

Infra-Red Absorption Spectra of SiD_3Cl , SiH_3F , and SiD_3F

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The infra-red absorption spectra of SiD_3Cl , SiH_3F , and SiD_3F are recorded in the 667—3 000 cm^{-1} region on a rock-salt instrument. Observed and estimated values of the fundamental vibrational frequencies are (estimated values in parenthesis): for SiD_3Cl : $\nu_1 = 1\ 619$; $\nu_2 = 848$; ($\nu_3 = 500-560$); $\nu_4 = 1\ 584$; $\nu_5 = 696$; ($\nu_6 = 470-520$); for SiH_3F : $\nu_1 = 2\ 215$; ($\nu_2 \sim 1\ 350$); $\nu_3 = 874$; $\nu_4 = 2\ 215$; $\nu_5 = 980$; $\nu_6 = 739$; for SiD_3F : $\nu_1 = 1\ 610$; $\nu_2 = 959$; $\nu_3 = 885$; $\nu_4 = 1\ 570$; $\nu_5 = 704$; ($\nu_6 \sim 506$). All frequencies are in cm^{-1} .

In connection with microwave work on the silyl halides^{1,2} the infrared absorption spectra of SiD_3Cl , SiH_3F , and SiD_3F were recorded as a check of the purity of the compounds. Because of the small quantities prepared² the gas-pressures which could be obtained were rather small (see experimental part). The spectra are, therefore, by no means complete but in view of the fact that no other investigations of the vibrational spectra of these compounds have so far been published it was decided to give the observed frequencies together with an assignment of them.

FUNDAMENTAL VIBRATION FREQUENCIES OF SiD_3Cl

In this case the assignment may, with relative ease, be made by using the results obtained by Monfils for SiH_3Cl ^{3,4}. His assignment of the fundamental vibrational frequencies of SiH_3Cl is indisputable since it is based on studies of the fine-structure of the bands. Because practically no fine-structure features could be seen by us with our instrument (Beckmann I.R. II) in the case of SiD_3Cl , the assignment which follows (Table I) has been based on several kinds of calculations (1°, 2°, 3°).

1°. Valence-force calculations

With reference to Fig. 1 the potential function used was:

$$\Delta 2V = f_1 (\Delta r_1)^2 + 3 f_2 (\Delta r_2)^2 + 3d_1 (r_1 \Delta \gamma)^2 + 3d_2 (r_2 \Delta \beta)^2 \quad (\text{I})$$

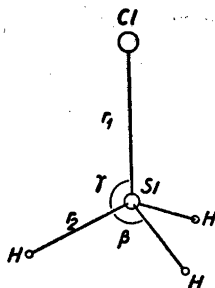


Fig. 1. Showing molecular geometrical parameters of SiH₃Cl.

The corresponding six equations which connect observed frequencies and the constants f_1 , f_2 , d_1 , and d_2 have been given by Wagner⁵. Setting ν_1 , ν_2 , ν_3 (frequencies of totally symmetric vibrations) = 2 196, 1 097.5, 551 from the SiH₃Cl spectrum⁴ we calculate $f_1 = 3.00 \cdot 10^5$, $f_2 = 2.82 \cdot 10^4$, and $D = 0.64 \cdot 10^5$ dynes / cm where D is given by

$$D = \frac{r_1}{r_2} d_1 + 9 \frac{\sin^2 \gamma \cos^2 \gamma}{\sin^2 \beta} d_2^2 \quad (\text{II})$$

Using ν_4 , ν_5 , ν_6 (frequencies of twofold degenerate vibrations) = 2 147.4, 951.2, 666.2 (likewise from the SiH₃Cl spectrum) we get $f_2 = 2.54$, $d_1 = 0.32$, and $d_2 = 0.12$ in units of 10^5 dynes/cm. The deviation between the two values of f_2 does not exceed what must be expected in the valence-force approximation. If the calculated values of d_1 and d_2 are inserted in (II) using $r_1 = 2.048$, $r_2 = 1.48$ Å; $\beta = 110.18^\circ$, $\gamma = 108.75^\circ$ one calculates $D = 0.55 \cdot 10^5$ dynes/cm which, too, is sufficiently consistent with the value of D ($0.64 \cdot 10^5$) calculated above. Now, at the pre-calculation of ν_1 , ν_2 , ν_3 for SiD₃Cl we have used f_1 , f_2 , $D = (3.00; 2.82; 0.64) \cdot 10^5$ dynes/cm while f_2 , d_1 , $d_2 = (2.54; 0.32; 0.12) \cdot 10^5$ dynes/cm were used at the pre-calculation of ν_4 , ν_5 , ν_6 for SiD₃Cl. This might

Table 1. Observed and calculated normal vibration frequencies of SiD₃Cl.

Observed frequencies (cm ⁻¹)		Calculated normal vibration frequencies for SiD ₃ Cl (cm ⁻¹)			
SiH ₃ Cl ⁴	SiD ₃ Cl	Valence-force calc.	Noether's rule ⁶		Teller's rule ⁷
			(A)	(B)	
2 196	1 619	$\nu_1 = 1 564$	1 595	1 600	
1 097.5	848	$\nu_2 = 831$		834	
551	Not obs.	$\nu_3 = 523$	557	523	495
2 147.5	1 584	$\nu_4 = 1 542$	1 525	1 614	
951.2	696 *	$\nu_5 = 651$	683	692	
666.2	Not obs.	$\nu_6 = 519$		509	474

* Maximum of optical density. \perp -band structure observed.

seem inconsistent but it must be remembered that no *precise* physical meaning can be ascribed to the constants in the abbreviated potential function which is used at 'valence-force' calculations. The results of the calculations are given in the third column of Table 1. It is consistent with the assignment suggested in the second column of the same table.

2°. Application of Noether's rule⁶

Noether's semi-empirical rule was originally applied successfully by him in cases such as (III):

$$\frac{\nu_i(\text{CH}_3\text{Cl})}{\nu_i(\text{CD}_3\text{Cl})} = \frac{\nu_i(\text{CH}_3\text{Br})}{\nu_i(\text{CD}_3\text{Br})} \quad (\text{III})$$

Here, the rule was used in its original form (A) and in a slightly deviating form (B):

$$\frac{\nu_i(\text{SiH}_3\text{F})}{\nu_i(\text{SiD}_3\text{F})} = \frac{\nu_i(\text{SiH}_3\text{Cl})}{\nu_i(\text{SiD}_3\text{Cl})} \quad (\text{A}) \qquad \frac{\nu_i(\text{CH}_3\text{Cl})}{\nu_i(\text{CD}_3\text{Cl})} = \frac{\nu_i(\text{SiH}_3\text{Cl})}{\nu_i(\text{SiD}_3\text{Cl})} \quad (\text{B})$$

The silyl fluoride frequencies necessary for the use of (A) are given in Table 2. The methyl halide frequencies were taken from Herzberg⁸.

3°. Application of Teller's rule

Teller's theoretically well-established rule was used in the form

$$\frac{\text{Product of } \left\{ \begin{array}{l} \text{totally symmetric} \\ \text{twofold degenerate} \end{array} \right\} \text{ vibration frequencies of SiD}_3\text{Cl}}{\text{Product of } \left\{ \begin{array}{l} \text{totally symmetric} \\ \text{twofold degenerate} \end{array} \right\} \text{ vibration frequencies of SiH}_3\text{Cl}} = \left\{ \begin{array}{l} S \\ E \end{array} \right.$$

where $S = \frac{m_{\text{H}}}{m_{\text{D}}} \sqrt{\frac{M(\text{SiD}_3\text{Cl})}{M(\text{SiH}_3\text{Cl})}}$ and $E = \left(\frac{m_{\text{H}}}{m_{\text{D}}}\right)^{3/2} \sqrt{\frac{M(\text{SiD}_3\text{Cl})B(\text{SiH}_3\text{Cl})}{M(\text{SiH}_3\text{Cl})B(\text{SiD}_3\text{Cl})}}$

Here, m_{H} is the mass of hydrogen, $M(\text{SiH}_3\text{Cl})$ the mass of SiH_3Cl etc. while $B(\text{SiH}_3\text{Cl})$ is the rotational constant of SiH_3Cl corresponding to rotation about an axis perpendicular to the threefold axis of symmetry. Inserting the values of the masses and $B(\text{SiH}_3\text{Cl}) = 6\,674 \text{ MHz}$, $B(\text{SiD}_3\text{Cl}) = 5\,918 \text{ MHz}^{1,2}$ we get $S = 0.512$ and $E = 0.384$. Taking three observed frequencies from the SiH_3Cl spectrum and two observed frequencies from the SiD_3Cl spectrum, ν_3 and ν_6 for SiD_3Cl were calculated. Since observed frequencies, rather than frequencies corrected for anharmonicity had to be used, the calculated values of ν_3 and ν_6 probably represent *lower* limits to the true values. It is seen from Table 1 that all calculated frequencies agree pretty well with the observed spectral lines.

FUNDAMENTAL VIBRATION FREQUENCIES OF SiH_3F AND SiD_3F

To the best of our knowledge no infra-red absorption spectrum of 'light' and 'heavy' silyl fluoride has hitherto been reported. In spite of the small quantities of the silyl fluorides prepared by us we were able to localize five of

the six fundamentals in each of the spectra. Furthermore sufficient fine-structure features could here be seen to warrant an assignment independent of any calculations. The calculations carried out (following the same scheme as above) were undertaken in order to get a check on the assignment made and, too, to get a reasonable good prediction of the localization of the still unobserved fundamental vibrational frequencies.

1°. Valence-force calculations

The straight-forward application of Wagner's formulae to 'light' and 'heavy' silyl fluoride soon leads into trouble such as imaginary force-constants etc. This might perhaps most easily be recognized by observing that $\nu_3(\text{SiD}_3\text{F})$ is larger than $\nu_3(\text{SiH}_3\text{F})$ (see Table 2). The following procedure was, therefore, adopted: since evidently the effect of isotopic substitution is small on ν_3 , we introduced $\nu_3(\text{SiH}_3\text{F}) = \nu_3(\text{SiD}_3\text{F})$ in Wagner's formulae.

Table 2. Observed and calculated normal vibration frequencies of SiH₃F and SiD₃F (cm⁻¹):

Observed frequencies		Calculated frequencies			
SiH ₃ F	SiD ₃ F	Valence-force calc.	Noether's rule (A)	Teller's rule	
2 215 ± 20	1 610 ± 10	$\nu_1(\text{SiD}_3\text{F}) = 1\ 575$	$\nu_1(\text{SiH}_3\text{F}) = 2\ 186$	$\nu_2(\text{SiH}_3\text{F}) = 1\ 370$	
Not obs.	959 ≠	$\nu_2(\text{SiH}_3\text{F}) = 1\ 350$	$\nu_2 \quad \gg = 1\ 240$		
874 ≠	885 ≠	$\nu_3(\text{SiD}_3\text{F}) = 874$	$\nu_4 \quad \gg = 2\ 130$		
2 215 ± 20	1 570 ± 10	$\nu_4(\text{SiD}_3\text{F}) = 1\ 575$	$\nu_5 \quad \gg = 961$		
980 *	704 *	$\nu_5(\text{SiD}_3\text{F}) = 762$			$\nu_6(\text{SiD}_3\text{F}) = 570$
739	Not obs.	$\nu_6(\text{SiD}_3\text{F}) = 506$			

≠ P, Q, and R-branches observed. Calculated P-R separation for SiH₃F: 32.5 cm⁻¹, found for 874-band: 34.5. Calculated for SiD₃F: 33.4 cm⁻¹. Found for 885-band: 33.0, for 959-band about 30 cm⁻¹ (weak band).

* Maximum of optical density. ⊥-band structure observed.

This simplification results in the formulae (V) and (VI) which are given together with (IV), an approximative formula introduced by Wagner himself:

$$\kappa_1^2 = \frac{f_2}{m_2} \left(1 + \frac{3m_2}{M} \cos^2 \alpha \right) \quad (\text{IV}) \quad \kappa_2^2 = \frac{D}{m_2} \left(1 + \frac{3m_2}{M} \right) \quad (\text{V}) \quad \kappa_3^2 = \frac{f_1}{m_1} \left(1 + \frac{m_1}{M} \right) \quad (\text{VI})$$

(Wagner's notation)

From (IV)—(VI) we calculate $f_1 = 5.11 \cdot 10^5$, $f_2 = 2.87 \cdot 10^5$, and $D = 0.892 \cdot 10^5$ dynes/cm. Furthermore, since ν_1 and ν_4 practically coincide we also equalize κ_1 and κ_4 and introduce this simplification in Wagner's formulae for the two-fold degenerate vibrations together with $f_2 = 2.87 \cdot 10^5$ just calculated. Using 'light' frequencies and ignoring a small imaginary part of d_1 we find

$d_1 = 0.314 \cdot 10^5$ and $d_2 = 0.165 \cdot 10^5$ dynes/cm. These force-constants give rise to the precalculated, twofold degenerate 'heavy' frequencies of Table 2. The value of D corresponding to d_1 and d_2 is $0.494 \cdot 10^5$ dynes/cm.

2°, 3°. Application of Noether's and Teller's rules is self-explanatory in this case.

COMPILATION OF FORCE-CONSTANTS FOR METHANE AND SILANE AND MONO-CHLORO AND MONO-FLUORO DERIVATIVES

Table 3 shows that by at large consistent values of stretching and deformation constants are obtained for the group of molecules in question.

Table 3. Force-constants for CH_4 , CH_3F , CH_3Cl , SiH_4 , SiH_3F and SiH_3Cl (in units of 10^5 dynes/cm).

	Carbon } -Halogen Silicon } stretching		Carbon } -Hydrogen Silicon } stretching		Hydrogen- Carbon- (or Silicon)- Halogen deformation	Hydrogen- Carbon (or Silicon)- Hydrogen deformation
	I	II	I	II		
CH_4			5.04	4.66		0.461
CH_3F	5.64 b	5.44	4.71 b	4.50	0.946 b	0.517 b
CH_3Cl	3.34 a	3.25	4.96 a	4.74	0.340 a	0.414 a
‡	3.35 b	3.25	4.90 b	4.74	0.701 b	0.523 b
SiH_4			2.84 a	2.63		0.189 a
SiH_3F	5.11 a	5.32	2.87 a	2.86	0.314 a	0.165 a
SiH_3Cl	3.00 a	2.96	2.82 a	2.77	0.32 a	0.12 a
‡	5.13 c	2.96	2.66 c	2.77	0.28 c	0.19 c

I: Quadratic potential function used; a: valence-force system; b: valence-force system improved by one constant of interaction; c: valence-force system improved by two constants of interaction. II: $\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}$, valid for diatomic molecules, used, considering e. g. CH_3F as consisting of F and a methyl'atom' (group).

It is seen that fairly independent of the approximative potential function assumed, the stretching constants come out almost identical. They represent, therefore, probably not only a mathematical but also a physical quantity (the force necessary to stretch the bonds 1 cm) in contrast to the deformation constants in which several effects seem to merge. The value $5.13 \cdot 10^5$ given by Monfils for the silicon-chlorine stretching constant may be due to a misprint (3.13?) or a computational error since all the other constants given by Monfils agree very well with our results.

Unfortunately, no theoretically derived rule exists connecting observed force-constants with interatomic distances, electron configuration etc. But the

force-constants found here are in agreement with the empirically very well-established rule by Badger⁹:

$$f = \frac{1.86}{(r - \Delta_{ij})^3} 10^5 \text{ dynes/cm. } r \text{ in } \text{Å units.}$$

where f is the stretching constant, r the length of the bond considered and Δ_{ij} depends on the *periods* (rows) in the periodic table to which the two atoms involved belong. In the present case we get:

	Stretching constant	Δ_{ij}	Interatomic distance (Å)	
			Calc. by Badger's rule	Observed
SiH ₄	2.84 10 ⁵	0.59	1.46	1.46
SiH ₃ F	5.11 »	0.90	1.62	1.59
SiH ₃ Cl	3.00 »	1.18	2.03	2.05

EXPERIMENTAL PART

The infrared spectra were taken on a Beckmann I.R. II spectrophotometer using NaCl optics. The length of the gas-cell was 10 cm. At the experiments with SiD₃Cl, SiH₃F, and SiD₃F the pressure was, respectively, 11, 6, and 10 mm of Hg. The temperature was 20° C. Details of the preparation of the samples used are given in reference 2.

Acknowledgments. We are indebted to professor Duchesne, University of Liège, Belgium, who drew our attention to the fact that the publication of the data presented here might be useful. We are indebted to professor Langseth of this laboratory for the loan of the infra-red equipment.

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Received February 9, 1954.