The Vibrational Spectra and Structures of Hexachlorodisiloxane and Trifluorotrichlorodisiloxane II.

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Abstract

The infrared spectra of Cl₃SiOSiCl₃ and F₃SiOSiCl₃ in gaseous state are measured and the Raman spectra of the molecules are reexamined using Ar⁺ laser. The new results support the author's original contention concerning the structures of these molecules, but require some minor adjustments in the earlier assignments. The vibrational spectrum of Cl₃SiOSiCl₃ has been measured, and it has been reported that the symmetry was C₂ᵥ (bent). However, the present observations seem to show that the vibrational bands obtained can be explained according to D₃d selection rules (linear). Because the irreducible representation of C₂ᵥ point group is 7A₁ (R, p; IR) + 4A₂(R) + 6B₁(R; IR) + 4B₂(R; IR), that is, all 21 fundamentals are allowed in the Raman effect (7 of them as polarized lines) and that 17 fundamentals are allowed in infrared absorption. On the other hand, that of D₃d point group is 3A₁g(R, p) + 3A₂u(IR) + 3E_g(R) + 4E_u(IR). Accordingly, the bands obtained are too simple to be ones of C₂ᵥ model, and it is against C₂ᵥ one that the obtained spectra are mutually exclusive in Raman and infrared.

The vibrational spectrum of F₃SiOSiCl₃ should be assigned according to C₃ᵥ (linear) or Cₛ (bent) model. The irreducible representation of C₃ᵥ point group is 6A₁ (R, p; IR) + 7E(R; IR) and that of Cₛ, 13A' (R, p; IR) + 8A" (R; IR). The vibrational spectrum of F₃SiOSiCl₃ obtained seems to be assigned according to C₃ᵥ selection rules, compared with those of structurally related molecules, Cl₅SiOSiCl₅, F₂SiCl and FSiCl₃. However, the final decision must await the results of the further studies, because it is very important whether Si-O-Si chain is linear or not.

The Raman spectra are recorded on JEOL JRS-SIB spectrophotometer using argon ion laser and the infrared spectra are measured with Shimadzu IR-450 spectrometer, whose gas cell had a path of 10 cm and KRS-5 windows.

1. Introduction

The D₃d model for hexachlorodisiloxane (Cl₅SiOSiCl₅) has six Raman active fundamentals and seven infrared active ones, which are mutually exclusive in the
Raman and infrared, whereas less symmetric model $C_{2v}$ would give twenty-one fundamentals, all of which are Raman active and seventeen of which are both Raman and infrared active.

It appears doubtful that the vibrational bands of Cl$_3$SiOSiCl$_3$ have been assigned according to $C_{2v}$ selection rules as indicated in the previous literatures$^{1-14}$, except the literatures describing that the symmetry of disiloxane (H$_3$SiOSiH$_3$) was $D_{3d}$$^{13}$ (linear Si-O-Si) and that of Cl$_3$SiOSiCl$_3$, $D_{3d}$$^{14}$ (linear Si-O-Si). Because only nine of 21 fundamental bands can be found in the Raman spectrum obtained, some of which may correspond to overtone or combination bands, and this fact seems to be sufficient to exclude the $C_{2v}$ model which should have 21 fundamentals which are Raman active. The present author has therefore found it worthwhile to investigate the structure of Cl$_3$SiOSiCl$_3$ by measuring the vibrational spectra and by comparing the spectra with those of structurally related molecules; F$_3$SiOSiCl$_3$$^{15}$, F$_3$SiCl and F$_3$SiCl$_3$$^{16,17}$.

The assignments of the vibrational spectra of F$_3$SiOSiCl$_3$ which would supply useful informations for the structure of Cl$_3$SiOSiCl$_3$ as well as that of F$_3$SiOSiCl$_3$ is the first example.

2. Experimental

A compound Cl$_3$SiOSiCl$_3$ was purchased from commercial source and purified by distillation. In order to synthesize F$_3$SiOSiCl$_3$, Cl$_3$OSiCl$_3$ was fluorinated using SbF$_3$ and incorporating SbCl$_5$ as a catalyst$^{18}$, and the synthesized F$_3$SiOSiCl$_3$ was separated by fractional distillation.

Raman spectra are recorded on JEOL JRS-SIB spectrometer using argon ion laser, and the infrared spectra are measured with Shimadzu IR-450 spectrometer, whose gas cell had a path of 10 cm and KRS-5 windows.

3. Results and Discussion

3-1. Vibrational Spectra of Cl$_3$SiOSiCl$_3$

The Raman and infrared spectra of Cl$_3$SiOSiCl$_3$ are given in Fig. 1. It is clearly seen that the spectra indicate the lack of coincidence between Raman and infrared frequencies which means that the molecule has a center of symmetry, and are too simple to be interpreted according to $C_{2v}$ symmetry which has 21 Raman active fundamentals and 17 infrared active ones, as shown in the irreducible representation of $C_{2v}$; $7A_1(R; p) + 4A_2(R) + 6B_1(R; IR) + 4B_2(R; IR)$. The spectra of Cl$_3$SiOSiCl$_3$ observed are in excellent agreement with the selection rules expected for $D_{3d}$ model$^{*1}$, the irreducible representation of which is $3A_1g(R; p) + 3A_2g(IR) + 3E_g(R) + 4E_u(IR)$.

$^*$1 A $D_{3h}$ symmetry, the irreducible representation of which is $3A_1^\prime(R; p) + 3A_2^\ast(IR) + 4E^\prime(R; IR) + 3E^\ast(R)$ is reasonable for linear Cl$_3$SiOSiCl$_3$, too, but $D_{3h}$ symmetry does not have a symmetry center.
3-I-I. *A*$_{1g}$ Bands  These are Raman active, polarized and infrared inactive. The Raman band of FSiCl$_3$\textsuperscript{16, 17} that corresponds to (p)728 cm\textsuperscript{-1} Raman band of Cl$_3$SiOSiCl$_3$ does not exist, but (p)672 cm\textsuperscript{-1} Raman band of F$_3$SiOSiCl$_3$ seems to correspond to the (p)728 cm\textsuperscript{-1} one of Cl$_3$SiOSiCl$_3$. Accordingly the (p)728 cm\textsuperscript{-1} band should be due to Si-O-Si stretching or bending which does not exist
for FSiCl₃. On the basis of the polarization state, the (p) 728 cm⁻¹ band can be assigned
to symmetric Si-O-Si stretching (νₛSi-O-Si)*² It is well known that a band of symmetric
Si-Cl stretching (νₛSiCl)*² would be very strong band which is polarized, lying at 450
cm⁻¹ region.*¹, *⁴ For example, the very intensive and polarized band at 464 cm⁻¹
of FSiCl₃ is assigned to νₛSiCl.*¹⁶, *¹⁷ So the (p) 422 cm⁻¹ band of Cl₂SiOSiCl₃ can be
assigned to νₛSiCl, where the lowering frequency than expected might be due to the
coupling of νₛSiCl (A₁g) and δSiCl₃(A₁g).*¹⁴ There remains symmetric SiCl₃
deformation(δ₃SiCl₃), and the polarized bands at 330, 351 and 389 cm⁻¹ could be
considered as δ₃SiCl₃ mode. Compared with the δ₃SiCl₃ bands of F₃SiOSiCl₃ and
FSiCl₃,*³ the (p) 330 cm⁻¹ band is assigned to δ₃SiCl₃.*⁴

3-1-2. A₂α Bands These are infrared active and Raman inactive. The
asymmetric Si-O-Si stretching modes of substituted disiloxanes have been found to
exhibit relative constancy from one compound to the next.*²¹ For example, bands
arising from this mode of vibration appear at 1107 cm⁻¹ in the spectrum of
H₃SiOSiH₃,*¹³ at 1060 cm⁻¹ in that of Me₃SiOSiMe₃,*²² at 1075 cm⁻¹ in that of
φ₃SiOSiφ₃,*²³ (Me=methyl, φ=phenyl), and at 1175 cm⁻¹ in that of F₃SiOSiCl₃ as
shown in Fig.1. The only band appearing in the spectrum of Cl₂SiOSiCl₃ within this
wave number region is the strong infrared band at 1180 cm⁻¹. Therefore this band is
confidently assigned to νₐₐSi-O-Si. The Raman counterpart is unobserved. If Cl₂SiOSiCl₃
has C₃ᵥ symmetry, νₐₐSi-O-Si band should appear in Raman. Therefore this strongly
supports D₃d for Cl₃SiOSiCl₃, too.

Molecule Cl₂SiOSiCl₃ is considered as a derivative in which SiCl₃ group is
connected to FSiCl₃ in opposite direction along the z axis and an oxygen atom is
inserted between the two SiCl₃ groups instead of a fluorine atom. Consequently the
νₛSiCl in FSiCl₃ is split to νₛSiCl(A₁g) and νₐₐSiCl (A₂α) in Cl₂SiOSiCl₃, and so the
νₐₐSiCl of Cl₂SiOSiCl₃ would appear near νₛSiCl of FSiCl₃ and Cl₂SiOSiCl₃ in
frequencies.*⁵ Accordingly the strong 480 cm⁻¹ band is assigned to asymmetric SiCl₃
stretching(νₐₐSiCl), compared with the frequency(422 cm⁻¹) of νₛSiCl(A₁g). The 339
cm⁻¹ band can be assigned to asymmetric SiCl₃ deformation (δₐₐSiCl₃) in a similar
manner as above.*⁵

3-1-3. Eₐ Bands These are Raman active, depolarized, and infrared
inactive. The bands at 613, 220 and 133 cm⁻¹, all of which are depolarized, are

*²) Some literatures *⁸, *¹² have assigned intensive and polarized 422 cm⁻¹ band to νₛSi-O-Si,
but the band should be assigned to νₛSiCl.

*³) It is well known that the frequencies of νₛCH₃, νₐₐCH₃ and δₐₐCH₃ are remarkably
constant throughout the series of molecule CH₃X(X=F, Cl, Br, I)*¹⁹, *₂⁰. This is, also, the
case for compounds containing SiCl₃ and SiF₃ groups.

*⁴) The literature*¹⁴ has assigned 330 cm⁻¹ to νₛSi-O-Si.

*⁵) In the other words, the similar vibration modes which belong to the similar species are
close to each other in frequencies.
assigned to $\nu_{as}$SiCl, $\delta_{as}$SiCl$_3$ and SiCl$_3$ rocking ($\rho_{SiCl_3}$) respectively, compared with those of FSiCl$_3$\(^*3\) and $E_{a}$ bands of Cl$_3$SiOSiCl$_3$\(^*5\).

3-1-4. $E_{a}$ Bands

These are infrared active and Raman inactive. The bands at 642, 247\(^*6\) and 179\(^*6\) cm$^{-1}$ are assigned to $\nu_{as}$SiCl, $\delta_{as}$SiCl$_3$ and $\rho_{SiCl_3}$ respectively, compared with those of FSiCl$_3$\(^*3\) and $E_{g}$ bands of Cl$_3$SiOSiCl$_3$\(^*5\). The 180 cm$^{-1}$ Raman band\(^*7\) found in liquid Cl$_3$SiOSiCl$_3$ may be the infrared fundamental at 179 cm$^{-1}$, appearing in the Raman effect through a breakdown of the selection rules due to intermolecular force active in the liquid. That is to say, this frequency would actually be permitted in the Raman effect even if the selection rules appropriate to $D_{3d}$ configuration apply to Cl$_3$SiOSiCl$_3$\(^2.4\). An absorption intensity of a fundamental vibrational transition which is infrared active is related to the dipole moment derivative, and then the intensity of Si-O-Si bending ($\delta_{Si-O-Si}$) of Cl$_3$SiOSiCl$_3$ would be expected to be weak, because of same end groups. On the other hand, the intensity of $\delta_{Si-O-Si}$ of F$_3$SiOSiCl$_3$, to be not weak, because of different end groups. The very intensive band at 410 cm$^{-1}$ of F$_3$SiOSiCl$_3$ can be assigned to $\delta$Si-O-Si, and the very weak band lying at 400 cm$^{-1}$ of Cl$_3$SiOSiCl$_3$ could be assigned to $\delta$Si-O-Si. This is in agreement with expectations for $\delta$Si-O-Si as mentioned above.

3-1-5. Overtone and Combination Bands

The infrared bands at 1173 and 1130 cm$^{-1}$ would neither $P$ nor $R$ branch of rotation-vibrational band, because the difference of 43 cm$^{-1}$ seems to be too large to be considered as $P-R$ separation value, for molecule having large moment of inertia like Cl$_3$SiOSiCl$_3$. These bands could be interpreted as due to Fermi resonance. Thus 1130($A_{2u}$) is in resonance with 480($A_{2u}$) + 2 x 339($A_{2u}$), the intensity of which is enhanced anomalously by Fermi resonance and is comparable to that of fundamental band. The center of Fermi doublet coincides very nearly with the wave number of combination band. This indicates the resonance of Fermi resonance. The Raman bands at 351 and 389 cm$^{-1}$ could be considered as combination of 220($E_g$) + 133($E_g$) and of 613($E_g$) + 220 ($E_g$), respectively.

Table 1 lists tentative assignments for the fundamental bands observed together with symmetry species and selection rules of $D_{3d}$.

3-2. Vibrational Spectra of F$_3$SiOSiCl$_3$

The Raman and infrared spectra of F$_3$SiOSiCl$_3$ are shown in Fig.1. The symmetry of F$_3$SiOSiCl$_3$ is $C_{3v}$ or $C_{3}$ for linear model and $C_{3}$ for bent one. The irreducible representations of skeletal modes are $6A_1$($R; p; IR$) + 7$E(R; IR)$ in $C_{3v}$, 7$A$($R; p; IR$) + 7$E(R; IR)$ in $C_{3}$.

*6) The bands at 247 and 179 cm$^{-1}$ are out of observational limit due to KRS-5 optics, but the frequencies are cited from the literature.$^3$

*7) In the literature$^{14}$, this 180 cm$^{-1}$ band is assigned to $\delta_{as}$SiCl$_3$. However this line is observed to be depolarized, therefore the above assignment seems to be doubtful. Because the band for totally symmetric deformational mode, $\delta$SiCl$_3$ should be polarized.
Table 1 Symmetry Species and Selection Rules of $D_3d$ and Frequency Assignments of Cl₃SiOSiCl₃

<table>
<thead>
<tr>
<th>Species</th>
<th>Normal Vibrational Modes</th>
<th>Cl₃SiOSiCl₃ (Raman)</th>
<th>Cl₃SiOSiCl₃ (IR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>Si-O-Si sym. str.</td>
<td>($p$) 728w</td>
<td>(ia)</td>
</tr>
<tr>
<td></td>
<td>Si-Cl sym. str.</td>
<td>($p$) 422vs</td>
<td>(ia)</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ sym. def.</td>
<td>($p$) 330m</td>
<td>(ia)</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>Torsion</td>
<td>(ia)</td>
<td>(ia)</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>Si-O-Si asym. str.</td>
<td>(ia)</td>
<td>1130vs</td>
</tr>
<tr>
<td></td>
<td>SiCl asym. str.</td>
<td>(ia)</td>
<td>480s</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ asym. def.</td>
<td>(ia)</td>
<td>339m</td>
</tr>
<tr>
<td>$E_g$</td>
<td>SiCl asym. str.</td>
<td>613w</td>
<td>(ia)</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ asym. def.</td>
<td>220s</td>
<td>(ia)</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ rock.</td>
<td>133vs</td>
<td>(ia)</td>
</tr>
<tr>
<td>$E_u$</td>
<td>SiCl asym. str.</td>
<td>(ia)</td>
<td>642vs</td>
</tr>
<tr>
<td></td>
<td>Si-O-Si bend.</td>
<td>(ia)</td>
<td>~400vww</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ asym. def.</td>
<td>(ia)</td>
<td>(247)*</td>
</tr>
<tr>
<td></td>
<td>SiCl₃ rock.</td>
<td>180**</td>
<td>(179)*</td>
</tr>
</tbody>
</table>

*) This band is out of observational limit, but the frequency is cited from reference 3).

**) This band would be forbidden, but the selection rules forbidding it may be somewhat less rigorous in the liquid due to intermolecular action.

(ia) means inactive.

$7E(R;IR)$ in $C_3$ and $13A^+(R;IR) + 8A^+(R;IR)$ in $C_{3v}$.

The spectra observed seem to be too simple to be interpreted on the basis of $C_3$, selection rules, which has 21 Raman fundamentals, of which 13 ones are polarized and 21 infrared fundamentals. Accordingly the symmetry of F₃SiOSiCl₃ is $C_{3v}$ or $C_3$. It is difficult to differentiate $C_{3v}$ model from $C_3$ one on the basis of the vibrational bands obtained, but $C_{3v}$ model would energetically be preferable to $C_3$ one.

3-2-1. $A_l$ Bands  These are active in both Raman and infrared, and polarized in Raman. The vibrational bands which belong to $A_l$ species are assigned as shown in Table 2, compared with structurally related compounds, Cl₃SiOSiCl₃, FSiCl₃ and F₃SiCl₃ (3). The assignments of Si-O-Si stretching modes of F₃SiOSiCl₃ are discussed previously (3-1-1 and 3-1-2).

3-2-2 $E$ Bands  These are active in both Raman and infrared, and depolarized in Raman. These are assigned as listed in Table 2 in a similar manner...
as above. The assignment of δSi-O-Si is discussed in section 3-1-4.

Table 2  Symmetry Species and Selection Rules of $D_{3d}$ and Frequency Assignments of Fundamentals of $F_3SiOSiCl_3$, $F_3SiCl$ and $FSiCl_3$

<table>
<thead>
<tr>
<th>Normal Vibrational Modes</th>
<th>Species $A_1$</th>
<th>Species $E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
</tr>
<tr>
<td>SiF$_3$ asym. str.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>SiF$_3$ sym. str.</td>
<td>$(p)997w$</td>
<td>902s</td>
</tr>
<tr>
<td>SiF$_3$ asym. def.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>SiF$_3$ sym. def.</td>
<td>$(p)497s$</td>
<td>501s</td>
</tr>
<tr>
<td>SiF$_3$ rock.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>Si-O-Si asym. str.</td>
<td>$(p)1164w$</td>
<td>1175vs</td>
</tr>
<tr>
<td>Si-O-Si sym. str.</td>
<td>$(p)672w$</td>
<td>659m</td>
</tr>
<tr>
<td>Si-O-Si bend.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>SiCl$_3$ asym. str.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>SiCl$_3$ sym. str.</td>
<td>$(p)458w$</td>
<td>458s</td>
</tr>
<tr>
<td>SiCl$_3$ asym. def.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
<tr>
<td>SiCl$_3$ sym. def.</td>
<td>$(p)344m$</td>
<td>340m</td>
</tr>
<tr>
<td>SiCl$_3$ rock.</td>
<td>$(ia)$</td>
<td>$(ia)$</td>
</tr>
</tbody>
</table>

$F_3SiCl$

<table>
<thead>
<tr>
<th>Species</th>
<th>Raman</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(p)73w$</td>
<td>883vs</td>
<td>$(*)$</td>
</tr>
<tr>
<td>265m</td>
<td>(*)</td>
<td>352s</td>
</tr>
<tr>
<td>222m</td>
<td>$(*)$</td>
<td></td>
</tr>
</tbody>
</table>

$FSiCl_3$

<table>
<thead>
<tr>
<th>Species</th>
<th>Raman</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(p)804w$</td>
<td>466w</td>
<td></td>
</tr>
<tr>
<td>278m</td>
<td>$(*)$</td>
<td></td>
</tr>
<tr>
<td>$(p)23w$</td>
<td>$(*)$</td>
<td></td>
</tr>
<tr>
<td>165s</td>
<td>$(*)$</td>
<td></td>
</tr>
</tbody>
</table>

$(ia)$ means inactive, and $(*)$ means out of observational limit.

3-2-3. Overtone and Combination Bands  The 1220 cm$^{-1}$ infrared band could be interpreted as due to Fermi resonance in similar manner as that of the 1173 cm$^{-1}$ band of Cl$_3$SiOSiCl$_3$. Thus 1175(A$_1$) is in resonance with 501(A$_1$)+2×340(A$_1$), the intensity of which is enhanced anomalously by Fermi resonance. The center of Fermi doublet coincides very nearly with the frequency of the combination band. The intensive infrared band at 957 cm$^{-1}$ may be one of Fermi doublet due to 902(A$_1$) and 2×458(A$_1$). The 681 cm$^{-1}$ infrared band can be considered as first overtone of 340 cm$^{-1}$ one; 436, as that of 220, and 359, as that of 177 cm$^{-1}$.

3-2-4. Impurity  The $(p)800$ cm$^{-1}$ band may be due to SiF$_4$ included in $F_3SiOSiCl_3$ as impurity, since the most intensive Raman band of SiF$_4$ is $(p)800$ cm$^{-1}$ band assigned to $\nu_3^{n}SiF$.

4. Conclusion

From the observed spectra, it would be clear that the Si-O-Si skeleton is linear in both Cl$_3$SiOSiCl$_3$ and $F_2SiOSiCl_3$, for coincidence between Raman and infrared
frequencies which are the spectral feature of $C_{2v}$ symmetry (bent Si-O-Si) for Cl$_3$SiOSiCl$_3$ does not occur and less fundamentals of F$_3$SiOSiCl$_3$ appear for $C_{2v}$ linear model to be acceptable. The only argument against linear Si-O-Si is that the Si-O-Si chain should be bent, on the basis of the fact that —O— is bent in H$_2$O molecule, but some literatures support experimentally a linear —O— for gaseous Z-O-H (Z = K, Rb, Cs). In addition it is possible to consider the 2s and 2$^p_z$ orbitals in oxygen atom as being hybridized to be linear.\textsuperscript{8)}

Table 2 lists the tentative assignments for the fundamental bands observed together with symmetry species and selection rules.

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\textsuperscript{8)} The ground state of the oxygen atom is $1s^22s^22p^4$. In order to display a linear valence of two, the oxygen atom must have two electrons with uncoupled spins. The way to obtain this condition is to excite one of the 2s electrons into 2$p$ state, and to have the resulting 2$p_z$ electron with uncoupled spin, and 2$p_x$ and 2$p_y$ electrons with coupled spins. Then the 180° bond angle in Si-O-Si could be produced by mixing 50 per cent 2$s^1$ and 50 per cent 2$p_z^2$. 
References