Determination of element-deuterium bond lengths in Zintl phase hydrides by $^2$H-NMR

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Dependency of $C_Q$ regarding the dihedral Si-chain to D angle

Figure S1: Changes of $C_Q$ and $\eta$ regarding to the dihedral angle of the plane of the Si zig-zag chain towards deuterium. The BaSiD$_2$-structure was used as a model system. Results are shown for the DFT-optimised bond length $d(\text{Si-D}) = 157$ pm and two additional values. The DFT-optimised structure exhibits a bond angle of $95.6^\circ$ which is indicated by the grey lines.
Evaluation of Si-D bond lengths from experimental $C_Q$ values

Figure S2: Empirical fits to DFT-derived $C_Q$-distance curves for the silicon systems.
Table S1: Si-D-distances calculated from experimental C_Q values using the C_Q-distance dependencies as given in Fig. S2.

<table>
<thead>
<tr>
<th>compound</th>
<th>C_Q,exp / kHz</th>
<th>d_{calc}(Si-D) / Å</th>
<th>d_{exp}(Si-D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiD_4-model</td>
<td>CaSiD_{4/3}-model</td>
<td>BaSiD_2-model</td>
</tr>
<tr>
<td>CaSiD_{4/3-x}</td>
<td>69(1) 1.552(3)</td>
<td>1.566(3)</td>
<td>1.562(3)</td>
</tr>
<tr>
<td>SrSiD_{5/3-x}</td>
<td>63(1) 1.572(4)</td>
<td>1.584(3)</td>
<td>1.581(4)</td>
</tr>
<tr>
<td>BaSiD_{2-x}</td>
<td>78(3) 1.526(8)</td>
<td>1.540(8)</td>
<td>1.536(8)</td>
</tr>
<tr>
<td></td>
<td>58(2) 1.589(7)</td>
<td>1.601(7)</td>
<td>1.597(7)</td>
</tr>
<tr>
<td>SiD_4</td>
<td>95</td>
<td>1.482</td>
<td>1.493</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;SiD</td>
<td>90(2) 1.494(5)</td>
<td>1.509(5)</td>
<td>1.505(5)</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;5&lt;/sub&gt;SiD</td>
<td>91(2) 1.492(5)</td>
<td>1.507(5)</td>
<td>1.502(4)</td>
</tr>
<tr>
<td>β-KSiD&lt;sub&gt;3&lt;/sub&gt;</td>
<td>72.0(5) 1.543(2)</td>
<td>1.557(2)</td>
<td>1.553(2)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Typical bond lengths. Determined for disilane (Si<sub>2</sub>H<sub>6</sub>).<sup>34</sup>
Evaluation of Ge-D bond lengths from experimental $C_Q$ values

![Graphs showing empirical fits to DFT-derived $C_Q$-distance curves for the germanium systems.]

Figure S3: Empirical fits to DFT-derived $C_Q$-distance curves for the germanium systems.

Table S2: Ge-D-distances calculated from experimental $C_Q$ values using the $C_Q$-distance dependencies as given in Fig. S3.

<table>
<thead>
<tr>
<th>compound</th>
<th>$C_{Q,exp}$ / kHz</th>
<th>$d_{calc}$(Ge-D) / Å</th>
<th>$d_{exp}$(Ge-D) / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GeD$_4$-model</td>
<td>SrGeD$_{4/3}$-model</td>
</tr>
<tr>
<td>SrGeD$_{4/3-x}$</td>
<td>52(2)</td>
<td>1.642(8)</td>
<td>1.652(8)</td>
</tr>
<tr>
<td>BaGeD$_{5/3-x}$</td>
<td>51(2)</td>
<td>1.646(8)</td>
<td>1.659(8)</td>
</tr>
<tr>
<td></td>
<td>61(2)</td>
<td>1.609(7)</td>
<td>1.620(7)</td>
</tr>
<tr>
<td>GeD$_4$</td>
<td>82(5)$^a$</td>
<td>1.545(14)</td>
<td>1.558(13)</td>
</tr>
<tr>
<td>CH$_3$GeD$_3$</td>
<td>82(2)$^a$</td>
<td>1.545(7)</td>
<td>1.558(6)</td>
</tr>
</tbody>
</table>

$^a$Typical bond lengths. Determined from germane (GeD$_4$)$^a$ and digermane (Ge$_2$H$_6$)$^a$.
Sn-D: C_Q-distance dependency according to SnD_4 model

Figure S4: Empirical fit to the DFT-derived C_Q-distance curve of SnD_4. The experimental reference data are: SnD_4: d(Sn-D) = 1.706(3) Å (at 5 K), C_Q = 66(5) kHz. BaSnD_{4/3-x}: d(Sn-D) = 1.858(8) Å, C_Q = 38(2) kHz (this work).

A evaluation of the Sn-D bond length from experimental C_Q-values according to the empirically fitted curve gives:

SnD_4: d(Sn-D) = 1.721(18) Å.

BaSnD_{4/3-x}: d(Sn-D) = 1.846(12) Å.
$^2$H MAS spectra at slow spinning showing spinning sideband pattern

Figure S5: $^2$H MAS spectrum of BaSiD$_{2-x}$ recorded with a spinning frequency of 4 kHz. The central line is vertically cut for better visibility of sideband intensities.

Figure S6: $^2$H MAS spectrum of SrSiD$_{5/3-x}$ recorded with a spinning frequency of 3.4 kHz. The central line is vertically cut for better visibility of sideband intensities.
Figure S7: $^2$H MAS spectrum of CaSiD$_{4/3-x}$ recorded with a spinning frequency of 8 kHz. The central line is vertically cut for better visibility of sideband intensities.

Figure S8: $^2$H MAS spectrum of BaGeD$_{5/3-x}$ recorded with a spinning frequency of 3.4 kHz. The central line is vertically cut for better visibility of sideband intensities.
Figure S9: $^2$H MAS spectrum of SrGeD$_{4/3-x}$ recorded with a spinning frequency of 1.5 kHz. The central line is vertically cut for better visibility of sideband intensities.

Figure S10: $^2$H MAS spectrum of BaSnD$_{4/3-x}$ recorded with a spinning frequency of 3.4 kHz. The central line is vertically cut for better visibility of sideband intensities.
References


