

A BRIEF OVERVIEW OF THE RAMAN SPECTRA OF GRAPHENE

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ABSTRACT

This paper is a review of the Raman scattering studies in Graphene - the new wonder material with innumerable desirable properties and applications. Raman spectroscopy has become a powerful and non-invasive technique for the characterization of Graphene and related materials. Several essential physical processes such as the phonon dispersion, the scattering mechanisms and the different resonances at play are dealt in this paper. Discussion of the significant changes in the salient features of the Raman spectra for the change in number of layers is also done. Moreover, the ability of this technique to differentiate between the armchair and zigzag edges has been discussed. A couple of selected, allied, basic concepts have also been highlighted in this paper and thus would serve to be beneficiary, especially for the novice readers of this field of study.

Keyword - Raman spectrum, Graphene, reciprocal space of Graphene, phonon dispersion, resonance mechanism, Graphene edges.

1. INTRODUCTION

In the year 2004, Andre Geim and his colleagues at the University of Manchester in the UK showed that the two major previously established beliefs about Graphene - a) that the thermal and other fluctuations would upset the stability of a sheet of Graphene and b) that even if stable, it would be impossible to isolate them for conducting research, were false. They made single graphene sheets by peeling them off a graphite substrate using a scotch tape! This paved the way for the extensive research, both theoretical and experimental, on this material. Raman spectroscopy has been long used as the primary technique for the structural characterization of graphitic materials, and now has also become a powerful tool for understanding the behavior of electrons and phonons in graphene.

The basics of reciprocal space and the phenomenon of Raman Effect, which are vital in the understanding of several parallel concepts, are addressed in this section.

1.1 Basics of Reciprocal space

Given a crystal, invariant under the linear translation of the form $T = i_1a_1 + i_2a_2 + i_3a_3$, where i_1, i_2, i_3 are some integers and a_1, a_2, a_3 are the crystal axes, any local physical property of the crystal, like the charge concentration, electron number density, or magnetic moment density is invariant under T . The electron number density, given by the function $n(r)$, is a periodic function of r with period a_1, a_2, a_3 in the directions of the three crystal axes respectively. Thus,

$$n(r + T) = n(r) \quad \text{---(1)}$$

Such periodicity creates an ideal situation for Fourier analysis since any periodic function can be expressed as a series of the sum of sine and cosine functions. The Fourier components of the electron density are related to the most

significant and fascinating properties of the crystal. First, we consider a function $n(x)$ in one dimension with period “a” along the x-axis. We then expand $n(x)$ in a Fourier series of sines and cosines:

$$n(x) = n_0 + \sum [C_p \cos(2 \pi p x / a) + S_p \sin(2 \pi p x / a)] \quad \text{----(2)}$$

Where, the p can take the value of positive integers and C_p , S_p are real constants, called the Fourier coefficients of the expansion. The factor $2 \pi / a$ in the arguments ensures that $n(x)$ has period a. It is usually taken that $(2 \pi p / a)$ is a point in the reciprocal lattice or Fourier space of the crystal. These points lie on a line in one dimension. The allowed terms in the Fourier series in (2) is decided by the reciprocal lattice points. A term is allowed if it is consistent with the periodicity of the crystal as shown in figure 1. It is convenient to write the series (2) in the exponential (compact) form as shown below,

$$n(x) = \sum n_p \exp(i 2 \pi p x / a) \quad \text{----(3)}$$

Where, the summation is over all integers. The coefficients n_p are now complex numbers [1].

The extension of the Fourier analysis to periodic functions $n(r)$ in three dimensions is straightforward. We need to find a set of vectors G such that

$$n(r) = \sum n_g \exp(iG \cdot r) \quad \text{----- (4)}$$

is invariant under all crystal translations T that leave the crystal invariant. Further, we must find the vectors G of the Fourier sum in (4). We do this by constructing the axis vectors b_1 , b_2 , b_3 of the reciprocal lattice with the basic relation below:

$$b_1 = 2 \pi ((a_2 \times a_3) / (a_1 \cdot a_2 \times a_3)) \quad \text{----- (5)}$$

A similar relation holds true for b_2 and b_3 . If a_1 , a_2 , a_3 are the primitive vectors of the real space crystal lattice, then b_1 , b_2 , b_3 are the primitive vectors of reciprocal lattice. Points in the reciprocal lattice are mapped by the set of vectors $G = i_1 b_1 + i_2 b_2 + i_3 b_3$, where i_1 , i_2 , i_3 are integers. A vector G of this form is a reciprocal lattice vector. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal. Vectors in the reciprocal lattice have the dimensions of $[1/\text{length}]$ as opposed to vectors in the direct lattice which have the dimensions of $[\text{length}]$. The reciprocal lattice is a lattice in the Fourier space associated with the crystal [1].

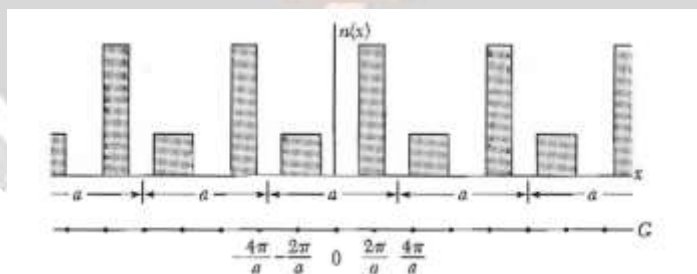


Fig -1: An arbitrary periodic function with a period “a”. The reciprocal lattice points are shown and they denote the allowed terms in (2).

1.2 Basics of Raman Effect

Raman Effect was discovered by the renowned Indian Physicist Sir Chandrasekhara Venkata Raman in 1928. In the spectroscopic technique based on this effect, first, a laser light of a certain frequency (ν_0) is incident on a sample. While most of the scattering is elastic in nature (Rayleigh scattering), only a very small fraction of the incident photons undergo inelastic scattering (Raman scattering). If the emitted photon has a lesser energy compared to the incident photon then it is the Stokes's Raman scattering. While if it is the other way around, it is the Anti-Stokes's scattering.

Consider a photon being incident on a crystal with energy $E = \hbar \omega$. After scattering from the crystal, the energy of the photon would be equal to $E = \hbar \omega'$ and let the energy of the emitted vibrational wave in the crystal be $E = \hbar \Omega$. This means that the emitted photon energy is the difference between the incident photon energy and the vibrational

wave's energy, i.e. $E = \hbar \omega' = \hbar (\omega - \Omega)$ and thus has a wavelength greater than the incident photon. The spectrum at this shifted wavelength (usually plotted in wavenumber units for convenience) gives the frequencies of vibrations, which is in turn related to the material's structure.

But why should there be a change in frequency (sometimes) as a result of the interaction of the photon with the crystal? Now, to understand that, consider an incoming electromagnetic radiation $E = E_0 e^{-i\omega t}$ which is incident on a molecule of dipole moment $P = \chi E$ which is the measure of the electrical polarity of the system and χ on the RHS is the susceptibility which indicates the degree of polarization in response to an applied electric field. Since E has an oscillatory exponential function and because classically an oscillating charge produces an electromagnetic field, the dipole moment oscillates with E and it acts like a tiny antenna that re-radiates at the same frequency. Hence the scattered light, in this case, has the same frequency as the incident EM wave. However, what if the molecule (or the site of incidence in general) is vibrating with some frequency, say Ω , initially? The vibrations modulate the susceptibility: $\chi = \chi_0 + \chi_1 (e^{-i\Omega t})$. Hence, the equation of the dipole moment is $P = \chi_0 (E_0 e^{-i\omega t}) + \chi_1 (E_0 e^{-i(\omega - \Omega)t})$ and the second term re-radiates at frequency $\omega' = \omega - \Omega$. An EM wave can gain energy from the vibration (Anti-Stokes event), or loose energy to a vibration (the Stokes process) [2]. The basic necessary condition for observing the Raman scattering is that the polarizability must change during vibrations of the molecules.

Raman spectroscopy is the foundation of research in diverse fields such as engineering, physics, chemistry and even biology. In fact, several of the papers and articles published every year on carbon materials have at least one Raman spectrum in them. An ideal characterization tool would be fast and nondestructive, offering high resolution, and giving structural and electronic information. All these requirements are satisfied by Raman spectroscopy. About 40 years ago, the Raman spectrum of graphite was first recorded. Raman spectroscopy had become one of the most popular techniques for the characterization of disordered and amorphous carbons, fullerenes, nanotubes, diamonds, carbon chains, and poly-conjugated molecules, by the time the Raman spectrum of graphene was measured for the first time in 2006 [3].

2. RECIPROCAL SPACE OF GRAPHENE

It was theoretically predicted about 60 years ago that the electronic band structure of graphene, should it ever be possible to produce it, would be very intriguing. $(1s)^2 (2s)^2 (2p)^2$ is the electronic structure of an isolated C atom. While the 1s electrons remain inert, the 2s and 2p electrons hybridize. One possible result is four sp^3 orbitals, which naturally tend to establish a tetrahedral bonding pattern. However, in case of the C atoms in Graphene an alternative hybridization of three sp^2 orbitals leaves over an almost pure p-orbital. The natural tendency for the sp^2 orbitals is to arrange themselves in a plane at 120° angles and the lattice thus formed is the honeycomb lattice as shown in figure 2a. Further, we see that the surroundings of the corresponding atoms are mirror images of one another and thus we have two inequivalent sub lattices, named A and B. Our Bravais lattice is chosen to have primitive lattice vectors a_1, a_2 for convenience and is given in (x, y) notation as:

$$a_1 = a/2 (3, \sqrt{3}) \quad a_2 = a/2 (3, -\sqrt{3}) \quad \text{----- (6)}$$

Where, a is the C-C spacing ($1.42 \text{ \AA}$). The reciprocal lattice vectors b_1, b_2 defined by the condition $a_i \cdot b_j = 2\pi \delta_{ij}$ are then

$$b_1 = 2\pi/3a (1, \sqrt{3}) \quad b_2 = 2\pi/3a (1, -\sqrt{3}) \quad \text{----- (7)}$$

We define the first Brillouin zone of the reciprocal lattice as bounded by the planes bisecting the vectors to the nearest reciprocal lattice points. This gives a FBZ of the same form as the original hexagons of the honeycomb lattice, but rotated with respect to them by $\pi/2$ (see figure 2b) [4]. Notice the two inequivalent points labelled as K and K' and their positions in momentum space are given by

$$k_1 = 2\pi/3a (1, 1/\sqrt{3}) \quad k_2 = 2\pi/3a (1, -1/\sqrt{3}) \quad \text{----- (8)}$$

The unit cell in the reciprocal space is shown in the figure 3a which shows some high symmetry points and the connecting lines within the first Brillouin zone of monolayer graphene. The gamma point at the zone centre labelled by Γ , the M points in the middle of the hexagonal sides and the K and K' points at the corner of the hexagons are shown. Connecting lines such as T connecting Γ to k, Σ connecting Γ to M and T' connecting K to M are shown. The two primitive vectors b_1 and b_2 , in reciprocal lattice, are shown. The two vectors on the top of the three hexagons shown in figure 3a denote the reciprocal space coordinate axes (for clarity). On the other hand, Graphite

has 4 atoms per unit cell. Only half the carbons have fourth neighbors that lie directly above or below in adjacent layers. Therefore, the two atoms of the unit cell in each layer are now inequivalent.

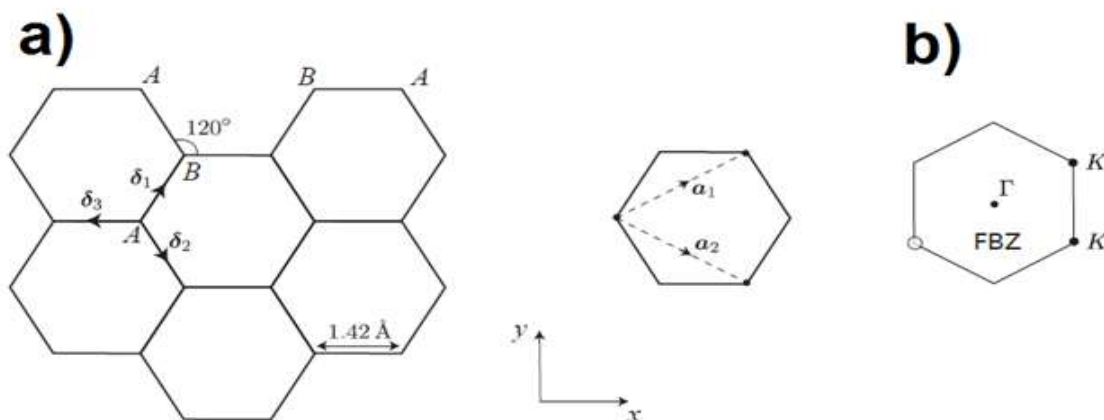


Fig -2: a) Direct lattice of Graphene with primitive lattice vectors in real space a_1 and a_2 . X and Y coordinates are shown for reference. b) The First Brillouin Zone of the reciprocal space of Graphene with Zone centre Γ and points K and K'. Adapted from reference [5]

3. PHONON DISPERSION IN GRAPHENE

In order to interpret the Raman spectra of Graphene, an understanding about the concept of phonon and their dispersion in graphene is vital. A phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter materials. Also, just as a photon is the quantum of electromagnetic or light energy, a phonon is a definite discrete unit or quantum of vibrational mechanical energy [6]. An acoustic phonon is a vibration in the crystal lattice where all moving components are about the same mass. Hence if we take the crystal's unit cell as a single object, the three different ways the unit cells of Graphene can move with respect to each other (two transverse one longitudinal) are the acoustic phonon modes. On the other hand, in case of the optical phonon we consider the constituents within the unit cell, where the dissimilar atoms often have a slight charge difference. Because of this charge difference, an electric field could interact with the pair of atoms within this unit cell - in particular an electromagnetic wave would interact with this two-atom dipole, hence the term "optical". The ways these atoms within the unit cell can move are again two transverse & one longitudinal. The number of optical phonon modes supported by the crystal raises with the number of different constituents of the unit cell [7].

The phonon dispersion curve, which is the plot of the frequency as a function of wavelength denoting the normal modes of vibration of a crystal, is usually plotted as frequency vs wave vector (wavelength^{-1}) (for mere convenience), across the Brillouin zone. There are six phonon dispersion bands as shown in figure 3b since the unit cell of monolayer graphene contains two carbon atoms, A and B, as shown in figure 2a. There are three acoustic branches (A) and three optic (O) phonon branches. As we have discussed above, for one acoustic branch (A) and one optic (O) phonon branch, the atomic vibrations are perpendicular to the graphene plane, and they correspond to the out- of plane (o) phonon modes. The vibrations are in-plane for two acoustic and two optic phonon branches. The directions of the vibrations are considered with respect to the direction of the nearest carbon-carbon atoms and hence the phonon modes are assorted as longitudinal (L) or transverse (T) based on whether the vibrations are parallel with or perpendicular to, respectively, the AB carbon-carbon directions. Therefore, the six phonon dispersion curves shown in the figure 3b are assigned to LO, iTO, oTO, LA, iTA, and oTA phonon modes, along the high symmetry Γ M and Γ K directions shown in 3a [8].

The in-plane iTO and LO optic modes, which are Raman active, correspond to the vibrations of the sub lattice A against the sub lattice B (as it should for optical phonons as mentioned above), and are degenerate near the center Γ (gamma) point. It can also be seen from the figure that for points inside the first Brillouin zone (BZ) of graphene, the degeneracy of the LO and iTO phonon modes disappear. Moreover, at the K-point, the phonon which comes from the iTO branch is non-degenerate. The phonon modes around the K point are very significant as the D-band and G'-band (discussed in the next section) are associated to phonon modes around the K point. Also, the LO and

LA phonon branches meet each other at the K point giving rise to a doubly degenerate phonon. It must be noted that for a bilayer graphene, separation of the phonon branches of monolayer graphene into two, is the result of the in-phase (symmetric) or out-of-phase (anti-symmetric) vibrations of the atoms in the two different layers [8].

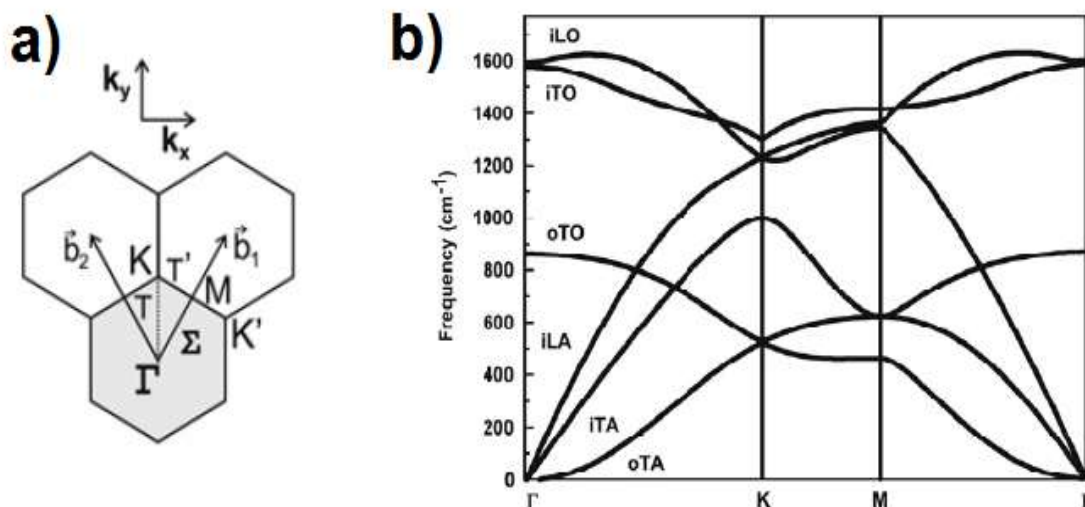


Fig- 3: a) The unit cell of the reciprocal lattice of graphene showing the high symmetry points and lines b) Phonon dispersion curves of Graphene showing different phonon modes along the high symmetry Γ M and Γ K directions.

4. RAMAN SCATTERING IN GRAPHENE

Raman spectrum is plotted with intensity in y-axis and the frequency difference, equivalent to the frequency of the lattice vibration (usually in cm^{-1}), in the x-axis. In the Raman spectra of monolayer Graphene, the most remarkable feature is the G-band which is associated with the doubly degenerate (iTO and LO) phonon mode at the Brillouin zone centre. It must be noted that the G-band is the only band arising from the first order Raman scattering process in graphene. The figure 4a also shows the G'-band (Also known as the 2D band but doesn't involve a defect and hence to avoid confusion G' is preferred). The disorder-induced D-band, at about half the frequency of the G'-band, is active for a disordered sample or at the edge of a Graphene sample. Unlike the G band, the G' and D-bands come from a second order process. The process for G'-band incorporates two iTO phonons near the K point, while for the D-band it involves one iTO phonon and one defect. There is also a weak disorder-induced feature known as the D' band. The 2D' peak is the D' overtone [9].

The dispersive behavior of the D and G'-bands is evident from the change in the frequency as a function of the energy of the incident electromagnetic radiation in the Raman spectra. The origin of the above behavior and the bands exhibiting them is attributed to the double resonance (DR) scattering mechanism, wherein the wave-vectors q of the phonons (with respect to the K point) associated with D and G'-bands would couple to the electronic states with wave-vector k (with respect to the K point) with $q \approx 2k$. The wave vector is a vector pointing in the direction of the propagation of the wave and having a magnitude equal to the wave number. The cones at the K and K' points at the edge of the first Brillouin zone (FBZ), shown in figure 4b, are the schematic of the electronic dispersion in Graphene (Dirac cones). An electron of wave vector k around K absorbing a photon (energy- E_{photon}) marks the onset of the double resonance process as shown in the middle of the figure 3b. Subsequently, inelastic scattering of the electron by a phonon or a defect with wave-vector q (energy- E_{phonon}) sends it to a point in a circle around the K' point, with wave-vector $k+q$. Upon being scattered back to a k state and recombining with a hole there, a photon is emitted. Since the above process connects points in the circles around the inequivalent K and K' Dirac points in the FBZ of Graphene, it is called an "intervalley" process. The two scattering processes include one elastic scattering by the defects in the crystal and one inelastic scattering by absorbing or emitting a phonon for the D-band. On the other hand, both processes are inelastic scattering involving two phonons in the case of the G'-band. If the double resonance process connects two points of the same circle around the K point (or K' point), it is an intra-valley process as in the case of the D' band [9], [10].

Moreover, scattering of holes can also happen in a Raman process. Since the valence and conduction bands are mirror images of one another for Graphene, it exhibits the triple resonance (TR) Raman process. Here, instead of the electron being scattered back by a phonon with wave-vector $-q$, the hole will be scattered by a wave-vector $+q$. Finally, the electron-hole recombination occurs at the opposite side with respect to the K point (that is near the K' point). The electron and hole scattering processes will be resonant. The triple-resonance mechanism holds the reason for why the G'-band is more intense than the G-band in monolayer graphene. Although the G'-band does not involve a first order process (which is predominant and hence usually intense) unlike the G-band, it is more intense than the G-band since it is contributed by two mechanisms (DR and TR) [11].

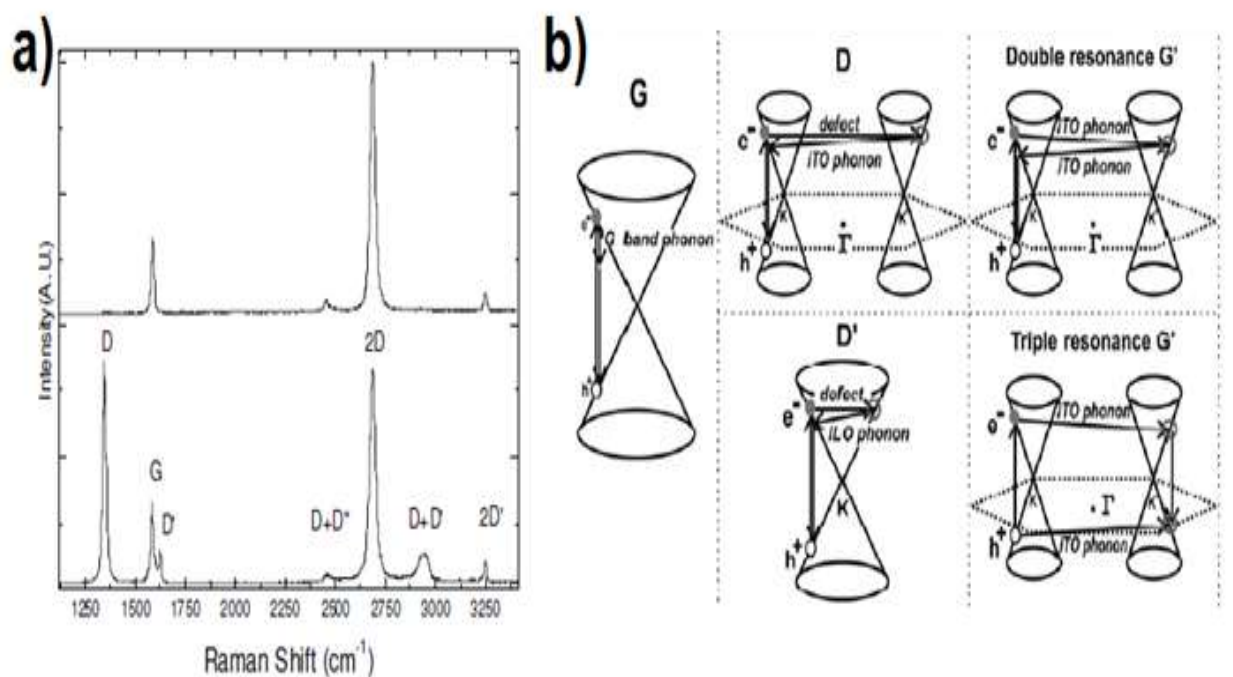


Fig- 4: a) The major bands arising from the Raman spectra of pristine (top) and defected (bottom) graphene b) Different Raman scattering processes labelled with the different bands that they are responsible for. Adapted from reference [11]

5. NUMBER OF LAYERS

The shape and intensity of the D peak varies with the number of Graphene layers in the sample under study as shown in the figure 5b. The same holds for the G' peak [12] (also known as 2D band) and the figure 5a describes the change in the 2D for the change in the number of layers. It has been found that the G' peak in Graphite has two components of varying intensities. What is more interesting is that the bi-layered Graphene (BLG) has a G' (2D) peak different from that of the single layered Graphene (SLG) as well as Graphite. $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$, are its four components of which two have higher intensities, namely $2D_{1A}$, $2D_{2A}$. The spectrum is almost identical to that of Graphite for number of layers greater than 5 [14].

The reasoning for the above assertion is as follows. The conduction and the valence band for a SLG are the π^* and π bands named after the π -bond and are formed due to the lateral overlap of the p_z orbitals of the unhybridized electron of the neighbouring Carbon atoms [13]. The interaction of the two Graphene layers, in case of the BLG, causes the division of π^* and π bands into 4, as shown in the figure 5d. While the incident radiation couples with only two of the four bands, the two degenerate TO phonons can couple all the bands. Thus there are four processes and the momenta of the phonons involved, q_{1B} , q_{1A} , q_{2A} and q_{2B} are shown in the figure. q_{1A} , q_{2A} are associated with processes more intense than q_{1B} and q_{2B} and they link bands of the same type unlike the latter. This accounts for the four components of the 2D (G') peak in BLG, as shown in figure 5c, since the four processes all correspond to different frequencies [14]

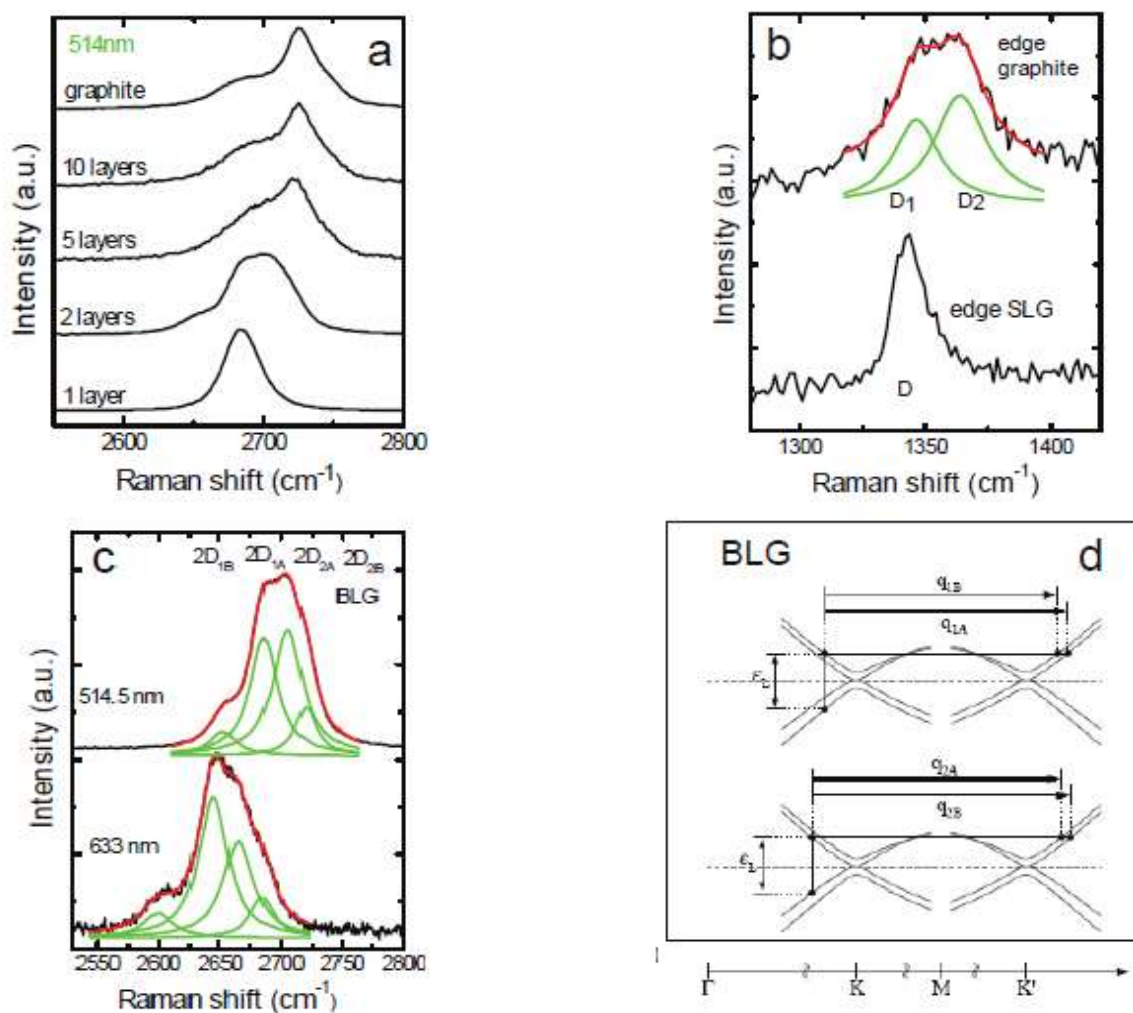


Fig- 5: a) The variation of the 2D peak as a function of N. b) The D peak at the edge of graphite and SLG. c) 2D peak of BLG with the green curves denoting the individual components and the red curve is the superposition of the components. (d) Phonon wave vectors responsible for the 2D peak in BLG. Adapted from reference [14]

6. EDGES

There are two possible edges in case of pristine Graphene namely Zigzag and Armchair as shown in the figure 6a and b. The electronic properties of graphene based materials at the nanometre scale are influenced by the specific types of edges and hence the study of their properties is essential. Raman spectroscopy has the potential to find the type and measure the quality of the edges.

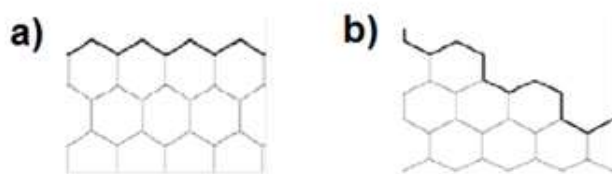


Fig- 6: a) Zigzag edge of Graphene b) Armchair edge of Graphene

Even if a Graphene sample has macroscopically smooth edges that are perfectly oriented, they are usually microscopically disordered consisting of Zigzag and Armchair segments. Although a perfect Zigzag and Armchair edge preserves the translational symmetry, this is not usually the case practically. They are thus considered as extended defects, violating the translational symmetry. Consequently, this leads to the activation of D and D' peaks. However, a perfect Zigzag edge cannot produce a D peak. The reasoning is as follows: In case of the D band which arises from an intervalley double resonance mechanism (see section 4), we let the phonon wave-vector be q . Moreover, the electron must be scattered elastically by a phonon with wave-vector $d = -q$ back to K from K', so as to conserve momentum. The defect wave-vectors d_a and d_z , which are normal to the armchair and zigzag edges (for the same reason as the hexagon corresponding to the FBZ was rotated by $\pi/2$ with respect to the real space honeycomb lattice- see section 2) respectively, are shown in the real space lattice in the figure 7a. The first Brillouin zone of graphene, oriented in accordance with the real space lattice, is shown in the adjacent figure 7b from which it is realized that the armchair wave-vector (d_a) connects the points around the K and K' and thus the Armchair edge exhibits the intervalley double resonance process. Since the K and K' points are not connected by the zigzag defect wave-vector (d_z), for the double resonance Raman process, the elastic electron scattering by the defect lacks the momentum for spanning points K and K' and thus for conserving momentum [15]. Thus, for a perfect graphene edge, D band would be found in the Armchair edge and not the Zigzag edge. Hence, a weak D-band is observed at a zigzag edge and a strong D-band intensity is obtained for the Armchair edge. On the other hand, the D' band is found in both the edges since it is based on the intravalley process connecting k points in the vicinity of the same K point (applicable for K' also) [16].

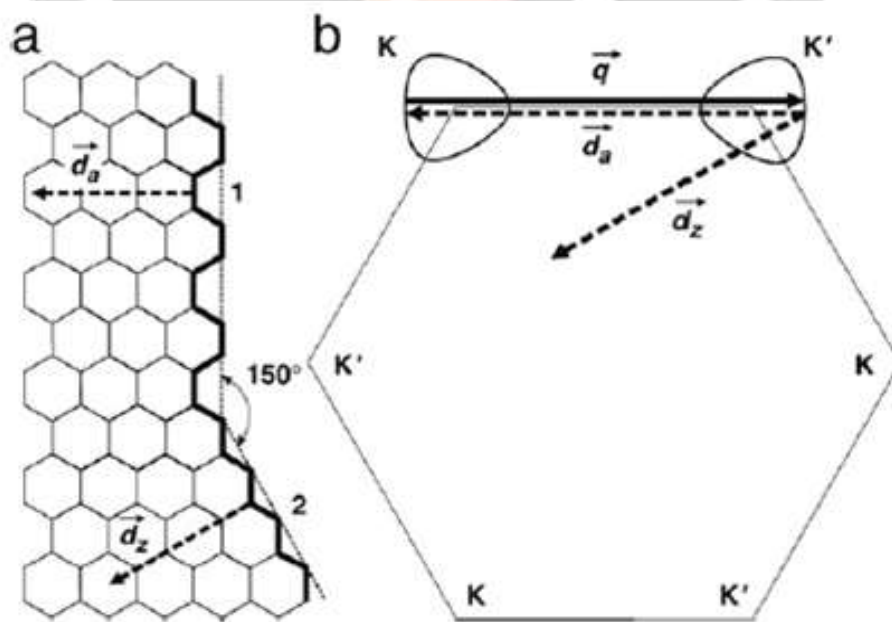


Fig- 7: a) The direct honeycomb lattice of Graphene illustrating the different types of edges along with the defect wave vectors. b) The reciprocal lattice showing the FBZ along with the defect wave vectors. The intervalley double resonance mechanism is present in an Armchair edge connecting the K and K' points while absent in a Zigzag edge which fails to do so. Taken from reference [15]

7. REAL SPACE RAMAN SCATTERING

All the scattering processes discussed in section 3 and applied in other sections are explained in the context of reciprocal space. The magnitude of the vectors in a reciprocal space does not correspond to distances but are wavenumbers proportional to the momentum of the wave. A final basic description of the main idea behind these processes in the real space context is included for better understanding. The promotion of an electron with momentum $p = \hbar k$ from π band to π^* band is due to the excitation photon, which creates a hole in the π band with momentum $-p$. This process (as shown by a streak in the figure 8a and b) takes place in a specific point in space.

Classical trajectories are followed by the electron and the hole with the group velocities deciding their directions. They may emit phonons or scatter on defects or edges. The condition for the electron and hole recombination to take place in order to produce the scattered photon is that they encounter each other after travelling for the same time at a given point in the real space, with opposite momenta k' , $-k'$ [17].

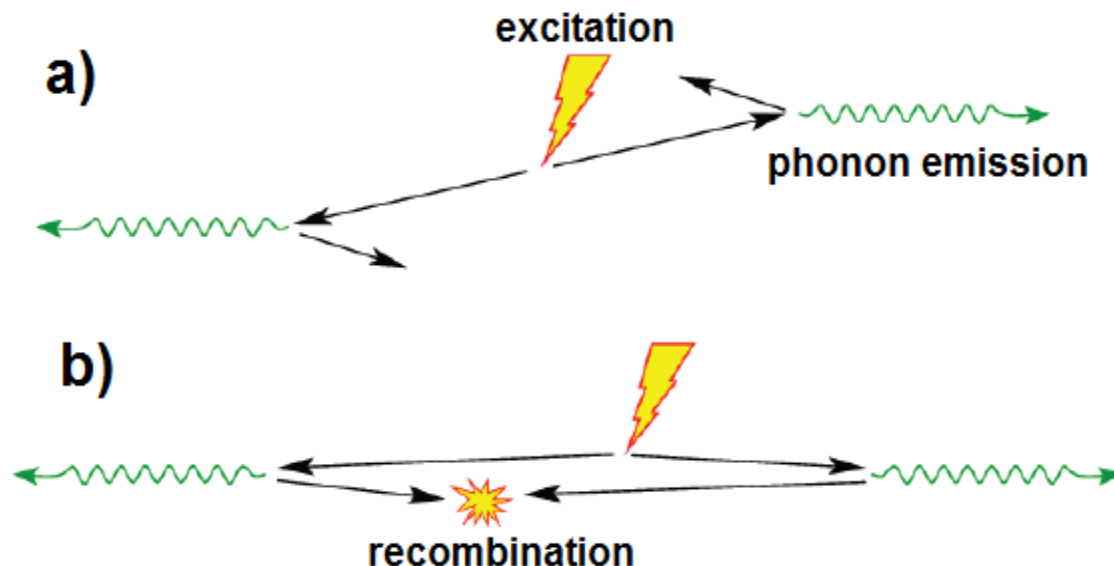


Fig- 8: a) Illustration of a real space Raman process wherein the electron hole recombination is impossible, since their trajectories do not meet at a point after the scattering by emission of phonon. b) Real space Raman process denoting the trajectory leading to the 2D band. Adapted from [17]

8. CONCLUSION

In summary, the basics of reciprocal space in general, reciprocal space of Graphene and the Raman scattering were touched upon. Also, the theoretical background of the phonon dispersion, first order Raman process, different resonances at play and the corresponding bands produced in the spectra were discussed. Further, the scope of the Raman spectroscopy in the estimation of number of Graphene layers and the quality and type of the edge was explained along with the reasoning and the several processes involved. Finally, the Raman process was also discussed in the context of the real lattice.

Raman spectroscopy is the most important characterization technique for several Carbon based compounds. The interest in this characterization was further increased by the synthesis of single and few layered Graphene. The discovery of other layered materials and thus the estimation of their Raman spectrum has just begun. Also, full-fledged research in order to understand the nanoscale structure of the Graphene and to put to use its marvellous properties is taking place. Hence, Raman spectroscopy has an important role to play in the above said research. Therefore, better theoretical understanding and practical instrumentation of both the characterisation technique and the sample is essential and hence requires further research in this field.

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