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Abstract

Raman spectroscopy is one of the most powerful tools for the study of carbonaceous materials, especially sp^2 or close to sp^2 carbon materials such as graphite, carbon nanotubes, and graphene. It is a quick, non-destructive, vibrational spectroscopy method which does not require significant effort for sample preparation. Furthermore, through resonance effects, the Raman spectrum also gives information about the electronic structure of the material. One must keep in mind, therefore, that the Raman spectrum reflects more than simply the phonon density of states of the material. In this study, I present the Raman spectra and analysis of an experimentally fabricated hBN/BLG/hBN heterostructure.

1. DFT Results

LA (longitudinal acoustic), **LO** (longitudinal optical) → vibrations along the propagation direction; **TA** (transverse acoustic), **TO** (transverse optical) → vibrations perpendicular to propagation direction but in-plane; **ZA**, **ZO** → vibrations out-of-plane

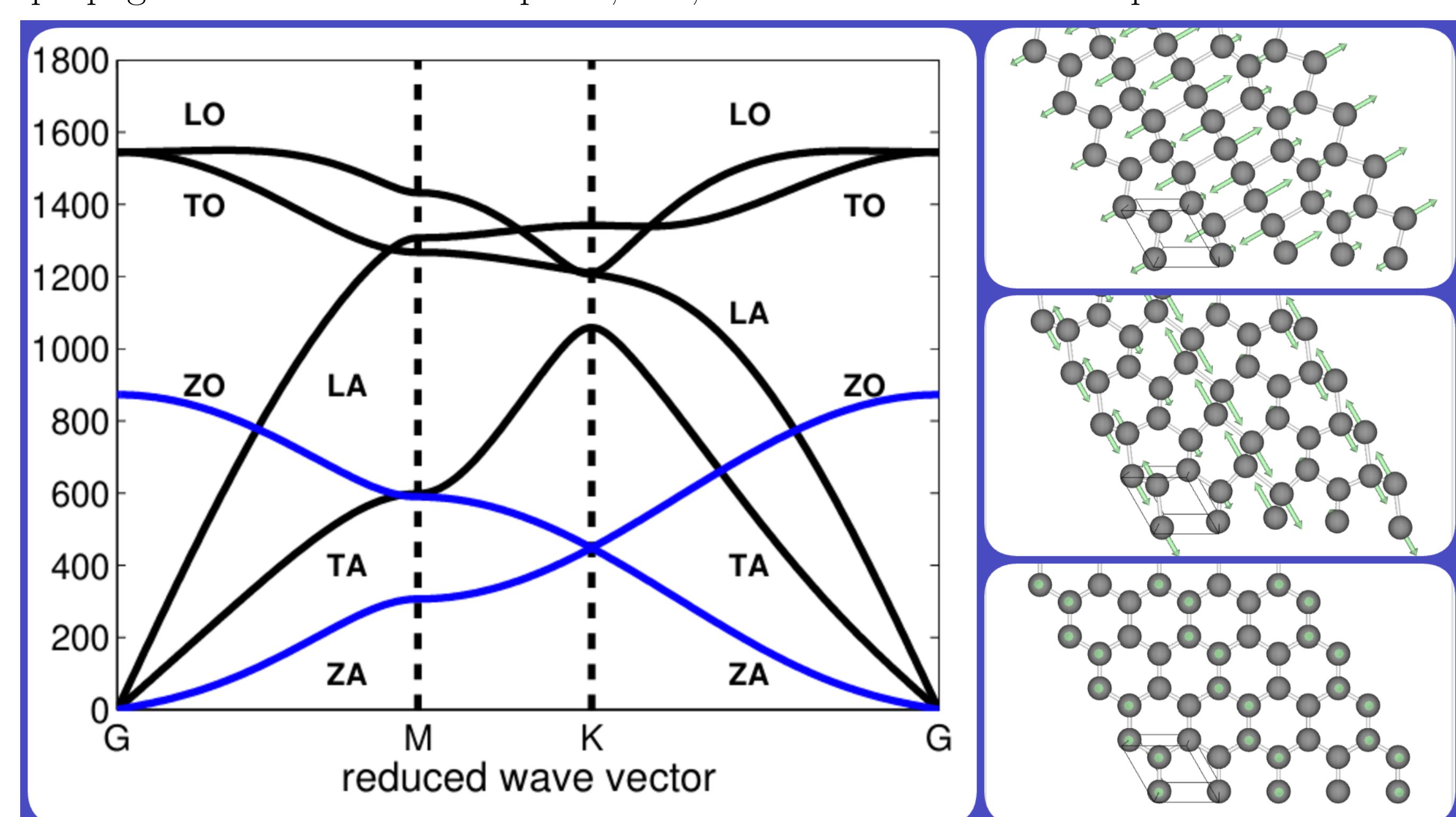


Fig. 1: Simulated phonon dispersion of AB bilayer graphene using GGA functional. [1, 2].

3. Raman Spectra

The device was fabricated by exfoliating HOPG graphene and pure hBN flakes [3] on a Si/SiO₂ substrate. Graphene is encapsulated between hBN layers.

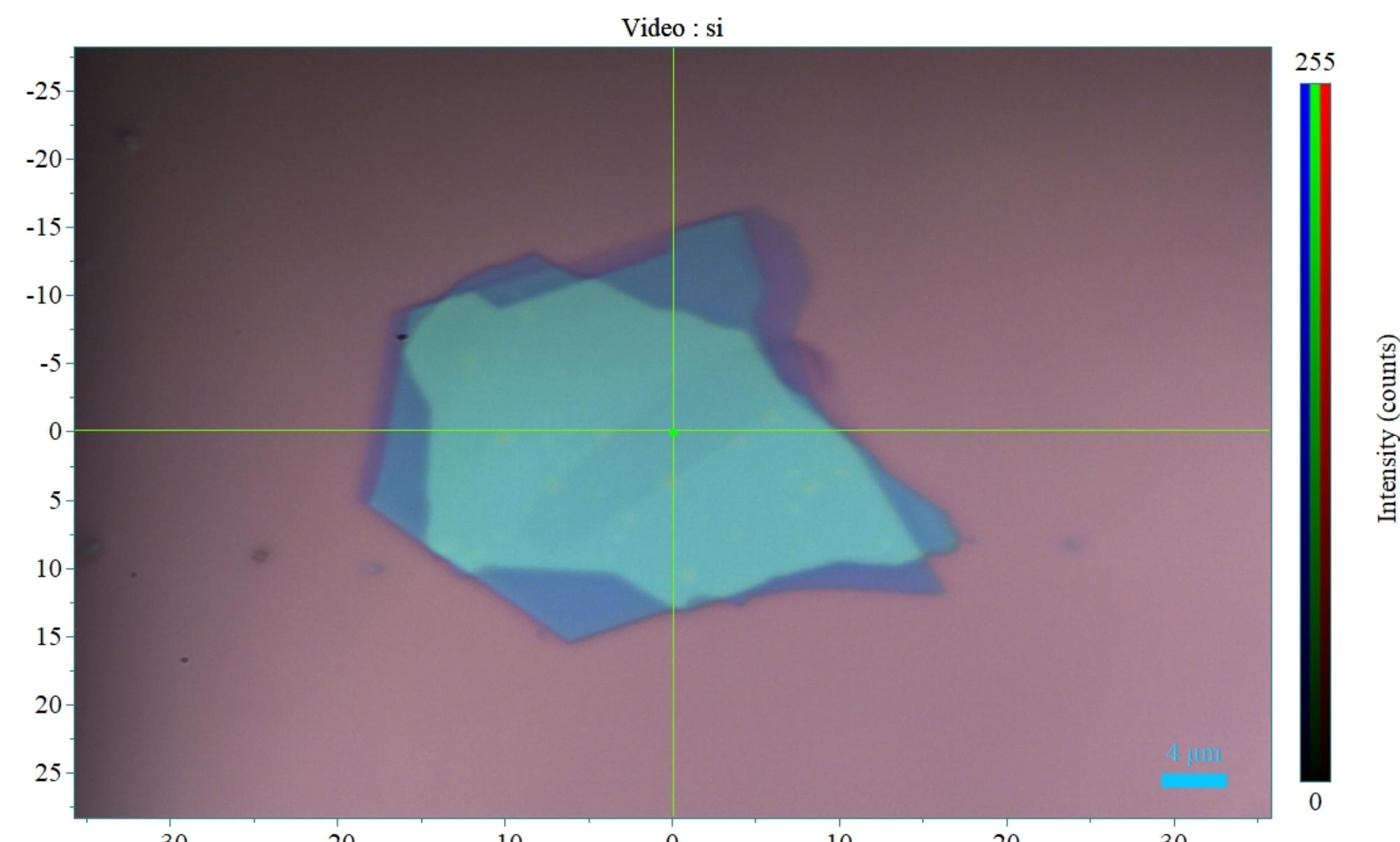


Fig. 2: Image of the device under 100× magnification under an optical microscope.

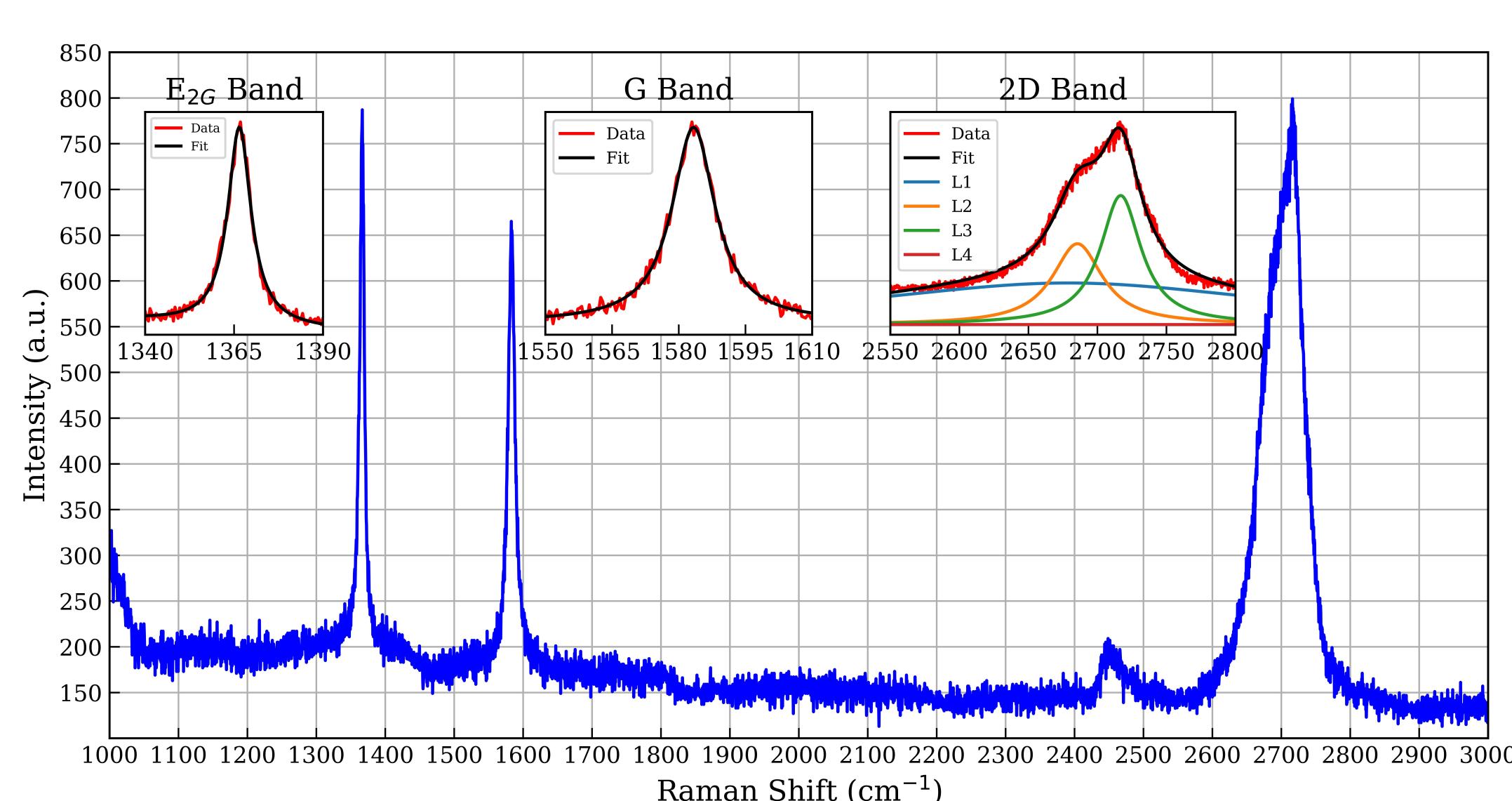


Fig. 3: Raman spectra of hBN/BLG/hBN.

E_{2G} band of hBN and G band of graphene is fit to a **single Lorentzian** while the 2D band of graphene is fit to **4 Lorentzians**.

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2. Raman Scattering

The Raman spectra of pure strain-free graphene are dominated by two bands: one at $\approx 1580\text{ cm}^{-1}$, and another at $\approx 2700\text{ cm}^{-1}$. The former is called the **G Band** and the latter the **2D Band**. G Band is a result of the in-plane vibration of two degenerate E_{2G} phonons: LO and TO at the Brillouin zone centre. This vibrational mode is a tell-tale characteristic of sp^2 bonded carbon networks and a result of the stretching and bending of the carbon-carbon bonds within the honeycomb lattice. The G band intensity is further enhanced by the **resonant Raman scattering** where the LASER energy matches an electronic transition in graphene.

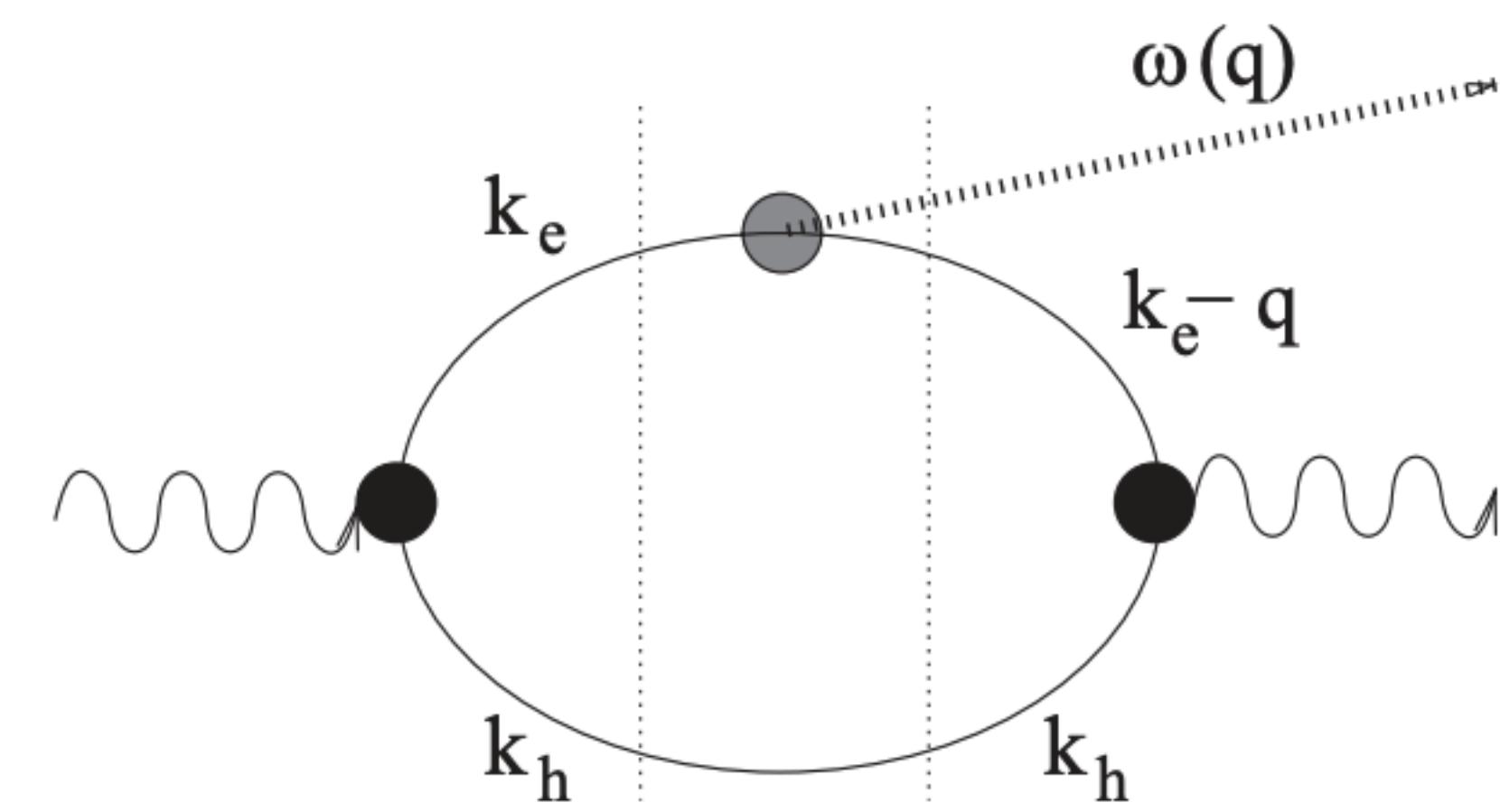


Fig. 4: Feynman-Goldstone diagram of the 1st order Raman process.

The 2D band is not a fundamental vibrational mode and is necessarily either a combination band or an overtone band as no single phonon has a frequency higher than 1650 cm^{-1} . The 2D band in graphene arises from a **double resonance Raman scattering** process involving two TO phonons around the K point in the Brillouin zone. This process involves two phonons with opposite momenta near the K point in the Brillouin zone, and the interaction is enhanced by a virtual electron-hole state, leading to the “double resonance”. The 2D band intensity is particularly strong in single and double-layer graphene, and can be used to characterise the layer thickness and strain.

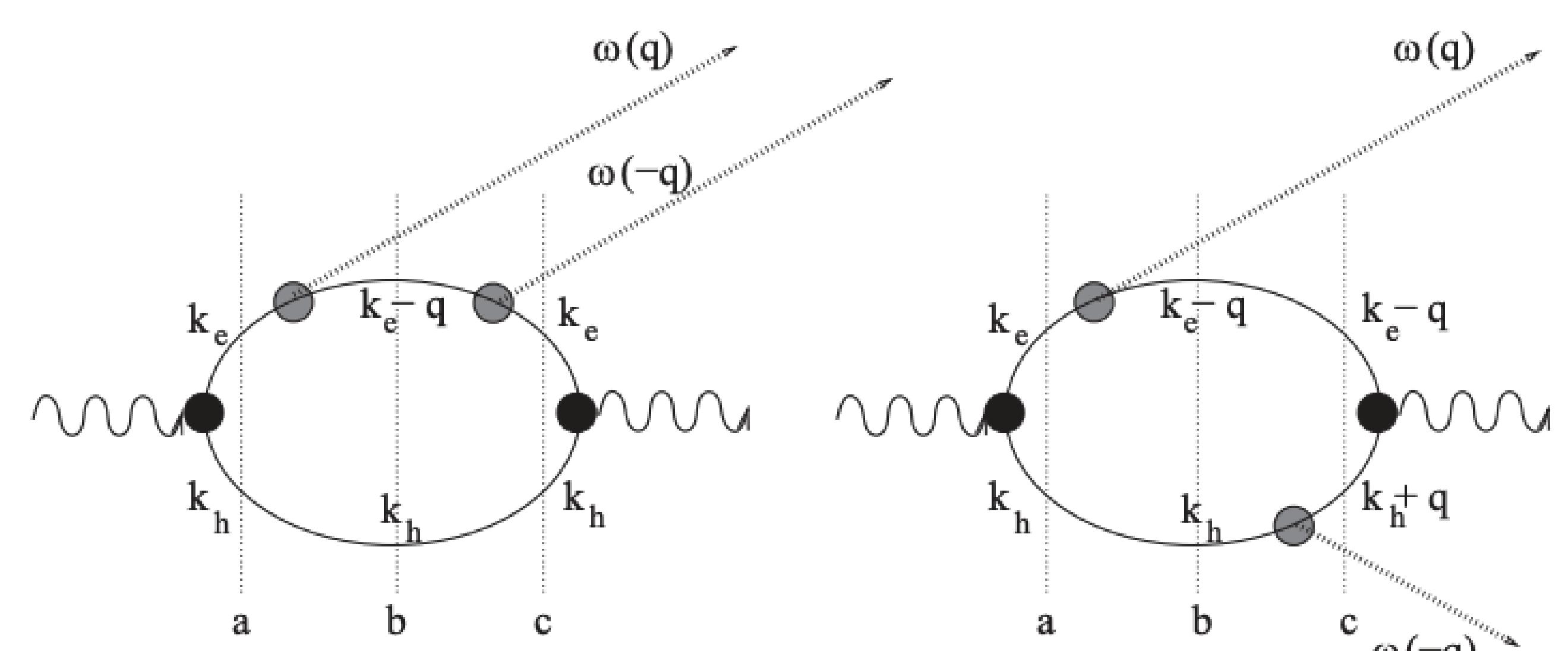


Fig. 5: Feynman-Goldstone diagrams of 2nd order Raman involving two phonons.

The D band in graphene, typically appearing around 1350 cm^{-1} , is a Raman scattering peak that arises from the presence of defects and disorder in the graphene's sp^2 -hybridised carbon network. It is not a fundamental vibrational mode of perfect graphene but is activated by structural imperfections like grain boundaries, edges, or vacancies. The D band originates from a **double resonance Raman scattering** where an incident photon excites an electron, which then interacts with a phonon and scatters to another location in the Brillouin zone, ultimately leading to the emission of another photon and the observation of the D band in the Raman spectrum. The location of the D band can vary slightly depending on the type of defect and the excitation LASER used. The ratio of D band to G band intensity (I_D/I_G) is used to quantify the degree of disorder in graphene.

References

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