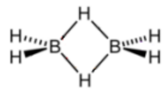
6.4: Diborane

Diborane - D_{2h} Symmetry



Diborane has 18 vibrational degrees of freedom. Nine modes are Raman active and eight are IR active. The experimental results are provided in the table below. Do a symmetry analysis to confirm the assignments given below, and identify stretches and bends.

$$\begin{pmatrix} D_{2h} & A_g & A_g & A_g & A_g & B_{1g} & B_{1g} & B_{2g} & B_{2g} & B_{3g} \\ \frac{\text{Raman}}{\text{cm}} & 2524 & 2104 & 1180 & 794 & 1768 & 1035 & 2591 & 920 & 1012 \\ D_{2h} & A_u & B_{1u} & B_{1u} & B_{1u} & B_{2u} & B_{2u} & B_{3u} & B_{3u} & B_{3u} \\ \frac{\text{IR}}{\text{cm}} & 0 & 2612 & 950 & 368 & 1915 & 973 & 2525 & 1606 & 1177 \end{pmatrix}$$

$$\begin{array}{cccccccc} E & C_2^z & C_2^y & C_2^x & i & \sigma_{xy} & \sigma_{xz} & \sigma_{yz} \end{array}$$

$$\mathrm{C}_{D2h} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 1 & -1 & 1 & 1 & -1 \end{pmatrix} \quad \begin{array}{l} A_g:\ x^2,\ y^2,\ z^2 \\ \mathrm{B}_{1g}:\ R_z,\ xy \\ \mathrm{B}_{2g}:\ R_y,\ xz \\ \mathrm{B}_{3g}:\ R_x, yx \\ \mathrm{A}_u \\ \mathrm{B}_{1u}:\ z \\ \mathrm{B}_{2u}:\ y \\ \mathrm{B}_{3u}:\ x \end{array} \quad \mathrm{D2h} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad \Gamma_{uma} = \begin{pmatrix} 8 \\ 0 \\ 2 \\ 2 \\ 0 \\ 4 \\ 6 \\ 2 \end{pmatrix} \quad \Gamma_{bonds} = \begin{pmatrix} 8 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4 \\ 4 \\ 0 \end{pmatrix}$$

$$\mathrm{A}_g = (\mathrm{C}_{D4h}^T)^{<1>} \quad \mathrm{B}_{2g} = (\mathrm{C}_{D4h}^T)^{<2>} \quad \mathrm{B}_{2g} = (\mathrm{C}_{D4h}^T)^{<3>} \quad \mathrm{B}_{3g} = (\mathrm{C}_{D4h}^T)^{<4>}$$

$$\mathrm{A}_u = (\mathrm{C}_{D4h}^T)^{<5>} \quad \mathrm{B}_{1u} = (\mathrm{C}_{D4h}^T)^{<6>} \quad \mathrm{B}_{2u} = (\mathrm{C}_{D4h}^T)^{<7>} \quad \mathrm{B}_{3u} = (\mathrm{C}_{D4h}^T)^{<8>} \quad h = \sum \mathrm{D2h}$$

$$\Gamma_{trans} = B_{1u} + B_{2u} + B_{3u} \qquad \Gamma_{tot} = B_{1g} + B_{2g} + B_{3g} \qquad \Gamma_{tot} = \overrightarrow{(\Gamma_{uma}\Gamma_{trans})}$$

$$\Gamma_{vib} = \Gamma_{tot} - \Gamma_{trans} - \Gamma_{rot} \qquad \Gamma_{vib}^T = \begin{pmatrix} 18 & 2 & 0 & 0 & 0 & 4 & 6 & 2 \end{pmatrix} \qquad i = 1..8$$

$$\Gamma_{stretch} = \Gamma_{bonds} \qquad \Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch}$$

$$\mathrm{Vib}_i = \frac{\sum \overrightarrow{[D2h(C_{D2h}^T)^{<i>}\Gamma_{vib}]}}{h} \quad \mathrm{Stretch}_i = \frac{\sum \overrightarrow{[D2h(C_{D2h}^T)^{<i>}\Gamma_{stretch}]}}{h} \quad \mathrm{Bend}_i = \frac{\sum \overrightarrow{[D2h(C_{D2h}^T)^{<i>}\Gamma_{bend}]}}{h}$$

$$\mathrm{Vib} = \begin{pmatrix} 4 \\ 2 \\ 2 \\ 1 \\ 1 \\ 3 \\ 2 \\ 3 \end{pmatrix} \begin{array}{l} A_g:\ x^2,\ y^2,\ z^2 \\ \mathrm{B}_{1g}:\ R_z,\ xy \\ \mathrm{B}_{2g}:\ R_y,\ xz \\ \mathrm{B}_{3g}:\ R_x, yx \\ \mathrm{A}_u \\ \mathrm{B}_{1u}:\ z \\ \mathrm{B}_{2u}:\ y \\ \mathrm{B}_{3u}:\ x \end{array} \quad \mathrm{Stretch} = \begin{pmatrix} 2 \\ 1 \\ 1 \\ 0 \\ 0 \\ 1 \\ 1 \\ 2 \end{pmatrix} \begin{array}{l} A_g:\ x^2,\ y^2,\ z^2 \\ \mathrm{B}_{1g}:\ R_z,\ xy \\ \mathrm{B}_{2g}:\ R_y,\ xz \\ \mathrm{B}_{3g}:\ R_x, yx \\ \mathrm{A}_u \\ \mathrm{B}_{1u}:\ z \\ \mathrm{B}_{2u}:\ y \\ \mathrm{B}_{3u}:\ x \end{array} \quad \mathrm{Bend} = \begin{pmatrix} 2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \end{pmatrix} \begin{array}{l} A_g:\ x^2,\ y^2,\ z^2 \\ \mathrm{B}_{1g}:\ R_z,\ xy \\ \mathrm{B}_{2g}:\ R_y,\ xz \\ \mathrm{B}_{3g}:\ R_x, yx \\ \mathrm{A}_u \\ \mathrm{B}_{1u}:\ z \\ \mathrm{B}_{2u}:\ y \\ \mathrm{B}_{3u}:\ x \end{array}$$

This analysis is in agreement with the experimental data. There are 9 Raman active modes and 8 IR active modes. Furthermore there are 4 Raman stretches at 2524 (Ag), 2104 (Ag), 1768 (B1g), and 2591 (B2g). The five Raman bends occur at 1180 (Ag), 794 (Ag), 1035 (B1g), 920 (B2g), and 1012 (B3g).

The 4 IR stretches occur at 2612 (B1u), 1915 (B2u), 2525 (B3u), and 1606 (B3u). The bends appear at 950 (B1u), 368 (B1u), 973 (B2u), 1177 (B3u).