6.3: Xenon Tetrafluoride

Xenon tetrafluoride is a chemical compound with chemical formula XeF_4. It was the first discovered binary compound of a noble gas. It is produced by the chemical reaction of xenon with fluorine, F_2, according to the chemical equation:

$$Xe + 2\,F_2 \rightarrow XeF_4$$

The infrared spectrum of XeF_4 has absorptions at 161, 291, and 586 cm^{-1} (two bends, one stretch), while the Raman spectrum has peaks at 218, 524, and 554 cm^{-1} (one bend, two stretches). Is its molecular structure tetrahedral or square planar?

Tetrahedral Symmetry - T_d

$$\begin{array}{c} E \quad C_3 \quad C_2 \quad S_4 \quad \sigma \\ \text{CIh} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & 1 & -1 \\ 3 & 0 & -1 & -1 & 1 \end{bmatrix} \end{array} \begin{array}{l} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2y^2, x^2-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x, y, z)(xy, xz, yz) \end{array} \quad \text{Td} = \begin{bmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{bmatrix} \quad \Gamma_{uma} = \begin{bmatrix} 5 \\ 2 \\ 1 \\ 1 \\ 3 \end{bmatrix}$$

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

$$T_2 = (C_{Td}^T)^{<5.} \quad \Gamma_{tot} = \overrightarrow{\Gamma_{uma} T_2} \quad h = \sum Td \quad \Gamma_{tot}^T = (15 \quad 0 \quad -1 \quad -1 \quad 3)$$

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

This analysis predicts two IR active modes ($2T_2$) and four Raman active modes (A_1, E, $2T_2$). It also suggests that the IR and Raman should have the two T_2 modes in common. Thus, tetrahedral geometry is not consistent with the spectroscopic data. Further detail can be obtained by noting that the stretching vibrations have the same symmetry properties as the chemical bonds. This allows the vibrational modes to be decomposed further into the symmetry of the stretches and bends.

Square Planar Geometry - D_{4H}

$$\begin{array}{c} E \quad C_4 \quad C_2 \quad C_2' \quad C_2'' \quad i \quad S_4 \quad \sigma_h \quad \sigma_v \quad \sigma_v \\ \text{CIh} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 \\ 2 & 0 & -2 & 0 & 0 & 2 & 0 & -2 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 2 & 0 & -2 & 0 & 0 & -2 & 0 & 2 & 0 & 0 \end{bmatrix} \end{array} \begin{array}{l} A1g: x^2+y^2+z^2 \\ \text{A2g: Rz} \\ \text{B1g: } x^2-y^2 \\ \text{B2g: xy} \\ \text{Eg: (Rx, Ry), xz, yz)} \\ \text{A1u} \\ \text{A2u: z} \\ \text{B1u} \\ \text{B2u} \\ \text{Eu: (x, y)} \end{array} \quad \text{D4h} = \begin{bmatrix} 1 \\ 2 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 2 \end{bmatrix} \quad \Gamma_{uma} = \begin{bmatrix} 5 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 3 \\ 1 \end{bmatrix} \quad \Gamma_{bonds} = \begin{bmatrix} 4 \\ 0 \\ 0 \\ 2 \\ 0 \\ 0 \\ 0 \\ 4 \\ 2 \\ 0 \end{bmatrix}$$

$$A_{1g} = (C_{D4h}^T)^{<1>} \quad A_{2g} = (C_{D4h}^T)^{<2>} \quad B_{1g} = (C_{D4h}^T)^{<3>} \quad B_{2g} = (C_{D4h}^T)^{<4>} \quad E_g = (C_{D4h}^T)^{<5>}$$

$$A_{1u} = (C_{D4h}^T)^{<6>} \quad A_{2u} = (C_{D4h}^T)^{<7>} \quad B_{1u} = (C_{D4h}^T)^{<8>} \quad B_{2u} = (C_{D4h}^T)^{<9>} \quad E_u = (C_{D4h}^T)^{<10>}$$

$$h = \sum D4h \quad \Gamma_{trans} = A_{2u} + E_u \quad \Gamma_{rot} = A_{2g} + E_g \quad \Gamma_{tot} = \overrightarrow{(\Gamma_{uma} \Gamma_{trans})}$$

$$\Gamma_{vib} = \Gamma_{tot} - \Gamma_{trans} - \Gamma_{rot} \quad \Gamma_{stretch} = \Gamma_{bonds} \quad \Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} \quad i = 1..10$$

$$\text{Vib}_i = \frac{\sum \overrightarrow{[D4h(C_{D4h}^T)^{<i>}\Gamma_{vib}]}}{h} \quad \text{Stretch}_i = \frac{\sum \overrightarrow{[D4h(C_{D4h}^T)^{<i>}\Gamma_{stretch}]}}{h} \quad \text{Bend}_i = \frac{\sum \overrightarrow{[D4h(C_{D4h}^T)^{<i>}\Gamma_{bend}]}}{h}$$

$$\text{Vib} = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 2 \end{bmatrix} \begin{matrix} A1g: x^2+y^2+z^2 \\ \text{A2g: Rz} \\ \text{B1g: } x^2-y^2 \\ \text{B2g: xy} \\ \text{Eg: (Rx, Ry), xz, yz)} \\ \text{A1u} \\ \text{A2u: z} \\ \text{B1u} \\ \text{B2u} \\ \text{Eu: (x, y)} \end{matrix} \quad \Gamma_{uma} = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \begin{matrix} A1g: x^2+y^2+z^2 \\ \text{A2g: Rz} \\ \text{B1g: } x^2-y^2 \\ \text{B2g: xy} \\ \text{Eg: (Rx, Ry), xz, yz)} \\ \text{A1u} \\ \text{A2u: z} \\ \text{B1u} \\ \text{B2u} \\ \text{Eu: (x, y)} \end{matrix} \quad \Gamma_{bonds} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 1 \end{bmatrix} \begin{matrix} A1g: x^2+y^2+z^2 \\ \text{A2g: Rz} \\ \text{B1g: } x^2-y^2 \\ \text{B2g: xy} \\ \text{Eg: (Rx, Ry), xz, yz)} \\ \text{A1u} \\ \text{A2u: z} \\ \text{B1u} \\ \text{B2u} \\ \text{Eu: (x, y)} \end{matrix}$$

This analysis predicts three IR active modes (A_{2u}, $2E_u$) and three Raman active modes (A_{1g}, B_{1g}, B_{2g}). It also indicates that there are no coincidences between the IR and Raman spectra. Thus, square planar geometry is consistent with the spectroscopic data. Examining the symmetry of the stretches and bends adds further support to this conclusion.

This analysis also predicts two Raman (A_{1g}, B_{1g}) and one IR (E_u) active stretches, and two IR (A_{2u}, E_u) and one Raman (B_{2g}) active bends. This is also consistent with the experiemental data.

References

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- *J. Phys. Chem*. **1971**, *54*, 5247.