

# Tetrahedral Symmetry for Methane

The infrared spectrum of methane shows two absorptions: a bend at 1306 cm<sup>-1</sup> and a stretch at 3019 cm<sup>-1</sup>. 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.

E	C <sub>3</sub>	C <sub>2</sub>	S <sub>4</sub>	σ					
$C_{Td} := \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & 1 & -1 \\ 3 & 0 & -1 & -1 & 1 \end{bmatrix}$	$A_1: x^2 + y^2 + z^2$					$Td := \begin{bmatrix} 1 \\ 8 \\ 3 \\ 6 \\ 6 \end{bmatrix}$	$\Gamma_{uma} := \begin{bmatrix} 5 \\ 2 \\ 1 \\ 1 \\ 3 \end{bmatrix}$	$\Gamma_{bonds} := \begin{bmatrix} 4 \\ 1 \\ 0 \\ 0 \\ 2 \end{bmatrix}$	
	$A_2$								
	$E: 2z^2 - x^2 - y^2, x^2 - y^2$								
	$T_1: (R_x, R_y, R_z)$								
	$T_2: (x, y, z), (xy, xz, yz)$								

$A_1 := (C_{Td}^T)^{\langle 1 \rangle}$	$A_2 := (C_{Td}^T)^{\langle 2 \rangle}$	$E := (C_{Td}^T)^{\langle 3 \rangle}$	$T_1 := (C_{Td}^T)^{\langle 4 \rangle}$	
$T_2 := (C_{Td}^T)^{\langle 5 \rangle}$	$\Gamma_{tot} := \overrightarrow{(\Gamma_{uma} \cdot T_2)}$	$h := \sum Td$	$\Gamma_{tot}^T = (15 \ 0 \ -1 \ -1 \ 3)$	$i := 1..5$

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

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

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

Thus the vibrational modes have A<sub>1</sub>, E, and T<sub>2</sub> symmetry. Only the two T<sub>2</sub> modes are infrared active which is consistent with the experimental data quoted above. One of the T<sub>2</sub> modes is a stretch (3019 cm<sup>-1</sup>) and the other is a bend (1306 cm<sup>-1</sup>).

This symmetry analysis predicts that all of vibrational modes are Raman active - one singly degenerate mode (A<sub>1</sub>), one doubly degenerate mode (E), and two triply degenerate modes (T<sub>2</sub>). Indeed four Raman active modes are found at 3019, 2917, 1534, and 1306 cm<sup>-1</sup>. Note, as expected from the symmetry analysis, there are two coincidences between the IR and Raman spectra.