The Molecular Vibrations and Rotational Isomerism of Chloro(chloromethyl)silane[1)]

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The infrared spectra of chloro(chloromethyl)silane, $ClCH_2SiH_2Cl$, and its deuterated species, $ClCH_2SiD_2Cl$, have been measured in the gaseous, liquid, and crystalline states. The Raman spectra have also been measured in the liquid state. The vibrational spectra have shown that two rotational isomers coexist in the gaseous and liquid states, while only one isomer persists in the crystalline state. The fundamental vibrations have been assigned for each isomer. The product rule, the calculation of the skeletal frequencies, and the band contours have indicated that the isomer persisting alone in the crystalline state is the *trans* form and that the other isomer is the *gauche* form. The solvent effects of the spectra have shown that the *gauche* form is more polar than the *trans* form. The normal vibrations have been calculated in a modified Urey-Bradley force field, and the force constants have been adjusted to predict well the observed frequencies for the isomers of both the parent and its deuterated species.

Many studies have been accumulated concerning the rotational isomerism of 1,2-substituted ethanes.[2)] We have taken an interest in studying organosilicon compounds of these homologous series, in which the height of the potential barrier around a C–Si bond may be lower than that around a C–C bond.[3)] Investigations of such organosilicon compounds as chloroethylsilane,[4)] (chloromethyl)methylsilane,[5)] and ethylmethylsilane[5)] have been reported previously. Chloro(chloromethyl)silane is a molecule in which both the substituents around the C–Si bond are chlorine atoms; it is a homologous molecule of 1,2-dichloroethane, which has previously been investigated in detail.[6)]

Therefore, in this paper, we will deal with the molecular vibrations of chloro(chloromethyl)silane in relation to the rotational isomerism in order to compare the results with those of 1,2-dichloroethane and the analogues of alkylsilanes. By methods similar to those used for 1,2-dichloroethane; that is, the product rule and the calculation of the skeletal frequencies, the molecular forms of the isomers will be determined. The normal vibration calculation will also be carried out for each molecular form in a modified Urey-Bradley force field, and the force constants will be adjusted by a least-squares method in order to predict the observed frequencies well.

Experimental

Tetrachlorosilane was treated with diazomethane,[7)] and the product ($ClCH_2SiCl_3$) was reduced with $LiAlH_4$ or $LiAlD_4$ in *n*-butyl ether.[8)] Chloromethylsilane was then reacted with $HgCl_2$ in a vacuum.[9)] The sample of chloro(chloromethyl)silane was purified by distillation in a dry nitrogen atmosphere; bp 75—76 °C/760 mmHg.

The infrared spectra were recorded on a Perkin-Elmer instrument (Model 621) in the 200—4000 cm^{-1} region and on a Hitachi Fis-3 far-infrared spectrophotometer in the 40—300 cm^{-1} region. The spectra in the liquid state were recorded in CsI and polyethylene cells. The spectra in the gaseous state were measured at room temperature with a 10-cm gas cell fitted with CsI windows. In the crystalline state, the vapor of the sample was condensed on a CsI window cooled with liquid nitrogen in a vacuum and was then annealed near the melting point. The solution spectra were measured using a sealed KRS-5 cell (0.2 mm thick), with *n*-hexane and acetonitrile as the solvents. The Raman spectra in the liquid state were measured with a JEOL Raman spectrometer (Model JAS-O2AS), using an argon-ion laser (488.0 nm) for excitation.

Results and Discussion

Rotational Isomerism. It has been determined by microwave studies that such molecules as chloromethylsilane[10)] and dimethylsilane[11)] have a staggered con-

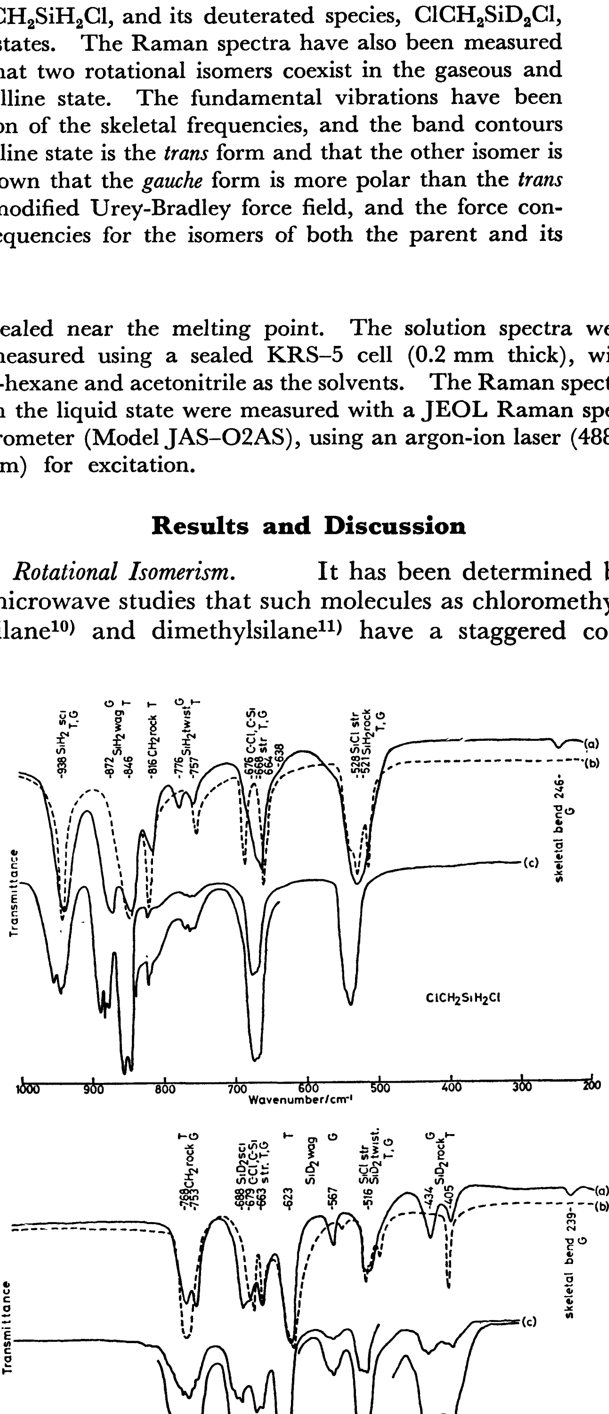

Fig. 1. Infrared spectra of chloro(chloromethyl)silane in the 200—1000 cm^{-1} region; (a): in the liquid state, (b): in the crystalline state, (c): in the gaseous state.

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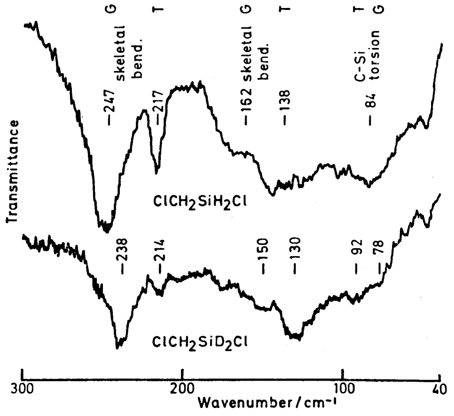

Fig. 2. Far-infrared spectra of chloro(chloromethyl)-silane in the liquid state in the 40—300 cm^{-1} region.

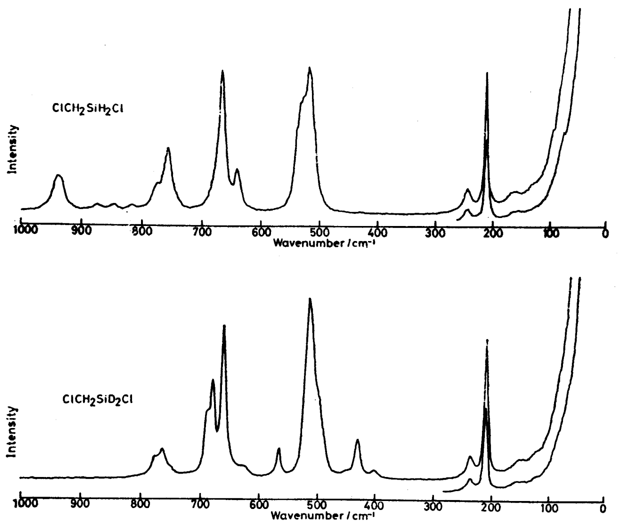

Fig. 3. Raman spectra of chloro(chloromethyl)silane in the liquid state in the region below 1000 cm^{-1}.

figuration around a C–Si bond. Therefore, in this substance, two rotational isomers of the *trans* and *gauche* forms can be expected. If this substance had a unique molecular form, it would show eighteen fundamental frequencies in both the infrared and Raman spectra.

Figures 1—2 and Fig. 3 show the infrared spectra in the 40—1000 cm^{-1} region and the Raman spectra in the region below 1000 cm^{-1} respectively. In the vibrational spectra, too many bands for one isomer are observed in the liquid state, while the absence of some of the bands in the crystalline state shows the existence of the rotational isomers in the liquid state. In the crystalline state, however, the existence of only one isomer is sufficient to account for the number of observed bands.

The vibrational assignments of this substance are made on the basis of the spectra of (chloromethyl)silane[12] and chloromethylsilane,[13] the relative intensities of both the infrared and Raman bands, and the infrared-band contours in the gaseous state. From the assignments of the observed spectra, given in Table 1, the sums of the squares of the fundamental frequencies are found to be:

$$\begin{array}{l}\sum\nu_i^2 = 3.638\times10^7\\ \sum\nu'^2_i = 3.639\times10^7\end{array} \quad (0.1\%\ \text{difference})$$

for $ClCH_2SiH_2Cl$ and:

$$\begin{array}{l}\sum\nu_i^2 = 3.044\times10^7\\ \sum\nu'^2_i = 3.038\times10^7\end{array} \quad (0.2\%\ \text{difference})$$

for $ClCH_2SiD_2Cl$, where ν_i and ν'_i indicate the frequencies of the isomers persisting and disappearing in the crystalline state respectively. From the above results, the assignments in Table 1 can be considered as acceptable.

Band Contours. The principal moments of inertia are calculated from the following parameters: C–Cl= 1.788 Å, C–Si=1.889 Å, Si–Cl=2.052 Å, C–H=1.096 Å Si–H=1.477 Å, tetrahedral bond angles, and the internal rotation angles of 180° (*trans*) and 60° (*gauche*). The bond lengths are transferred from those of (chloromethyl)silane[10] and chloromethylsilane[14] determined by microwave studies. Figure 4 shows the *trans* and *gauche* forms of chlorochloromethylsilane in the principal axis system. The *trans* form of this substance may have the C_s symmetry. The 18 normal vibrations are reduced to 11 vibrations of the A′ species and 7 of A″. The a and b internal axes are in the plane of symmetry, while the c axis is perpendicular to it. The A′ vibrations may have either a-, b-, or ab-type infrared-band contours in the case of an asymmetric top. The A″ vibrations, on the other hand, have c-type band contours. The *gauche* form may have no symmetry (point group C_1). All the 18 normal vibrations are of the same symmetry of A.

The principal moments of inertia of I_a, I_b, and I_c calculated are 31.742 (38.838), 424.52 (427.66), and 447.17 (451.55) amu·Å^2 for the *trans* form of $ClCH_2SiH_2(-D_2)Cl$ and 87.086 (95.978), 275.95 (281.16), and 338.37 (346.60) amu·Å^2 for the *gauche* form. The Ray asymmetry parameters, κ, are −0.9918 (−0.9895) and −0.8432 (−0.8218) for the *trans* and *gauche* forms of $ClCH_2SiH_2(-D_2)Cl$ respectively; these values show both the forms to be prolate asymmetric top molecules. The expected PR separations are calculated by the use of the method of Seth-Paul and Dijkstra.[15] The

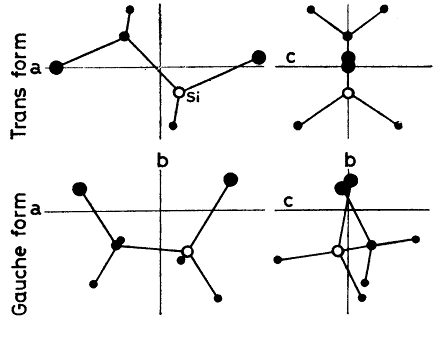

Fig. 4. Possible molecular forms of chloro(chloromethyl)-silane in the principal axis system.

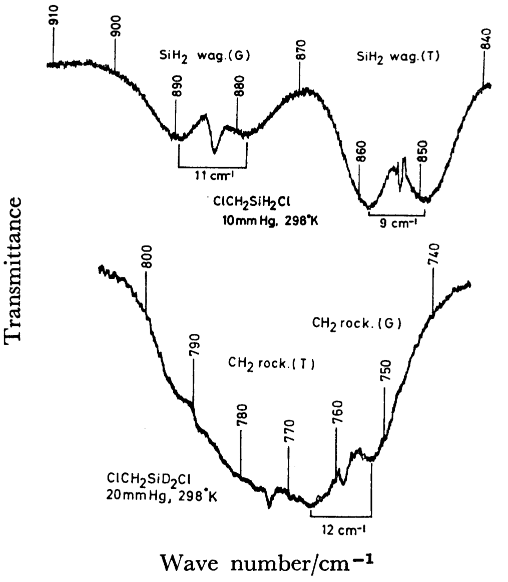

Fig. 5. Infrared band contours of the SiH_2 wagging vibration for $ClCH_2SiH_2Cl$ and the CH_2 rocking vibration for $ClCH_2SiD_2Cl$.

PR separations of the a-, b-, and c-type band contours at the temperature of 298 K are estimated to be 9.6 (9.6), 8.0 (8.0), and 14.4 (14.3) cm^{-1} for the *trans* form of $ClCH_2SiH_2(-D_2)Cl$ and 11.6 (11.6), 9.5 (9.4), and 17.5 (17.4) cm^{-1} for the *gauche* form, where the c-type band contours are expected to produce a PQR structure featuring a sharp Q branch but ill-defined P and R branches.[16)]

The PR separations of $ClCH_2SiH_2(-D_2)Cl$ observed are between 8 and 12 cm^{-1}, as is shown in Fig. 5 and Table 1. Especially, for the bands assigned to the SiH_2 wagging vibration, the PR separation of the band at 883 cm^{-1} (11 cm^{-1}) is larger than that of the band at 853 cm^{-1} (9 cm^{-1}), where the former disappears in the crystalline state. The bands assigned to the CH_2 and SiD_2 rocking vibrations and persisting in the crystalline state (the band at 820 cm^{-1} for $ClCH_2SiH_2Cl$ and the bands at 774 and 403 cm^{-1} for $ClCH_2SiD_2Cl$) have c-type band contours, while the corresponding bands disappearing in the crystalline state (the bands at 759 and 436 cm^{-1} for $ClCH_2SiD_2Cl$) feature PQR structures with PR separations of 11—12 cm^{-1}. The results are consistent with the determination of the molecular forms using the product rule and the calculation of the skeletal frequencies to be described below.

Molecular Forms of Isomers. It has been mentioned by Mizushima *et al.*[6)] that the product rule and the calculation of the skeletal frequencies are useful for the determination of the molecular forms of the rotational isomers.

The products of the fundamental frequencies are:

$$\pi\nu_i'/\pi\nu_i = 1.146$$

for $ClCH_2SiH_2Cl$ and:

$$\pi\nu_i'/\pi\nu_i = 1.099$$

for $ClCH_2SiD_2Cl$, where ν_i and ν_i' indicate the frequencies of the isomers persisting and disappearing in the crystalline state respectively. When it is assumed that the force field is identical for both the rotational isomers, the relationship between the frequencies of the two isomers is:

$$\pi\nu_i'/\pi\nu_i = (|G(\nu')|/|G(\nu)|)^{1/2}.$$

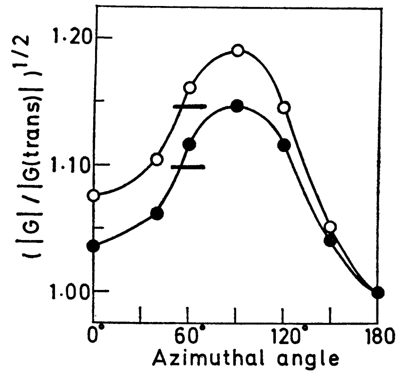

Fig. 6. The calculated values of $(|G'|/|G(trans)|)^{1/2}$ and the observed values of $\pi\nu'/\pi\nu(trans)$;
—○—: $(|G'|/|G(trans)|)^{1/2}$ for $ClCH_2SiH_2Cl$,
—●—: $(|G'|/|G(trans)|)^{1/2}$ for $ClCH_2SiD_2Cl$,
——: observed values.

Figure 6 gives the calculated values of $(|G|/|G(trans)|)^{1/2)}$ of a different azimuthal angle, where it is assumed that this substance has a staggered configuration. This shows that the bands persisting in the crystalline state are attributable to the *trans* form and that the bands disappearing in the crystalline state are attributable to the *gauche* form.

In order to confirm the above results, the skeletal frequencies of the parent species are calculated on the basis of the simple Urey-Bradley force field. The force constants used are K(C–Cl)=2.90, K(C–Si)=2.80, K(Si–Cl)=2.59, H(Cl–C–Si)=0.093, H(C–Si–Cl)=0.117, F(Cl·C·Si)=0.21, and F(C·Si·Cl)=0.16 md/Å. The bending and repulsion force constants are transferred from those of (chloromethyl)silane[12)] and

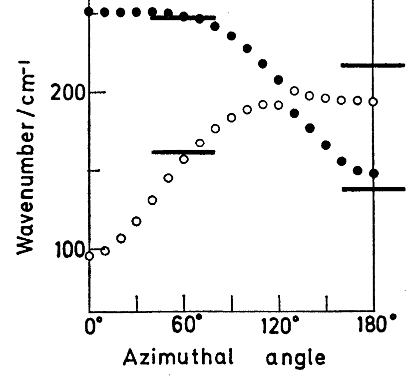

Fig. 7. Dependence of skeletal deformation frequencies of azimuthal angle;
○: calculated frequencies of the symmetric mode,
●: calculated frequencies of the antisymmetric mode, ——: observed frequencies.

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF CHLORO(CHLOROMETHYL)SILANE[a] (cm^{-1})

Infrared			Raman liquid	Calculated		P. E. D.[b]
Gas Int.	Liquid Int.	Crystal Int.	Int.	T form	G form	
			$\mathrm{ClCH_2SiH_2Cl}$			
	3000 vw	2999 vw	2997 mw	2998 A″	2998	$\nu_a\mathrm{CH_2}$ (100)
			2989 mw			
2960 w 2950	2945 vw	2945 vw	2945 s	2945 A′		$\nu_s\mathrm{CH_2}$ (100)
2933 b vw	2936 vw	—	2936 s		2945	$\nu_s\mathrm{CH_2}$ (100)
2227 sh 2222 s 2217		2232 s 2221		2222 A″	2222	$\nu_a\mathrm{SiH_2}$ (100)
2208 s 2198 s 2185	2208 b s		2200 vs	2220 A′	2220	$\nu_s\mathrm{SiH_2}$ (100)
1412 1408 m 1402	1398 m	1398 m	1398 w	1396 A′		$s\mathrm{CH_2}$ (92)
	1392 sh	—	1392 sh w		1396	$s\mathrm{CH_2}$ (92)
1180 1175 vw 1170	1180 sh w	—	1179 w		1162	$w\mathrm{CH_2}$ (100)
	1174 w	1171 m	1174 w	1157 A′		$w\mathrm{CH_2}$ (100)
1112 1107 vw 1101	1106 w	—	1105 w		1116	$t\mathrm{CH_2}$ (84)
	1097 sh w	1092 m	1096 w	1116 A″		$t\mathrm{CH_2}$ (85)
954 s 945	938 s	940 s	938 m	953 A′	951	$s\mathrm{SiH_2}$ (95)
941 sh s 933						
889 883 s 878	872 vs	—	873 vw	873 vw	902	$\omega\mathrm{SiH_2}$ (85), $r\mathrm{CH_2}$ (10)
858 853 vs 849	846 vs	846 vs	846 vw	885 A′		$\omega\mathrm{SiH_2}$ (99)
822 w	816 m	818 vs	816 vw	835 A″		$r\mathrm{CH_2}$ (51), $t\mathrm{SiH_2}$ (30)
817 w					776	$t\mathrm{SiH_2}$ (37), $r\mathrm{CH_2}$ (32)

Table 1. Continued

Infrared			Raman Liquid Int.	Calculated		P. E. D.[b]
Gas Int.	Liquid Int.	Crystal Int.		T form	G form	
770	776 w	—	774 mw		708	$r\mathrm{CH}_2$ (40), $t\mathrm{SiH}_2$ (33)
764 w						
758	757 w	753 m	757 m	674 A″		$t\mathrm{SiH}_2$ (51), $r\mathrm{CH}_2$ (20), $r\mathrm{SiH}_2$ (23)
677	676 sh m	684 s		685 A′		νC-Cl (53), νC-Si (41)
671 m	668 sh m	—			686	νC-Si (48), νC-Cl (36)
667	664 s	657 s	664 s	640 A′		νC-Si (47), νC-Cl (33)
	638 vw	—	638 w		645	νC-Si (37), $r\mathrm{SiH}_2$ (23)
575 sh vw						
567 sh vw	567 vw					
546 sh		534 sh s		536 A′		νSi-Cl (95)
539 s	528 b s	527	528 s		514	νSi-Cl (89)
535	521 sh s	512 s	517 s	511 A″		$r\mathrm{SiH}_2$ (42), $r\mathrm{CH}_2$ (32)
					500	$r\mathrm{SiH}_2$ (50), νC-Cl (35)
	247 vw	—	245 w		253	δClCSi (55), δClSiC (28)
	217 vvw		212 s	205 A′		δClSiC (31), δClCSi (27)
	162 b vvw		160 w		161	δClSiC (43), δClCSi (20), τ (24)
	138 b vw			134 A′		δClCSi (52), δClSiC (46)
	84 b vvw		92 vw ?	92 A″		τ (87)
			78 vw		78	τ (56), δClCSi (21), δClSiC (20)
			$\mathrm{ClCH_2SiD_2Cl}$			
	2998 vw	3000 vw	2997 mw	2998 A″	2998	$\nu_a\mathrm{CH}_2$ (100)
			2988 mw			
2962 m 2953	2947 m	2947 vw	2947 s	2945 A′		$\nu_s\mathrm{CH}_2$ (100)
2935 sh w	2936 m	—	2937 s		2945	$\nu_s\mathrm{CH}_2$ (100)
1627						
1623 s	1618 s	1630 s	1619 m	1604 A″	1604	$\nu_a\mathrm{SiD}_2$ (100)
1616						
1605 s						
1594 s	1591 s	1602 s	1591 vs	1588 A′	1587	$\nu\mathrm{SiD}_2$ (100)
1584			1563 w			
1408						
1404 m	1394 m	1395 m	1394 w	1396 A′		$s\mathrm{CH}_2$ (92)
1398	1391 m	—	1391 w		1396	$s\mathrm{CH}_2$ (92)
1179						
1177 w	1178 sh m	—	1178 w		1159	$w\mathrm{CH}_2$ (100)
1168	1172 m	1169 m	1173 w	1156 A′		$\omega\mathrm{CH}_2$ (100)
1110						
1104 vw	1103 w	—	1104 w		1114	$t\mathrm{CH}_2$ (84)
1099	1084 b w	1089 w	1094 w	1114 A″		$t\mathrm{CH}_2$ (85)

Table 1. Continued

Infrared			Raman Liquid Int.	Calculated		P. E. D.[b]
Gas Int.	Liquid Int.	Crystal Iint.		T form	G form	
1059 1052 vw 1048						
	856 w	859 vw				
844 b mw	839 w					
824 mw 815	822 sh w					
			777 mw			
774 s	768 s	767 s 762	767 mw	785 A″		rCH$_2$ (79)
765 759 s 753	753 s	—	754 sh w		778	rCH$_2$ (71), wSiD$_2$ (16)
703					703	νC-Cl (48), νC-Si (21), sSiD$_2$ (28)
699 s	688 s	675 s	688 m	714 A′		νC-Si (32), νC-Cl (32), wSiD$_2$ (30)
					681	sSiD$_2$ (67), νC-Cl (26)
692	679 sh	671	681 m	700 A′		sSiD$_2$ (77)
					676	νC-Si (48), sSiD$_2$ (38)
672 s 663	663 s	659 s	663 s	637 A′		νC-Cl (58), wSiD$_2$ (32)
640 635 vs 630	623 vs	618 vs	629 sh w	618 A′		ωSiD$_2$ (32), νC-Si (42), sSiD$_2$ (16)
567 m	567 m	—	568 mw		596	wSiD$_2$ (48), νC-Si (18), rCH$_2$ (11)
		552 vw				
530 525 s	516 m	517 m	517 vvs	523 A′		νSi-Cl (88)
521		512			509	νSi-Cl (39), tSiD$_2$ (47)
		500 w	500 sh s	502 A″		tSiD$_2$ (74)
					504	tSiD$_2$ (30), νSi-Cl (52)
442 436 m 431	434 m	—	434 mw		412	rSiD$_2$ (66), νC-Cl (22)
403 w	405 w	405 m	405 w	407 A″		rSiD$_2$ (54), tSiD$_2$ (18)
	238 vw	—	239 mw		246	δClCSi (58), δClSiC (23)
	214 vvw		212 s	204 A′		δClSiC (28), δClCSi (28)
	150 b vvw		150 w		151	δClSiC (53), δClCSi (20), τ (32)
	130 b vw		129 vw	132 A′		δClCSi (52), δClSiC (47)
	92 b vvw ?			91 A″		τ (88)
	78 b vvw ?				78	τ (58), δClCSi (20)

a) Int.=intensity; s, m, w=strong, medium, weak; v=very; b=broad; sh=shoulder; T=the *trans* isomer; G=the *gauche* isomer; A′, A″=A′ symmetry species, A″ symmetry species; P.E.D.=potential energy distributions; and ν, s, w, t, r, δ, τ=stretching, scissoring, wagging, twisting, rocking, deformation, torsion. b) Only contributions greater than 20% are included.

chloromethylsilane.[13] Figure 7 shows the dependence of the calculated skeletal frequencies for a different azimuthal angle, where the highest-frequency band observed vanishes in the crystalline state. If this substance had a staggered configuration, the isomer disappearing in the crystalline state would be the *gauche* form, though the calculated frequencies do not satisfactorily reproduce the observed frequencies. Therefore, the previous conclusion of the molecular form determined from the product rule is confirmed.

Solvent Effects of the Spectra. The solvent effects of the infrared spectra are measured using the pair band assigned to the SiD_2 rocking vibrations at 434 and 405 cm^{-1}, where the former disappears in the crystalline state. The band at 434 cm^{-1} increases in its relative intensity when it is mixed with a polar solvent such as acetonitrile, while the band at 405 cm^{-1} increases in its relative intensity in a mixture with a non-polar solvent such as *n*-hexane, as is shown in Fig. 8. Therefore, it can be concluded that the isomer persisting in the crystalline state (the *trans* form) is less polar than the other (the *gauche* form).

On the basis of these results, if the C–Cl bond moment is assumed to have the direction of C^+–Cl^-, the group moment of the $CSiH_2(-D_2)Cl$ group should be mainly in the direction of Si^+–Cl^-, though it has been reported that, for (chloromethyl)methylsilane,[5] the group moment of the C_2SiH_2 group is $+{}^{C}_{C}\!>\!Si\!<\!{}^{H}_{H}-$ on the bisector of the C–Si–C angle. Therefore, the bond moment of SiCl may be larger than the group moment of C_2SiH_2.

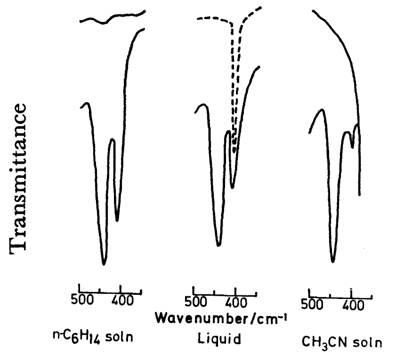

Fig. 8. Solvent effects of the infrared spectra.

Normal Vibration Calculation. The normal vibrations of chloro(chloromethyl)silane were calculated in order to get a reliable set of force constants. The bond lengths and angles used were of the same values used in the calculation of the moments of inertia.

First, we attempted to determine the force constants in the modified Urey-Bradley force field for (chloromethyl)silane[12] and chloromethylsilane[13] and their deuterated species, $ClCH_2SiD_3$ and CH_3SiD_2Cl, in order to get a set of transferable force constants. Second, we tested it for the case of this substance and found that, among the calculated frequencies, the skeletal vibrational frequencies were not in good agreement with the observed frequencies especially. Therefore, the force constants were adjusted by a least-squares method in order to predict well the observed frequencies for both the *trans* and *gauche* forms of the parent and its deuterated species as the assumption that the repulsion force constants were transferable. Modifications of the force field were also made as follows: 1) the bond interaction force constant, p(C–H), was introduced in order to reproduce the observed C–H stretching frequencies and 2) the *trans* coupling constants, $t(CH_2, SiH_2)$, t(SiCCl, SiH_2), and t(CSiCl, SiCCl) were introduced in order to reproduce satisfactorily the observed frequencies of the CH_2 and SiH_2 groups and the skeletal deformation frequencies, where the *gauche* couplings were assumed to be $g=-0.5t$. As a fair agreement was obtained between the observed and calculated frequencies, no further adjustments of the force constants were made.

The calculated frequencies are given in Table 1, together with the predominant internal symmetry coordinates in the potential energy distributions. The force constants obtained are given in Table 2, together

TABLE 2. FORCE CONSTANTS FOR CHLORO(CHLOROMETHYL)SILANE[a]

Force const.	$ClCH_2SiH_2Cl$	$ClCH_2SiH_3$[b]	CH_3SiH_2Cl[c]	Force const.	$ClCH_2SiH_2Cl$	$ClCH_2SiH_3$[b]	CH_3SiH_2Cl[c]
K(C-H)	4.393	4.390	4.453	$\kappa(CH_2)$	0.024	0.027	−0.008
K(Si-H)	2.607	2.638	2.565	$\kappa(SiH_2)$	0.138	0.056	0.112
K(C-Cl)	1.510	1.697		Y(C-Si)	0.130	0.080	
K(C-Si)	1.580	1.991	2.393	$t(CH_2, SiH_2)$[d]	0.086	0.081	0.067
K(Si-Cl)	2.205		2.272	$t(SiH_2$, SiCCl)[d]	−0.107	0.032	
p(C-H)	−0.098	—	−0.082	t(CSiCl, SiCCl)[d]	0.178		
H(Si-C-H)	0.103	0.104	0.123	F(Si·C·H)	0.271	0.271	0.271
H(Cl-C-H)	0.147	0.147		F(Cl·C·H)	0.558	0.558	
H(H-C-H)	0.331	0.349	0.353	F(H·C·H)	0.200	0.200	0.200
H(Si-C-Cl)	0.071	0.093		F(Si·C·Cl)	0.210	0.210	
H(Cl-Si-H)	0.077		0.077	F(Cl·Si·H)	0.243		0.243
H(C-Si-H)	0.101	0.113	0.102	F(C·Si·H)	0.149	0.149	0.149
H(H-Si-H)	0.170	0.170	0.170	F(H·Si·H)	0.041	0.041	0.041
H(C-Si-Cl)	0.096		0.117	F(C·Si·Cl)	0.160		0.160

a) The units of the force constants are in md/Å for stretching, K; bending, H; repulsion, and F; bond interaction, p; and in md·Å for intramolecular tension, κ; and *trans* coupling, t. b) Ref. 12. c) Ref. 13. d) The *gauche* coupling constants are assumed to be $g=-0.5\,t$.

with those of (chloromethyl)silane and chloromethylsilane. The values of the adjusted force constants, except for these of the skeleton, are similar to those of such analogues as (chloromethyl)silane and chloromethylsilane; under the repulsion-force constants we fixed the transferred values. However, all the values of the skeletal stretching constants are considerably smaller than those of the analogues. It is interesting to note that the higher-frequency band for the SiH_2 wagging vibration and the lower-frequency band for the SiD_2 wagging vibration vanish in the crystalline state. The potential energy distributions indicate that this is mainly due to the coupling with the CH_2 rocking vibration in the 750—820 cm^{-1} region. The tendency of the $SiH_2(-D_2)$ wagging and SiD_2 rocking vibrations between the liquid and crystalline states is the same as those of (chloromethyl)methylsilane and ethylmethylsilane.[5]

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