

Solutions: Selection Rules in C_{6v} (Graphene Example)

1 Point group C_{6v} and its character table

The point group C_{6v} describes systems with a sixfold rotation axis (C_6) about z and six vertical mirror planes. It is the natural symmetry group for ideal hexagonal lattices such as graphene (when inversion is ignored).

The group has twelve elements arranged in six conjugacy classes:

$$C_{6v} = \{E, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d\},$$

where

- E is the identity,
- C_6 is rotation by $\pm 60^\circ$ about the z axis,
- C_3 is rotation by $\pm 120^\circ$,
- C_2 is rotation by 180° ,
- σ_v are vertical mirrors that contain the x (or bond) axes,
- σ_d are vertical mirrors that bisect the angles between the σ_v planes.

There are six irreducible representations: four one dimensional (A_1, A_2, B_1, B_2) and two two dimensional (E_1, E_2). The character table can be written as

	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0

For later use in selection rules it is convenient to list common basis functions that transform according to each irreducible representation. A typical choice is

Irrep	Example basis functions
A_1	$z, x^2 + y^2, z^2$
A_2	R_z (rotation about z)
B_1	— (no simple low order polynomial in Cartesian form)
B_2	—
E_1	$(x, y), (R_x, R_y)$
E_2	$(x^2 - y^2, 2xy)$

Here (x, y, z) are components of a polar vector such as the position or dipole moment, and (R_x, R_y, R_z) are components of an axial vector such as the angular momentum. In graphene, the in plane components of the electric dipole operator transform as E_1 , while the out of plane component z transforms as A_1 . This is the starting point for analyzing optical selection rules and Raman activity of modes.

1. Dipole selection rules in C_{6v} : in-plane vs out-of-plane light

(a) Symmetry condition for a non-zero dipole matrix element

For a matrix element

$$\langle f | \hat{\mu} | i \rangle,$$

the relevant representation is

$$\Gamma_{\text{prod}} = \Gamma_i \otimes \Gamma_\mu \otimes \Gamma_f.$$

Necessary condition for the transition to be symmetry-allowed:

Γ_{prod} must contain the totally symmetric irrep (A_1 in C_{6v}).

If A_1 does not appear in the decomposition of this product, the dipole matrix element must vanish by symmetry.

(b) Case $\Gamma_i = A_1, \Gamma_f = E_1$

(i) Light polarized along z (operator irrep A_1)

Here

$$\Gamma_i = A_1, \quad \Gamma_f = E_1, \quad \Gamma_\mu = A_1.$$

Then

$$\Gamma_{\text{prod}} = \Gamma_i \otimes \Gamma_\mu \otimes \Gamma_f = A_1 \otimes A_1 \otimes E_1.$$

Since A_1 is the identity for direct products,

$$A_1 \otimes A_1 = A_1, \quad A_1 \otimes E_1 = E_1,$$

so

$$\Gamma_{\text{prod}} = E_1.$$

This product does *not* contain A_1 . Therefore the transition

$$A_1 \xrightarrow[\mu_z]{A_1} E_1$$

is **forbidden** by symmetry.

(ii) **In-plane polarization (operator irrep E_1)**

Now

$$\Gamma_i = A_1, \quad \Gamma_f = E_1, \quad \Gamma_\mu = E_1.$$

Then

$$\Gamma_{\text{prod}} = A_1 \otimes E_1 \otimes E_1.$$

Again A_1 acts as identity, so

$$A_1 \otimes E_1 = E_1, \quad \Rightarrow \quad \Gamma_{\text{prod}} = E_1 \otimes E_1.$$

In C_{6v} (and similarly in many hexagonal groups), one has the direct product rule

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2.$$

This *does* contain the totally symmetric irrep A_1 .

Therefore the transition

$$A_1 \xrightarrow[\mu_{x,y}]{E_1} E_1$$

is **allowed** by symmetry (for suitable in-plane polarization).

(iii) **Justification via direct products**

Summary of the key products used:

$$A_1 \otimes X = X \quad \text{for any irrep } X,$$

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2.$$

Hence:

$$A_1 \otimes A_1 \otimes E_1 = E_1 \quad (\text{no } A_1),$$

$$A_1 \otimes E_1 \otimes E_1 = E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2 \quad (\text{contains } A_1).$$

Only the second case is symmetry-allowed.

(c) **Connection to π / σ bands and polarization in graphene**

In a 2D hexagonal crystal like graphene:

- The out-of-plane p_z orbitals form the π and π^* bands. Their symmetry at Γ is associated with an irrep that transforms like an out-of-plane function (often A_1 -type or related, depending on the full space group).
- In-plane sp^2 -like orbitals (p_x, p_y mixed with s) form the σ bands and transform mainly as E_1 -type (in-plane vector) representations.
- Our result shows that polarization selection matters:
 - z -polarized light (A_1 operator) couples initial and final states only when $A_1 \otimes A_1 \otimes \Gamma_f$ contains A_1 .
 - In-plane polarized light (E_1 operator) can couple $A_1 \leftrightarrow E_1$ and mixes strongly with in-plane (E_1 -type) orbitals.

Thus, symmetry analysis explains why in a strictly 2D system the response to in-plane vs out-of-plane polarization is different, and why certain transitions between π and σ bands are allowed or suppressed depending on the polarization direction.

2. Raman selection rules in C_{6v} and the E_2 “G-mode”

(a) Classify quadratic functions and identify Raman-active irreps

From a standard C_{6v} character table, the typical assignments are:

- A_1 : $z, z^2, x^2 + y^2$,
- A_2 : R_z (no simple quadratic coordinates),
- E_1 : $(x, y), (xz, yz)$,
- E_2 : $(x^2 - y^2, 2xy)$.

Therefore we can classify:

$$\begin{aligned} z^2, x^2 + y^2 &\sim A_1, \\ x^2 - y^2, 2xy &\sim E_2, \\ xz, yz &\sim E_1. \end{aligned}$$

(Pure x^2 and y^2 can be written as linear combinations of $x^2 + y^2$ and $x^2 - y^2$, so they are mixtures of A_1 and E_2 .)

The **Raman tensor** transforms like the set of *all* quadratic functions, so the Raman-active irreps in C_{6v} are:

$$A_1, E_1, E_2.$$

Any vibrational mode transforming as one of these irreps can be Raman active in suitable polarization geometries.

(b) Show that an E_2 mode (graphene G-mode) is Raman active

The in-plane G-mode in graphene transforms as an E_2 -type irrep of the hexagonal point group. We have just shown that the Raman tensor in C_{6v} contains components transforming as E_2 :

$$(x^2 - y^2, 2xy) \sim E_2.$$

Since the Raman operator (effective polarizability tensor) has an E_2 component, and the vibrational mode also has symmetry E_2 , the corresponding matrix element

$$\langle 1_{E_2} | \hat{\alpha}_{ij} | 0 \rangle$$

does not vanish by symmetry. Therefore an E_2 vibrational mode is **Raman active**.

(c) Why the E_2 G-mode gives a strong Raman line

Qualitative points:

- An E_2 vibrational mode is *doubly degenerate*, meaning there are two orthogonal displacement patterns with the same frequency (often drawn as two perpendicular in-plane distortions).

- The Raman tensor also has two independent E_2 components (like $x^2 - y^2$ and $2xy$). For different choices of incident and scattered polarization, the light probes different linear combinations of these tensor components.
- In many polarization configurations, at least one linear combination of the E_2 tensor components couples strongly to the E_2 vibrational displacement. Thus, instead of suppressing intensity, the degeneracy provides more ways for the phonon to couple to light.
- As a result, the E_2 G-mode in graphene typically produces a **strong and robust Raman line** across many experimental geometries.

1. Character-table derivation

We now derive the product rule

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2$$

purely from the character table of C_{6v} .

The point group C_{6v} has $|G| = 12$ elements, arranged into six conjugacy classes:

Class	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
N_R	1	2	2	1	3	3

where N_R is the number of elements in each class.

The characters of the 2D irrep E_1 (the in-plane vector representation) are

$$\chi_{E_1}(R) = (2, 1, -1, -2, 0, 0),$$

in the order $(E, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d)$.

For a tensor product of representations, the character is the product of characters:

$$\chi_{E_1 \otimes E_1}(R) = \chi_{E_1}(R) \chi_{E_1}(R) = \chi_{E_1}(R)^2.$$

Thus we obtain

$$\chi_{E_1 \otimes E_1}(R) = (4, 1, 1, 4, 0, 0).$$

To decompose $E_1 \otimes E_1$ into irreducible representations, we use the standard inner-product formula for multiplicities:

$$n_\alpha = \frac{1}{|G|} \sum_R N_R \chi_\alpha^*(R) \chi_{E_1 \otimes E_1}(R),$$

where α labels an irrep and $|G| = 12$ for C_{6v} .

We only need the rows for A_1 , A_2 , and E_2 :

$$\begin{aligned} \chi_{A_1}(R) &= (1, 1, 1, 1, 1, 1), \\ \chi_{A_2}(R) &= (1, 1, 1, 1, -1, -1), \\ \chi_{E_2}(R) &= (2, -1, -1, 2, 0, 0). \end{aligned}$$

Multiplicity of A_1 .

$$\begin{aligned} n_{A_1} &= \frac{1}{12} [1 \cdot (1 \cdot 4) + 2 \cdot (1 \cdot 1) + 2 \cdot (1 \cdot 1) + 1 \cdot (1 \cdot 4) + 3 \cdot (1 \cdot 0) + 3 \cdot (1 \cdot 0)] \\ &= \frac{1}{12} (4 + 2 + 2 + 4) = 1. \end{aligned}$$

Multiplicity of A_2 .

$$\begin{aligned} n_{A_2} &= \frac{1}{12} [1 \cdot (1 \cdot 4) + 2 \cdot (1 \cdot 1) + 2 \cdot (1 \cdot 1) + 1 \cdot (1 \cdot 4) + 3 \cdot ((-1) \cdot 0) + 3 \cdot ((-1) \cdot 0)] \\ &= \frac{1}{12} (4 + 2 + 2 + 4) = 1. \end{aligned}$$

Multiplicity of E_2 .

$$\begin{aligned} n_{E_2} &= \frac{1}{12} [1 \cdot (2 \cdot 4) + 2 \cdot ((-1) \cdot 1) + 2 \cdot ((-1) \cdot 1) + 1 \cdot (2 \cdot 4) + 3 \cdot (0 \cdot 0) + 3 \cdot (0 \cdot 0)] \\ &= \frac{1}{12} (8 - 2 - 2 + 8) = 1. \end{aligned}$$

All other irreps yield zero multiplicity, so we conclude

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2.$$

This matches the intuitive tensor decomposition: the product of two in-plane vectors yields a scalar (A_1), a pseudoscalar (A_2), and a symmetric traceless rank-2 tensor (E_2) under C_{6v} .

Raman activity of an E_2 vibrational mode

A standard group-theoretical selection rule for matrix elements is:

A matrix element

$$\langle f | \hat{O} | i \rangle$$

can be nonzero only if the direct product of irreps

$$\Gamma_f \otimes \Gamma_O \otimes \Gamma_i$$

contains the totally symmetric irrep A_1 .

For Raman scattering, the relevant operator is the (effective) polarizability tensor $\hat{\alpha}_{ij}$, which transforms as a rank-2 symmetric tensor in the in-plane vector space. In C_{6v} , the in-plane vector transforms as E_1 , so the tensor product

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2$$

shows that the polarizability tensor decomposes as

$$\Gamma_\alpha = A_1 \oplus A_2 \oplus E_2.$$

In particular, it contains an E_2 component.

Now consider a one-phonon Raman process involving an E_2 vibrational mode:

- The vibrational ground state $|0\rangle$ is totally symmetric: $\Gamma_i = A_1$.
- The one-phonon excited state of symmetry E_2 is denoted $|1_{E_2}\rangle$, so $\Gamma_f = E_2$.
- We focus on the E_2 component of the Raman operator: $\Gamma_\alpha = E_2$.

The symmetry condition for the Raman matrix element

$$\langle 1_{E_2} | \hat{\alpha}_{ij} | 0 \rangle$$

is therefore determined by

$$\Gamma_f \otimes \Gamma_\alpha \otimes \Gamma_i = E_2 \otimes E_2 \otimes A_1.$$

Since A_1 is the identity representation, this is equivalent to

$$E_2 \otimes E_2.$$

For C_{6v} , the tensor square of E_2 decomposes as

$$E_2 \otimes E_2 = A_1 \oplus A_2 \oplus E_2.$$

This direct product *contains* the totally symmetric irrep A_1 , hence the matrix element

$$\langle 1_{E_2} | \hat{\alpha}_{ij} | 0 \rangle$$

is not forced to vanish by symmetry.

Therefore, an E_2 vibrational mode is *Raman active*: its symmetry matches an E_2 component of the polarizability tensor in such a way that the overall product contains A_1 , allowing a nonzero Raman transition amplitude.