Chlorine-35 NQR of Hexachlorodisilane, Hexachlorodisiloxane, and Hexachlorodisilazane

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Abstract

Chlorine-35 NQR of Cl₃SiSiCl₃, Cl₃SiOSiCl₃, and Cl₃SiN(H)SiCl₃ are measured with a superregenerative spectrometer. All samples exhibit the complex chlorine NQR spectra and the average frequencies for Cl₃SiSiCl₃, Cl₃SiOSiCl₃, and Cl₃SiN(H)SiCl₃ are 19.29, 19.85 and 19.63 MHz, respectively. Only a very little difference among the average of NQR frequency values of three compounds may be due to the difference of ionic character for Si-Cl bond.

Experimental

Materials. Hexachlorodisilane and hexachlorodisiloxane are obtained from commercial sources. Hexachlorodisilazane are synthesized as follows*: An ammonia gas diluted with a nitrogen gas was passed through ether containing silicon tetrachloride at -75°C. The product are purified by distillation.

Measurements. Hexachlorodisilane is measured at -196°C with a superregenerative spectrometer*, whose resonance frequencies are measured with DELICA GRID-DIP meter(HAM-310), and the others are done in Professor M.A. Whitehead's laboratory.

Results and Discussion

Table 1 gives the results of measurements.

The increasing nuclear quadrupole resonance frequencies in the sequence Cl₃SiSiCl₃, Cl₃SiN(H)SiCl₃, Cl₃SiOSiCl₃ to SiCl₄ may reflect a decrease in ionic character in the Si-Cl bond. This is consistent with the view that the replac-

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Table 1  Cl₃NQR Frequencies of Cl₃SiSiCl₃, Cl₃SiOSiCl₃, and Cl₃SiN(H)SiCl₃ at -197°C

<table>
<thead>
<tr>
<th>Cl₃SiSiCl₃(*) MHz</th>
<th>Cl₃SiOSiCl₃(*) MHz</th>
<th>Cl₃SiN(H)SiCl₃(*) MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.45±0.03</td>
<td>19.957±0.001</td>
<td>19.725±0.001</td>
</tr>
<tr>
<td>19.28</td>
<td>19.895</td>
<td>19.704</td>
</tr>
<tr>
<td>19.22</td>
<td>19.865</td>
<td>19.665</td>
</tr>
<tr>
<td>(**)</td>
<td>19.849</td>
<td>19.655</td>
</tr>
<tr>
<td>(**) average</td>
<td>19.85</td>
<td>19.63</td>
</tr>
</tbody>
</table>

(*1) measured with DELICA GRID-DIP meter.
(*2) Few very weak resonances seem to appear below 19.22 MHz.
(*5) Few very weak resonances exist below 19.849 MHz.

ing a chlorine of SiCl₄ by the groups whose electronegativity strengths decrease in the order Cl>Cl₃SiO>Cl₃SiN(H)>Cl₃Si gives a progressively smaller competition for Si electrons and hence an increased ionic character in Si-Cl.

When chlorine is replaced by fluorine a still larger increase of NQR frequency would be expected since fluorine is much more electronegative than chlorine. NQR frequency of trichloromonofluorosilane is 19.753 MHz\(^5\), which is less than the average frequency of SiCl₄, 20.390 MHz\(^5\). This is not the case in progressing from SiCl₄ to Cl₃SiOSiCl₃ and so on. It has been proposed\(^7\), in order to explain such a consequence unexpected, that there is an increase in double bond character due to contributions of resonant structures of the type F-Si=Cl\(^+\). Since double bond character is in the direction of decreasing NQR frequency, this effect would be in the same direction to the ionic character effect discussed above and could explain the decrease of NQR frequency when chlorine is replaced by fluorine.

It would be of interest to obtain NQR frequencies of F₃SiCl₂ and FₙSiCl, but the NQR measurements for them have been unsuccessful\(^5\).

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4) M.A. Whitehead, Private Communication