Van Hove singularity and apparent anisotropy in the electron-phonon interaction in graphene

Cheol-Hwan Park,[1,2,*] Feliciano Giustino,[1,2] Jessica L. McChesney,[3] Aaron Bostwick,[3] Taisuke Ohta,[3] Eli Rotenberg,[3] Marvin L. Cohen,[1,2] and Steven G. Louie[1,2]

[1]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*

[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[3]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

(Received 21 February 2008; published 27 March 2008)

We show that the electron-phonon coupling strength obtained from the slopes of the electronic energy vs wave vector dispersion relations, as often done in analyzing angle-resolved photoemission data, can differ substantially from the actual electron-phonon coupling strength due to the curvature of the bare electronic bands. This effect becomes particularly important when the Fermi level is close to a van Hove singularity. By performing *ab initio* calculations on doped graphene, we demonstrate that, while the apparent strength obtained from the slopes of experimental photoemission data is highly anisotropic, the angular dependence of the actual electron-phonon coupling strength in this material is negligible.

DOI: 10.1103/PhysRevB.77.113410 PACS number(s): 73.61.Wp, 73.20.At, 79.60.Dp

The energies and lifetimes of charge carriers in solids are significantly affected by many-body interactions including those with electron-hole pairs, plasmons, and phonons. Angle-resolved photoemission spectroscopy has emerged as an ideal tool for directly probing the effects of these interactions on the electron quasiparticle dynamics with good energy and momentum resolution.[1]

In particular, the low-energy electron dynamics at metal surfaces,[2] in layered materials, such as magnesium diboride,[3] graphite,[4] and cuprate superconductors,[1] and in single layer graphene[5–16] is significantly affected by the electron-phonon interaction. Since the electron-phonon interaction generally manifests itself as a kink in the quasiparticle dispersion relations measured by angle-resolved photoemission spectroscopy,[17,18] it is common practice to determine the strength of the electron-phonon coupling by taking the ratio between the group velocity at the Fermi level and below the phonon-induced kink.[8,19–21] In the cases where this simple procedure is not applicable, more complicated self-consistent algorithms[22,23] become necessary to extract the electron-phonon coupling strength. However, the application of these methods requires knowledge of several adjustable parameters and is subject to some arbitrariness. Therefore, assessing in the first instance the validity of extraction procedures based on the linear slopes of the photoemission data is an important issue.

Graphene[24–28] is an ideal system to investigate these effects. Indeed, the Fermi level of graphene can be tuned over a wide energy range by chemical doping[5,8] or by gating,[26,27,29] and can almost be aligned with the van Hove singularity at the M point of the two-dimensional Brillouin zone.[8]

In this work, we show that the apparent electron-phonon coupling strength in doped graphene obtained from the linear slopes of the renormalized quasiparticle dispersions, as calculated from first principles, is highly *anisotropic*, which is in good agreement with experimental results.[8] On the other hand, the phonon-induced electron self-energy is found to be only weakly dependent on the wave vector in the Brillouin zone. As a consequence, the actual electron-phonon coupling strength is *isotropic*. The apparent anisotropy of the electron-phonon interaction is shown to arise from the curvature of the bare electronic bands of graphene, which is strongly enhanced in the proximity of the van Hove singularity at the M point. Our findings are relevant to the interpretation of photoemission spectra in materials where the Fermi level is aligned with a van Hove singularity, such as the hole-doped cuprates at optimal doping.

The mass-enhancement parameter or electron-phonon coupling strength $\lambda_{\mathbf{k}}$ of an electronic state with wave vector $\mathbf{k}$ on the Fermi surface can be expressed through the energy derivative of the real part of the self-energy arising from the electron-phonon interaction[30] as follows:

$$\lambda_{\mathbf{k}} = -\left.\frac{\partial \,\mathrm{Re}\,\Sigma_{\mathbf{k}}(E)}{\partial E}\right|_{E=E_{\mathrm{F}}}, \tag{1}$$

with E_{F} being the Fermi level. Within the Migdal approximation, which corresponds to considering the noncrossing electron-phonon self-energy diagrams, this quantity can be calculated by[17,31]

$$\lambda_{\mathbf{k}} = \sum_{m,\nu}\int \frac{d\mathbf{q}}{A_{\mathrm{BZ}}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2\left[\frac{n_{\mathbf{q}\nu}+1-f_{m\mathbf{k}+\mathbf{q}}}{(E_{\mathrm{F}}-\epsilon_{m\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\nu})^2} + \frac{n_{\mathbf{q}\nu}+f_{m\mathbf{k}+\mathbf{q}}}{(E_{\mathrm{F}}-\epsilon_{m\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\nu})^2}\right], \tag{2}$$

where $\epsilon_{n\mathbf{k}}$ is the energy of an electron in the band n with wave vector $\mathbf{k}$, $\omega_{\mathbf{q}\nu}$ the energy of a phonon in the branch ν with wave vector $\mathbf{q}$, and $f_{n\mathbf{k}}$ and $n_{\mathbf{q}\nu}$ are the Fermi–Dirac and Bose–Einstein occupations, respectively. The integration is performed within the two-dimensional Brillouin zone (BZ) of area A_{BZ}. The electron-phonon matrix element $g_{mn,\nu}(\mathbf{k},\mathbf{q})=\langle m\mathbf{k}+\mathbf{q}|\Delta V_{\mathbf{q}\nu}|n\mathbf{k}\rangle$ is the amplitude for the transition from an electronic state $|n\mathbf{k}\rangle$ to another state $|m\mathbf{k}+\mathbf{q}\rangle$ induced by the change in the self-consistent potential $\Delta V_{\mathbf{q}\nu}$ generated by the phonon $|\mathbf{q}\nu\rangle$. The technical details of the calculations are reported in Ref. 13.

It can be shown[17] that the actual electron-phonon coupling strength in Eq. (1) can also be written as

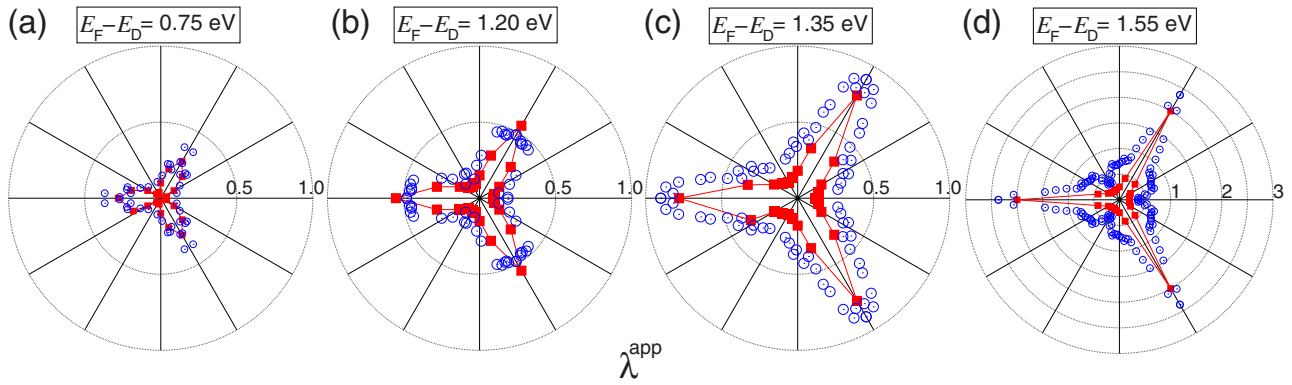

FIG. 1. (Color online) Polar plots of the apparent electron-phonon coupling strength $\lambda_{\mathbf{k}}^{app}$ on the Fermi surface around the K point in the Brillouin zone. Filled red squares and empty blue circles represent the results from the *ab initio* calculation and from the experimental photoemission spectra, respectively. The lines are included as a guide for the eye. Different panels correspond to different doping levels. Note that the scale in (d) is different from that in (a)–(c).

$$\lambda_{\mathbf{k}} = \frac{v_{\mathbf{k}}^0(E_F)}{v_{\mathbf{k}}(E_F)} - 1, \tag{3}$$

where $v_{\mathbf{k}}(E_F)$ and $v_{\mathbf{k}}^0(E_F)$ are the renormalized and bare velocities at the Fermi level, respectively. While Eq. (3) is useful for theoretical analyses, it cannot be used directly in determining the electron-phonon coupling strength from the experimental data since the bare group velocity is merely a conceptual tool and cannot be measured. To circumvent this difficulty, from the experimentally measured low-energy photoemission spectrum, the electron-phonon coupling strength is usually extracted[1,8] by taking the ratio of the renormalized velocity below and above the phonon kink. This procedure rests on the assumptions that (i) well beyond the phonon energy scale, the bare velocity is fully recovered and that (ii) the bare band is linear over the energy range considered. We denote the value obtained from this procedure as the apparent electron-phonon coupling strength:

$$\lambda_{\mathbf{k}}^{app} = \frac{v_{\mathbf{k}}(E_F - \Delta E)}{v_{\mathbf{k}}(E_F)} - 1, \tag{4}$$

where ΔE is taken to be slightly larger than the phonon energy ω_{ph} so that the energy $E=E_F-\Delta E$ falls below the phonon kink.

In Fig. 1, we compare the apparent coupling strength $\lambda_{\mathbf{k}}^{app}$ obtained from our first-principles calculations and that extracted from the experimental photoemission spectra of graphene at four different levels of doping.[8] To determine $v_{\mathbf{k}}(E_F-\Delta E)$ in Eq. (4) from our first-principles calculations, we considered the slope of the quasiparticle band at the energy $\Delta E=0.3$ eV below the Fermi level.[32] We have checked that as the energy range ΔE varies within the interval 0.2–0.4 eV, the apparent strength λ^{app} changes by less than 10% along both the KM and $K\Gamma$ directions. Theory and experiment are in good agreement with each other for all doping levels considered. For graphene at the highest doping level ($E_F-E_D=1.55$ eV, where E_D is the energy at the Dirac point), the agreement between theory and experiment is slightly worse along the $K\Gamma$ direction.

Figure 2(a) shows the calculated apparent strength λ^{app} [Eq. (4)] as a function of doping for two different directions in the Brillouin zone of graphene. The apparent electron-phonon coupling strength is highly anisotropic and can become as large as $\lambda^{app}=2$ along the KM direction for the doping levels considered here.

Now we consider the actual electron-phonon coupling strength λ as obtained from Eq. (2) [Fig. 2(b)]. The actual strength monotonically increases with doping, reaching $\lambda=0.22$ when $E_F-E_D=1.5$ eV. At variance with the apparent strength, the actual strength λ does not depend on the direction of the wave vector $\mathbf{k}$. We have checked that this holds for any path through the K point. The present results indicate that the actual electron-phonon coupling strength in doped graphene is extremely isotropic. Thus, the actual strength can substantially differ from the apparent strength, more so as the Fermi surface approaches the van Hove singularity at the M point.

In order to analyze in detail the angular dependence of the electron-phonon coupling in graphene, we calculated the phonon-induced electron self-energy using Eq. (1) of Ref.

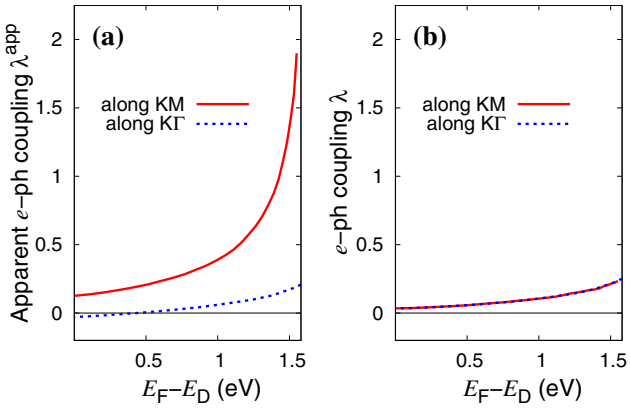

FIG. 2. (Color online) (a) The apparent strength λ^{app} and (b) the actual electron-phonon coupling strength λ calculated along two different directions in the two-dimensional Brillouin zone of graphene: along KM (solid red lines) and along $K\Gamma$ (dashed blue lines). Along the $K\Gamma$ direction, λ^{app} can even become negative [cf. discussion around Eq. (5)].

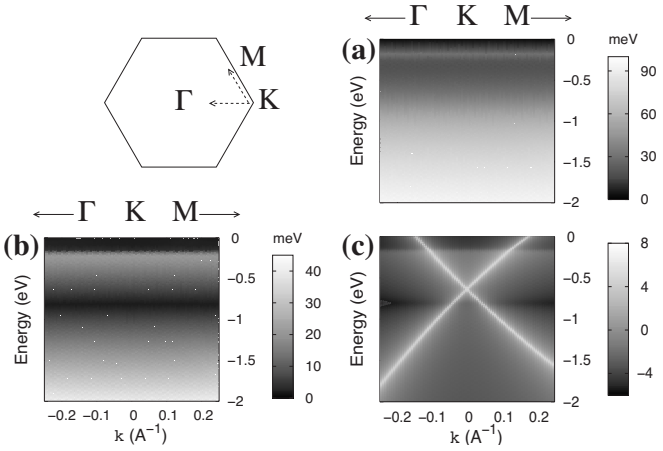

FIG. 3. Calculated (a) real and (b) imaginary parts of the electron self-energy $\Sigma(E,\mathbf{k})$ and (c) logarithm of the corresponding spectral function $A(E,\mathbf{k})$ arising from the electron-phonon interaction in n-doped graphene ($E_F-E_D=0.64$ eV), along two different directions KM and $K\Gamma$ in the Brillouin zone.

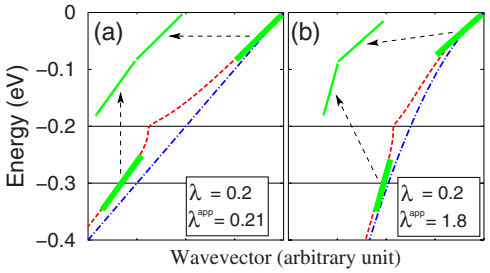

FIG. 4. (Color online) Quasiparticle band structures of model systems including the electron-phonon interaction (dashed red lines). In (a) and (b), the bare electronic bands (dash-dotted blue lines) are assumed to be linear and quadratic, respectively. In each case, the actual electron-phonon coupling strength is set to $\lambda=0.2$. The horizontal solid lines represent the phonon energy $\omega_{\mathrm{ph}}=0.2$ eV, and the energy $\Delta E=0.3$ eV below the Fermi level ($E_{\mathrm{F}}=0$), at which the slope is taken to calculate the apparent strength λ^{app}. The solid green line segments are tangential to the quasiparticle band structure at $E=0$ or $E=-\Delta E$.

13. While in Ref. 13 the electron self-energy was evaluated under the constraint $E=\epsilon_{\mathbf{k}}$, here we consider the complete energy-dependent self-energy $\Sigma_{\mathbf{k}}(E)$. Figures 3(a) and 3(b) show the real and imaginary parts of the electron self-energy in n-doped graphene ($E_F-E_D=0.64$ eV). The wave vector is varied along two different paths indicated in the upper left corner of Fig. 3. The dependence of the self-energy on the wave vector $\mathbf{k}$ is found to be extremely weak, with the variation along the path considered in Fig. 3 being less than 3 meV for a given energy E. The insensitivity of the electron-phonon coupling strength $\lambda_{\mathbf{k}}$ to the wave vector $\mathbf{k}$ [see Fig. 2(b)] is fully consistent with the finding on the self-energy. Figure 3 also shows that, while the self-energy is highly isotropic, the corresponding spectral function exhibits significant angular dependence due to the anisotropic dispersion of the energy bands in graphene.

Recently, the observed anisotropy[8] in the apparent electron-phonon coupling strength has been related to foreign atoms based on calculations of CaC_6 layers with the dopants arranged periodically in atop sites on the graphene plane.[14] Our calculations clearly show that the anisotropy in the apparent strength λ^{app} is already present without invoking the possible effect of the dopants.

Our investigation of doped graphene allows us to discuss some general aspects of the extraction of the electron-phonon coupling parameters from angle-resolved photoemission data. By expanding the energy dependence of the velocity to first order, we can rewrite approximately the apparent electron-phonon coupling strength in Eq. (4) as

$$\lambda_{\mathbf{k}}^{\mathrm{app}} \approx \lambda_{\mathbf{k}} - \frac{v_{\mathbf{k}}'^{0}(E_{\mathrm{F}})}{v_{\mathbf{k}}(E_{\mathrm{F}})}\Delta E. \tag{5}$$

In Eq. (5), $v_{\mathbf{k}}'^{0}(E_{\mathrm{F}})$ is the energy derivative of the bare velocity, and we assumed that well below the phonon kink, the bare and renormalized velocities coincide. Equation (5) shows that whenever the band velocity decreases with decreasing binding energy (i.e., $v_{\mathbf{k}}'^{0}<0$), as is the case for graphene along the KM direction, the apparent electron-phonon coupling strength always exceeds the actual strength.

To illustrate this point, we consider in Fig. 4 the quasiparticle band structure for a model system obtained by assuming an Einstein phonon spectrum with phonon energy $\omega_{\mathrm{ph}}=0.2$ eV, a constant density of states near the Fermi level, and a constant electron-phonon coupling strength $\lambda=0.2$. Within this model, the real part of the electron self-energy due to electron-phonon interaction reads[18]

$$\mathrm{Re}\,\Sigma(E) = -\frac{\lambda\omega_{\mathrm{ph}}}{4}\log\left|\frac{(E+\omega_{\mathrm{ph}})^2+\Gamma^2}{(E-\omega_{\mathrm{ph}})^2+\Gamma^2}\right|, \tag{6}$$

having included broadening $\Gamma=10$ meV for convenience. As shown in Fig. 4(a), the apparent strength $\lambda^{\mathrm{app}}=0.21$ constitutes a good approximation to the actual strength $\lambda=0.2$ when the slope of the bare electronic band does not change appreciably within the phonon energy scale, i.e., $v_{\mathbf{k}}'^{0}(E_{\mathrm{F}})\Delta E \ll v_{\mathbf{k}}(E_{\mathrm{F}})$. However, in the case where the bare velocity decreases with decreasing binding energy, the apparent strength $\lambda^{\mathrm{app}}=1.8$ differs significantly from the actual electron-phonon coupling strength $\lambda=0.2$, which is consistent with Eq. (5) [Fig. 4(b)]. In the limiting situation where the Fermi level is aligned with the van Hove singularity (as in heavily doped graphene), the velocity at the Fermi level vanishes, while the velocity below the phonon kink energy remains finite. As a result, the apparent strength obtained through Eq. (4) becomes exceedingly large.

In conclusion, we have shown that while the phonon-induced electronic self-energy of graphene is isotropic and, consequently, the angular dependence of the electron-phonon coupling strength is negligible, the apparent electron-phonon coupling strength extracted from the experimental angle-resolved photoemission spectra using Eq. (4) exhibits significant anisotropy due to the curvature of the underlying bare electronic bands. Our analysis indicates that the band curvature is a crucial ingredient for the interpretation of angle-resolved photoemission spectra. For example, the present re-

sult may carry implications in the interpretation of many-body renormalization effects along the antinodal cuts in the photoemission spectra of cuprate superconductors due to the presence of a saddle-point van Hove singularity along the Cu-O bond directions.[33,34]

This work was supported by NSF Grant No. DMR07-05941 and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering Division, U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Computational resources have been provided by the National Partnership for Advanced Computational Infrastructure (NPACI) and the National Energy Research Scientific Computing Center (NERSC). The calculations were performed using the QUANTUM-ESPRESSO (Ref. 35) and WANNIER (Ref. 36) packages.

*cheolwhan@civet.berkeley.edu

[1] A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. **75**, 473 (2003).
[2] E. W. Plummer, J. Shi, S. J. Tang, E. Rotenberg, and S. D. Kevan, Prog. Surf. Sci. **74**, 251 (2003).
[3] S. Souma, Y. Machida, T. Sato, T. Takahashi, H. Matsui, S.-C. Wang, H. Ding, A. Kaminski, J. C. Campuzano, S. Sasaki, and K. Kadowaki, Nature (London) **423**, 65 (2003).
[4] S. Y. Zhou, G.-H. Gweon, J. Graf, A. V. Fedorov, C. D. Spataru, R. D. Diehl, Y. Kopelevich, D.-H. Lee, S. G. Louie, and A. Lanzara, Nat. Phys. **2**, 595 (2006).
[5] A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg, Nat. Phys. **3**, 36 (2007).
[6] T. Ohta, A. Bostwick, J. L. McChesney, T. Seyller, K. Horn, and E. Rotenberg, Phys. Rev. Lett. **98**, 206802 (2007).
[7] A. Bostwick, T. Ohta, J. L. McChesney, K. V. Emtsev, T. Seyller, K. Horn, and E. Rotenberg, New J. Phys. **9**, 385 (2007).
[8] J. McChesney, A. Bostwick, T. Ohta, K. Emtsev, T. Seyller, K. Horn, and E. Rotenberg, arXiv:0705.3264 (unpublished).
[9] T. Ohta, F. E. Gabaly, A. Bostwick, J. McChesney, K. V. Emtsev, A. K. Schmid, T. Seyller, K. Horn, and E. Rotenberg, New J. Phys. **10**, 023034 (2008).
[10] M. Mucha-Kruczynski, O. Tsyplyatyev, A. Grishin, E. McCann, V. I. Fal'ko, A. Bostwick, and E. Rotenberg, arXiv:0711.1129 (unpublished).
[11] S. Zhou, D. Siegel, A. Fedorov, and A. Lanzara, Nat. Mater. **6**, 770 (2007).
[12] S. Zhou, D. Siegel, A. Fedorov, and A. Lanzara, arXiv:0801.3862 (unpublished).
[13] C.-H. Park, F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **99**, 086804 (2007).
[14] M. Calandra and F. Mauri, Phys. Rev. B **76**, 161406(R) (2007).
[15] M. Calandra and F. Mauri, Phys. Rev. B **76**, 205411 (2007).
[16] W.-K. Tse and S. Das Sarma, Phys. Rev. Lett. **99**, 236802 (2007).
[17] G. Grimvall, in *The Electron-Phonon Interaction in Metals*, edited by E. Wohlfarth, Selected Topics in Solid State Physics (North-Holland, New York, 1981).
[18] S. Engelsberg and J. R. Schrieffer, Phys. Rev. **131**, 993 (1963).
[19] M. Hengsberger, D. Purdie, P. Segovia, M. Garnier, and Y. Baer, Phys. Rev. Lett. **83**, 592 (1999).
[20] M. Hengsberger, R. Frésard, D. Purdie, P. Segovia, and Y. Baer, Phys. Rev. B **60**, 10796 (1999).
[21] E. Rotenberg, J. Schaefer, and S. D. Kevan, Phys. Rev. Lett. **84**, 2925 (2000).
[22] A. Kaminski and H. M. Fretwell, New J. Phys. **7**, 98 (2005).
[23] A. A. Kordyuk, S. V. Borisenko, A. Koitzsch, J. Fink, M. Knupfer, and H. Berger, Phys. Rev. B **71**, 214513 (2005).
[24] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
[25] K. S. Novoselov, D. Jiang, F. Schedin, T. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. U.S.A. **102**, 10451 (2005).
[26] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005).
[27] Y. Zhang, J. W. Tan, H. L. Stormer, and P. Kim, Nature (London) **438**, 201 (2005).
[28] C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).
[29] A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).
[30] S. Nakajima and M. Watabe, Prog. Theor. Phys. **29**, 341 (1963).
[31] F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. B **76**, 165108 (2007).
[32] This specific value of $\Delta E=0.3$ eV was chosen under a reasonable assumption that $v_{\mathbf{k}}(E_F-\Delta E)$ appearing in Eq. (3) is obtained as the average slope between $E=E_F-\omega_{\mathrm{ph}}$ and $E=E_F-2\omega_{\mathrm{ph}}$. We have checked that as the energy range ΔE varies within the interval 0.2–0.4 eV, the apprent strength λ^{app} changes by less than 10% along both KM and $K\Gamma$ directions.
[33] A. A. Kordyuk, S. V. Borisenko, T. K. Kim, K. A. Nenkov, M. Knupfer, J. Fink, M. S. Golden, H. Berger, and R. Follath, Phys. Rev. Lett. **89**, 077003 (2002).
[34] A. D. Gromko, Y.-D. Chuang, A. V. Fedorov, Y. Aiura, Y. Yamaguchi, K. Oka, Y. Ando, and D. S. Dessau, arXiv:cond-mat/0205385 (unpublished).
[35] S. Baroni, S. de Gironcoli, A. D. Corso, P. Gianozzi, and F. Mauri, computer code QUANTUM-ESPRESSO, 2006, http://www.quantum-espresso.org
[36] A. Mostofi, J. R. Yates, N. Marzari, I. Souza, and D. Vanderbilt, computer code WANNIER, 2006, http://www.wannier.org