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Real-Time Observation of Interlayer Vibrations in Bilayer and Few-Layer Graphene

Davide Boschetto,*[,†,‡] Leandro Malard,[†] Chun Hung Lui,[†] Kin Fai Mak,[†] Zhiqiang Li,[†] Hugen Yan,[†] and Tony F. Heinz*[,†,§]

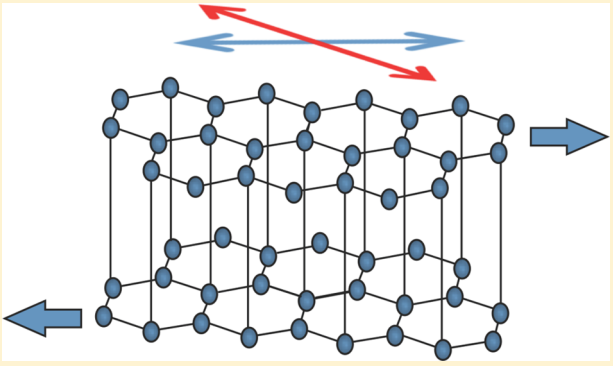
[†]Department of Physics, Columbia University, New York, New York 10027, United States

[‡]Laboratoire d'Optique Appliquée, ENSTA ParisTech/Ecole Polytechnique, 91762 Palaiseau, France

[§]Department of Electrical Engineering, Columbia University, New York, New York 10027, United States

Supporting Information

ABSTRACT: We report real-time observation of the interlayer shearing mode, corresponding to the lateral oscillation of graphene planes, for bi- and few-layer graphene. Using a femtosecond pump−probe technique, we have followed coherent oscillations of this vibrational mode directly in the time domain. The shearing-mode frequency, as expected for an interlayer mode, exhibits a strong and systematic dependence on the number of layers, varying from 1.32 THz for the bulk limit to 0.85 THz for bilayer graphene. We explored the role of interactions with the external environment on this vibrational mode by comparing the response observed for graphene layers supported by different substrates and suspended in free space. No significant frequency shifts were observed.



KEYWORDS: *Graphene, ultrafast spectroscopy, coherent phonon dynamics, adlayer and substrate interactions*

The distinctive electronic properties[1−4] of graphene and the associated potential for novel devices[5−8] have evoked great interest. Lattice vibrations in graphene have been the subject of much research, both because of their importance in characterizing properties of graphene and because of the role of strong electron−phonon interactions in the system.[9−12] While the high-frequency phonons in both single- and few-layer graphene have been extensively investigated,[3,9−11,13] our knowledge of the low-frequency phonons is much more limited. In graphite, the interlayer shearing mode is the lowest-energy optical phonon. At the center of the Brillouin zone, it has an energy of 5.5 meV or a frequency of 1.32 THz; it consists of rigid lateral displacements of adjacent graphene planes (schematic in Figure 1). Although this phonon is Raman active, its low energy renders it difficult to observe by conventional Raman spectroscopy, particularly for the reduced amount of material in few-layer graphene (FLG) samples. A recent paper has reported observation of this mode in FLG.[12]

In this paper, we investigate the shearing mode in few-layer graphene directly in the time domain by means of coherent phonon spectroscopy. Using this femtosecond pump−probe technique,[14] we are able to probe in real time the shearing mode in FLG from 15 layers down to the bilayer. The measurements provide both the shearing mode frequency and damping rate. The frequency is found to drop with decreasing thickness from the bulk value of 1.32 THz to 0.85 THz for bilayer graphene (BLG), while the damping rate remains essentially unchanged. We examine the influence of the external environment through studies of FLG deposited on different solid substrates, covered by overlayers, and suspended away from substrates.

We implemented coherent phonon spectroscopy in FLG by pumping the samples with 200 fs pulses at a photon energy of 3.1 eV (400 nm wavelength), generated as the second-harmonic of a femtosecond modelocked Ti:sapphire laser. In FLG samples, this photon energy produces $\pi \rightarrow \pi^*$ electronic transitions but does not induce transitions to other electronic bands.[15] Since the pump pulses are shorter than the oscillation period, these pulses can excite the shearing mode coherently, that is, with a well-defined phase. The resulting lattice vibrations lead to a modulation of the optical dielectric function of the FLG proportional to the magnitude of the vibration. We detect the shearing-mode vibrations by the induced changes in the reflectivity of time-synchronized 800 nm pulses from the Ti:sapphire laser. One of the challenges in the measurement is to detect the weak modulation of the coherent phonons in the presence of a stronger change in the dielectric function arising from the photoexcited electrons. We overcome this problem using a polarization-sensitive detection technique in which the reflectivity of probe beams polarized

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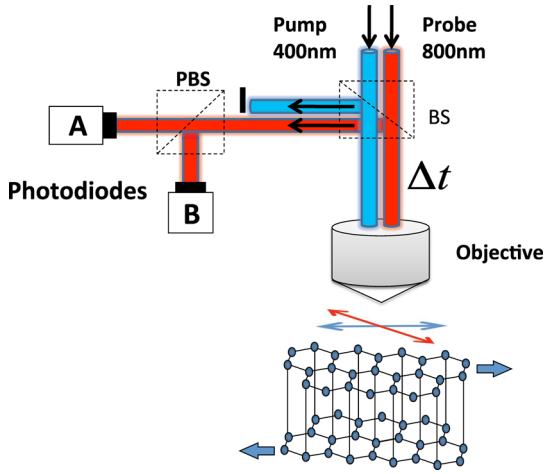

Figure 1. Experimental setup for pump and probe spectroscopy of the interlayer shearing mode in FLG graphene. The femtosecond probe pulses (red, at 800 nm) are polarized at 45° with respect to the pump pulses (blue, at 400 nm). We use a beam splitter (BS) to redirect the reflected probe beam into a polarized beam splitter (PBS), to separate the polarization components parallel and perpendicular to the pump beam. We detect the difference in intensity between the two components of the reflected probe pulses as a function of delay time. The schematic of BLG shows the displacements of the shearing mode.

parallel and perpendicular to the pump beam are compared (Figure 1). This arrangement eliminates the isotropic electronic response, while doubling the contribution of coherent phonons of the E_{2g} symmetry of the shearing mode.[16,17] (Further details about the experimental technique and the preparation of the FLG samples are provided in the Section 1 of the Supporting Information.)

We have measured the time-resolved differential reflectivity for BLG, FLG, and bulk graphite (Figure 2). In all cases, there is a clear oscillatory response with a frequency around 1 THz. In contrast, for single-layer graphene, no oscillatory response is observed, as expected for a signal from the interlayer shearing mode. For bulk graphite, the oscillations can be identified as arising from the interlayer shearing mode.[16,17] This assignment

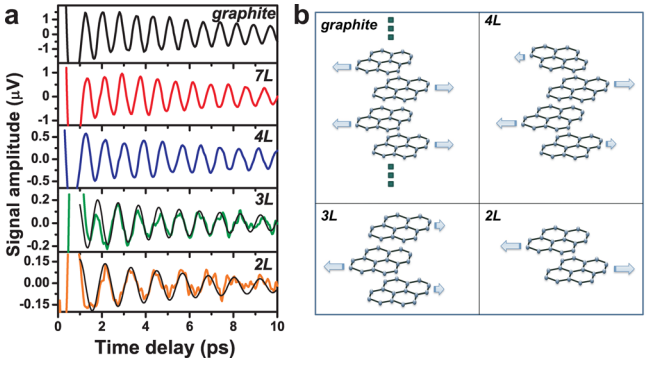

Figure 2. Real-time measurements of shearing mode oscillations and schematic representations of corresponding vibrations for FLG and graphite. (a) Transient reflectivity signals for samples of differing number of layers. For the 2L and 3L plots, the solid lines are fits using an exponentially decaying sinusoid. (b) Schematic of the high-frequency shearing vibrations for FLG and bulk graphite. The length of the arrow indicates the amplitude of the motion of the corresponding layer.

is based on symmetry restriction of our experimental arrangement, which allows only the detection of E_{2g} modes, the symmetry of the interlayer shearing mode. Further, the measured phonon frequency (1.32 THz) matches that of the shearing mode as determined by conventional Raman spectroscopy.[18] The measured frequency and damping time are also in good agreement with previous studies of bulk graphite by coherent phonon spectroscopy.[16,17] For our FLG samples, we also assign the observed oscillations to interlayer shearing mode vibrations, since the measured frequencies evolve continuously from that of the bulk limit.

In FLG, the frequency of the shearing mode is seen to decrease monotonically with decreasing the number of graphene layers (Figure 3a). We find a direct correspondence

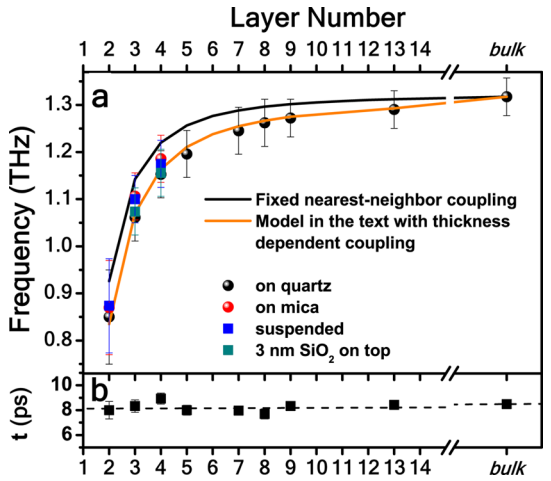

Figure 3. Dependence of the shearing-mode frequency and damping time on the number of layers of FLG samples. (a) Shearing mode frequency versus number of layers for FLG deposited on fused quartz. Also shown are shearing-mode frequencies for 2L, 3L, and 4L graphene in different environments: on fused quartz and mica, freely suspended, and on a quartz substrate with the FLG covered by an overlayer of 3 nm of SiO_2. The black line is the prediction for coupled identical harmonic oscillators; the orange line is the fit that includes a slight relaxation of the lattice spacing, as discussed in the text. (b) Damping time for the amplitude of shearing mode oscillations as a function of number of layers.

between the shearing-mode frequency and the number of layers, indicating that this phonon mode can be used to identify the FLG thickness, up to at least 10 layers. On the other hand, we observe no significant dependence of the phonon damping time on the number of layers (Figure 3b). We also remark that the data are consistent with a sine wave response. While our measurements do not provide a detailed picture of the pathway by which the coherent phonons are generated from the pump pulse, the phase of the sinusoidal response is compatible with an impulsive-stimulated Raman scattering process.[16]

As the simplest description of the shearing modes in FLG, we examine a coupled oscillator model in which we consider only interactions between adjacent layers and treat all layers as identical. We can then readily obtain frequencies for the $N - 1$ different normal modes for rigid in-plane displacements of the graphene layers, corresponding to the different branches of the shearing mode in FLG. The branch with the highest frequency corresponds to oppositely directed motion of all adjacent pairs of layers. This is the nearest analogue to the (zone-center) shearing mode in bulk graphite and is likewise Raman active.

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The frequency of this branch of the shearing mode for N-layer graphene is given by[19]

$$\omega_N = \omega_\infty \cos(\pi/2N) \quad (1)$$

where ω_∞ is the shearing-mode frequency in the bulk limit. This treatment accounts very well for the trend of the experimental data (Figure 3a). In particular, the analysis shows that the shearing-mode decreases in frequency with decreasing number of layers as a consequence of the reduced number of interlayer forces $(N - 1)$ compared to the number of graphene planes (N). The asymptotic behavior predicts that the shearing-mode frequency in BLG is lower than that of the bulk by a factor of $\sqrt{2}$. The experimental results are close to this prediction.

In our model, we have only taken into account the nearest-neighbor interlayer interactions. The influence of next-nearest neighbor interactions is reduced in the case of the shearing modes in question, since the layer displacements of next-nearest neighbor planes will be similar to one another and thus will generate little or no restoring force. The dependence of shearing-mode frequency on the number of graphene layers has been previously investigated by first-principles studies,[20−22] which yielded results similar to those presented here.

In graphite, the symmetry of the interlayer-shearing mode corresponds to the E_{2g} irreducible representation. We note that for the case of bi- and trilayer graphene, only the indicated (high-frequency) shearing mode vibration is relevant to our measurements. For BLG, only one shearing mode exists, while for trilayer graphene, there is only one shearing mode that has E_{2g}-like symmetry. For FLG with increased number of layers, however, additional Raman-active shearing modes exist. Among the different shearing-modes branches, we expect the high-frequency mode to produce the strongest Raman response. All of the other normal modes have displacements that compensate one another, reducing partially or fully the corresponding change in the susceptibility and, hence, the Raman response. The experimental data are compatible with the assumption that the high-frequency shearing mode dominates the Raman response, with no observable signal arising from other Raman-active shearing modes.

Our discussion up to this point has neglected the role of interactions of the FLG with the environment. Especially for samples of just a few layers' thickness, one would intuitively expect that the lateral motion of the exterior graphene planes could be significantly altered by the presence of a substrate or of adsorbates. One might consider, for example, a layer in contact with the massive substrate to be immobilized, thus effectively reducing the thickness of the sample and inducing a significant modification of the shearing mode frequency. To investigate these issues experimentally, we prepared graphene samples suspended over quartz trenches, as well as samples deposited on different (SiO_2 and mica[4]) substrates. To address the role of adsorbates, we examined the shearing mode in graphene samples both before and after the deposition of a 3-nm-thick SiO_2 layer on the top surface. Remarkably, for all of these modified environments we found no significant change of the shearing-mode frequency (Figure 3a). We further performed measurements in the ambient air environment and in dry nitrogen. We expect in this fashion to alter the concentration of adsorbed water molecules on the FLG. We also failed in this case to observe any meaningful change in the shearing-mode frequency.

How do we understand this seemingly counterintuitive insensitivity of the shearing mode to these very different external environments? The first observation is that the ∼1 THz shearing mode frequency is actually quite high compared to typical frequencies for frustrated translational motion of physisorbed molecules. We consequently expect the coupling of the shearing mode to such adsorbates to be relatively weak. For interactions of the graphene with solids explored experimentally, we note the absence of lattice matching between the graphene layer and the substrate. The lattice structures being incommensurate, there will for an idealized system be no overall resulting restoring force exerted on the exterior planes of the FLG sample by the substrate. Accordingly, no change in shearing-mode frequency is expected. We note, however, that very different behavior would be anticipated either for lattice-matched interactions or for strongly (chemisorbed) adlayers. A further experimental and theoretical investigation of these issues is clearly warranted.

Since we have seen that environmental factors do not significantly alter the measured shearing mode frequencies (Figure 3a), we return to an examination of the measured shearing-mode frequencies as a function of the number of layers. Although the simple coupled oscillator model provides very good overall agreement with experiment (Figure 3a), we observed a small, but systematic red shift of the experimental frequencies with respect to the predictions of this model, especially for the thin layers.

Here we propose an explanation for the discrepancy between the coupled oscillator model and the observed frequencies. We first note that in other experiments involving coherent phonon generation by excitation with ultrashort laser pulses, red-shifts have been observed associated with an electronically induced weakening of the bonds.[14] Such an explanation does not apply in this case, since the pump excitation fluence is held sufficiently low to avoid any such perturbation in the interlayer potential (see Supporting Information for more details). Rather we can explain the effect in terms of a small change in interlayer coupling with layer thickness. From measurements of the bulk behavior of the shearing mode frequency with pressure, we know that the frequency is sensitive to the interlayer spacing of the graphene planes, as described by the mode Grüneisen parameter γ. The observed decrease in the shearing mode frequencies for thin samples, in this picture, can then be attributed to a slight increase in the interlayer spacing for such samples. Just this effect is anticipated based on the nature of long-range van-der-Waals interactions between the graphene layers. As the number of layers decreases, there are fewer interlayer interactions that act to compress the sample, which leads to a very slight relaxation in the interlayer spacing. An analysis based on Lennard−Jones interactions (see Supporting Information for more details) suggests, for example, that the bilayer interlayer spacing would be increased by about 1.3% relative to bulk graphite, in agreement with a previous theoretical calculation.[23] From this analysis and an assumed mode Grüneisen parameter $\gamma = 1.72$, we fit the experimental dependence of the shearing mode frequency with the number of layers very well (Figure 3a). Further discussion of this analysis and of the value of γ is provided in the Supporting Information.

In conclusion, we have observed directly in the time domain the motion of graphene planes of the interlayer shearing-mode for bi- and few-layer graphene samples. The mode frequency was found to be insensitive to the presence and nature of

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different (incommensurate) substrates and overlayers, but to increase strongly and systematically with the number of layers. The overall behavior can be reproduced well by a system of coupled harmonic oscillators. Observed deviations from the predicted frequencies may reflect the role of a slight relaxation of the interlayer spacing in thin samples of FLG. The shearing mode response provides a natural signature of thickness in FLG, but, more importantly, opens up new possibilities for exploring the subtleties of interlayer interactions both within FLG and with the external environment. The observed insensitivity of the shearing mode to the external environment is not, for example, expected to apply for strongly bonded or commensurate systems. Since the coherently excited shearing mode corresponds to a lateral displacement of a graphene sheet, further investigations of this mode provide a route to study nanomechanical interactions in the terahertz frequency range.

■ ASSOCIATED CONTENT

Supporting Information

Details on samples preparation, ultrafast spectroscopy experiments, data analysis, and the theoretical model. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: Davide.Boschetto@ensta.fr.
*E-mail: tony.heinz@columbia.edu.

Author Contributions

D.B. and L.M. contributed equally.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

FLG, few-layer graphene; BLG, bilayer graphene

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