1-1-2009

Strong nonlinear optical response in graphene in terahertz regime

Anthony Wright
University of Wollongong, arw75@uow.edu.au

Xuguang Xu
Chinese Academy of Science

J. C. Cao
Chinese Academy of Science

Chao Zhang
University of Wollongong, czhang@uow.edu.au

Strong nonlinear optical response of graphene in the terahertz regime

A. R. Wright,[1] X. G. Xu,[2] J. C. Cao,[2] and C. Zhang[1,a)]
[1]*School of Engineering Physics, University of Wollongong, New South Wales 2552, Australia*
[2]*State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, CAS, Shanghai 200050, People's Republic of China*

(Received 13 July 2009; accepted 24 July 2009; published online 17 August 2009)

We demonstrate that within the model of massless Dirac fermions, graphene has a strong nonlinear optical response in the terahertz regime. It is found that the nonlinear contribution significantly alters both the single frequency and frequency tripled optical response at experimentally relevant field strengths. The optical activity of single layer graphene is significantly enhanced by nonlinear effects, and the frequency tripled response opens the gateway to photonic and optoelectronic device applications. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3205115]

The first intentional production of graphene flakes occurred in 2003.[1] Since then a considerable amount of riveting work on single layer graphene (SLG) and graphene nanoribbons has been performed.[2,3] For example, the prediction and observation of electron-hole symmetry and half-integer quantum Hall effect,[4–6] finite conductivity at zero charge-carrier concentration,[4] the strong suppression of weak localization,[7–9] and ac and dc universal conductance.[10–12]

The optical conductance of graphene based systems in the terahertz to far infrared (FIR) regime has been a topic of some interest due to the ongoing search for viable terahertz detectors and emitters, as well as the ubiquitous research being undertaken within the infrared frequencies used for telecommunications purposes. Graphene is traditionally a poor conductor in this part of the spectrum, with the universal conductivity $\sigma_0=e^2/4\hbar$ leading to a transmittance of $\approx 4\%$. At higher energies we know this is not the case.[13] At low energies this problem is alleviated in the case of bilayer graphene where the conductivity is as much as $8\sigma_0$.[14] The problem is even further alleviated in the case of SLG nanoribbons in a magnetic field where the conductance can be as much as two orders of magnitude higher than that for SLG,[15] and recently it was shown that a subclass of bilayer nanoribbons is similarly active in the terahertz-FIR regime even without a magnetic field.[16] Nevertheless, for a sheet of SLG, the optical conductance in the terahertz-FIR regime is essentially confined to σ_0. This has put a severe limitation on graphene's potential application to electronics and photonics.

The purpose of this letter is to demonstrate that strong nonlinear effects can exist in intrinsic graphene ($\mu=0$) in the terahertz to infrared frequency regime under a moderate electric field intensity. Within the classical picture, it has been shown that frequency upconversion can be achieved within the Dirac description,[17] although the field response has been restricted to the linear E term. Here we shall adopt an approach that treats the coupling of the Dirac electron to the time-dependent electric field quantum mechanically to calculate the nonlinear terms, both in high order electrical field and in multiple frequencies. We determine the required field strength to induce non-negligible nonlinear effects, and investigate the temperature dependence of these terms as well.

Let's consider intrinsic graphene under an applied field, $\mathbf{E}(t)=\mathbf{E}e^{i\omega t}$ whose direction is along the x-axis. The tight binding Hamiltonian in the low energy regime is given by

$$H=v_F\begin{pmatrix}0 & p_-+eA_-\\ p_++eA_+ & 0\end{pmatrix}, \tag{1}$$

where $v_F\approx c/300$, $p_\pm=p_x\pm ip_y$, and $A_\pm=A=\frac{E}{i\omega}e^{i\omega t}$. The time-dependent two-component wave functions can be expanded in the basis set

$$\psi(\mathbf{p},t)=\sum_{n=0}^{\infty}\phi(\mathbf{p},n)e^{in\omega t}e^{-i\epsilon t}, \tag{2}$$

where $\epsilon=|\mathbf{p}|$, and $\phi(\mathbf{p},n)$ is a spinor given by

$$\phi(\mathbf{p},n)=\begin{bmatrix}\alpha_n(\mathbf{p})\\ \beta_n(\mathbf{p})\end{bmatrix}. \tag{3}$$

By substituting Eq. (2) into the Schrödinger equation $i\hbar\partial\psi/\partial t=H\psi$, we obtain

$$-\hbar\sum_{n=0}^{\infty}\phi(\mathbf{p},n)(n\omega-\epsilon)e^{i(n\omega-\epsilon)t}=\begin{pmatrix}0 & p_-+\frac{eE}{i\omega}e^{i\omega t}\\ p_++\frac{eE}{i\omega}e^{i\omega t} & 0\end{pmatrix}\sum_{n=0}^{\infty}\phi(\mathbf{p},n)e^{i(n\omega-\epsilon)t}. \tag{4}$$

The above equation contains information of all multiple photon process in intrinsic graphene. Due to the orthonormal relation of $e^{in\omega t}$, we can write the coupled recursion relations for the spinor components,

$$(\epsilon-n\omega)\alpha_n(\mathbf{p})=p_+\beta_n(\mathbf{p})+\frac{E}{2i\omega}\beta_{n-1}(\mathbf{p}),$$

$$(\epsilon-n\omega)\beta_n(\mathbf{p})=p_-\alpha_n(\mathbf{p})+\frac{E}{2i\omega}\alpha_{n-1}(\mathbf{p}). \tag{5}$$

The recursion relation couples the n photon processes to the $n-1$ photon processes. From the solutions to Eq. (5) we can calculate the nth order total current which is given by

a)Electronic mail: czhang@uow.edu.au.

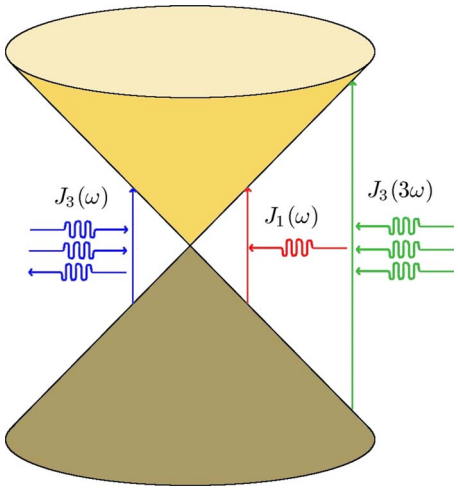

FIG. 1. (Color online) A schematic illustration of linear and nonlinear optical processes in intrinsic graphene. The universal conductance is described by $\mathbf{J}_1$. The two third order terms are $\mathbf{J}_3(\omega)$ and $\mathbf{J}_3(3\omega)$. The latter is a frequency tripling term which is the dominant nonlinear current at room temperature.

$$\mathbf{J}_{\mathbf{n}}^{\nu} = \frac{1}{4\pi^2}\int \mathrm{d}\mathbf{p}\mathbf{j}_{\mathbf{n}}^{\nu}N(\epsilon). \tag{6}$$

Here $N(\epsilon)=n_F(-\epsilon)-n_F(\epsilon)=\tanh(\epsilon/2k_BT)$, and $\mathbf{j}_{\mathbf{n}}^{\nu}=\psi^{\dagger}v_{\nu}\psi$, where $v_{\nu}=(\partial H)/(\partial p_{\nu})$ is the current operator with $\nu=x, y$. The choice of ν is arbitrary due to the simplicity of the Hamiltonian. The nth order current becomes

$$\mathbf{J}_{\mathbf{n}} = \frac{1}{2\pi^2}\int N(\epsilon)p\mathrm{d}p\mathrm{d}\theta\,\mathrm{Re}\left(\sum_{i=0}^{n}\alpha_i^*\beta_{n-i}+\beta_i^*\alpha_{n-i}\right). \tag{7}$$

In the absence of the electric field, only $n=0$ terms are nonzero and the solution of Eq. (5) is the usual wave functions for the massless Dirac fermion, $\alpha_0(\mathbf{p})=1/\sqrt{2}$, $\beta_0(\mathbf{p})=p_-/\sqrt{2}p$. The one photon term solution is given by,

$$\alpha_1 = C_1[(p_- + p_+)p - \omega p_-],$$

$$\beta_1 = C_1(p^2 - \omega p + p_-^2), \tag{8}$$

where $C_1=A/\sqrt{2}\omega p(\omega-2p)$. The total current calculated with $n=1$ terms is equivalent to the linear response result obtained from the Kubo formula,[10,11,13] $\mathbf{J}_1=e^2E/4$. Upon converting to real units, it results in the universal conductance $\mathbf{J}_1=\sigma_1 E$, where $\sigma_1=e^2/4\hbar$. The second order solution makes no contribution due to time-reversal symmetry. We now proceed to calculate the third order current,

$$\mathbf{J}_3 = \frac{\sigma_1 e^2 v_F^2 E_0^2}{\hbar^2\omega^4}[N_3(\omega)e^{3i\omega t}+N_1(\omega)e^{i\omega t}] = \mathbf{J}_3(3\omega)+\mathbf{J}_3(\omega), \tag{9}$$

where the thermal factors N_i are given by $N_1(\omega)=N(\omega)$ and $N_3(\omega)=13N(\omega/2)/48-N(\omega)/3+45N(3\omega/2)/48$.

The third order current, then, is a superposition of a term oscillating with frequency ω, $J_3(\omega)$, and a frequency tripling term, $J_3(3\omega)$. The electronic processes represented by these two terms are shown in Fig. 1. The linear "universal conductivity" is a single photon process where an electron absorbs a photon making a transition from the valence band to the conduction band. The two third order terms are both three-photon processes. The term oscillating with frequency ω corresponds to a process where two incoming photons are absorbed, followed by the immediate emission of a third photon. The frequency tripling term corresponds to simultaneous absorption of three photons and the total transition energy is $3\hbar\omega$. The latter two terms are inversely proportional to ω^4, and proportional to E_0^2 which is the power of the field.

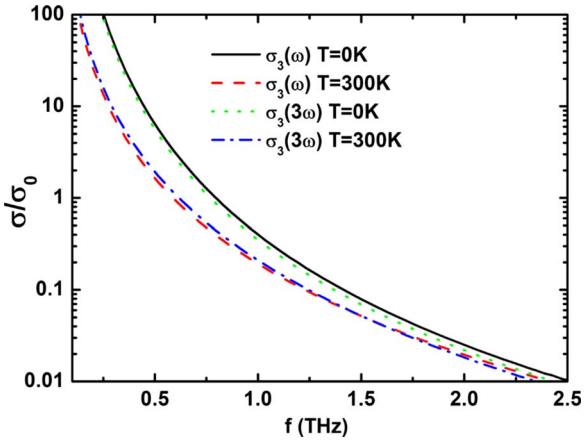

FIG. 2. (Color online) The frequency dependent nonlinear current. Both the single frequency and frequency tripling terms decrease as ω^{-4}, and with increasing temperature.

By using the same method we can obtain $\alpha_n(\mathbf{p})$ and $\beta_n(\mathbf{p})$ for any n, and thus the full nonlinear current of the system at arbitrary electric field can be obtained. In general the nth order term is proportional to E_0^{n-1}/ω^{2n}. This means that at sufficiently high field strength and low frequency, the nonlinear terms are relevant.

In Fig. 2, we plot the frequency dependent nonlinear current relative to the linear current. Both nonlinear terms decrease rapidly with frequency, and at low frequencies, are approximately an order of magnitude lower at room temperature than at zero temperature. For weak fields and high frequencies, the linear current dominates and the two nonlinear terms are approximately equal in magnitude.

The point at which the nonlinear conductance dominates over the linear conductivity is given by the simple expression $\sigma_3^j/\sigma_1>1$ which gives a critical field strength of

$$E_C^{i\omega} = \frac{\hbar\omega^2}{ev_F\sqrt{N_i}}. \tag{10}$$

For a beam of frequency $\omega=1$ THz, at zero temperature, this gives a critical field strength of $E_C^{\omega}\approx 1600$ V/cm for the single frequency term, and $E_C^{3\omega}\approx 1700$ V/cm for the frequency tripling term. These field strengths can easily be achieved in a laboratory. For the same beam at room temperature, the critical field strength becomes $E_C^{\omega}\approx 2350$ V/cm and $E_C^{3\omega}\approx 2250$ V/cm. This means there is a crossover point where the single frequency term ceases to dominate over the tripling term. At zero temperature, both critical fields increase as ω^2. At room temperature, the two critical fields have rather different ω-dependence. Figure 3(a) shows the change of critical field $\Delta E_C=E_C(300\text{ K})-E_C(0\text{ K})$ as a function of frequency. Both critical fields increase as temperature increases, indicating that thermal ex-

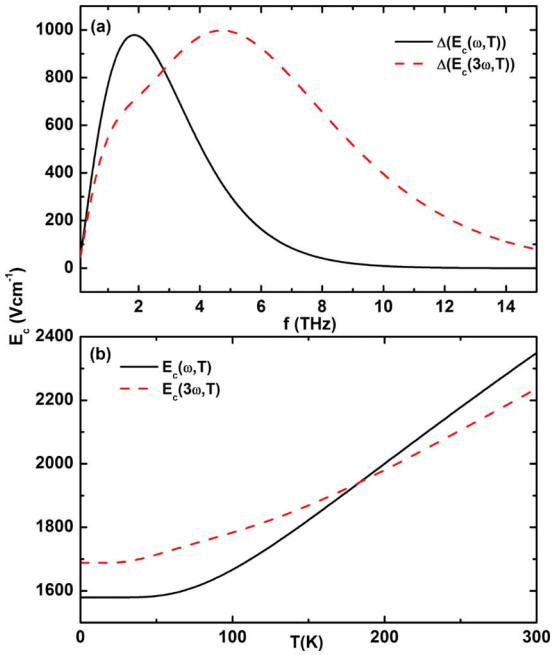

FIG. 3. (Color online) (a) The difference between the critical fields at 0 and 300K as a function of frequency [i.e., $\Delta E_c = E_c(300\ \mathrm{K}) - E_c(0\ \mathrm{K})$]. There is a maximum discrepancy for each nonlinear contribution which indicates the frequency where thermal effects are most significant. (b) The temperature dependence of the critical field strength at fixed frequency of 1 THz. At low temperatures the single frequency nonlinear current dominates over the frequency tripling term. At ≈180 K however, the situation is reversed such that at room temperature, the frequency tripling term is the dominant nonlinear contribution.

citation can reduce the nonlinear effect. For each ΔE_C, there exists a frequency at which the thermal effect is strongest. For $\Delta E_C(\omega)$, this frequency is around $k_B T/4$ and for $\Delta E_C(3\omega)$ it is around $3k_B T/4$.

Figure 3(b) shows the temperature dependence of the critical field at $\omega = 1$ THz. There are two distinctive temperature regimes separated by the temperature $T_1 \approx$ 180 K. Below T_1, $J_3(\omega)$ dominates the nonlinear effect while above T_1, $J_3(3\omega)$ is more dominant. This behavior is useful for frequency upconversion device applications since the use of the frequency tripling term is more effective at room temperature than at low temperature.

These results demonstrate that graphene is a rather strong nonlinear material. There are two third order nonlinear terms, $J_3(\omega)$ and $J_3(3\omega)$. The first contributes to the current oscillating with ω. This adds a correction to the response function such that $\sigma(\omega) = \sigma_0 + (e^2 v_F^2/\hbar^2)(E^2/\omega^4)$. Therefore the universal conductance will be destroyed at a field strength of around 10^3 V/cm and frequency around 1 THz. This effect is rather robust from low to room temperatures. The second nonlinear contribution is a frequency tripling term. This term is similar in strength to its complement, and at higher frequencies is higher than the single frequency term. This term's relative strength makes graphene a potential candidate as a terahertz emitter/detector at frequencies which are traditionally difficult to obtain by using an existing emitter at one third the frequency. For sufficiently strong fields the loss rate could be minimized even in a cascading situation.

In conclusion, we have shown that SLG exhibits a strong nonlinear effect in the terahertz to far infrared regime under an electric field of around 10^3 V/cm. In particular, a moderate field can induce the frequency tripling term at room temperature. This could be of potential use in device application for frequency upconversion.

This work is supported by the Australian Research Council, the National Basic Research Program of China (Project No. 2007CB310402), the National Natural Science Foundation of China (Project No. 60721004), and the major project and Hundred Scholar Plan of the Chinese Academy of Sciences.

[1] 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).
[2] A. K. Geim and K. S. Novoselov, Nature Mater. **6**, 183 (2007).
[3] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
[4] 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).
[5] Y. Zhang, Y. W. Tan, H. L. Störmer, and P. Kim, Nature (London) **438**, 201 (2005).
[6] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Konrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).
[7] H. Suzuura, and T. Ando, Phys. Rev. Lett. **89**, 266603 (2002).
[8] S. V. Morozov, K. S. Novoselov, M. I. Katsnelson, F. Schedin, L. A. Ponomarenko, D. Jiang, and A. K. Geim, Phys. Rev. Lett. **97**, 016801 (2006).
[9] D. V. Khveshchenko, Phys. Rev. Lett. **97**, 036802 (2006).
[10] V. P. Gusynin, S. G. Sharapov, and J. P. Carbotte, Phys. Rev. Lett. **96**, 256802 (2006).
[11] A. B. Kuzmenko, E. van Heumen, F. Carbone, and D. van der Marel, Phys. Rev. Lett. **100**, 117401 (2008).
[12] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, Science **320**, 1308 (2008).
[13] C. Zhang, L. Chen, and Z. Ma, Phys. Rev. B **77**, 241402 (2008).
[14] A. R. Wright, F. Liu, and C. Zhang, arXiv:0907.0504v1 (unpublished).
[15] J. Liu, A. R. Wright, C. Zhang, and Z. Ma, Appl. Phys. Lett. **93**, 041106 (2008).
[16] A. R. Wright, J. C. Cao, and C. Zhang, arXiv:0905.4304v1 (unpublished).
[17] S. A. Mikhailov and K. Ziegler, J. Phys.: Condens. Matter **20**, 384204 (2008).