

Group Theory for Dodecahedrane

When Paquette's group synthesized dodecahedrane, $C_{20}H_{20}$, they measured its infrared and Raman spectra (JACS 1983, 105, 5446-5450). They found three IR active bands at 2945, 1298, and 728 cm^{-1} and eight Raman frequencies at 2924, 2938, 1324, 1164, 1092, 840, 676, and 480 cm^{-1} . Use group theory to show that these data are consistent with the fact that dodecahedrane has icosahedral symmetry.

$CI_h :=$	E	C_5	C_5^2	C_3	C_2	i	S_{10}	S_{10}^3	S_6	σ	
1	1	1	1	1	1	1	1	1	1	1	$Ag: x^2 + y^2 + z^2$
3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	-1	$T1g: Rx, Ry, Rz$
3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	-1	$T2g$
4	-1	-1	1	0	4	-1	-1	1	0	0	Gg
5	0	0	-1	1	5	0	0	-1	1	1	$Hg: 2z^2 - x^2 - y^2, x^2 - y^2, xy, yz, xz$
1	1	1	1	1	-1	-1	-1	-1	-1	-1	Au
3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	-3	$-\frac{1-\sqrt{5}}{2}$	$-\frac{1+\sqrt{5}}{2}$	0	1	1	$T1u: x, y, z$
3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	-3	$-\frac{1+\sqrt{5}}{2}$	$-\frac{1-\sqrt{5}}{2}$	0	1	1	$T2u$
4	-1	-1	1	0	-4	1	1	-1	0	0	Gu
5	0	0	-1	1	-5	0	0	1	-1	-1	Hu

$$I_h := (1 \ 12 \ 12 \ 20 \ 15 \ 1 \ 12 \ 12 \ 20 \ 15) \quad I_h := I_h^T \quad \Gamma_{uma} := (40 \ 0 \ 0 \ 4 \ 0 \ 0 \ 0 \ 0 \ 0 \ 8) \quad \Gamma_{uma} := \Gamma_{uma}^T$$

$$\Gamma_{bonds} := (50 \ 0 \ 0 \ 2 \ 2 \ 0 \ 0 \ 0 \ 0 \ 8) \quad \Gamma_{bonds} := \Gamma_{bonds}^T \quad \Gamma_{stretch} := \Gamma_{bonds}$$

$$Ag := (CI_h^T)^{\langle 1 \rangle} \quad T1g := (CI_h^T)^{\langle 2 \rangle} \quad T2g := (CI_h^T)^{\langle 3 \rangle} \quad Gg := (CI_h^T)^{\langle 4 \rangle} \quad Hg := (CI_h^T)^{\langle 5 \rangle}$$

$$Au := (CI_h^T)^{\langle 6 \rangle} \quad T1u := (CI_h^T)^{\langle 7 \rangle} \quad T2u := (CI_h^T)^{\langle 8 \rangle} \quad Gu := (CI_h^T)^{\langle 9 \rangle} \quad Hu := (CI_h^T)^{\langle 10 \rangle}$$

$$h := \sum I_h \quad h = 120 \quad \Gamma_{tot} := (\Gamma_{uma} \cdot T1u) \quad \Gamma_{vib} := \Gamma_{tot} - T1g - T1u \quad \Gamma_{bend} := \Gamma_{vib} - \Gamma_{stretch} \quad i := 1..10$$

$$\text{Vib}_i := \sum_h \left[\text{Ih} \cdot (\text{CIh}^T)^{\langle i \rangle} \cdot \Gamma \text{vib} \right]$$

$$\text{Stretch}_i := \sum_h \left[\text{Ih} \cdot (\text{CIh}^T)^{\langle i \rangle} \cdot \Gamma \text{stretch} \right]$$

$$\text{Bend}_i := \sum_h \left[\text{Ih} \cdot (\text{CIh}^T)^{\langle i \rangle} \cdot \Gamma \text{bend} \right]$$

$$\text{Vib} = \begin{bmatrix} 2 \\ 1 \\ 2 \\ 4 \\ 6 \\ 0 \\ 3 \\ 4 \\ 4 \\ 4 \end{bmatrix} \begin{array}{l} \text{Ag: } x^2 + y^2 + z^2 \\ \text{T1g: Rx, Ry, Rz} \\ \text{T2g} \\ \text{Gg} \\ \text{Hg: } 2z^2 - x^2 - y^2, x^2 - y^2, xy, yz, xz \\ \text{Au} \\ \text{T1u: x, y, z} \\ \text{T2u} \\ \text{Gu} \\ \text{Hu} \end{array}$$

$$\text{Stretch} = \begin{bmatrix} 2 \\ 0 \\ 0 \\ 2 \\ 3 \\ 0 \\ 2 \\ 2 \\ 2 \\ 1 \end{bmatrix} \begin{array}{l} \text{Ag: } x^2 + y^2 + z^2 \\ \text{T1g: Rx, Ry, Rz} \\ \text{T2g} \\ \text{Gg} \\ \text{Hg: } 2z^2 - x^2 - y^2, x^2 - y^2, xy, yz, xz \\ \text{Au} \\ \text{T1u: x, y, z} \\ \text{T2u} \\ \text{Gu} \\ \text{Hu} \end{array}$$

$$\text{Bend} = \begin{bmatrix} 0 \\ 1 \\ 2 \\ 2 \\ 3 \\ 0 \\ 1 \\ 2 \\ 2 \\ 3 \end{bmatrix} \begin{array}{l} \text{Ag: } x^2 + y^2 + z^2 \\ \text{T1g: Rx, Ry, Rz} \\ \text{T2g} \\ \text{Gg} \\ \text{Hg: } 2z^2 - x^2 - y^2, x^2 - y^2, xy, yz, xz \\ \text{Au} \\ \text{T1u: x, y, z} \\ \text{T2u} \\ \text{Gu} \\ \text{Hu} \end{array}$$

According to the usual selection rules only the three T_{1u} vibrations are IR active. The A_g and H_g vibrations are Raman active giving a total of eight frequencies in the Raman spectra. This analysis is in agreement with the experimental spectroscopic results quoted by Paquette. Note also that, as is usual for molecules with a center of inversion, there are no coincidences between the IR and Raman active modes.