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Strain-induced graphene phonon softening and phonon band splitting are indeed fascinating, which were attributed to the phonon double resonant scattering without intrinsic involvement of C-C bond relaxation. Here, we show that the lengthening and weakening of the C-C bond softens the phonon and that the mismatching between the uniaxial strain and the C_{3v} bond geometry splits the band. In addition to the force constant of 11.8 N/m for a C-C bond in graphene, consistency between theory and measurements derives that if the strain is along a bond, maximal band splitting happens; if the strain is perpendicular, no band splitting occurs. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4935604]

Overwhelming contributions have been made in recent years toward exploring the Raman shifts of the single- and the few-layer graphenes and their nanoribbons under various stimuli such as the uniaxial tensile strains (ε).[1–3] The Raman 2D band[4,5] undergoes the red-shift associated with a band splitting. The vibronic behavior of atoms in graphene is not only of fundamental significance to processes such as electron phonon coupling, phonon photon interaction, phonon transport, and thermal conductivity,[6–8] but also of technical importance to practical applications in fields such as short wavelength light emitting, high temperature, high power electronic, and thermal devices.[9,10] Although there have been experimental analyses assuming isotropic TO phonon softening[3] and theoretical studies on the 2D band under strain,[11] but, all the work explained the phenomena using the hypothetic concept of "two-phonon double resonant scattering"[4] that describes only the extrinsic process of light scattering without intrinsic involvement of the C-C bond that undergoes relaxation under strain.

In this letter, we show that an incorporation of the bond order-length-strength (BOLS) correlation[12] into the sophisticated measurements has led to formulation of the Raman shifts depending functionally only on the oriented strain in terms of the response of the length and energy of the bond, being independent of the process of phonon or electron scattering. Strikingly, agreement between the BOLS formulation and the measurements has led to the force constant of the C–C bond in graphene with a deeper insight into the mechanism behind the strain-induced fascinations.

The BOLS notion[13] indicates that bonds between under-coordinated atoms become shorter and stronger, which follows the relations:

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

The subscripts z and b denote an atom with z coordination neighbors (CN) 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 bond nature index $m = 2.56$ for carbon.[14] Using the length of 0.154 nm for the C-C bond 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). For the C atom in the bulk diamond, the effective CN is 12 instead of 4 because the diamond structure is an interlock of two fcc unit cells. By the relation of $E_z = C_z^{-m} E_b$, and the known atom cohesive energy of diamond, 7.37 eV,[15] the single C-C bond energy in the diamond is $E_b = 7.37/12 = 0.614$ eV, and it is $E_3 = 1.039$ eV in the monolayer graphene of z = 3. Combining the uniaxial tensile strains, $\varepsilon = \Delta x / x_0$ and Eq. (1), it can obtain the strain, $\varepsilon_{CN} = (d_z - d_b)/d_b = C_z - 1$. According to the BOLS notion, the C-C bond in graphene is subject to a compression strain ($\Delta\varepsilon$), as given in Table I.

TABLE I. Instrumental information derived from the BOLS theory, in the carbon allotropes.

Parameters	C_{60}	SWCNT	Graphene	Graphite	CNB	Diamond
CN	2.465	3	3	5.335	5.605	12.00
d (nm)	0.118	0.125	0.125	0.142	0.143	0.154
C_z	0.763	0.814	0.814	0.922	0.929	1
$\Delta\varepsilon_{2D}$	0.237	0.186	0.186	0.078	0.071	0

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Equaling the vibration energy of a harmonic system to the third term in the Taylor series of the interatomic potential, in the first order approximation, we can derive the phonon frequency shift as a function of atomic CN, bond length, bond energy, and the reduced mass of the dimer atoms (z, d_z, E_z, μ) with $\mu = m_1 m_2 / (m_1 + m_2)$[14]

$$\frac{1}{2}\mu(\Delta\omega)^2 x^2 \cong \frac{1}{2}\frac{\partial u(r)}{\partial r^2}\bigg|_{r=d_z} x^2 \propto \frac{1}{2}\frac{E_z}{d_z^2}x^2,$$

and

$$\Delta\omega(z,\varepsilon) = \omega(z,\varepsilon) - \omega(1,0) \propto \frac{z}{d(z,\varepsilon)}\left(\frac{E(z,\varepsilon)}{\mu}\right)^{1/2}.$$

The $\omega(1)$ is the reference point from which the Raman shift proceeds. For a given specimen, the z and the reduced mass do not change unless phase transition occurs. Hence, the energy shift of the specific Raman mode is only bond-length and bond-energy dependent, irrespective of the extrinsic processes of phonon scattering. The uniaxial tensile

strains is $\varepsilon = \Delta x / x_0$; therefore, the change of bond length $d(z,\varepsilon)$ and the bond energy $E(z,\varepsilon)$ follows the relations

$$\begin{cases} d(z,\varepsilon) = d_b\left\{[1 + (C_z - 1)]\left(1 + \int_0^\varepsilon d\varepsilon\right)\right\} \\ E(z,\varepsilon) = E_b\left\{1 + \left[(C_z^{-2.56} - 1) - d_z^2\int_0^\varepsilon \kappa(\varepsilon)\varepsilon d\varepsilon\right]\Big/E_b\right\}, \end{cases}$$
(2)

where $k(\varepsilon)$ and E_b are the force constant and the bond energy for the C-C bond in graphene, respectively.

For the clarity and convenience, here we focus on the 2D mode that is the secondary term of the solution, in the form of Fourier series, to the Hamiltonian of the harmonic system. The 2D frequency is ideally double that of the primary D mode rather than it is a combination of two independent phonons. With the given Raman frequencies of the 2D peak shifting from $\omega(z_g = 5.335$ for graphite$) = 2720$ to $\omega(z = 3$ for graphene$) = 2680$ cm^{-1},[16–18] we can determine the reference frequency $\omega(1,0)$ from Eq. (2)

$$\begin{cases} \dfrac{\omega(3,0) - \omega(1,0)}{\omega(z_g,0) - \omega(1,0)} = \dfrac{3}{z_g}\left(\dfrac{C_z}{C_{z_g}}\right)^{-(2.56/2+1)} = \dfrac{3.0}{5.335}\left(\dfrac{0.8147}{0.9220}\right)^{-2.28} = 0.7458 = A \\ \omega(1,0) = \dfrac{\omega(3,0) - \omega(z_g,0)A}{1-A} = 2562.6\ \text{cm}^{-1} \\ \omega(3,0) = \omega(z,0) = \omega(1,0) + A \times \big(\omega(z_g,0) - \omega(1,0)\big). \end{cases}$$
(3)

The strain-effect on the 2D band softening and splitting follows

$$\begin{aligned} \frac{\omega(z,\varepsilon) - \omega(1,0)}{\omega(z,0) - \omega(1,0)} &= \frac{d(z,0)}{d(z,\varepsilon)}\left(\frac{E(z,\varepsilon)}{E(z,0)}\right)^{1/2} \\ &= \frac{\left(1 - d_z^2\int_0^\varepsilon \kappa\varepsilon d\varepsilon/E_z\right)^{1/2}}{1+\varepsilon} \\ &\cong \frac{(1 - \kappa'\varepsilon^2)^{1/2}}{(1+\varepsilon)}, \end{aligned}$$

$$\begin{aligned} \omega(3,\varepsilon) &= \omega(1,0) + A \times \big[\omega(5.335,0) - \omega(1,0)\big] \\ &\quad \times (1 - \kappa'\varepsilon^2)^{1/2} \times (1+\varepsilon)^{-1} \\ &= 2562.6 + 0.7458 \times 157.4\frac{(1-\kappa'\varepsilon^2)^{1/2}}{1+\varepsilon}, \end{aligned} \quad (4)$$

with $\kappa = 2E_z\kappa'd_z^{-2}$ being the force constant of the C-C bond between the given z-coordinated atoms.

Practically, one can measure the average strain of the entire specimen other than that of the individual bond as illustrated in Fig. 1. The numbers indicate atoms bonding to the atom at the origin. θ is the angle between the strain and the direction along a certain bond. There are two extreme situations: at $\theta = 0°$, $\varepsilon_1 = \varepsilon_3 < \varepsilon_2$; at $\theta = 30°$, $\varepsilon_1 = \varepsilon_2 > \varepsilon_3 \sim 0$. Due to the symmetry, the angle is limited to $0° < \theta < 30°$.

The magnitudes of the strain and the strain energy of each bond vary with the relative direction between the strain and the bond orientation. It is expected that at $\theta = 0°$ and $30°$, maximal and minimal (zero) band splitting happens, respectively; at $0° < \theta < 30°$, situations are between both extremes. It is therefore not surprising that some measurements revealed band splitting[4] and some did not.[5,19]

The well measured Raman shifts[4,5] as a function of the tensile strain enabled the verification of the derived formulations. In the numerical calculations, the known effective bond length $d_g = 0.142$ nm and the $z_g = 5.335$ for bulk graphite, the $z = 3$ for the single layer graphene, and the $m = 2.56$ for carbon were taken as input parameters. We also assume all the experimental data used are sufficiently accurate.
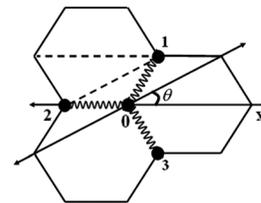

FIG. 1. Illustration of the anisotropic response of the C-C bonds to the uniaxial strain (arrowed line) applied to the C_{3v} graphene. The numbers indicate the atoms bonding to the atom at the origin. There are two extreme situations: at $\theta = 0°$, $\varepsilon_1 = \varepsilon_3 < \varepsilon_2$; at $\theta = 30°$, $\varepsilon_1 = \varepsilon_2 > \varepsilon_3 = 0$. Due to the symmetry, the angle is limited to $0° < \theta < 30°$.
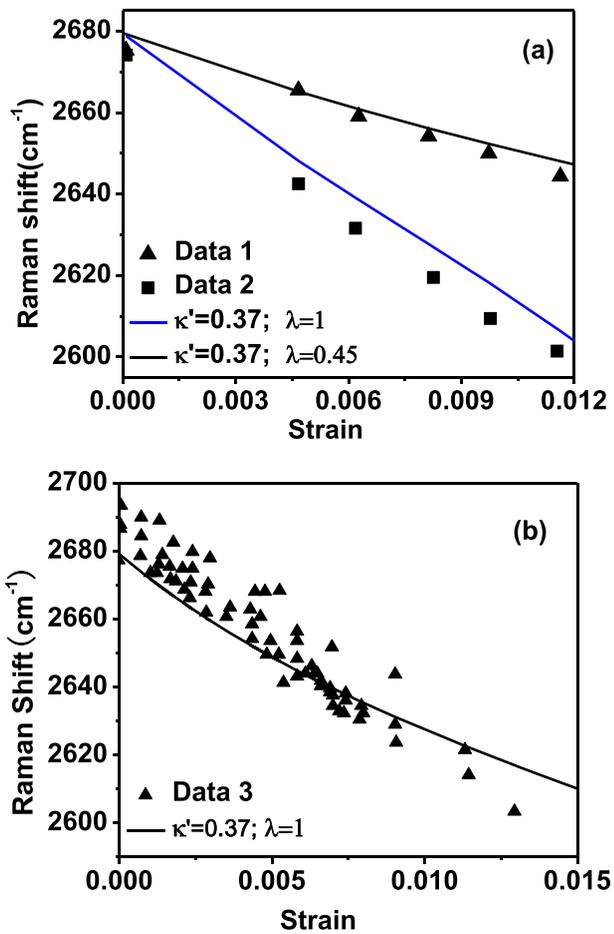
FIG. 2. BOLS reproduction of the measured uniaxial and tensile strain dependence of the 2D Raman shifts (a) $\theta = 0°$ with (Data 1 and 2)[4] and (b) $\theta = 30°$ without band splitting (Data 3).[1] $k' = 0.37$ is the reduced and $k = 11.8$ N/m the force constant of the C-C bond. The $\varepsilon' = \lambda\varepsilon$ is an effective strain of the branch of the slower-shift in (a).

Errors in measurements will affect the derivatives but not the nature and the trends of the observations. Modeling reproduction of the measured ε dependence[4,5] of the Raman shift, as shown in Fig. 2, leads to the estimation of the $\kappa' = \kappa d_z^2/(2E_z) = 0.37$, and the $\kappa = 7.87$ N/m. From the C_{3v} bond configuration shown in Fig. 1, and the derived effective force constant $\kappa = 7.87$ N/m, we can estimate the force constant of the C-C bond in the single layer graphene. We may define the C-C bond force constant k_0, the bonds labeled 1 and 3 are approximated as in parallel and the resultant $\kappa_{13} = 2\ \kappa_0$. This resultant bond connects with bond 2 in series, and therefore, the resultant force constant of the three bonds is $\kappa_{123} = \kappa = 2\kappa_0/3$. Hence, the force constant for the single C-C bond is $\kappa_0 = 3\kappa/2 \sim 11.8$ N/m.

Hence, an extension of the BOLS notion to including the directional strain has enabled us to clarify that: (i) the elongating and weakening of the C-C bond dominates the phonon softening and (ii) the mismatching between the uniaxial strain and the C_{3v} bond geometry dictates the phonon band splitting. If the strain is along a certain bond, maximal band splitting happens; if the strain is perpendicular to a bond, no band splitting occurs. Consistency between predictions and measurements has led to the quantitative information of the force constant of the C-C bond in the graphene to be 11.8 N/m, which is beyond the scope of available approaches.

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