# The Microwave Spectrum, Structure, Quadrupole Coupling Constants, and Barrier to Internal Rotation of Methyldichlorosilane

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The microwave spectra of the $^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$ isotopic species of $CH_3SiHCl_2$ have been investigated in the frequency region from 12 to 40 GHz. The rotational constants and centrifugal distortion constants have been determined and were used to calculate the structure of the molecule. The structural parameters determined are:

$$r(\text{Si–C}) = 1.850\,\text{Å}, \quad \angle\text{C–Si–Cl} = 109.8°,$$
$$r(\text{Si–Cl}) = 2.040\,\text{Å}, \quad \angle\text{Cl–Si–Cl} = 108.8°.$$

A few high-J R-branch transitions are split into doublets because of the methyl internal rotation. These splittings give a barrier to internal rotation of $1.69\pm0.05$ kcal/mol. An analysis of the $^{35}Cl_2$ quadrupole splittings leads to quadrupole coupling constants of $\chi_{aa}=-19.1\pm0.3$ MHz, $\chi_{bb}=5.4\pm1.3$ MHz, $\chi_{cc}=13.7\pm1.4$ MHz, $\chi_{bond}=-41.2\pm2.0$ MHz, and $\eta_{bond}=0.16\pm0.03$.

A comparison of the molecular structures in various substituted fluorosilane molecules reveals that both the Si–C and Si–F bond distances decrease upon the substitution of the fluorine atoms for the hydrogen atoms attached to the silicon.[1–4] Furthermore, it is interesting to note that the barrier to internal rotation decreases markedly with an increase in the number of fluorine atoms, while the barriers to internal rotation of various fluoroethane molecules have almost the same values.[5]

The chloro derivatives of methylsilane also provide a group of molecules that may be used to test the changes in the molecular constants with the substitution of the chlorine atoms for the hydrogen atoms. However, $CH_3SiHCl_2$ has not been studied by microwave spectroscopy, and only incomplete molecular structures have been determined for $CH_3SiH_2Cl$ and $CH_3SiCl_3$. $CH_3SiCl_3$ was first investigated by Mockler *et al.*,[6] and the primitive molecular structure was presented on the basis of an analysis of the spectra of $CH_3Si^{35}Cl_3$ and $CH_3Si^{37}Cl_3$. Although the data for its isotopic species were added by Mitzlaff *et al.*,[7] they did not determine the molecular structure, since they failed to observe the silicon isotopic species. Recently the present authors suceeded in observing the spectrum of the $^{29}Si$ species, and the molecular structure has been analyzed.[8] Zeil *et al.* investigated the microwave spectrum of $CD_3SiH_2Cl$ and presented the partial $r_s$ structure of Si–Cl.[9] Though they recently reported about normal species, $CH_3SiD_2Cl$, and $CD_3SiD_2Cl$,[10] the molecular structure has not yet been determined.

The barrier to internal rotation of $CH_3SiCl_3$ has been obtained from the intensity measurement of the microwave spectral lines,[7] and that of $CH_3SiH_2Cl$ has been determined by the observation of the far-infrared spectrum,[11] while the barrier height of $CH_3SiHCl_2$ in the vapor phase has not been obtained. In the present study, we measured the microwave spectrum of $CH_3SiHCl_2$ and determined the molecular structure and the barrier to internal rotation.

## Experimental

The sample of $CH_3SiHCl_2$ was obtained from a commercial source and was used without further purification. The $CH_3SiH^{35}Cl^{37}Cl$ and $CH_3SiH^{37}Cl_2$ isotopic apecies were observed in their natural abundances. Since the sample decomposed gradually in the cell, it was continuously introduced into the cell and pumped out during the measurement. The spectrometer used in this reseach was a conventional 100 kHz Stark modulation type, with a 3 m X-band waveguide cell cooled with Dry Ice. The frequency accuracy is estimated to be ±0.1 MHz.

## Analysis of the Spectra

The spectrum of $CH_3SiHCl_2$ was predicted from an approximate structure based on the structures of $CH_3SiHF_2$[3] and $CH_3SiH_2Cl$.[9] The $\chi_{bond}$ values (quadrupole coupling constants in coordinate system with z axis along the Si–Cl bond) were assumed to be the same as in $CH_3SiH_2Cl$. The predicted spectrum indicated that the c- and b-type transitions are allowed and that the b-type transitions are stronger if the large bond moments are assumed along the Si–Cl bonds. The prediction also showed that the b-type R-branch transitions with low $K_{-1}$ numbers make the strongest series and have very small splittings due to hyperfine structures, and that they should have large Stark effects because of the nearly degenerate $K$-type doublet levels which are coupled with the $\mu_c$ dipole component. In fact, the clear $K$-doublet patterns for the $9_{09}\leftarrow8_{18}$ and $9_{19}\leftarrow8_{08}$ transitions were observed first under very small Stark modulation voltages. Between these two $K$-doublet lines, unusual spectral lines showing only Stark components were observed, as is shown in Fig. 1. These lines were identified as $9_{09}\leftarrow8_{08}$ and $9_{19}\leftarrow8_{18}$. Since this molecule lacks the $\mu_a$ component, these transitions are prohibited at the zero-field duration time of the square-wave modulation. On the other hand, the transitions are allowed at the other duration time in which the electric field is applied, because of the breakdown of the selection rule caused by the mixing of the energy levels by the $\mu_c$ component. This mechanism is illustrated schematically in Fig. 2. The similar transitions were observed also for $J=8\leftarrow7$, $J=10\leftarrow9$, and

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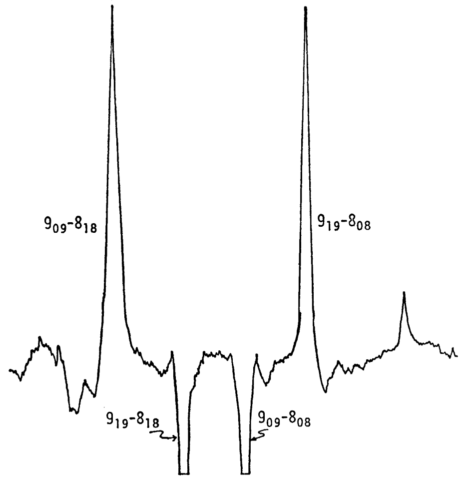

Fig. 1. The $9_{09}\leftarrow8_{08}$, $9_{19}\leftarrow8_{18}$ prohibited transitions.

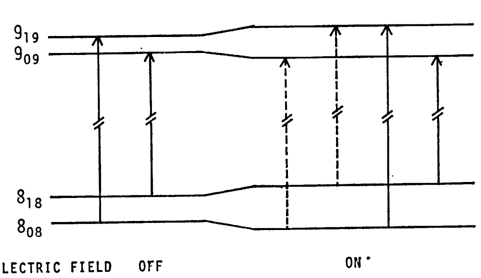

Fig. 2. Schematical illustration for breakdown of the prohibited transitions. Dotted lines represent prohibited transitions which is allowed only when an electric field is applied.

$J=11\leftarrow10$ R-branch *K*-type doublets. Subsequently, Q-branch transitions were searched for in the region predicted from the rotational constants roughly determined by the R-branch transitions, and assigned by means of their characteristic hyperfine structures.

The unsplit frequencies of the observed transitions, which were obtained by a method to be described later, are listed in Table 1. The rotational constants and the centrifugal distortion constants of the $CH_3SiH^{35}Cl_2$ species were determined by a least squares fit calculation using the formula presented by Watson.[12] The determined constants are given in Table 2. The rotational constants of the $^{35}Cl^{37}Cl$ and $^{37}Cl_2$ species were determined by assuming the same centrifugal distortion constants as those of the $^{35}Cl_2$ species.

Table 1. Observed and calculated frequencies of methyldichlorosilane (MHz)

| Transition | | $\nu_{obsd}$ | $\nu_{obsd}-\nu_{calcd}$ |
|---|---|---|---|
| $CH_3SiH^{35}Cl_2$ | | | |
| $3_{1\,3}$ | $2_{0\,2}$ | 12583.45 | 0.23 |
| $4_{4\,0}$ | $4_{3\,1}$ | 15493.42 | −0.04 |
| $4_{1\,4}$ | $4_{0\,3}$ | 15620.39 | 0.07 |
| $4_{0\,4}$ | $3_{1\,3}$ | 14425.55 | 0.03 |
| $5_{4\,1}$ | $5_{3\,2}$ | 15047.81 | 0.06 |
| $5_{1\,5}$ | $4_{0\,4}$ | 18744.28 | 0.07 |
| $5_{0\,5}$ | $4_{1\,4}$ | 18166.36 | −0.16 |
| $6_{1\,6}$ | $5_{0\,5}$ | 21993.24 | 0.07 |
| $6_{0\,6}$ | $5_{1\,5}$ | 21739.76 | −0.23 |
| $6_{1\,5}$ | $6_{0\,6}$ | 13596.78 | 0.12 |
| $6_{2\,5}$ | $6_{1\,6}$ | 14944.88 | −0.06 |
| $6_{4\,3}$ | $6_{3\,4}$ | 15824.25 | −0.11 |
| $6_{5\,1}$ | $6_{4\,2}$ | 19856.25 | 0.24 |
| $7_{2\,6}$ | $6_{1\,5}$ | 29175.62 | −0.05 |
| $7_{1\,6}$ | $7_{0\,7}$ | 16731.74 | 0.04 |
| $7_{2\,6}$ | $7_{1\,7}$ | 17444.50 | −0.12 |
| $7_{1\,7}$ | $6_{0\,6}$ | 25327.84 | 0.13 |
| $7_{0\,7}$ | $6_{1\,6}$ | 25223.72 | 0.00 |
| $8_{1\,7}$ | $8_{0\,8}$ | 19742.98 | 0.24 |
| $8_{2\,7}$ | $8_{1\,8}$ | 20084.24 | −0.26 |
| $8_{1\,8}$ | $7_{0\,7}$ | 28706.38 | 0.26 |
| $8_{0\,8}$ | $7_{1\,7}$ | 28665.31 | 0.05 |
| $8_{2\,7}$ | $7_{1\,6}$ | 32058.76 | −0.17 |
| $9_{1\,9}$ | $8_{0\,8}$ | 32104.52[a] | 0.35 |
| $9_{0\,9}$ | $8_{1\,8}$ | 32088.37[a] | −0.23 |
| $9_{2\,8}$ | $8_{1\,7}$ | 35164.14 | −0.04 |
| $9_{1\,8}$ | $8_{2\,7}$ | 34653.72 | −0.18 |
| $9_{2\,7}$ | $8_{3\,6}$ | 35141.16 | −0.33 |
| $10_{1\,10}$ | $9_{0\,9}$ | 35510.62[a] | 0.25 |
| $10_{0\,10}$ | $9_{1\,9}$ | 35504.58[a] | 0.00 |
| $10_{1\,9}$ | $10_{0\,10}$ | 25494.36 | −0.10 |
| $10_{2\,8}$ | $10_{1\,9}$ | 21067.00 | −0.08 |
| $10_{3\,8}$ | $10_{2\,9}$ | 22033.16 | −0.21 |
| $10_{4\,6}$ | $10_{3\,7}$ | 11286.27 | 0.12 |
| $10_{4\,7}$ | $10_{3\,8}$ | 19664.20 | 0.24 |
| $10_{5\,5}$ | $10_{4\,6}$ | 15931.73 | −0.13 |
| $10_{5\,6}$ | $10_{4\,7}$ | 20313.84 | 0.03 |
| $10_{6\,4}$ | $10_{5\,5}$ | 23090.72 | −0.11 |
| $10_{6\,5}$ | $10_{5\,6}$ | 23895.28 | −0.11 |
| $10_{7\,3}$ | $10_{6\,4}$ | 28516.92 | 0.03 |
| $10_{7\,4}$ | $10_{6\,5}$ | 28578.48 | 0.11 |
| $11_{1\,10}$ | $11_{0\,11}$ | 28306.54 | 0.22 |
| $11_{2\,10}$ | $11_{1\,11}$ | 28333.20 | 0.11 |
| $CH_3SiH^{35}Cl^{37}Cl$ | | | |
| $3_{1\,3}$ | $2_{0\,2}$ | 12388.10 | −0.03 |
| $5_{2\,4}$ | $5_{1\,5}$ | 12497.86 | −0.12 |
| $6_{1\,5}$ | $6_{0\,6}$ | 13216.84 | −0.06 |
| $7_{1\,6}$ | $7_{0\,7}$ | 16313.85 | 0.00 |
| $7_{2\,6}$ | $7_{1\,7}$ | 17125.19 | 0.14 |
| $7_{1\,7}$ | $6_{0\,6}$ | 24825.00 | 0.10 |
| $7_{0\,7}$ | $6_{1\,6}$ | 24703.00 | 0.05 |
| $8_{1\,8}$ | $7_{0\,7}$ | 28128.80 | −0.06 |
| $8_{0\,8}$ | $7_{1\,7}$ | 28079.60 | 0.09 |
| $9_{1\,9}$ | $8_{0\,8}$ | 31455.00 | 0.13 |
| $9_{0\,9}$ | $8_{1\,8}$ | 31435.46 | −0.05 |
| $10_{1\,10}$ | $9_{0\,9}$ | 34790.28 | −0.05 |
| $10_{0\,10}$ | $9_{1\,9}$ | 34782.80 | −0.13 |
| $CH_3SiH^{37}Cl_2$ | | | |
| $6_{0\,6}$ | $5_{1\,5}$ | 20827.10 | 0.13 |
| $7_{0\,7}$ | $6_{1\,6}$ | 24189.35 | −0.12 |
| $7_{1\,7}$ | $6_{0\,6}$ | 24330.39 | −0.06 |
| $8_{0\,8}$ | $7_{1\,7}$ | 27502.00 | −0.15 |
| $8_{1\,8}$ | $7_{0\,7}$ | 27560.91 | 0.12 |
| $9_{0\,9}$ | $8_{1\,8}$ | 30791.80 | −0.15 |
| $9_{1\,9}$ | $8_{0\,8}$ | 30815.84 | 0.26 |
| $10_{0\,10}$ | $9_{1\,9}$ | 34072.10 | 0.17 |
| $10_{1\,10}$ | $9_{0\,9}$ | 34081.00 | −0.20 |

a) "*A*" component of internal rotation.

TABLE 2. ROTATIONAL CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF METHYLDICHLOROSILANE (MHz)

| | $CH_3SiH^{35}Cl_2$ | $CH_3SiH^{35}Cl^{37}Cl$ | $CH_3SiH^{37}Cl_2$ |
|---|---|---|---|
| A | 4342.16(06) | 4313.75(09) | 4285.39(3.30) |
| B | 2433.28(03) | 2370.94(02) | 2311.39(0.68) |
| C | 1706.05(02) | 1671.23(02) | 1636.85(0.87) |
| $d_J$ | −0.00157 | | |
| $d_{JK}$ | −0.02646 | | |
| $d_K$ | −0.02027 | | |
| $d_{WJ}$ | $0.106\times10^{-5}$ | | |
| $d_{WK}$ | $0.109\times10^{-4}$ | | |

The assignment was also confirmed by the observation of the double-resonance effects between the transitions of $7_{25}\leftarrow7_{16}$ and $8_{27}\leftarrow7_{16}$, and between those of $9_{36}\leftarrow9_{27}$ and $9_{27}\leftarrow8_{36}$. The spectral line of $8_{27}\leftarrow7_{16}$ or $9_{27}\leftarrow8_{36}$ was observed on a cathode ray tube, and the transition of $7_{25}\leftarrow7_{16}$ or $9_{36}\leftarrow9_{27}$ was saturated. About 30% of the intensity decrease was observed when the exact pumping frequency was applied.

## Hyperfine Structure

The hyperfine structures of the spectrum due to the two chlorine nuclei were analyzed on the basis of the theory presented by Robinson and Cornwell.[13] A typical pattern of the hyperfine structure and an observed spectrum, when the moments of the two chlorine nuclei are identical, are given in Fig. 3. As is shown in the figure, the strongest line, which consists of four degenerate components, always exists at the unsplit value. Therefore, the unsplit values can be determined simply by measuring the strongest lines in the hyperfine structures. Although this degenerate line splits into four components when the two quadrupole coupling constants are not identical, as in the case of the $^{35}Cl^{37}Cl$ species, the strongest lines without splittings were always observed for the spectrum of $CH_3SiH^{35}Cl^{37}Cl$. Therefore, the unsplit frequencies of the spectrum were approximated by the center frequencies of the unresolved lines for this species.

The values of the $\chi$ tensor for $CH_3SiH^{35}Cl_2$ were determined from the analysis of the five Q-branch transitions. The obtained values are listed in Table 3, along with the values of $\chi_{zz}$ and $\eta$. Since the off-diagonal elements of the tensor in the principal axis system of the molecule were not obtained, $\chi_{zz}$ and $\eta$ were calculated by the use of the transformation coefficients determined from the structure obtained in the present study. In this coordinate system, the z axis is along the Si–Cl bond, the x axis is in the Cl–Si–Cl plane, and the y axis is perpendicular to these two. The obtained values of this $\chi_{zz}$ may be compared with that of $SiH_3Cl$ ($eQq=-40.0$ MHz).[14]

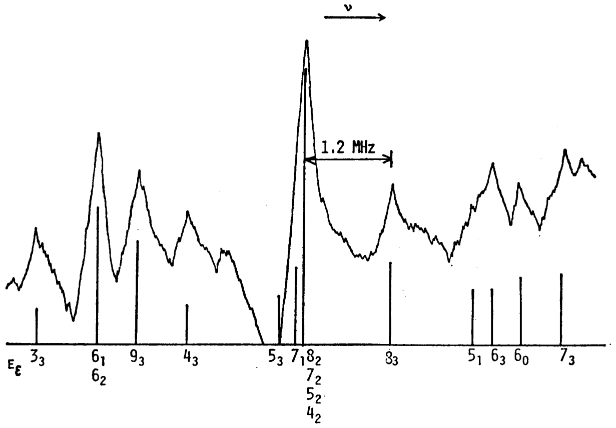

Fig. 3. Recorded spectrum and predicted hyperfine structure for the $6_{51}\leftarrow6_{42}$ transition in $CH_3SiH^{35}Cl_2$.

TABLE 3. QUADRUPOLE COUPLING CONSTANTS OF $CH_3SiH^{35}Cl_2$

| | |
|---|---|
| $\chi_{aa}$ | $-19.1\pm0.3$ MHz |
| $\chi_{bb}$ | $5.4\pm1.3$ MHz |
| $\chi_{cc}$ | $13.7\pm1.4$ MHz |
| $\chi_{bond}$ | $-41.2\pm2.0$ MHz |
| $\eta_{bond}$ | $-0.16\pm0.03$ |

## Internal Rotation

The low-$J$ lines in the spectrum of this molecule are of rigid asymmetric top. Some of the high-$J$ R-branch transitions, however, shows splittings due to the interaction between the internal rotation and the over-all rotation. These splittings have been analyzed to determine the barrier to internal rotation using the structure shown in Table 5. Table 4 lists the frequencies, $\nu_A$, the frequency differences, $\nu_A-\nu_E$, and the calculated values of $V_3$ for four transitions in $CH_3SiH^{35}Cl_2$. The splittings due to the quadrupole coupling are very small and are not observed for these transitions.

TABLE 4. BARRIER HEIGHT OF $CH_3SiHCl_2$

| Transition | $\nu_A$ (MHz) | $\nu_A-\nu_E$ (MHz) | $V_3$ (kcal/mol) |
|---|---|---|---|
| $8_{1\,9}$ $8_{0\,8}$ | 32104.52 | 0.79 | 1.70 |
| $9_{0\,9}$ $8_{1\,8}$ | 32088.37 | −0.89 | 1.68 |
| $10_{1\,10}$ $9_{0\,9}$ | 35510.62 | 2.01 | 1.69 |
| $10_{0\,10}$ $9_{1\,9}$ | 35504.58 | −2.02 | 1.68 |

Internal rotation parameters
$I_\alpha=3.2$ amu Å$^2$ (assumed)
$\lambda_b=0.902585$
$\lambda_c=0.430511$
$F=160.26$ GHz

Results
Average $s=49.16$
Average $V_3=1.69\pm0.05$ kcal/mol

Durig and Hawley measured the vibrational spectra of gaseous and solid $CH_3SiHCl_2$,[11] and they estimated that the very weak band at 173 cm$^{-1}$ in solid phase arose from the methyl torsion. This value leads to 2.09 kcal/mol as the barrier height; this value is consistent with our value considering that the barrier in the solid phase is always higher than that in the gas phase.[11]

## Molecular Structure

Since only three isotopic species ($^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$) were measured, and since the $^{37}Cl_2$ species gives essentially the same informations as to the molecular structure as does the $^{35}Cl^{37}Cl$ species, it is necessary to assume some parameters in order to determine the molecular structure. The partial structures of the $CH_3$ and SiH groups were chosen as those to be assumed, because the probable errors in the assumed structures cause little errors in the other parameters. In principle, it is possible to determine the four parameters of the C–Si and Si–Cl bond lengths and the Cl–Si–Cl and C–Si–Cl angles from six rotational constants. Although this was tried first, the obtained values were changed appreciably by the small deviations of the rotational constants. Therefore, the Si–C length was also assumed for the analysis of the molecular structure. The C–Si bond distances in methylsilane and methylfluorosilanes have been determined precisely by the substitution method. Durig *et al.*[4] have revealed that both the Si–C and Si–F bond distances decrease with a further substitution of the fluorine atoms for the hydrogen atoms attached to the silicon. In Fig. 4 the change in the Si–C bond distances in methylfluorosilanes versus the number of fluorine atoms is plotted. A similar shortening of Si–C distances in methylcholorosilanes can also be expected by the substitution of the chlorine atoms for the hydrogen atoms, while the amount of the shortening is expected to be about a half of that in the case of fluorine. Therefore, we estimated that the C–Si bond distance of methyldichlorosilane should be about 1.850 Å, which is the average value of the C–Si bond distances in methylsilane and methyldifluorosilane. This estimation is supported by the results of the structure analysis for the halogen derivatives of hydrocarbones. The Cl–Si length, and the C–Si–Cl and Cl–Si–Cl angles were determined, using this assumed value, by means of a least-squares method. The obtained values are listed in Table 5.

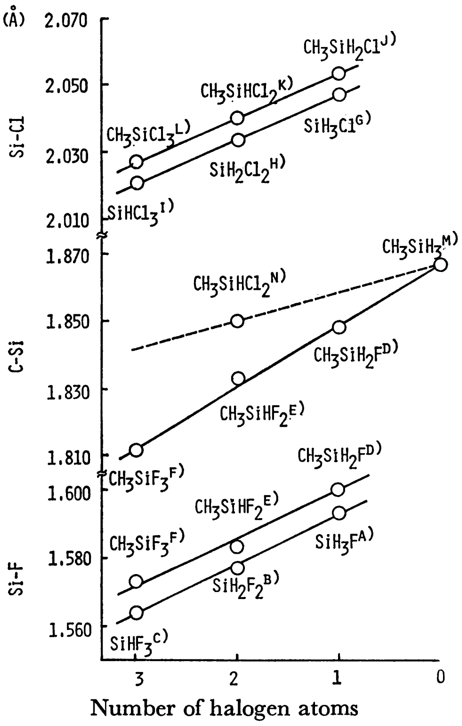

Fig. 4. The change of bond distances due to substitution of the halogen atoms for the hydrogen atoms in halosilanes and methylhalosilanes.
A), G) R. Kewley, P. M. McKinney, and A. G. Robiette, *J. Mol. Spectrosc.*, **34**, 390 (1970). B) V. W. Laurie, *J. Chem. Phys.*, **26**, 1359 (1957). C) G. A. Heath, L. F. Tomas, and J. Sheridan, *Trans. Faraday Soc.*, **50**, 779 (1954). D), E) L. C. Krisher and L. Pierce, *J. Chem. Phys.*, **32**, 1619 (1960). F) Ref. 4. H) R. W. Davis and M. C. L. Gerry, *J. Mol. Spectrosc.*, **60**, 117 (1976). I), L) Ref. 8. J) Ref. 9. K) This work. M) Ref. 1. N) Assumed values: see text.

Table 5. Molecular structure of methyldichlorosilane

| Assumed structural parameters | | | |
|---|---|---|---|
| *r* Si–C | 1.850 Å | ∠ Si–C–H | 109.5° |
| *r* Si–H | 1.467 Å | ∠ C–Si–H | 110.9° |
| *r* C–H | 1.093 Å | | |
| $C_{3v}$ symmetry for methyl group | | | |
| Fitted structural parameters | | | |
| *r* Si–Cl | 2.040 Å | | |
| ∠ C–Si–Cl | 109.8° | | |
| ∠ Cl–Si–Cl | 108.8° | | |
| Calculated rotational constants (MHz) | | | |
| | *A* | *B* | *C* |
| $CH_3SiH^{35}Cl_2$ | 4342.18 | 2433.62 | 1706.04 |
| $CH_3SiH^{35}Cl^{37}Cl$ | 4313.70 | 2371.20 | 1671.20 |
| $CH_3SiH^{37}Cl_2$ | 4283.32 | 2310.85 | 1636.90 |

## Discussion

The obtained Si–Cl bond distance is compared with those of chlorosilanes and other methylchlorosilanes in Fig. 4. Zeil *et al.* have presented two Si–Cl bond distances, 2.049±0.013 Å and 2.052±0.005 Å by combining the rotational constants of $CD_3{}^{28}SiH_2{}^{35}Cl$, $CD_3{}^{29}SiH_2{}^{35}Cl$, $CD_3{}^{30}SiH_2{}^{35}Cl$, and $CD_3{}^{28}SiH_2{}^{37}Cl$. When we choose 2.052 Å for the plot of Si–Cl bond distances in Fig. 4, it can clearly be seen that the Si–Cl bond distances decrease with the substitution of chlorine atoms for the hydrogen atoms and that the change is quite regular. It should be noted that the slopes of chlorosilanes and methylchlorosilanes have almost the same gradient.

In Table 6, the barrier of $CH_3SiHCl_2$ determined in this study is compared with a few values of methylsilanes and methylhalosilanes which have been determined by microwave and infrared spectroscopy. In the $CH_3SiH_3$,

Table 6. Comparison of barriers to internal rotation in methylhalosilane

| Molecule | $V_3$(kcal/mol) | Method |
|---|---|---|
| $CH_3SiH_3$ | 1.70[a)] | Mw split |
| $CH_3SiH_2F$ | 1.559[b)] | Mw split |
| $CH_3SiHF_2$ | 1.255[c)] | Mw split |
| $CH_3SiF_3$ | 0.93[d)] | Mw intensity |
| $CH_3SiH_2Cl$ | 1.84,[e)] 2.25[e)] | IR gas, IR solid |
| $CH_3SiHCl_2$ | 1.69, 2.09[e)] | This work, IR solid |
| $CH_3SiCl_3$ | 0.58[f)] | Mw intensity |

a) Ref. 1. b) Ref. 2. c) Ref. 3. d) Ref. 4. e) Ref. 11. f) Ref. 7.

$CH_3SiH_2F$, $CH_3SiHF_2$, $CH_3SiF_3$ series, it can clearly be observed that the substitution of a fluorine for a hydrogen causes a significant decrease in the barrier to internal rotation. The $CH_3SiH_3$, $CH_3SiH_2Cl$, $CH_3SiHCl_2$, $CH_3SiCl_3$ series, however, shows that the substitution of a chlorine for a hydrogen does not cause any significant effect on the barrier except $CH_3SiCl_3$. A similar comparison of the barriers for chloro and fluoroethanes has revealed that the substitution of a chlorine with a hydrogen increases the barrier, while the change in the barrier is small in the case of fluorine. Therefore, one might assume that the nonbonded Cl···H interaction is always larger than the nonbonded F···H interaction. From this point of view, it is very difficult to explain the remarkably low barrier of $CH_3SiCl_3$. Since the barrier of 0.58 kcal/mol for $CH_3SiCl_3$ was obtained by the microwave intensity method, it is probable that there was a confusion in the assignment of the tortional state; a careful re-investigation of the microwave spectrum may, therefore, be necessary.

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