

The Raman Spectrum of Hexachlorodisilane

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where $\omega=1000^\circ$. The slope would be 0 for the first group and 434 for the second one. The average for $\bar{x}_{Av}=0.33$, according to (24) would be about 150. This is incompatible with the observed slopes of about 5. The basic idea of this argument is that the r.l.f. averages x and the terminal slope of the loops averages $(1000)^\circ$; these two averages are quite different. This argument, therefore, proves again the basic idea of paper I, that the value of x observed is essentially a single grain feature.

VIII. CONCLUSION

The theoretical considerations in this paper yield these conclusions: (1) The available data for isodense and iso-exposure sequence loops are described quantitatively by the theory in terms of l.i.f. The latter in turn was covered in paper I in terms of the fundamental processes in the grain. (2) The number of Ag atoms in a just developable speck seems to vary somewhat according to circumstances between 4 and 10. (More data may reveal even larger values.)

The Raman Spectrum of Hexachlorodisilane

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The Raman spectrum of hexachlorodisilane was observed in the liquid state and the normal vibrations of this molecule were calculated by use of the Urey-Bradley field. The seven observed Raman frequencies could be assigned to the fundamental vibrations and the molecule was found to belong to the D_{3h}' symmetry. This means that the molecule exerts internal free rotation around the Si-Si bond as axis. This is in conformity with the experimental result of the electron diffraction investigation.

DURING the last few years many investigations of the molecules of ethane type have been made in connection with the mutual position of the two methyl groups and the potential barrier restricting internal rotation about the carbon-carbon single bond as axis. It would be interesting from this point of view to study the internal rotation of hexachlorodisilane $\text{Cl}_3\text{Si}-\text{SiCl}_3$ about the Si-Si single bond, whose length is much greater than that of the C-C bond, so that the interaction potential of the two rotating groups would decrease considerably. L. O. Brockway and J. Y. Beach¹ concluded by electron diffraction investigation that this molecule has a staggered form, but recently more accurate analysis of the electron diffraction pattern showed that this molecule exerts almost free internal rotation about the Si-Si axis.²

F. Stitt and D. M. Yost³ observed the frequencies, relative intensities and depolarization factors of the Raman lines of this molecule, but they could not decide whether the molecular configuration corresponds to D_{3d} or D_{3h}' . It is the object of this paper to determine the configuration of this molecule by the measurement of the Raman effect together with the calculation of normal vibrations.

EXPERIMENTAL

The apparatus for the measurement of the Raman effect was previously described.⁴ The hexachlorodisilane

(b.p. 36.0°C at 10 mm Hg) kindly prepared by Professor K. Yamasaki by the reaction between metallic silicon and chlorine gas² was distilled into the Raman tube in vacuum. To avoid the decomposition of the sample by ultraviolet rays dilute solution of sodium nitrite was used as a filter. The observed Raman frequencies ($\Delta\nu$) and visually estimated intensities (I) are shown in Table I, which agree well with the results obtained by Stitt and Yost. The minor differences are that we observed one broad line at 379 cm^{-1} instead of the two lines at 377 cm^{-1} and 387 cm^{-1} and that we assigned the e - 565 cm^{-1} line reported by them as f - 622 cm^{-1} .

CALCULATION OF NORMAL VIBRATION AND ASSIGNMENT OF FREQUENCIES

This molecule consisting of eight atoms has twelve normal frequencies, of which six correspond to doubly degenerate vibrations. One of these corresponds to the internal rotation of SiCl_3 groups about the Si-Si bond as axis and is inactive both in the Raman effect and the infra-red. The selection rule for the remaining eleven vibrations is shown in the left part of Table II, from which we see that six fundamental frequencies will be observed in the Raman effect if the molecule belongs to D_{3d} symmetry (staggered form), while nine frequencies will be expected both for D_{3h} (eclipsed form) and D_{3h}' symmetry (free rotation). Stitt and Yost considered that one cannot discriminate D_{3h}' from D_{3d} by the Raman data, because the frequencies of E_g vibrations coincide with those of E_u vibrations so that only six fundamentals become Raman active in both cases. Their reasoning is not, however, sound, since it

¹ L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **60**, 1836 (1938).

² Yamasaki, Kotera, Tatematsu, and Iwasaki, J. Chem. Soc. Japan **69**, 104 (1947).

³ F. Stitt and D. M. Yost, J. Chem. Phys. **5**, 90 (1937).

⁴ S. Mizushima and Y. Morino, Proc. Ind. Acad. Sci. **8**, 351 (1938).

TABLE I. The Raman spectrum of hexachlorodisilane.

Present data			Stitt and Vost's data		
$\Delta\nu$ cm ⁻¹	I	excitation	$\Delta\nu$ cm ⁻¹	I	ρ
124	8	$e\pm, k\pm, i$	124	8	
132	8	$e\pm, k\pm, i$	132	5	0.72 ± 0.02
179	5	e	179	0.4	
211	8	$e\pm, k\pm, i$	212	4	0.86 ± 0.02
354	10	$e\pm, k\pm, i, f, g$	354	10	0.05
379	3b	e	377	1	
			387	1	
420	4	e	421	$<<< 1$	
454	3	e	460	$<<< 1$	
484	3	e	487	$<<< 1$	
			565	$<< 1$	
588	6b	$e\pm, k\pm, i, f$	590	3	0.88 ± 0.03
622	6	$e\pm, k\pm, i, f$	625	2	< 0.5
651	1	e			
710	2	e	706	$<<< 1$	

will be evident from the following calculation that all the frequencies of E_u vibrations do not coincide with those of E_g vibrations. Furthermore, as shown in Table II, E_u vibrations are Raman-active for D_{3h} , while they are not for D_{3d} . Therefore, the determination of molecular configuration can at once be made by observing if the E_u -type vibrations appear in the Raman effect or not.

For the assignment of the Raman line we have calculated the normal vibrations of this molecule, using the Urey-Bradley field, which has been shown to be successful in obtaining the normal frequencies for various molecules.⁵ The potential energy in the present case is thus expressed as follows:

$$\begin{aligned}
 V = & \{K'_{\text{SiSi}}R_0\Delta R + \frac{1}{2}K_{\text{SiSi}}(\Delta R)^2\} \\
 & + \sum_{i=1}^6 \{K'_{\text{SiCl}}r_0\Delta r_i + \frac{1}{2}K_{\text{SiCl}}(\Delta r_i)^2\} \\
 & + \sum_{j=1}^6 \{H'_{\text{ClSiSi}}r_0^2\Delta\alpha_j + \frac{1}{2}H_{\text{ClSiSi}}r_0^2(\Delta\alpha_j)^2\} \\
 & + \sum_{k=1}^6 \{H'_{\text{ClSiSi}}r_0R_0\Delta\beta_k + \frac{1}{2}H_{\text{ClSiSi}}r_0R_0(\Delta\beta_k)^2\} \\
 & + \sum_{l=1}^6 \{F'_{\text{ClCl}}q_0\Delta q_l + \frac{1}{2}F_{\text{ClCl}}(\Delta q_l)^2\} \\
 & + \sum_{m=1}^6 \{F'_{\text{ClSi}}p_0\Delta p_m + \frac{1}{2}F_{\text{ClSi}}(\Delta p_m)^2\}, \quad (1)
 \end{aligned}$$

where R and r_i are the bond distances of Si—Si and Si—Cl, α_j and β_k the interbond angles $\angle \text{Cl—Si—Cl}$ and $\angle \text{Cl—Si—Si}$, q_l the distances between Cl-atoms bonded to the same Si-atom, p_m those between Si and Cl not bonded directly, and R_0 , r_0 , q_0 and p_0 the equilibrium values of R , r , q , and p . They are shown in Fig. 1. The first and the second terms of Eq. (1) are the potentials for the change of bond distances, and the third and the fourth terms are those for the change of interbond

⁵ T. Simanouti, J. Chem. Phys. 17, 245, 734 (1949).

TABLE II. The normal vibrations of hexachlorodisilane.

Irreducible representation			Selection rule for the Raman effect			Calculated frequencies (cm ⁻¹)	Observed frequencies (cm ⁻¹)	ρ
D_{3d}	D_{3h}	D_{3h}	D_{3d}	D_{3h}	D_{3h}			
A_{1g}	A_1	A_1'	$\nu(\text{Si-Si})^a$	p^o	p	626	622(6)	$\rho < 0.5$
			$\nu(\text{Si-Cl})$	p	p	375	354(10)	p
			$\nu(\text{Si-Cl})$	p	p	127	124(8)	p
E_g	\bar{E}	E'	$\nu(\text{Si-Cl})$	d^d	d	625	622(6)	
			$\delta(\text{Si-Cl})^b$	d	d	145	132(8)	
			$\delta(\text{Si-Cl})$	d	d	202	211(8)	d
A_{2u}	\bar{A}_2	A_2''	$\nu(\text{Si-Cl})$	i^e	i	478		
			$\delta(\text{Si-Cl})$	i	i	249		
E_u	E	E''	$\nu(\text{Si-Cl})$	i	d	588	588(6b)	d
			$\delta(\text{Si-Cl})$	i	d	80	—	
			$\delta(\text{Si-Cl})$	i	d	188	179(5)	

^a ν : valency vibration.

^b δ : deformation vibration.

^c p : Raman-active and polarized.

^d d : Raman-active and depolarized.

^e i : Raman-inactive.

TABLE III. Force constants (10^5 dynes/cm) and molecular parameters of hexachlorodisilane used in the calculation of normal vibration.

$$\begin{aligned}
 K_{\text{SiSi}} = 2.20, & H_{\text{ClSiCl}} = 0.04, F'_{\text{ClCl}} = -0.06, F'_{\text{SiCl}} = -0.05, \kappa = 0.15, \\
 K_{\text{SiCl}} = 2.60, & H_{\text{ClSiSi}} = 0.05, F_{\text{ClCl}} = 0.30, F_{\text{SiCl}} = 0.1, \\
 R_0(\text{Si-Si}) = 2.34\text{\AA}, & \alpha \} = \text{tetrahedral angles} \\
 r_0(\text{Si-Cl}) = 2.02\text{\AA}, & \beta \}
 \end{aligned}$$

angles. The last two terms refer to the repulsions between non-bonded atoms. The interaction between Cl-atoms attached to different Si-atoms is neglected, because if the repulsive force constant between two chlorine atoms bonded to the different Si-atoms is calculated from Eq. (3) to be described below, it is found to be less than 0.01×10^5 dynes/cm. The secular equation is calculated by the method presented by Wilson.⁶

$$|\mathbf{GF} - \lambda \mathbf{E}| = 0, \quad (2)$$

of which the G - and F -matrices are given in Eqs. (4) and (6) in the preceding paper.⁷ So far as we neglect the interaction between atoms bonded to different Si-atoms, we can at once show that the frequencies of the normal vibrations of ethane-like molecules are independent of the angle of internal rotation, since the G - and F -matrices are the same for all internal positions.

For the calculation of the vibrational frequencies from this secular equation using the potential function stated above, nine force constants, K_{SiSi} , K_{SiCl} , H_{ClSiCl} , H_{ClSiSi} , F'_{ClCl} , F_{ClCl} , F'_{SiSi} , F_{SiSi} and an intramolecular tension κ are necessary.* Four of these constants, K_{SiCl} , H_{ClSiCl} , F'_{ClCl} , and F_{ClCl} , can be obtained directly from

⁶ E. Bright Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

⁷ T. Simanouti, J. Chem. Phys. 17, 848 (1949).

* For the significance of κ refer to T. Simanouti, J. Chem. Phys. 17, 245 (1949). The other constants K' and H' are represented in terms of F' and κ .

TABLE IV. Assignment of the combination tones and overtones of hexachlorodisilane.

Observed frequency (cm ⁻¹)	Assignment	Symmetry and selection rule for the Raman effect			
		D_{3h}'		D_{3d}	
377	124×3=372	A_1	active	A_{1g}	active
387	132×3=396	$\bar{A}_1+\bar{A}_2+\bar{E}$	active	$A_{1g}+A_{2g}+E_g$	active
	211+179=390	$\bar{A}_1+\bar{A}_2+\bar{E}$	active	$A_{1u}+A_{2u}+E_u$	inactive
420	211×2=422	A_1+E	active	$A_{1g}+E_g$	active
	179+124×2=427	E	active	E_u	inactive
454	211+124×2=459	\bar{E}	active	E_g	active
484	354+124=478	A_1	active	A_{1g}	active
	354+132=486	\bar{E}	active	E_g	active
	211+132×2=475	$\bar{A}_1+\bar{A}_2+2\bar{E}$	active	$A_{1g}+A_{2g}+2E_g$	active
651	354+179+124=657	E	active	E_u	inactive
	211+179+132×2=654	$2\bar{A}_1+2\bar{A}_2+4\bar{E}$	active	$2A_{1u}+2A_{2u}+4E_u$	inactive
	179×3+124=661	A_1+A_2+E	active	$A_{1u}+A_{2u}+E_u$	inactive
	132×4+124=652	$\bar{A}_1+2\bar{E}$	active	$A_{1g}+2E_g$	active
	132×5=660	$\bar{A}_1+\bar{A}_2+2\bar{E}$	active	$A_{1g}+A_{2g}+2E_g$	active
710	354×2=708	A_1	active	A_{1g}	active
	354+179×2=712	A_1+E	active	$A_{1g}+E_g$	active
	354+211+132=697	A_1+A_2+E	active	$A_{1g}+A_{2g}+E_g$	active

the normal frequencies of SiCl₄.⁷ As to the other five we have taken the values shown in Table III so as to give the best fit with the observed frequencies.

In Table II are shown the calculated frequencies which are in good agreement with those observed, if these are assigned as in the last column of that table. The most remarkable difference between our assignment and that of Stitt and Yost lies in that for the vibration of $\nu(\text{Si}-\text{Si})$. Assuming both SiH₃ and SiCl₃ as one particle, Stitt and Yost calculated this frequency as 200 cm⁻¹ by use of the force constants 1.7×10^5 dynes/cm obtained from the analysis of the spectra of disilane Si₂H₆, and they assigned the observed frequency of 179 cm⁻¹ to the $\nu(\text{Si}-\text{Si})$ vibration. Our calculation has given 626 cm⁻¹ as the frequency of $\nu(\text{Si}-\text{Si})$ of Si₂Cl₆, so that the observed frequency of 622 cm⁻¹ should be assigned to this vibration, while the line at 179 cm⁻¹ is assigned to the deformation vibration of E_u type† computed as 188 cm⁻¹. The

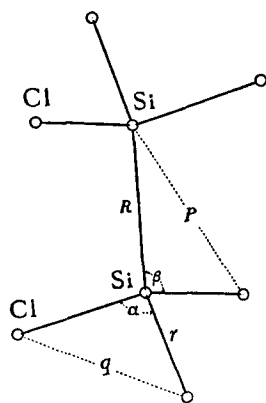


FIG. 1. Coordinates used for hexachlorodisilane.

† Naming the symmetry of the vibrations in accord with the D_{3d} configuration is not to be interpreted as eliminating the D_{3h}' or D_{3h} possibility.

valency vibration of E_g type, computed by the calculation as 625 cm⁻¹, seems to overlap with the frequency 626 cm⁻¹ of A_{1g} type. This assignment is justified by the fact reported by Stitt and Yost that the degree of depolarization of this line is larger than the other two frequencies of A_{1g} type.

The weak lines observed in the Raman spectra may correspond to combination tones or overtones. Their possible assignments and the selection rules are given in Table IV, which shows that almost all the Raman lines are well explained by the model of D_{3h}' as well as by that of D_{3d} except the frequency of 651 cm⁻¹. As to this frequency there are many possibilities of assignment, but all the higher harmonics of the Raman-active vibrations of the model of D_{3d} do not probably appear in the Raman effect. This fact favors the model of D_{3h}' (freely rotating model).

Stitt and Yost assumed the existence of the frequency of 252 cm⁻¹ to explain combination tones. Since this frequency is not observed in the Raman spectra, it must belong to the class of \bar{A}_2 for the model of D_{3h}' and to that of A_{2u} or E_u for the model of D_{3d} . Accordingly, some of their assignments of the combination tones are not acceptable from the selection rules. We did not use such an unobserved frequency in our assignment, and could explain all of the observed frequencies without any contradiction to the selection rules.

DISCUSSION

The most important point of our assignment refers to the fact that the frequencies 588 cm⁻¹ and 179 cm⁻¹ of E_u type for D_{3d} are observed in the Raman effect. This shows that the molecule is not of the staggered form, since E_u frequencies are not Raman-active for D_{3d} symmetry as shown in Table II. Of course they might be explained by the eclipsed form (D_{3h}), but this

possibility is excluded by the result of the electron diffraction experiment described below. Accordingly, we have to conclude that this molecule should belong to the D_{3h}' symmetry.

As to the electron diffraction investigation Brockway and Beach¹ observed four halos in the region of $s=2\sim 8$, and by comparing the calculated intensity curves with the observed result they concluded that this molecule has the staggered form. The eclipsed form was excluded by their result, and also by the recent investigation by Yamasaki, Kotera, Tatematsu, and Iwasaki.²

The experiment of Brockway and Beach is not sufficient for the final determination of the molecular form, because in the region of scattering angle corresponding to $s=2\sim 8$, there is no difference between the intensity curve for the staggered form and that for the freely rotating model. In the next outer region, however, there is a conspicuous difference between the staggered and freely rotating models,² i.e., the staggered form must have a halo of $s=11$, while the freely rotating model has none. Yamasaki, Kotera, Tatematsu, and Iwasaki ascertained that there is no halo of $s=11$, which is a conclusive evidence for the freely rotating model. The result obtained by the Raman effect stated above also confirms this conclusion.

For hexachloroethane Cl_3CCl_3 it was concluded from the investigation of the Raman spectrum^{8,9} and electron diffraction¹⁰ that the equilibrium configuration is the staggered form (D_{3d}), and that the forces stabilizing this form result mainly from the steric repulsion between chlorine atoms. As we have shown above, hexachlorodisilane exerts free internal rotation, which can be explained from the greater distance between the chlorine atoms of different rotating groups. In fact, if

we calculate the interatomic potential between chlorine atoms by use of the potential function

$$V = -\frac{1.515 \times 10^{-10}}{r^6} + \frac{1.620 \times 10^{-7}}{r^{12}} \quad \text{erg/molecule } (r \text{ in } \text{\AA} \text{ unit}), \quad (3)$$

which¹¹ was obtained from the second virial coefficient of chlorine gas, we can show that the hindering potential is negligibly small for hexachlorodisilane, while its barrier amounts to 12 kcal./mole for hexachloroethane.

One might consider that owing to the free rotation around the Si—Si axis the Raman lines would become broad. If, however, we neglect the interaction between atoms bonded to different Si-atoms, the frequencies of the normal vibrations are independent upon the angle of internal rotation, and the said interaction is expected to be very small, as stated before. Therefore, even in the case of free rotation the Raman lines do not necessarily become broad.

As the Raman spectra reported above were observed in the liquid state, the intermolecular forces might deform the molecule as in the case of liquid benzene¹² and the selection rule for the D_{3d} symmetry might be broken. This deformation would, however, take place most probably through the internal rotation of SiCl_3 -groups about the Si—Si axis. We need not, therefore, change our explanation of the Raman spectra of hexachlorodisilane, even if we take into account such intermolecular forces in the liquid state.

ACKNOWLEDGMENT

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⁸ Mizushima, Morino, Kawano, and Otiai, J. Chem. Soc. Japan **65**, 127 (1944); Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **42**, 1 (1944).

⁹ D. T. Hamilton and F. F. Cleveland, J. Chem. Phys. **12**, 249 (1944).

¹⁰ Morino, Yamaguchi, and Mizushima, Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **42**, 5 (1944); Y. Morino and M. Kimura, J. Chem. Soc. Japan **68**, 77 (1947); Y. Morino and M. Iwasaki, J. Chem. Phys. **17**, 216 (1949).

¹¹ Y. Morino and I. Miyagawa, J. Chem. Soc. Japan **68**, 62 (1947).

¹² C. K. Ingold, Proc. Roy. Soc. A**169**, 149 (1939).