Second-Order Overtone and Combination Raman Modes in Bilayer Graphene: First-Principles Calculations

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Double-resonant Raman (DRR) spectroscopy is a very important characterization tool for graphitic materials. In general, the 2D band is the most intense DRR peak in this kind of material. The 2D band involves the creation of two optical phonons with wave-vector close to the K-point of the Brillouin Zone. Nevertheless, there are several other DRR peaks in graphitic materials that may be useful in these materials characterization.

Here, we present *ab-initio* calculations for intensities, positions and line shapes of small intensity DRR peaks in bilayer graphene. We use the methodology presented in detail in [1], where density functional theory calculations were used to investigate the 2D band in bilayer graphene.

Recently, several experimental papers reported results for small intensities DRR peaks in bilayer graphene. The fisrt measurements appeared in Refs. [2] and [3]. In these works the Raman spectra for bilayer graphene between 1650 and 2300 cm^{-1} were reported. In this region of the spectra it is possible to identify several DRR bands. More recently, these DRR bands were measured with several different laser energies [4.5].

In bilayer graphene there are also DRR bands in the region of the spectra between 160 and 200 cm^{-1}[6]. These bands are due to layer breathing phonon modes. Additionally, Stokes-anti-Stokes bands measurements have been also reported recently [7].

In our calculations we are able to reproduce the experimental measurements reported in Refs. [2] to [7] with excellent agreement. In FIG. 1, for instance, our results are shown, in the region of the spectra between 1650 and 2400 cm^{-1}, for three different laser energies. More importantly our calculations allow a full interpretation of the experimental results. We are able to unambiguously determine the origin of all DRR processes concerning the phonons branches, wave-vectors and relevant electronic processes.

References
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FIG 1 – Calculated DRR bands for bilayer graphene for three different laser energies.