

Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene

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Gate-modulated low-temperature Raman spectra reveal that the electric field effect (EFE), pervasive in contemporary electronics, has marked impacts on long-wavelength optical phonons of graphene. The EFE in this two-dimensional honeycomb lattice of carbon atoms creates large density modulations of carriers with linear dispersion (known as Dirac fermions). Our EFE Raman spectra display the interactions of lattice vibrations with these unusual carriers. The changes of phonon frequency and linewidth demonstrate optically the particle-hole symmetry about the charge-neutral Dirac point. The linear dependence of the phonon frequency on the EFE-modulated Fermi energy is explained as the electron-phonon coupling of massless Dirac fermions.

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The interaction between electrons and quantized lattice vibrations in a solid is one of the most fundamental realms of study in condensed matter physics. In particular, the electron-phonon interaction in graphene and its derivatives plays an important role in understanding anomalies of photoemission spectra observed in graphite [1] and graphene [2], the nonlinear high energy electron transport in carbon nanotubes [3–7], as well as phonon structures in graphite [8,9] and carbon nanotubes [9–11].

Traditionally, electron-phonon interactions are investigated through chemical doping, in which the charge carrier density is varied by the introduction of impurities. The electric field effect (EFE) is an alternative method for changing the charge carrier density effectively in low-dimensional systems. The EFE has proven very successful in graphene, a single atomic sheet of graphite, where an unconventional integer quantum Hall effect [12,13] has revealed physics linked to the uniqueness of the electronic band structure near the charge-neutral Dirac points [Fig. 1(a)].

We measured Raman spectra of optical phonons in graphene, where large densities of free electrons or free holes are modulated by the EFE. We discovered that the even parity long-wavelength optical phonon (the graphene G band) has a marked dependence on gate voltage and the induced charge density. The dependence of the phonon frequency and linewidth on the EFE-induced charge density demonstrates that the intriguing physics of massless Dirac fermions with particle-hole symmetry is encoded in the electron-phonon interaction.

Raman studies of graphite [14] are at the forefront of research on carbon-based materials. The recent availability of few-layer and single-layer graphene [15,16] has stimulated great interest in Raman scattering in such novel and exciting systems. For example, dimensional crossover was observed in Raman spectra of thin graphitic films as a function of multilayer thickness [17–19]. In the work reported here, Raman spectroscopy emerges as an insight-

ful method to probe the EFE in a single atomic layer and the phonon dynamics that are associated with the two-dimensional (2D) Dirac fermions.

We focus on the doubly degenerate optical phonon of E_{2g} symmetry at $\sim 1580\text{ cm}^{-1}$, known as the G band. We also report on the smaller impact of the EFE on the second-order band at $\sim 2700\text{ cm}^{-1}$, known as the D^* band. These two bands are prominent Raman features in graphene [17–19]. The G band is the optical phonon at long wavelengths, and the D^* band is associated with a two-phonon state in which each phonon has a large wave vector. Our experiments demonstrate that the G band is markedly sensitive to coupling with Dirac fermion excitations at small wave vectors (long wavelengths), while the reduced impact of

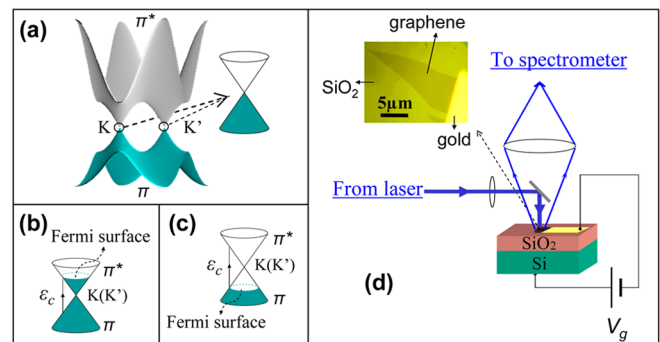


FIG. 1 (color online). (a)–(c) Electronic band structure of graphene and (d) experimental setup. (a) π and π^* bands of graphene in momentum space. K and K' (Dirac points) are the corner points of the first Brillouin zone. For neutral graphene, the π band is completely filled, shown as blue shading in this diagram. Near Dirac points, the band structure exhibits isotropic linear dispersion, shown as two cones at K and K' . (b) shows the region near Dirac points in n -type graphene. ϵ_c is the onset energy for vertical electron-hole pair transitions. (c) is like (b) for p -type graphene. (d) Upper left is an optical image of the sample.

the EFE on the D^* band offers insights on the coupling to particle-hole pairs at large wave vectors.

The interaction of the G phonon with small wave vector particle-hole pairs has a crucial dependence on the onset energy ε_c for vertical transitions (zero momentum transfer) of an electron from a π valence band to a π^* conduction band state as shown in Figs. 1(b) and 1(c). The $\pi \rightarrow \pi^*$ transitions need to satisfy the requirements of the Pauli principle. For this reason, ε_c is directly linked to the position of the Fermi surface as $\varepsilon_c = 2|E_F|$, where $|E_F|$ is the absolute value of the Fermi energy with respect to the Dirac point. The response of the G phonon to the EFE is thus inextricably related to the electronic band structure in the vicinity of the Dirac point.

Graphene samples were deposited on degenerately doped p -type silicon with a 300-nm-thick SiO_2 as the gate dielectric using the mechanical method described in Ref. [20]. The single layers were identified by their color under an optical microscope and confirmed by Raman spectroscopy [17–19]. A gold electrode was thermally evaporated on one end of the graphene layer to contact it to the electrical ground [Fig. 1(d)]. A gate bias voltage V_g was applied to the silicon substrate to induce charge carriers in the sample by the EFE. The sample was mounted in a variable temperature cryostat with optical access, where it was cooled by a continuous flow of cold helium gas. The Raman measurements were performed in a backscattering configuration [Fig. 1(d)] with the 488-nm line of an argon-ion laser as exciting radiation. The laser spot size on the sample was $\sim 25 \mu\text{m}$ in diameter, and the power was kept below 5 mW. The scattered light was collected into a Spex-1404 0.85-m double grating spectrometer, and spectra were recorded by a liquid-nitrogen-cooled CCD camera. The spectral resolution in these measurements is $\sim 2 \text{ cm}^{-1}$.

Typical spectra showing G and D^* bands at cryostat cold finger temperatures $\sim 10 \text{ K}$ are displayed in Fig. 2. Remarkably, both the peak position and the linewidth are found to be modulated by the gate voltage. The changes induced by the EFE are much larger for the G mode than for the second-order D^* band. We also show for comparison a G band for thick ($>10 \text{ nm}$) samples [Fig. 2(b)] taken under similar experimental conditions with no gate voltage applied, which serves as a bulk sample spectrum.

The EFE-induced charge in the single layer of graphene can be modulated by gate voltage according to the relation $n = C_g(V_g - V_{\text{Dirac}})/e$, where C_g , e , and V_{Dirac} are the gate capacitance, electron charge, and the gate voltage corresponding to the charge-neutral Dirac point, respectively. The changes in graphene Raman spectra as a function of V_g demonstrate that the EFE-modulated charge density results in significant changes in the frequency and lifetime of phonons.

Figure 3 displays the G -mode frequency ω_G and width Γ_G as a function of V_g . It is remarkable that $\omega_G(V_g)$ and $\Gamma_G(V_g)$ both exhibit nearly symmetric changes relative to the value of $V_g \sim 18 \text{ V}$. This symmetry is naturally linked

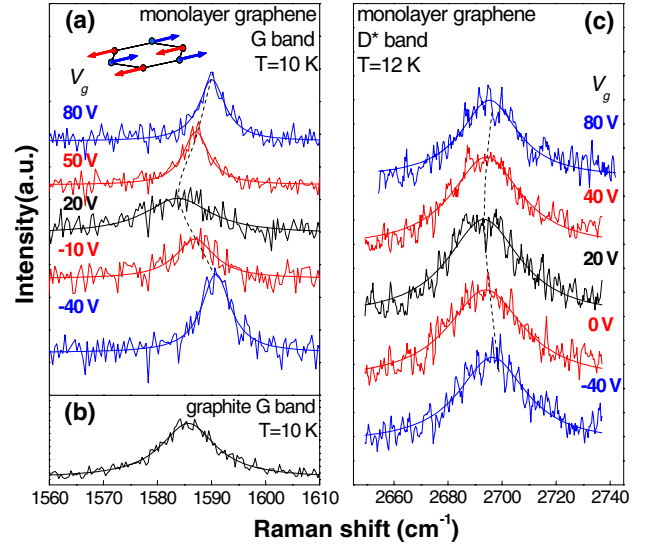


FIG. 2 (color online). Low-temperature Raman spectra and their Lorentzian fits (smooth overlapping curves). (a) Evolution of the G band of a graphene monolayer with gate voltage V_g . The upper left inset is a schematic representation of carbon atom motion in the G band. The dashed line is a guide to the eye. (b) Spectrum of the G band of a thick ($>10 \text{ nm}$) graphite layer. (c) Evolution of the D^* two-phonon band of a graphene monolayer with V_g .

to the symmetry of the electronic band structure that occurs at the Dirac point shown in Fig. 1(a), from which we determine $V_{\text{Dirac}} = 18 \pm 2 \text{ V}$ [21]. In particular, $\omega_G(V_g)$ has a minimum near the Dirac point, revealing that increases in charge density of either sign result in stiffening of the G mode. On the other hand, Γ_G sharply decreases as

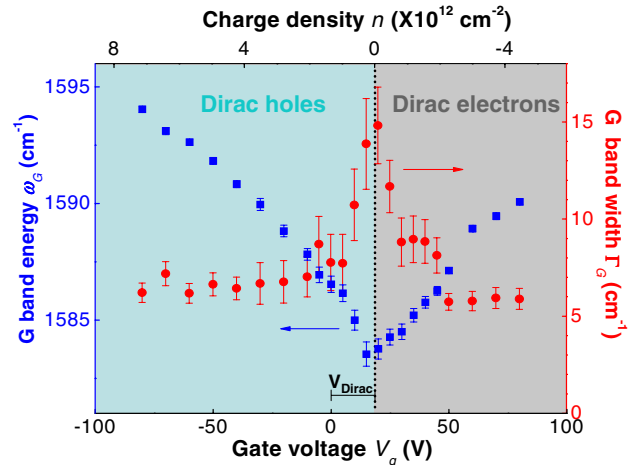


FIG. 3 (color online). G band energy (squares) and G band width (circles) extracted from Fig. 2(a). The vertical dotted line is the approximate position of the charge-neutral Dirac point that is estimated from the symmetry of the data. The upper scale is obtained with $n = C_g(V_g - V_{\text{Dirac}})/e$, where $C_g = 115 \text{ aF}/\mu\text{m}^2$ [12,13].

$|V_g - V_{\text{Dirac}}|$ increases, showing that longer phonon lifetimes are linked to higher particle or hole density. These results offer key insights into the coupling of Dirac fermions to lattice vibration modes, as discussed below.

We first consider Γ_G shown in Fig. 4(a). Its marked reduction (from 15 to 6.5 cm^{-1}) at higher carrier densities can be understood as a Landau damping of phonons in which the mode decays into particle-hole pairs. Examples of such processes are shown in the inset in Fig. 4(a) and in Fig. 4(b). Phonon decay processes are real transitions that conserve energy and momentum. The small wave vector G phonon can decay only into particle-hole pairs represented by vertical transitions that have vanishingly small wave vector transfer [Fig. 4(b)]. When charge carriers are induced by EFE in ideal graphene at low temperatures, the Fermi level E_F changes as $E_F(n) = -\text{sgn}(n)\hbar v_F \sqrt{(\pi|n|)}$, where $v_F = 10^6$ m/sec [12,13] is the Fermi velocity and n is charge density. To satisfy the Pauli principle, Landau damping is allowed only when $|E_F| < \hbar\omega_G/2$ [Figs. 4(b) and 4(c)]. This is the relatively low density regime in which G band phonons are damped via decay into vertical particle-hole pairs.

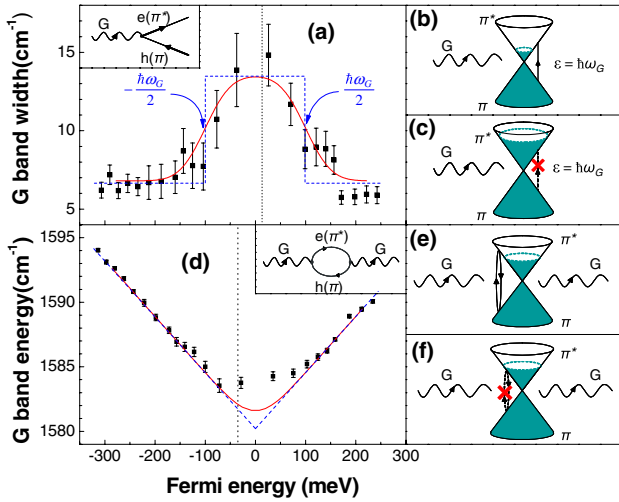


FIG. 4 (color online). (a)–(c) Graphene G band damping and (d)–(f) energy renormalization. In (a) and (d), dashed blue lines and solid red lines are the fits for ideal and nonuniform graphene, respectively. In all cases, the same electron-phonon coupling strength ($D = 12.6$ eV/Å) is assumed. The vertical dotted lines are the determinations of the Dirac point shown in Fig. 3. The insets are Feynman diagrams for electron-phonon coupling applicable to the case of the G phonon. (b) represents the broadening of the G phonon due to decay into particle-hole pairs. (c) indicates that the G -phonon decay into the electron-hole pair is forbidden by the Pauli principle at high EFE-induced charge densities. (e) is for the renormalization of the G -phonon energy by interaction with virtual electron-hole pairs. (f) shows that virtual electron-hole pair transitions with energy ranging from 0 to $2|E_F|$ are forbidden. Only the diagrams for n -type graphene are shown in (b), (c), (e), and (f). Diagrams for the p -type cases are similar.

The total change in Γ_G is written as $\Delta\Gamma_G = \Gamma_G(V_{\text{Dirac}}) - \Gamma_G^0$, where Γ_G^0 is the residual linewidth from processes that are not related to Landau damping. The Landau damping phonon decay rate $\Delta\Gamma_G$ is the probability of creating energetically allowed electron-hole pairs via the electron-phonon coupling in unit time. Therefore, the electron-phonon coupling strength can be estimated from $\Delta\Gamma_G$. A calculation based on the Fermi golden rule yields [9]

$$\Delta\Gamma_G = \frac{A_{\text{uc}}}{8Mv_F^2} D^2, \quad (1)$$

where A_{uc} is the area of the graphene unit cell, M is the carbon atom mass, and D is the electron-phonon coupling strength. The measured 8.5 cm^{-1} $\Delta\Gamma_G$ yields $D = 14.1$ eV/Å, which seems to be consistent with the value predicted by density functional theory [22].

The results in Fig. 4(a) exhibit that the measured Γ_G has departures from the steplike function (dashed blue line) expected for ideal graphene with uniform charge density distribution. In graphene samples, however, there are presumably local density variations due to self-doping [23], chemical adsorption [15], and charged impurities trapped in the substrate [24,25]. Different locations of the graphene sheet have thus different local contributions to damping of G phonons, smoothing out the sudden changes at $\pm\hbar\omega_G/2$. Considering a nonuniform spatial variation of $\sim \pm 3 \times 10^{11}$ cm^{-2} in charge density, we obtained a reasonable fit for Γ_G shown as the solid red curve in Fig. 4(a).

The EFE modulation of ω_G , which has a minimum near the Dirac point, is shown in Fig. 4(d) as a function of Fermi energy. For carrier densities above $\sim \pm 5 \times 10^{11}$ cm^{-2} where nonuniformity is no longer dominant, the G band phonon energy increases linearly with changes in Fermi energy. This intriguing result directly links the EFE-modulated ω_G to 2D Dirac fermion properties, as discussed below.

The coupling between G -phonon lattice vibrations and Dirac fermions is allowed by graphene lattice symmetry. The carriers residing in the honeycomb lattice respond to the dynamical perturbation of G mode lattice vibration by creation and annihilation of virtual long-wavelength electron-hole pairs across the gapless Dirac point, which, in turn, renormalizes the G -phonon energy. The energy range of the virtual electron-hole pairs allowed by the Pauli principle is decided by the position of the Fermi level [Figs. 4(e) and 4(f)]. When the graphene is charge-neutral, the onset energy is zero. If graphene is doped with electrons or holes, the onset energy is twice the Fermi energy. The difference of the G band energy in neutral and charged graphene is thus given by the renormalization of electron-hole pairs with energy ranging from 0 to $2|E_F|$.

Carrying out the calculation explicitly with time-dependent perturbation theory [26] and the linear dispersion near the Dirac point, we find that the change of G band phonon energy is described by

$$\hbar\omega_G - \hbar\omega_G^0 = \lambda \left\{ |E_F| + \frac{\hbar\omega_G}{4} \ln \left| \frac{2|E_F| - \hbar\omega_G}{2|E_F| + \hbar\omega_G} \right| \right\}, \quad (2)$$

where ω_G^0 is ω_G at the Dirac point, $\lambda = A_{uc}D^2/2\pi\hbar\omega_G Mv_F^2$ [27]. In the high density limit, the linear term dominates over the logarithm term. A fit of the linear segments in Fig. 4(d) (dashed blue lines) with the linear term in Eq. (2) gives $D = 12.6$ eV/Å, close to the value 14.1 eV/Å determined above from the analysis of the ω_G data. The solid red line in Fig. 4(d) is the fit that takes into account the impact of nonuniformity described above.

It is worth noting that $\Delta\Gamma_G/\lambda = \pi\hbar\Gamma_G/4 \approx 154$ meV, which depends only on one parameter. Our experimental result gives 195 meV.

Finally, we consider the impact of the EFE on the D^* Raman mode shown in Fig. 2(c). Although both the peak position and the width of the G and D^* bands exhibit similar gate dependence behavior, the magnitudes of the changes seen in Fig. 2(c) are only $\sim 10\%$ of those of the G band. This smaller gate response can be explained by the impact of electron-phonon interactions for the two large wave vector phonons that contribute to the second-order Raman D^* band. The renormalization of the phonon frequency due to electron-phonon interactions is inversely proportional to the energy of particle-hole transitions at the phonon wave vector [26]. In this context, the weaker response of the D^* band to the EFE suggests that relevant EFE-modulated particle-hole transitions here have energies about an order of magnitude larger than those in the renormalization of the G band [28]. Further quantitative description could be carried out by the analysis of the doubly resonant Raman processes in the D^* band [14].

In conclusion, we observed EFE-tunable electron-phonon coupling in Raman spectra of single-layer graphene. The gate voltage dependence of phonon frequency and damping reveals charge-tunable interactions of optical phonons with Dirac fermion transitions across a vanishing band gap. These results uncover physics that links the EFE with electron-phonon coupling and demonstrate venues to probe fundamental interactions and to characterize atomic scale structures and devices.

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Note added.—Recently, we became aware of related work on similar systems from other groups [29–32].

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