

C_{3v} Symmetry - BCl₃

The infrared spectrum of BCl₃ shows vibrational bands at 995, 480, and 244 cm⁻¹, while Raman bands appear at 995, 471, and 244 cm⁻¹. Is the geometry of the molecule trigonal pyramid (C_{3v}) or trigonal planar (D_{3h})? Is your answer to this question consistent with chemical bonding principles (VSEPR)? Assign symmetry labels to the vibrational bands and identify the stretches and bends.

$$\begin{array}{l}
 \text{E } C_3 \sigma_v \\
 C_{C3v} := \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \\ 2 & -1 & 0 \end{pmatrix} \quad \begin{array}{l} A_1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x,y), (R_x,R_y), \\ (x^2 + y^2, xy)(xz,yz) \end{array}
 \end{array}
 \quad
 \begin{array}{l}
 C_{3v} := \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{l}
 \Gamma_{\text{uma}} := \begin{pmatrix} 4 \\ 1 \\ 2 \end{pmatrix}
 \end{array}
 \quad
 \begin{array}{l}
 \Gamma_{\text{bonds}} := \begin{pmatrix} 3 \\ 0 \\ 1 \end{pmatrix}
 \end{array}$$

$$A_1 := (C_{C3v}^T)^{\langle 1 \rangle} \quad A_2 := (C_{C3v}^T)^{\langle 2 \rangle} \quad E := (C_{C3v}^T)^{\langle 3 \rangle} \quad h := \sum C_{3v}$$

$$\Gamma_{\text{tot}} := \overline{\Gamma_{\text{uma}} \cdot (A_1 + E)} \quad \Gamma_{\text{tot}}^T = (12 \ 0 \ 2) \quad \Gamma_{\text{vib}} := \Gamma_{\text{tot}} - A_1 - A_2 - 2E$$

$$\begin{array}{l}
 i := 1..3 \\
 \text{Vib}_i := \frac{\sum \left[C_{3v} \cdot (C_{C3v}^T)^{\langle i \rangle} \cdot \Gamma_{\text{vib}} \right]}{h}
 \end{array}
 \quad
 \begin{array}{l}
 \text{Vib} = \begin{pmatrix} 2 \\ 0 \\ 2 \end{pmatrix} \quad \begin{array}{l} A_1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x,y), (R_x,R_y), \\ (x^2 + y^2, xy)(xz,yz) \end{array}
 \end{array}$$

$$\begin{array}{l}
 \Gamma_{\text{stretch}} := \Gamma_{\text{bonds}} \\
 \text{Stretch}_i := \frac{\sum \left[C_{3v} \cdot (C_{C3v}^T)^{\langle i \rangle} \cdot \Gamma_{\text{stretch}} \right]}{h}
 \end{array}
 \quad
 \begin{array}{l}
 \text{Stretch} = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \begin{array}{l} A_1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x,y), (R_x,R_y), \\ (x^2 + y^2, xy)(xz,yz) \end{array}
 \end{array}$$

$$\begin{array}{l}
 \Gamma_{\text{bend}} := \Gamma_{\text{vib}} - \Gamma_{\text{stretch}} \\
 \text{Bend}_i := \frac{\sum \left[C_{3v} \cdot (C_{C3v}^T)^{\langle i \rangle} \cdot \Gamma_{\text{bend}} \right]}{h}
 \end{array}
 \quad
 \begin{array}{l}
 \text{Bend} = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \begin{array}{l} A_1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x,y), (R_x,R_y), \\ (x^2 + y^2, xy)(xz,yz) \end{array}
 \end{array}$$

This analysis predicts that there should be 4 IR and 4 Raman active vibrations. It also predicts that the IR and Raman vibrations should be coincident. This is not in agreement with the experimental data, so BCl₃ does not have trigonal pyramidal geometry.

This analysis also predicts that the stretches should have A₁ and E symmetry, but since it has already been concluded that the molecule does not have C_{3v} symmetry this result will not be discussed further.

D_{3h} Symmetry - BCl₃

| | | | | |
|---|---|--|--|--|
| $C_{D3h} := \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & 0 & 2 & -1 & 0 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & -1 & 1 \\ 2 & -1 & 0 & -2 & 1 & 0 \end{bmatrix}$ | $A_1': x^2 + y^2, z^2$ $A_2': Rz$ $E': (x,y), (x^2 - y^2, xy)$ $A_1'':$ $A_2'': z$ $E'': (Rx, Ry), (xz, yz)$ | $D_{3h} := \begin{bmatrix} 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \end{bmatrix}$ | $\Gamma_{uma} := \begin{bmatrix} 4 \\ 1 \\ 2 \\ 4 \\ 1 \\ 2 \end{bmatrix}$ | $\Gamma_{bonds} := \begin{bmatrix} 3 \\ 0 \\ 1 \\ 3 \\ 0 \\ 1 \end{bmatrix}$ |
|---|---|--|--|--|

$$A_1 := (C_{D3h}^T)^{\langle 1 \rangle} \quad A_2 := (C_{D3h}^T)^{\langle 2 \rangle} \quad E := (C_{D3h}^T)^{\langle 3 \rangle} \quad A_{11} := (C_{D3h}^T)^{\langle 4 \rangle}$$

$$A_{21} := (C_{D3h}^T)^{\langle 5 \rangle} \quad E_1 := (C_{D3h}^T)^{\langle 6 \rangle} \quad h := \sum D_{3h} \quad \Gamma_{tot} := \overline{\Gamma_{uma} \cdot (A_{21} + E)}$$

$$\Gamma_{tot}^T = (12 \quad 0 \quad -2 \quad 4 \quad -2 \quad 2) \quad \Gamma_{vib} := \Gamma_{tot} - A_2 - E - A_{21} - E_1 \quad i := 1..6$$

$$\Gamma_{stretch} := \Gamma_{bonds} \quad \Gamma_{bend} := \Gamma_{vib} - \Gamma_{stretch}$$

$$Vib_i := \frac{\sum [D_{3h} \cdot (C_{D3h}^T)^{\langle i \rangle} \cdot \Gamma_{vib}]}{h} \quad Stretch_i := \frac{\sum [D_{3h} \cdot (C_{D3h}^T)^{\langle i \rangle} \cdot \Gamma_{stretch}]}{h} \quad Bend_i := \frac{\sum [D_{3h} \cdot (C_{D3h}^T)^{\langle i \rangle} \cdot \Gamma_{bend}]}{h}$$

| | | |
|---|---|--|
| $Vib = \begin{bmatrix} 1 \\ 0 \\ 2 \\ 0 \\ 1 \\ 0 \end{bmatrix} \begin{matrix} A_1': x^2 + y^2, z^2 \\ A_2': Rz \\ E': (x,y), (x^2 - y^2, xy) \\ A_1'' : \\ A_2'': z \\ E'': (Rx, Ry), (xz, yz) \end{matrix}$ | $Stretch = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{matrix} A_1': x^2 + y^2, z^2 \\ A_2': Rz \\ E': (x,y), (x^2 - y^2, xy) \\ A_1'' : \\ A_2'': z \\ E'': (Rx, Ry), (xz, yz) \end{matrix}$ | $Bend = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{bmatrix} \begin{matrix} A_1': x^2 + y^2, z^2 \\ A_2': Rz \\ E': (x,y), (x^2 - y^2, xy) \\ A_1'' : \\ A_2'': z \\ E'': (Rx, Ry), (xz, yz) \end{matrix}$ |
|---|---|--|

This analysis shows that there are 3 IR active modes (2E', A₂'') and 3 Raman active modes (A₁', E'). It also show that there are two coincidences (2E'). Thus, D_{3h} symmetry for BCl₃ is consistent with the spectroscopic data.

Thus the specific assignments are: A₁' = 471; A₂'' = 480; E' = 995; E' = 244. From the analysis above it can be seen that the stretches occur at 995 and 471, and the bends are at 480 and 244 cm⁻¹.

VSEPR theory would predict a trigonal planar arrangement of chlorine atoms around the electron deficient boron, so the symmetry analysis and the bonding theory are in agreement with each other and the spectroscopic measurements.