Journal of Fluorine Chemistry, 7 (1976) 385 - 396

Received: July 4, 1975; in revised form August 15, 1975

THE VIBRATIONAL SPECTRUM AND STRUCTURE OF TRIFLUOROTRICHLORODISILOXANE

K. HAMADA

Faculty of Education, Nagasaki University, Nagasaki 852 (JAPAN)

SUMMARY

The vibrational spectrum of trifluorotrichlorodisiloxane ($F_3SiOSiCl_3$) is reported, analyzed and assigned in terms of a linear C_{3v} model, by comparison with that of structurally related hexachlorodisiloxane($Cl_3SiOSiCl_3$). This is the first assignment of the vibrational spectrum for this molecule. The vibrational spectrum of $Cl_3SiOSiCl_3$ is assigned on the basis of a linear D_{3d} model, which is different from a bent C_{2v} model in the previous literature.

INTRODUCTION

The D_{3d} model for $Cl_3SiOSiCl_3$ has six Raman active fundamentals and seven infrared active ones, which are mutually exclusive in the Raman and infrared. The less symmetric model C_{2v} would give twenty-one fundamentals, all of which are Raman active and seventeenth of which are infrared active. Most previous assignment [1-11] of the vibrational bands of $Cl_3SiOSiCl_3$ have been based on C_{2v} selection rules. One paper [12] has assigned D_{3h} symmetry to $Cl_3SiOSiCl_3$ and another [13] has assigned D_{3d} symmetry to disiloxane($H_3SiOSiH_3$). However since only nine of twenty-one fundamental bands can be found in the observed Raman spectrum of $Cl_3SiOSiCl_3$ and some of those may correspond to overtone or combination bands, it seems likely that the C_{2v} model which should have twenty-one fundamentals which are Raman active is incorrect. The present author has therefore found it worthwhile to investigate the structure of $Cl_3SiOSiCl_3$ by measuring the vibrational spectrum and comparing the spectra with those of the structurally related molecules; $F_3SiOSiCl_3$ [14], F_3SiCl and $FSiCl_3$[15,16]. The assignment of the vibrational spectrum of $Cl_3SiOSiCl_3$ would supply useful information for the structure of $F_3SiOSiCl_3$, too.

EXPERIMENTAL

The compound $Cl_3SiOSiCl_3$ was purchased from a 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 [17] and synthesized $F_3SiOSiCl_3$ was separated by fractional distillation.

Raman spectra were recorded on a JEOL JRS S1B spectrometer using argon ion laser, and the infrared spectra were measured with a Shimadzu IR-450 spectrometer. The gas cell had a path of 10 cm and KRS-5 windows. The infrared spectra were measured both in the gaseous and the liquid states. The differences between the patterns of the spectra in both states are hardly discernible and those between the wave numbers in both states are very small.

RESULTS AND DISCUSSION

VIBRATIONAL SPECTRUM 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 centre of symmetry, and are too simple to be interpreted according to C_{2v} symmetry which should have 21 Raman active fundamentals and 17 infrared active ones, as shown in the irreducible representation of C_{2v} ; $7A_1(R,p:IR)+4A_2(R)+6B_1(R:IR)+4B_2(R:IR)$. The spectra of $Cl_3SiOSiCl_3$ observed are in agreement with the selection rules expected for D_{3d} model[*1]

[*1] A D_{3h} symmetry, the irreducible representatios of which is $3A_1'(R,p)+1A_1''(inac.)+3A_2''(IR)+4E'(R:IR)+3E''(R)$ is reasonable for linear $Cl_3SiOSiCl_3$, too, but does not have a symmetry center.

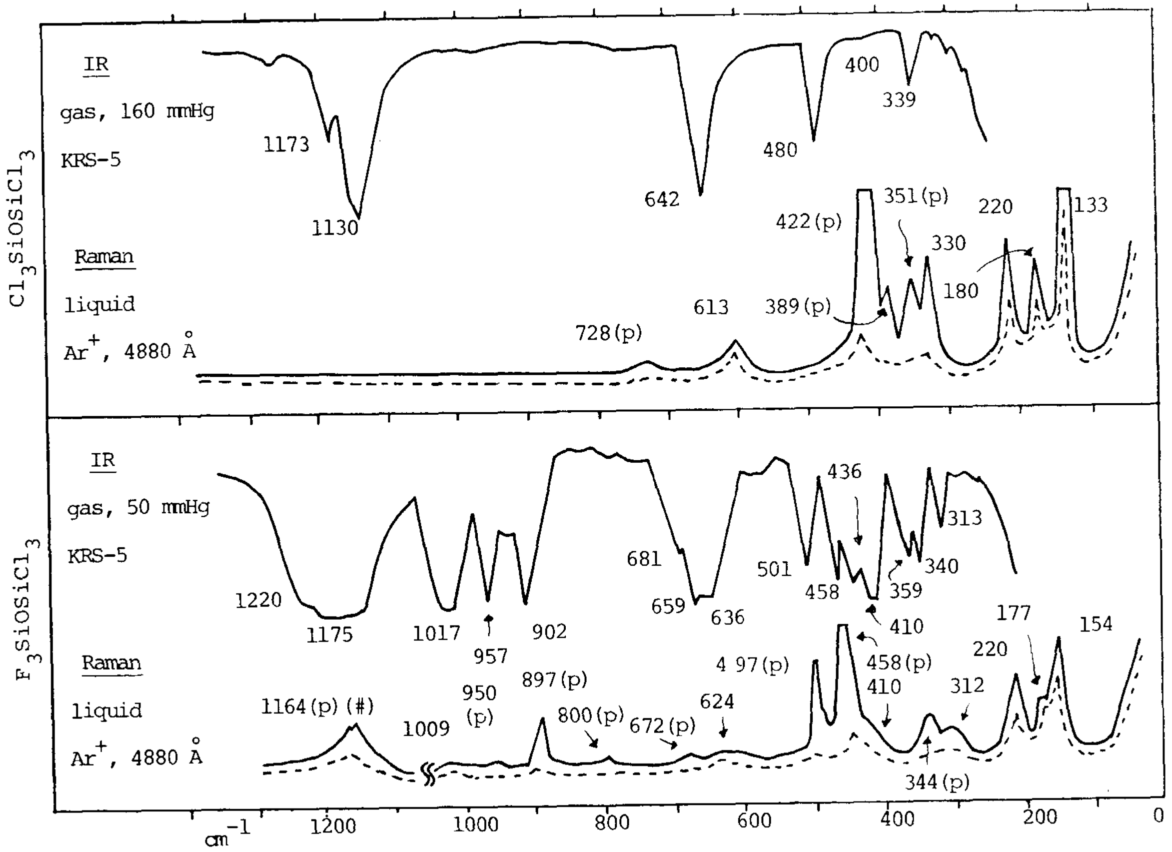

Fig. 1 Raman and infrared spectra of $Cl_3SiOSiCl_3$ and $F_3SiOSiCl_3$ (#), in high sensitivity

the irreducible representations of which is $3A_{1g}(R,p)+1A_{1u}$(inac.) $+3A_{2u}(IR)+3E_{g}(R)+4E_{u}(IR)$.

(a) A_{1g} bands

These are Raman active and polarized and infrared inactive. The Raman band of $FSiCl_3$[15,16] that corresponds to the 728 cm^{-1} Raman band(p) of $Cl_3SiOSiCl_3$ does not exist, but the 672 cm^{-1} Raman band(p) of $F_3SiOSiCl_3$ seems to correspond to the 728 cm^{-1} band(p) of $Cl_3SiOSiCl_3$. Accordingly the 728 cm^{-1}band(p) should be due to SiOSi stretching or bending which is absent in $FSiCl_3$. By considering the polarization state, the 728 cm^{-1} band(p) can be assigned to symmetric SiOSi stretching, ν_s(SiOSi). Some workes [2,11] have assigned the intense and polarized 422 cm^{-1} band to ν_s(SiOSi). However the most prominent band in the Raman spectra of such compounds has been observed to arise from ν_s(SiCl). This band is always strong and highly polarized and occurs in 450 cm^{-1} wave number region [18], with which ν_s(SiCl) would be identified. Thus the 422 cm^{-1} band(p) of $Cl_3SiOSiCl_3$ should be assigned to ν_s(SiCl), where the lower frequency as expected($\sim$450 cm^{-1}) might be due to the coupling of ν_s(SiCl)(A_{1g}) and $\delta_s(SiCl_3)(A_{1g})$ [13]. The stretching force constants of ν_s(SiCl) are approximately calculated from the experimental vibration frequencies. That is, the values of the force constants for compounds containing $SiCl_3$ group(s) are calculated, using about 450 cm^{-1} of ν_s(SiCl) as shown in Fig. 2, to be 2.2$\sim$2.5 x10^{-5} dyne/cm [*2], which seem to be reasonable value by comparing with 2.7 x10^{-5} of $SiCl_4$ [19] and 2.6 x10^{-5} dyne/cm of $Cl_3SiOSiCl_3$ [20].

The literature [12] has assigned the 330 cm^{-1} band(p) instead of 728 cm^{-1} band(p) to ν_s(SiOSi). However the 330 cm^{-1} band(p) seems to appear in frequency region of $\delta_s(SiCl_3)$. There remains the symmetric $SiCl_3$ deformation mode, $\delta_s(SiCl_3)$, and polarized bands at 330, 351 and 389 cm^{-1} could be considered arising from this $\delta_s(SiCl_3)$ mode. By comparison with the $\delta_s(SiCl_3)$ bands of the compounds having $SiCl_3$ group(s) shown in Fig. 2, the 330 cm^{-1} band(p) seems to be assigned to $\delta_s(SiCl_3)$. It is well know that the

---

[*2] The anomalous low frequency of ν_s(SiCl) of $Cl_3SiSiCl_3$ may be due to the intensive coupling of ν_s(SiCl) and $\delta_s(SiCl_3)$.

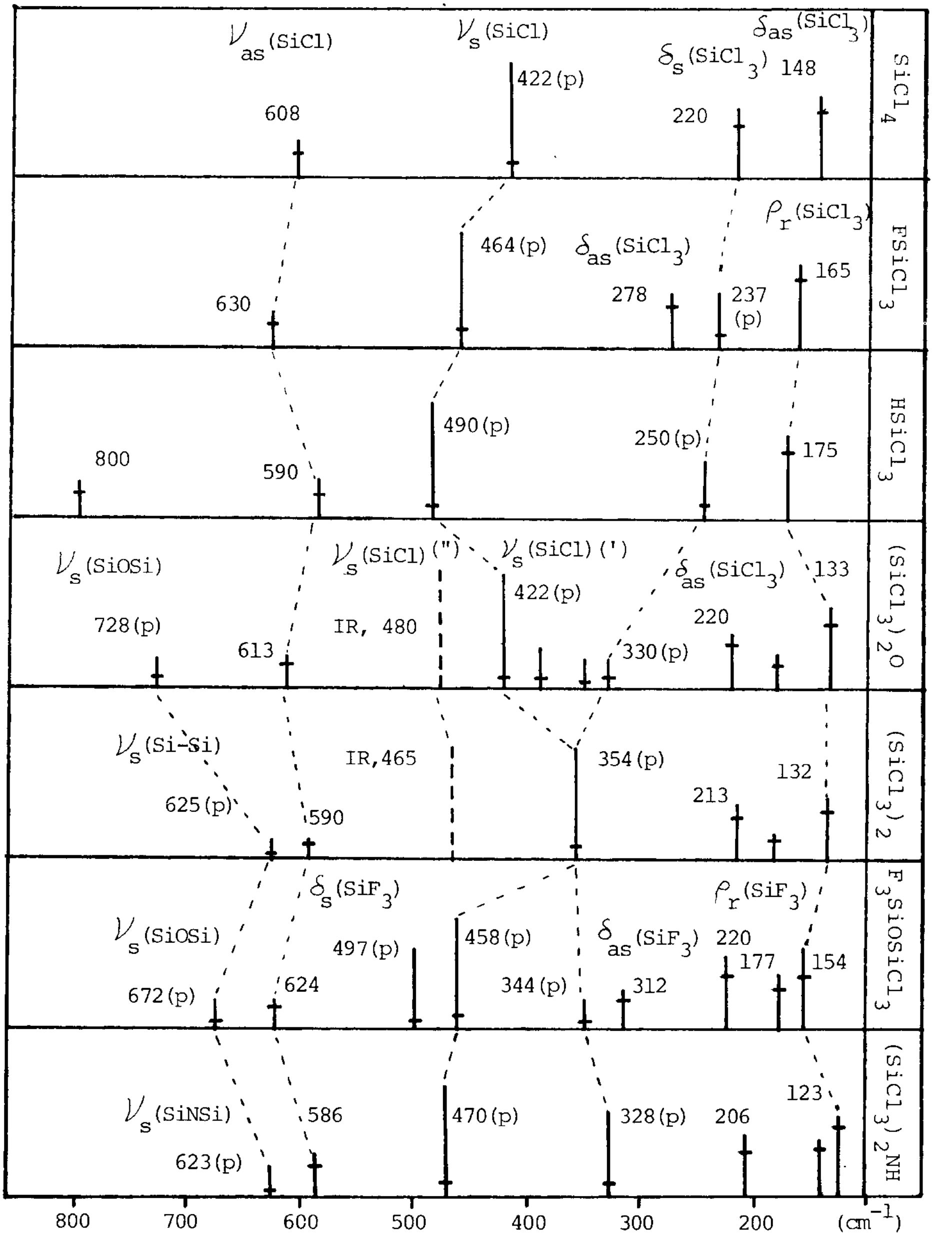

Fig. 2 Schematic Raman spectra of compounds with $SiCl_3$ or/and SiF_3. Intensity of (∥) band is shown by vertical line and top of (⊥) band, by horizontal bar. Dotted line shows infrared band of $_{as}$(SiCl)(A_{2u}) which is Raman inactive. ('),in phase; ("),out of phase

frequencies of $\nu_s(CH_3)$, $\nu_{as}(CH_3)$ and $\delta_s(CH_3)$ are remarkably constant throughout the series of molecule CH_3-Z(Z=F,Cl,Br,I)[21]. This is also the case for compounds containing $SiCl_3$ and/or SiF_3 group(s) as shown in Fig. 2.

(b) A_{2u} bands

These are infrared active and Raman inactive. The asymmetric SiOSi stretching modes of substituted disiloxanes have been found to exhibit relative constancy from one compound to the next [22]. For example, bands arising from this mode of vibration appear at 1107 cm^{-1} in the spectrum of $H_3SiOSiH_3$ [13], at 1060 cm^{-1} in that of $Me_3SiOSiMe_3$ [23], at 1075 cm^{-1} in that of $\Phi_3SiOSi\Phi_3$ [24] (Me=methyl, Φ=phenyl), and at 1175 cm^{-1} in that of $F_3SiOSiCl_3$. The only band appearing in the spectrum of $Cl_3SiOSiCl_3$ within this wave number region is the strong infrared band at 1130 cm^{-1}. Therefore, this band is assigned to ν_{as}(SiOSi). The Raman counterpart is not observed. If $Cl_3SiOSiCl_3$ has C_{2v} symmetry, ν_{as}(SiOSi) band should appear in the Raman. Accordingly this further supports the D_{3d} structure for $Cl_3SiOSiCl_3$.

The molecule $Cl_3SiOSiCl_3$ may be considered as a derivative of $FSiCl_3$: the $SiCl_3$ linked to an oxygen atom replaced the fluorine atom. Thus ν_s(SiCl) in $FSiCl_3$ is split to give to ν_s(SiCl)(in phase) and ν_s(SiCl)(out of phase) in $Cl_3SiOSiCl_3$, and the ν_s(SiCl) (out of phase) of $Cl_3SiOSiCl_3$ would appear near ν_s(SiCl) of $FSiCl_3$ and that(in phase) of $Cl_3SiOSiCl_3$. Accordingly the strong 480 cm^{-1} band is assigned to ν_s(SiCl)(out of phase), compared with the frequency(422 cm^{-1}) of ν_s(SiCl)(in phase). The 339 cm^{-1} band is assigned to $\delta_{as}(SiCl_3)$ by comparison with $\delta_s(SiCl_3)$(330 cm^{-1}).

(c) E_g bands

These are Raman active and depolarized, and infrared active. The bands at 613, 220 and 133 cm^{-1}, all of which are depolarized, are assigned to ν_{as}(SiCl), $\delta_{as}(SiCl_3)$ and $\rho_r(SiCl_3)$ respectively, by comparison with those of $FSiCl_3$ and the E_u bands of $Cl_3SiOSiCl_3$.

(d) E_u bands

These are infrared active and Raman inactive. The bands at 642, 247 [*3] and [*3] cm^{-1} are assigned to ν_{as}(SiCl),

---

[*3] These are beyond the range of KRS-5, but are cited from ref.[2].

$\delta_{as}(SiCl_3)$ and $\rho_r(SiCl_3)$ respectively, compared with those of $FSiCl_3$ and E_g bands of $Cl_3SiOSiCl_3$. The 180 cm^{-1} band found in liquid $Cl_3SiOSiCl_3$ 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 in the liquid[25].

The intensity of the SiOSi bending mode, $\delta(SiOSi)$ of $Cl_3SiOSiCl_3$ with same end groups would be expected to be weak, so the very weak band lying at about 400 cm^{-1} in $Cl_3SiOSiCl_3$ could be assigned to $\delta(SiOSi)$, which is absent in $FSiCl_3$ and $HSiCl_3$. The intensity of this $\delta(SiOSi)$ band of $Cl_3SiOSiCl_3$ is in contrast to the intensity of $\delta(SiOSi)$ of $F_3SiOSiCl_3$ with different end groups, as mentioned below.

(e) Overtone and combination bands

The infrared bands at 1173 and 1130 cm^{-1} may arise from Fermi resonance between $1130(A_{2u})$ and $480(A_{2u}) + 2x239(A_{2u})$. The Raman bands at 351 and 389 cm^{-1} could be considered as combinations of $220(E_g) + 133(E_g)$ and of $613(E_g) - 220(E_g)$, respectively The Raman bands at 351 and 389 cm^{-1} of $Cl_3SiOSiCl_3$ which do not appear in infrared should be overtone or combination band. If these bands would be fundamentals, the molecule, $Cl_3SiOSiCl_3$ would have a lower symmetry having more fundamentals than a D_{3d} and all(or most) of the fundamentals in Raman and infrared should coincide with each other in frequencies. However the obtained spectra are mutually exclusive in Raman and infrared. The Raman 180 cm^{-1} band [*4,25] of $Cl_3SiOSiCl_3$ which has the infrared counterpart is considered as the fundamental appearing in the Raman effect due to a breakdown of D_{3d} selection rules. Table 1 lists the assignment for the fundamental bands observed together with symmetry species and selection rules of D_{3d}.

[*4] In the literature [12], this 180 cm^{-1} band is assigned to $\delta_s(SiCl_3)$. However this band is observed to be depolarized, therefore the above assignment seems to be doubtful. Because $\delta_s(SiCl_3)$ should be polarized.

Speceis	Normal Vibr. Modes	$SiCl_3OSiCl_3$	
		Raman	IR
A_{1g}	ν_s(SiOSi)	728(p,w)	---
	ν_s(SiCl) (')	422(p,vs)	---
	$\delta_s(SiCl_3)$ (')	330(p,m)	---
A_{1u}	Torsion	---	---
A_{2u}	ν_{as}(SiOSi)	---	1130(vs)
	ν_s(SiCl) ('')	---	480(s)
	δ_s(SiCl) ('')	---	339(m)
E_g	ν_{as}(SiCl)	613(d,w)	---
	$\delta_{as}(SiCl_3)$	220(d,s)	---
	$\rho_r(SiCl_3)$	133(d,vs)	---
E_u	ν_{as}(SiCl)	---	642(vs)
	δ(SiOSi)	---	400(vw)
	$\delta_{as}(SiCl_3)$	---	247(*)
	$\rho_r(SiCl_3)$	180(**)	179(*)

(a) $Cl_3SiOSiCl_3$

Vibr. Modes	$F_3SiOSiCl_3$			
	Speceies A_1		Speceis E	
	Raman	IR	Raman	IR
ν_{as}(SiF)	---	---	1009(w)	1017(vs)
ν_s(SiF)	897(w)	902(s)	---	---
$\delta_{as}(SiF_3)$	---	---	312(w)	313(m)
$\delta_s(SiF_3)$	497(s)	501(s)	---	---
$\rho_r(SiF_3)$	---	---	177(m)	(*)
ν_{as}(SiOSi)	1164(vw)	1175(vs)	---	---
ν_s(SiOSi)	672(w)	659(m)	---	---
δ(SiOSi)	---	---	410(vw)	410(vs)
$\nu_{as}(SiCl_3)$	---	---	624(w)	636(vs)
$\nu_s(SiCl_3)$	458(vs)	458(s)	---	---
$\delta_{as}(SiCl_3)$	---	---	220(s)	(*)
$\delta_s(SiCl_3)$	344(m)	340(m)	---	---
$\rho_r(SiCl_3)$	---	---	154(s)	(*)

(b) $F_3SiOSiCl_3$

F_3SiCl [15,16]	
Raman	IR
990(d,vw)	1005(msh)
873(p,w)	883(vs)
265(d,m)	(*)
347(p,m)	352(s)
222(d,m)	(*)

$FSiCl_3$ [15,16]	
Raman	IR
630(d,w)	630(vs)
464(p,vs)	466(w)
278(d,m)	(*)
237(p,m)	(*)
165(d,s)	(*)

(c) F_3SiCl & $FSiCl_3$

TABLE 1 Symmetry speceies and selection rules of D_{3d} and C_{3v}, and frequency assignments of compounds; (a), (b) and (c)

(*); This is beyond the the range of KRS-5, but the figure is cited from ref. [2]. (**); This would be forbidden in Raman, but may appear through a breakdown of the selection rules due to intermolecular force in liquid. ('); in phase (''); out of phase

VIBRATIONAL SPECTRUM OF $F_3SiOSiCl_3$

The Raman and infrared spectra of $F_3SiOSiCl_3$ are shown in Fig. 1. The symmetry of $F_3SiOSiCl_3$ is C_{3v} or C_3 for the linear model and C_s for the bent one. The irreducible representations of the skeletal modes are $6A_1$(R,p)+$1A_2$(inac.)+7E(R:IR) for C_{3v}, 7A(R,p:IR)+7E(R:IR) for C_3 and 13A'(R,p:IR)+8A"(R:IR) for C_s. The spectra observed seem 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 $F_3SiOSiCl_3$ may be C_{3v} or C_3. It is difficult to differentiate the C_{3v} model from C_3 one, on the basis of the vibrational bands obtained, but the C_{3v} model would energetically be preferable to C_3 one.

(a) A_1 bands

These are active in both Raman and infrared, and polarized in the Raman. The vibrational bands which belong to A_1 species are assigned as shown in Table 2, compared with those for the structurally related compounds, $Cl_3SiOSiCl_3$, $FSiCl_3$ and F_3SiCl. The assignments of SiOSi stretching modes of $F_3SiOSiCl_3$ have been discussed previously. In the case of $Cl_3SiOSiCl_3$, the Raman counterpart of ν_{as}(SiOSi) is not observed. However, in the case of $F_3SiOSiCl_3$, the Raman counterpart is observed to be 1164 cm^{-1}(p If $Cl_3SiOSiCl_3$ has a bent model, ν_{as}(SiOSi) band should appear in the Raman. The lack of the Raman band of ν_{as}(SiOSi) for $Cl_3SiOSiCl_3$ strongly supports a linear D_{3d} model. In the case of $F_3SiOSiCl_3$, ν_{as}(SiOSi) is active in both Raman and infrared even in a linear C_{3v} model.

(b) E bands

These are active in both Raman and infrared, but depolarized in the Raman. The assignments of $\nu_{as}(SiF_3)$, $\delta_{as}(SiF_3)$, $\nu_{as}(SiCl_3)$ and $\delta_{as}(SiCl_3)$ can be easily assigned in a similar manner as above mentioned for $\nu_s(SiF_3)$, $\delta_s(SiF_3)$, $\nu_s(SiCl_3)$ and $\delta_s(SiCl_3)$.

The absorption intensity of a fundamental transition which is infrared active is related to the dipole moment derivative, so the intensity of δ(SiOSi) of $F_3SiOSiCl_3$ with different end groups would be expected to be not too weak. On the other hand, that of

$Cl_3SiOSiCl_3$ with same end groups would be expected to be very weak. Therefore, the intense band at 410 cm^{-1} of $F_3SiOSiCl_3$ can be assigned to δ(SiOSi). This is in agreement with expectations for δ(SiOSi) as mentioned above.

The $\rho_r SiF_3$ and $\rho_r SiCl_3$ can be assigned as shown in Table 1, compared with those of F_3SiCl and $FSiCl_3$ and considered the polarization data.

(c) Overtone and combination bands

The 1220 cm^{-1} infrared band seems to be interpretable as due to Fermi resonance between 1175 $cm^{-1}(A_1)$ and $501(A_1) + 2x340$ (A_1). The center of the Fermi doublet coincides very nearly with the frequency of the combination band. The intense infrared band at 957 cm^{-1} may be one of a Fermi doublet due to $902(A_1)$ and $2 \times 458(A_1)$. The 681 cm^{-1} infrared band can be considered as the first overtone of the 340 cm^{-1}; the band at 436, as that of 220; and the band at 359 as that of 177 cm^{-1}. The infrared bands at 681, 436 and 359 cm^{-1} of $F_3SiOSiCl_3$ which do not have the Raman counterpart should be overtone or combination band. If they should be fundamental, the symmetry of $F_3SiOSiCl_3$ have to be less symmetry, C_s having more fundamentals than C_{3v}. The obtained spectra are too simple to be C_s.

(e) Impurity

The 800 cm^{-1} band(p) may be due to SiF_4 included in $F_3SiOSiCl_3$ as an impurity, since the most intense Raman band of SiF_4 is the 800 cm^{-1} band(p) assigned to ν_s(SiF).

HYBRIDIZED LINEAR ORBITAL

From the observed spectra, it may be that the SiOSi skeleton is linear in both $Cl_3SiOSiCl_3$ and $F_3SiOSiCl_3$, for coincidence between Raman and infrared frequencies which are the spectral feature of C_{2v} symmetry(bent SiOSi) for $Cl_3SiOSiCl_3$ does not occur and less fundamentals of $F_3SiOSiCl_3$ appear for C_{3v} linear model to be acceptable.

The only argument against linear SiOSi is that the SiOSi chain should be bent, on the basis of the fact that — O — is bent in H_2O molecule, but some literature[26-29] support experimentally a linear — O — for gaseous Z - O - H(Z=K,Rb,Cs). In addition, it is theoretically possible to consider the 2s and $2p_z$ orbitals in oxygen atom as being hybridized to be linear, as follows. 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° bond angle in SiOSi could be produced by mixing 50 per cent $2s^1$ and 50 per cent $2p_z^1$ [30].

ACKNOWLEDGEMENTS

Grateful appreciation is expressed for financial support of this work by the Science Research Fund of the Ministry of Education of Japan and for assistance of Mr. Morishita of this Faculty in making the Raman and infrared measurements.

REFERENCES

1 W.R. Thorson and I. Nakagawa, J. Chem. Phys., 33 (1960) 994

2 J.E. Griffiths and D.F. Sturman, Spectrochim. Acta, 25A (1969) 1415

3 H. Bürger, K. Burczyk, F. Höfler and W. Sawodny, Spectrochim. Acta, 25A (1969) 1891

4 C.C. Certo, J.L. Lauer and H.C. Beachell, J. Chem. Phys., 22 (1954) 1

5 I. Simon and H.O. Mahon, J. Chem. Phys., 20 (1952) 905

6 N. Wright and M.J. Hunter, J. Amer. Chem. Soc., 69 (1947) 803

7 H. Kriegsman, Z. f. Electrochem., 61 (1957) 1088

8 A.L. Smith, Spectrochim. Acta, 19 (1963) 849

9 J.R. Aronson, R.C. Lord and D.M. Robinson, J. Chem. Phys., 33 (1960) 1004

10 T.F. Tenisheva and A.N. Lazarev, Izv. Akad. Nouk, SSSR, Morgan, Mat, 4 (1968) 1952

11 J.E. Griffiths, Spectrochim. Acta, 30A (1974) 945

12 J.R. Durig and K.L. Hellams, Inorg. Chem., 8 (1969) 944

13 R.C. Lord, D.W. Robinson and W.C. Schumb, J. Amer. Chem. Soc., 78 (1956) 1327

14 K. Hamada, J. Phys. Soc. Japan, 36 (1974) 617

15 K. Hamada, G.A. Ozin and E.A. Robinson, Can. J. Chem., 49 (1971) 477

16 K. Hamada, G.A. Ozin and E.A. Robinson, Bull. Chem. Soc. Japan, 44 (1971) 2555

17 H.S. Booth and R.A. Osten, J. Amer. Chem. Soc., 67 (1945) 1092

18 J.R. Durig and K.L. Hellams, Appl. Spectry., 22 (1968) 153

19 G.A. Ozin, J. Chem. Soc.(A), 2952(1969)

20 M. Katayama, T. Shimanouchi, Y. Morino and S. Mizushima, J. Chem. Phys., 18 (1950) 506

21 W.H. Bennet and C.F. Meyer, Phys. Rev., 32 (1928) 888

22 J.G. Moorhead, Phys. Rev., 39 (1932) 788

23 R.J. Gillespie and E.A. Robinson, Can. J. Chem., 42 (1964) 2496

24 D.W. Scott, J.F. Messerly, S.S. Todd, G.B. Guthrie, J.A.Hossenlop R.T. Moore, Ann Osborn, W.T. Berg and J.P. McCullough, J. Phys. Chem., 65 (1961) 1320

25 B.L. Crowford, Jr., W.H. Avery and J.W. Linnett, J. Chem. Phys. 6 (1938) 682

26 D.R. Lide, Jr. and R.L. Kuczkowski, J. Chem. Phys., 46 (1967) 4768

27 C. Matsumura and D.R. Lide, Jr., J. Chem. Phys., 50 (1969) 71

28 D.R. Lide, Jr. and C. Matsumura, J. Chem. Phys., 50 (1969) 3080

29 E.P. Pearson and M.B. Trueblood, J. Chem. Phys., 58 (1973) 826

30 W.J. Moore, Physical Chemistry, Prentice-Hall, Inc., New York, 1962, p. 537