Emergence of a ZO Kohn anomaly in quasi-freestanding epitaxial graphene

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In neutral graphene, two prominent cusps known as Kohn anomalies are found in the phonon dispersion of the highest optical phonon at \( q = \Gamma \) (LO branch) and \( q = K \) (TO branch), reflecting a significant electron-phonon coupling to undoped Dirac electrons. In this work, high-resolution electron energy loss spectroscopy is used to measure the phonon dispersion around the \( \Gamma \) point in quasi-freestanding graphene epitaxially grown on Pt(111). The Kohn anomaly for the LO phonon is observed at finite momentum \( q \sim 2k_F \) from \( \Gamma \), with a shape in excellent agreement with the theory and consistent with known values of the EPC and the Fermi level. More strikingly, we also observe a Kohn anomaly at the same momentum for the out-of-plane optical phonon (ZO branch). This observation is the first direct evidence of the coupling of the ZO mode with Dirac electrons, which is forbidden for freestanding graphene but becomes allowed in the presence of a substrate. Moreover, we estimate the EPC to be even greater than that of the LO mode, making graphene on Pt(111) an optimal system to explore the effects of this new coupling in the electronic properties.

Introduction - Kohn anomalies (KAs) are kinks in the phonon dispersion of a material produced by abrupt variations in the screening of atomic vibrations by gapless electrons [1-3]. The properties of these anomalies are completely determined by the electron-phonon coupling (EPC) and the shape of the Fermi surface, and their observation thus offers a window to study the interplay between electronic properties and phonon dynamics.

As a paradigmatic example, in graphite [4-7] and graphene [8-15], Kohn anomalies are realized as linear cusps in the dispersion of the highest optical phonon branches at \( \Gamma \) (the \( E_2g \) phonon) and at \( K \) (the \( A_1^\prime \) phonon). The form and position of this cusp is determined by the Dirac fermion dispersion of the electronic \( \pi \) bands around \( K \) and the Fermi level \( \mu \approx 0 \). These two in-plane phonon branches are commonly accepted to be the only ones with a significant EPC in graphene [16]. Within a tight-binding picture, these are the only branches that modify the nearest neighbor hopping integrals, so other in-plane phonons require a different mechanism to couple to electrons.

For the case of out-of-plane phonons, the EPC is strongly constrained by the presence of mirror symmetry with respect to the horizontal plane which forbids a first order coupling to electrons, at least in free-standing graphene. When graphene is supported by a substrate a first order EPC becomes allowed in principle [17,18], but it has remained unknown whether its strength is large enough to produce any significant effect. In particular, for the out-of-plane optical mode (the ZO mode), it has been speculated that a finite coupling could be responsible for a Peierls instability to a spontaneous buckling of the lattice [19,20], which has not been observed so far. The observation of a Kohn anomaly for the ZO phonon [21] would represent a definitive proof of the existence of the EPC for this phonon branch and would allow an estimate of it. Herein, we demonstrate the existence of precisely this Kohn anomaly by means of high-resolution electron energy loss spectroscopy (HREELS) measurements on monolayer graphene grown on Pt(111). In addition, we also present evidence of the expected Kohn anomaly for the \( E_2g \) phonon branch.

Graphene on Pt(111) is an ideal playground for investigating the possible emergence of a ZO Kohn anomaly, as it is characterized by the weakest graphene-substrate interaction [22]. The graphene-Pt distance (3.31 Å) lies close to the c-axis spacing in graphite. Moreover, the electronic structure of graphene on Pt(111) resembles that of isolated graphene [23], with the Dirac fermion dispersion of \( \pi \) bands preserved. Angle-resolved photoemission spectroscopy (ARPES) experiments [23] do not show any significant hybridization of the graphene \( \pi \) states with Pt \( d \)-states, which simply superpose in energy with minimal interaction between them. This is in contrast to the case of, for example, graphene on Ni(111), where the hybridization of the graphene \( \pi \)-states with the Ni \( d \) bands has a very strong effect on the \( \pi \) bands [24]. The graphene sheet grown on Pt(111) is p-doped with a shift by 0.30 ± 0.15 eV of the Fermi level from the Dirac point.

Experimental methods - Experiments were carried out in an ultra-high vacuum (UHV) chamber operating at a base pressure of 5·10\(^{-9}\) Pa. The sample was a single crystal of Pt(111). The substrate was cleaned by repeated cycles of ion sputtering and annealing at 1300 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Graphene was attained by dosing ethylene onto the clean Pt(111) substrate held at 1150 K. The completion of the first layer...
was reached upon an exposure of $3 \times 10^{-8}$ mbar for ten minutes ($24\ L, 1\ L = 1.33 \times 10^{-6}$ mbars). The graphene layer was characterized by Raman spectroscopy, low-energy electron diffraction, and scanning electron microscopy experiments, as reported elsewhere [25]. In particular, Raman measurements indicate the unique presence of monolayer graphene domains.

HREELS experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS) with an energy resolution ranging from 1 to 3 meV. The dispersion of the peaks in the energy loss $E_{\text{loss}}$ was measured by moving the analyzer while keeping the sample and the monochromator fixed. The phonon in-plane momentum was determined from $q_\parallel = \vec{k}_i \sin \theta_i - \vec{k}_s \sin \theta_s$ as

$$q_\parallel = \sqrt{2mE_p} \left( \sin \theta_i - \sqrt{1 - E_{\text{loss}}/E_p \cos \theta_s} \right)$$

(1)

where $\theta_i$ and $\theta_s$ are the incident and scattering angles, and we set $\hbar = 1$. The impinging energy $E_p$ and the incident angle $\theta_i$ were chosen so as to obtain the highest signal-to-noise ratio. A primary beam energy of $E_p = 20$ eV provided the best compromise among surface sensitivity, the highest cross-section for mode excitation and momentum resolution. The angular acceptance of the apparatus was $\alpha = \pm 0.5^\circ$, which determines the momentum resolution as

$$\Delta q_\parallel = \sqrt{2mE_p} \left( \cos \theta_i + \sqrt{1 - E_{\text{loss}}/E_p \cos \theta_s} \right) \alpha$$

(2)

For the investigated range of $q_\parallel$, $\Delta q_\parallel$ was found to range from 0.005 near $\Gamma$ to 0.022 Å$^{-1}$ at $K$. To obtain the energies of loss peaks, a polynomial background was subtracted from each spectrum. The resulting spectra were fitted by a Gaussian line shape (not shown herein). All measurements were made at room temperature.

**Experimental results** - The phonon spectrum in graphene is composed by six phonon branches. Four vibrate in-plane and are labeled transverse and longitudinal acoustic (TA and LA) and optical (TO and LO). The other two are acoustic and optical out-of-plane vibrations (ZA and ZO). Fig. 1 shows a map of the EELS intensity as a function of energy and momentum, where four phonon branches (ZA, ZO, LA, LO) can be clearly observed. Their dispersion is consistent with previous works [24, 26, 27]. The other two phonon branches (TO and TA) are practically absent because a selection rule that forbids the emission of odd phonons under reflections by the scattering plane [28]. This is also clearly observed in Fig. 2 where the energy loss is plotted for a selected angle, and four peaks are clearly identified.

We now focus on the dispersion of the ZO and LO modes around $\Gamma$. As usual, the ZO mode is significantly softened compared to the LO mode, due to the higher freedom for atom motion perpendicular to the plane with respect to the in-plane motion. The intensity of the ZO phonon at small momenta has very low weight, as shown in the intensity plot reported in Fig. 1. To enhance the signal-to-noise ratio from the ZO phonon in the nearness of $\Gamma$, each spectrum was acquired for several days. While this allowed to resolve the ZO loss peak, the error bars for its frequency are still in general larger than for other branches. Experimental frequencies for the LO and ZO phonons for small momenta are

![FIG. 2. Selected phonon spectrum from the dataset of Fig 1 at $\theta_i = 47^\circ$. The TA and TO modes are not observed due to a selection rule.](image-url)
The dispersions of the phonons can be expanded as

$$\omega \approx \frac{\hbar}{\sqrt{2 M}} \sqrt{\frac{a^2}{2}} \left( \frac{4 k_F}{\sqrt{3}} \right) \left( e^{i q \cdot r} + e^{-i q \cdot r} \right),$$

where $i = \text{LO}, \text{TO}, \text{ZO}$ and $a_c = 3 \sqrt{3} a^2 / 2$ is the nearest neighbor distance. The dispersions of the phonons $\omega_i(q)$ are analytic in the absence of EPC. For momenta close to the $\Gamma$ point they can be expanded as $\omega_i(q) = \omega_i^0 + c_i q^2 + c'_i q^4$, where $\omega_i^0$, $c_i$ and $c'_i$ are parameters to be fitted from experimental data. The coupling between electrons and phonons is described by

$$H_{e-ph} = F_i \int d^2 r u_i \psi^\dagger \mathcal{M}_i \psi,$$

with $F_i$ the electron-phonon coupling. The matrix $\mathcal{M}_i$ for the different phonons is equal to $\mathcal{M}_{LO} = \hat{q} \times \hat{\sigma}, \mathcal{M}_{TO} = \hat{q} \cdot \hat{\sigma}, \mathcal{M}_{ZO} = \sigma_3$. Following Ref. [16], it is customary to introduce a dimensionless EPC as

$$\lambda_i = \frac{F_i^2 a_c}{2 M \omega_i v_F^2}.$$

The electron-phonon coupling induces a phonon self-energy $\Pi_i(q)$ that corrects the dispersion according to

$$\omega_{R,i} = \omega_i^0 + a_i q^2 + b_i q^4 + \frac{\lambda_i}{2} \Pi_i(q/k_F).$$

In the static approximation, the self-energies for the different phonon branches in terms of the dimensionless

![Graph showing phonon dispersions close to the $\Gamma$ point, showing cusps around $q_c \approx 0.13 \text{ Å}^{-1}$. Top: Dispersion of the LO phonon. A fit to Eq. (8) (full line) gives an EPC $\lambda_{LO} = 0.029$. Bottom: Dispersion of the ZO phonon. A fit to Eq. (8) (full line) gives an EPC $\lambda_{ZO} = 0.087$.](image)
variable \( x = q/k_F \) are given by \cite{31}

\[
\Pi_{LO}(x) = \frac{g_s v_H}{4\pi} \left( \sqrt{1 - \frac{4}{x^2} + \frac{x}{2} \arccos(2/x)} \right) \theta(2 - x),
\]

(9)

\[
\Pi_{TO}(x) = 0,
\]

(10)

\[
\Pi_{ZO}(x) = \frac{g_s v_H}{4\pi} \left( 2 + x \arccos(2/x) \theta(2 - x) \right).
\]

(11)

These expressions can be used to fit the cusps in the experimental curves to obtain an estimate for the different electron-phonon couplings. To do so, we have fitted the dispersion parameters for both curves and determined the optimal Fermi level as \( E_F = v_F q_\varepsilon/2 \approx 0.401 \) eV, which corresponds to a cusp momentum of \( q_\varepsilon = 0.133 \) Å\(^{-1}\). The fits are shown in Fig. 5 with the experimental dispersion, and the result for the LO EPC is \( \lambda_{LO} = 0.292 \), in excellent agreement with the estimates obtained from Raman, \( \lambda_{LO} = 0.207 - 0.034 \) \cite{16}. The fit for the ZO gives \( \lambda_{ZO} = 0.087 \), an even greater value.

**Discussion** - Since this is the first work to observe the effects of electron-phonon coupling to the ZO mode in graphene, there are no measurements of \( \lambda_{ZO} \) available to compare with. Theoretically, this coupling has only been estimated for a SiO\(_2\) substrate in Ref. \cite{19}, giving a maximum value of \( F_{ZO} = 7 \) eVÅ or \( \lambda_{ZO} = 0.011 \) \cite{32}. Our significantly higher value reflects the fact that the substrate is metallic and that, while direct hybridization with graphene is small, the surface electric field induces a stronger breaking of reflection symmetry which is responsible for the EPC.

Our finding that \( \lambda_{ZO} \) has a significant magnitude implies that its effects should also be observable in other experiments. For example, the EPC is visible in the electron dispersion, in the form of a kink at the phonon frequency that is observable by ARPES \cite{9}. The existence of \( \lambda_{ZO} \) would be responsible for an extra kink at \( \omega_{ZO} \) that could be resolved in future experiments. One could also expect a finite \( \lambda_{ZO} \) to induce new Raman peaks. A peak at \( \omega_{ZO} \) from a first order Raman process (analog of the \( G \) peak) for the ZO is not allowed because the ZO transforms as \( B_2 \), which is not contained in \( E_1 \times E_1 \). However, a second order process (analogous to the 2\( D' \) peak \cite{16}) is in principle allowed by symmetry. This process would give a peak at roughly \( 2\omega_{ZO} \), which unfortunately may be difficult to detect because of its overlap with the \( G \) peak. Therefore, either Raman or ARPES could provide an independent confirmation of electron-phonon coupling for the ZO mode.

A related system where the standard (LO and TO) Kohn anomalies have been observed is graphene on Ir(111) \cite{27}. According to ARPES \cite{33}, the Fermi level in this system is \( E_F \approx 0.1 \) eV which corresponds to \( 2k_F \approx 0.03 \) Å\(^{-1}\). Kohn anomalies at such small momentum are probably too difficult to resolve, which is consistent with the observed broadened dip around \( \Gamma \) instead of a cusp. Similarly, if the ZO EPC in this system is significant, such a feature should be observed for the ZO around \( \Gamma \). The data in Ref. \cite{27} are inconclusive on this matter. Finite momentum Kohn anomalies will be more likely to be found in graphene on metals more similar to Pt(111), with weak hybridization but large charge transfer \cite{34}. In metallic substrates with stronger hybridization such as as Ni(111), Kohn anomalies are not present for the LO and TO phonons \cite{35,39} because the coupling of the graphene \( \pi \) bands with the Ni \( d \) orbitals completely rearranges the electron bands. A Kohn anomaly for the ZO is therefore not expected in this type of system.

Finally, a finite \( \lambda_{ZO} \) is also possible in the presence of insulating substrates, as originally conjectured in Ref. \cite{19}. For an undoped graphene sample on such a substrate, the Coulomb interaction is unscreened and this gives rise to a strong renormalization of \( \lambda_{ZO} \) and to the existence of a power-law Kohn anomaly with an exponent that depends on the Coulomb interaction, in the same way as what happens for the TO phonon at \( K \) \cite{13,15,30}. This effect would be remarkable to observe if a substrate inducing a large \( \lambda_{ZO} \) were available.

In summary, in this work we have shown that the presence of a substrate induces a significant electron-phonon coupling to ZO phonons in graphene, which is responsible for a strong Kohn anomaly at \( q = 2k_F \). This finding paves the way to explore the many implications of the coupling of flexural phonons to Dirac electrons in supported graphene samples and graphene with metallic contacts.

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\begin{thebibliography}{9}
\bibitem{1} W. Kohn, Phys. Rev. Lett. 2, 393 (1959).
\bibitem{2} J. Braun, P. Rugar, G. Zhang, J. P. Toennies, and G. Benedek, Phys. Rev. B 79, 205423 (2009).
\bibitem{3} P. Aynajian, T. Keller, L. Boeri, S. Shapiro, K. Habicht, and B. Keimer, Science 319, 1509 (2008).
\bibitem{4} J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, and P. Ordejón, Phys. Rev. Lett. 92, 075501 (2004).
\bibitem{5} S. Piscanec, M. Lazzeri, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. Lett. 93, 185503 (2004).
\bibitem{6} M. Lazzeri, S. Piscanec, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. B 73, 155426 (2006).
\bibitem{7} M. Mohr, J. Maultzsch, E. Dobardžić, S. Reich, I. Milešević, M. Damjanović, A. Bosak, M. Krisch, and C. Thomsen, Phys. Rev. B 76, 035439 (2007).
\bibitem{8} M. Lazzeri and F. Mauri, Phys. Rev. Lett. 97, 266407 (2006).
\bibitem{9} S. Y. Zhou, D. A. Siegel, A. V. Fedorov, and A. Lanzara, Phys. Rev. B 78, 193404 (2008).
\end{thebibliography}
[10] W.-K. Tse, B. Y.-K. Hu, and S. Das Sarma, Phys. Rev. Lett. 101, 066401 (2008).

[11] K.-i. Sasaki, M. Yamamoto, S. Murakami, R. Saito, M. S. Dresselhaus, K. Takai, T. Mori, T. Enoki, and K. Wakabayashi, Phys. Rev. B 80, 155450 (2009).

[12] D. L. Mafla, L. M. Malard, S. K. Doorn, H. Htoon, J. Nilsson, A. H. Castro Neto, and M. A. Pimenta, Phys. Rev. B 80, 241414 (2009).

[13] I. Milošević, N. Kepčija, E. Dobardžić, M. Mohr, J. Maultzsch, C. Thomsen, and M. Damnjanović, Phys. Rev. B 81, 233410 (2010).

[14] F. de Juan and H. A. Fertig, Phys. Rev. B 85, 085441 (2012).

[15] D. M. Basko, S. Piscanec, and A. C. Ferrari, Phys. Rev. B 79, 125418 (2008).

[16] T. L. Linnik, J. Phys.: Condens. Matter 24, 205302 (2012).

[17] D. M. Basko, Phys. Rev. B 78, 125418 (2008).

[18] J.-N. Fuchs and P. Lederer, Phys. Rev. Lett. 98, 016803 (2007).

[19] K. Ziegler, E. Kogan, E. Majerníková, and S. Shpyrko, Phys. Rev. B 84, 073407 (2011).

[20] A. Shikin, D. Farias, V. Adamchuk, and K.-H. Rieder, Surf. Sci. 424, 155 (1999).

[21] A. Shikin, D. Farias, and K. Rieder, EPL 44, 44 (1998).

[22] T. Aizawa, R. Souda, Y. Ishizawa, H. Hirano, T. Yamada, K. ichi Tanaka, and C. Oshima, Surf. Sci. 237, 194 (1990).
SUPPLEMENTARY MATERIAL: EMERGENCE OF A ZO KOHN ANOMALY IN QUASI-FREESTANDING EPITAXIAL GRAPHENE

Phonon self-energy

All calculations are performed at $T = 0$. Room temperature (300 K) corresponds to 25 meV, which is much smaller than $E_F$ or the optical phonon frequencies. With the definitions given in Eqs. [4]-[7] in the main text, the phonon propagator is written as

$$G_i(\omega, q) = \frac{2\omega_i(q)}{\omega^2 - \omega_i(q)^2 - 2\omega_i(q)\Sigma_i(\omega, q)}, \quad (12)$$

where $\Sigma_i(\omega, q) = \frac{\lambda_i}{2}\Pi_i(\omega, q)$ is the self-energy, and $i = LO, TO, ZO$ as in the text. The dispersion relation for the phonon can be obtained by solving for the pole in Eq. (12) for small $\lambda_i$, so that the renormalized phonon dispersion relation is given by

$$\omega_{R,i}(q) \approx \omega_i(q) + \frac{\lambda_i}{2}\Pi_i(\omega_i, q), \quad (13)$$

which yields Eq. [5] in the text. The response function $\Pi_i$ for a particular phonon is given by

$$\Pi_i(E, \bar{q}) = g_{s,v}i \int \frac{d\omega d^2k}{(2\pi)^3} \text{tr} \mathcal{M}_iG(\omega, \bar{k})\mathcal{M}_iG(\omega + E, \bar{k} + \bar{q}), \quad (14)$$

where $g_{s,v} = 4$ accounts for spin and valley degeneracy, $\mathcal{M}_i$ is the electron-phonon coupling matrix as defined in the text, and

$$G(\omega, \bar{k}) = \frac{\omega + \mu + \vec{\sigma}\cdot\vec{k}}{\omega(1+i\epsilon) + \mu) + \bar{k}^2}, \quad (15)$$

is the electron propagator, where we set $v_F = 1$. Evaluating the trace in Eq. (14) we obtain

$$\Pi_i(E, \bar{q}) = g_{s,v}i \int \frac{d\omega d^2k}{(2\pi)^3} \frac{N_i}{[\omega(1+i\epsilon) + \mu)^2 - \bar{k}^2]}. \quad (16)$$

where the numerators $N_i$ for the different phonons are given by

$$N_{LO} = 2[\omega(\omega + E) - \bar{k} \cdot (\bar{k} + \bar{q}) + 2(\bar{k} \cdot \bar{q})^2/q^2 + 2\bar{k} \cdot \bar{q}], \quad (17)$$

$$N_{TO} = 2[\omega(\omega + E) - \bar{k} \cdot (\bar{k} + \bar{q}) + 2(\bar{k} \times \bar{q})^2/q^2], \quad (18)$$

$$N_{ZO} = 2[\omega(\omega + E) - \bar{k} \cdot (\bar{k} + \bar{q})], \quad (19)$$

The frequency integral is performed with the residue method, giving

$$\Pi_i(E, \bar{q}) = g_{s,v} \int \frac{d^2k}{(2\pi)^2} \left[ \frac{\theta(k - \mu)N_i|_{\omega = k - \mu}}{2|k|[(k + E + 1 + i\epsilon)^2 - |k + \bar{q}|^2]} + \frac{\theta(k + \bar{q} - \mu)N_i|_{\omega = k + \bar{q} + \mu}}{2|k + \bar{q}|[(k + \bar{q})^2 + E(1 + i\epsilon) + |k + \bar{q}|^2]} \right], \quad (20)$$

Since these integrals are ultraviolet divergent as power counting reveals, it is customary to split them into the contribution coming from the undoped Dirac cone plus a finite correction induced by finite chemical potential. This is done by replacing $\theta(k - \mu) = 1 - \theta(\mu - k)$ in the integrals, giving

$$\Pi_i(E, \bar{q}) = \Pi_{i=0}^\mu(E, \bar{q}) - \Delta\Pi_i(E, \bar{q}), \quad (21)$$

with

$$\Delta\Pi_i(E, \bar{q}) = g_{s,v} \int \frac{d^2k}{(2\pi)^2} \left[ \frac{\theta(\mu - k)N_i|_{\omega = k - \mu}}{2|k|[(k + E + 1 + i\epsilon)^2 - |k + \bar{q}|^2]} + \frac{\theta(\mu - \bar{k} + \bar{q} - \mu)N_i|_{\omega = k + \bar{q} + \mu}}{2|k + \bar{q}|[(k + \bar{q})^2 + E(1 + i\epsilon) + |k + \bar{q}|^2]} \right]. \quad (22)$$
\( \Pi_{\mu=0}(E, \mathbf{q}) \) can then be computed with dimensional regularization methods giving \([5, 16]\)

\[
\Pi_{LO}^{\mu=0} = \frac{g_{s,v}}{16} \sqrt{-E^2 + q^2},
\]

\[
\Pi_{TO}^{\mu=0} = -\frac{g_{s,v}}{16} \frac{E^2}{\sqrt{-E^2 + q^2}},
\]

\[
\Pi_{ZO}^{\mu=0} = \frac{g_{s,v}}{8} \sqrt{-E^2 + q^2}.
\]

The correction terms become complicated expressions but can be computed analytically in the static approximation \((E = 0)\) giving \([10]\)

\[
\Delta \Pi_{LO} = \frac{g_{s,v}}{4\pi} \left[ \frac{q^2}{4} \left( \frac{q}{2} \arccos \left( \frac{2\mu}{q} \right) + \frac{\mu}{q} \sqrt{q^2 - 4\mu^2} \right) \theta(q - 2\mu) \right],
\]

\[
\Delta \Pi_{TO} = 0,
\]

\[
\Delta \Pi_{ZO} = \frac{g_{s,v}}{4\pi} \left[ \frac{q^2}{2} - 2\mu - q \arccos \left( \frac{2\mu}{q} \right) \theta(q - 2\mu) \right].
\]

Combining the two contributions, Eq. 21, we finally get

\[
\Pi_{LO}(E = 0) = \frac{g_{s,v}}{4\pi} \left[ \frac{q^2}{2} \arccos \left( \frac{2\mu}{q} \right) + \frac{\mu}{q} \sqrt{q^2 - 4\mu^2} \right] \theta(q - 2\mu),
\]

\[
\Pi_{TO}(E = 0) = 0,
\]

\[
\Pi_{ZO}(E = 0) = \frac{g_{s,v}}{4\pi} \left[ 2\mu + q \arccos \left( \frac{2\mu}{q} \right) \theta(q - 2\mu) \right].
\]

The results in the main text are obtained by recovering \(v_F\) and setting \(x = q/(v_F\mu)\). Note that the functional dependence of the \(\mu = 0\) part for the ZO was anticipated in Ref. \([21]\), and by symmetry arguments \([15]\), it is the same as that of the TO phonon at the \(K\) point \([18]\).