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Vibrational assignments and torsional barrier heights of some methylsilylchlorides

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The infrared spectra of gaseous chloromethyl-, dichloromethyl-, and methyldichlorosilane have been obtained from 4000 to 33 cm⁻¹ and the far infrared spectrum of gaseous methylchlorosilane has been recorded from 350 to 33 cm⁻¹. The far infrared spectrum of the low temperature solids $(-190^{\circ}C)$ have also been recorded from 350 to 33 cm⁻¹. The Raman spectra of the liquids have been measured, with quantitative depolarization ratios, from 4000 to 100 cm⁻¹. Assignments for all of the fundamentals for each of the molecules are proposed on the basis of depolarization ratios, band contours, and group frequencies. The bands corresponding to the torsional modes are assigned as appearing at 172, 177, 175, and 184 cm⁻¹ in the infrared spectra of the solids and give corresponding barriers of 3.00, 3.69, 2.25 and 2.09 kcal/mole for chloromethyl-, dichloromethyl-, metylchloro-, and methyldichlorosilane, respectively. The results are discussed in terms of present theory.

I. INTRODUCTION

There have appeared in the literature numerous attempts to predict torsional barriers utilizing both semiempirical¹⁻⁻⁶ and quantum mechanical approaches.⁷⁻¹³ The quantum mechanical calculations, particularly those utilizing the self-consistent field approach, have often led to surprisingly good results when compared to experiment. However, because of the very nature of SCF-MO calculations, the results do not readily lend themselves to discussion in more classical terms, such as electronegativity and induction effects. For the localized MO calculations the errors in the total energy are sometimes several times greater than the energy associated with the torsion, making analysis based on these results somewhat questionable. Of the functions developed utilizing the more empirical approach, some have been shown to give reasonably good correlation to the barriers in a number of molecules^{1,2}; however, they have consistently predicted barriers which are too low for those molecules containing chlorine atoms.

It has been shown that chlorine and bromine have an appreciable effect on the barrier to internal rotation¹⁴⁻¹⁶; therefore, it would seem that a study of molecules containing these atoms would serve as a critical test for those theories already developed and might lead to suggestions as to modifications which are necessary to improve these formulations.

It is generally agreed that the microwave splitting technique offers the greatest accuracy available for the determination of barrier heights for those molecules for which this technique is applicable. Because of the complexities created by quadrupole coupling, however, molecules containing multichlorine or bromine atoms are not readily analyzed by this technique. Torsional transitions have been directly observed in the far infrared spectrum of the gas^{16–18}; however, because of the anharmonicity associated with these vibrations and their inherent low intensity, their observation in the fluid states is usually difficult. Also, in molecules which contain multiple halogen substitution, the broad intense bands associated with the bending modes often obscure the torsional modes. These problems are often eliminated by going to the low temperature solid since the $0 \rightarrow 1$ transition of the torsion becomes more pronounced and there is a general sharpening of all the low frequency bands. We have thus utilized this technique in a study of the torsional oscillations in chloromethyl-, dichloromethyl-, methylchloro-, and methyldichlorosilane. These molecules were studied to demonstrate the effect of chlorine substitution on the barriers of these molecules relative to methylsilane and the effect of the longer C-Si bond distance on the nonbonded interactions of these molecules relative to the chloroethanes.

II. EXPERIMENTAL SECTION

The sample of CH_3SiHCl_2 was purchased from Pierce Chemical Company and contained the usual siloxane and HCl impurities. The siloxane was removed by trap to trap distillation of the CH_3SiHCl_2 from a dry iceethanol bath to a trap cooled by liquid nitrogen. The HCl was then removed by pumping on the CH_3SiHCl_2 trap, which was cooled by a *n*-pentane slush (-131°C).

The CH₃SiH₂Cl was prepared by the diisobutyl aluminum hydride reduction of CH₃SiHCl₂. In the preparation, 9.5 g of diisobutyl aluminum hydride were placed in an addition funnel with 200 ml of di-*n*-butyl ether. Approximately 5 g of CH₃SiHCl₂ were contained in a 500 ml flask, which was connected through two traps to a vacuum system. The first trap was cooled by dry ice-ethanol and the second by liquid nitrogen. Before the addition was begun, the system was purged with dry nitrogen, the reaction flask cooled with an ice-ethanol mixture ($\sim -10^{\circ}$ C) and finally the system was pumped to a pressure of 200 mm Hg. The diisobutyl aluminum hydride was then added over a period of two



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FIG. 1. Far infrared spectra of CH_3SiH_2Cl . A. Generalized background absorption. B. Far infrared spectrum of gaseous CH_3SiH_2Cl ; path length—6.4 m, pressure—4 torr. C. Far infrared spectrum of gaseous CH_3SiH_2Cl ; path length—8.2 m, pressure—38 torr. D. Generalized background absorption. E, F. Far infrared spectrum of solid CH_3SiH_2Cl with additional sample deposit. Abscissa in arbitrary units of absorption.

hours. When the addition was completed the reaction flask was allowed to warm to room temperature and the remaining product collected. The product collected in the dry ice-ethanol trap was then purified on a low temperature sublimation column. The CH₃SiH₂Cl was collected at a temperature of -110° C and a pressure of 280 μ of Hg. 2 ml of pure sample were collected giving a reaction yield of approximately 60%. The vapor pressure of the collected sample was checked against the published data.¹⁹

Methylsilane was prepared by trapping methyldichlorosilane into a vessel containing a 3.5M solution of LiAlH₄ in diethylether. A 10% excess of LiAlH₄ was used. The system was allowed to warm to room temperature and the methylsilane was trapped as it was formed. The collection trap was then cooled with an isopentane slush (-161°C) and pure methylsilane was pumped into a trap cooled with liquid N₂. The unreacted CH₃SiHCl₂ was then trapped back into the reaction flask and the procedure repeated. The yield was essentially quantitative.

The CH₂ClSiH₃ and CHCl₂SiH₃ were prepared by the LiAlH₄ reduction of CH₂ClSiCl₃ and CHCl₂SiCl₃, respectively.²⁰ Both compounds were purified using a low temperature sublimation column. The CH₂ClSiH₃ was collected at -90° C and a pressure of 260 μ of Hg, and the CHCl₂SiH₈ was collected at -73° C and a pressure of 170 μ Hg. Vapor pressures of the collected samples were checked against the literature values.²⁰

Because of the high sensitivity to moisture of the methylchloro- and methyldichlorosilane, special care was taken in handling these compounds. All sample manipulations were carried out in a high vacuum system which contained no greased stopcocks or joints. The low temperature distillations were carried out on a 5 ft sublimation column, which was cooled by liquid nitrogen boil off. The pressures were monitored during the distillations via a thermocouple pressure gauge mounted at the top of the column at the take-off point.

The infrared spectra of the gases were recorded from 4000 to 250 cm⁻¹ on a Perkin-Elmer Model 621 spectrophotometer, which was continuously purged with dry air. The instrument was calibrated using standard gases.²¹ Spectra of the sample vapors were recorded using a 20 cm-path cell equipped with CsBr windows.

The far-infrared spectra were recorded from 33 to 350 cm^{-1} with a Beckman Model IR-11 spectrophotometer, which was flushed with dry air. The instrument was calibrated using atmospheric water vapor.²² Spectra of the gases were obtained utilizing a Beckman 10 m multipass cell. Spectra of the solids were obtained using a low temperature cell, which has been described previously.²³ A thermocouple mounted on the sample block was used to monitor the temperature. The samples were deposited on a wedged optically polished silicon substrate utilizing conventional vacuum deposition techniques. After deposition the samples were annealed until no further changes occurred in the spectra. All infrared frequencies are expected to be accurate to $\pm 1 \text{ cm}^{-1}$.

The Raman spectra were recorded on a Cary Model 81 Raman spectrophotometer equipped with a Spectra-Physics helium-neon laser which has an excitation wavelength of 6328 Å. Depolarization ratios were obtained using a Spex Ramalogin spectrophotometer. The liquid samples were sealed in vacuo in Pyrex capillaries. Raman frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$.

III. RESULTS

A. Methylchlorosilane (CH_3SiH_2Cl)

Assignments for the fundamental vibrations of methylchlorosilane have been previously proposed on the basis of the infrared spectrum (4000 to 400 cm⁻¹ prism resolution) of the gas.²⁴ However, there has not appeared in the literature any report of Raman data for this molecule. Also because of instrumental limits, there was no assignment proposed for the skeletal deformation nor the methyl torsion in the previous study.

The far-infrared spectra of gaseous and solid CH_3SiH_2Cl are shown in Fig. 1 and the Raman spec-





trum of the liquid in Fig. 2. The Raman data are essentially in agreement with the assignments of Ebsworth et al.24 except that there appears in the Raman spectrum only one band in the 900 cm^{-1} region. This depolarized band corresponds to the 912 cm⁻¹ infrared band and is assigned as the antisymmetric CH3 rock. The symmetric CH3 rock is assigned, as did Ebsworth et al.,²⁴ to the band at 870 cm⁻¹. A rather strong polarized Raman line occurs at 700 cm⁻¹ that has no infrared counterpart. This band is assigned as the SiH₂ wag. This assignment seems to be preferable to that proposed by Ebsworth et al.²⁴ in that the relative frequencies of the other SiH₂ bending modes are more compatible with this assignment. Both the infrared and Raman data support our assignment for this normal mode (see Tables I and II).

The skeletal deformation appears as a *B*-type band in the infrared spectrum of the gas at 212 cm⁻¹ and as a polarized Raman line also at 212 cm⁻¹. The methyl torsion gives rise to two weak *Q* branches at 165 (0 \rightarrow 1) and 147 (1 \rightarrow 2) cm⁻¹. With an *F* value of 5.58 cm⁻¹, a barrier of 1.84 kcal/mole is calculated for the torsional motion for both the 0 \rightarrow 1 and 1 \rightarrow 2 transitions. This indicates that the assumption, that the V₆ and higher order terms are negligible, is a valid one. The torsion occurs in the solid at 184 cm^{-1} . This frequency leads to a calculated barrier of 2.25 kcal/mole, which indicates that there must be an appreciable intermolecular perturbation of the torsional potential in the crystalline state.

B. Methyldichlorosilane (CH₃SiHCl₂)

Two papers have appeared in the literature in which Raman data are reported for methyldichlorosilane.^{25,26} However, a number of normal vibrations are not assigned and it was felt that a more unambiguous assignment of all the fundamentals might be made with both the infrared and Raman data. Like the other molecules of this study, the only possible element of symmetry is a reflection plane; therefore the molecular symmetry must be either C_s or C_1 . Our assignments are made assuming C_s symmetry. For C_s symmetry there will be 11 A' fundamentals, which will appear as polarized Raman lines and should appear in the gas phase infrared as mixed B-C hybrids. There will also be 7 A'' modes, which should be depolarized in the Raman and have pure A type contours in the infrared spectrum of the gas.

The infrared spectrum of methyl dichlorosilane vapor is shown in Fig. 3 and the Raman spectrum of the

| Gas | | Solid | | | Raman | | |
|--|--------------|-----------------------|--------------|-----------------------------------|------------------------|-----------------|---------------------------------------|
| ν (cm ⁻¹) | Rel. int. | ₩ (cm ⁻¹) | Rel. int. | $\Delta \nu \ (\mathrm{cm}^{-1})$ | Liquid Rel. int. | Depol. ratio | Assignment |
| 252 <i>R</i> 246 <i>Q</i> 239 <i>P</i> | W | | | | | | $\nu_8 - \nu_{17} = 241$ |
| 213 R 198 P | w | 212 | w | 212 | m | 0.63 | r11, CSiCl deformation |
| 165 $(0 \rightarrow 1) Q$ 147 $(1 \rightarrow 2) Q$ | vw | 184 82 | w m | | | | v18, CH3 torsion Lattice vibration |

TABLE I. Far infrared and low frequency Raman data and assignments for methylchlorosilane.

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| Frequency | Rel. int. | Depol. ratio | Assignment |
|--------------|--------------|-----------------|---|
| 2973 | 10 | 0.72 | v1 and v12, CH3 antisymmetric stretches |
| 2909 | 81 | 0.02 | v ₂ , CH ₃ symmetric stretch |
| 2184 | 100 | 0.06 | v3 and v13, SiH2 stretches |
| 1444 | <1 | ? | v4, CH3 antisymmetric deformation |
| 1413 | 1 | 0.72 | ν14, CH3 antisymmetric deformation |
| 1259 | 2 | <0.01 | v5, CH3 symmetric deforma- tion |
| 956 | <1 | 0.73 | ν_6 , SiH ₂ deformation |
| 900 | <1 | 0.75 | P15, CH3 antisymmetric rock |
| 870 | <1 | 0.75 | ₽7, CH ₃ symmetric rock |
| 748 | 7 | 0.07 | v ₈ , Si–C stretch |
| 700 | 5 | 0.38 | ν_9 , SiH ₂ wag |
| 685 | <1 | ? | v16, SiH2 twist |
| 527 * | | | v17, SiH2 rock |
| 508 | 10 | 0.12 | v10, SiCl stretch |
| 212 | 2 | 0.63 | ν_{11} , CSiCl deformation |

TABLE II. Raman frequencies and assignments for methylchlorosilane.

* Taken from the infrared data of Ref. 24.

liquid in Fig. 4. The observed frequencies and their assignments are given in Table III. The A' and A'' antisymmetric C-H stretches are, as expected, degenerate and appear in the Raman as a depolarized Raman line at 2981 cm⁻¹. The symmetric C-H stretch gives rise to a polarized Raman line at 2912 cm⁻¹ and an infrared band of no discernible contour centered at 2917 cm⁻¹. The SiH stretch appears as a very strong Raman line at 2216 cm⁻¹ and in the infrared as a mixed B-C hybrid centered at 2222 cm⁻¹.

Under the local C_{3v} symmetry of the methyl group the A' and A'' antisymmetric CH₃ deformations correspond to a degenerate E mode and are not greatly affected by any over-all molecular asymmetry. Thus, these two modes are assigned as being accidentally degenerate and correspond to the Raman line appearing at 1396 cm⁻¹ and the infrared band at 1400 cm⁻¹. The symmetric CH₃ deformation gives rise to an infrared band centered at 1267 $\rm cm^{-1}$ with a *B*-type envelope and a strongly polarized Raman line at 1261 cm⁻¹. The methyl rocks also correspond to an E mode under C_{3v} (top) symmetry; however, they are usually split by a lower molecular symmetry. The bands, appearing at 884 and 839 cm⁻¹ in the Raman spectrum of the liquid and centered at 884 and 841 cm⁻¹ in the infrared spectrum of the vapor, have very similar intensities in both the infrared and Raman spectra and have exactly the same depolarization ratios. The band centered at 884 cm^{-1} , however, has a *B*-type envelope and on this basis is assigned to the A' CH₃ rocking motion. The A-type band with the Q branch occurring at 841 cm^{-1} is then assigned to the A'' rock.

The C–Si stretch gives rise to a rather strong Raman line at 785 cm⁻¹ and an intense infrared band at 755 cm⁻¹. This corresponds very nicely with the frequency of 751 cm⁻¹ found by Ebsworth and co-workers for the corresponding mode in methylchlorosilane.²⁴ The shoulder appearing in the Raman spectrum at 744 cm⁻¹ is assigned as the in-plane SiH bend. These assignments may be reversed; however, because of the proximity of the bands, there is probably a considerable mixing of these two normal modes and their distinction may be rather moot. The out-of-plane SiH bending occurs as a depolarized Raman line at 683 cm⁻¹.

As expected the SiCl stretches give rise to relatively strong bands in the infrared spectrum. The infrared band centered at 568 cm⁻¹, which corresponds to the depolarized Raman line at 554 cm⁻¹, is assigned as the antisymmetric SiCl stretch. The symmetric SiCl stretch corresponds to the 501 cm⁻¹ infrared band and the intense, strongly polarized Raman line at 485 cm⁻¹. It is worth noting that both the 568 and 501 cm⁻¹ bands appearing in the infrared spectrum of the gas show an appreciable shift to lower frequency (14 and 16 cm⁻¹) on condensation. These large shifts are attributed to association in the liquid phase.

In the vibrational assignment of 1,1-dichloroethane, the deformation was assigned as occurring at the highest frequency of the CCl₂ bending modes.²⁷ By analogy the SiCl₂ deformation is assigned to the polarized Raman line at 252 cm⁻¹. The depolarized Raman line at 198 cm⁻¹ corresponds to the 204 cm⁻¹ band in the infrared spectrum of the gas and is assigned to the SiCl₂ wag. The remaining bending mode, the SiCl₂ rock appears as a *B*-type band centered at 181 cm⁻¹ in the infrared spectrum of the gas.

The far infrared spectrum of solid methyldichlorosilane is shown in Fig. 5. Of the four bands occurring outside the lattice region only the band at 173 cm^{-1} does not have a Raman counterpart. Torsional oscillations almost never appear in the Raman spectrum and on this basis the 173 cm⁻¹ band is thought to arise from the methyl torsion. It should be pointed out, because of the proximity of the 173 cm^{-1} band in the infrared spectrum of the solid to the band appearing at 180 cm⁻¹ in the Raman spectrum of the liquid, that the bands corresponding to skeletal bendings and methyl torsions generally shift to higher frequency on solidification. Because of this, the 180 cm⁻¹ Raman line most certainly corresponds to the 188 cm⁻¹ band in the infrared spectrum of the solid. The two bands appearing in the far infrared spectrum of the solid at 95 and 71 cm⁻¹ are assigned as lattice vibrations; however, in the absence of data on isotopic species, it cannot be ascertained whether these bands correspond to translational or librational motions. Because of the appearance of these two medium intensity low frequency bands, it is possible that the 173 cm^{-1} band, assigned as the torsion, could actually correspond to a two phonon process involving the lattice modes. In the absence of any

| Infrared | | | | Raman | | |
|-----------------------|-------------|------|------------------------|--------|------|--|
| | Gas | | Liquid | | | |
| (-1) | Band | Rel. | | Depol. | Rel. | |
| ν (cm ⁻¹) | type | int. | Δν (cm ⁻¹) | ratio | int. | Assignment |
| 2978 R | A | m | 2981 | 0.75 | 31 | \$\nu_1\$ and \$\nu_{12}\$, CH\$ antisymmetric stretches |
| 2984 Q 2080 P | | | | | | |
| 2989 P 2917 ctr | ? | w | 2912 | 0.15 | 100 | v. CH ₂ symmetric stretch |
| 1016 B | РС | _ | 0016 | 0.10 | | |
| 2220 R 2219 P | <i>B</i> -C | S | 2210 | 0.10 | 00 | v ₃ , SIH stretch |
| 1508 R | A | w | | | | $2 \times 755 = 1510$ |
| 1500 Q | | | | | | |
| 1494 P | | | | | | |
| 1410 R | A | m | 1396 | 0.76 | 6 | v_4 and v_{13} , CH ₂ antisymmetric |
| 1400 Q | | | | | - | deformations |
| 1394 P | | | | | | |
| 1271 R | В | s | 1261 | 0 | 3 | v5. CH ₂ symmetric deformation |
| 1263 P | | | | | - | •••• |
| 937 ctr | ? | m | | | | 185+755=940 |
| 891 R | В | s | 884 | 0.76 | 3 | ve. CHa symmetric rock |
| 882 P | | | | | | |
| 850 <i>R</i> | A | e | 830 | 0 76 | 2 | . CH. antigurgmetric rock |
| 841 Q | | 5 | | 0.70 | 2 | M, CHI anusymmetric rock |
| 836 P | | | | | | |
| 758 R | | | | | | |
| 750 O | ? | s | 758 | 0.28 | 15 | w C-Sistretch |
| 746 P | - | 2 | 744 sh | ? | 11 | vs. SiH in-plane bend |
| 690 Q | ? | m | | | | 180 + 501 = 682 fermi |
| 680 Q | ? | m | 683 | 0.74 | 6 | v15, SiH, out-of-plane bend |
| 619 ctr | 5 | w | | | | 2×755-886=624 |
| 568 ctr | A | s | 554 | 0.74 | 4 | 16, Si-Cl antisymmetric stretch |
| 501 Q | С | S | 487 | 0.03 | 48 | v9, Si–Cl symmetric stretch |
| 254 ctr (258) | ? | m | 252 | 0.42 | 7 | 110, SiCl2 deformation |
| 204 ctr (206) | ? | w | 198 | 0.76 | 8 | v17, SiCl ₂ wag |
| 186 R (188) 176 P | В | m | 180 | 0.70 | 11 | v11, SiCl ₂ rock |
| (173) | | w | | | | P18, CH3 torsion |
| (95) | | m | | | | Lattice vibration |
| (71) | | m | | | | Lattice vibration |

TABLE III. Assignment of the observed infrared and Raman frequencies for methyldichlorosilane.*

^a Abbreviations: w=weak, m=medium, s=strong, ctr=band center, sh=shoulder.

^b () indicates frequencies taken from the solid state $(-190^{\circ}C)$.

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FIG. 3. Infrared spectrum of gaseous CH₂SiHCl₂; path length—20 cm, pressure—3 torr. Abscissa in arbitrary units of absorption.

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knowledge of the dispersion curve, this is, however, somewhat speculative. Also, on performing a variable temperature study, the intensity and bandwidth of the lattice bands showed a considerably higher temperature dependence than did the 173 cm⁻¹ band and it is, thus, believed to be due to the torsional mode. With the assignment of the 173 cm⁻¹ band as the torsion and with an F value of 5.32 cm⁻¹, calculated from the assumed structural parameters of Table IV, the barrier height is calculated to be 2.09 kcal/mole. This compares with a value of 2.90 kcal/mole determined from heat capacity measurements.³¹ Since it has been found previously that the torsion always shifts to higher frequency on solidification, the barrier determined herein is an upper limit; thus, the barrier determined by the thermodynamic method is in error.

C. Chloromethylsilane (CH₂ClSiH₃)

There has previously appeared a paper in which assignments were proposed for most of the fundamentals of chloromethylsilane³²; however, the treatment was rather cursory and incomplete. Because of this we propose an assignment of all the fundamentals of this molecule on the basis of both the infrared and Raman data. The infrared spectrum of the gas is shown in Fig. 6 and the Raman spectrum of the liquid in Fig. 7. Again the molecular symmetry is assumed to be C_s , thus giving rise to 7 A'' and 11 A' modes.

The antisymmetric CH₂ stretch gives rise to a depolarized Raman line at 2989 cm⁻¹ and a band of C contour centered at 2994 cm⁻¹ in the infrared spectrum

of the gas. The infrared band corresponding to the CH₂ symmetric stretch is a *B*-type envelope with a central Q branch at 2952 cm⁻¹. The A' and A'' antisymmetric SiH₃ stretches are expected to be nearly degenerate and are assigned to the *C*-type band occurring at 2198 cm⁻¹ in the infrared spectrum. The symmetric SiH₃ stretch corresponds to the strong infrared band at 2168 cm⁻¹ and the Raman counterpart at 2172 cm⁻¹. The 2172 cm⁻¹ band is the only Raman line appearing in this spectral region and does not appear to be asymmetric. Thus, the antisymmetric stretches either do not give rise to a Raman band of significant intensity or they become essentially degenerate with the symmetric stretch in the liquid (see Table V).

There are nine fundamentals that may be classified as hydrogen bends-four CH₂ and five SiH₃. The CH₂ deformation occurs in the infrared as a band of A contour at 1409 cm⁻¹. The CH₂ wag is assigned to the Btype infrared band centered at 1180 cm⁻¹. The depolarized Raman line at 1107 cm⁻¹ is assigned as arising from the CH_2 twist. The A and E deformations of the SiH₃ group in methylsilane are assigned as degenerate and occur at 945 cm^{-1.33} The molecular asymmetry of chloromethylsilane does not appreciably effect this degeneracy and these three SiH₃ deformations are assigned to the 936 cm⁻¹ Raman line and the infrared band centered at 925 cm⁻¹. The infrared band does show a slight shoulder on the high frequency side; however, this shoulder could not be clearly resolved. Thus the deformations are essentially degenerate. It should be noted that the 936 cm⁻¹ Raman line is depolarized



FIG. 4. Raman spectrum of liquid CH₃SiHCl₂. Abscissa in arbitrary units of scattering intensity.

FIG. 5. Far infrared spectra of CH₃-SiHCl₂ A. Typical background absorption. B. Far infrared spectrum of gaseous CH₃SiHCl₂; path length—8.2 m, pressure—5 torr. C. Far infrared spectrum of solid CH₃SiHCl₂. Abscissa in arbitrary units of absorption.



and may be due only to the antisymmetric deformations and the 925 cm⁻¹ infrared band, of apparent *B* contour, could then correspond to the symmetric mode. However, it seems unlikely that the antisymmetric mode would appear in the Raman and not the symmetric; conversely it is equally unlikely that the symmetric mode should appear in the infrared and not the antisymmetric mode. The prominent *Q* branch occurring in the infrared spectrum of the gas at 816 cm⁻¹ is assigned to the CH₂ rock. The SiH₃ rocks are split by the molecular asymmetry with the symmetric rock appearing in the infrared spectrum at 556 cm⁻¹ and the antisymmetric rock appearing as a shoulder at 508 cm⁻¹.

The C-Si stretch gives rise to the Raman line at 755 cm⁻¹ with an infrared counterpart at 753 cm⁻¹. Carbon-chlorine stretches generally occur between 700 and 750 cm⁻¹; thus, this mode is assigned to the 712 cm⁻¹ Raman line. The band corresponding to the C-Si-Cl deformation appears in the Raman spectrum as a polarized Raman line at 200 cm⁻¹ and in the infrared spectrum of the gas as a band of *B*-type contour centered at 192 cm⁻¹. The methyl torsion is then

assigned to the weak shoulder appearing in the infrared at 161 cm⁻¹. Again there is no corresponding band at this frequency in the Raman spectrum. In the far infrared spectrum of the solid the bands appearing at 128, 120, 95, 67, 61, and 52 cm⁻¹ are assigned as arising from lattice modes (see Fig. 8).

The barrier to internal rotation for chloromethylsilane has been previously determined from an analysis of the splittings produced by internal rotation on the rotational lines of the molecule in the first excited torsional state.³¹ The barrier determined in that study was 2.55 kcal/mole. This would indicate that the $0 \rightarrow 1$ torsional transition should occur in the far infrared spectrum of the gas at 159 cm⁻¹. The discrepancy of this value with the observed frequency of 161 cm⁻¹ may be due to an error in the frequency measurement but it is probably due, in part, to the fact that the microwave barrier was calculated from splittings observed in the torsional excited state. Using the Fvalue of 3.48 cm⁻¹ obtained in the microwave study²⁹ and the frequency of 161 cm⁻¹ the barrier is calculated to be 2.65 kcal/mole. The $1\rightarrow 2$ torsional transition is

| | _ | | | | | | | |
|------------------------------------|----------|-------|--------------|-------|---------------|------|----------------|--|
| | fсн | rcs i | 7 CC1 | ₹BiH | 7 8iCl | F | V ₃ | |
| CH₃SiH₂Cl | 1.093 | 1.889 | ••• | 1.485 | 2.050 | 5.58 | 1.84 | |
| CH ₈ SiHCl ₂ | 1.093 | 1.878 | ••• | 1.485 | 2.042 | 5.32 | 2.09° | |
| CH2ClSiH3 | 1.093 | 1.889 | 1.788 | 1.485 | ••• | 3.48 | 2.65 | |
| CHCl ₂ SiH ₃ | 1.093 | 1.878 | 1.779 | 1.485 | ••• | 2.95 | 3.69° | |

TABLE IV.ª Structural parameters and calculated barrier heights.^b

* Structural parameters assumed from CH₂SiH₃,²⁸ CH₂ClSiH₃,²⁹ and SiH₂Cl.⁵⁰

^b All angles assumed tetrahedral.

° Indicates barriers determined from frequencies observed in the spectra of the solids.

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TABLE V. Assignment of the observed infrared and Raman frequencies for chloromethylsilane.

| | Infrared | | | Raman | | |
|---|---------------------|--------------|------------------------------|---------------------------|--------------|--|
| ν (cm ⁻¹) | Gas Band type | Rel. int. | $\Delta \nu ~({ m cm}^{-1})$ | Liquid Depol. ratio | Rel. int. | Assignment |
| 3120 ctr | ? | w | | | | 2198+925=3123 |
| 2994 Q | С | m | 2989 | 0.73 | 5 | v_{12} , CH ₂ antisymmetric stretch |
| 2960 <i>R</i> 2945 <i>P</i> | В | m | 2942 | 0.03 | 47 | v1, CH2 symmetric stretch |
| 2799 | ? | w | L. | | | $2 \times 1409 = 2818$ |
| 2198 Q | С | m | | | | \$\nu_2\$ and \$\nu_{13}\$, SiH_3\$ antisymmetric stretches |
| 2176 <i>R</i> 2168 <i>Q</i> 2162 <i>P</i> | А-В | S | 2172 | 0.07 | 100 | r3, SiH2 symmetric stretch |
| 1632 ctr | ? | w | | | | 2×816=1632 |
| 1416 <i>R</i> 1409 <i>Q</i> 1402 <i>P</i> | A | m | 1402 | 0.57 | 2 | <i>v</i> ₄ , CH ₂ symmetric deformation |
| 1328 <i>R</i> 1315 <i>P</i> | В | w | | | | 1109+210=1319 |
| 1278 <i>R</i> 1265 <i>P</i> | А-В | w | | | | 716+556=1272 |
| 1187 <i>R</i> 1173 <i>P</i> | В | w | 1178 | 0.07 | 2 | 15, CH2 wag |
| 1109 Q | С | m | 1107 | 0.78 | 1 | 14, CH2 twist |
| 930 <i>R</i> 920 <i>P</i> | В | S | 936 | 0.76 | 6 | ν_6 , ν_7 , and ν_{15} , SiH ₃ deformations |
| 816 Q | С | m | 810 | ? | <0.1 | v16, CH2 rock |
| 753 sh | ? | w-m | 755 | 0.63 | 4 | v8, C–Si stretch |
| 724 R or Q 711 P | A-B | m | 712 | 0.04 | 6 | v9, Si–Cl stretch |
| 564 R 548 P | В | S | 550 | 0.10 | 13 | ν10, SiH3 symmetric rock |
| 508 Q | С | m | | | | v17, SiH2 antisymmetric rock |
| 199 R (213) 184 P (208) | В | S | 200 | 0.24 | 1 | ν_{11} , Cl–C–Si deformation |
| $\begin{array}{c} 161 \ Q \ Q \rightarrow 1 \\ 152 \ Q \ 1 \rightarrow 2 \end{array}$ | С | w | | | | 128, SiH3 torsion |
| (128) | | m | | | | lattice vibration |
| (120) | | m | | | | lattice vibration |
| (92) | | w | | | | lattice vibration |
| (67) | | w | | | | lattice vibration |
| (61) | | w | | | | lattice vibration |
| (52) | | w | | | | lattice vibration |

* Abbreviations: See Table III.

^b () indicates frequencies taken from the solid state $(-190^{\circ}C)$.

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FIG. 6. Infrared spectrum of gaseous CH_2ClSiH_3 ; path length—20 cm, pressure—2 torr with insert—60 torr. Abscissa in arbitrary units of absorption.

observed for this system at 152 cm⁻¹ and again the agreement between the barriers calculated from the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions supports the neglect of the higher order terms in the potential energy expression. It is seen from Table VII that on going to the solid the torsional frequency shifts to 172 cm⁻¹. Using this frequency, the barrier in the solid is calculated to be 3.00 kcal/mole. Because there are six lattice frequencies observed, there is obviously more than one molecule per unit cell. This is also evidenced by the fact that the ClCSi deformation is split into a doublet in the solid with frequencies of 213 and 208 cm⁻¹. Because of the 11 cm⁻¹ shift in the torsional frequency on going from the gas to the solid and the 5 cm^{-1} correlation field splitting observed for the skeletal deformation, it is obvious that there is appreciable intermolecular interaction. In a previous study of the halogenated ethanes,15 it was shown that when factor group splitting was observed, there was a significant gas to solid shift in the frequency of the torsional mode. Thus, when factor group splitting is possible, a qualitative evaluation of the effect of intermolecular perturbation on the torsional potential may be made from the magnitude of the splitting.

D. Dichloromethylsilane (CHCl₂SiH₃)

Dichloromethylsilane has 18 internal fundamental vibrations and is assumed to have C_s symmetry. The A'' fundamentals in CHCl₂SiH₃ should give rise to infrared bands of *B*-type contour and the A' fundamentals should lead to bands of mixed A-C contour. The infrared spectra of the gas are shown in Figs. 9 and 10, and the Raman spectrum of the liquid in

Fig. 11. The observed frequencies and assignments are given in Table VI.

The CH stretch gives rise to an infrared band at 2990 cm⁻¹ and a Raman line at 2978 cm⁻¹. The symmetric SiH₃ stretch gives rise to an infrared band at 2215 cm⁻¹. The antisymmetric SiH₃ stretches are assigned to the infrared band centered at 2193 cm⁻¹. These assignments for the 3 SiH₃ stretches are made on the basis of the infrared band contours; however, it is noted that only one Raman line appears in this frequency region at 2183 cm⁻¹. Because of the intensity of this Raman line and its depolarization ratio it is felt that this band is mainly due to the symmetric SiH₃ stretches become degenerate and occur at 2183 cm⁻¹.

The out-of-plane CH bend gives rise to an infrared band of *B*-type contour centered at 1201 cm⁻¹ and a depolarized Raman line at 1197 cm⁻¹. The in-plane CH bend is assigned to the polarized Raman line at 1145 cm⁻¹. The symmetric SiH₃ deformation appears in the infrared as a *C*-type band at 942 cm⁻¹. The antisymmetric SiH₃ deformations are assigned as degenerate and occur in the infrared as a *B*-type band at 920 cm⁻¹.

The antisymmetric CCl_2 stretch occurs in the infrared spectrum of the gas at 807 cm⁻¹. In all the other molecules studied in this work, the C–Si stretch has occurred at ~750 cm⁻¹; thus, this mode is assigned in dichloromethylsilane to the band occurring at 745 cm⁻¹ in the Raman. These two assignments require that the CCl₂ antisymmetric stretch be assigned to an infrared band of inordinately low relative intensity and also require a rather large frequency separation between the A' and A'' CCl₂ stretches relative to the separation observed for the corresponding modes in 1,1-dichloroethane.



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FIG. 7. Raman spectrum of CH_2 -ClSiH₂ liquid. Abscissa in arbitrary units of scattering intensity.

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FIG. 8. Far infrared spectra of CH₂-ClSiH₈. A. Generalized background absorption. B. Far infrared spectrum of gaseous CH₂ClSiH₃; path length—4.6m, pressure—10 torr. C. Far infrared spectrum of gaseous CH₂ClSiH₃; path length—8.2 m, pressure—30 torr. D. Generalized background absorption. E, F. Far infrared spectrum of CH₂ClSiH₃ solid with additional sample deposit. Abscissa in arbitrary units of absorption.

WAVENUMBER CM-1

Thus, these two assignments may be reversed; however, because of the invariance in the frequency in the C-Si stretch in analogous systems, the former assignment is preferred. The relatively strong polarized Raman line at 711 cm⁻¹ is assigned to the symmetric CCl₂ stretch.

The A'' SiH₈ rock gives rise to a strong infrared band centered at 613 cm⁻¹ and a depolarized Raman line at 608 cm⁻¹. The symmetric SiH₈ rock occurs as a highly polarized Raman line at 512 cm⁻¹. Again by analogy with 1, 1-dichloroethane,²⁷ the highest frequency skeletal mode is expected to be the CCl₂ deformation and appears in the Raman spectrum at 300 cm⁻¹. The CCl₂ rock is then assigned to the Raman band at 228 cm⁻¹. The CCl₂ wag gives rise to a depolarized Raman line at 182 cm⁻¹ and an infrared band at 180 cm⁻¹. The silyl torsion is assigned to the weak band appearing in the far infrared spectrum of the solid at 177 cm⁻¹. Again this is the only low frequency band occurring outside the lattice region which does not have a Raman counterpart. As mentioned earlier bending modes do not shift to lower frequencies on solidification; thus, the 177 cm⁻¹ infrared band does not correspond to the 182 cm⁻¹ Raman line. The possibility exists that the 177 cm⁻¹ band is the overtone of the strong lattice mode occurring at 89 cm⁻¹; however, since overtones of lattice modes are not frequently observed, this latter assignment seems unlikely. The other two low frequency bands at 60 and 55 cm⁻¹ occurring in the infrared spectrum of the solid are assigned as lattice modes.

No previous determination of the barrier to internal rotation has been made for this molecule. With the assignment of the torsion at 177 cm⁻¹ and an F value of 2.95 calculated from the assumed structure given in Table IV, a torsional barrier of 3.69 kcal/mole is obtained.

E. Methylsilane (CH₃SiH₃)

The spectrum of methylsilane in the solid state was obtained in the hope that the torsional mode would become active under the factor group symmetry of the



FIG. 9. Infrared spectrum of gaseous CHCl₂SiH₃; path length—20 cm, pressure—5 torr with insert—45 torr. Abscissa in arbitrary units of absorption.

| Infrared | | | Raman | | | |
|-----------------------------------|---------------------|--------------|-----------------------------------|---------------------------|--------------|---|
| ν (cm ⁻¹) | Gas Band type | Rel. int. | $\Delta \nu \ (\mathrm{cm}^{-1})$ | Liquid Depol. ratio | Rel. int. | Assignment |
| 2990 ctr | ? | w | 2978 | 0.19 | 11 | r1, CH stretch |
| 2948 R 2937 Q | C | w | | | | 2190+748=2938 |
| 2224 <i>R</i> 2215 Q | A | S | | | | ν_2 , SiH ₃ symmetric stretch |
| 2197 <i>R</i> 2190 <i>P</i> | В | S | 2183 | 0.10 | 100 | v8 and v12, SiH8 antisymmetric stretches |
| 1217 ctr | ? | w | | | | 2×613=1226 |
| 1205 <i>R</i> 1197 <i>P</i> | В | w | 1197 | 0.76 | <0.1 | ν_{13} , CH out-of-plane bend |
| 1140 ctr | ? | w | 1145 | 0.52 | 1 | ν_4 , CH in-plane bend |
| 942 Q | С | s | 935 | 0.77 | 5 | v5, SiH3 symmetric deformation |
| 923 <i>R</i> 916 <i>P</i> | В | s | 915 sh | 2 | 1 | v ₆ and v ₁₄ , SiH ₃ antisymmetric deformation |
| 807 ctr | ? | w | 805 | 0.72 | 2 | 15, CCl2 antisymmetric stretch |
| 748 ctr | ? | m | 735 | 0.73 | 2 | ₽7, C–Si stretch |
| 718 R 709 Q 698 P | A | m | 711 | 0.06 | 4 | 28, CCl ₂ symmetric stretch |
| 617 R 610 P | В | s | 608 | 0.77 | 2 | ν_{16} , SiH ₈ antisymmetric rock |
| 511 ctr | ? | m | 512 | 0.03 | 10 | v9, SiH3 symmetric rock |
| 305 R (304) ^b 290 P | В | w | 300 | 0.11 | 5 | ν_{10} , CCl ₂ deformation |
| 220 ctr (228) | ? | m | 228 | 0.62 | 2 | 11, CCl ₂ wag |
| 180 ctr (190) | ? | w | 182 | 0.75 | <0.1 | v17, CCl ₂ rock |
| (177) | | vw | | | | 18, SiH2 torsion |
| (89) | | s | | | | Lattice vibration |
| (60) | | m | | | | Lattice vibration |
| (55) | | m | | | | Lattice vibration |

TABLE VI. Assignments for the observed infrared and Raman frequencies of dichloromethylsilane.^a

* Abbreviations: See Table III.

crystal. Unfortunately this does not appear to be the case, since only three bands appear in the spectrum of the solid and these are all in the lattice region. Bands were observed at 85, 105, 129 cm⁻¹ and in the absence of isotopic data they are assigned simply as lattice modes.

IV. CONCLUSIONS AND RESULTS

Of the molecules studied herein only the barrier in chloromethylsilane has been predicted theoretically. Lowe and Parr, using an electrostatic model, predicted a barrier of 2.44 kcal/mole for chloromethylsilane.⁷



FIG. 10. Far infrared spectra of CHCl₂-SiH₃ A. Generalized background absorption. B. Far infrared spectrum of gaseous CHCl₂SiH₃; path length—6.4 m, pressure—6 torr. C. Far infrared spectrum of gaseous CH₂ClSiH₃; path length—8.2 m, pressure—21 torr. D. Generalized background absorption. E, F, G. Far infrared spectrum of CHCl₂SiH₃ solid with successive sample additions. Abscissa in arbitrary units of absorption.

This is in good agreement with the gas phase barrier of 2.65 kcal/mole obtained in this work and the 2.55 kcal/mole obtained previously by the microwave splitting technique.²⁹ Because of this good agreement it is rather unfortunate that Lowe and Parr did not extend their calculations to the dichloride and the analogous silyl chlorides, so that a further evaluation of this method might be made.

One notices from Table VII that there is a gradual increase in the barrier in going from methylsilane to methyldichlorosilane and in the series methylsilane, chloromethylsilane, and dichloromethylsilane. This trend is in direct conflict with the trend observed for the ethane series where there is a discontinuity in the trend for 1,1-dichloroethane.¹⁶ In the work on 1,1dichloroethane, the torsion is assigned to frequency of 231 cm⁻¹ for both the gas and solid.¹⁶ This lack of shift in the torsional frequency on solidification is in conflict with the observations for the other chloroethanes. The present authors therefore feel the assignment of the torsion in 1,1-dichloroethane is somewhat suspect and a reinvestigation of this system seems warranted.

In methylchloro- and chloromethylsilane the torsions were observed both in the solid and the gas. From these data, one observes that there is a respective increase of 0.35 and 0.41 kcal/mole in going from the gas to the solid. These shifts are rather significant and indicate an appreciable intermolecular interaction. As was mentioned in the section on chloromethylsilane, large perturbation shifts in the torsional frequency usually occur when there is an observable factor group splitting of the internal fundamentals. Considering the large gas to solid shift in the torsional frequency, the failure to observe such splitting in the spectrum of methylchlorosilane indicates that there is most probably only one molecule per unit cell. This deduction is compatible



FIG. 11. Raman spectrum of CHCl₂-SiH₂ liquid. Abscissa in arbitrary units of scattering intensity.

with the observation of only one lattice mode in the far infrared spectrum of this molecule.

On examining Table VII it is noticed that by allowing a gas-solid shift in the barrier of 0.09 kcal/mole for dichloromethylsilane and a shift of 0.11 kcal/mole for methyldichlorosilane, the gas phase barrier for the mono and dichloro derivatives of each series would be strictly additive as compared to methylsilane (Fig. 12). This possibility is highly speculative; however, its implications are quite suggestive. On examining the ethane series one sees that on going from ethane to chloroethane the barrier increases by 0.75 kcal/mole. On admitting the possibility of the additivity of the barrier this would then imply that the gas phase barrier in 1,1-dichloroethane would be 4.53 kcal/mole and the barrier in methylchloroform would be 5.28 kcal/mole. This latter value of 5.28 kcal/mole is in good agreement with the 5.45 kcal/mole found for methylchloroform in the solid. It has always been observed that the barrier in the solid is higher than that for the gas phase; thus, the fact that the observed value of 5.45 is slightly higher than predicted is compatible with these observations. Thus, for the ethylchlorides, chloromethyl-, and methylchlorosilanes, the experimental data tend to indicate there may be a step wise increase in the barrier for successive additions of chlorine atoms. The exception to this trend is the 1,1-dichloroethane and the authors feel there is some question as to the correctness of the assignment for the torsion in this molecule.

There has appeared in the literature a paper in which the barrier in methyltrichlorosilane was determined to be less than 0.58 kcal/mole.⁴⁰ In light of the previous

TABLE VII. Summary of barriers for chloro-substituted ethane type molecules.^a

| | Barrier | | |
|-------------------------------------|-------------|-----------------------------------|---------------------|
| Molecule | (kcal/mole) | Method | Reference |
| CH₄CH₃ | 2.928 | IR | 34 |
| CH ₂ CH ₂ Cl | 3.68, 4.48 | MW _s , IR _s | 35, 15 ^b |
| CH ₂ CHCl ₂ | 3.50 | IR | 16 |
| CH ₃ CCl ₃ | 5.45 | IR, | 16 |
| CH ₃ SiH ₃ | 1.70 | MW _s , IR _s | 32, 36 ^b |
| CH ₃ SiH ₂ Cl | 1.84, 2.25 | IR, IR, | This work |
| CH ₃ SiHCl ₂ | 2.09 | IR. | This work |
| CH ₃ SiCl ₃ | 0.58 | MWi | 40 |
| CH ₂ ClSiH ₃ | 2.55, 2.65 | MW _s , IR _s | 31, This work |
| CHCl ₂ SiH ₈ | 3.69 | IR. | This work |
| CCl _a SiH _a | ••• | ••• | ••• |
| CH ₂ GeH ₃ | 1.24, 1.27 | MW _s , IR _s | 37, 36 ^b |
| CH ₃ GeCl ₃ | 1.30 | IR ₁ | 38 |
| CH ₂ SnH ₃ | 0.65 | MW, | 39 |

^a For abbreviations: IR_s =infrared gas, IR_s =infrared solid, IR_1 =infrared liquid, MW_s =microwave splitting. MW_i =micro-wave intensity.

^b The references are given in the respective order of the technique used.



FIG. 12. Graphical correlation of barrier heights for methylsilyl chlorides. Solid lines indicate experimental values; dash lines are extrapolated values. Abscissa: Barrier height in kcal/mole. Ordinate: Number of chlorine atoms on frame.

discussion this determination is questionable. This barrier was determined by the microwave intensity method and considering the magnitude of the complexity in the spectrum introduced by the large number of low frequency bending modes, such an error is easy to understand. Unfortunately the torsion, which is inactive under the molecular symmetry, did not appear in the spectrum of the solid.⁴¹

It has been shown herein and in previous work^{15,16} that the substitution of a chlorine for a hydrogen on carbon or silicon has a significant effect on the barrier to internal rotation. Therefore one might assume that this increase must arise from the increased electrostatic nonbonded Cl-H interaction or from an increase in the secondary overlap of the electrons of the X-Cl bond with the electrons of the Y-H bonds. In the chloromethyl- and methylchlorosilanes the nonbonded distances across the C-Si bond are approximately the same (the Cl···H nonbonded distance in chloromethylsilane is 3.36 Å whereas the corresponding distance in methylchlorosilane is 3.38 Å); however, there is a significant difference in the barriers for the corresponding members of each series. It hight be argued that because of the different electronegativities of carbon and silicon the differences in the barrier heights could be due to differences in the residual charges on the chlorines in the two systems. Alternatively, the lower barriers in the methylchlorosilanes could arise from the change of the electron density on the chlorine by $(p-d)\pi$ bonding between the silicon and the chlorine atoms. However, if these two factors do make a con-

tribution, they would tend to act in opposite directions. It would, therefore, require a complete analysis of the electron distributions in these molecules to see which factors actually predominate. Superficially, the results appear to discount purely electrostatic interactions as the major source of the barrier. The observations herein are, however, compatible with the secondary overlap concept. The highly diffuse electron cloud of the silicon-chlorine bonds do not have an appreciable effective overlap with the electron cloud of the carbonhydrogen bonds; thus, the barriers are somewhat low. However, the electron cloud of the C-Cl bonds appears to overlap more extensively with the electrons of the SiH bonds causing the barriers to be higher. The secondary overlap would seem to require a modification of the molecular orbitals to allow the electron density to be more spacially extensive than is generally assumed, to give an effect consistent with the observations herein.

- *Taken in part from the Ph.D. thesis of C. W. Hawley to be submitted to the Department of Chemistry.
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It would be interesting to see what modifications in the molecular orbital electron densities are required to reproduce the observed barriers.

In summary, these results would seem to indicate that further study of the barrier in 1,1-dichloroethane seems necessary. Also, to investigate the possibility of the additivity of barriers, studies of 1,1-dibromoethane and the methyl silyl bromides seem warranted.

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