Ultrafast Dynamics of Dirac Plasmon in Graphene

Dino Novko$^{1,2,*}$

$^1$ Institute of Physics, Bijenička 46, 10000 Zagreb, Croatia
$^2$ Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain

Exploring low-loss two-dimensional plasmon modes is considered central for achieving light manipulation at the nanoscale and applications in plasmonic science and technology. In this context, pump-probe spectroscopy is a powerful tool for investigating these collective modes and the corresponding energy transfer processes. Here, I present a first-principles study on non-equilibrium Dirac plasmon in graphene, wherein damping channels under ultrafast conditions are still not fully explored. The laser-induced blueshift of plasmon energy is explained in terms of thermal increase of the electron-hole pair concentration in the intraband channel. Interestingly, while damping pathways of the equilibrium graphene plasmon are entirely ruled by scatterings with acoustic phonons, the photoinduced plasmon predominantly transfers its energy to the strongly coupled hot optical phonons, which explains the experimentally-observed tenfold increase of the plasmon linewidth.

The present study paves the way for an in-depth theoretical comprehension of plasmon temporal dynamics in novel two-dimensional systems and heterostructures.

Understanding, and thus mastering, the temporal dynamics of charge carriers in graphene and related quasi-two-dimensional materials is pivotal, but highly challenging task in material science. Many recent studies were devoted to explore the time evolution of the laser-excited electrons by means of time-resolved photoemission [1–5] and pump-probe optical absorption spectroscopies [6–13] in graphene and graphite in order to reach the aforesaid goal. Precise time scales of ultrafast electron interactions were extracted, in particular, electron-electron scattering was shown to rule the dynamics below, while the coupling with the optical phonons (OP) above $\sim 50$ fs [1, 3–6]. However, underlying microscopic processes still remain largely unexplored, mostly due to a lack of accompanying first-principles methodology that can quantitatively capture these features.

Photoinduced plasmon excitation, i.e., collective electron oscillations under highly nonequilibrium condition, [14, 15] is one such ultrafast phenomena that requires further insights. In graphene and graphene-based heterostructures, two-dimensional plasmons show quite exceptional features, e.g., electrical tunability [16, 17] and low losses [18–20], making these materials promising building blocks for optoelectronic and plasmonic devices. Recently, the relaxation dynamics of laser-induced graphene plasmon was monitored with unprecedented temporal and spatial resolution by using antenna-based near-field nanoscopy [21, 22]. High electron temperatures achieved in these experiments are increasing the energy of graphene plasmon while concurrently increasing (decreasing) its linewidth (lifetime) [22]. The former was explained in terms of increase of the Drude weight, or equivalently increase of thermally excited electron-hole pairs, with elevated electron temperature, while the origin of the latter remains unresolved. Since the relaxation of equilibrium graphene plasmon was shown to be governed by the electron-phonon coupling [19, 20, 23, 24], mainly coupling with graphene acoustic phonons (AP) [19, 20, 23], it was speculated that the enhanced plasmon decay under non-equilibrium condition has the same origin [22]. However, projecting conclusions from the equilibrium situation might be premature, considering highly disparate thermal conditions in the two cases, but also having in mind the results extracted from time-resolved photoemission and optical absorption experiments where OP were proven to play a key role in relaxation processes [1, 3, 6].

In this Letter, I investigate the dynamics of laser-excited plasmon in lightly-doped graphene under nonequilibrium conditions by means of the robust ab initio methodology. The work conjoins the electron-phonon coupling theory and the Coulomb screening in random phase approximation to capture the temperature-dependent plasmon decay due to phonons [24–26], while the nonequilibrium electron and phonon temperatures are simulated within the effective temperature model [27–31]. I show, in agreement with previous reports [19, 20, 23], that graphene plasmon under equilibrium conditions (i.e., when electrons and phonons are thermalized) is predominantly decaying due to scattering with the AP. In particular, the obtained temperature dependence of the plasmon decay rate due to coupling with AP shows very good agreement with recent measurements done on high-mobility graphene [20]. However, the situation is drastically different for nonequilibrium conditions, where the majority of the laser-induced excess electron energy is transferred to the strongly coupled OP, creating hot phonon bath [6]. In this case, the results show that the low-energy plasmons (i.e., at $\sim 0.1$ eV), usually explored in the experiments [20–22], are mostly coupled to the hot OP, which is in contrast to the current belief [22]. The latter interaction is consequently responsible for the large time-dependent modifications of plasmon broadening. In addition, the laser excitation increases the phase space for the interband transitions (i.e., Landau damping), which in turn enhance the plasmon decay rate at higher energies (i.e., around 0.2 eV). Finally, the experimentally-
observed ultrafast blueshift of plasmon energy is to be induced by the transient increase of the electron-hole pair excitations in the intraband channel (i.e., increase of the Drude weight). All in all, I believe that the \textit{ab initio} methodology and conclusions outlined here will be useful not only for comprehending the interplay of plasmon and phonon dynamics in graphene, but as well in other similar systems hosting a two-dimensional plasmon [32, 33].

Ultrafast electron dynamics is explored here for the hole-doped graphene where the Fermi energy is $\varepsilon_F = -250$ meV, as it is the case, e.g., for graphene adsorbed on SiC surface [1] (note that the conclusions of the paper would be the same for lightly electron-doped graphene as in the graphene/SiO$_2$ system [22] due to electron-hole symmetry in the low-energy region of band structure). The corresponding electron and phonon band structures are shown in Figs. 1(a) and 1(b) (see SI for computational details). Additionally, Fig. 1(b) shows the results for the Eliashberg function that measures the degree of the electron-phonon coupling with energy resolution. As is well know [34], electrons are strongly coupled to OP at K and $\Gamma$ point of the Brillouin zone, i.e., $\omega \gtrsim 0.16$ eV where Eliashberg function shows two prominent peaks, while only weakly coupled to the rest of the modes (mostly low-energy AP). Accordingly, the plasmon excitations below 0.16 eV are weakly coupled to AP [23], while at higher energies plasmon decay is mostly due to the strong coupling with OP [24]. The graphene plasmon dispersion $\omega_{pl}$ and the corresponding decay regions are shown in Fig. 1(c).

Figures 2(a) and 2(b) further depict the energy renormalization $1 + \lambda_{ep}(\omega)$ and decay rate $\gamma_{ep}(\omega)$, respectively, of the electron-hole pairs due to coupling with phonons as a function of temperature [25, 35–37]. These quantities are computed by using density functional and density functional perturbation theories [38, 39] as in Refs. [24, 31, 40] (see SI for computational details). The Fermi energy is here chosen to be $\varepsilon_F = 300$ meV for the sake of comparison with the experiment [20] (the rest of the results are for $\varepsilon_F = -250$ meV as mentioned earlier). For plasmon energies, i.e., $\omega = \omega_{pl}$, the quantities $1 + \lambda_{ep}(\omega_{pl})$ and $\gamma_{ep}(\omega_{pl})$ are equivalent to the plasmon energy renormalization and plasmon decay rate due to coupling with phonons [24]. The results show that the plasmon energy is insignificantly renormalized due to electron-phonon coupling, with very small temperature modifications. The corresponding plasmon broadening is as well small (especially for $\omega_{pl} < 0.16$ eV, where electrons mostly couple to AP) but notable. For the temperature range presented here, the temperature-induced change in plasmon broadening is more pronounced for the lower energies since AP are more easily excited with temperature than the high-energy OP (i.e., $\omega_{OP} \gg k_B T$). Figure 2(c) shows the temperature dependence of the plasmon decay rate when $\omega_{pl} = 110$ meV. The results are in very good agreement with the decay rate extracted from the recent experiment done on high-mobility graphene [20]. Further analysis demonstrates that the decay rate of the equilibrium graphene plasmon and its temperature dependence predominantly comes from coupling with AP, in agreement with the previous studies [19, 20, 23].

I turn now to the study of the nonequilibrium condition, i.e., of the ultrafast electron dynamics in graphene. In order to simulate the laser-induced electron dynamics...
I utilize the three temperature model [29] with \textit{ab initio} input parameters (see Ref. [30] and SI for more details). Within this model, the temperature of graphene is divided among three subsystems, i.e., electron temperature \((T_e)\), temperature of the strongly coupled optical phonons \((T_{OP})\), and the remnant temperature that mostly belongs to AP \((T_{AP})\). The energy flow between electron and phonon degrees of freedom is then dictated by the electron-phonon coupling [27], while the thermalization between two phonon subsystems goes via anharmonic coupling. The resultant time evolution of these temperatures is shown in Fig. 3(a), where the laser with fluence of \(F = 8 \text{ J/m}^2\) excites the system at time delay \(t_d = 0\). Right after the laser excitation, the electron temperature \(T_e\) abruptly increases up to almost 3000 K and subsequently decays due to coupling with OP, in good agreement with the experiment [2]. Consequently, the temperature of the strongly coupled OP elevates above 1000 K, while the AP remain almost at the same temperature. Since the energy exchange rate between phonon and electron baths is proportional to \(\lambda \langle \omega^2 \rangle / C_{ph}\) (where \(\lambda\) is the electron-phonon coupling strength, \(\langle \omega^2 \rangle\) is the second moment of the phonon spectrum, and \(C_{ph}\) is the heat capacity of the relevant phonon subsystem) [27], the obtained dramatic difference between the OP and AP temperatures comes not only because the OP are coupled more strongly to the electrons than the AP \((\lambda_{OP} \langle \omega^2 \rangle_{OP} > \lambda_{AP} \langle \omega^2 \rangle_{AP}\)), but also because the strongly coupled OP subsystem consist of only very few modes around \(\Gamma\) and K points of the Brillouin zone [see Fig. 1(b)] and thus \(C_{OP} \ll C_{AP}\). Such laser-induced hot OP scenario was already discussed in various spectroscopy studies [1, 3, 6].

Figure 3(b) shows the ensuing charge density modifications \(\delta n\) as a function of time delay. As laser excites the system, electron-hole pair concentration increases both in intraband (electron and hole are in the same band) and interband (electron and hole are in different bands) channels. In fact, for the lightly-doped graphene with \(\varepsilon_F = -250 \text{ meV}\) it turns out that \(\delta n_{intra} \gg \delta n_{inter}\). The laser-induced changes of the electron-phonon coupling are shown in Figs. 3(c) and 3(d). In particular, time-dependent modifications of the electron-phonon decay rate \(\delta \gamma_{ep}\) and energy renormalization parameter \(1 + \lambda_{ep}\) are depicted for three different excitation energies \(\omega\). Since \(1 + \lambda_{ep}\) is already small for the equilibrium situation, it is not surprising that \(1 + \lambda_{ep}\) experiences only minor changes as a function of pump-probe time delay and excitation energy. One can also note that laser excitation reduces the energy renormalization parameter as a function of time. On the other hand, for the same laser conditions, the photoinduced decay rate modifications \(\delta \gamma_{ep}\) are relatively high [i.e., \(\delta \gamma_{ep} \gg \gamma_{ep}(T = 300 \text{ K})\)] and actually follow the variations of both \(T_e\) and \(T_{OP}\) (see the discussion below). Also, the overall intensity of \(\delta \gamma_{ep}\) over time is bigger for smaller excitation energies (i.e., for \(\omega = 0.1 \text{ eV}\) and \(0.2 \text{ eV}\), compared to \(\omega = 0.4 \text{ eV}\)). This is because for \(\omega \lesssim 0.2 \text{ eV}\) the equilibrium value of \(\gamma_{ep}\) is small and includes mostly the contributions from the weakly-coupled AP modes, while when both \(T_e\) and \(T_{OP}\) are elevated the probability of scattering on the OP, which are strongly coupled to electrons, increases significantly. A more rapid increase of electron-OP scattering probability when \(T \gtrsim 300 \text{ K}\) can, for example, be seen in Fig. 2(c). However, when \(\omega \gtrsim 0.2 \text{ eV}\) the probability of scattering on the OP is less altered for the present laser conditions, since \(\omega > T_e, T_{OP}\). Therefore, the relative modification of damping rate is less pronounced for \(\omega > 0.2 \text{ eV}\) compared to \(\omega \lesssim 0.2 \text{ eV}\).

The time dynamics of charge density and decay rate are relevant for comprehending the transient optical absorption, i.e., photoconductivity, as well as the relaxation mechanisms of nonequilibrium plasmons. Figure 3(e) depicts the time evolution of optical absorption \(\sigma_1(\omega)\) (i.e., the real part of optical conductivity \(\sigma\)) up to 0.7 eV (see SI for the corresponding methodology). The observed modifications are due to photoinduced variations of \(T_e\), and also due to changes in decay rate \(\delta \gamma_{ep}\) (note that \(\sigma_1(0) \propto n/\gamma_{ep}\) and \(\sigma_1(\omega > 0) \propto n_{ep}/(\omega^2 + \gamma_{ep}^2)\) [24, 35, 37]). In particular, the low-energy part of \(\sigma_1(\omega)\) decreases significantly around \(t_d = 0\) due to changes in \(\delta \gamma_{ep}\) and then it starts to increase back to its equilibrium value [see the inset in Fig 3(e)]. Contrary, for higher excitation energies up to around interband threshold \(2|\varepsilon_F|\) the photoinduced modifications of \(\sigma_1(\omega)\) are...
The processes underlying the plasmon decay rate $\delta_\gamma$ as a function of time delay are a bit more complex than the processes ruling $\delta\omega$. For plasmon energies $\omega_\text{pl} \approx 0.1 \text{ eV}$, it turns out that the increase of the plasmon broadening $\delta_\gamma$ is entirely ruled by electron-phonon coupling. What is intriguing and actually at odds with the previous assumptions [22], is that the photoinduced plasmon decays mostly due to scatterings with the OP modes [cf. green and purple dashed lines in Fig. 4(b)]. This is also in contrast with the decay mechanisms of the equilibrium plasmon, for which the scattering with the AP modes is the main loss channel [Fig. 2(c)].

The present analysis also shows that part of the electron-OP scattering contribution to the $\delta_\gamma$ is induced by the elevated $T_e$ and part by the elevated $T_\text{OP}$ [cf. purple and black dashed lines in Fig. 4(b)]. Namely, the laser heats the OP modes (i.e., elevates $T_e$), which in turn increases the electron phase space for the electron-OP scattering, especially when $T_e > \omega_\text{OP}$. In addition, hot electrons transfer the excess energy to the strongly-coupled OP, i.e., $T_\text{OP}$ rises substantially, which increases the number of thermally excited OP and therefore increases $\delta_\gamma$. All in all, the results show that the plasmon-OP scattering is behind the experimentally-observed plasmon broadening under non-equilibrium conditions. The coupling with the OP modes is generally much more stronger than with the AP modes. However, for equilibrium case the energy conservation condition $\omega_\text{pl} \geq \omega_\text{OP}$ must be met in order to activate this strong coupling. On the other hand, under the strong laser excitations, this energy conservation condition looses up considerably and graphene plasmons with energy $\omega_\text{pl} < \omega_\text{OP}$ couple strongly with the hot OP modes. When the plasmon energy is more closer to the interband threshold $2|\varepsilon_F|$, i.e., $\omega_\text{pl} \approx 0.2 \text{ eV}$, the plasmon energy predominantly come from the increase of electron-hole pair concentrations in the intraband channel $n_\text{intra}$ [see Figs. 4(a) and 4(d)]. In other words, laser elevates $T_e$, i.e., increases the number of thermally excited electrons in the intra-band channel [see also Fig. 3(b)], which in turn increases the Drude weight and thus the plasmon energy [21, 22]. As already discussed above, the renormalization of the plasmon energy due to electron-phonon coupling is insignificant [see also Fig. 3(d)].
Temporal dynamics of non-equilibrium plasmon under intense laser excitation was explored in lightly-doped graphene by means of density functional and density functional perturbation theories. By considering plasmon-phonon coupling, decay rates of graphene Dirac plasmon were studied under both equilibrium (i.e., electron and nuclear degrees of freedom are thermalized) and ultrafast (i.e., electrons and phonons are thermally excited and have disparate energies) conditions. Due to available phase space and energy constraints, equilibrium plasmon with energy \( \sim 0.1 \text{eV} \) and at ambient temperature is mostly damped due to scatterings with the acoustic phonon modes. Interestingly, the photoinduced non-equilibrium graphene plasmon is, on the other hand, underlain by completely different damping mechanism. Namely, the pump laser pulse increases the population of hot electrons, which in turn transfers the large portion of energy to the strongly coupled optical phonons, creating hot optical-phonon bath. Under such out-of-equilibrium condition phase space for electron scatterings and population of optical phonon modes are increased, as well as the energy constraints are loosened. Consequently, the broadening of the non-equilibrium plasmon is increased immediately after the laser excitation, mostly due to coupling with the hot optical phonons. The corresponding strong plasmon energy renormalization is explained in terms of photoinduced Drude weight increase. For energies \( \sim 0.2 \text{eV} \) damping pathways of non-equilibrium plasmon are again different and are due to photoinduced interband excitations (Landau damping). Present study might also help elucidate energy-transfer mechanisms under optical pumping in novel quasi-two-dimensional materials that support collective plasmon modes, like metallic transition metal dichalcogenides [47, 48], topological insulators [32, 33], borophene [49], or layered electrides [50, 51].

**ACKNOWLEDGMENTS**

The author acknowledges financial support from the Croatian Science Foundation (Grant no. UIP-2019-04-6869) and from the European Regional Development Fund for the “Center of Excellence for Advanced Materials and Sensing Devices” (Grant No. KK.01.1.1.01.0001). Financial support by Donostia International Physics Center (DIPC) during various stages of this work is also acknowledged. Computational resources were provided by the DIPC computing center.

[1] J. C. Johannsen, S. Ulstrup, F. Cilento, A. Crepaldi, M. Zacchigna, C. Cacho, I. C. E. Turcu, E. Springate, F. Fromm, C. Raidel, T. Seyller, F. Parmigiani, M. Grioni, and P. Hofmann, Phys. Rev. Lett. 111, 027403 (2013).
[2] I. Gierz, J. C. Petersen, M. Mitrano, C. Cacho, I. C. E. Turcu, E. Springate, A. Stöhr, U. Starke, and A. Cavalleri, Nature Mater. 12, 1119 (2013).
[3] A. Stange, C. Sohrt, L. X. Yang, G. Rohde, K. Janssen, P. Hein, L.-P. Oloff, K. Hanff, K. Rossnagel, and M. Bauer, Phys. Rev. B 92, 184303 (2015).
[4] S. Tan, A. Argondizzo, C. Wang, X. Cui, and H. Petek, Phys. Rev. X 7, 011004 (2017).
[5] G. Rohde, A. Stange, A. Müller, M. Behrendt, L.-P. Oloff, K. Hanff, T. J. Albert, P. Hein, K. Rossnagel, and M. Bauer, Phys. Rev. Lett. 121, 256401 (2018).
[6] T. Kampfrath, L. Perfetti, F. Schapper, C. Frischkorn, and M. Wolf, Phys. Rev. Lett. 95, 187403 (2005).
[7] D. Sun, Z.-K. Wu, C. Divin, X. Li, C. Berger, W. A. de Heer, P. N. First, and T. B. Norris, Phys. Rev. Lett. 101, 157402 (2008).
[8] S. Wimmer, M. Orlita, P. Plchocka, P. Kossacki, M. Potemski, T. Winzer, E. Malic, A. Knorr, M. Sprinkle, C. Berger, W. A. de Heer, H. Schneider, and M. Helm, Phys. Rev. Lett. 107, 237401 (2011).
[9] G. Jianwali, Y. Rao, H. Yan, and T. F. Heinz, Nano Lett. 13, 524 (2013).
[10] S. A. Jensen, Z. Mics, I. Ivanov, H. S. Varol, D. Turcincovich, F. H. L. Koppens, M. Bonn, and K. J. Tielrooij, Nano Lett. 14, 5830 (2014).
[11] A. J. Frenzel, C. H. Lui, Y. C. Shin, J. Kong, and N. Gedik, Phys. Rev. Lett. 113, 056602 (2014).
[12] Z. Mics, K.-J. Tielrooij, K. Parvez, S. A. Jensen, I. Ivanov, X. Feng, K. Millen, M. Bonn, and D. Turchinovich, Nature Communications 6, 7655 (2015).
[13] A. Tomadin, S. M. Hornett, H. I. Wang, E. M. Alexeev, A. Candini, C. Coletti, D. Turchinovich, M. Kläui, M. Bonn, F. H. L. Koppens, E. Hendry, M. Polini, and K.-J. Tielrooij, Science Advances 4, eaar5313 (2018).
[14] K. F. MacDonald, Z. L. Sässon, M. I. Stockman, and N. I. Zheludev, Nature Photonics 3, 55 (2008).
[15] M. A. Huber, F. Mooshammer, M. Plankl, L. Viti, F. Sandner, L. Z. Kastner, T. Frank, J. Fabian, M. S. Vitiello, T. L. Cocker, and R. Huber, Nature Nanotechnology 12, 207 (2016).
[16] L. Ju, B. Geng, J. Hornz, G. Girit, M. Martin, Z. Hao, H. A. Bechtel, X. Liang, A. Zettl, Y. R. Shen, and F. Wang, Nature Nanotechnology 6, 630 (2011).
[17] Z. Fei, A. S. Rodin, G. O. Andreew, W. Bao, A. S. McLeod, M. Wagner, L. M. Zhang, Z. Zhao, M. Thiemens, G. Dominguez, M. M. Fogler, A. H. C. Neto, C. N. Lau, F. Keilmann, and D. N. Basov, Nature 487, 82 (2012).
[18] H. Yan, T. Low, W. Zhu, Y. Wu, M. Freitag, X. Li, F. Guinea, P. Avouris, and F. Xia, Nature Photonics 7, 394 (2013).
[19] A. Woessner, M. B. Lundeberg, Y. Gao, A. Principi, P. Alonso-González, M. Carreca, K. Watanabe, T. Taniguchi, G. Vignale, M. Polini, J. Hone, R. Hillebrand, and F. H. L. Koppens, Nature Materials 14, 421 (2015).
[20] G. X. Ni, A. S. McLeod, Z. Sun, L. Wang, L. Xiong,
K. W. Post, S. S. Sunku, B.-Y. Jiang, J. Hone, C. R. Dean, M. M. Fogler, and D. N. Basov, Nature 557, 530 (2018).

[21] M. Wagner, Z. Fei, A. S. McLeod, A. S. Rodin, W. Bao, E. G. Iwinski, Z. Zhao, M. Goldflam, M. Liu, G. Dominguez, M. Thiemens, M. M. Fogler, A. H. Castro Neto, C. N. Lau, S. Amarie, F. Keilmann, and D. N. Basov, Nano Lett. 14, 894 (2014).

[22] G. X. Ni, L. Wang, M. D. Goldflam, M. Wagner, Z. Fei, A. S. McLeod, M. K. Liu, F. Keilmann, B. Özyilmaz, A. H. C. Neto, J. Hone, M. M. Fogler, and D. N. Basov, Nature Photonics 10, 244 (2016).

[23] A. Principi, M. Carrega, M. B. Lundeberg, A. Woessner, F. H. L. Koppens, G. Vignale, and M. Polini, Phys. Rev. B 90, 165408 (2014).

[24] D. Novko, Nano Letters 17, 6991 (2017).

[25] S. Shulga, O. Dolgov, and E. Maksimov, Physica C: Superconductivity 178, 266 (1991).

[26] D. Novko, M. Šunjič, and V. Despoja, Phys. Rev. B 93, 125413 (2016).

[27] P. B. Allen, Phys. Rev. Lett. 59, 1460 (1987).

[28] Z. Lin, L. V. Zhigilei, and V. Celli, Phys. Rev. B 77, 075133 (2008).

[29] L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, H. Eisaki, and M. Wolf, Phys. Rev. Lett. 99, 197001 (2007).

[30] F. Caruso, D. Novko, and C. Draxl, Phys. Rev. B 101, 035128 (2020).

[31] D. Novko, F. Caruso, C. Draxl, and E. Cappelluti, Phys. Rev. Lett. 124, 077001 (2020).

[32] S. Sim, H. Jang, N. Koirala, M. Brahlek, J. Moon, J. H. Sung, J. Park, S. Cha, S. Oh, M.-H. Jo, J.-H. Ahn, and H. Choi, Nature Commun. 6, 8814 (2015).

[33] C. In, S. Sim, B. Kim, H. Bae, H. Jung, W. Jang, M. Son, J. Moon, M. Saleki, S. Y. Seo, A. Soon, M.-H. Ham, H. Lee, S. Oh, D. Kim, M.-H. Jo, and H. Choi, Nano Lett. 18, 734 (2018).

[34] S. Piscanec, M. Lazzeri, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. Lett. 93, 185503 (2004).

[35] P. B. Allen, Phys. Rev. B 3, 305 (1971).

[36] P. B. Allen and R. Silberglitt, Phys. Rev. B 9, 4733 (1974).

[37] I. Kupčić, Phys. Rev. B 91, 205428 (2015).

[38] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).

[39] F. Giustino, Rev. Mod. Phys. 89, 015003 (2017).

[40] D. Novko, Phys. Rev. B 98, 041112 (2018).

[41] A. F. Page, F. Ballout, O. Hess, and J. M. Hamm, Phys. Rev. B 91, 075404 (2015).

[42] J. M. Hamm, A. F. Page, J. Bravo-Abad, F. J. García-Vidal, and O. Hess, Phys. Rev. B 93, 041408 (2016).

[43] Z. Sun, D. N. Basov, and M. M. Fogler, Phys. Rev. Lett. 117, 076805 (2016).

[44] R. Petersen, T. G. Pedersen, and F. Javier García de Abajo, Phys. Rev. B 96, 205430 (2017).

[45] J. Wilson, F. Santosa, M. Min, and T. Low, Phys. Rev. B 98, 081411 (2018).

[46] E. T. Jensen, R. E. Palmer, W. Allison, and J. F. Annett, Phys. Rev. Lett. 66, 492 (1991).

[47] K. Andersen and K. S. Thygesen, Phys. Rev. B 88, 155128 (2013).

[48] F. H. da Jornada, L. Xian, A. Rubio, and S. G. Louie, Nature Commun. 11, 1013 (2020).

[49] Y. Huang, S. N. Shirodkar, and B. I. Yakobson, J. Am. Chem. Soc. 139, 17181 (2017).

[50] D. L. Druffel, K. L. Kuntz, A. H. Woomer, F. M. Alcorn, J. Hu, C. L. Donley, and S. C. Warren, J. Am. Chem. Soc. 138, 16089 (2016).

[51] J. Wang, X. Sui, S. Gao, W. Duan, F. Liu, and B. Huang, Phys. Rev. Lett. 123, 206402 (2019).