

Step-by-Step Analysis of Normal Modes of Planar PtCl_4^{2-} (D_{4h})

Step 1: Count non-shifted atoms.



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
N_i	5	1	1	3	1	1	1	5	3	1

Step 2: Multiply by the contribution per non-shifted atom to generate Γ_{3n} .

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
N_i	5	1	1	3	1	1	1	5	3	1
χ_i	3	1	-1	-1	-1	-3	-1	1	1	1
Γ_{3n}	15	1	-1	-3	-1	-3	-1	5	3	1

Step 3: Reduce Γ_{3n}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
N_i	5	1	1	3	1	1	1	5	3	1		
χ_i	3	1	-1	-1	-1	-3	-1	1	1	1		
Γ_{3n}	15	1	-1	-3	-1	-3	-1	5	3	1	Σ	$\Sigma/16$
A_{1g}	15	2	-1	-6	-2	-3	-2	5	6	2	16	1
A_{2g}	15	2	-1	6	2	-3	-2	5	-6	-2	16	1
B_{1g}	15	-2	-1	-6	2	-3	2	5	6	-2	16	1
B_{2g}	15	-2	-1	6	-2	-3	2	5	-6	2	16	1
E_g	30	0	2	0	0	-6	0	-10	0	0	16	1
A_{1u}	15	2	-1	-6	-2	3	2	-5	-6	-2	0	0
A_{2u}	15	2	-1	6	2	3	2	-5	6	2	32	2
B_{1u}	15	-2	-1	-6	2	3	-2	-5	-6	2	0	0
B_{2u}	15	-2	-1	6	-2	3	-2	-5	6	-2	16	1
E_u	30	0	2	0	0	6	0	10	0	0	48	3

$$\Gamma_{3n} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

Step 4: Check that the sum of the dimensions of the found irreducible representations equals the dimension of the representation, $3n = 15$.

$$d = 1 + 1 + 1 + 1 + 2 + (2)(1) + 1 + (3)(2) = 15$$

Step 5: Identify species of translations and rotations from vector transformation listings in the penultimate column of the character table.

$$\Gamma_{\text{trans}} = A_{2u} + E_u \quad \Gamma_{\text{rot}} = A_{2g} + E_g$$

Step 6: Subtract translation and rotation species from Γ_{3n} to obtain Γ_{3n-6} , the species of the genuine normal modes of vibration.

$$\Gamma_{3n-6} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u = 7 \text{ frequencies}$$

Step 7: Determine infrared activity from the unit vector transformation listings. Determine Raman activity from the direct product listings. Any species of Γ_{3n-6} that do not match either of these are silent modes.

Infrared	$3 (A_{2u} + 2E_u)$
Raman	$3 (A_{1g} + B_{1g} + B_{2g})$
Polarized	$1 (A_{1g})$
Coincidences	0
Silent modes	$1 (B_{2u})$

Notes and questions about the results

1. Notice that no infrared active species are Raman active and vice versa. Why?
2. What does it mean in terms of the motions of the normal modes that all the infrared-active modes belong to *ungerade* species and all the Raman-active modes belong to *gerade* species.
3. Can you predict the motions of the normal modes on the basis of their symmetry designations (Mulliken symbols)?
4. How do the pairs of modes that comprise each of the two E_u frequencies differ from each other?
5. How does the pattern of infrared and Raman activity of a planar XY_4 molecule compare to a tetrahedral XY_4 molecule?

Normal Modes of Planar AX₄-Type Molecules

