6.8: CH_4

Tetrahedral Symmetry for Methane

The infrared spectrum of methane shows two absorptions: a bend at 1306 cm^{-1} and a stretch at 3019 cm^{-1}. Demonstrate that a symmetry analysis assuming tetrahedral symmetry for methane is consistent with this spectroscopic data. Also predict how many Raman active modes methane should have.

$$C_{Td} = \begin{matrix} E & C_3 & C_2 & S_4 & \sigma \end{matrix} \\ \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & 1 & -1 \\ 3 & 0 & -1 & -1 & 1 \end{bmatrix} \begin{matrix} A_1: x^2+y^2+z^2 \\ A_2 \\ E: 2z^2-x^2-y^2,\ x^2-y^2 \\ T_1: (R_x,\ R_y,\ R_z) \\ T_2: (x,\ y,\ z),\ (xy,\ xz,\ yz) \end{matrix} \quad Td = \begin{bmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{bmatrix} \quad \Gamma_{uma} = \begin{bmatrix} 5 \\ 2 \\ 1 \\ 1 \\ 3 \end{bmatrix} \quad \Gamma_{bonds} = \begin{bmatrix} 4 \\ 1 \\ 0 \\ 0 \\ 2 \end{bmatrix}$$

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

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

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

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

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

Thus the vibrational modes have A_1, E, and T_2 symmetry. Only the two T_2 modes are infrared active which is consistent with the experimental data quoted above. One of the T_2 modes is a stretch (3019 cm^{-1}) and the other is a bend (1306 cm^{-1}).

This symmetry analysis predicts that all of vibrational modes are Raman active - one singly degenerate mode (A_1), one doubly degenerate mode (E), and two triply degenerate modes (T_2). Indeed four Raman active modes are found at 3019, 2917, 1534, and 1306 cm^{-1}. Note, as expected from the symmetry analysis, there are two coincidences between the IR and Raman spectra.