

Number-of-layer discriminated graphene phonon softening and stiffening

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From the perspective of bond order-length-strength correlation and the local bond averaging approach, we have formulated the number-of-layer resolved Raman shifts of graphene, with quantification of the referential origins from which the Raman shifts proceed and clarification of their origins. It is found that the primary D mode and the secondary 2D mode are dominated by the interaction between a specific atom and its nearest neighbors while the G mode by the dimer interaction, and therefore red shift happens to the D/2D phonons and blue shift to the G mode upon the number-of-layer is reduced. © 2011 American Institute of Physics. [doi:10.1063/1.3656704]

Although the lattice dynamics of graphene and its number-of-layer (n) dependence of the Raman shift have been intensively investigated in recent years,^{1–12} the n -induced Raman trends need yet to be formulated and the mechanism underneath needs to be clarified. However, such an attempt from the perspective of bond relaxation and vibration is still lacking. A large graphene sheet manifests two Raman modes: the G band around $\sim 1580\text{ cm}^{-1}$ was suggested to arise from the in-plane vibrations of the sp^2 carbon network⁵; the 2D band around 2680 cm^{-1} was believed as a second-order process of double resonant Raman feature.⁶ In the presence of undercoordinated defect or edge atoms, a defect-induced D band at frequencies around 1345 cm^{-1} can be resolved with intensity being subject to the edge conditions.^{7,8} When the n is reduced, the D and the 2D modes are softened^{4,9,10} while the G mode is stiffened.^{10–12} Under the 514.5 nm light radiation, the D mode shifts from 1367 to 1344 cm^{-1} and the 2D mode changes from 2720 to 2680 cm^{-1} when the bulk graphite evolves into the monolayer graphene.¹¹ In contrast, the G mode shifts from 1582 to 1587 cm^{-1} when the n is reduced from 20 to one.^{10,11} When the n is increased from a few to multiple, the Raman vibration modes turn from the dominance of the monolayer component to the dominance of the bulk component.¹⁰ The conflicting n -dependent Raman trends indicate that the G mode and the D/2D modes are governed by different yet unclear physical mechanisms.

The objective of this contribution is to show that incorporating our original bond order-length-strength (BOLS) correlation mechanism^{13–16} and the local bond averaging (LBA) approach¹⁷ to the Raman spectroscopy, we have been able to formulate, clarify, and quantify the effects of the n on the Raman shifts of graphene. Agreement of modeling predictions to the measurements has led to consistent insight into the mechanism behind the fascinations with quantitative

information of the referential frequency, $\omega_x(1)$, and the effective coordination number (CN, or z) for the few-layer graphene.

The BOLS correlation^{13–16} indicates that the shorter and stronger bonds between undercoordinated atoms cause local densification and quantum entrapment of bonding electrons and binding energy, which modulate the local atomic cohesive energy, the binding energy density, the Hamiltonian of the entire specimen and the relevant properties such as mechanical strength, thermal stability, lattice dynamics, photonic, magnetic and dielectric properties associated with atomic undercoordination.¹³ The LBA approach suggests that any detectable quantity of a specimen be dependent functionally on the order, length, energy of the representative bond of entire specimen and their responses to the applied stimuli. The BOLS correlation is expressed as¹³

$$\begin{cases} d_z/d_b = C_z = 2/\{1 + \exp[(12-z)/8z]\} & \text{(bond contraction)} \\ E_z/E_b = C_z^{-m} & \text{(bond strengthening)} \end{cases} \quad (1)$$

The subscripts z and b denote an atom with z coordination neighbors and in the bulk as a standard, respectively. The bond contraction coefficient C_z varies only with the effective z of the atom of concern regardless of the nature of the bond or the solid dimension. The index $m = 2.56$ is the bond nature indicator of carbon.¹⁵ With the known C-C bond length of 0.154 nm in diamond and 0.142 nm in graphite, one can readily derive the effective CN for the bulk graphite as $z_g = 5.335$, according to Eq. (1). The effective CN of a C atom in diamond is 12 instead of 4 because the diamond structure is an interlock of two fcc unit cells.

Theoretical reproduction of the elastic modulus enhancement,^{15,19} melting point depression of the single-walled carbon nanotube,^{15,20} the C 1s binding energy shift of graphene edge, graphene, graphite, and diamond,^{21,22} the width dependence of the band gap expansion of graphene ribbon,²³ and the Dirac-Fermi polarons generation and

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hydrogenation¹⁴ have confirmed consistently that C–C bond between the 3-coordinated atoms contracts by 18.5% to 0.125 nm with a 68% increase of bond energy.^{15,19,24} The BOLS predicted bond contraction and bond strength gain has been evidenced by the observations of the elastic modulus ($\propto E/d^3$) enhancement of Au at the atomic scale²⁵ and the shell-resolved Au–Au bond contraction in a radial way at the outermost two atomic layers of Au nanocrystals.²⁶ From the fact that the modulus for the single attached Au atom is twice that of the bulk,²⁵ we can estimate that the Au–Au bond contraction by 16% ($Y_1/Y_b = 2 = C^{-4}$; $m = 1$).

Based on the BOLS theory and the LBA approach, we have recently¹⁸ formulated the thermally softened and the mechanically stiffened graphene phonons with confirmation of the C–C bond length in the single-layer graphene contracting from 0.154 to 0.125 nm and the binding energy increasing from 0.65 to 1.04 eV. Matching theory to the measured temperature- and pressure-dependent Raman shift has derived that the Debye temperature drops from 2230 to 540 K, the atomic cohesive energy drops from 7.37 to 3.11 eV/atom, and the binding energy density increases from 250 to 320 eV/nm³ compared with the respective quantities of bulk diamond.

It is emphasized that the solution to the Hamiltonian of a vibration system is a Fourier series with multiple terms of frequencies being folds of that of the primary mode.²⁷ Therefore, the frequency of the 2D mode is approximately twofold that of the D mode. This finding may clarify the intrinsic origin of the 2D mode that is often related to the double resonant Raman process. The fact that the n-reduction induced D peak shifting from 1367 to 1344 cm⁻¹ and the 2D peak shifting from 2720 to 2680 cm⁻¹ is right within this expectation.

Generally, one can measure the Raman resonance frequency as $\omega_x = \omega_{x0} + \Delta\omega_x$ ($x = D, 2D, G$), where ω_{x0} is the reference origin from which the Raman shift $\Delta\omega_x$ proceeds. By expanding the interatomic potential in a Taylor series around its equilibrium and considering the effective atomic z , we can derive the vibration frequency shift of the harmonic system as a function of $\Delta\omega_x(z, d_z, E_z, \mu)$. Equating the vibration energy to the third term in the Taylor series with omitting of the higher order contributions, we have

$$\frac{1}{2}\mu(\Delta\omega)^2x^2 \cong \frac{1}{2}\frac{\partial u(r)}{\partial r^2}\Big|_{r=d} x^2 \propto \frac{zE_z}{2d^2}x^2.$$

From the dimensionality analysis, the term $\partial u(r)/\partial r^2|_{r=d}$ is proportional to E_z/d^2 . The n-reduction induced opposite trends of the D, 2D, and the G mode Raman shifts suggest that the G mode be dominated by interaction between two neighboring atoms of a dimer while the D and 2D modes involve all the z neighbors of a specific atom

$$\begin{aligned} \Delta\omega_x(z, d_z, E_z, \mu) &= \omega_x(z, d_z, E_z, \mu) - \omega_x(1, d_b, E_b, \mu) \\ &= \omega = \sqrt{\frac{d^2u(r)}{\mu dr^2}\Big|_{r=d_z}} \propto \frac{1}{d_z} \left(\frac{E_z}{\mu}\right)^{1/2} \times \begin{cases} 1 & (\text{Gmode}) \\ z & (\text{D/2Dmode}) \end{cases}. \end{aligned} \quad (2)$$

We may rename, conveniently, ω_{x0} as $\omega_x(1)$ that is to be fixed from matching theory to the measurements. The reduced mass of the dimer μ remains a constant unless chemical adsorption or isotope is being involved.

Incorporating Eq (1) into (2) and taking z_g for the bulk graphite as a reference, we have the general form of the relative Raman shift, the reference $\omega_x(1)$, and the z -dependent frequency $\omega_x(z)$ for all the possible Raman modes

$$\begin{aligned} \frac{\omega_x(z) - \omega_x(1)}{\omega_x(z_g) - \omega_x(1)} &= \frac{zd(z_g)}{d(z)} \left(\frac{E(z)}{E(z_g)}\right)^{1/2} \\ &= \left(\frac{C_z}{C_{z_g}}\right)^{-(m/2+1)} \times \begin{cases} \frac{z}{z_g} = A_D(z, z_g) & (\text{D and 2D}) \\ 1 = A_G(z, z_g) & (\text{G mode}) \end{cases} \\ \begin{cases} \omega_x(1) = \frac{\omega_x(z) - \omega_x(z_g)A_x(z, z_g)}{1 - C_x(z, z_g)} \\ \omega_x(z) = \omega_x(1) + [\omega_x(z_g) - \omega_x(1)]A_x(z, z_g). \end{cases} & \quad (3) \end{aligned}$$

We calculated the z -dependent curves and calibrate them with the known vibration frequencies for the bulk graphite and the monolayer graphene. In numerical calculations, the known bond length $d_g = 0.142$ nm and $z_g = 5.335$ for the bulk graphite, $z = 3$ for the single-layer graphene, and $m = 2.56$ for carbon were taken as input parameters. With the given Raman frequencies of the 2D peak shifting from 2720 to 2680 cm⁻¹ and the D peak from 1367 to 1344 cm⁻¹ when the graphite (z_g) turns to be the monolayer ($z = 3$) graphene,^{9,10,28} and the G mode shifting from 1582 to 1587 cm⁻¹,^{10,11} we can calibrate the z -dependent relative shift of the possible modes

$$A_x(3, z_g) = \left(\frac{0.8147}{0.9220}\right)^{-2.28} \times \begin{cases} \frac{3.0}{5.335} = 0.7458(D, 2D) \\ 1 = 1.3260(G) \end{cases}.$$

The reference frequencies and the general expression for the z -dependency are derived as

$$\begin{aligned} \omega_x(1) &= \frac{\omega_x(3) - \omega_x(z_g)A_x(3, z_g)}{1 - A_x(3, z_g)} = \begin{cases} 1276.8 & (D) \\ 2562.6 & (2D) \\ 1566.7 & (G) \end{cases} (\text{cm}^{-1}), \\ \omega_x(z) &= \omega_x(1) + [\omega_x(z_g) - \omega_x(1)]A_x(z, z_g) \\ &= \begin{cases} 1276.8 + 90.2 \times A_D(z, z_b) & (D) \\ 2562.6 + 157.4 \times A_D(z, z_b) & (2D) \\ 1566.7 + 16.0 \times A_G(z, z_b) & (G) \end{cases} (\text{cm}^{-1}). \end{aligned} \quad (4)$$

Figure 1 shows the modeling reproduction of the z -dependent Raman frequencies of (a) the D and 2D modes^{10,29,30} and (b) the G mode.^{10,11} Panel (c) is the z - n correlation derived from (a) and (b). It is seen that when the n is greater than 6, the z reaches and then maintains almost the bulk graphite value of 5.335. The consistency between predictions and the measurements of the z -dependent Raman shifts and the z - n transformation function for the three modes evidences the essentiality and appropriateness of the proposed mechanisms for the lattice vibration in graphene.

We have thus formulated, clarified, and quantified the n -dependent Raman shifts of graphene, as a function depending on the BOLS correlation in terms of the response of the length and energy of the representative bond to the bond

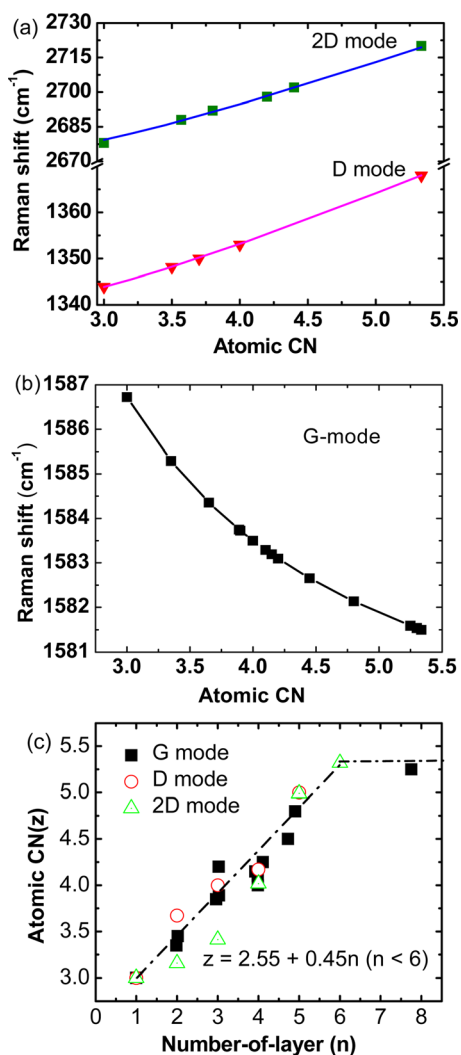


FIG. 1. (Color online) BOLS reproduction of the z dependence of the Raman shifts of (a) the D and the 2D modes (Refs. 9 and 10) and (b) the G mode with derivative of the referential vibration frequency for each. Panel (c) shows the correlation between the atomic CN(z) and the number-of-layer, n . For $n > 6$, the z approaches and maintains almost the bulk graphite value of 5.335.

order loss. Numerical reproduction of the measurements clarified that the D and 2D phonons involve interaction of a specific atom with all of its z neighbors while the G phonon involves only interaction with a dimer. Reproduction of the measurements has led to quantitative information of the referential frequencies for each mode from which the Raman shifts proceed and the effective coordination numbers for the few-layer graphene, which is of instrumental importance to the understanding of the unusual behavior of graphene. Findings and understandings demonstrate the essentiality of the proposed approach that has empowered the Raman spectroscopy

immensely in gaining quantitative information about the dynamics of the representative bond of a specimen.

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