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Anomaly of Hexachlorodisilane in Symmetric Si-Cl Stretching Frequency and Its Vibrational Assignments

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Abstract

The symmetric Si-Cl stretching of hexachlorodisilane, 352 cm^{-1} is found to be anomously low when a comparison with those of some compounds containing SiCl$_3$ groups is made. This anomaly seems due to intensive coupling of symmetric SiCl$_3$ deformation with symmetric Si-Cl stretching and/or Si-Si stretching mode. On the basis of the above consideration, the vibrational assignments of hexachlorodisilane are tentatively done.

1. Experimental

The compounds used are obtained from commercial sources, except trifluorotri-chlorodisiloxane (F$_3$SiOSiCl$_3$) and hexachlorodisilazane (Cl$_3$SiN(H)SiCl$_3$) synthesized according to the references.[1-3]

The Raman spectrum is recorded on *JEOL JRS-S1B* spectrophtometer using argon ion laser and the infrared spectrum is measured with *Shimadzu IR-450* spectrometer, whose window material is *KRS-5*.

2. Results and Discussion

The most prominent band in the Raman spectra of compounds containing SiCl$_3$ groups has been observed to arise from symmetric Si-Cl stretching mode(ν_sSiCl); this band is always strong and highly polarized and occurs in 450 cm^{-1} wave number region[4], with which ν_sSiCl would be identified. However there does not appear such a band in 450 cm^{-1} region for hexachlorodisilane(Cl$_3$SiSiCl$_3$). Therefore the very intensive and highly polarized band at 352 cm^{-1} can not help being assigned to the ν_sSiCl for Cl$_3$SiSiCl$_3$.[5-7] Figure 1 shows schematic Raman bands of some compounds containing SiCl$_3$ groups.

The stretching force constants of ν_sSiCl are approximately calculated from the

$$800 \quad 700 \quad 600 \quad 500 \quad 400 \quad 300 \quad 200 \quad 100 \quad cm^{-1}$$

SiCl₄: $\nu_{as}SiCl$, $\nu_{s}SiCl$ (p) 422, $\delta_{s}SiCl$ 220, $\delta_{as}SiCl$, 608, 148

FSiCl₃: (p) 464, $\delta_{as}SiCl_3$, (p) 237, $\rho_r SiCl_3$ 165, 630, 278

HSiCl₃: $\delta_{as}SiCl_3$ 800, (p) 490, (p) 250, 175, 590

Cl₃SiOSiCl₃: $\nu_{as}SiCl(A_{2u})$ i.r. 480, $\Delta\nu$ 58, (p) 422 (#), $\delta_{as}SiCl_3$ 220 (*), 133, $\nu_s Si$-O-Si (p) 728, 613, (#) (#), (p) 330

Cl₃SiSiCl₃: i.r. 465, $\Delta\nu$ 111, (p) 354, 132, $\nu_s Si$-Si (p) 625, 590, 213, (*)

F₃SiOSiCl₃: $\delta_s SiF_3$ (p) 497, (p) 458, $\delta_{as}SiF_3$ 312, 220, $\rho_r SiF_3$ 177, 154, $\nu_s Si$-O-Si (p) 672, 624, (p) 344

Cl₃SiNSiCl₃ (H): (p) 470, (p) 328, 206, 123, (*), $\nu_s Si$-N-Si (H) (p) 623, 586

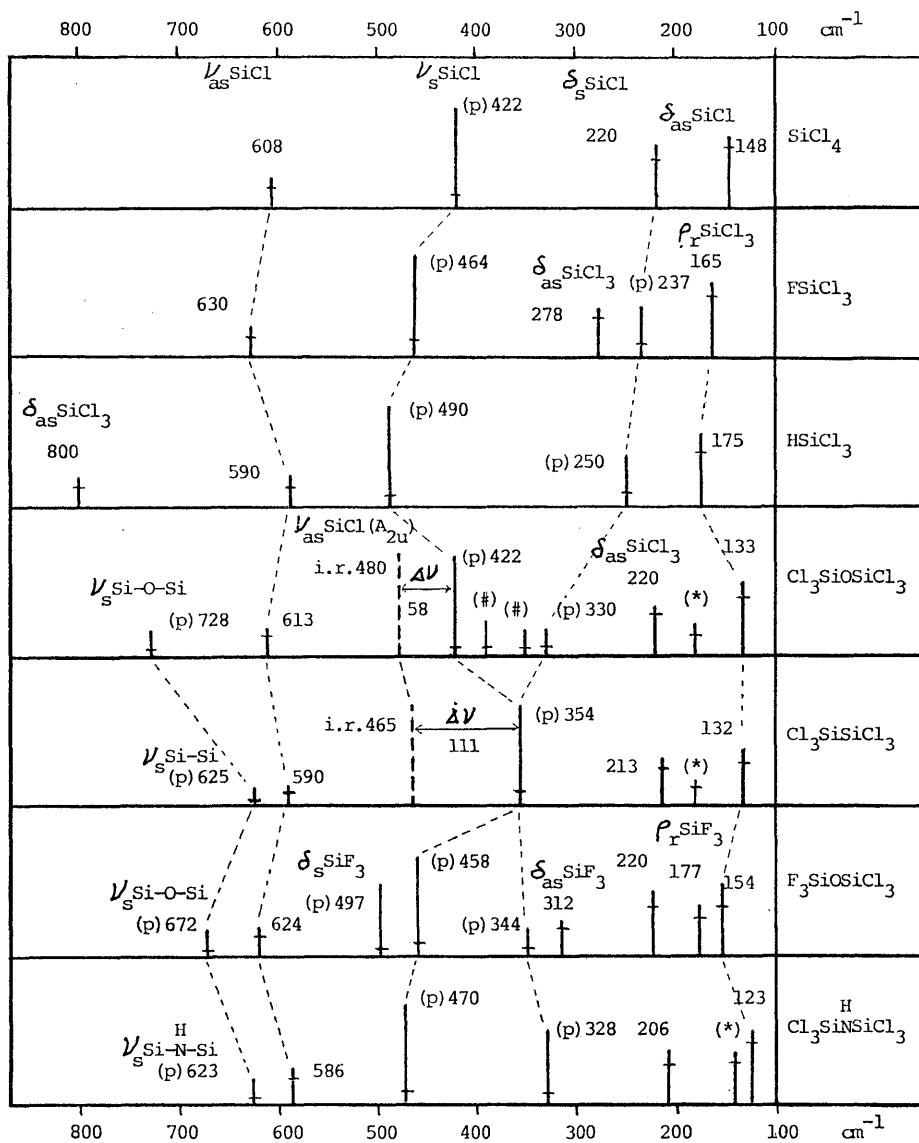$$800 \quad 700 \quad 600 \quad 500 \quad 400 \quad 300 \quad 200 \quad 100 \quad cm^{-1}$$

Fig. 1 Schematic Raman Spectra

Intensity of ($\parallel$) band is shown by vertical line and top of ($\perp$) band, by horizontal bar. Dotted line shows the infrared band of $\nu_{as}SiCl\,(A_{2u})$ which is Raman inactive. (*) indicates the band is Raman inactive but appears due to breakdown of selection rules. (#) indicates a combination band.

experimental vibration frequencies assuming XSi (X=O, N(H), Cl ,F, H) as one particle and the vibration as simple two-body vibration of (XSi)-Cl. The values of the force constant for these compounds except $Cl_3SiSiCl_3$ are calculated to be $2.21\sim2.55\times10^{-5}$ dyn/cm, which seem to be reasonable value, compared with 2.71×10^{-5} of $SiCl_4$[6] and 2.60×10^{-5} dyn/cm of $Cl_3SiOSiCl_3$[5]. However the force constant of $\nu_s SiCl$ for $Cl_3SiSiCl_3$ is calculated to be 1.15×10^{-5} dyn/cm using 352 cm^{-1} assigned to $\nu_s SiCl$

previously.[5-7] The calculated force constant is roughly a factor of two to two and a half times too small, which results from using too small frequency (352 cm^{-1}) for ν_sSiCl of $Cl_3SiSiCl_3$. The lowering of ν_sSiCl frequency may be due to the mixing of symmetry coordinates which results in the simultaneous raising and lowering of the frequencies of two of the A_{1g} fundamentals, as follows; ν_sSi-Si(A_{1g}) and $\delta_sSiCl_3(A_{1g})$, and $\nu_sSiCl(A_{1g})$ and $\delta_sSiCl_3 (A_{1g})$ are coupled intensively, and so ν_sSi-Si and ν_sSiCl stretches involve considerable δ_sSiCl_3 motion. Accordingly the frequencies of ν_sSi-Si and ν_sSiCl modes are lower than would be expected for isolated ν_sSi-Si and ν_sSiCl, and that of δ_sSiCl_3, higher due to a corresponding rising. Consequently ν_sSiCl and δ_sSiCl_3 bands would come closer to coalesce to be one band due to very strong coupling in $Cl_3SiSiCl_3$.

Even in $Cl_3SiOSiCl_3$, the coupling shall arise among ν_sSi-O-Si(A_{1g}) and δ_sSiCl_3 (A_{1g}), and $\nu_sSiCl(A_{1g})$ and $\delta_sSiCl_3(A_{1g})$, but it shall not be so strong in $Cl_3SiOSiCl_3$. Because in $Cl_3SiSiCl_3$, two silicon atoms are close together, whereas in Cl_3Si-O-$SiCl_3$, they are separated by oxygen atom.

In $Cl_3SiOSiCl_3$ and $Cl_3SiSiCl_3$, the asymmetric Si-Cl stretching mode$(\nu_{as}SiCl)$ (A_{2u}) is infrared active but silent in the Raman effect. The infrared band at 480 cm^{-1} is assigned to $\nu_{as}SiCl$ in $Cl_3SiOSiCl_3$. This mode lies well within the expected frequency range$(ca. 450$cm$^{-1})$, and the assignment of $\nu_{as}SiCl$ places the frequency of $\nu_{as}SiCl$ 58 cm^{-1} above 422 cm^{-1} of ν_sSiCl. Such a large separation is to be expected if ν_sSiCl

Species	Normal Vibrational Modes	Reference 6)		Present authors	
		Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)
A_{1g}	ν_sSi-Si	(p)627m	......	(p)625m	......
	ν_sSi-Cl	(p)356s	......	(p)354vs	......
	δ_sSiCl_3	(p)136m	......	(p)354vs	......
A_{1u}	Torsion	......	......	......	......
A_{2u}	$\nu_{as}SiCl$	......	464s	......	465s
	$\delta_{as}SiCl_3$	......	245m	......	( )
E_g	$\nu_{as}SiCl$	592m	......	590m	......
	$\delta_{as}SiCl_3$	215w	......	213m	......
	ρ_rSiCl_3	129m	......	132s	......
E_u	$\nu_{as}SiCl$	......	615vs	......	610vs
	$\delta_{as}SiCl_3$	......	179m	(*) 180w	( )
	ρ_rSiCl_3	......	75vvw	......	( )

Table 1 Symmetry Species and Selection Rules of D_{3d}, and Frequency Assignments of $Cl_3SiSiCl_3$

( ) means this band is out of observational limit. (*) shows this band would be forbidden, but appears due to breakdown of the selection rules caused by intermolecular action.

mode is coupled with $\delta_s SiCl_3$ one and the frequency of $\nu_s SiCl$ is lowered. Otherwise $\nu_s SiCl$ and $\nu_{as} SiCl$ modes should lie very close together.[9] In the case of $Cl_3 SiSiCl_3$, the separation between $\nu_s SiCl(A_{1g})$ and $\nu_{as} SiCl(465 \text{ cm}^{-1})(A_{2u})$ is 111 cm^{-1}. This shows, as above mentioned, that there occur very, very intensive coupling of the A_{1g} fundamentals of $Cl_3 SiSiCl_3$.

The frequencies of symmetric $SiCl_3$ deformation($\delta_s SiCl_3$) for $Cl_3 SiOSiCl_3$, $Cl_3 SiN$-$(H)SiCl_3$ and $F_3 SiOSiCl_3$ are 330, 328 and 344 cm^{-1}, respectively. On the other hand, the frequency of $\delta_s SiCl_3$ for $Cl_3 SiSiCl_3$ has been reported to be 136 cm^{-1}, as shown in Table 1, which seems to be very low, compared with those of $\delta_s SiCl_3$ for the structually similar molecules, $Cl_3 SiOSiCl_3$, $Cl_3 SiN(H)SiCl_3$ and $F_3 SiOSiCl_3$. If the band at 354 cm^{-1}, as above mentioned, would be considered as the coalescent band of $\nu_s SiCl$ and $\delta_s SiCl_3$, the frequency, 354 cm^{-1} is reasonable for $\delta_s SiCl_3$ mode, whose frequency is expected to lie within 330 cm^{-1} region, but is raised to 354 cm^{-1} due to coupling of A_{1g} fundamentals. If the band at 136 cm^{-1} is assigned to $\delta_s SiCl_3$ the band should be polarized one. Nevertheless the 132 cm^{-1} band obtained looks like depolarized one. On the basis of the above discussion, the vibrational spectra of $Cl_3 SiSiCl_3$ can be tentatively assigned as shown in Table 1. The new results require some minor adjustments in the earlier assignments.[10]

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