

# 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  $180^\circ$ ,
- $\sigma_v$  are vertical mirrors that contain the  $x$  (or bond) axes,
- $\sigma_d$  are vertical mirrors that bisect the angles between the  $\sigma_v$  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:*

$\Gamma_{\text{prod}}$  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

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

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  $\pi$  /  $\sigma$  bands and polarization in graphene**

In a 2D hexagonal crystal like graphene:

- The out-of-plane  $p_z$  orbitals form the  $\pi$  and  $\pi^*$  bands. Their symmetry at  $\Gamma$  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  $\sigma$  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  $\pi$  and  $\sigma$  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:

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

(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:

$$A_1, \quad E_1, \quad E_2.$$

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  $\alpha$  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.