Symmetry, Spectroscopy, and the Molecular Structure of 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? References: *J. Am. Chem. Soc*. **1963**, *85*, 1927; *J. Phys. Chem.* **1971**, *54*, 5247.

Tetrahedral Symmetry - T$_d$

$$
\begin{array}{ccccc}
E & C_3 & C_2 & S_4 & \sigma
\end{array}
$$

$$
C_{Td} := \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & 1 & -1 \\ 3 & 0 & -1 & -1 & 1 \end{bmatrix}
$$

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)

$$
Td := \begin{bmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{bmatrix}
\qquad
\Gamma_{uma} := \begin{bmatrix} 5 \\ 2 \\ 1 \\ 1 \\ 3 \end{bmatrix}
$$

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

$$T_2 := \left(C_{Td}^{\ T}\right)^{<5>} \qquad \Gamma_{tot} := \overrightarrow{\left(\Gamma_{uma} \cdot T_2\right)} \qquad h := \sum Td \qquad \Gamma_{tot}^{\ T} = (\ 15 \quad 0 \quad -1 \quad -1 \quad 3\ )$$

$i := 1..5$

$$\Gamma_{vib} := \Gamma_{tot} - T_1 - T_2 \qquad Vib_i := \frac{\overrightarrow{\sum\left[Td \cdot \left(C_{Td}^{\ T}\right)^{<i>} \cdot \Gamma_{vib}\right]}}{h} \qquad Vib = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 2 \end{bmatrix}$$

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)

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 Symmetry - D$_{4h}$

$$\text{E} \quad \text{C}_4 \quad \text{C}_2 \quad \text{C}_2' \quad \text{C}_2'' \quad \text{i} \quad \text{S}_4 \quad \sigma_h \quad \sigma_v \quad \sigma_d$$

$$
C_{D4h} := \begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 \\
1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\
1 & -1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 \\
2 & 0 & -2 & 0 & 0 & 2 & 0 & -2 & 0 & 0 \\
1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\
1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 \\
1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 \\
1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
2 & 0 & -2 & 0 & 0 & -2 & 0 & 2 & 0 & 0
\end{bmatrix}
$$

A1g: $x^2 + y^2$, z^2
A2g: Rz
B1g: $x^2 - y^2$
B2g: xy
Eg: (Rx, Ry), (xz, yz)
A1u:
A2u: z
B1u
B2u
Eu: (x, y)

$$
D4h := \begin{bmatrix} 1 \\ 2 \\ 1 \\ 2 \\ 2 \\ 1 \\ 2 \\ 1 \\ 2 \\ 2 \end{bmatrix}
\qquad
\Gamma_{uma} := \begin{bmatrix} 5 \\ 1 \\ 1 \\ 3 \\ 1 \\ 1 \\ 1 \\ 5 \\ 3 \\ 1 \end{bmatrix}
\qquad
\Gamma_{bonds} := \begin{bmatrix} 4 \\ 0 \\ 0 \\ 2 \\ 0 \\ 0 \\ 0 \\ 4 \\ 2 \\ 0 \end{bmatrix}
$$

$$A_{1g} := \left(C_{D4h}^{\ T}\right)^{<1>} \qquad A_{2g} := \left(C_{D4h}^{\ T}\right)^{<2>} \qquad B_{1g} := \left(C_{D4h}^{\ T}\right)^{<3>} \qquad B_{2g} := \left(C_{D4h}^{\ T}\right)^{<4>} \qquad E_{g} := \left(C_{D4h}^{\ T}\right)^{<5>}$$

$$A_{1u} := \left(C_{D4h}^{\ T}\right)^{<6>} \qquad A_{2u} := \left(C_{D4h}^{\ T}\right)^{<7>} \qquad B_{1u} := \left(C_{D4h}^{\ T}\right)^{<8>} \qquad B_{2u} := \left(C_{D4h}^{\ T}\right)^{<9>} \qquad E_{u} := \left(C_{D4h}^{\ T}\right)^{<10>}$$

$$h := \sum D4h \qquad \Gamma_{trans} := A_{2u} + E_u \qquad \Gamma_{rot} := A_{2g} + E_g \qquad \Gamma_{tot} := \overrightarrow{\left(\Gamma_{uma} \cdot \Gamma_{trans}\right)}$$

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

$$Vib_i := \frac{\sum \overrightarrow{\left[D4h \cdot \left(C_{D4h}^{\ T}\right)^{<i>} \cdot \Gamma_{vib}\right]}}{h}$$

$$Stretch_i := \frac{\sum \overrightarrow{\left[D4h \cdot \left(C_{D4h}^{\ T}\right)^{<i>} \cdot \Gamma_{stretch}\right]}}{h}$$

$$Bend_i := \frac{\sum \overrightarrow{\left[D4h \cdot \left(C_{D4h}^{\ T}\right)^{<i>} \cdot \Gamma_{bend}\right]}}{h}$$

$$
Vib = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 2 \end{bmatrix}
$$

A1g: $x^2 + y^2$, z^2
A2g: Rz
B1g: $x^2 - y^2$
B2g: xy
Eg: (Rx, Ry), (xz, yz)
A1u:
A2u: z
B1u
B2u
Eu: (x, y)

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

A1g: $x^2 + y^2$, z^2
A2g: Rz
B1g: $x^2 - y^2$
B2g: xy
Eg: (Rx, Ry), (xz, yz)
A1u
A2u: z
B1u
B2u
Eu: (x, y)

$$
Bend = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 1 \end{bmatrix}
$$

A1g: $x^2 + y^2$, z^2
A2g: Rz
B1g: $x^2 - y^2$
B2g: xy
Eg: (Rx, Ry), (xz, yz)
A1u
A2u: z
B1u
B2u
Eu: (x, y)

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.