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<tr>
<td>Author(s)</td>
<td>Hamada, Keinosuke; Morishita, Hirofumi</td>
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<td>長崎大学教育学部自然科学研究報告. vol.26, p.61-64; 1975</td>
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<td>Issue Date</td>
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**Example:**

久高海岸の研究で発見された新しい化学物質に関する詳細は、以下に掲載されています。

http://naosite.lb.nagasaki-u.ac.jp
Anomaly of Hexachlorodisilane in Symmetric Si-Cl Stretching Frequency and Its Vibrational Assignments

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(Received October 31, 1974)

Abstract

The symmetric Si-Cl stretching of hexachlorodisilane, 352 cm\(^{-1}\) is found to be anomalously 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 trifluorotrichlorodisiloxane (F\(_3\)SiOSiCl\(_3\)) and hexachlorodisilazane (Cl\(_3\)SiN(H)SiCl\(_3\)) synthesized according to the references.\(^1-5\)

The Raman spectrum is recorded on JEOL JRS-SIB spectrophotometer 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 (\(\nu_4\)SiCl); this band is always strong and highly polarized and occurs in 450 cm\(^{-1}\) wave number region\(^4\), with which \(\nu_4\)SiCl 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 \(\nu_4\)SiCl 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 \(\nu_4\)SiCl are approximately calculated from the
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$_3$SiSiCl$_3$ are calculated to be $2.21 \sim 2.55 \times 10^{-5}$ dyn/cm, which seem to be reasonable value, compared with $2.71 \times 10^{-5}$ of SiCl$_4$\(^6\)) and $2.60 \times 10^{-5}$ dyn/cm of Cl$_3$SiOSiCl$_3$\(^5\)). However the force constant of $\nu_4$SiCl for Cl$_3$SiSiCl$_3$ is calculated to be $1.15 \times 10^{-5}$ dyn/cm using 352 cm$^{-1}$ assigned to $\nu_4$SiCl
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 \(\nu_6\)SiCl of Cl\(_3\)SiSiCl\(_3\). The lowering of \(\nu_6\)SiCl 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; \(\nu_4\)Si–Si\((A_{1g})\) and \(\delta_6\)SiCl\(_3\)(\(A_{1g}\)), and \(\nu_6\)SiCl\((A_{1g}\) and \(\delta_6\)SiCl\(_3\)(\(A_{1g}\)), are coupled intensively, and so \(\nu_4\)Si–Si and \(\nu_6\)SiCl stretches involve considerable \(\delta_6\)SiCl\(_3\) motion. Accordingly the frequencies of \(\nu_4\)Si–Si and \(\nu_6\)SiCl modes are lower than would be expected for isolated \(\nu_4\)Si–Si and \(\nu_6\)SiCl, and that of \(\delta_6\)SiCl\(_3\), higher due to a corresponding rising. Consequently \(\nu_6\)SiCl and \(\delta_6\)SiCl\(_3\) bands would come closer to coalesce to be one band due to very strong coupling in Cl\(_3\)SiSiCl\(_3\).

Even in Cl\(_3\)SiOSiCl\(_3\), the coupling shall arise among \(\nu_6\)Si–O–Si\((A_{1g}\) and \(\delta_6\)SiCl\(_3\)\((A_{1g}\), and \(\nu_6\)SiCl\((A_{1g}\) and \(\delta_6\)SiCl\(_3\)(\(A_{1g}\), but it shall not be so strong in Cl\(_3\)SiOSiCl\(_3\). Because in Cl\(_3\)SiSiCl\(_3\), two silicon atoms are close together, whereas in Cl\(_3\)Si–O–SiCl\(_3\), they are separated by oxygen atom.

In Cl\(_3\)SiOSiCl\(_3\) and Cl\(_3\)SiSiCl\(_3\), 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\(_3\)SiOSiCl\(_3\). This mode lies well within the expected frequency range(ca. 450cm\(^{-1}\)), and the assignment of \(\nu_{as}\)SiCl places the frequency of \(\nu_{as}\)SiCl 58 cm\(^{-1}\) above 422 cm\(^{-1}\) of \(\nu_6\)SiCl. Such a large separation is to be expected if \(\nu_6\)SiCl

<table>
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Table 1 Symmetry Species and Selection Rules of \(D_{3d}\). and Frequency Assignments of Cl\(_3\)SiSiCl\(_3\)

\((\ )\) 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 $\delta_SiCl_3$ one and the frequency of $\nu_SiCl$ is lowered. Otherwise $\nu_SiCl$ and $\nu_{as}SiCl$ modes should lie very close together. In the case of Cl$_3$SiSiCl$_3$, the separation between $\nu_SiCl(A_{1g})$ and $\nu_{as}SiCl$(465 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 ($\delta_SiCl_3$) 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 $\delta_SiCl_3$ 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 $\delta_SiCl_3$ for the structurally 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 $\nu_SiCl$ and $\delta_SiCl_3$, the frequency, 354 cm$^{-1}$ is reasonable for $\delta_SiCl_3$ 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 $\delta_SiCl_3$ 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.

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References