Infra-Red Absorption Spectra of SiD₃Cl, SiH₃F, and SiD₃F

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The infra-red absorption spectra of SiD₃Cl, SiH₃F, and SiD₃F are recorded in the 687-3000 cm⁻¹ region on a rock-salt instrument. Observed and estimated values of the fundamental vibrational frequencies are (estimated values in parenthesis): for SiD₃Cl: \( v₁ = 1619; \) \( v₂ = 888; \) \( (v₃ = 560-560); \) \( v₄ = 1584; \) \( v₅ = 696; \) \( (v₆ = 470-520); \)

for SiH₃F: \( v₁ = 2215; \) \( (v₂ \sim 1350); \) \( v₃ = 874; \) \( v₄ = 2215; \) \( v₅ = 980; \)

\( v₆ = 739; \) for SiD₃F: \( v₁ = 1610; \) \( v₂ = 959; \) \( v₃ = 885; \) \( v₄ = 1570; \)

\( v₅ = 704; \) \( (v₆ \sim 506).\) All frequencies are in cm⁻¹.

In connection with microwave work on the silyl halides, the infrared absorption spectra of SiD₃Cl, SiH₃F, and SiD₃F were recorded as a check of the purity of the compounds. Because of the small quantities prepared, 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 SiD₃Cl

In this case the assignment may, with relative ease, be made by using the results obtained by Monfils for SiH₃Cl. His assignment of the fundamental vibrational frequencies of SiH₃Cl 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 SiD₃Cl, 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:

\[ \Delta 2V = f₁(\Delta r₁)² + 3 f₂(\Delta r₂)² + 3d₁(r₁\Delta γ)² + 3d₂(r₁\Delta β)² \]

(1)

Acta Chem. Scand. 8 (1954) No. 5
The corresponding six equations which connect observed frequencies and the constants \( f_1, f_2, d_1, \) and \( d_2 \) have been given by Wagner. Setting \( \nu_1, \nu_2, \nu_3 \) (frequencies of totally symmetric vibrations) = 2.198, 1.097.5, 551 from the \( \text{SiH}_3\text{Cl} \) spectrum we calculate \( f_1 = 3.00 \cdot 10^6, f_2 = 2.82 \cdot 10^4, \) and \( D = 0.64 \cdot 10^6 \) dynes/cm where \( D \) is given by

\[
D = \frac{r_1}{r_2} d_1 + 9 \frac{\sin^2 \gamma \cos^2 \gamma}{\sin^2 \beta} d_2^2
\]  

Using \( \nu_4, \nu_5, \nu_6 \) (frequencies of twofold degenerate vibrations) = 2.147.4, 951.2, 666.2 (likewise from the \( \text{SiH}_3\text{Cl} \) spectrum) we get \( f_2 = 2.54, d_1 = 0.32, \) and \( d_2 = 0.12 \) in units of \( 10^6 \) 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 \( r_1 = 2.048, \)
\( r_3 = 1.48 \text{ Å}; \beta = 110.18^\circ, \gamma = 108.75^\circ \) one calculates \( D = 0.55 \cdot 10^6 \) dynes/cm which, too, is sufficiently consistent with the value of \( D (0.64 \cdot 10^6) \) calculated above. Now, at the pre-calculation of \( \nu_1, \nu_2, \nu_3 \) for \( \text{SiD}_3\text{Cl} \) we have used \( f_1, f_2, D = (3.00; 2.82; 0.64) \cdot 10^6 \) dynes/cm while \( f_2, d_1, d_2 = (2.54; 0.32; 0.12) \cdot 10^6 \) dynes/cm were used at the pre-calculation of \( \nu_4, \nu_5, \nu_6 \) for \( \text{SiD}_3\text{Cl}. \) This might

<table>
<thead>
<tr>
<th>Table 1. Observed and calculated normal vibration frequencies of ( \text{SiD}_3\text{Cl} ).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Observed frequencies (cm^{-1})</strong></td>
</tr>
<tr>
<td><strong>Valence-force calc.</strong></td>
</tr>
<tr>
<td>SiH₃Cl</td>
</tr>
<tr>
<td>2.198</td>
</tr>
<tr>
<td>1.097.5</td>
</tr>
<tr>
<td>551</td>
</tr>
<tr>
<td>2.147.5</td>
</tr>
<tr>
<td>951.2</td>
</tr>
<tr>
<td>666.2</td>
</tr>
</tbody>
</table>

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

*Acta Chem. Scand. 8 (1954) No. 5*
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 rule

Noether's semi-empirical rule was originally applied successfully by him in cases such as (III):
\[
\frac{v_1 (\text{CH}_3\text{Cl})}{v_1 (\text{CD}_3\text{Cl})} = \frac{v_1 (\text{CH}_3\text{Br})}{v_1 (\text{CD}_3\text{Br})}
\]  

(III)

Here, the rule was used in its original form (A) and in a slightly deviating form (B):
\[
\frac{v_1 (\text{SiH}_3\text{F})}{v_1 (\text{SiD}_3\text{F})} = \frac{v_1 (\text{SiH}_3\text{Cl})}{v_1 (\text{SiD}_3\text{Cl})} \quad \text{(A)} \quad \frac{v_1 (\text{CH}_3\text{Cl})}{v_1 (\text{CD}_3\text{Cl})} = \frac{v_1 (\text{SiH}_3\text{Cl})}{v_1 (\text{SiD}_3\text{Cl})} \quad \text{(B)}
\]

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

3°. Application of Teller's rule

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

Product of [totally symmetric] vibration frequencies of SiD₃Cl
\[
\text{SiH₃Cl} = \left\{ \begin{array}{c} S \\ E \end{array} \right\}
\]

where

\[
S = \frac{m_H}{m_D} \sqrt{\frac{M(\text{SiD}_3\text{Cl})}{M(\text{SiH}_3\text{Cl})}} \quad \text{and} \quad E = \left(\frac{m_H}{m_D}\right)^{1/2} \sqrt{\frac{M(\text{SiD}_3\text{Cl})B(\text{SiH}_3\text{Cl})}{M(\text{SiH}_3\text{Cl})B(\text{SiD}_3\text{Cl})}}
\]

Here, \( m_H \) is the mass of hydrogen, \( M(\text{SiH}_3\text{Cl}) \) the mass of \( \text{SiH}_3\text{Cl} \) etc. while \( B(\text{SiH}_3\text{Cl}) \) is the rotational constant of \( \text{SiH}_3\text{Cl} \) corresponding to rotation about an axis perpendicular to the threefold axis of symmetry. Inserting the values of the masses and \( B(\text{SiH}_3\text{Cl}) = 6.674 \text{ MHz} \), \( B(\text{SiD}_3\text{Cl}) = 5.918 \text{ MHz} \) we get \( S = 0.512 \) and \( E = 0.384 \). Taking three observed frequencies from the \( \text{SiH}_3\text{Cl} \) spectrum and two observed frequencies from the \( \text{SiD}_3\text{Cl} \) spectrum, \( v_3 \) and \( v_6 \) for \( \text{SiD}_3\text{Cl} \) were calculated. Since observed frequencies, rather than frequencies corrected for anharmonicity had to be used, the calculated values of \( v_3 \) and \( v_6 \) 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 SiH₃F AND SiD₃F

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

Acta Chem. Scand. 8 (1954) No. 5
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 \( v_3(\text{SiD}_3\text{F}) \) is larger than \( v_3(\text{SiH}_3\text{F}) \) (see Table 2). The following procedure was, therefore, adopted: since evidently the effect of isotopic substitution is small on \( v_3 \), we introduced \( v_3(\text{SiH}_3\text{F}) = v_3(\text{SiD}_3\text{F}) \) in Wagner’s formulæ.

Table 2. Observed and calculated normal vibration frequencies of SiH\(_3\)F and SiD\(_3\)F (cm\(^{-1}\)):

<table>
<thead>
<tr>
<th>Observed frequencies</th>
<th>Valence-force calc.</th>
<th>Noether’s rule (A)</th>
<th>Teller’s rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH(_3)F</td>
<td>SiD(_3)F</td>
<td>( v_1 ) (SiD(_3)F) = 1 575</td>
<td>( v_1 ) (SiH(_3)F) = 2 186</td>
</tr>
<tr>
<td>2 215 ± 20</td>
<td>1 610 ± 10</td>
<td>( v_1 ) (SiH(_3)F) = 1 350</td>
<td>( v_2 ) (SiH(_3)F) = 874</td>
</tr>
<tr>
<td>Not obs.</td>
<td>959*</td>
<td>( v_2 ) (SiD(_3)F) = 762</td>
<td>( v_4 ) (SiH(_3)F) = 506</td>
</tr>
<tr>
<td>874 ≠</td>
<td>885 ≠</td>
<td>( v_2 ) (SiH(_3)F) = 874</td>
<td>( v_4 ) (SiH(_3)F) = 2 130</td>
</tr>
<tr>
<td>980</td>
<td>704*</td>
<td>( v_4 ) (SiH(_3)F) = 762</td>
<td>( v_4 ) (SiH(_3)F) = 961</td>
</tr>
<tr>
<td>739</td>
<td>Not obs.</td>
<td>( v_4 ) (SiH(_3)F) = 506</td>
<td>( v_4 ) (SiD(_3)F) = 570</td>
</tr>
</tbody>
</table>

≠ P, Q, and R-branches observed. Calculated P—R separation for SiH\(_3\)F: 32.5 cm\(^{-1}\), found for 874-band: 34.5. Calculated for SiD\(_3\)F: 33.4 cm\(^{-1}\). Found for 885-band: 33.0, for 959-band about 30 cm\(^{-1}\) (weak band).

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

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

\[ \chi_1^2 = \frac{f_2}{m_2} (1 + \frac{3m_3}{M} \cos^2 \alpha) \]  
\[ (IV) \]

\[ \chi_2^2 = \frac{D}{m_2} (1 + \frac{3m_3}{M}) \]  
\[ (V) \]

\[ \chi_3^2 = \frac{|f_1|}{m_1} (1 + \frac{m_1}{M}) \]  
\[ (VI) \]

(Wagner’s notation)

From (IV)—(VI) we calculate \( f_1 = 5.11 \times 10^5 \), \( f_2 = 2.87 \times 10^5 \), and \( D = 0.892 \times 10^3 \) dynes/cm. Furthermore, since \( v_1 \) and \( v_2 \) practically coincide we also equalize \( \chi_1 \) and \( \chi_2 \) and introduce this simplification in Wagner’s formulæ for the two-fold degenerate vibrations together with \( f_2 = 2.87 \times 10^5 \) just calculated. Using ‘light’ frequencies and ignoring a small imaginary part of \( d_1 \) we find

Acta Chem. Scand. 8 (1954) No. 5
\( d_1 = 0.314 \cdot 10^8 \) and \( d_2 = 0.165 \cdot 10^8 \) 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 \( 0.494 \cdot 10^8 \) 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 CH₂, CH₂F, CH₂Cl, SiH₂, SiH₂F and SiH₂Cl (in units of \( 10^8 \) dynes/cm).**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Halogen</td>
<td></td>
<td>- Silicon</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td></td>
<td>(or Silicon)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deformation</td>
</tr>
<tr>
<td></td>
<td>stretching</td>
<td>II</td>
<td>I</td>
</tr>
<tr>
<td>CH₄</td>
<td>I</td>
<td>II</td>
<td>5.64b</td>
</tr>
<tr>
<td>CH₂F</td>
<td>5.44b</td>
<td>4.50b</td>
<td>0.946b</td>
</tr>
<tr>
<td>CH₂Cl</td>
<td>3.34a</td>
<td>4.74a</td>
<td>0.340a</td>
</tr>
<tr>
<td></td>
<td>3.25b</td>
<td>4.74b</td>
<td>0.701b</td>
</tr>
<tr>
<td>SiH₂</td>
<td>I</td>
<td>II</td>
<td>2.84a</td>
</tr>
<tr>
<td>SiH₂F</td>
<td>5.32a</td>
<td>2.86</td>
<td>0.314a</td>
</tr>
<tr>
<td>SiH₂Cl</td>
<td>3.00a</td>
<td>2.77</td>
<td>0.32a</td>
</tr>
<tr>
<td></td>
<td>2.96c</td>
<td>2.77</td>
<td>0.28c</td>
</tr>
</tbody>
</table>

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: \( \nu = \frac{1}{2\pi c} \sqrt{\frac{I}{\mu}} \), valid for diatomic molecules, used, considering \( \text{e.g. CH₂F} \) 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 \( 5.13 \cdot 10^8 \) 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 Badger:

\[ f = \frac{1.86}{(r - A_{ij})^2} \times 10^5 \text{ dynes/cm.} \ r \text{ in Å units.} \]

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

<table>
<thead>
<tr>
<th></th>
<th>Stretching constant</th>
<th>( A_{ij} )</th>
<th>Interatomic distance (Å)</th>
<th>Calc. by Badger’s rule</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>2.84 \times 10⁴</td>
<td>0.59</td>
<td>1.46</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>SiH₂F</td>
<td>5.11</td>
<td>0.90</td>
<td>1.62</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>SiH₂Cl</td>
<td>3.00</td>
<td>1.18</td>
<td>2.03</td>
<td>2.05</td>
<td></td>
</tr>
</tbody>
</table>

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 SiD₄Cl, SiH₂F, and SiD₂F 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.

REFERENCES


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