

6.6: BCl₃

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.

$$\begin{aligned}
 C_{C_{3v}} &= \begin{pmatrix} C_3 & \sigma_v \\ 1 & 1 & 1 \\ 1 & 1 & -1 \\ 2 & -1 & 0 \end{pmatrix} \quad \begin{matrix} 1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x, y)(R_x, R_y), (x^2 + y^2, xy)(xz, yz) \end{matrix} & C_{3v} &= \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} & \Gamma_{uma} &= \begin{pmatrix} 4 \\ 1 \\ 2 \end{pmatrix} & \Gamma_{bonds} &= \begin{pmatrix} 3 \\ 0 \\ 1 \end{pmatrix} \\
 A_1 &= (C_{C_{3v}}^T)^{<1>} & A_2 &= (C_{C_{3v}}^T)^{<2>} & E &= (C_{C_{3v}}^T)^{<3>} & h &= \sum C_{3v} \\
 \Gamma_{tot} &= \overline{[\Gamma_{uma}(A_1 + E)]} & \Gamma_{tot}^T &= (12 & 0 & 2) & \Gamma_{vib} &= \Gamma_{tot} - A_1 - A_2 - 2E \\
 i = 1..3 & \text{Vib}_i &= \frac{\overline{\sum [C_{3v}(C_{C_{3v}}^T)^{<i>} \Gamma_{vib}]} & \text{Vib} &= \begin{pmatrix} 2 \\ 0 \\ 2 \end{pmatrix} \quad \begin{matrix} 1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x, y)(R_x, R_y), (x^2 + y^2, xy)(xz, yz) \end{matrix} \\
 \Gamma_{stretch} &= \Gamma_{bonds} & \text{Stretch}_i &= \frac{\overline{\sum [C_{3v}(C_{C_{3v}}^T)^{<i>} \Gamma_{stretch}]} & \text{Stretch} &= \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \begin{matrix} 1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x, y)(R_x, R_y), (x^2 + y^2, xy)(xz, yz) \end{matrix} \\
 \Gamma_{bend} &= \Gamma_{vib} - \Gamma_{stretch} & \text{Bend}_i &= \frac{\overline{\sum [C_{3v}(C_{C_{3v}}^T)^{<i>} \Gamma_{bend}]} & \text{Bend} &= \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad \begin{matrix} 1: z, x^2 + y^2, z^2 \\ A_2: R_z \\ E: (x, y)(R_x, R_y), (x^2 + y^2, xy)(xz, yz) \end{matrix}
 \end{aligned}$$

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

$$\begin{aligned}
 C_{C_{3v}} &= \begin{pmatrix} C_3 & C_2 & \sigma_h & S_3 & \sigma_v \\ 1 & 1 & 11 & 1 & 1 \\ 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & 0 & 2 & -1 & 0 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & 1 & \\ 2 & -1 & 0 & -2 & 1 & 0 \end{pmatrix} \quad \begin{matrix} 1': x^2 + y^2, z^2 \\ A_2': R_z \\ E': (x, y), (x^2 + y^2, xy) \\ A_1'': \\ A_2'': z \\ E'': (R_x, R_y), (xz, yz) \end{matrix} & D_{3h} &= \begin{bmatrix} 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \end{bmatrix} & \Gamma_{uma} &= \begin{bmatrix} 4 \\ 1 \\ 2 \\ 4 \\ 1 \\ 2 \end{bmatrix} & \Gamma_{bonds} &= \begin{bmatrix} 3 \\ 0 \\ 1 \\ 3 \\ 0 \\ 1 \end{bmatrix} \\
 A_1 &= (C_{D_{3h}}^T)^{<1>} & A_2 &= (C_{D_{3h}}^T)^{<2>} & E &= (C_{D_{3h}}^T)^{<3>} & A_{11} &= (C_{D_{3h}}^T)^{<4>} \\
 A_{21} &= (C_{D_{3h}}^T)^{<5>} & E_1 &= (C_{D_{3h}}^T)^{<6>} & h &= \sum D_{3h} & \Gamma_{tot} &= \overline{[\Gamma_{uma}(A_{21} + E)]} \\
 \Gamma_{tot}^T &= (12 & 0 & -2 & 4 & -2 & 2) & \Gamma_{vib} &= \Gamma_{tot} - A_2 - E - A_{21} - E_1 & i = 1..6 \\
 \Gamma_{stretch} &= \Gamma_{bonds} & \Gamma_{bend} &= \Gamma_{vib} - \Gamma_{stretch}
 \end{aligned}$$

$$\begin{aligned}
 \text{Vib}_i &= \frac{\sum [D_{3h}(C_{D_{3h}}^T)^{<i>}\Gamma_{\text{vib}}]}{h} \\
 \text{Stretch}_i &= \frac{\sum [D_{3h}(C_{D_{3h}}^T)^{<i>}\Gamma_{\text{stretch}}]}{h} \\
 \text{Bend}_i &= \frac{\sum [D_{3h}(C_{D_{3h}}^T)^{<i>}\Gamma_{\text{bend}}]}{h}
 \end{aligned}$$

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

This analysis shows that there are 3 IR active modes (2E', A2'') and 3 Raman active modes (A1', E'). It also shows 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.

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