Fine Tuning of Optical Transition Energy of Twisted Bilayer Graphene via Interlayer Distance Modulation

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Twisted bilayer graphene (tBLG) represents a family of unique materials with optoelectronic properties tuned by the rotation angle between the layers. In the presented work we show an additional way of tweaking of the electronic structure of tBLG: by modifying the interlayer

distance, for example by small uniaxial out-of-plane compression. We have focused on the optical transition energy, which shows a clear dependence on the interlayer distance, both experimentally and theoretically.

Since the discovery of graphene, the tuning of its electronic structure has been one of the strongest focal points of many researchers. However, the vision of exploiting the unique properties of graphene towards the replacement of silicon in logical circuits has so far been hampered by the inability of opening a sizeable band gap in a simple, controlled and cost-efficient manner [1]. To this end, bilayer graphene (BLG) holds more promise than monolayer graphene; it offers several routes of profiting from the interactions between the two layers [2-4], e.g., by dual gating [4,5], molecular doping [6] or theoretically by mechanical deformation [7]. Similarly, the appealing concept of Bilayer Pseudo-Spin Field Effect Transistor (BiSFET) still exists only on the theoretical level [3,8,9]. It is worth noting that the interlayer distance could be one of the most important parameters controlling the excitonic gap in BiSFET [10].

Twisted bilayer graphene (tBLG), i.e. a system where the alignment of the two graphene layers deviates from the periodic (AB) Bernal stacking, has recently attracted an increased attention because in fact every tBLG with a particular twist angle represents a unique material in terms of optoelectronic properties [11]. The relative rotation of the layers leads to the formation of superlattices, which manifest themselves as Moiré patterns in high-resolution transmission electron microscopy [12] or scanning tunneling microscopy [13] studies. Importantly, the interference superlattices give rise to van Hove singularities (vHs's) in the density of states (DOS), with their energy gap dependent of the twist angle [12-14]. The vHs's cause optical coloration of the tBLG [11] and a strong enhancement of the Raman G mode when the laser excitation matches

the vHs's energy [12,15,16]. As mentioned above, the interaction between the two layers depends on the twist angle; however, the influence of the interlayer distance has never been accounted for in detail. Moreover, the interlayer space in stacked two dimensional materials provides an additional feature through the so-called van der Waals pressure acting upon molecules or crystals trapped in between the layers [17,18]. The phenomenon is, however, yet to be fully explained and understood.

In the present work, we have studied tBLG of various origin under direct uniaxial out-of-plane compression in a low stress regime. The simultaneous in-situ Raman spectroscopy measurement revealed a clear modulation of the G band enhancement indicating changes in the resonance conditions, hence in the energy of vHs's. In order to evaluate the effect of compression, we have performed theoretical calculations of the DOS of tBLG modulating both the interlayer and the in-plane C-C distance. Our calculations reveal variations of vHs's energy in dependence on the interlayer distance, as large as 200 meV, while no sizable variations are detected when decreasing the *a* lattice parameter.

Experiments. Single layer graphene samples of ^{12}C and ^{13}C were prepared by CVD method, described elsewhere [19]. Labelled bilayer graphene was obtained by sequential transfer of individual monolayers from the copper foil to a sapphire disc, using the reported wet transfer method with polymethylmethacrylate [20]. Additionally, as-grown and exfoliated ^{12}C BLG samples were studied for comparison. The experimental setup consists of a gem anvil cell coupled to a Raman spectrometer. (LabRAM HR, Horiba Jobin-Yvon). In order to perform direct out-of-plane compression a modified sapphire cell is used, where one of the anvil is substituted by a sapphire disc containing the sample. In such conditions, the use of conventional stress marker is inadequate and the stress is estimated from the evolution of the Raman features of sapphire.[21]

Raman spectra and maps were registered using an Ar/Kr laser working at 488.0 nm, 514.5 nm, 532.0 nm and 647.1 nm, keeping the power in the sample below 1 mW. A 50x objective provided a laser spot on the sample of ~1 μm. Each 0.1 and 0.5 GPa compression steps single spectrum and Raman maps (40x40 μm^2, 4-5 μm sampling steps) were registered, respectively, in selected grains fulfilling the resonant conditions at the corresponding laser excitation energy.

Calculations. A commensurate structure of tBLG is characterized by two integers (n,m). In the calculation, we use primitive vectors $\boldsymbol{T}_1=n\boldsymbol{a}_1+m\boldsymbol{a}_2$ and $\boldsymbol{T}_2=(n+m)\boldsymbol{a}_1-n\boldsymbol{a}_2$ for (n,m) tBLG [14]. Here $\boldsymbol{a}_1=a(\sqrt{3}/2,1/2)$, $\boldsymbol{a}_2=a(\sqrt{3}/2,-1/2)$, $a=|\boldsymbol{a}_1|=|\boldsymbol{a}_2|$ are the primitive vectors and lattice constant of monolayer graphene, respectively. The electronic structure and DOS of tBLG are calculated using the tight binding method [22,23] with different interlayer distance and in-plane lattice constant in order to evaluate compression effect. The adopted tight binding parameter is a function of the distance between carbon atoms [22]. The optical transition energy, corresponding to the enhancement effect of the Raman intensity, is estimated from the results. Note that optical transition between the saddle points of electronic structure is not allowed [24].

The Raman spectrum of labelled BLG has been previously reported [25]. The phonon frequency (ω) is inversely related to the atomic mass and, therefore, the Raman peaks coming from each layer can be distinguished [26]. Thus, the Raman spectrum of labelled BLG is dominated by 4 peaks: two G bands (1525 and 1590 cm^{-1}) and two 2D bands (2620 and 2710 cm^{-1}), with the lower frequency peaks being the ones corresponding to the ^{13}C [26]. Analogously, in the case that lattice disorder is present in the sample, two D bands appear at ~ 1303 and 1347 cm^{-1} (2.54 eV excitation energy).

As stated above, tBLG shows vHs´s in the density of states, with their energy gap dependent on the twist angle. When the excitation wavelength matches the energy difference between these vHs's (the optical transition energy), an enhancement of the G band intensity is observed, and the intensity ratio G/2D increases about 15 times, see Figure S1 [27]. In order to locate tBLG grains in resonance with the excitation energy used, Raman maps of 40×40 μm^2 were measured where regions with the enhanced G band can be distinguished (see Figure S2a). In Figure 1a we show the single Raman spectra acquired in the center of a tBLG grain, fulfilling the resonant conditions at 2.54 eV excitation energy, i.e. ~13º rotation angle [12], with sequentially increasing the out-of-plane compression up to 1.5 GPa, approximately. The behavior under compression in a larger stress range is presented and discussed in the Supporting Information [27]. The use of isotopically labeled tBLG allows us to expose potential disharmony in the evolution of the two layers during the high stress experiment; however, Fig. 1a shows none such. Thus, both layers in the examined tBLG (and in all other experimental runs mentioned further) manifest the same treatment.

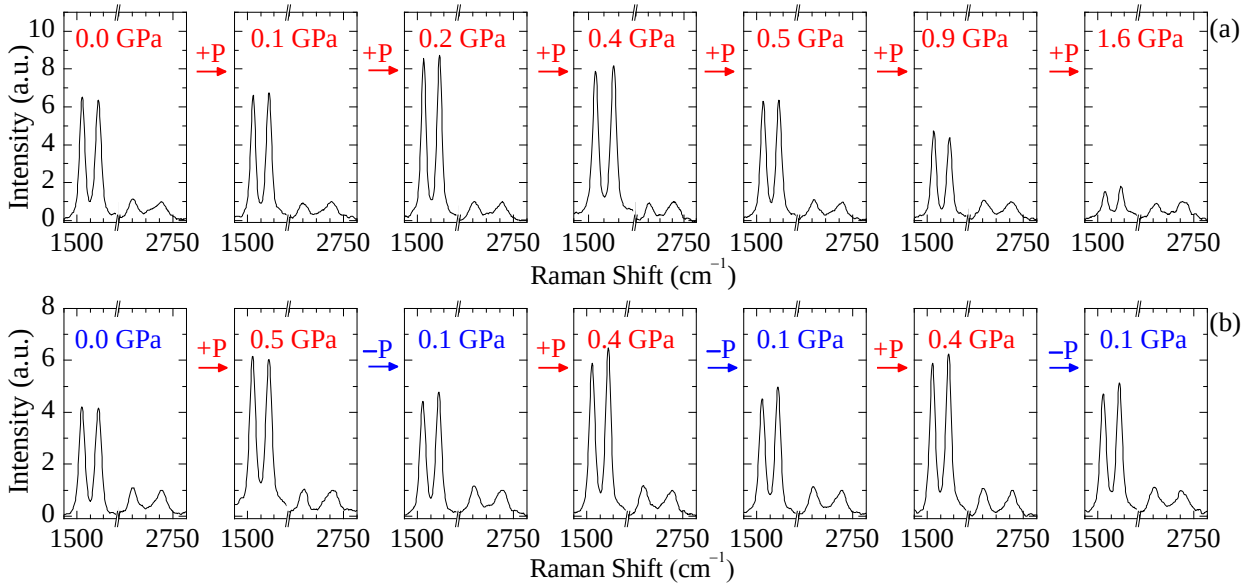

FIG. 1. Evolution of Raman spectra of $^{13}C/^{12}C$ tBLG (a) with compression up to 1.6 GPa, and (b) with stress cycling of ±0.4 GPa, approximately. Laser excitation energy of 488.0 nm.

As found out for graphite [28] and other layered materials [29] the out-of-plane compression decreases preferentially the distance between the layers, in other words, the out-of-plane compressibility is much higher than the in-plane compressibility, owing to the weak interlayer forces. At the initial stages of compression (up to 0.4 GPa) we observe an increase of the G band enhancement by a factor of about 1.5 (the G band enhancement can reach a factor of 4, depending on the sample, see Figure 2a) which is reduced to the original value at about 1 GPa. Such variation is indicating that the decrease of the interlayer distance is modifying the resonance conditions, *i.e.* modulating the electronic properties of the system. At the later stages of compression, above 1 GPa, the enhancement continues to decrease due to other factors entering the play, such as the sample disorder, as reported before [30] and discussed in the Supporting Information, Figure S4 [27].

The G band enhancement within the 0.5 GPa range warrants further investigation. In Figure 1b we present the stress performance during consecutive compression cycles of a tBLG grain. We observe that the behavior described above is reversible in the low stress range. Such reversibility confirms that the change in the interlayer distance is the main factor of the modulation of the tBLG electronic properties. While charge doping has been shown to modify the electron resonance in tBLG [31], a possible change in the doping state induced by an irreversible purging of impurities (remnant from the transfer) from the interlayer space, can be ruled out based on the reversible behavior shown in Figure 1b. A change of the rotation angle with shear stress can also be excluded

in view of Figure 1b. Moreover, additional observations based on Finite Elements (FE), compiled in the Supporting Information [27], point to only insignificant shear stresses, at least three orders of magnitude smaller than the out-of-plane compressive forces, hence no appreciable relative movement of the layers is expected.

In order to prove the universality of our findings additional experiments were performed by employing several excitation energies and analyzing different tBLG samples. In Figure 2a we present the G/2D intensity ratio evolution with stress for labelled tBLG with different twisting angles; each of them excited with the corresponding resonant laser energy in order to observe the G band enhancement. We observe that the variation of the resonant conditions is qualitatively analogous regardless the rotation angle and the excitation energy. For sure, for grains with a different twist angle the magnitude of the energy band-gap modulation may be not the same, as evidenced by the varying enhancement factor and the position of the enhancement maximum for the different excitation wavelengths in Figure 2a, and demonstrated by our theoretical calculations later on.

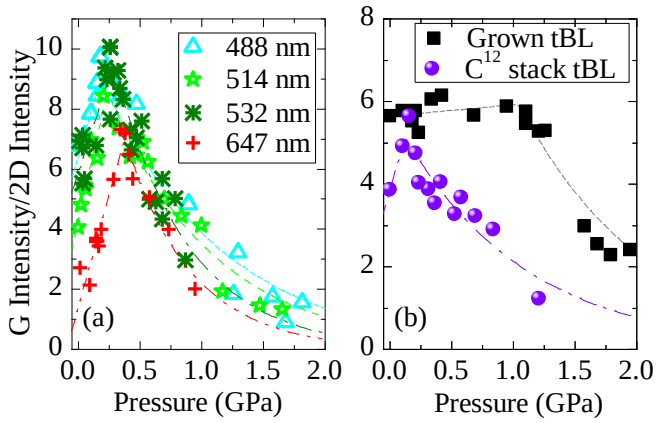

FIG. 2. Evolution of the intensity ratio G/2D with increasing stress. (a) Labelled tBLG with rotation angles of 13.0, 12.3, 11.9 and 9.8 degrees excited with 488.0, 514.5, 532.0 and 647.1 nm

laser energy, respectively, to achieve the G band enhancement in each sample [12]. The intensity ratio is obtained as $(AG_{12}+AG_{13})/(A2D_{12}+A2D_{13})$. (b) Intensity ratio G/2D with stress for ^{12}C CVD BLG (squares) and $^{12}C/^{12}C$ stack BLG (circles); both measured in a region resonant with the 488.0 nm excitation energy. Dotted lines are guides to the eye.

In Figure 2b we compare the compression behavior of as-grown ^{12}C tBLG with that prepared by a sequential transfer of two monolayers. The latter shows a compression behavior analogous to the labelled tBLG. Note that before compression, the sample consists of two layers of graphene sequentially transferred, in which remnant polymers or other impurities from the transfer may hinder a closer contact between them (see AFM analysis in the Supporting Information [27]). However, in the as-grown tBLG sample the graphene layers are originally in closer contact, and therefore the increase of the of the G band enhancement is almost absent. It is also worth noting that the maximum stress-induced enhancement in sequentially transferred tBLG is the same as the initial enhancement in the as-grown tBLG.

To further prove the effect that the interlayer distance has on the resonant conditions and therefore on the electronic properties of tBLG we perform a single compression cycle up to 0.6 GPa on a tBLG grain with a G band enhancement manifested for both the 488.0 and 514.5 nm excitation energies. Note that the G band enhancement is not the maximum possible for either of the excitation energies, which indicates that the rotation angle of the measured grain is between 13.0 and 12.3 degrees, see Figure 3. When increasing the stress, thereby reducing the interlayer distance, the resonant conditions are changed in a way that the same grain better fulfils the resonance conditions for the 488.0 nm energy, while the enhancement at 514.5 nm line

simultaneously. This result indicates that the optical transition energy for the analyzed tBLG grain has increased upon compression, becoming closer to 2.54 eV (488.0 nm).

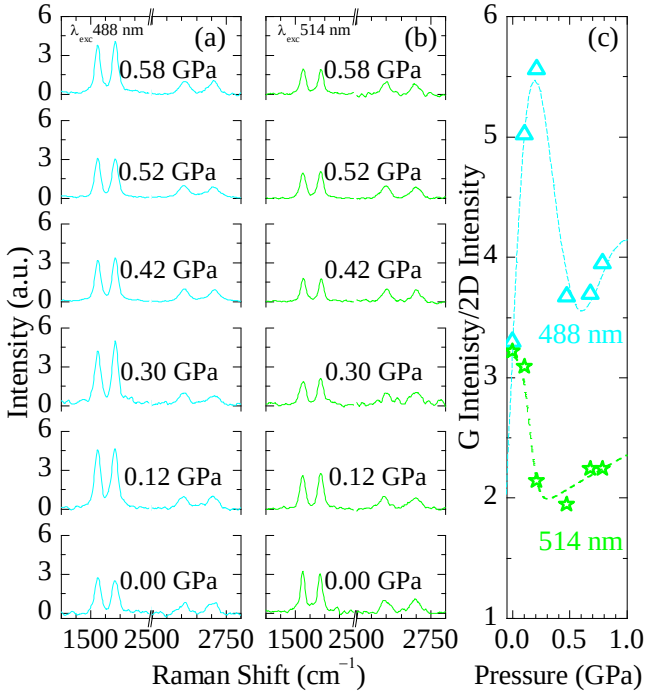

FIG. 3. Evolution of the Raman spectra of $^{13}C/^{12}C$ tBLG with compression up to 0.6 GPa. The same tBLG grain is measured with (a) 488.0 nm and (b) 514.5 nm excitation energy. (c) Intensity ratio G/2D as a function of increasing stress.

Finally, the modulation of the electronic structure of tBLG in the low stress regime, manifested by the G band enhancement, is examined with the aid of calculations, based on the tight-binding method. As an example, in Figure 4a we present the DOS of the (3,2) tBLG structure (corresponding to a ~13° rotation angle, in resonance with the 488.0 nm excitation energy [14]) at selected interlayer distances (*d*) ranging from 0.50 to 0.25 nm. We scan a wide *d* interval, of ± 0.15 nm the interlayer distance in natural BLG, in order to account for all possible experimental facts:

the decrease of *d* by means of stress and the larger *d* of pristine samples due to the preparation method [27]. We observe that both the DOS and the vHs's energy are modified by *d*. Specifically, in Figure 4b, we see that upon decreasing the interlayer distance to ~0.45 nm the optical transition energy reaches a maximum, and starts decreasing when further moving the layers closer to each other. Along the whole analyzed range of interlayer distances the optical transition energy shows variations as large as 200 meV, for the given twist angle. This variation of the optical transition energy with *d* alters the resonance conditions, thereby explaining the experimental observations where at a particular excitation energy the G band enhancement changes with stress. The theoretical behavior of (1,5) tBLG, which is slightly further of the resonance with the 488.0 nm laser (twist angle of ~15°) has been also checked; the optical transition energy follows a similar trend as in the (3,2) case, albeit with smaller energy differences, up to 80 meV.

As noted above, the tBLG under out-of-plane compression demonstrates certain, despite lower, in-plane compressibility [32], proved by the blue-shift of the Raman spectrum [27]. The influence that the in-plane compression has on the electronic properties of tBLG is presented in Figure S5 [27]. The DOS was calculated for the same (3,2) structure at a fixed interlayer distance (0.35 nm) with decreasing *a* lattice parameter values, from the equilibrium, 0.2460 nm, down to 0.24565 nm (corresponding to a >1.5 GPa in-plane compression, obtained from the equation of state of graphite) [33]. Within this *a* range only a negligible increase of the vHs's, ~1meV, is observed. Moreover, when decreasing more drastically the *a* parameter, to 0.2435 nm (estimated stress of ~10 GPa), the increase of vHs's energy obtained theoretically is lower than 10 meV, which is 20 times smaller than the observed with the interlayer distance modulation. Thus, according to our calculations, the in-plane stress as the reason for the modulation of the resonance conditions in tBLG can be discarded.

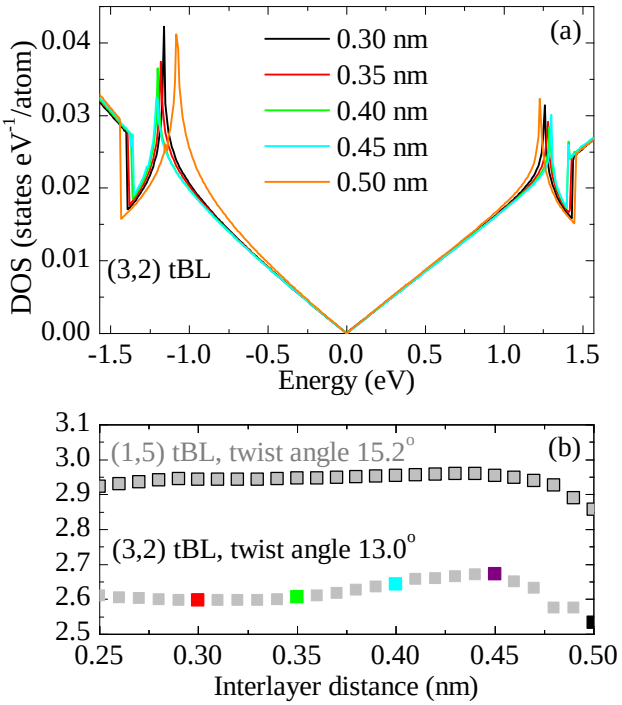

FIG. 4. (a) Density of states of (3,2) tBLG at different interlayer distances. (b) Optical transition energy as a function of the interlayer distance for (3,2) and (1,5) tBLG, squares and circles, respectively. The filled points in the (3,2) graph correspond to the curves in (a) with the same gray color.

In summary, we have shown the dependence of the energy of van Hove singularities on the interlayer distance in twisted bilayer graphene. The tight binding calculations reveal an initial increase of the optical transition energy upon decreasing the interlayer distance to ~0.45 nm, where the maximum energy is reached, followed by a gradual decrease with further moving the layers closer to each other. The theoretical results are corroborated by a compression experiment, which shows an increase of the Raman G band enhancement reflecting the changes in the resonance conditions caused by the altered vHs´s energy. The tight binding calculations also show that in-plane compression of the graphene layers is not responsible for the changes in the optical transition

energy. The sensitivity of tBLG to the interlayer distance can prove highly useful in optoelectronic applications and it might also explain the differences in the magnitude of the G band enhancement observed at a particular laser excitation for differently prepared samples.

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