Effects of Layer Stacking on the Combination Raman Modes in Graphene

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Abstract We have observed new combination modes in the range from 1650 to 2300 cm⁻¹ in single-(SLG), bi-, few-layer and incommensurate bilayer graphene (IBLG) on silicon dioxide substrates. A peak at ~1860 cm⁻¹ (iTALO) is observed due to a combination of the in-plane transverse acoustic (iTA) and the longitudinal optical (LO) phonons. The intensity of this peak decreases with increasing number of layers and this peak is absent for bulk graphite. The overtone of the out-of-plane transverse optical (oTO) phonon at ~1750 cm⁻¹, also called the M band, is suppressed for both SLG and IBLG. In addition, two previously unidentified modes at ~2200 and ~1880 cm⁻¹ are observed in SLG. The 2220 cm⁻¹ (1880 cm⁻¹) mode is tentatively assigned to the combination mode of in-plane transverse optical (iTO) and TA phonons (oTO+LO phonons) around the K point in the graphene Brillouin zone. Finally, the peak frequency of the 1880 (2220) cm⁻¹ mode is observed to increase (decrease) linearly with increasing graphene layers.

Keywords: Graphene - Raman - spectroscopy - double resonance - combination

Single layer (SLG) and bilayer graphene (BLG) have recently attracted much attention from the research community, mainly due to their extraordinary electronic properties, which are interesting for both fundamental and applied sciences. SLG and BLG are quite different from each other with respect to their band structure. SLG is a semimetal with a vanishing density of states at the Fermi level, while AB-stacked BLG possesses massive Dirac fermions with a transverse field-tunable band gap. On the other hand, incommensurate BLG (IBLG) behaves in a similar fashion as SLG with reduced Fermi velocities.

Raman spectroscopy is the standard technique to distinguish between SLG, BLG, IBLG, and graphene samples with a few layers (FLG). The most commonly used Raman signature for layer thickness is a peak occurring at ~2700 cm⁻¹ called the 2D (also called the G' band), which is an overtone of the disorder-induced D band located at ~1350 cm⁻¹. Both the D and 2D bands occur due to an intervalley double resonance Raman process where the D band phonon scattering is a second order process mediated by a defect, while the 2D band occurs due to scattering by two phonons and does not need any defects for activation. The 2D band in SLG can be fit to a single Lorentzian peak and its intensity has been found to be much higher than that of the G band (located at ~1580 cm⁻¹) for SLG; hence it is often used as an indicator of an SLG region. On the other hand, the 2D band in BLG can be clearly deconvoluted into four Lorentzian peaks and its intensity is lower than that of the 2D band in SLG on silicon dioxide. As the number of layers increase to more than 3 the 2D band evolves into a two-peak structure along with a concomitant decrease in intensity with respect to the G band. It has recently been shown that IBLG can be distinguished between SLG and BLG by the presence of a new defect-induced peak (I band) located on the high-frequency side of the D band (Figure 1a). The I band appears due to one layer imposing a perturbation on the other and is a signature for the presence of non-AB stacked graphene. Moreover, the frequency of the I band depends on the angle of orientation between the folded and parent graphene layer. In another recent report, other weak intensity peaks between 1650 and 2150 cm⁻¹ have been observed from SLG and IBLG. These weak intensity peaks were assigned to combination modes that occur due to a double resonance Raman scattering process involving the in-plane transverse optical (iTO), longitudinal optical (LO), and in-plane transverse acoustic (iTA) phonons. We have performed detailed investigations of the combination modes involving iTO, LO, and iTA phonons in SLG, BLG, FLG, and IBLG and report three new features in
the region between 1650 and 2300 cm$^{-1}$. (1) We observe a previously unidentified dispersive mode at $\sim$1880 cm$^{-1}$ (iTALO$^-$) when excited with $E_{\text{laser}} = 2.33$ eV in SLG, which strongly depends on the number and stacking order of graphene layers. This mode is tentatively assigned as a combination of the out-of-plane transverse optical and longitudinal optical (oTO + LO) phonons around the K point in the graphene Brillouin zone. (2) Another previously unidenti-

died mode is observed at $\sim$2220 cm$^{-1}$ in SLG (when excited with $E_{\text{laser}} = 2.33$ eV). This mode has a negative dispersion with respect to laser energy and is tentatively assigned as a combination of the ITA and iTA phonons (iTOTAL mode) around the K point. (3) The combination modes involving the LO phonon (iTALO$^-$, iTALO$^+$, and LOLA modes) upshift in frequency with increase in the number of graphene layers, while the iTOTAL mode frequency downshifts with increasing graphene layers. An additional stiffening of all the combination modes is observed for IBLG.

RESULTS AND DISCUSSION

Figure 1a shows the D and G band region and the G$'$ band regions from the graphene samples collected using $E_{\text{laser}} = 2.33$ eV. Also included in Figure 1 are spectra collected from bulk graphite (HOPG). The D band intensity is very low across all graphene samples and is negligible for HOPG. Not surprisingly, the $I_D/I_G$ value for IBLG is the highest and it decreases in general as the number of layers increase as shown in the inset in Figure 1a. In addition, a second peak in the D band region can be observed in the IBLG spectrum. This peak, called the I band, appears at 1374 cm$^{-1}$ and can be used as a metric for identification of IBLG (see Figure S1 in the Supporting Information for a magnified view of the I band). The 2D band from SLG, BLG, FLG, and HOPG can be fit to 1, 4, 2, and 2 Lorentzian peaks, respectively, thus confirming the presence of 1, 2, few layer graphene and bulk graphite (Figure 1b). The Raman signature from IBLG is different from both SLG and BLG, where the 2D band intensity is higher than the G band, but reverts to a single Lorentzian peak similar to SLG with a blue-shifted (3–7 cm$^{-1}$) frequency.$^{14,15}$

Figure 2a shows peaks in the region between the G and G$'$ bands (1650–2300 cm$^{-1}$), which are typically much lower in intensity compared to the other peaks in the Raman spectra of graphene. The strong dependence of peak frequencies and intensities of these modes on the number of layers can be observed clearly in Figure 2a. The lowest frequency peak in Figure 2a appearing at $\sim$1750 cm$^{-1}$ is a double peak feature called the M band, which is an overtone of the oTO phonon and has been observed in graphite and single-walled nanotube (SWNT) samples.$^{16,17}$ The M band, which is activated by strong coupling between graphene layers, is suppressed for SLG and IBLG as observed previously.$^{14}$ In addition, the lower frequency peak in the M band (M$^-$) is downshifted by $\sim$20 cm$^{-1}$ in BLG compared to FLG or HOPG (vertical dashed line in Figure 2a). The peak at $\sim$1860 cm$^{-1}$ in SLG has been assigned to a combination of the iTA phonon and the LO phonon and can be called the iTALO$^-$ mode.$^{14,16}$ However, instead of a single peak as reported in previous studies,$^{14,16}$ we observe a two-peak structure for this mode. Furthermore, the intensity of both peaks clearly decreases with increasing layers in graphene. We also observe these peaks in SLG samples on other substrates such as mica and quartz, confirming that the peaks are intrinsic to graphene and not a substrate effect. The third set of peaks in the range shown in Figure 2a occur due to combinations between the iTA + LA (lower frequency peak) and LO + LA phonons (higher frequency peak).$^{14}$ It has recently been shown that the higher frequency LOLA peak is more sensitive to defects and decreases in intensity upon heat treatment.$^{18,19}$ Finally a previously unidentified peak at $\sim$2220 cm$^{-1}$ is observed in all graphene samples and its origin is discussed below.

Two novel features can be observed from Figure 2a. A new mode appears at $\sim$1880 cm$^{-1}$ (iTALO$^-$) as a shoulder on the higher frequency side of the iTALO$^-$ peak in SLG. In addition, this new mode is greatly suppressed in IBLG in contrast with SLG and BLG, indicating that it is very sensitive to the stacking order of graphene layers. As such, we refer to the absence of this mode as an indicator for IBLG. We tentatively assign this peak to a combination of the oTO and LO phonons around the K point of the graphene Brillouin zone, as explained below. The second new feature in...
Figure 2a is the appearance of a peak at \( \sim 2220 \text{ cm}^{-1} \) that has not been seen previously in graphene samples. This peak has, however, been observed in single-walled carbon nanotubes (SWNTs)\(^{20}\) and is tentatively assigned as a combination of the iTA and iTO phonons around the K point in the graphene Brillouin zone.

Figure 2b plots the frequencies of all the combination modes between 1650 and 2300 \( \text{cm}^{-1} \) (iTALO\(^-\), iTALO\(^+\), ITOLA, LOLA, and iTOTA modes) for graphene samples with increasing layers. The iTALO\(^-\) mode is absent for HOPG. The peaks involving the LO phonon, namely the iTALO\(^-\) and LOLA peaks, increase in frequency due to increasing layers, while the iTOLA peak at \( \sim 1970 \text{ cm}^{-1} \) remains more or less at the same position. The iTALO\(^+\) peak is also observed to increase in frequency, suggesting that it occurs due to the involvement of the LO phonon, analogous to the iTALO\(^-\) and LOLA modes. In addition, the frequency of the iTOTA mode at \( \sim 2220 \text{ cm}^{-1} \) (inset in Figure 2b) is observed to decrease with increasing graphene layers. The frequency increases of the iTALO\(^-\), iTALO\(^+\), and LOLA modes indicate a high degree of sensitivity of these modes to the stacking order of graphene layers. All the combination modes in IBLG are further upshifted in frequency compared to both SLG and BLG. While multiple mechanisms may be involved in the added frequency upshift observed in IBLG, the possibility of compressive strain (or change in restoration force for the phonon vibrations) is higher for incommensurately stacked graphene layers as opposed to AB-stacked graphene. Hence, the upshift may occur due to added stiffening of the vibrational modes. We confirmed that the relative shift of all the combination modes is maintained between the unfolded SLG and IBLG regions on the same sample, suggesting that the results shown in Figure 2b are not due to variations in electronic doping of different samples.

Interestingly, we find that all the combination mode frequencies exhibit an almost linear dependence on \( 1/n \) according to the following relationship: \( \omega(n) = \omega(\infty) + \beta/n \), where \( n \) is the number of graphene layers, and \( \beta \) is a constant (Figure 3). Such a linear dependence on \( 1/n \) has been observed previously for the G band phonons in exfoliated graphene.\(^{10}\) As seen in Figure 3, the values of \( \beta \) for the iTALO\(^-\) (\( \sim 13 \text{ cm}^{-1} \)) and LOLA (\( \sim 21 \text{ cm}^{-1} \)) are comparable to shifts caused by the van der Waals interactions (\( \sim 12-13 \text{ cm}^{-1} \)) in the radial breathing modes of bundled SWNTs,\(^{21}\) indicating that the upshifts of these modes are due to van der Waals interactions caused by layer stacking rather than changes in the electronic band structure. On the other hand, the high \( \beta \) value for the iTALO\(^+\) mode (\( \sim 68 \text{ cm}^{-1} \)), which occurs due to a higher frequency shift with increasing graphene layers, suggests that this mode may be more sensitive to the electronic structure of graphene, similar to the 2D band.

The dispersion of the combination modes discussed above versus laser energy is shown in Figure 4. The iTOLA and LOLA modes upshift with laser energy by 204 and 223 \( \text{cm}^{-1}/\text{eV} \), respectively. These dispersions are similar to the peak dispersions of the iTOLA and LOLA modes in graphite and SWNTs.\(^{17,19,22}\) In addition, the dispersion of the iTALO\(^-\) mode is \( \sim 140 \text{ cm}^{-1}/\text{eV} \), similar to the value reported recently by Cong et al.\(^{14}\) while the dispersion of the iTALO\(^+\) mode is a little
higher (∼150 cm$^{-1}$/eV). One could consider the two peaks around 1860 cm$^{-1}$ to occur in a similar fashion as the M band at ∼1750 cm$^{-1}$, which also consists of two peaks. The two-peak structure of the M band has been explained in the context of double resonance Raman scattering with the lower frequency (M$^{-}$) peak attributed to scattering by a phonon with a momentum double that of the scattered electron ($q \approx 2k$), and the higher frequency (M$^{+}$) peak due to scattering by a phonon with near-zero momentum ($q \approx 0$). This explains the fact that the M$^{+}$ peak does not disperse with laser energy while the M$^{-}$ peak downshifts with increasing laser energy. However, both the iTALO$^{-}$ and iTALO$^{+}$ modes are observed to shift with laser energy with similar dispersions, ruling out the $q \approx 0$ phonon within the framework of double resonance theory. Furthermore, the relative intensity between the iTALO$^{-}$ and iTALO$^{+}$ modes changes dramatically for IBLG. The inset in Figure 4 shows the ratio of peak intensities of the iTALO$^{+}$ and iTALO$^{-}$ modes plotted for SLG, IBLG, BLG, and FLG. An obvious decrease in the ratio for IBLG can be observed, suggesting that the iTALO$^{+}$ peak is quite sensitive to the interlayer interaction of individual graphene layers.

A recent theoretical study predicted the absence of infrared modes in non-AB-stacked graphene. The suppression of the iTALO$^{+}$ mode in IBLG could therefore occur due to the involvement of the infrared active oTO phonon. In addition, the iTALO$^{+}$ mode is observed to upshift with increasing graphene layers in a similar fashion as the iTALO$^{-}$ and LOLA modes (Figure 2b), suggesting that the LO phonon could be responsible for the iTALO$^{+}$ mode. In fact, for the iTALO$^{+}$ peak in HOPG at ∼1940 cm$^{-1}$ (see Figure 2b), a good agreement can be found for a combination of the oTO (∼620 cm$^{-1}$) and LO phonon (∼1350 cm$^{-1}$) around the K point of the graphene Brillouin zone. Moreover, for the excitation ranges used in this study, the dispersions of the oTO and LO phonons around the K point are both positive and could account for the ∼150 cm$^{-1}$/eV dispersion of the iTALO$^{+}$ mode. On the basis of the above arguments we tentatively assign the iTALO$^{+}$ mode as a combination of the oTO and LO phonons around the K point of the graphene Brillouin zone.
zone. It is worth mentioning that second order modes with large dispersions (such as the iTOLA and LOLA modes) typically occur due to the combination of an acoustic and optical phonon, yet these other modes do not fit our data. Further theoretical and experimental studies are needed to understand why this particular combination mode appears for single layer and AB-stacked graphene but not IBLG.

The second previously unidentified mode in SLG at ∼2220 cm⁻¹ (for \(E_{\text{laser}} = 2.33\) eV) has a negative dispersion with laser energy and the peak frequency downshifts with increasing excitation energy by ∼−56 cm⁻¹/eV (Figure 4). A peak at ∼2200 cm⁻¹ has been observed in SWNTs but was left unassigned. Moreover, as shown in Figure 2b, the peak at ∼2200 cm⁻¹ downshifts in frequency with increasing graphene layers in contrast to the other modes involving the LO phonon. The iTA branch around the K point has a negative dispersion and peaks around 1100 cm⁻¹ corresponding to the iTA phonon have been observed in graphite whiskers and carbon nanotubes. However, the dispersion of the iTA branch is ∼−75 to 100 cm⁻¹/eV, which implies that the dispersion of its overtone would be twice as much. This makes it unlikely for the 2220 cm⁻¹ peak to be the overtone of the iTA phonon. On the other hand, a combination of the iTA phonon (at ∼940 cm⁻¹) and iTO phonon (∼1350 cm⁻¹) around the K point could account for the 2200 cm⁻¹ mode. The iTO phonon branch has a positive dispersion (∼50 cm⁻¹/eV) while the iTA branch has slight negative dispersion (∼−20 cm⁻¹/eV) around the K point of the graphene Brillouin zone. However, there is limited experimental data available for the iTO phonon branch around the K point of graphite (or graphite) and this ambiguity could account for the −56 cm⁻¹/eV dispersion observed for the 2220 cm⁻¹ combination mode. We thus assign this mode as a combination of the iTA and iTO phonon (hence the name iTOTA) around the K point of the graphene Brillouin zone.

CONCLUSIONS
In summary, we have observed changes in various combination modes in the Raman spectra of graphene that depend on the number and stacking of layers. The overtone of the infrared active oTO phonon, also called the M band, disappears for SLG and non-AB-stacked bilayer samples, indicating that the M band is strongly dependent on stacking order of graphene layers. In addition, the lower frequency peak within the M band (M⁻ peak) downshifts by ∼20 cm⁻¹ for BLG compared to FLG and HOPG. A peak at ∼1860 cm⁻¹ is attributed to iTA + LO phonons, and its intensity is observed to decrease with increasing graphene layers. Moreover, the iTALO band can be deconvoluted into two peaks, with similar dispersions versus laser energy. The higher frequency peak at ∼1880 cm⁻¹ has a similar dispersion as the iTALO band and shows a strong dependence on the stacking order of graphene layers. This peak is assigned to a combination of the oTO and LO phonons around the K point in the graphene Brillouin zone. A peak at ∼2200 cm⁻¹ is observed for all graphene samples and is assigned to a combination of the iTA and iTO phonons around the K point. The peak frequencies of all the combination modes involving the LO phonon are observed to increase linearly with increasing graphene layers, indicating a strong coupling of the LO phonon between graphene layers.

METHODS
The graphene samples having various layers were prepared by using the standard mechanical exfoliation method from HOPG on 280 nm SiO₂/Si substrates (see Figures S2 and S3 in the Supporting Information for optical microscope images of the samples). The presence of SLG, IBLG, BLG, and few layer graphene (FLG) areas were confirmed by atomic force microscopy (AFM) and micro-Raman spectroscopy. Raman spectra were acquired with a Renishaw InVia Raman microscope using \(E_{\text{laser}} = 1.96, 2.33,\) and 2.41 eV. The incident laser beam was focused by a 50× objective and the laser power on the samples was kept to a minimum to avoid heating. All the Raman spectra...
were normalized with respect to the G band intensity and were baseline corrected prior to Lorentzian line shape analysis.

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Supporting Information Available: Raman spectra in the D band region from IBLG and SLG showing the I band at 1374 cm$^{-1}$ in IBLG and optical microscope images (50× magnification) of the SLG, BLG, FLG, and IBLG samples used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


