Successful isolation of graphene and subsequent experiments that reveal its special properties have generated excitement to explore the novel properties of the two-dimensional (2D) crystal from various disciplines. Advances in synthesis and experimental techniques enable the finding of other 2D crystals and the artificial fabrication of multiply-stacked structures. Often, the stacking structures lead to very unusual electronic properties different from those of constituent 2D crystals depending on how they are piled up. Among them, bilayer graphene (BLG), which is a stacked structure of two single-layer-graphene (SLG) sheets, is unique in electronic structure and exhibits colorful variation in low energy states when its layer stacking is changed. The in-plane three-fold rotational and mirror symmetries and the decoupling of strong $\pi$ and weak $\sigma$ bonds of carbon atoms authorize the uniqueness of graphene systems. As such, the interlayer coupling in BLG, while a weak van der Waals type, produces interesting variations in low energy band structures upon changes of stacking geometries. For example, its low-energy states in the Bernal stacked pristine form has quadratic energy bands but change to have linear bands when it has a rotational stacking fault. And, a sensitive electronic topological transition is also predicted for sliding systems. Interplay of the interlayer interaction, the electron-phonon coupling, and the stacking fault by layer slidings are thus expected to produce drastic changes in its low energy properties. Control of its electronic property is also enabled by manipulating such changes.

Recently, an epitaxially grown BLG on the vicinal surfaces of silicon carbide shows misalignment between two graphene layers exhibiting a complex nature of its electronic structures. Moreover, recent experiments on CVD bi- and trilayer graphene also reveal possible misaligned layers at the domain walls in between two ideally stacked graphene systems. Immediate questions are how such structural variations are reflected in spectroscopic features and whether the misalignment of layers can be detected or not. Raman and infrared (IR) spectroscopies have proven to be powerful non-destructive methods to study physical and chemical properties of 2D crystals. Physical properties of graphene under various conditions such as doping or mechanical strains have been verified using such tools. In consideration of the rapid progress of research in this field, comprehensive analysis of the spectroscopic features of sliding BLG will provide key information on the stacking geometry, the electron-phonon interactions, and low energy excitations.

In this paper, we study long wave-length optical phonon modes responsible for Raman and IR spectrum when two layers of BLG slide each other. We investigate how the tiny atomic misalignment between two layers changes its phonon frequencies and spectroscopic spectrum using first-principles calculations. It is found that the degeneracy of IR-active modes is immediately lifted by the sliding and each mode changes separately depending on sliding geometries. Unlike the behavior of IR modes, the frequencies of doubly degenerate Raman-active optical phonons do not change at all in all sliding circumstances. Such unconventional optical phonon splittings originate from the difference in their frequency renormalizations due to interlayer couplings, which is confirmed by our effective model Hamiltonian calculations. Moreover, we demonstrate that, owing to its changes in the crystal-symmetry, non-resonant Stokes Raman-scattering intensities associated with Raman-active phonons exhibit a strong polarization dependence so that they can be used to detect sub-Angstrom misalignment between two layers in sliding BLG.

RESULTS AND DISCUSSION

Figure 1 illustrates the sliding geometry of graphene layers in BLG. When the sliding vector $\vec{d}$ is along $-\vec{d}_1$, the BLG gradually transforms from its pristine form of
AB-stacking (designated as AB-BLG) to AA-stacking ($d = -\delta_1$) in which all carbon atoms are right on top of each other (AA-BLG). For the sliding along $+\delta_1$, the AB-BLG becomes upside-down AB-stacked BLG (BA-BLG). Equivalent layer stackings are arranged by other sliding vectors along either $\pm \delta_2$ or $\pm \delta_3$ direction. Also combination of the sliding vectors is possible as drawn in Fig. 1(a).

Among the phonon modes at $\Gamma$-point in the Brillouin zone (BZ) of AB-BLG, high-frequency $E_g$ [Fig. 1(b)] and $E_u$ optical modes [Fig. 1(c)] are responsible for the Raman G-band and IR-peak, respectively \cite{17, 18}. The in-plane atomic motions in the upper and lower layers [Figs. 1(b) and (c)] are in-phase and out-of-phase for $E_g$ and $E_u$ mode, respectively. These modes are doubly degenerate as denoted by thick red arrows for longitudinal optical (LO) mode and by blue ones for transverse optical (TO) mode as shown in Figs. 1(b) and (c). Our calculated phonon frequencies of $E_u$ and $E_g$ modes in AB-BLG are 1592 cm$^{-1}$ and 1585 cm$^{-1}$, respectively (Fig. 2), in good agreement with previous studies \cite{21, 22}. As these two modes involve with the interlayer stacking as well as the crystal symmetry, the sliding motion of two graphene will imprint its effect on these modes.

First, we find that the sliding in AB-BLG lifts the degeneracy of optical phonon modes immediately with the splitting size depending on both the sliding geometries and the symmetry of the phonon modes [Fig. 2]. The degeneracy is recovered when the sliding ends up in AA-BLG [Fig. 2]. This finding is readily understood from the crystal symmetry of AB- and AA-BLG that guarantee the degeneracy of TO and LO modes for $E_u$ and $E_g$ phonons. However, $E_g$ and $E_u$ phonon modes exhibit completely different responses to the sliding because of their atomic motions (one in-phase and the other out-of-phase). The frequencies of IR-active $E_u$ phonon modes are apparently split into two modes upon sliding with a strong dependence on the sliding vectors [Fig. 2]. On the other hand, the frequencies of Raman-active $E_g$ modes are seemingly unaffected at all by the sliding motion although the exact degeneracy does not hold any more as Fig. 2 illustrates. We observe that the splitting between TO and LO phonons is as large as 20 cm$^{-1}$ for $E_u$ mode but no more than 1 cm$^{-1}$ for $E_g$ mode.

To understand the intriguing behavior of optical phonons upon the sliding, we construct a minimal model of the phonon modes in sliding BLG. From our \textit{ab initio} calculations for in-plane atomic displacements, we find that the interlayer ion-ion interaction energy changes very little (less than 10%) compared with the interlayer ion-electron interaction. So, additional force constants that account for the renormalization of in-plane phonon frequencies by the interlayer electronic hopping are sufficient to include into the conventional force-constant model. Within the harmonic approximation, the phonon frequency of BLG ($\omega_\alpha$ for $E_g(u)$ mode) at $\Gamma$-point can be expressed as $\omega_\alpha^2 = \omega_\alpha^2 + \xi_\alpha/m_c$, where $\omega_\alpha$ is the frequency of $E_{2g}$ phonon modes of SLG and $\xi_\alpha$ is the effective force constant for the $E_g(u)$ phonon-renormalization owing to the interlayer electron hopping in BLG ($m_c \simeq 1.99 \times 10^{-25}$g is the mass of carbon atom) \cite{24}. The Hamiltonian for BLG with a sliding vector $d = (d_x, d_y)$ \cite{11, 12} can be written as $H_{\text{total}} = H_{\text{intra}} + H_{\text{inter}}$ where the intralayer Hamiltonian is $H_{\text{intra}} = \sum_\alpha \Pi \hat{c}_{B\alpha}^\dagger (\vec{p}) \hat{c}_{A\alpha} (\vec{p}) + (\text{h.c.})$ and interlayer interaction $H_{\text{inter}} = \pi \langle \delta \rangle c_{B1}^\dagger (\vec{p}) c_{A2} (\vec{p}) - \gamma_1 c_{A1}^\dagger (\vec{p}) c_{B2} (\vec{p}) + (\text{h.c.})$. Here $c_{\alpha \alpha}^\dagger (c_{\alpha \alpha}^\dagger)$ is an annihilation (creation) op-

![FIG. 1: (color online) (a) $\delta_i (i = 1, 2, 3)$ are vectors connecting the nearest neighbor carbon atoms in each layer. The sliding vector in the upper layer is denoted by $\vec{d}$. From the left to the right, top views of BLG for $d = 0, \frac{1}{2} \delta_1, -\frac{1}{2} \delta_1$, and $\frac{1}{4} (\delta_1 - \delta_2)$. (b) and (c), in-plane atomic displacements for $E_g$ and $E_u$ optical phonons, respectively. For each phonon mode, doubly-degenerate atomic motions are denoted by red (LO-mode) or blue (TO-mode) arrows with carbon atoms of the same color moving in the same direction. Vertical dashed-lines are guides for eyes to the nearest interlayer carbon atoms (A2 and B1).](image)

![FIG. 2: (color online) Variation of optical phonon frequencies as a function of sliding distance and direction. Red filled circles (blue filled rectangles) are frequencies for IR-active LO (TO) modes and black empty circles and empty rectangles denote two Raman-active modes. The sliding vectors are shown in the bottom abscissa and corresponding stacking geometries in the top. The $\alpha$- ($d = \frac{1}{2} \delta_1$) and $\beta$-stacking ($d = -\frac{1}{2} \delta_1$ or $\frac{1}{4} (\delta_1 - \delta_2)$) geometries are shown in the second and third panels of Fig. 1(a), respectively.](image)
phonon frequency. Since E, the interlayer nn distance, γ₁(t/10) and γ₃(γ₁) the nn and the next nn interlayer-hoppings, respectively, and β ~ αₙ²

With an intralayer-electron-phonon coupling constant of g ≃ 58 eV/nm, we investigate their spec-

tations explain the different responses of Raman-active optical phonon modes, respectively, which can be
defined as Πₓ = Πₓ(u) ≃ γ₁(u) + γ₃(u), Πᵧ = Πᵧ(u) ≃ γ₁(u) + γ₃(u) [29–31]. Here u is the amplitude of E₂g phonon modes in SLG and then the atomic displacements at A and B sites in the layer α are given as \( u_{Aα} = -u_{Bα} = u_α(= u\hat{x}) \) for the LO (TO) mode [Fig. 1(b)]. With γ₁(3)(u) ≃ γ₁(3) + (Ω/2), ξₓ is obtained from the energy variation with respect to the atomic displacement,

\[ ξₓ = \frac{1}{2} gₓgₓ \int d\nu \left[ \xi_{\nu}^{∥}(u) - \xi_{\nu}^{∥}(u) \right], \quad (1) \]

where \( \xi_{\nu}^{∥}(u) = -\left[ Πₓ(u)² + Πᵧ(u)² \right] + γ₁(3)(u) + 2|Πₓ(u)Πᵧ(u) + γ₁(3)(u)|^{1/2} \) and \( \xi_{\nu}^{∥}(u) = -2|Πₓ(u)|. \)

This can be demonstrated easily by shifting \( \hat{p} - (2\nu gₓ, 0, 0) \) and \( \hat{p} + (2\nu gₓ, 0, 0) \) for LO and TO E₂g modes in Eq. (1), respectively. So, this explains the reason why sliding does not change the frequency of E₂g modes. In contrast, for Eₓu modes of AB-BLG without sliding, we find ξₓ ≃ \( \frac{3}{4}\pi gₓ² \) so that \( \omega_(d = 0) - ω_+ ≃ \frac{1}{2}\pi gₓ² mₓ c₂² \) ≃ 10 cm⁻¹ in a good agreement with our calculation in Fig. 2. With sliding along \( d = α₁(α₁ ≪ 1) \), we find that \( \Delta ω - (d) \equiv \omega - (d) - ω_- (d = 0) \propto +\frac{1}{2}\frac{γ₁(3)(u)}{mₓ c₂²} \) for the LO (TO) E₃u mode (here Λ is a dimensionless constant), which shows the splitting of two degenerate IR-active modes upon sliding as shown in Fig. 2. These calculations explain the different responses of Raman-active and IR-active phonon modes in sliding BLG.

Having understood the origin of the anomalous optical phonon splittings upon sliding, we investigate their spectroscopic consequences. Our calculations readily indicate that the sliding systems have different IR reflectivity and Raman spectrum when it is placed on insulating substrates with top or bottom gates. The single Fano-like IR spectra of gated BLG [18] will turn into the double-peak spectrum upon sliding because of the splitting in E₃u phonon frequencies. Also, its anomalous splitting in Raman G-band [23, 27, 28] due to mixing between E₉ and E₃u modes will be affected by sliding. The splitting of Raman G-band (or spectral transfer between opposite parity optical phonon modes) of gated BLG is known to originate from the inversion-symmetry breaking by the gate electric field [23, 28]. Therefore, we expect that the splitting in E₃u mode upon sliding will generate a more complex Raman spectrum in the gated structure, e.g., a three-peak structure. While the gated structure is the most straightforward way to observe the sliding-induced splitting of optical phonons, more generic ways are desirable of detecting tiny sliding on arbitrary substrates without the need of heavy doping using the field-effect transistor structure. We present below conventional Raman techniques with polarizers indeed can detect sub-

Table I: Calculated Raman tensors for various sliding vectors \( \hat{d} \). G is the Schoenflies notation of the point-group symmetry for each sliding geometry. Here, \( δ_M = δ₁ - δ₂ \). The components of all Raman tensors expressed in the vibrational symmetry-group notations are normalized to AB-BLG Raman tensor.
We directly calculate the derivative of $\chi_{ij}$ with respect to the atomic displacements corresponding to the $\nu$-th modes. Assuming an incident light with an energy of 2.41 eV, calculated Raman tensors for various sliding geometries are summarized in Table I together with corresponding crystal-symmetry groups and vibrational symmetries. Our calculations of Raman tensors for AB-BLG and AA-BLG reproduce the well-known results with $E_g$ and $E_{2g}$ symmetries. Upon sliding, changes in the crystal symmetry produce correspondingly distinctive Raman tensors. With $e_i = e_{a} = (\cos \theta, \sin \theta)$, the polarized Raman intensity for AB-BLG is given as $I = |c(\cos^2 \theta - \sin^2 \theta)|^2 + |2e \sin \theta \cos \theta|^2 = I_{AB}$ so that the intensity does not depend on the polarization angle $\theta$ [Fig. 3(a)]. This behavior is also the same for AA-BLG while with a different intensity. When the sliding direction ($\vec{d}$) is along $\pm \delta_1$, the polarized Raman intensity is given as $I(\theta)/I_{AB} = (\delta a - b)^2 \cos 4\theta + a^2 - b^2 - a^2 \cos 2\theta + I_0$ ($a$, $b$, and $d$ are given in Table I and $I_0$ is a constant). $I(\theta)$ has an elliptic shape for $a \approx b$ or quadrupolar form otherwise as shown in Fig. 3. When $\vec{d}$ deviates from the direction of $\pm \delta_1$, the polarized intensity tends to rotate as shown in Fig. 3(c). In case that the overall shape of the polarized intensity looks similar, its magnitude has a strong dependence on the sliding size [Fig. 3(b)].

**CONCLUSIONS**

In conclusion, we have shown theoretically that tiny sliding of the layers in BLGs can induce anomalous splitting of optical phonon that changes the spectroscopic features significantly. We have shown that the frequencies of the degenerate in-phase optical phonons ($E_g$ mode) are hardly changed irrespective of sliding distance and direction. On the other hand, the polarization-dependent Raman intensity associated with $E_g$ mode is modified strongly so that the sub-Angstrom misalignment between two graphene layers can be resolved by spectroscopic methods. We expect that this study will provide essential information for spectroscopic measurements and for linking local atomic structures to novel electronic properties of stacked 2D atomic crystals.

**THEORETICAL METHODS**

We calculated electronic structures and phonon dispersions of the sliding BLGs using first-principles methods with a plane-wave basis set. The local density approximation is adopted for the exchange-correlation functional, and the phonon frequencies are calculated using the density functional perturbation theory. Computations are also repeated using the atomic-orbital basis set, the generalized gradient approximation (GGA), and frozen phonon method to find almost identical results. In calculating electronic structures and phonon dispersions with the atomic orbital basis set, the basis-set superposition errors were removed by including two ghost atoms in the unit cell. A semi-empirical correction of van der Waals (vdW) forces is added to all our calculations following Grimme’s proposal, which is essential to obtain the correct interlayer distance of sliding BLGs. We note that our methods accurately describe the phonon frequencies of graphitic systems when the appropriate interlayer-distance is provided.

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