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Identification of mono- and few-layer graphene: Raman study

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Abstract : In this theoretical work, the Raman spectra were analyzed by considering the origin of the G peak, its shape, position and relative intensity as a function of the number of graphene layers. By using the spectral moment's method, the Raman spectra of mono, bi and few-layers of graphene are calculated and a good agreement was found with group theory concerning the number of the Raman-active modes and the Raman measurements. Our results provide a Raman analysis to evaluate the number of layers in multilayer graphene.

Keywords : RAMAN SPECTROSCOPY, GRAPHENE, GRAPHITE

Introduction

Since its discovery, graphene has attracted considerable interest due to some of its extraordinary properties [1, 2]. Graphene can be synthesized using micromechanical cleavage of graphite [1, 2], epitaxial growth [3, 4], chemical vapour deposition [4, 5] or to be appealing, a characterization tool must be nondestructive, fast and give the maximum structural and electronic information. Raman spectroscopy can fulfill these requirements.

Raman spectroscopy has thus become a standard characterization tool in the fast growing field of graphene studies. The difficult point in Raman measurements of graphene is spectral interpretation. The Raman spectra of all carbon systems show only a few prominent features. The spectra appear deceptively simple: just a couple of very intense bands in the 1000-2000 cm^{-1} spectral range and some other bands at 2500-2800 cm^{-1} . However, the accurate analysis of their shape, intensity and positions allow discriminating between hard amorphous carbon or metallic and semiconductor nanotubes. This has resulted in an enormous amount of work on the vibrational spectroscopy of graphene [7, 8, 9, 10] and also renewed the interest in its vibrational properties. The relation of phonon dispersion and the vibrational density of states (VDOS) are still an open issue

in the field, as it can be ascertained from several publications. Gruneis et al.[11] parameterized the popular 4th-nearest-neighbor force constant (4NNFC) approach [7]. Dubay and Kresse [12] performed calculations using density-functional theory (DFT) within the local-density approximation (LDA) for the exchange correlation function.

In this work, using the spectral moments method (SMM) [14, 15, 16, 17], and in the framework of the bond-polarization theory, the polarized Raman spectra of mono-, bi- and tri-layer graphene, were calculated. The dependence of the Raman active modes on the number of sheets was investigated. The results of calculations were compared with experimental Raman data.

Models and methods

Most models used to describe the phonon bands, the valence force field (VFF) method, and the force constant model (FCM). The latter has the lowest computation time requirements. In the FCM model, the dynamics of atoms are simply described by a few force springs connecting an atom to its surroundings up to a given number of neighbours. In contrast, the VFF method is based on the evaluation of the force constants, which requires longer computational times. FCM uses a small set of empirical measurements. Despite its simplicity, it can provide accurate and robust tools to investigate thermal properties of crystals and

in particular graphene nanostructures. The FCM employed model involves a fourth

nearest neighbor approximation. This model was previously used by our group to study the nonresonant Raman spectra of (single walled carbon nanotubes (SWNTs), double walled carbon nanotubes (DWNTs), dimers of two SWNTs and oligomers encapsulated in graphene (pT@G). [18, 19, 20, 21, 22, 23, 22].

We also performed calculations of the potential reliefs of interlayer interaction energy in bi-layer and tri-layer graphene, as well as in graphite using the Lennard-Jones potential.

$$V(\mathbf{r}) = 4\epsilon[(\sigma/\mathbf{r})^{12} - (\sigma/\mathbf{r})^6] \quad (1)$$

The values of Lennard-Jones parameters are $\epsilon = 2.964$ and $\sigma = 3.407$. Note that the Lennard-Jones potential was successfully used to describe the van der Waals energy in graphite-based systems [24].

The Raman efficiency of modes was calculated according to the nonresonant Raman scattering approach by using the bond-polarizability (BP) model [25, 26, 27]. In this model, the polarization is only modulated by the nearest-neighbor bonds and the components of the induced polarizability tensor [26, 27].

Results and discussions

The calculations were first performed on an infinite sheet of graphene which was obtained by applying periodic conditions on the unit cells of the graphene. Figure 1 shows the calculated ZZ polarized Raman spectra of infinite graphene. The symmetries of the Raman active modes were directly derived from the polarized ZZ in the spectra. Indeed, it was established that the A_{1g} Raman mode of graphene is active in the ZZ polarization. The number of calculated active modes is in agreement with group theory calculations [28]. The ZZ polarized spectrum is dominated by a strong A_{1g} Raman active mode calculated in the Tangential Mode (TM) region calculated around 1588 cm^{-1} . The Raman spectrum of graphene bilayer (2-LG) was also calculated with Bernal AB layer stacking. The G-band is calculated to occur 1588.4 cm^{-1} and corresponds to the atomic motion of nearest neighbor carbon atoms moving against each other within the plane and in phase between the two layers (figure 2-d).

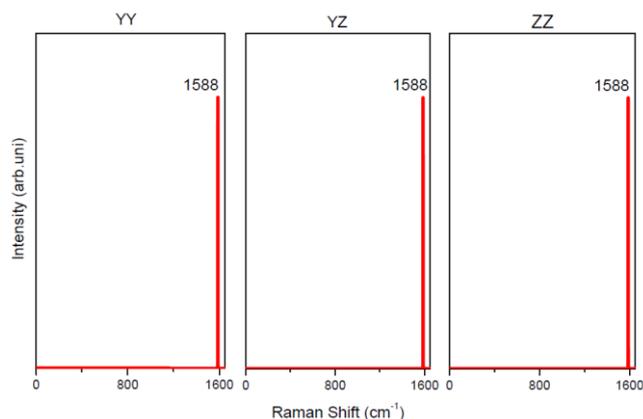


Figure1: Raman spectra of graphene mono-layer.

1-LG	-	-	-	-	-	-	1588cm ⁻¹
2-LG	-	-	-	58cm ⁻¹	89cm ⁻¹	866cm ⁻¹	1588.4cm ⁻¹
3-LG	42cm ⁻¹	64cm ⁻¹	74cm ⁻¹	112cm ⁻¹	866cm ⁻¹	1588.4cm ⁻¹	1589.06cm ⁻¹

Table 1: The Raman active modes in 1-LG, 2-LG and 3-LG

Three other Raman active modes are found, one located at 58 cm^{-1} and the two others at 89 cm^{-1} and 866 cm^{-1} . Figure 2 shows the eigenvector displacements of the Raman active modes in a graphene bi-layer. The van der Waals interactions lead to new Raman active modes associated to single-layer graphene. Note that the atomic motion of the mode located at 89 cm^{-1} (figure 5-a) is similar to that of the counter phase radial breathing mode of double walled carbon nanotubes [32].

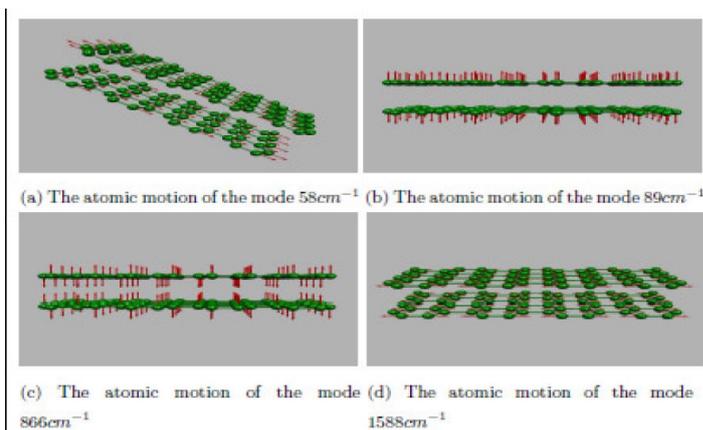


Figure2: The atomic motions of Raman active modes in graphene bi-layer.

For the Trilayer graphene (3-LG), the G-band mode is calculated at 1589 cm^{-1} . As in the case of bi-layer graphene, additional Raman active modes are also calculated in 3-LG. The atomic motion of these Raman active modes is shown in Figure 3. In table 1, we present calculated Raman active mode frequencies in 1-LG, 2-LG and 3-LG systems. We note that our calculated

frequencies of the Raman-active modes are in good agreement with group theory predictions [28].

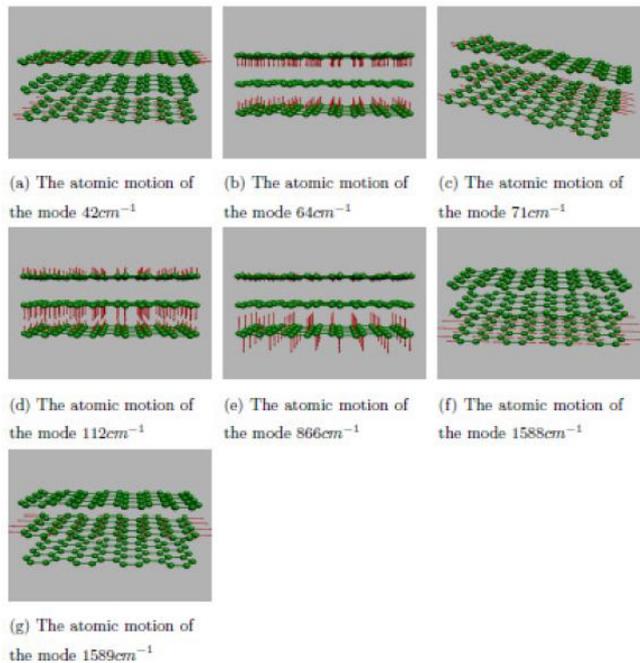


Figure3: The atomic motions of Raman active modes in graphene tri-layer.

Finally, we calculate the ZZ Raman spectrum of graphite. Figure 4 presents the G-bands of the Raman spectrum of mono-layer, bi-layer, tri-layer graphene and graphite. We found that the A_{1g} mode up-shifted with increasing number of layers. The G peak also showed a small shift upon increasing the number of layers. For instance, the G band frequency

$\omega(G)$ of single-layer graphene is 1588cm^{-1} , that of bi-layer graphene is 1588.4cm^{-1} and for trilayer is 1589.4cm^{-1} .

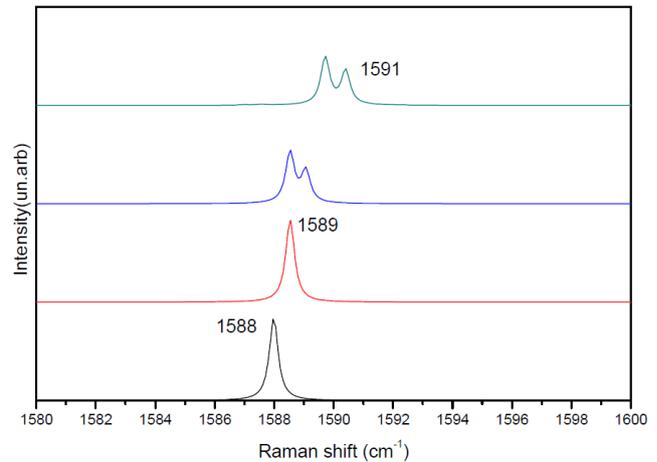


Figure4: Raman spectra of graphene mono-, bi- and tri-layer and graphite.

Conclusion

In this paper, the evolution of calculated Raman active modes as a function of the number of graphene layers are analyzed and general good agreement is found between our calculations and group theory. The high frequency regions of the Raman spectra of graphene multilayer are characterized by a splitting of the A_{1g} mode of graphene mono-layer. The additional modes that originate from the monolayers A_{1g} modes are strongly coupled through the van der Waals interlayer interactions. These predictions are useful for understanding the experimental Raman spectra of multilayer graphene.

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