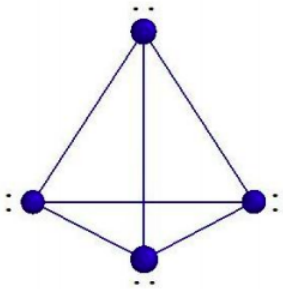
6.9: P_4

T_d - Tetrahedral Symmetry for P_4

The following Raman and IR frequencies have been observed for the tetrahedral P_4 molecule. Is the assignment of tetrahedral geometry to this molecule in agreement with the spectroscopic data? Explain.

$$\begin{pmatrix} R & R & R, IR \\ \frac{614}{\text{cm}} & \frac{372}{\text{cm}} & \frac{466}{\text{cm}} \end{pmatrix}$$



$$C_{Td} = \begin{matrix} E & C_3 & C_2 & S_4 & \sigma \end{matrix} \quad \begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & 1 & -1 \\ 3 & 0 & -1 & -1 & 1 \end{pmatrix} \quad \begin{matrix} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2-y^2,\ x^-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x,\ y,\ z),\ (xy,\ xz,\ yz) \end{matrix} \quad Td = \begin{pmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{pmatrix} \quad \Gamma_{uma} = \begin{pmatrix} 4 \\ 1 \\ 0 \\ 0 \\ 2 \end{pmatrix} \quad \Gamma_{bonds} = \begin{pmatrix} 6 \\ 0 \\ 2 \\ 0 \\ 2 \end{pmatrix}$$

$$A_1 = (C_{Td}^T)^{<1>} \quad A_2 = (C_{Td}^T)^{<2>} \quad E = (C_{Td}^T)^{<3>} \quad T_1 = (C_{Td}^T)^{<4>}$$

$$T_2 = (C_{Td}^T)^{<5>} \quad \Gamma_{tot} = \overrightarrow{(\Gamma_{uma}\, T_2)} \quad h = \sum Td \quad \Gamma_{tot}^T = (12 \quad 0 \quad 0 \quad 0 \quad 2) \quad i = 1..5$$

$$\Gamma_{vib} = \Gamma_{tot} - T_1 - T_2 \qquad \text{Vib}_i = \frac{\sum \overrightarrow{\left[Td (C_{Td}^T)^{<i>} \Gamma_{vib}\right]}}{h} \qquad \text{Vib} = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} \begin{matrix} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2-y^2,\ x^-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x,\ y,\ z),\ (xy,\ xz,\ yz) \end{matrix}$$

$$\Gamma_{stretch} = \Gamma_{bonds} \qquad \text{Stretch}_i = \frac{\sum \overrightarrow{\left[Td (C_{Td}^T)^{<i>} \Gamma_{stretch}\right]}}{h} \qquad \text{Stretch} = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} \begin{matrix} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2-y^2,\ x^-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x,\ y,\ z),\ (xy,\ xz,\ yz) \end{matrix}$$

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} \qquad \text{Bend}_i = \frac{\sum \overrightarrow{\left[Td (C_{Td}^T)^{<i>} \Gamma_{bend}\right]}}{h} \qquad \text{Bend} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \begin{matrix} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2-y^2,\ x^-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x,\ y,\ z),\ (xy,\ xz,\ yz) \end{matrix}$$

The group theoretical analysis assuming tetrahedral geometry is in excellent agreement with the spectroscopic data. Group theory predicts one IR active mode, and that it is coincident with a Raman frequency. This is observed with the T_2 vibration. In addition theory predicts that there are two additional Raman active modes A_1 and E.