_0$
		750	m	C–Si str. T
747	ms	746	m	$-d_0$, $-d_2$
724	ms	727	m	$-d_2$
710	ms	714	s	Si–H def. T
700	ms	700	m	$-d_0$
682	s	687	m	C–Cl str. T
668 sh	m	675	m	$-d_2$
644	w	646	w	$-d_2$
637 sh	w	—		$-d_2$
617 sh	w	—		$-d_0$
607	m	607	m	$-d_0$
595 sh	w	—		C–Si str. G
579 sh	w	—		$-d_0$
567	m	568	m	$-d_2$
539	m	—		$-d_2$
502 sh	mw	—		Si–D def. G
494	m	498	m	Si–D def. T
487	m	489	m	$-d_0$
475 sh	mw	—		$-d_2$
433	m	—		SiHD rock. G
425	m	423	m	SiHD rock. T
401	m	—		$-d_2$
389 sh	w	391	m	$-d_2$

a) The region from 810 to 4000 cm^{-1} is omitted.
b) Assignments for the d_0 and d_2 species are omitted.

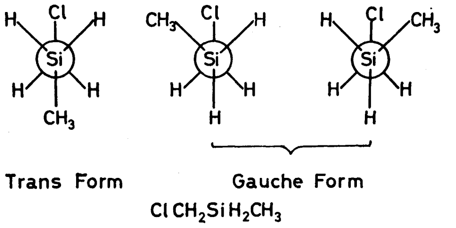


Fig. 1. Molecular forms of (chloromethyl)methylsilane.

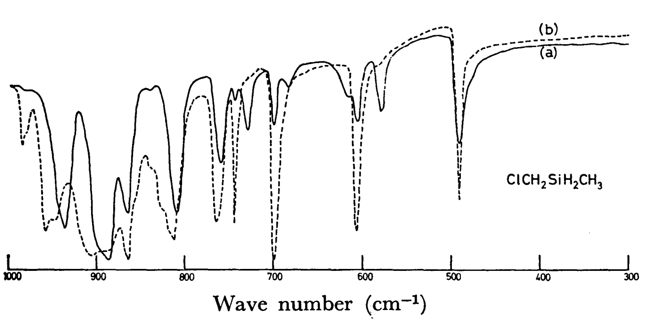


Fig. 2. Infrared spectra of $ClCH_2SiH_2CH_3$.
(a): in the liquid state,
(b): in the crystalline state.

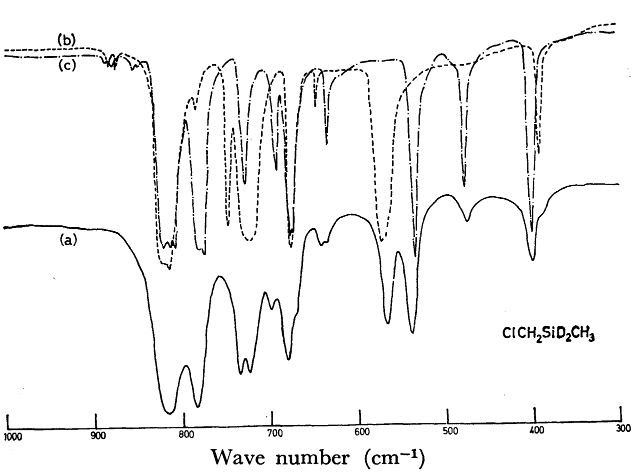


Fig. 3. Infrared spectra of $ClCH_2SiD_2CH_3$.
(a): in the liquid state,
(b): in the stable crystalline state,
(c): in the metastable crystalline state.

A comparison of the observed spectra in the liquid state with those in the crystalline state reveals the existence of rotational isomers in this substance, since some of the infrared bands vanish in the crystalline state.

Especially, it is to be noted that, for $ClCH_2SiD_2CH_3$, a different spectral pattern is sometimes obtained in the crystalline state before annealing the sample enough, as is shown in (c) of Fig. 3; furthermore, the superposition of these two kinds of spectral patterns, (b) and (c), coincides with the spectral pattern in the liquid state.

This is understandable if the persisting isomer has different molecular forms for $ClCH_2SiD_2CH_3$ in the metastable and stable crystalline states.

In the cases of ethylmethylsilane and its deuterated species, the existence of the rotational isomers has been proved from the lower-frequency mode of two Si–C stretchings and the SiH_2 rocking, SiD_2 rocking, and SiD_2 wagging modes appearing in the region from 300 to 650 cm^{-1}.[3] The spectra assigned to these modes have been observed for ethylmethylsilane as pairs which consist of two bands attributable to the *trans* and *gauche* isomers respectively.

These modes are also expected for (chloromethyl)-methylsilane in the same region as those for ethylmethylsilane; that is, for $ClCH_2SiH_2CH_3$, the lower-frequency mode of the two C–Si stretchings and the SiH_2 rocking mode are expected around 620 and 490 cm^{-1} respectively, and for $ClCH_2SiD_2CH_3$, the C–Si stretching, the SiD_2 wagging, and the SiD_2 rocking modes are expected around 640, 560, and 400 cm^{-1} respectively. In this region, for $ClCH_2SiH_2CH_3$ three bands are seen in the liquid state; one of them accompanies a shoulder on the higher-frequency side, while two bands persist in the crystalline state.

For $ClCH_2SiD_2CH_3$ five bands are seen in the liquid state; two of them accompany a shoulder on the lower-frequency side, while there are four and three bands persisting in the metastable and stable crystalline states respectively.

Although some of these bands can be regarded as pairs, only single bands can be found for the other modes. However, these single bands can be regarded as unresolved pairs of two bands, since these bands are reduced in their relative intensities in the crystalline state; this fact can be understood if one of two unresolved bands vanishes in the crystalline state. The possibility of the unresolved bands in a pair is also supported by the fact that even the resolved bands in a pair actually have much smaller spacings than those for ethylmethylsilane.[3)]

Because of the smallness of the spacing of the bands in the pair, the existence of the rotational isomers cannot be concluded from the SiH_2 rocking mode for $ClCH_2SiH_2CH_3$. However, for $ClCH_2SiD_2CH_3$, definite evidence is obtained from the SiD_2 wagging and the SiD_2 rocking modes. The pair at 567 and 537 cm^{-1} assigned to the SiD_2 wagging mode, and that at 401 and 389 cm^{-1} assigned to the SiD_2 rocking mode, are seen in the liquid state, where the bands at 537 and 401 cm^{-1} disappear in the stable crystalline state. This is the same as in the case of ethylmethylsilane.

Therefore, if the bands in the pair appear in the same order as in the case of ethylmethylsilane, the bands disappearing in the stable crystalline state are attributable to the *gauche* isomer and the bands persisting in the stable crystalline state are attributable to the *trans* isomer.

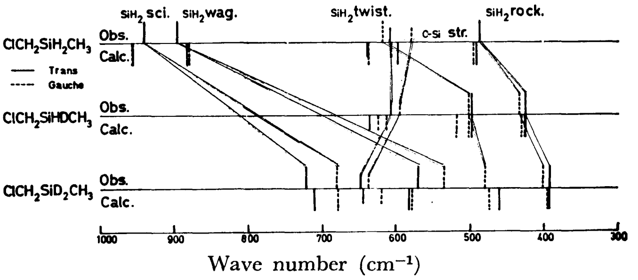


Fig. 4. Observed and calculated frequencies of the SiH_2, SiD_2, and SiHD deformation modes and the lower frequency C–Si stretching mode.

As is shown in Fig. 4, this conclusion is also confirmed by the normal vibration calculation, as will be described later.

The pair at 608 and 579 cm^{-1} for $ClCH_2SiH_2CH_3$ and that at 644 and 637 cm^{-1} for $ClCH_2SiD_2CH_3$ are seen in the liquid state, where one of two bands in each pair (579 and 637 cm^{-1}) disappears in the crystalline state. These are assigned to the lower-frequency mode of C–Si stretching from the results of the calculations.

Usually, the spectra of an asymmetrically deuterated species such as $ClCH_2SiHDCH_3$ give difinite experimental evidence on the molecular forms of the rotational isomers. For $ClCH_2SiHDCH_3$ and $CH_3CH_2SiHDCH_3$, since the two *gauche* forms come to be not equivalent, the spectra of the *gauche* isomer are expected to be split into doublets, while the spectra of the *trans* isomer remain singlets.

This is actually the case with ethylmethylsilane.[3)] For the present case of $ClCH_2SiHDCH_3$, however, this is not actually the case.

As is shown in Fig. 5 although the doublet at 433 and 425 cm^{-1} assigned to the SiHD rocking mode is seen in the liquid state, one of the components, that at 433 cm^{-1}, disappears in the crystalline state. This component can be regarded as two unsplit bands due to two different pairs of *gauche* forms.

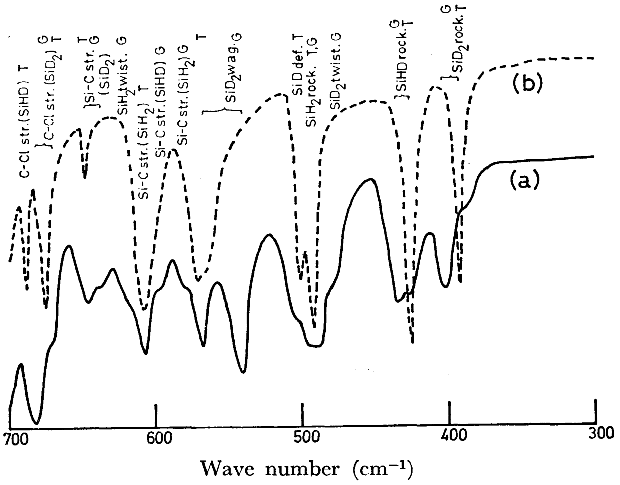


Fig. 5. Infrared spectra of the mixture of $ClCH_2SiHDCH_3$, $ClCH_2SiH_2CH_3$, and $ClCH_2SiD_2CH_3$.
(a): in the liquid state,
(b): in the crystalline state.

The existence of the rotational isomers in the gaseous state can also be proved from a comparison of the spectra in the gaseous and liquid states.

In the case of $ClCH_2SiD_2CH_3$, in the crystalline state it is concluded from the above discussions of the molecular forms of the isomers that the *gauche* isomer persists alone in the metastable state, while the *trans* isomer persists alone in the stable state.

As no appreciable changes in the relative absorption intensities between the spectra at low temperatures (*ca.* −100°C) and those at room temperature (*ca.* 23°C) were observed, the energy difference between the isomers can be disregarded in the liquid state. In the gaseous state, the larger overlapping of the key bands prevents the measurement of the relative intensities of the bands.

The Solvent Effects of the Spectra

The solvent effects of the spectra were measured using the pair of Si–C stretching bands at 608 and 579 cm^{-1} for $ClCH_2SiH_2CH_3$ and the pair of SiD_2 wagging bands at 567 and 537 cm^{-1} for $ClCH_2SiD_2CH_3$, where the higher-frequency bands of each pair are due to the *trans* isomer and the lower bands are due to the *gauche* isomer.

The bands for the *trans* isomer increase in their relative intensities when a mixture is made with a polar solvent such as acetonitrile, while the bands for the *gauche* isomer increase in their relative intensities in a mixture with a non-polar solvent such as carbon disulfide, as is shown in Fig. 6. Therefore, it can be concluded that the *trans* isomer is more polar than the *gauche* isomer.

From these results, if the C–Cl bond moment is assumed to have the direction of C^{+}–Cl^{-}, the group

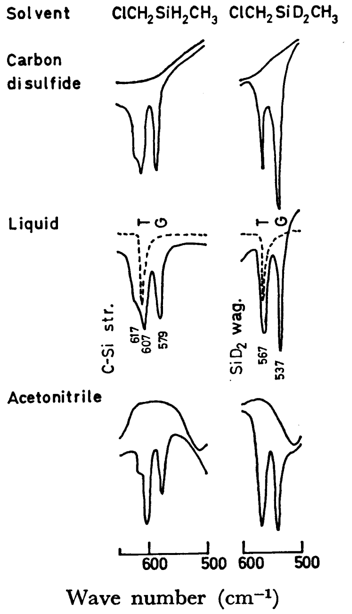
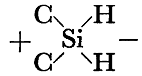


Fig. 6. Solvent effects of the infrared spectra for (chloromethyl)-methylsilane.

moment of the C_2SiH_2 group should be in the direction of  $+\!\!\begin{smallmatrix}C & & H\\ & Si & \\ C & & H\end{smallmatrix}\!\!-$ on the bisector of the C–Si–C angle.

The Normal Vibration Calculation and the Vibrational Assignments

In order to confirm the molecular forms of the rotational isomers and the assignments of the observed spectra, the normal vibration calculation for (chloromethyl)methylsilane was carried out using a modified Urey-Bradley force field.

The force constants used were transferred from those for chloromethylsilane[1] and dimethylsilane[2] except for the two force constants of H(Cl–C–Si) and F(Cl···C···Si), which were adjusted in order to predict the observed Cl–C–Si bending vibration, which had not been observed for chloromethylsilane.

The modified Urey-Bradley force field used in the calculation was the same type as in the cases of chloromethylsilane and dimethylsilane, where the internal rotation force constants for the CH_3–Si and CH_2–Si groups were taken so as to predict the observed barrier height of 1.65 kcal/mol for dimethylsilane[5] by microwave spectroscopy.

The structural parameters were transferred from those of chloromethylsilane[6] and dimethylsilane[5] determined by microwave studies. However, the valency angles were assumed to be tetrahedral without regard to the reported values.

The force constants used in the calculation are listed in Table 4. The observed and calculated frequencies of (chloromethyl)methylsilane and its deuterated species are given in Tables 5—7, together with their predominant symmetry coordinates in the potential energy

TABLE 4. FORCE CONSTANTS FOR (CHLOROMETHYL)-METHYLSILANE[a)]

K(C–H), CH_2	4.390	$\kappa(CH_2)$	0.027
K(C–H), CH_3	4.403	$\kappa(CH_3)$	0.014
K(Si–H)	2.462	$\kappa(SiH_2)$	0.104
K(C–Cl)	1.697	Y(C–Si)	0.051
K(C–Si)	1.991	p(C–H)	−0.084
H(Si–C–Cl)	0.030	F(Si·C·Cl)	0.280
H(Si–C–H), CH_2	0.104	F(Si·C·H), CH_2	0.271
H(Cl–C–H)	0.147	F(Cl·C·H)	0.558
H(H–C–H)	0.349	F(H·C·H)	0.200
H(C–Si–C)	0.133	F(C·Si·C)	0.040
H(C–Si–H), CH_3	0.092	F(C·Si·H), CH_3	0.149
H(C–Si–H), CH_2	0.113	F(C·Si·H), CH_2	0.149
H(H–Si–H)	0.180	F(H·Si·H)	0.041
H(Si–C–H), CH_3	0.102	F(Si·C·H), CH_3	0.271
t(Si–C–Cl, SiH_2)[b)]	0.017	t(C–Si–C, CH)[b)]	0.030
t(CH_2, SiH_2)[b)]	0.082	t(CH_3, SiH_2)[b)]	0.057

a) Force constants are transferred from those of dimethylsilane and chloromethylsilane except H(Si–C–Cl) and F(Si·C·Cl) which are adjusted so as to reproduce the observed frequency of the Si–C–Cl bending mode. The units of the force constants are in mdyn/Å for the streching, K; the bending, H; the repulsion, F; and the bond interaction, p, and in mdyn·Å for the internal rotation, Y; the *trans* coupling, t; and the intramolecular tension, k.

b) The *gauche* coupling constants are assumed to be $g=-0.5t$.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES OF $ClCH_2SiH_2CH_3$

	No.	*Trans* form		*Gauche* form		P. E. D.[a)]
		Obsd	Calcd	Obsd	Calcd	
A'	1	2966	2964	2966	2964	CH_3 asym. str.
	2	2942	2949	2942	2949	CH_2 sym. str.
	3	2913	2901	2913	2901	CH_3 sym. str.
	4	2156	2147	2156	2147	SiH_2 sym. str.
	5	1416	1413	1416	1413	CH_3 asym. def.
	6	1394	1420	1394	1421	CH_2 sci.
	7	1256	1254	1256	1254	CH_3 sym. def.
	8	1179	1168	1179	1168	CH_2 wag.
	9	940	955	940	956	SiH_2 sci.
	10	895	882	895	879	SiH_2 wag., CH_3 rock.
	11	761	777	761	770	CH_3 rock., SiH_2 wag.
	12	745	730	736	729	C–Si str., C–Cl str.
	13	699	688	685	695	C–Cl str., C–Si str.
	14	608	639	579	606	C–Si str., C–Cl str.
	15	—	212	—	251	Skeletal bend.
	16	—	158	—	148	Skeletal bend.
A''	17	2966	2994	2966	2993	CH_2 antisym. str.
	18	2966	2964	2966	2964	CH_3 asym. str.
	19	2156	2148	2156	2148	SiH_2 antisym. str.
	20	1416	1413	1416	1413	CH_3 asym. def.
	21	1109	1109	1109	1112	CH_2 twist.
	22	867	846	867	842	CH_3 rock., SiH_2 twist.
	23	809	824	761	776	CH_2 rock., CH_3 rock., SiH_2 twist.
	24	—	597	618	637	SiH_2 twist., CH_2 rock.
	25	487	492	487	496	SiH_2 rock.
	26	—	169	—	178	CH_3–Si torsion
	27	—	66	—	67	CH_2–Si torsion

a) Only the predominant symmetry coordinates are shown.

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Table 6. Observed and calculated frequencies of $ClCH_2SiD_2CH_3$

	No.	*Trans* form		*Gauche* form		P. E. D.[a]
		Obsd	Calcd	Obsd	Calcd	
A'	1	2966	2964	2967	2964	CH_3 asym. str.
	2	2944	2949	2931	2949	CH_2 sym. str.
	3	2904	2901	2909	2901	CH_3 sym. str.
	4	1563	1536	1555	1536	SiD_2 sym. str.
	5	1420	1413	1409	1413	CH_3 asym. def.
	6	1396	1420	1398	1421	CH_2 sci.
	7	1250	1254	1248	1254	CH_3 sym. def.
	8	1168	1167	1178	1166	CH_2 wag.
	9	819	822	822	823	CH_3 rock.
	10	747	749	732	731	C–Si str.
	11	722	711	680	678	SiD_2 sci.
	12	675	672	697	712	C–Cl str., C–Si str.
	13	648	645	637	619	C–Si str.
	14	570	582	535	578	SiD_2 wag.
	15	—	210	240	248	Skeletal bend.
	16	—	154	—	145	Skeletal bend.
A''	17	2966	2994	2977	2993	CH_2 antisym. str.
	18	2966	2964	2967	2964	CH_3 asym. str.
	19	1581	1552	1573	1552	SiD_2 antisym. str.
	20	1427	1413	1419	1413	CH_3 asym. def.
	21	1107	1107	1111	1110	CH_2 twist.
	22	814	817	815	816	CH_3 rock.
	23	784	780	784	759	CH_2 rock.
	24	—	460	479	474	SiD_2 twist.
	25	392	393	401	395	SiD_2 rock.
	26	—	168	—	175	CH_3–Si torsion
	27	—	65	—	65	CH_2–Si torsion

a) Only the predominant symmetry coordinates are shown.

Table 7. Observed and calculated frequencies of $ClCH_2SiHDCH_3$

	No.	*Trans* form		*Gauche* form(G)[a]		*Gauche* form(G′)[b]		P. E. D.[c]
		Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	
A	1		2994		2993		2993	CH_2 antisym. str.
	2		2964		2964		2964	CH_3 asym. str.
	3		2964		2964		2964	CH_3 asym. str.
	4		2949		2949		2949	CH_2 sym. str.
	5		2901		2901		2901	CH_3 sym. str.
	6		2148		2147		2147	Si–H str.
	7		1544		1544		1544	Si–D str.
	8		1420		1421		1421	CH_2 sci.
	9		1413		1413		1413	CH_3 asym. def.
	10		1413		1413		1413	CH_3 asym. def.
	11		1254		1254		1254	CH_3 sym. def.
	12		1168		1166		1168	CH_2 wag.
	13		1108		1112		1110	CH_2 twist.
	14		869		876		855	SiHD sci.
	15		858		857		858	CH_3 rock., SiHD def.
	16		812		814		812	CH_3 rock.
	17	805	794		715		723	CH_2 rock. [d]
	18	750	753		746		731	C–Si str. [d]
	19	714	703		762		769	Si–H def. [d]
	20	687	686		668		690	C–Cl str. [d]
	21	607	636	595	613	595	624	C–Si str., C–Cl str.
	22	498	498	502	519	502	502	Si–D def.
	23	425	425	433	430	433	425	SiHD rock.
	24		211		248		251	Skeletal bend.
	25		168		176		176	CH_3–Si torsion
	26		156		146		147	Skeletal bend.
	27		66		66		66	CH_2–Si torsion

a) The chlorine atom occupies the *trans* position to the deuterium of the SiHD group.

b) The chlorine atom occupies the *trans* position to the hydrogen of the SiHD group.

c) Only the predominant symmetry coordinates are shown.

d) These four frequencies have the complicated mixing modes of the four symmetry coordinates of the CH_2 rocking, C–Si stretching, Si–H deformation, and C–Cl stretching. However, the correspondence of the observed frequencies to these symmetry coordinates can be found as is shown in the table from the comparison with those for the other species.

distribution.

A fair agreement is obtained between the observed and calculated frequencies. The deviation is within 3% for almost all of the modes. However, a little larger deviations (~5%) are seen for the C–Si and C–Cl stretching modes for $ClCH_2SiH_2CH_3$ and $ClCH_2SiHDCH_3$ and for the SiD_2 wagging mode for $ClCH_2SiD_2CH_3$. Although these larger deviations indicate the limitation of the transferability of the force constants, further adjustments of the force constants were not attempted.

From the calculated potential energy distribution, the mixings of the modes were found to be complicated among the C–Si and C–Cl stretchings and some of the hydrogen deformation modes of the CH_3, CH_2, and SiH_2 groups.

As is shown in Tables 1 and 2, according to the present assignments the frequency differences between the CH_3 rocking modes belonging to the A′ and A″ species are found to be more than 100 cm^{-1} for $ClCH_2SiH_2CH_3$ in both the *trans* and *gauche* forms, while those for $ClCH_2SiD_2CH_3$ are less than 10 cm^{-1}. The situation is the same with the CH_3 rocking modes for dimethylsilane[2] and ethylmethylsilane,[3] as has been reported in previous papers.

This is understandable for the following reasons. For $ClCH_2SiH_2CH_3$, as the SiH_2 wagging mode is found at a frequency close to the expected frequency for the CH_3 rocking mode belonging to the A′ species, the CH_3 rocking mode receives a strong coupling from the SiH_2 wagging mode and is pushed down to the lower-frequency side. On the other hand, for $ClCH_2SiD_2CH_3$, as the SiD_2 wagging mode is far from the frequency for the CH_3 rocking mode, the coupling becomes negligible.

This is also supported by the calculated potential energy distribution for these modes.

As has been already pointed out in the cases of dichlorosilane,[7] dimethylsilane,[2] and ethylmethylsilane,[3] for $ClCH_2SiHDCH_3$ the calculated potential energy distribution also shows that the SiHD rocking mode keeps its original mode, while the SiHD twisting mode should be more properly called the SiD deformation mode.

The vibrational assignments for the other modes can be obtained by taking into account the results of the normal vibration calculations and by comparing the observed spectra with those of similar molecules, such as dimethylsilane,[8–10] chloromethylsilane,[1] and ethylmethylsilane.[3] The results are shown in Tables 1—3.

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