Phonon switching and combined Fano-Rice effect in optical spectra of bilayer graphene

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Recent infrared measurements of phonon peaks in gated bilayer graphene reveal two striking signatures of electron-phonon interaction: an asymmetric Fano lineshape and a giant variation of the peak intensity as a function of the applied gate voltage. In this Letter we provide a unified theoretical framework which accounts for both these effects and unveils the occurrence of a switching mechanism between the symmetric ($E_g$) and anti-symmetric ($E_u$) phonon modes as dominant channel in the optical response. A complete phase diagram of the optical phonon response is also presented, as a function of both the charge density and the bandgap.

Single and multi-layer graphenes are among the most promising systems for the development of carbon-based devices in electronics. Bilayer graphene is of particular interest because a controlled tunable gap in the electronic spectrum can be there induced by applying one (or more) external gate voltages [1,2] as observed by transport [3] and optical measurements [4–7]. The potential interest in application has triggered also an intense research on the vibrational properties, that can be used for instance for a careful characterization of the number of layers, the charge doping and the amount of disorder [8,9]. Large part of the work in this context has focused on the properties of the in-plane $E_g$ mode at $\omega \approx 0.2$ eV which is present in single as well as in bilayer systems, and which can be probed by Raman spectroscopy [8,10].

Recently, phonon peaks in the energy range $\omega \approx 0.2$ eV have been reported also in infrared (IR) optical measurements of bilayer graphene [11,12], showing a rather different phenomenology with respect to Raman spectroscopy. In particular, the observed IR phonon peak presents a strong dependence of the intensity and of the Fano-like asymmetry as a function of the applied gate voltage [15,16]. These features have been attributed respectively to a charged-phonon effect for the $E_u$ anti-symmetric (A) mode [15], or, at $n = 0$, to the emergence of a Fano profile for the $E_g$ symmetric (S) mode, whose optical activity can be triggered by the electrostatic potential difference $\Delta$ between the two carbon planes [16]. However, the possible connection between these two alternative views is still unclear.

In this Letter we provide a unified microscopic framework that allows us to elucidate the relative role of the $E_u$ and $E_g$ phonon modes in bilayer graphene, with regards to the infrared activity and the Fano asymmetry of the observed phonon peaks. We present a complete phase diagram for the strength of the phonon modes and their Fano properties as functions of the chemical potential and $\Delta$, showing that a switching mechanism between the dominance of the $E_u$ or $E_g$ mode can be controlled by the external gate voltage. Our work permits thus reconciling within a unique approach the phonon-peak features observed by different experimental groups [15,16].

To compute the conductivity of bilayer graphene we work in the $4 \times 4$ basis of the atomic orbitals $\Psi_k = (a_{1k}^\dagger, b_{1k}^\dagger, a_{2k}^\dagger, b_{2k}^\dagger)$, where $a_{1k}^\dagger$ and $b_{1k}^\dagger$ operators create an electron in the layer $i$ and on the sublattice A or B, respectively. In this basis, the Hamiltonian for bilayer graphene near the K point reads [17]:

$H_k = \left\{ \hbar v k \cdot \vec{I}(\sigma) + (\Delta/2) \hat{z} + (\gamma/2) \left[ \hat{x}(\hat{y} + \hat{y}) + \hat{y}(\hat{x} + \hat{x}) \right] \right\},$

where $\hat{\sigma}_i$ and $\hat{I}$ are $2 \times 2$ Pauli matrices and the unit matrix respectively, and $A(\bar{B}) \equiv A \otimes \bar{B}$. Here $v$ is the Fermi velocity for single-layer graphene and $\gamma$ is the interlayer hopping. The electrostatic potential difference $\Delta$ induces a gap in the diagonalized bands $\varepsilon_{k,n}$, labeled according to Fig. 1a. We set the electric field of the infrared radiation along the $x$-axis, so that the electric current reads $j = \sum_k \psi_{k,\sigma}^{\dagger} j_{\sigma} \psi_k \equiv \sum_k \psi_{k,\sigma}^{\dagger} \psi_k$ where $j_{\sigma} = -e v I(\hat{\sigma}_x)$. The two $E_u$ and $E_g$ in-plane optical phonons have degenerate longitudinal and transverse polarization at zero momentum $\mathbf{q} = 0$ [17]. We can write the electron-phonon interaction for these modes as:

$H_{\text{ep}} = \sum_{\nu} V_{\nu} \phi_{\nu},$

where $\phi_{\nu}$ is the dimensionless lattice displacement for the $\nu$=A,S branch at $\mathbf{q} = 0$, $V_{\nu} = \sum_k \Psi_k^{\dagger} \nu \nu \Psi_k$ is the corresponding electron-phonon scattering operator. For a choice of the longitudinal polarization along $x$, one finds $\tilde{V}_{\lambda} = i g \hat{z}(\hat{y})$ and $\Delta_{ij} = j \cdot \Psi_{A}^{\dagger} \tilde{V}_{\lambda} \Psi_{A} + \text{h.c.}$.

FIG. 1: (a) Scheme of the band structure. (b)-(d) Relevant diagrams entering the optical conductivity for $\Delta = 0$: Dashed, solid and wavy lines represent the photon, the electron and phonon Green’s functions, respectively. Squares and circles are the current and the electron-phonon scattering matrices $j$, $\tilde{V}_{\lambda}$, respectively.
\[ \hat{V}_S = ig\hat{I} (\hat{\sigma}_y) \] 17, where \( g \) is the electron-phonon coupling.

Let us consider first the case of ungapped bilayer graphene (\( \Delta = 0 \)), where only the A mode is optically active. Since graphene is a non-polar system, the bare dipole induced by the rigid shift of the valence charges upon the A lattice distortion is extremely small 13. Nevertheless, an optical phonon response can be still mediated by the conduction charges in the presence of the electron-phonon interaction, as suggested by M.J. Rice in the context of organic and fullerene compounds 18. The total optical conductivity of the system is computed as \( \sigma(\omega) = -\chi_{jj}(\omega)/\omega \), where \( \chi_{jj}(\omega) = -(j\langle j^\dagger j \rangle) \) is the current-current response function. In the presence of electron-phonon interaction, one can identify two classes of contributions in \( \chi_{jj}(\omega) \), namely \( \chi_{jj}^\dagger(\omega) = \chi_{jj}^e(\omega) + \chi_{jj}^p(\omega) \). The former, depicted in Fig. 1b, describes electronic excitations (see, for example, Ref. 14), while the latter encompasses all the diagrams which can be split in two by cutting one phonon propagator (Fig. 1c) 18. We can write thus

\[
\chi_{jj}^{\text{ep}}(\omega) = \chi_{jA}(\omega) D_{AA}(\omega) \chi_{A^jA}(\omega),
\]

where \( \chi_{jA}(\omega) = -(\langle jV_A^\dagger j \rangle)/(\omega - \omega_A + i\Gamma_A/2) \) are the mixed current-phonon response functions, and \( D_{AA}(\omega) = -(\langle \phi_A^\dagger \phi_A \rangle)/(\omega - \omega_A + i\Gamma_A/2)^{-1} \) is the phonon propagator with frequency \( \omega_A \) and linewidth \( \Gamma_A \) renormalized by the phonon self-energy \( \chi_{AA}^{\dagger A} \) (Fig. 1b). It should be emphasized that two different response functions, \( \chi_{jj}^e \) and \( \chi_{jA} \), enter in the above decomposition of \( \sigma(\omega) \). This distinction, that has been neglected in the original formulation 18, is however crucial, because it implies that the allowed particle-hole excitations of the system will contribute in a different way to the electronic optical background, related to \( \chi_{jj}^e \), to the phonon renormalization, controlled by \( \chi_{jA}^{\dagger A} \), or to the electron-phonon optical response, controlled by \( \chi_{jA} \).

Eq. (1) leads to the onset, in the real part of the optical conductivity \( \sigma_{\text{ep}}^{\text{re}}(\omega) \), of a phonon peak at \( \omega_A \). Indeed, using the relation \( \chi_{jA}^{\dagger j\dagger}(\omega) = \chi_{jA}(\omega) \), and taking the real and imaginary part of each element in Eq. (1), we get

\[
\sigma_{\text{ep}}^{\text{re}}(\omega) \bigg|_{\omega=\omega_A} \approx \frac{2}{\omega_A \Gamma_A} \frac{\left[\chi_{jA}(\omega_A)\right]^2}{\left[q_A^2 - 1 + 2q_A z\right]/\left(1 + z^2\right)}.
\]

where \( z = 2(\omega - \omega_A)/\Gamma_A \) and where

\[
q_A = -\frac{\chi_{jA}(\omega_A)}{\chi_{jA}^{\dagger}(\omega_A)}
\]

Eq. (2) has exactly the same structure as the Fano formula 20. The derivation of Eqs. (2)-(4) shows not only that in bilayer graphene the Fano effect originates from a correct implementation of the charged-phonon Rice theory, but it provides a compelling procedure to evaluate on microscopic grounds the shape and the intensity of the phonon peak. For instance from Eqs. (2)-(4) we can identify the \( \omega \)-integrated peak area as

\[
\sigma_A = \pi |\chi_{jA}(\omega_A)|^2/\omega_A = \left(1 - 1/q_A^2\right)|\chi_{jA}^{\dagger A}(\omega_A)/\omega_A|.
\]

Since the sign of \( q_A \) depends on \( q_A \), it can be convenient, as done in Ref. 13, to define a “bare” intensity as \( W_A = \pi |\chi_{jA}(\omega_A)/\omega_A| \), which coincides with \( W_A \) in the limit \( |q_A| \to \infty \), when Eq. (2) reduces to a conventional Lorentzian peak with weight \( W_A \). Note however that in the opposite case \( |q_A| \approx 1 \) one recovers from Eqs. (2)-(4) a completely negative Lorentzian peak, of intensity \(-\pi |\chi_{jA}^{\dagger A}(\omega_A)/\omega_A|^2 \), so that the definition of ‘intensity’ of the phonon peak can be ambiguous in the presence of the Fano effect. A more convenient quantity to parameterize the strength of the phonon peak is \( P_{\text{ph}} = \pi |\chi_{jA}(\omega_A)|^2/\omega_A = W_A(1 + 1/q_A^2) \), which is always positive and vanishes when the phonon peak is completely absent.

Eqs. (2)-(4) can be computed analytically by using the non-interacting electron Green’s functions. The quantity \( \chi_{jA} \) has the typical structure of a particle-hole Lindhard response function, with proper coherence factors \( C_{jA}^{nm} \) weighting the contributions of the various excitations between the \( n \) and \( m \) bands. In particular, using the explicit matrix expressions of the \( \hat{J} \) and \( \hat{V}_A \) operators, one gets

\[
\chi_{jA}(\omega) = \chi_{jA}^{12}(\omega) + \chi_{jA}^{13}(\omega) - \chi_{jA}^{24}(\omega) - \chi_{jA}^{34}(\omega),
\]

where

\[
\chi_{jA}^{nm}(\omega) = \pi_{jA}^{nm}(\omega) - \pi_{jA}^{nm}(\omega),
\]

and

\[
\pi_{jA}^{nm}(\omega) = \sum_k C_{jA}^{nm} f\left(\epsilon_{k,m} - \mu\right) - f\left(\epsilon_{k,n} - \mu\right) \epsilon_{k,n} - \epsilon_{k,m} + \hbar\omega + i\eta.
\]

Here \( f(x) = 1/[\exp(x/T) + 1] \) is the Fermi function, \( C_{jA}^{nm} = (\text{gcd} N_s N_v)\gamma\hbar/4(\hbar v F)^2 + \gamma^2 \) for \( n, m \) as in Eq. (4) and zero otherwise, \( \mu \) is the chemical potential, \( N_s = N_v = 2 \) are the spin and valley degeneracies, and the \( \eta \) factor takes into account broadening effects due to impurities and inhomogeneities. In the clean limit, \( \eta = 0 \), we obtain the analytical expressions valid for \( T = 0 \) and
\[ |\mu| < \gamma: \]
\[ \chi_{j\lambda}(\omega) = A \left\{ \ln \left[ \frac{(1 + u)(1 - u + 2w)}{(1 - u)(1 + u + 2w)} \right] + \frac{4uw}{(1 - u^2)} \right\} \]
\[ \chi_{j\lambda}''(\omega) = \pi A \left\{ \theta(|u| - 1)\theta(1 - |u| + 2w) + 2w\delta(|u| - 1) \right\} \]
where \( A = g\epsilon\gamma/4\pi \hbar v, \ u = \hbar\omega/\gamma \) and \( w = |\mu|/\gamma \). Similar analytical expressions can be obtained for \( \mu > \gamma \).

To compute the optical conductivity \( \sigma(\omega) \) we evaluate the complex function \( \chi_{j\lambda}(\omega) \) at the phonon resonance \( \omega_A \approx 0.2 \text{ eV} \), using standard values for \( \hbar v = 6.74 \text{ eV} \) and \( \gamma = 0.39 \text{ eV} \). From the value \( \alpha = 6.4 \text{ eV} \AA^{-1} \) of the deformation potential we get \( g = 0.27 \text{ eV} \), corresponding to the dimensionless parameter \( \lambda = (\sqrt{3}/\pi)g^2/|\hbar v/\alpha|^2 = 6 \times 10^{-3} \) \cite{17}, in agreement with the experimental estimates given in Refs. \cite{13, 15}.

The resulting spectral weight \( W_{\lambda} \) as evaluated from Eq. \( \text{(2)} \) and Eqs. \( \text{(4)-(5)} \) is shown in Fig. \( \text{2} \) for \( \eta = 0 \) and \( \eta = 30 \text{ meV} \), along with the experimental data \( W_{\text{exp}} \), \( W'_{\text{exp}} \) taken from Ref. \cite{15}. Note that the only possible electron-hole excitations at the phonon energy \( \omega_A \) (\(< \gamma \)), namely the 2-3 multiband transitions, are not allowed in Eq. \( \text{(4)} \).

Thus in the clean limit \( \chi_{j\lambda}''(\omega_A) \approx 0 \), so that no Fano effect \( (\eta_A = -\infty) \) is found and \( W''_{\lambda} = W_{\lambda} \), while for \( \eta \neq 0 \) a small contribution to \( \chi_{j\lambda}''(\omega_A) \) from the other interband transitions gives rise to a weak Fano asymmetry, and hence \( W''_{\lambda} \leq W_{\lambda} \), as shown in Fig. \( \text{2} \). Both the magnitude of \( W_{\lambda} \), which is proportional to the dimensionless coupling \( \lambda \), and its doping dependence are in excellent agreement with \( W_{\text{exp}} \), pointing out that the \( E_u \) mode is the main responsible for the phonon infrared intensity reported in Ref. \cite{12} at large \( n \). On the other hand, even in the presence of a large \( \eta \), the above calculations do not account for the negative integrated weight \( W''_{\lambda} \) observed around \( n \approx 0 \) (Fig. \( \text{2} \)), which has been attributed in Ref. \cite{16} to the onset of the \( E_g \) mode in the presence of a finite potential asymmetry \( \Delta \). These observations suggest thus that different phonon modes can be optically relevant in different regions of the phase space.

Our theoretical framework allows us to investigate the possibility of such phonon switching by taking into account explicitly the role of \( \Delta \). When \( \Delta \neq 0 \) two effects must be taken into account: \( i \) the phonon eigenmodes of the systems do not correspond any more to \( E_u \) and \( E_g \), even though the new phonon eigenfrequencies \( \omega_{\pm} \) follow closely the doping dependence of the \( \omega_{AS} \) of the uncoupled modes \cite{22, 23}. As a consequence the phonon propagator \( D_{AA} \) can develop at large \( \Delta \) a second peak with weaker intensity at approximately the frequency \( \omega_{AS} \) of the \( E_g \) mode. Note however that according to Eq. \( \text{(1)} \) the infrared activity of the \( D_{AA} \) phonon propagator is still ruled by the strength \( p_A \). Since, as we shall see below, \( p_A \) vanishes for \( n \rightarrow 0 \) also when \( \Delta \neq 0 \), the appearance of the IR phonon structures at \( n \approx 0 \) \cite{12, 16} cannot be accounted for by the mixing of the modes; \( ii \) in addition to the previous effect, the presence of a finite \( \Delta \) leads also to a finite mixed response function \( \chi_{JS}(\omega) = -\langle \mu S \rangle/\omega \neq 0 \). Eq. \( \text{(1)} \) must be thus generalized as:

\[ \chi_{JS}(\omega) = \chi_{j\lambda}(\omega)D_{AA}(\omega)\chi_{\lambda j}(\omega) + \chi_{JS}(\omega)D_{SS}(\omega)\chi_{\lambda j}(\omega) + [\chi_{j\lambda}(\omega)D_{AS}(\omega)\chi_{\lambda j}(\omega) + \text{h.c.}] \]

where \( \chi_{\lambda j}(\omega) = \chi_{\lambda j}(\omega) \), and \( D_{\nu
u'}(\omega) = -\langle \phi_{\nu'}\phi_{\nu} \rangle/\omega \) are the phonon propagators, calculated including the hybridized phonon self-energy \( \chi_{\nu} \) for finite \( \Delta \) \cite{22, 23}. Eq. \( \text{(8)} \) shows how, due to the \( \chi_{JS} \) response triggered by the finite \( \Delta \), a direct coupling channel to the symmetric \( E_g \) mode vibrations (the \( D_{SS} \) phonon propagator) appears in the optical spectroscopy. Similar expressions as Eqs. \( \text{(4)-(5)} \) can be derived for \( \chi_{JS} \), where however the coefficients \( C_{\nu \nu k}^{nm} \), as well as \( C_{\nu \nu k}^{nm} \), have a more complex structure for \( \Delta \neq 0 \).

To elucidate the competition between the different optical channels in Eq. \( \text{(8)} \) we compute explicitly \( \chi_{j\lambda} \) and \( \chi_{JS} \) for generic \( \Delta \) and \( \mu \), giving a complete phase diagram that can be explored in double-gated samples. To parameterize the strengths of the relative channels we use the quantities \( \omega_{\nu} = \sqrt{|\chi_{\nu}|^2}/\omega_{\nu} \) for \( \nu = A, S \) and \( p_{AS} = \sqrt{|\chi_{j\lambda}\chi_{JS}|}/\omega_{\nu} \) for the mixed channel, where \( \omega_{\nu} \) is the average frequency of the two poles of the phonon propagators \cite{22, 23}. For a direct comparison with experimental data, we set \( T = 10 \text{ K} \) and \( \eta = 30 \text{ meV} \), which is halfway between \( \eta = 18 \text{ meV} \) reported in Ref. \cite{7} and \( \eta = 40 \text{ meV} \) in Ref. \cite{16}. The results for the phonon strengths and Fano factors are plotted as a color-map in the \( \Delta\mu \) space in Fig. \( \text{3} \), where also the \( \Delta\mu \) location of the available IR data \cite{13, 16} are shown. Fig. \( \text{3} \) shows that the main parameter tuning the strength of the \( E_u \) mode is the charge doping whereas the \( E_g \) mode is active mainly around the neutrality point, with a strength that is tuned by the asymmetry gap \( \Delta \). The strength of the mixed optical structure (third line in Eq. \( \text{(8)} \), shown in Fig. \( \text{3} \)), satisfies \( p_{AS} \ll p_A, p_S \) in a large part of the phase diagram so that only the \( A \) and \( S \) channels [first two lines in Eq. \( \text{(8)} \)] are active. The relative intensity \( R_{AS} = (p_A - p_S)/(p_A + p_S) \) is summarized in Fig. \( \text{3} \) where \( R_{AS} \approx 1 \) corresponds to a dominant \( E_u \) mode, while \( R_{AS} \approx -1 \) gives a dominant \( E_g \) resonance. Note that the region \( R_{AS} \approx 0 \) where the two strengths of the optical structures have similar magnitude is quite narrow and difficult to resolve experimentally. In Fig. \( \text{3} \) we plot also the relative Fano factor \( q_0 \) for the \( A \) and \( S \) modes. As one can see, \( q_0 \) is essentially doping independent while \( q_0 \) shows a sizeable dependence as function of \( \mu \). These behaviors can be understood considering that the structure of Eq. \( \text{(1)} \) for \( \chi_{j\lambda} \) is still valid for \( \Delta \neq 0 \), so that the low-energy \( 2 \rightarrow 3 \) interband transitions are missing and the weak Fano asymmetry of the \( A \) mode is only due to a finite broadening due to \( \eta \) on the remaining transitions. On the contrary all the interband
plot the spectra for $\mu = 0$, showing the evolution of the optical intensity and of the Fano asymmetry for increasing $\Delta$. These features are related uniquely to the $E_g$ S mode, consistently with panels (a) and (b). On the contrary the spectra in Fig. 3i, evaluated at the doping levels and electrostatic potentials of Ref. 15, are expected to show a continuous switching between the A and S modes, depending on the values of $\mu$ and $\Delta$. To investigate deeper this issue, we plot in Fig. 3 the theoretical spectral weights $W_\nu$ for both the $E_u$ and $E_g$ modes evaluated on the set of experimental data $\Delta$-$\mu$ of Refs. 15. The size of the symbols is proportional to the peak strength $p_\nu$. The switch between the $E_u$ phonon peak and the $E_g$ one in the regime $n \in [-1:3] \times 10^{12}$ cm$^{-2}$ is evident and is reflected in a total spectral weight $W_\nu = W'_A + W'_S$ which becomes negative in such $n$-region, in good agreement with the experimental $\omega$-integrated weight $W_\nu^{\exp}$. A similar phonon switch is also evident from the analysis of the Fano asymmetry, reported in Fig. 3j. Also here one can distinguish the crossover between a constant $\nu$ behavior at large $n$, which we can attribute to the $E_u$ mode, and a drop of $|\nu|$ at small $n$ in the region where the $E_g$ mode becomes dominant. The experimental fit, done with a single mode Fano formula, presents a similar trend.

We stress that the switching between the $E_u$ and $E_g$ modes in the optical conductivity discussed here is not related to the possible appearance at large $\Delta$ of a double-peak structure in each of the $D_{AA}$ or $D_{SS}$ propagators 13, 14, 22, 23. Even though the two effects could be present simultaneously at large gap values, the optical data available so far are outside the region where the two peaks can be resolved.

In conclusion, in this paper we presented a complete theoretical description of the phonon resonance in bilayer graphene, that accounts for both the intensity and the Fano-asymmetry variations as functions of the density and the gap. We also showed that an optical switching from $E_u$ to $E_g$ can be induced in a controlled way, providing a full understanding of the experimental data.

The derived phase diagram for the optical properties offers a roadmap for the characterization of graphenic systems. For instance the measurement of the IR intensity of the phonon peak can provide a useful tool to determine the doping level in contact-free samples.

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