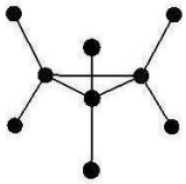
6.12: Cyclopropane

D_{3h} Symmetry - C_3H_6

The following IR and Raman spectroscopic data is available for cyclopropane, C_3H_6. Demonstrate that this data is consistent with a D_{3h} symmetry assignment for cyclopropane.



$$\begin{pmatrix} \text{Frequency} & 3038 & 1479 & 1188 & 3025 & 1438 & 1029 & 866 & 3103 & 854 & 3082 & 1188 & 734 \\ \text{Activity} & R & R & R & R, IR & R, IR & R, IR & R, IR & IR & IR & R & R & R \\ \text{Type} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

$$E_{D3h} = \begin{array}{c} \begin{matrix} C_3 & C_2 & \sigma_h & S_3 & \sigma_v \end{matrix} \\ \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & - & 2 & -1 & 0 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & -1 & 1 \\ 2 & -1 & 0 & -2 & 1 & 0 \end{pmatrix} \end{array} \begin{matrix} 1' : x^2+y^2,\ z^2 \\ A2' : Rz \\ E' : (x,\ y),\ (x^2-y^2,\ xy) \\ A1'' : \\ A2'' : z \\ E' : (Rx, Ry),\ (xz,\ yz) \end{matrix} \quad D3h = \begin{pmatrix} 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \end{pmatrix} \quad \Gamma_{uma} = \begin{pmatrix} 9 \\ 0 \\ 1 \\ 3 \\ 0 \\ 3 \end{pmatrix} \quad \Gamma_{bounds} = \begin{pmatrix} 9 \\ 0 \\ 1 \\ 3 \\ 0 \\ 3 \end{pmatrix}$$

$$A_1 = (C^T_{D3h})^{<1>} \quad A_2 = (C^T_{D3h})^{<2>} \quad E = (C^T_{D3h})^{<3>} \quad A_{11} = (C^T_{D3h})^{<4>}$$

$$A_{21} = (C^T_{D3h})^{<5>} \quad E_1 = (C^T_{D3h})^{<6>} \quad h = \sum D3h \quad \Gamma_{tot}\overrightarrow{[\Gamma_{uma}(A_{21}+E)]}$$

$$\Gamma^T_{tot} = (27 \quad 0 \quad -1 \quad 3 \quad 0 \quad 3) \quad \Gamma_{vib} = \Gamma_{tot} - A_2 - E - A_{21} - E_1 \quad i = 1..6$$

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

$$\text{Vib}_i = \frac{\sum \overrightarrow{\left[D3h(C^T_{D3h})^{<i>}\Gamma_{vib}\right]}}{h} \quad \text{Stretch}_i = \frac{\sum \overrightarrow{\left[D3h(C^T_{D3h})^{<i>}\Gamma_{bend}\right]}}{h} \quad \text{Bend}_i = \frac{\sum \overrightarrow{\left[D3h(C^T_{D3h})^{<i>}\Gamma_{bend}\right]}}{h}$$

$$\text{Vib} = \begin{pmatrix} 3 \\ 1 \\ 4 \\ 1 \\ 2 \\ 3 \end{pmatrix} \begin{matrix} 1' : x^2+y^2,\ z^2 \\ A2' : Rz \\ E' : (x,\ y),\ (x^2-y^2,\ xy) \\ A1'' : \\ A2'' : z \\ E' : (Rx, Ry),\ (xz,\ yz) \end{matrix} \quad \text{Stretch} = \begin{pmatrix} 2 \\ 0 \\ 2 \\ 0 \\ 1 \\ 1 \end{pmatrix} \begin{matrix} 1' : x^2+y^2,\ z^2 \\ A2' : Rz \\ E' : (x,\ y),\ (x^2-y^2,\ xy) \\ A1'' : \\ A2'' : z \\ E' : (Rx, Ry),\ (xz,\ yz) \end{matrix}$$

$$\text{Bend} = \begin{pmatrix} 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \end{pmatrix} \begin{matrix} 1' : x^2+y^2,\ z^2 \\ A2' : Rz \\ E' : (x,\ y),\ (x^2-y^2,\ xy) \\ A1'' : \\ A2'' : z \\ E' : (Rx, Ry),\ (xz,\ yz) \end{matrix}$$

$$\begin{pmatrix} \text{Frequency} & 3038 & 1479 & 1188 & 3025 & 1438 & 1029 & 866 & 3103 & 854 & 3082 & 1188 & 734 \\ \text{Activity} & R & R & R & R, IR & R, IR & R, IR & R, IR & IR & IR & R & R & R \\ \text{Type} & S & S & B & S & S & B & B & S & B & S & B & B \\ \text{Symmetry} & A1' & A1' & A1' & E' & E' & E' & E' & A2'' & A2'' & E'' & E'' & E'' \end{pmatrix}$$

There are 9 Raman active modes, 2 IR active modes, 8 IR/Raman active, and 2 modes that are neither Raman or IR active. This gives a total of 21 vibrational modes which is consistent with the total degrees of freedom (27=3x9) minus 6 for translation and rotation.
