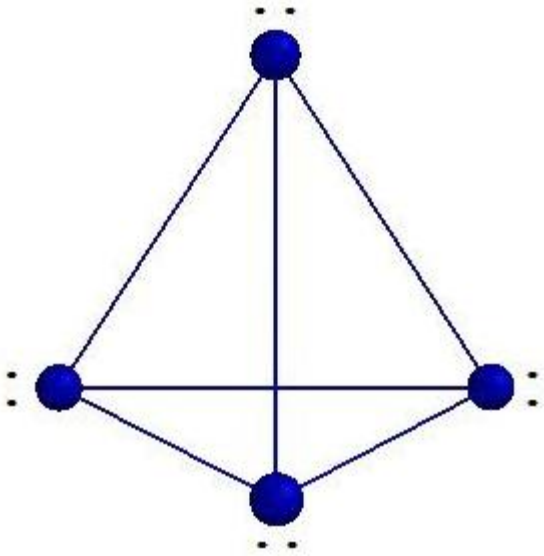
Td - Tetrahedral Symmetry for P_4

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.

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



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

$$Td := \begin{pmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{pmatrix} \qquad \Gamma_{uma} := \begin{pmatrix} 4 \\ 1 \\ 0 \\ 0 \\ 2 \end{pmatrix} \qquad \Gamma_{bonds} := \begin{pmatrix} 6 \\ 0 \\ 2 \\ 0 \\ 2 \end{pmatrix}$$

$$A_1 := \left(C_{Td}^{\,T}\right)^{\langle 1 \rangle} \qquad A_2 := \left(C_{Td}^{\,T}\right)^{\langle 2 \rangle} \qquad E := \left(C_{Td}^{\,T}\right)^{\langle 3 \rangle} \qquad T_1 := \left(C_{Td}^{\,T}\right)^{\langle 4 \rangle}$$

$$T_2 := \left(C_{Td}^{\,T}\right)^{\langle 5 \rangle} \qquad \Gamma_{tot} := \overrightarrow{\left(\Gamma_{uma} \cdot T_2\right)} \qquad h := \sum Td \qquad \Gamma_{tot}^{\,T} = (12 \quad 0 \quad 0 \quad 0 \quad 2) \qquad i := 1 .. 5$$

$$\Gamma_{vib} := \Gamma_{tot} - T_1 - T_2 \qquad Vib_i := \frac{\sum \overrightarrow{\left[Td \cdot \left(C_{Td}^{\,T}\right)^{\langle i \rangle} \cdot \Gamma_{vib}\right]}}{h}$$

$$Vib = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} \quad \begin{array}{l} A_1\text{: } x^2 + y^2 + z^2 \\ A_2 \\ \text{E: } 2z^2 - x^2 - y^2,\ x^2 - y^2 \\ T_1\text{: } (R_x, R_y, R_z) \\ T_2\text{: } (x, y, z),\ (xy, xz, yz) \end{array}$$

$\Gamma_{stretch} := \Gamma_{bonds}$

$$Stretch_i := \frac{\sum \overrightarrow{\left[Td \cdot \left(C_{Td}{}^{T} \right)^{\langle i \rangle} \cdot \Gamma_{stretch} \right]}}{h}$$

$$Stretch = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}$$

A_1: $x^2 + y^2 + z^2$

A_2

E: $2z^2 - x^2 - y^2$, $x^2 - y^2$

T_1: (R_x, R_y, R_z)

T_2: (x, y, z), (xy, xz, yz)

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

$$Bend_i := \frac{\sum \overrightarrow{\left[Td \cdot \left(C_{Td}{}^{T} \right)^{\langle i \rangle} \cdot \Gamma_{bend} \right]}}{h}$$

$$Bend = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

A_1: $x^2 + y^2 + z^2$

A_2

E: $2z^2 - x^2 - y^2$, $x^2 - y^2$

T_1: (R_x, R_y, R_z)

T_2: (x, y, z), (xy, xz, yz)

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.