The Analysis of the Raman Spectra of Si2Cl6(l) and of Si2H6(g)

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The Analysis of the Raman Spectra of $Si_2Cl_6(l)$ and of $Si_2H_6(g)$*

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The Raman spectra of $Si_2H_6(g)$ and of $Si_2Cl_6(l)$ have been photographed. Polarization measurements of the stronger lines of Si_2Cl_6 have been made. From a consideration of the relations among the modes of vibration of similar molecules having different symmetry, the analysis of the observed lines is facilitated by a knowledge of the assignments of the fundamental frequencies of SiH_4, $HSiCl_3$ and $BrSiCl_3$. A definite assignment is made for the three observed lines of Si_2H_6. A tentative assignment of the observed lines of Si_2Cl_6 is made and some evidence is presented for the existence of internal rotation in this molecule at room temperature.

IN addition to determining and assigning some of the fundamental vibration frequencies of disilane and of disilicon hexachloride, we have attempted in this investigation to determine whether or not internal rotation is present in the Si_2Cl_6 molecule at room temperature.

EXPERIMENTAL

The disilane used was obtained from Professor Johnson of the University of Chicago, and we wish to express our gratitude to him for his kindness in making the material available to us. It was quite pure, showing, according to Professor Johnson, a molecular weight of 62.6; the formula weight is 62.2.

The disilicon hexachloride was prepared by treating ferrosilicon[1] with chlorine and fractionally distilling the product four or five times. It boiled at $145° \pm 0.5°$.

The spectrum of gaseous disilane was photographed with radiation from a mercury arc. A Pyrex Raman tube was used to avoid possible decomposition since Hg 2537A was found to decompose SiH_4.[2] When the Si_2Cl_6 was photographed in a Pyrex tube without a filter it showed some decomposition with the appearance of small brown flakes of silicon. An acid quinine chloride solution as filter absorbed almost completely all lines of the mercury arc of higher frequency than the Hg 4358 group, and no decomposition occurred. As Raman lines excited by the

FIG. 1. Experimental arrangement for polarization measurements. M, half-wave mica plate; N, Nicol prism; S, step weakener on slit of spectrograph; T, Raman tube; L, condensing lens; B, parallel black screens.

4047 group were observed in the absence of the filter, the decomposition was probably due to the Hg 3650 group.

Polarization measurements were made on the stronger lines of Si_2Cl_6 (l). The experimental arrangement used for these measurements is shown in Fig. 1. This arrangement suffers the disadvantage that a separate exposure must be made for the parallel and perpendicular components,[3] but possesses the two following important advantages: (1) The use of a step weakener on the slit[4] automatically calibrates the photographic plate, the blackening along the length of each spectral line varying in steps of known relative intensity of illumination. Thus both the source and the exposure time for calibration are the same as for the image, an important factor where low intensities and long exposure times are involved. (2) The use of a half-wave mica plate[5] preceding

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[1] Quig and Wilkinson, J. Am. Chem. Soc. **48**, 902 (1926); Martin, J. Chem. Soc. **105**, 2836 (1914).

[2] Stitt and Yost, J. Chem. Phys. **4**, 82 (1936).

[3] An arrangement eliminating this disadvantage is obtained if, in Fig. 1, M and N be removed and a large aperture Wollaston prism be introduced into the collimator tube of the spectrograph. Correction for polarization due to the spectrograph may then be eliminated by rotating the Wollaston 45° about the axis of the tube from the position in which the two beams emerging from it are in a vertical plane. The mercury arc is placed so that with the Raman tube it determines a plane at 45° to the vertical. This arrangement was not used because a suitable Wollaston prism was not available.

[4] We are indebted to Professor Houston and Dr. C. M. Lewis for allowing us to use a step weakener made by them. See Phys. Rev. **44**, 903 (1933).

[5] We are indebted to Dr. John Strong for suggesting the use of a half-wave plate.

the Nicol prism eliminates the correction for polarization due to the apparatus, and also allows each component to be photographed passing through the spectrograph with the electric vector in the horizontal plane, thus minimizing the loss due to reflection by the prism faces.

For photographing one component (the ∥-component for illumination in a vertical plane) the axis of the Nicol prism is horizontal and the axis of the mica plate parallel to that of the Nicol. The only alteration necessary for photographing the other component is to rotate the half-wave plate through 45°, thus rotating by 90° the electric vector of the light passing through it. Tests showed that a 0.048 mm mica sheet serves as a half-wave plate with practically no error from 4400A to 5000A. Only for high frequency shifts from Hg 4358A as an exciting line need a different thickness plate be used.

The step weakener was calibrated at a number of different wave-lengths. For the calibration a low voltage Mazda lamp, such as used in street lights, served as constant source of illumination, and the small, spiral, vertical filament served as a good point source. The inverse square law of illumination was assumed throughout. Five positions giving relative intensities of 1, 0.8, 0.6, 0.4, 0.2 were used, each with exactly one hour exposure time. By microphotometering these continuous spectra at any wave-length the calibration for that wave-length could be made. Eight

TABLE I. Raman spectrum of Si_2H_6 (g). Pressure approximately 2 atmos.

$\Delta\tilde{\nu}$ IN CM^{-1}	NO. OF EXCITING LINES	DESCRIPTION
2163	6	Strong; sharp.
910 to 955	2	Weak; diffuse.
434.5	3	Medium intensity; sharp; appeared also as an anti-Stokes line.

steps were used having relative transmission values of 1.00, 0.85, 0.61, 0.45, 0.34, 0.26, 0.19, 0.14 at 4384A.

A Raman tube of rectangular cross section was employed in order to minimize reflection of incident light. Parallel black screens for making the incident light approximately parallel were so spaced that only light within about 15° of the vertical could enter the Raman tube. For $\rho = 0.86$ the error in ρ is less than 0.02 for incident light at an angle of 20° with the vertical.[6] Eastman I−O plates were used.

The mercury arc was run at constant voltage and showed little fluctuation in current over long periods of time. A 48-hour exposure of each component was taken, the illumination probably being very nearly the same for both components. However, it should be pointed out that, for this work, it is not necessary that the illumination be precisely the same for the two components for accurate results. For practically all compounds

[6] G. Placzek, "Rayleigh-Streuung und Raman-Effekt," Handbuch der Radiologie, Band II, Teil 2 (Leipzig, 1934), p. 244.

TABLE II. Raman spectrum of Si_2Cl_6 (l). (Anti-Stokes lines not included.)

ν IN CM^{-1}	$\Delta\tilde{\nu}$ IN CM^{-1}	RELATIVE INTENSITY	POLARIZATION RATIO (ρ)	DESCRIPTION
22806	124	8 }	0.72±0.02	Double line; diffuse. Not resolved in polarization measureurements. 132 cm^{-1} portion seems slightly less diffuse than 124 cm^{-1} portion.
22814	132	5 }		
22759	179	~0.4		Sharp.
22726	212	4	0.86±0.02	Sharp.
22685	354	< <1	—	Hg 4047 as exciting line.
22641	354	< <1		Hg 4339 as exciting line.
22584	354	10	<0.05	Sharp.
22561	377 }	1		Double; similar to 124, 132 cm^{-1} doublet. 388 cm^{-1} portion seems slightly more intense and less diffuse than 377 cm^{-1} portion.
22551	387 }			
22517	421	< < <1		Broad; too broad to be $\Delta\nu = 425$ cm^{-1} of $SiCl_4$.
22478	460	< < <1		Very weak; moderately diffuse.
22451	487	< < <1		Very broad. Strongest of < < <1 lines. Too intense to be $\Delta\nu = 588$ cm^{-1} from Hg 4339.
22405	590	< < <1		Hg 4347 as exciting line.
22373	565	< <1		Moderately diffuse. Too intense for $\Delta\nu = 625$ cm^{-1} from Hg 4347 as exciting line.
22348	590	3	0.88±0.03	Rather diffuse.
22313	625	2	<0.5	Moderately diffuse.
22232	706	< < <1		Very weak; moderately diffuse.

TABLE III. *Relations among the irreducible representations of certain symmetry groups.*

T_d	C_{3v}	C_3	D_3	D_{3h}	C_{3v} or D_3	D_{3d}
$\left.\begin{array}{l}A_1\\A_2\\E\end{array}\right\}$	$\left.\begin{array}{l}A_1\\A_2\\E\end{array}\right\}$	$\begin{array}{l}A\\E_{1,2}\end{array}$	$\left\{\begin{array}{l}A_1\\A_2\\E\end{array}\right.$	$\left.\begin{array}{l}A_1'\\A_2''\end{array}\right\}$	A_1	$\left\{\begin{array}{l}A_{1g}\\A_{2u}\end{array}\right.$
$T_1\}$	A_2+E			$\left.\begin{array}{l}A_1''\\A_2'\end{array}\right\}$	A_2	$\left\{\begin{array}{l}A_{2g}\\A_{1u}\end{array}\right.$
$T_2\}$	A_1+E			$\left.\begin{array}{l}E'\\E''\end{array}\right\}$	E	$\left\{\begin{array}{l}E_g\\E_u\end{array}\right.$

some Raman lines have $\rho = 6/7$ for ordinary incident light. If the exposure is somewhat different for the two components, one may find an accurate correction factor to use with the observed ρ values from the fact that the highest ρ is probably actually $6/7$. In the present work, the observed values for two lines were 0.86 within narrow limits thus confirming our assumption that the illumination was the same for the two exposures.

On plotting the microphotometer reading for each step as ordinate against the percentage transmission for that step as abscissa for each component, the depolarization ρ is the ratio of the abscissas for the same ordinate on the two curves. (Correction for background was unnecessary as the background was negligible. Note the background radiation also is reduced in known ratios.) The values of ρ thus found choosing different ordinates agreed quite well.

The experimental results are summarized in Tables I and II.

THEORETICAL

Wigner[7] has shown that the normal coordinates for vibrations of a system of point particles belong to (that is, have the linear transformation properties of) definite irreducible representations (IR) of the point group representing the symmetry of the system. The methods for determining, for a given model, how many vibrational frequencies belong to each of the IR of the appropriate group and for determining the selection rules in the Raman and infrared spectrum are now well known.[8]

[7] *Göttingen Nachrichten* (1930), p. 133.

[8] See reference 6, 7; also E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934), J. Chem. Phys. **2**, 432 (1934) and references given there.

It is instructive to follow (a) how the fundamental frequencies for a model with a given number of atoms are distributed among the IR of the appropriate point group as the symmetry of the model is changed from that of one point group to that of another, and (b) and (c) how the new modes of vibration introduced when the number of atoms in a model is increased, with and without altering the point group symmetry, distribute themselves among the IR of the appropriate point group. The use of such considerations for correlation and assignment of frequencies is frequently very helpful. We will restrict ourselves here to a discussion of examples related to the interpretation of the spectra of Si_2H_6 and Si_2Cl_6.

For studying the distributions referred to in the preceding paragraph the methods already referred to[8] are employed, supplemented by some further considerations. When the symmetry is lowered to that of a subgroup of the original group, those IR of the original group possessing the same characters with respect to the operations of the subgroup merge to form a single IR of the subgroup. Mulliken[9] has published tables showing some of these relations. When the symmetry is altered so that the new point group is not a subgroup of the original one, a correlation between the two is then obtained by seeing how the IR of each reduce to those of the group possessing all elements of symmetry common to the two. For our present purposes we are interested in these relations for the point groups C_{3v}, D_3, D_{3d}, D_{3h}, and T_d; these are shown in Table III. IR designated by A are one dimensional, and frequencies associated with them are nondegenerate; those

TABLE IV. *Irreducible representations to which the fundamental frequencies of certain models belong, and selection rules for Raman and infrared spectra.*

FORMULA	SYMMETRY	FREQUENCIES	RAMAN ACTIVE	INFRARED ACTIVE
XY_3	C_{3v}	$2A_1$, $2E$	$2A_1$, $2E$	$2A_1$, $2E$
XY_4	T_d	A_1, E, $2T_2$	A_1, E, $2T_2$	$2T_2$
XY_3Z	C_{3v}	$3A_1$, $3E$	$3A_1$, $3E$	$3A_1$, $3E$
X_2Y_6	D_{3d}	$3A_{1g}$, A_{1u}, $2A_{2u}$ $3E_g$, $3E_u$	$3A_{1g}$, $3E_g$	$2A_{2u}$, $3E_u$
X_2Y_6	D_{3h}	$3A_1'$, A_1'', $2A_2''$ $3E'$, $3E''$	$3A_1'$, $3E'$, $3E''$	$2A_2''$, $3E'$
X_2Y_6	D_3	$4A_1$, $2A_2$, $6E$	$4A_1$, $6E$	$2A_2$, $6E$

Note: By active is meant only that a frequency is permitted to appear, and not that it necessarily does appear.

[9] Phys. Rev. **43**, 294 (1933).

designated with letters **E** and **T** are two and three dimensional, respectively, and the frequencies associated with them are doubly and triply degenerate.

In Table IV are shown the distribution of the fundamental vibrations for several models among the IR of the appropriate point group, and also the selection rules for the fundamentals in their infrared and Raman spectra. For those vibrations belonging to the completely symmetric IR (A_1 of D_3, A_1 of C_{3v} and of T_d, A_1' of D_{3h}, and A_{1g} of D_{3d}) the corresponding Raman lines have a polarization ratio $\rho < 6/7$; for all others $\rho = 6/7$.

In Table V are shown the Raman selection rules for first overtones and one-one combinations for these same models.

Coordinates belonging to appropriate IR for a given model of X_2Y_6 may be constructed readily from similar coordinates for the XY_3 model. (The normal coordinate for a given vibration is a linear combination of those symmetry coordinates belonging to the IR with which that vibration is associated.) The method is as follows: For each symmetry coordinate of XY_3 construct two for X_2Y_6. In both of these each $-XY_3$ radical vibrates with the XY_3 symmetry coordinate, but in one the two radicals vibrate in phase, in the other 180° out of phase. This will be made clear by reference to Fig. 2, in which are shown the symmetry coordinates thus[10] found from the symmetry coordinates formulated by Howard and Wilson[11] for XY_3. The "in phase" coordinates (those with subscript s) are unchanged by rotation about a twofold axis of the X_2Y_6 model,

FIG. 2. Symmetry coordinates for X_2Y_6 from those for XY_3.

whereas the same operation changes the "out of phase" coordinates (those with subscript a) by 180° in phase. The equilibrium configuration for X_2Y_6 shown in Fig. 2 is that for symmetry D_{3d}, but beneath each coordinate is noted the IR of the point groups D_{3d}, D_{3h} and D_3, respectively, to which the suitably drawn coordinate belongs when the $-XY_3$ radicals are combined to form molecules of these symmetries. These coordinates have been given designations for future reference.

In the following discussion we shall refer to these coordinates as if they were normal coordinates. The symmetry coordinates of AB_3 have been chosen so that each one involves primarily a bending or a stretching of the bonds. For most AB_3 molecules the large difference in the frequencies of the two vibrations belonging to either A_1 or E of C_{3v} show that the normal coordinates are probably very similar to these symmetry coordinates. The same is probably true of the coordinates shown for A_2B_6. This would be expected to be true, especially for the degenerate modes, in case of free internal rotation.

TABLE V. *Raman selection rules for first overtones and for one-one combinations of fundamental frequencies of X_2Y_6 models. All are allowed except those shown.*

SYMMETRY	FORBIDDEN RAMAN LINES
D_3	$A_1 + A_2$
D_{3d}	(A_{1g} or A_{1u})+(A_{2g} or A_{2u}), $A_{1g}+E_u$, $A_{1u}+E_g$, $A_{2g}+E_u$, $A_{2u}+E_g$.
D_{3h}	(A_1' or A_1'')+(A_2' or A_2'')

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[10] Slight modification of the XY_3 coordinate may be necessary to eliminate over-all rotation as in forming τ_s of Fig. 2 from ω_x, ω_y of XY_3, or to avoid distortion as in forming ω_x, ω_y of X_2Y_6 in Fig. 2 from T_x, T_y of XY_3. We wish to thank Dr. J. B. Howard for calling our attention to this.

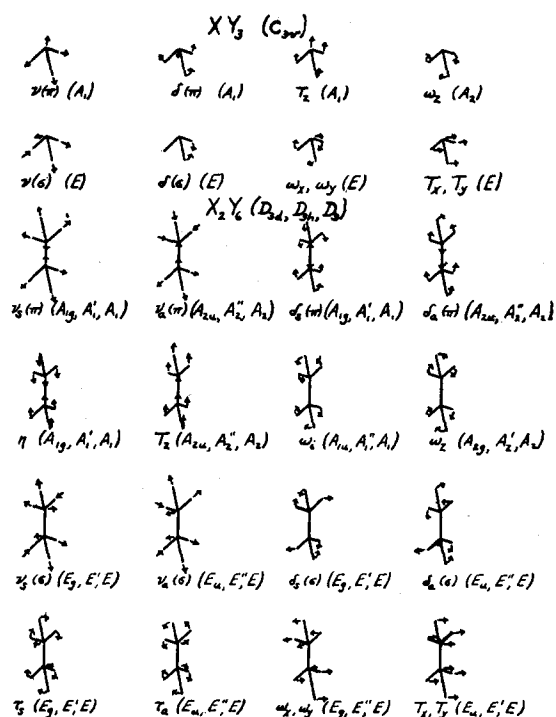[11] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **3**, 630 (1934).

DISCUSSION

Si₂H₆

There is no question as to the presence of internal rotation in Si_2H_6. In ethane the difference in stability of the D_{3h} and D_{3d} configurations is considerably less than kT at room temperature so that the internal rotation is almost free.[12] In Si_2H_6, due to the greater distance between the two central atoms than in C_2H_6, rotation of the two halves of the molecule with respect to each other must be even less hindered than in ethane.

$\Delta\nu = 2163$ cm^{-1} is doubtless due to $\nu_s(\pi)$ because of its great intensity, its sharpness, and its numerical proximity to $\nu(\pi) = 2187$ cm^{-1} of SiH_4.[2]

$\Delta\nu = 910$ to 955 cm^{-1} is probably $\delta(\sigma)$. In SiH_4 we have assigned[2] $\nu = 910$ cm^{-1} to IR T_2 of T_d, $\nu = 978$ cm^{-1} to E of T_d, and of these two frequencies only $\Delta\nu = 978$ cm^{-1} was observed with appreciable intensity in its Raman spectrum. On the assumption that the intensities of the Raman lines of Si_2H_6 are related to those of SiH_4, in accordance with Table III we conclude $\Delta\nu = 910$ to 955 cm^{-1} of Si_2H_6 probably belongs to E of D_3, hence is probably $\delta(\sigma)$ rather than $\delta(\pi)$.

$\Delta\nu = 434.5$ cm^{-1} is very likely η. The fundamental frequencies of SiH_4 indicate that all the fundamental frequencies of Si_2H_6 are in the neighborhood of either 1000 cm^{-1} or 2000 cm^{-1} except η, ω_i and τ. ω_i is probably zero as nearly free internal rotation is present. η would be expected to be sharp, and perhaps of appreciable intensity because of its appearance in the Raman spectrum of $C_2H_6'(g)$.[13] If it is assumed that 434.5 cm^{-1} is the frequency of vibration of two rigid $-SiH_3$ groups with respect to each other, a stretching force constant of 1.7×10^5 dynes/cm is found for the $Si-Si$ bond.

Si₂Cl₆

In Si_2Cl_6 the situation as to internal rotation is not so clear. The electrostatic interaction due to assuming a positive charge of 4.5×10^{-10} e.s.u. on each Si atom and a negative charge of 1.5×10^{-10} e.s.u. on each Cl atom (corresponding to the high value of 3.0 Debyes for the dipole moment of the

Si$-$Cl bond)[14] results in stabilizing the D_{3d} configuration by 475 cal./mole with respect to the D_{3h} configuration. The van der Waals attraction between the Cl atoms tends to stabilize the D_{3h} configuration by an amount of the order of 450 cal./mole.[15] Due to the mutual repulsion of the Cl atoms, there is a barrier of the order at 500 cal./mole between the two configurations.[16] Hence it seems probable that resistance to internal rotation at room temperature is probably of the order of $k\mathbf{T}$, the D_{3d} configuration being somewhat more stable than the D_{3h} one.

In accordance with Table IV we see that if Si_2Cl_6 possesses a rigid staggered (D_{3d}) structure, six distinct fundamental frequencies are permitted in the Raman spectrum, three of which would have a polarization ratio $\rho < (6/7)$. If Si_2Cl_6 possesses a rigid structure having a symmetry plane perpendicular to the threefold axis, nine distinct fundamental frequencies are permitted to be Raman active, and three of these would have $\rho < (6/7)$.[17] If free internal rotation occurs the symmetry of the molecule is only D_3 most of the time. For a rigid D_3 model Table IV shows that ten distinct fundamental frequencies are permitted to be Raman active. However, if free rotation is present, one of these, ω_i, is zero, and intuitively it seems very likely that under such conditions the corresponding "in phase" and "out of phase" vibrations not symmetric with respect to the threefold axis (the degenerate vibrations) would become indistinguishable, thus resulting in only six distinct fundamental frequencies permitted in the Raman spectrum.

[12] Eucken and Weigert, Zeits. f. physik. Chemie **B23**, 266 (1933); Eucken and Parts, *Göttingen Nachrichten* (1932), p. 274; Zeits. f. physik. Chemie **B18**, 61 (1932); Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

[13] Teller and Topley, J. Chem. Soc. 885 (1935).

[14] Distances used: Si$-$Cl $= 2.00A$, the SiCl$_4$ value. Si$-$Si $= 2.34A$ the value recently found in Si$_2$H$_6$ by electron diffraction. (Dr. Brockway, private communication.) The C$-$Cl dipole moment is about 1.5 Debyes and the Si$-$Cl separation is about twice the C$-$Cl separation on Pauling's electronegativity scale (See J. Am. Chem. Soc. **54**, 3570 (1932)).

[15] See Slater and Kirkwood, Phys. Rev. **37**, 682 (1931).

[16] If for the repulsive potential between two bound Cl atoms, the expression $\phi(r) = be^{(2\gamma_0 - \gamma)/\rho}$ is used, with $b = 10^{-12}$ erg, $\rho = 0.2091A$, and $\gamma_0 = 1.370A$, the calculated barrier is about 350 cal./mole. These values of b and ρ were used to give the best fit for neon (see Bleick and Mayer, J. Chem. Phys. **2**, 252 (1934)) and γ_0 was chosen by comparison with γ_0 for neon and for the alkali and halide ions (see Huggins and Mayer, J. Chem. Phys. **1**, 643 (1933)). The barrier (exclusive of Coulomb interaction) calculated if the Cl atoms are assumed to be chloride ions is about 2000 cal./mole. (See Huggings and Mayer, above.) The correct value is probably nearer that calculated for bound chlorine atoms.

[17] By rigid here is meant that resistance to internal rotation is sufficiently great so that only small vibrations about the equilibrium position may occur.

In addition to the selection rules, we have some knowledge of the fundamental frequencies of $HSiCl_3$[18] and of $BrSiCl_3$[19] to aid us in our analysis of the Si_2Cl_6 spectrum. In Table VI are shown the observed Raman frequency shifts for these compounds and the assignment of the frequencies. The assignment shown for the $HSiCl_3$ frequencies is that of Mecke.[20] The analysis of the $BrSiCl_3$ frequencies we have made by analogy to Mecke's analysis[20] of the $HSiCl_3$, HCX_3 and CH_3X frequencies (X=halogen). The designations ν and δ refer to vibrations roughly approximated by the symmetry coordinates shown in Fig. 2 for XY_3 where X now becomes a rigid $H-Si$ (or $Br-Si$) group, and $\eta(\pi)$ and $\eta(\sigma)$ refer, respectively, to vibrations in which the motion is essentially a stretching or a bending with respect to the $-SiCl_3$ group of the $H-Si$ (or $Br-Si$) bond. Calculation of $\eta(\pi)$ for $BrSiCl_3$, assuming it to involve only a vibration of the Br atom relative to a rigid $-SiCl_3$ group and assuming the stretching force constant of the $Si-Br$ bond to be unchanged from its value in $SiBr_4$, yields 314 cm^{-1}.

Considering both $BrSiCl_3$ and Si_2Cl_6 as a $-SiCl_3$ group with a rather large mass attached along the threefold axis, one would expect the $\nu(\pi)$ and $\delta(\pi)$ vibrations in one to be of approximately the same frequency as in the other. Without concluding as to the symmetry of Si_2Cl_6, this prediction coupled with the selection rules and the values of ρ for these lines lead us to assign 354 cm$^{-1} = \nu(\pi)$ and either 124 or 132 cm$^{-1} = \delta(\pi)$ in Si_2Cl_6.

Since the mass of the H atom is so small relative to that of Si or Cl, the frequencies of $HSiCl_3$

TABLE VI. *Assignment of the fundamental vibration frequencies of $HSiCl_3$ and of $BrSiCl_3$.*

HSiCl₃		IR	Designation	BrSiCl₃
489	(6.6)	A_1	$\nu(\pi)$	362 (v. str.)
249	(2.6)	A_1	$\delta(\pi)$	123
2256	(8.3)	A_1	$\eta(\pi)$	325
587	(1)	E	$\nu(\sigma)$	410
179	(4)	E	$\delta(\sigma)$	183 (str.)
797	(1)	E	$\eta(\sigma)$	201

[18] de Hemptinne and Peeters, Bull. Sci. Acad. Roy. Belg. **17**, 1107 (1931); Urey and Bradley, Phys. Rev. **37**, 843 (1931).
[19] de Hemptinne, Wouters and Fayt, Bull. Sci. Acad. Roy. Belg. **19**, 318 (1933).
[20] *Handbuch und Jahrbuch der Chem. Phys.* (Leipzig, 1934), Band 9, Teil II, p. 390.

(omitting $\eta(\pi)$ and $\eta(\sigma)$)[21] are very nearly those of a free $-SiCl_3$ group. If nearly free internal rotation is present in Si_2Cl_6, the perpendicular vibrations $\nu(\sigma)$ and $\delta(\sigma)$ would be expected to be of nearly the same frequency as those of a free $-SiCl_3$ group, since then the net instantaneous momentum in any direction perpendicular to the threefold axis would be essentially zero for each half of the molecule. This condition need not obtain for a rigid[17] configuration. The appreciable intensity, the polarization ratio of 6/7, and the numerical value of 590 cm^{-1} in Si_2Cl_6 indicate that it is $\nu(\sigma)$. This proximity to the value of $\nu(\sigma) = 587$ cm^{-1} in $HSiCl_3$ favors the conclusion that there is nearly free internal rotation in Si_2Cl_6. The appreciable intensity and ρ value of 212 cm^{-1} lead to its assignment as $\delta(\sigma)$. This is slightly higher than $\delta(\sigma)$ in either $HSiCl_3$ (179 cm^{-1}) or $BrSiCl_3$ (183 cm^{-1}).

We are unable to make definite assignments of more than these four lines as fundamental frequencies of Si_2Cl_6. The relation of these assignments to the analyses of the frequencies of $HSiCl_3$, $BrSiCl_3$ and $SiCl_4$ from the viewpoint of Table III is shown in Table VII.

Several of the weaker lines observed may be assigned as combinations or overtones:

421 cm^{-1}: The first overtone of 212 cm^{-1}.
487 cm^{-1}: Combination 132 cm$^{-1} + 354$ cm^{-1}.
565 cm^{-1}: Combination 212 cm$^{-1} + 354$ cm^{-1}.
706 cm^{-1}: First overtone of 354 cm^{-1}.

The remaining weak lines, $\Delta\nu = 377$, 387 and 460 cm^{-1}, are also probably due to combinations or overtones. Numerically they agree with 124, 132 and 212 cm^{-1}, respectively, combining with a frequency of about 252 cm^{-1}. As fundamentals we can see no feasible assignment for them.

The component of the 124, 132 cm^{-1} doublet which is not $\delta(\pi)$ may well be τ with a polarization ratio of 6/7. The observed $\rho = 0.72$ is an over-all value for both lines.

Two possibilities suggest themselves for 179 cm^{-1}: (1) It may be η; (2) If the correct configuration is a rigid[17] one, it may be $\delta_a(\sigma)$, its numerical value being practically the same as $\delta(\sigma)$ in $HSiCl_3$ and $BrSiCl_3$. If η is assumed to be the vibration of two rigid $-SiCl_3$ groups with respect to each other, and if the $Si-Si$ bond stretching

[21] This is equivalent to calling the symmetry coordinates described above for $\eta(\pi)$ and $\eta(\sigma)$ normal coordinates.

TABLE VII. *Correlation of fundamental frequencies of SiCl$_4$, HSiCl$_3$, BrSiCl$_3$ and Si$_2$Cl$_6$.*

SiCl$_4$ (T$_d$)	HSiCl$_3$ (C$_{3v}$)	BrSiCl$_3$	Si$_2$Cl$_6$	(D$_3$, D$_{3d}$)(?)
A 425 (10)	489 (7)⎫ 250 (3)⎬A$_1$	⎧362 (v. str.) ⎨123	354 (10)⎫ 124 (8)⎬ or	A$_1$, A$_{1g}$
608 (2)	2258 (8)⎭	⎩325	132 (5)⎭	
T$_2$ 220 (5)				
	799 (1)⎫	⎧201		
E 150 (5)	587 (1)⎬E	⎨410	590 (3)⎫	E, E$_g$
	179 (4)⎭	⎩183 (str.)	212 (4)⎬	

TABLE VIII. *Assignment of the Raman frequencies of Si$_2$Cl$_6$, assuming internal rotation.*[25]

Δν cm^{-1}	INTENSITY	ASSIGNMENT (See Fig. 2)
	FUNDAMENTALS	
354	10	$\nu_s(\pi)$
132 (or 124)	5 (or 8)	$\delta_s(\pi)$
179	0.4	η (?)
590	3	$\nu(\sigma)$
212	4	$\delta(\sigma)$
124 (or 132)	8 (or 5)	τ (?)
	COMBINATIONS AND OVERTONES	
421	<<<1	$2\delta(\sigma)$
487	<<<1	$\delta_s(\pi)+\nu_s(\pi)$
565	<<1	$\delta(\sigma)+\nu_s(\pi)$
706	<<<1	$2\nu_s(\pi)$
377	<<1	124 cm^{-1}+252 cm^{-1} (?)
387	<<1	132 cm^{-1}+252 cm^{-1} (?)
460	<<<1	$\delta(\sigma)+252$ cm^{-1} (?)
625	2	$\nu_s(\pi)+252$ cm^{-1} or (?) in accidental deg. with $\nu(\sigma)$ (?)

force constant is that calculated above from Si$_2$H$_6$, its frequency should be 201 cm^{-1}. (A similar calculation using C$_2$H$_6$[13] and C$_2$Cl$_6$[22] data predicts a frequency of 354 cm^{-1} for η of C$_2$Cl$_6$, and a line belonging to the completely symmetric IR is observed at 342 cm^{-1}.) Since the frequency corresponding to the η vibration in C$_2$H$_6$, Si$_2$H$_6$ and C$_2$Cl$_6$ in each case appears with appreciable intensity in its Raman spectrum, we should expect it to appear also in Si$_2$Cl$_6$. Therefore it seems to us more likely that 179 cm^{-1} is η rather than $\delta_a(\sigma)$.

The observed line at $\Delta\nu=625$ cm^{-1} appears with considerable intensity, yet it does not seem possible to us that it is due to a fundamental frequency. Its polarization ratio shows that it is not due to a degenerate fundamental frequency. Reference to Table IV shows that only $\nu_s(\pi)$, $\delta_s(\pi)$, η, and ω_i are permitted to be Raman active among the nondegenerate fundamentals in any of the models considered. Of these only $\nu_s(\pi)$ would be expected to be of relatively high frequency, but 354 cm^{-1} is definitely assigned as $\nu_s(\pi)$. $\Delta\nu=625$ cm^{-1} must therefore be due to a combination or overtone. Its intensity then indicates that it probably corresponds to a level in accidental degeneracy with 590 cm^{-1}. Since 590 cm^{-1} shows a ρ value of 6/7 and 625 cm^{-1} a ρ value of <0.5, and since interaction between two levels may occur only if their wave functions belong to representations including the same IR, then the wave function corresponding to 625 cm^{-1} must belong to a representation including both A$_1$ and E of the appropriate point group. Of the first overtones or one-one combinations for each of the symmetries D$_3$, D$_{3d}$ and D$_{3h}$ only an overtone of a degenerate fundamental or a combination of two degenerate fundamentals belonging to the same IR satisfy this requirement.[23] If this

interpretation is correct[24] either $2\delta(\sigma)$, 2τ or $\delta(\sigma)+\tau$ should be approximately 608 cm^{-1}, although this is not the case for the present proposed assignment. It is interesting to note that combination of 354 cm^{-1} with the hypothetical 252 cm^{-1} frequency gives a level at approximately 608 cm^{-1}, but this level would not satisfy the requirements just mentioned.

The above analysis does not permit a definite answer to the question of internal rotation in Si$_2$Cl$_6$ at room temperature, but affords some evidence for its existence. In Table VIII is shown a tentative assignment of the observed lines under the assumption that free rotation does exist.[25]

In conclusion we wish to thank Professor E. B. Wilson, Jr. and Dr. J. B. Howard for valuable criticism and discussion.

Note added in proof. Very recently Kemp and Pitzer (J. Chem. Phys. 4, 749 (1936)) have presented evidence for the existence of a potential barrier of about 3150 cal./mole between the D$_{3d}$ and D$_{3h}$ configurations in ethane. Since the Si—Si distance (2.34A) in Si$_2$H$_6$ and Si$_2$Cl$_6$ is considerably greater than the C—C distance (1.52A) in ethane, their conclusions would not appear to exclude the possibility of internal rotation in Si$_2$H$_6$ and Si$_2$Cl$_6$.

[22] Heidenreich, Zeits. f. Physik 97, 277 (1935).
[23] See Tisza, Zeits. f. Physik 82, 48 (1933).

[24] In this case the numerical agreement between 587 cm^{-1} of HSiCl$_3$ and 590 cm^{-1} of Si$_2$Cl$_6$ loses some of its significance as evidence for free rotation.
[25] If instead a rigid (reference 17) D$_{3d}$, or even D$_{3h}$, structure exists, subscripts s on the degenerate frequency designations in Table VIII would be the only change necessary for the appropriate new tentative assignments.