

Symmetry Analysis for Cubane

Cubane, C_8H_8 , has 42 vibrational degrees of freedom, but only three IR active modes. Cubane belongs to the octahedral point group. Show that group theory predicts three IR active modes. Determine how many vibrational modes will be Raman active. Will there be any coincidences between the IR and Raman active modes? The synthesis and characterization of cubane was reported in 1964 by Philip Eaton and Thomas Cole in JACS **1964**, *86*, 3157-3158. They reported three IR bands at 3000, 1231, and 851 cm^{-1} .

$i := 1..10$

$C_{Oh} :=$	E C ₃ C ₂ C ₄ C ₂ " i S ₄ S ₆ σ _h σ _d							
$\left[\begin{array}{cccccccccc} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 \\ 2 & -1 & 0 & 0 & 2 & 2 & 0 & -1 & 2 & 0 \\ 3 & 0 & -1 & 1 & -1 & 3 & 1 & 0 & -1 & -1 \\ 3 & 0 & 1 & -1 & -1 & 3 & -1 & 0 & -1 & 1 \\ 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 \\ 2 & -1 & 0 & 0 & 2 & -2 & 0 & 1 & -2 & 0 \\ 3 & 0 & -1 & 1 & -1 & -3 & -1 & 0 & 1 & 1 \\ 3 & 0 & 1 & -1 & -1 & -3 & 1 & 0 & 1 & -1 \end{array} \right]$		A1g: $x^2 + y^2 + z^2$	$Oh :=$	$\left[\begin{array}{c} 1 \\ 8 \\ 6 \\ 6 \\ 6 \\ 3 \\ 1 \\ 6 \\ 8 \\ 3 \\ 6 \end{array} \right]$	$\Gamma_{uma} :=$	$\left[\begin{array}{c} 16 \\ 4 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 8 \end{array} \right]$	$\Gamma_{bonds} :=$	$\left[\begin{array}{c} 20 \\ 2 \\ 2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4 \\ 6 \end{array} \right]$
		A2g						
		Eg: $2z^2 - x^2 - y^2, x^2 - y^2$						
		T1g: Rx, Ry, Rz						
		T2g: xy, xz, yz						
		A1u:						
		A2u						
		Eu						
		T1u: x, y, z						
		T2u						

$$A_{1g} := (C_{Oh}^T)^{\langle 1 \rangle} \quad A_{2g} := (C_{Oh}^T)^{\langle 2 \rangle} \quad E_g := (C_{Oh}^T)^{\langle 3 \rangle} \quad T_{1g} := (C_{Oh}^T)^{\langle 4 \rangle} \quad T_{2g} := (C_{Oh}^T)^{\langle 5 \rangle}$$

$$A_{1u} := (C_{Oh}^T)^{\langle 6 \rangle} \quad A_{2u} := (C_{Oh}^T)^{\langle 7 \rangle} \quad E_u := (C_{Oh}^T)^{\langle 8 \rangle} \quad T_{1u} := (C_{Oh}^T)^{\langle 9 \rangle} \quad T_{2u} := (C_{Oh}^T)^{\langle 10 \rangle}$$

$$h := \sum Oh \quad \Gamma_{tot} := \overrightarrow{(\Gamma_{uma} \cdot T_{1u})} \quad \Gamma_{vib} := \Gamma_{tot} - T_{1u} - T_{1g} \quad \Gamma_{stretch} := \Gamma_{bonds} \quad \Gamma_{bend} := \Gamma_{vib} - \Gamma_{stretch}$$

$$Vib_i := \frac{\sum \left[Oh \cdot (C_{Oh}^T)^{\langle i \rangle} \cdot \Gamma_{vib} \right]}{h} \quad Stretch_i := \frac{\sum \left[Oh \cdot (C_{Oh}^T)^{\langle i \rangle} \cdot \Gamma_{stretch} \right]}{h} \quad Bend_i := \frac{\sum \left[Oh \cdot (C_{Oh}^T)^{\langle i \rangle} \cdot \Gamma_{bend} \right]}{h}$$

$Vib =$	$\left[\begin{array}{c} 2 \\ 0 \\ 2 \\ 1 \\ 4 \\ 0 \\ 2 \\ 2 \\ 3 \\ 2 \end{array} \right]$	$\left[\begin{array}{l} A1g: x^2 + y^2 + z^2 \\ A2g \\ Eg: 2z^2 - x^2 - y^2, x^2 - y^2 \\ T1g: Rx, Ry, Rz \\ T2g: xy, xz, yz \\ A1u: \\ A2u \\ Eu \\ T1u: x, y, z \\ T2u \end{array} \right]$	$Stretch =$	$\left[\begin{array}{c} 2 \\ 0 \\ 1 \\ 0 \\ 2 \\ 0 \\ 1 \\ 0 \\ 2 \\ 1 \end{array} \right]$	$\left[\begin{array}{l} A1g: x^2 + y^2 + z^2 \\ A2g \\ Eg: 2z^2 - x^2 - y^2, x^2 - y^2 \\ T1g: Rx, Ry, Rz \\ T2g: xy, xz, yz \\ A1u: \\ A2u \\ Eu \\ T1u: x, y, z \\ T2u \end{array} \right]$	$Bend =$	$\left[\begin{array}{c} 0 \\ 0 \\ 1 \\ 1 \\ 2 \\ 0 \\ 1 \\ 2 \\ 1 \\ 1 \end{array} \right]$	$\left[\begin{array}{l} A1g: x^2 + y^2 + z^2 \\ A2g \\ Eg: 2z^2 - x^2 - y^2, x^2 - y^2 \\ T1g: Rx, Ry, Rz \\ T2g: xy, xz, yz \\ A1u: \\ A2u \\ Eu \\ T1u: x, y, z \\ T2u \end{array} \right]$
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Only the three T_{1u} vibrational modes are IR active, which is consistent with the spectroscopic data. The character table indicates that the A_{1g} , E_g , and T_{2g} modes are Raman active. Thus there should be 8 Raman active modes. These have been observed at 2996, 2978, 1185, 1081, 1002, 912, 826, and 665 cm^{-1} (*J. Phys. Chem.* **1981**, 85, 2186). There should be no coincidences between the IR and Raman modes because cubane has a center of inversion.

The vibrational modes can be sorted into stretches and bends by determining how the chemical bonds transform under the symmetry operations of the octahedral group. The symmetry of the stretching modes is the same as the symmetry of the bonds.

This analysis tells us that there are two IR active stretches ($2T_{1u}$) and five Raman active stretches ($2A_{1g}$, E_g , and $2T_{2g}$). This is consistent with the experimental spectra in that stretches generally occur at a higher frequency than bends.