

# The Vibrational Spectra and Structures of Hexachloro- disiloxane and Trifluorotrichlorodisiloxane II.

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## Abstract

The infrared spectra of  $\text{Cl}_3\text{SiOSiCl}_3$  and  $\text{F}_3\text{SiOSiCl}_3$  in gaseous state are measured and the Raman spectra of the molecules are reexamined using  $\text{Ar}^+$  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.<sup>1-a)</sup>

The vibrational spectrum of  $\text{Cl}_3\text{SiOSiCl}_3$  has been measured, and it has been reported that the symmetry was  $C_{2v}$  (bent). However the present observations seem to show that the vibrational bands obtained can be explained according to  $D_{3d}$  selection rules (linear). Because the irreducible representation of  $C_{2v}$  point group is  $7A_1(R, p; IR) + 4A_2(R) + 6B_1(R; IR) + 4B_2(R; IR)$ , 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  $D_{3d}$  point group is  $3A_{1g}(R, p) + 3A_{2u}(IR) + 3E_g(R) + 4E_u(IR)$ . Accordingly the bands obtained are too simple to be ones of  $C_{2v}$  model, and it is against  $C_{2v}$  one that the obtained spectra are mutually exclusive in Raman and infrared.

The vibrational spectrum of  $\text{F}_3\text{SiOSiCl}_3$  should be assigned according to  $C_{3v}$  (linear) or  $C_s$  (bent) model. The irreducible representation of  $C_{3v}$  point group is  $6A_1(R, p; IR) + 7E(R; IR)$  and that of  $C_s$ ,  $13A'(R, p; IR) + 8A''(R; IR)$ . The vibrational spectrum of  $\text{F}_3\text{SiOSiCl}_3$  obtained seems to be assigned according to  $C_{3v}$  selection rules, compared with those of structurally related molecules,  $\text{Cl}_3\text{SiOSiCl}_3$ ,  $\text{F}_3\text{SiCl}$  and  $\text{FSiCl}_3$ . 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-S1B* 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  $D_{3d}$  model for hexachlorodisiloxane ( $\text{Cl}_3\text{SiOSiCl}_3$ ) 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  $Cl_3SiOSiCl_3$  have been assigned according to  $C_{2v}$  selection rules as indicated in the previous literatures<sup>1, b) - 14)</sup>, except the literatures describing that the symmetry of disiloxane ( $H_3SiOSiH_3$ ) was  $D_{3d}^{13)}$  (linear Si-O-Si) and that of  $Cl_3SiOSiCl_3$ ,  $D_{3h}^{14)}$  (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  $Cl_3SiOSiCl_3$  by measuring the vibrational spectra and by comparing the spectra with those of structurally related molecules;  $F_3SiOSiCl_3^{15)}$ ,  $F_3SiCl$  and  $FSiCl_3^{16, 17)}$

The assignments of the vibrational spectra of  $F_3SiOSiCl_3$  which would supply useful informations for the structure of  $Cl_3SiOSiCl_3$  as well as that of  $F_3SiOSiCl_3$  is the first example.

## 2. Experimental

A compound  $Cl_3SiOSiCl_3$  was purchased from commercial source and purified by distillation. In order to synthesize  $F_3SiOSiCl_3$ ,  $Cl_3SiOSiCl_3$  was fluorinated using  $SbF_3$  and incorporating  $SbCl_5$  as a catalyst<sup>18)</sup>, and the synthesized  $F_3SiOSiCl_3$  was separated by fractional distillation.

Raman spectra are recorded on *JEOL JRS-S1B* 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 $Cl_3SiOSiCl_3$

The Raman and infrared spectra of  $Cl_3SiOSiCl_3$  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  $C_{2v}$ ;  $7A_1(R, \rho; IR) + 4A_2(R) + 6B_1(R; IR) + 4B_2(R; IR)$ . The spectra of  $Cl_3SiOSiCl_3$  observed are in excellent agreement with the selection rules expected for  $D_{3d}$  model<sup>\*1)</sup>, the irreducible representation of which is  $3A_{1g}(R, \rho) + 3A_{2u}(IR) + 3E_g(R) + 4E_u(IR)$ .

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\*1) A  $D_{3h}$  symmetry, the irreducible representation of which is  $3A_1'(R, \rho) + 3A_2''(IR) + 4E'(R; IR) + 3E''(R)$  is reasonable for linear  $Cl_3SiOSiCl_3$ , too, but  $D_{3h}$  symmetry does not have a symmetry center.

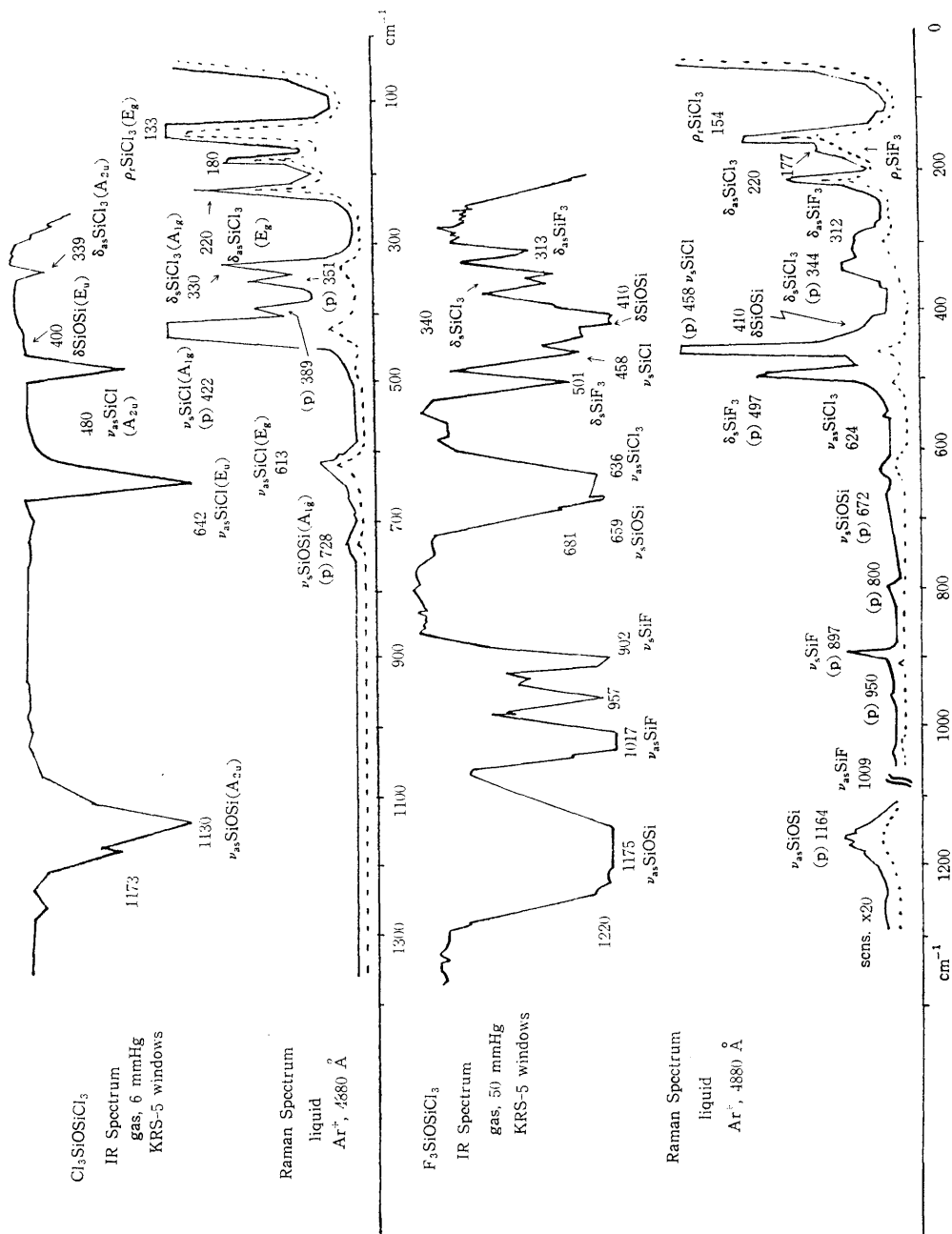


Fig. 1 Raman and Infrared Spectra of  $\text{Cl}_3\text{SiOSiCl}_3$  and  $\text{F}_3\text{SiOSiCl}_3$

3-1-1.  $A_{1g}$  Bands ..... These are Raman active, polarized and infrared inactive. The Raman band of  $\text{FSiCl}_3$ <sup>16, 17)</sup> that corresponds to (*p*)728  $\text{cm}^{-1}$  Raman band of  $\text{Cl}_3\text{SiOSiCl}_3$  does not exist, but (*p*) 672  $\text{cm}^{-1}$  Raman band of  $\text{F}_3\text{SiOSiCl}_3$  seems to correspond to the (*p*)728  $\text{cm}^{-1}$  one of  $\text{Cl}_3\text{SiOSiCl}_3$ . Accordingly the (*p*)728  $\text{cm}^{-1}$  band should be due to Si-O-Si stretching or bending which does not exist

for  $\text{FSiCl}_3$ . On the basis of the polarization state, the (*p*)728  $\text{cm}^{-1}$  band can be assigned to symmetric Si-O-Si stretching ( $\nu_s\text{Si-O-Si}$ )\*<sup>2)</sup> It is well known that a band of symmetric Si-Cl stretching ( $\nu_s\text{SiCl}$ )\*<sup>2)</sup> would be very strong band which is polarized, lying at 450  $\text{cm}^{-1}$  region.<sup>14, 19)</sup> For example, the very intensive and polarized band at 464  $\text{cm}^{-1}$  of  $\text{FSiCl}_3$  is assigned to  $\nu_s\text{SiCl}$ .<sup>16, 17)</sup> So the (*p*)422  $\text{cm}^{-1}$  band of  $\text{Cl}_3\text{SiOSiCl}_3$  can be assigned to  $\nu_s\text{SiCl}$ , where the lowering frequency than expected might be due to the coupling of  $\nu_s\text{SiCl}(A_{1g})$  and  $\delta_s\text{SiCl}_3(A_{1g})$ .<sup>14)</sup> There remains symmetric  $\text{SiCl}_3$  deformation( $\delta_s\text{SiCl}_3$ ), and the polarized bands at 330, 351 and 389  $\text{cm}^{-1}$  could be considered as  $\delta_s\text{SiCl}_3$  mode. Compared with the  $\delta_s\text{SiCl}_3$  bands of  $\text{F}_3\text{SiOSiCl}_3$  and  $\text{FSiCl}_3$ ,\*<sup>3)</sup> the (*p*)330  $\text{cm}^{-1}$  band is assigned to  $\delta_s\text{SiCl}_3$ .\*<sup>4)</sup>

3-I-2.  $A_{2u}$  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.<sup>21)</sup> For example, bands arising from this mode of vibration appear at 1107  $\text{cm}^{-1}$  in the spectrum of  $\text{H}_3\text{SiOSiH}_3$ <sup>13)</sup>, at 1060  $\text{cm}^{-1}$  in that of  $\text{Me}_3\text{SiOSiMe}_3$ <sup>22)</sup>, at 1075  $\text{cm}^{-1}$  in that of  $\phi_3\text{SiOSi}\phi_3$ <sup>23)</sup> (Me=methyl,  $\phi$ =phenyl), and at 1175  $\text{cm}^{-1}$  in that of  $\text{F}_3\text{SiOSiCl}_3$  as shown in Fig.1. The only band appearing in the spectrum of  $\text{Cl}_3\text{SiOSiCl}_3$  within this wave number region is the strong infrared band at 1180  $\text{cm}^{-1}$ . Therefore this band is confidently assigned to  $\nu_{as}\text{Si-O-Si}$ . The Raman counterpart is unobserved. If  $\text{Cl}_3\text{SiOSiCl}_3$  has  $C_{2v}$  symmetry,  $\nu_{as}\text{Si-O-Si}$  band should appear in Raman. Therefore this strongly supports  $D_{3d}$  for  $\text{Cl}_3\text{SiOSiCl}_3$ , too.

Molecule  $\text{Cl}_3\text{SiOSiCl}_3$  is considered as a derivative in which  $\text{SiCl}_3$  group is connected to  $\text{FSiCl}_3$  in opposite direction along the  $z$  axis and an oxygen atom is inserted between the two  $\text{SiCl}_3$  groups instead of a fluorine atom. Consequently the  $\nu_s\text{SiCl}_3$  in  $\text{FSiCl}_3$  is split to  $\nu_s\text{SiCl}(A_{1g})$  and  $\nu_{as}\text{SiCl}(A_{2u})$  in  $\text{Cl}_3\text{SiOSiCl}_3$ , and so the  $\nu_{as}\text{SiCl}$  of  $\text{Cl}_3\text{SiOSiCl}_3$  would appear near  $\nu_s\text{SiCl}$  of  $\text{FSiCl}_3$  and  $\text{Cl}_3\text{SiOSiCl}_3$  in frequencies.\*<sup>5)</sup> Accordingly the strong 480  $\text{cm}^{-1}$  band is assigned to asymmetric SiCl stretching( $\nu_{as}\text{SiCl}$ ), compared with the frequency(422  $\text{cm}^{-1}$ ) of  $\nu_s\text{SiCl}(A_{1g})$ . The 339  $\text{cm}^{-1}$  band can be assigned to asymmetric  $\text{SiCl}_3$  deformation ( $\delta_{as}\text{SiCl}_3$ ) in a similar manner as above.\*<sup>5)</sup>

3-I-3.  $E_g$  Bands ----- These are Raman active, depolarized, and infrared inactive. The bands at 613, 220 and 133  $\text{cm}^{-1}$ , all of which are depolarized, are

\*2) Some literatures <sup>8, 12)</sup> have assigned intensive and polarized 422  $\text{cm}^{-1}$  band to  $\nu_s\text{Si-O-Si}$ , but the band should be assigned to  $\nu_s\text{SiCl}$ .

\*3) It is well known that the frequencies of  $\nu_s\text{CH}_3$ ,  $\nu_{as}\text{CH}_3$  and  $\delta_{as}\text{CH}_3$  are remarkably constant throughout the series of molecule  $\text{CH}_3\text{X}(\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I})$ <sup>19, 20)</sup>. This is, also, the case for compounds containing  $\text{SiCl}_3$  and  $\text{SiF}_3$  groups.

\*4) The literature<sup>14)</sup> has assigned 330  $\text{cm}^{-1}$  to  $\nu_s\text{Si-O-Si}$ .

\*5) In the other words, the similar vibration modes which belong to the similar species are close to each other in frequencies.

assigned to  $\nu_{as}\text{SiCl}_3$ ,  $\delta_{as}\text{SiCl}_3$  and  $\text{SiCl}_3$  rocking ( $\rho_r\text{SiCl}_3$ ) respectively, compared with those of  $\text{FSiCl}_3$ \*<sup>3)</sup> and  $E_u$  bands of  $\text{Cl}_3\text{SiOSiCl}_3$ \*<sup>5)</sup>

*3-1-4.  $E_u$  Bands* ----- These are infrared active and Raman inactive. The bands at 642, 247\*<sup>6)</sup> and 179\*<sup>6)</sup>  $\text{cm}^{-1}$  are assigned to  $\nu_{as}\text{SiCl}_3$ ,  $\delta_{as}\text{SiCl}_3$  and  $\rho_r\text{SiCl}_3$  respectively, compared with those of  $\text{FSiCl}_3$ \*<sup>3)</sup> and  $E_g$  bands of  $\text{Cl}_3\text{SiOSiCl}_3$ \*<sup>5)</sup>. The 180  $\text{cm}^{-1}$  Raman band\*<sup>7)</sup> found in liquid  $\text{Cl}_3\text{SiOSiCl}_3$  may be the infrared fundamental at 179  $\text{cm}^{-1}$ , 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  $\text{Cl}_3\text{SiOSiCl}_3$ \*<sup>24)</sup>. 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 ( $\delta\text{Si-O-Si}$ ) of  $\text{Cl}_3\text{SiOSiCl}_3$  would be expected to be weak, because of same end groups. On the other hand, the intensity of  $\delta\text{Si-O-Si}$  of  $\text{F}_3\text{SiOSiCl}_3$ , to be not weak, because of different end groups. The very intensive band at 410  $\text{cm}^{-1}$  of  $\text{F}_3\text{SiOSiCl}_3$  can be assigned to  $\delta\text{Si-O-Si}$ , and the very weak band lying at 400  $\text{cm}^{-1}$  of  $\text{Cl}_3\text{SiOSiCl}_3$  could be assigned to  $\delta\text{Si-O-Si}$ . This is in agreement with expectations for  $\delta\text{Si-O-Si}$  as mentioned above.

*3-1-5. Overtone and Combination Bands* ----- The infrared bands at 1173 and 1130  $\text{cm}^{-1}$  would neither  $P$  nor  $R$  branch of rotation-vibrational band, because the difference of 43  $\text{cm}^{-1}$  seems to be too large to be considered as  $P$ - $R$  separation value, for molecule having large moment of inertia like  $\text{Cl}_3\text{SiOSiCl}_3$ . These bands could be interpreted as due to Fermi resonance. Thus 1130( $A_{2u}$ ) is in resonance with 480( $A_{2u}$ ) + 2 × 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  $\text{cm}^{-1}$  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 $\text{F}_3\text{SiOSiCl}_3$

The Raman and infrared spectra of  $\text{F}_3\text{SiOSiCl}_3$  are shown in Fig.1. The symmetry of  $\text{F}_3\text{SiOSiCl}_3$  is  $C_{3v}$  or  $C_3$  for linear model and  $C_s$  for bent one. The irreducible representations of skeletal modes are  $6A_1(R,p;IR) + 7E(R;IR)$  in  $C_{3v}$ ,  $7A(R,p;IR) +$

\*6) The bands at 247 and 179  $\text{cm}^{-1}$  are out of observational limit due to  $KRS-5$  optics, but the frequencies are cited from the literature.<sup>2)</sup>

\*7) In the literature<sup>14)</sup>, this 180  $\text{cm}^{-1}$  band is assigned to  $\delta_s\text{SiCl}_3$ . However this line is observed to be depolarized, therefore the above assignment seems to be doubtful. Because the band for totally symmetric deformational mode,  $\delta_s\text{SiCl}_3$  should be polarized.

**Table 1** Symmetry Species and Selection Rules of  $D_{3d}$  and Frequency Assignments of  $\text{Cl}_3\text{SiOSiCl}_3$ 

Species	Normal Vibrational Modes	$\text{Cl}_3\text{SiOSiCl}_3$	
		Raman	IR
$A_{1g}$	Si-O-Si sym. str.	( <i>p</i> )728w	( <i>ia</i> )
	Si-Cl sym. str.	( <i>p</i> )422vs	( <i>ia</i> )
	$\text{SiCl}_3$ sym. def.	( <i>p</i> )330m	( <i>ia</i> )
$A_{1u}$	Torsion	( <i>ia</i> )	( <i>ia</i> )
$A_{2u}$	Si-O-Si asym. str.	( <i>ia</i> )	1130vs
	SiCl asym. str.	( <i>ia</i> )	480s
	$\text{SiCl}_3$ asym. def.	( <i>ia</i> )	339m
$E_g$	SiCl asym. str.	613w	( <i>ia</i> )
	$\text{SiCl}_3$ asym. def.	220s	( <i>ia</i> )
	$\text{SiCl}_3$ rock.	133vs	( <i>ia</i> )
$E_u$	SiCl asym. str.	( <i>ia</i> )	642vs
	Si-O-Si bend.	( <i>ia</i> )	~400vww
	$\text{SiCl}_3$ asym. def.	( <i>ia</i> )	(247)*)
	$\text{SiCl}_3$ rock	180**)	(179)*)

\*) 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  $13A'(R,p;IR) + 8A'(R;IR)$  in  $C_s$ .

The spectra observed seem to be too simple to be interpreted on the basis of  $C_s$  selection rules, which has 21 Raman fundamentals, of which 13 ones are polarized and 21 infrared fundamentals. Accordingly the symmetry of  $\text{F}_3\text{SiOSiCl}_3$  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.  $A_1$  Bands ----- These are active in both Raman and infrared, and polarized in Raman. The vibrational bands which belong to  $A_1$  species are assigned as shown in Table 2, compared with structurally related compounds,  $\text{Cl}_3\text{SiOSiCl}_3$ ,  $\text{FSiCl}_3$  and  $\text{F}_3\text{SiCl}^{*3)}$ . The assignments of Si-O-Si stretching modes of  $\text{F}_3\text{SiOSiCl}_3$  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  $\delta\text{Si-O-Si}$  is discussed in section 3-1-4.

**Table 2** Symmetry Species and Selection Rules of  $D_{3d}$  and Frequency Assignments of Fundamentals of  $\text{F}_3\text{SiOSiCl}_3$ ,  $\text{F}_3\text{SiCl}$  and  $\text{FSiCl}_3$

Normal Vibrational Modes	Species $A_1$		Species $E$		$\text{F}_3\text{SiCl}$	
	<i>Raman</i>	<i>IR</i>	<i>Raman</i>	<i>IR</i>	<i>Raman</i>	<i>IR</i>
$\text{SiF}_3$ asym. str.	( <i>ia</i> )	( <i>ia</i> )	1009vw	1017vs	990vw	1005msh
$\text{SiF}_3$ sym. str.	( <i>p</i> )897w	902s	( <i>ia</i> )	( <i>ia</i> )	( <i>p</i> )873w	883vs
$\text{SiF}_3$ asym. def.	( <i>ia</i> )	( <i>ia</i> )	312m	313m	265m	(*)
$\text{SiF}_3$ sym. def.	( <i>p</i> )497s	501s	( <i>ia</i> )	( <i>ia</i> )	( <i>p</i> )347m	352s
$\text{SiF}_3$ rock.	( <i>ia</i> )	( <i>ia</i> )	177m	(*)	222m	(*)
Si-O-Si asym. str.	( <i>p</i> )1164vw	1175vs	( <i>ia</i> )	( <i>ia</i> )		
Si-O-Si sym. str.	( <i>p</i> )672w	659m	( <i>ia</i> )	( <i>ia</i> )		
Si-O-Si bend.	( <i>ia</i> )	( <i>ia</i> )	410vw	410vs		
$\text{SiCl}_3$ asym. str.	( <i>ia</i> )	( <i>ia</i> )	624w	636vs	630w	630vs
$\text{SiCl}_3$ sym. str.	( <i>p</i> )458vs	458s	( <i>ia</i> )	( <i>ia</i> )	( <i>p</i> )464vs	466w
$\text{SiCl}_3$ asym. def.	( <i>ia</i> )	( <i>ia</i> )	220s	(*)	278m	(*)
$\text{SiCl}_3$ sym. def.	( <i>p</i> )344m	340m	( <i>ia</i> )	( <i>ia</i> )	( <i>p</i> )237m	(*)
$\text{SiCl}_3$ rock.	( <i>ia</i> )	( <i>ia</i> )	154s	(*)	165s	(*)

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

**3-2-3. Overtone and Combination Bands** ----- The  $1220\text{ cm}^{-1}$  infrared band could be interpreted as due to Fermi resonance in similar manner as that of the  $1173\text{ cm}^{-1}$  band of  $\text{Cl}_3\text{SiOSiCl}_3$ . Thus  $1175(A_1)$  is in resonance with  $501(A_1)+2\times 340(A_1)$ , 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  $957\text{ cm}^{-1}$  may be one of Fermi doublet due to  $902(A_1)$  and  $2\times 458(A_1)$ . The  $681\text{ cm}^{-1}$  infrared band can be considered as first overtone of  $340\text{ cm}^{-1}$  one; 436, as that of 220, and 359, as that of  $177\text{ cm}^{-1}$ .

**3-2-4. Impurity** ----- The (*p*) $800\text{ cm}^{-1}$  band may be due to  $\text{SiF}_4$  included in  $\text{F}_3\text{SiOSiCl}_3$  as impurity, since the most intensive Raman band of  $\text{SiF}_4$  is (*p*)  $800\text{ cm}^{-1}$  band assigned to  $\nu_3\text{SiF}$ .

#### 4. Conclusion

From the observed spectra, it would be clear that the Si-O-Si skeleton is linear in both  $\text{Cl}_3\text{SiOSiCl}_3$  and  $\text{F}_3\text{SiOSiCl}_3$ , for coincidence between Raman and infrared

frequencies which are the spectral feature of  $C_{2v}$  symmetry (bent Si-O-Si) for  $\text{Cl}_3\text{SiOSiCl}_3$  does not occur and less fundamentals of  $\text{F}_3\text{SiOSiCl}_3$  appear for  $C_{3v}$  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  $\text{H}_2\text{O}$  molecule, but some literatures support experimentally a linear —O— for gaseous Z-O-H (Z=K,Rb,Cs).<sup>25-28)</sup> In addition it is possible to consider the 2s and  $2p_z$  orbitals in oxygen atom as being hybridized to be linear.\*8)

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

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\*8) The ground state of the oxygen atom is  $1s^2 2s^2 2p^4$ . 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 2p state, and to have the resulting  $2p_z$  electron with uncoupled spin, and  $2p_x$  and  $2p_y$  electrons with coupled spins. Then the  $180^\circ$  bond angle in Si-O-Si could be produced by mixing 50 per cent  $2s^1$  and 50 per cent  $2p_z^1$ .



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