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.

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

$$Td := \begin{bmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{bmatrix} \qquad \Gamma_{uma} := \begin{bmatrix} 5 \\ 2 \\ 1 \\ 1 \\ 3 \end{bmatrix} \qquad \Gamma_{bonds} := \begin{bmatrix} 4 \\ 1 \\ 0 \\ 0 \\ 2 \end{bmatrix}$$

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

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

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

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

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

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 T2 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.