

Gate Modulated Raman Spectroscopy of Graphene

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| URL | http://hdl.handle.net/10097/00097237 |

Gate Modulated Raman Spectroscopy of Graphene

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Background

Single atomic layer of graphite (graphene) becomes the most fundamental material to study electrons and phonons of two dimensional (2D) systems [Science **306**, 666 (2004)]. A combination of electronic gating and inelastic scattering of light (Raman spectroscopy) elucidates interplay of electron, phonons, and photons in graphene because we can tune the Fermi energy (E_F) of graphene while simultaneously probing phonon excitation [Solid State Commun. **175-176**, 18 (2013)]. Spectral properties such as intensity, spectral linewidth, peak position, and lineshape of the Raman spectra can be modified by varying E_F , indicating an interplay of the electron-phonon interaction. However, the physical consequence behind the change of spectral properties measured by experiment cannot be understood unless a theoretical calculation of Raman intensity is performed. Understanding detailed mechanism underlying the change of Raman spectral properties mentioned above is essential for the progress of solid state physics, in particular, for the description of the electron-photon, electron-phonon, and electron-electron interactions of graphene.

Purposes

The purpose of this thesis is to investigate the gate modulated Raman spectroscopy in graphene and to find the origin of the changes of spectral properties as a function of E_F .

Theoretical Methods and Results

Raman intensity. Raman scattering processes consist of (1) an optical transition of an electron from the valence to the conduction bands, (2) the electron-phonon interactions by emitting a single (or two) phonon(s) and (3) the electron relaxation back to the valence band by emitting a photon as shown in Fig. 1(a) and (b). The phonon excited by the Raman process can have either a zero momentum $\mathbf{q} = 0$ [Fig. 1(a)] or a non-zero momentum $\mathbf{q} \neq 0$ [Fig. 1(b)]. The first-order Raman process corresponds to $\mathbf{q} = 0$ phonon emission [Fig. 1(a)] while the second-order Ra-

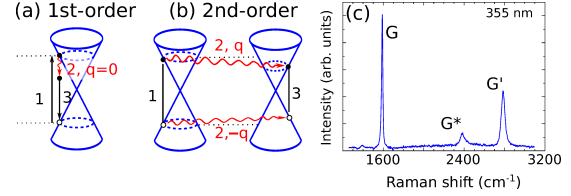


Figure 1: (a) First-order and (b) second-order Raman processes. (c) Raman spectra of graphene at excitation wavelength 355 nm by Liu et al. [Carbon **81**, 807 (2015)].

man process corresponds to $\mathbf{q} \neq 0$ phonon and $-\mathbf{q}$ phonon emission processes [Fig. 1(b)] so as the photoexcited electron to recombine with the hole. Figure 1(c) shows Raman spectra of graphene at excitation wavelength 355 nm by Liu et al. [Carbon **81**, 807 (2015)]. The G band occurring at $\sim 1600 \text{ cm}^{-1}$ is assigned to the first-order Raman process while the G^* ($\sim 2400 \text{ cm}^{-1}$) and G' ($\sim 2800 \text{ cm}^{-1}$) bands are assigned to the second-order Raman process. We calculated intensities for both the first- and second-order Raman processes as a function of E_F by employing the perturbation theory.

E_F dependence of peak position and linewidth. Several works reported the changes of Raman peak position and spectral linewidth upon varying E_F [e.g. Nat Nano **3**, 210 (2008), Phys. Rev. Lett. **98**, 166802 (2007)]. Araujo et al. found experimentally that the peak position [linewidth] of the G band shows a “V” [“Λ”] shape as a function of E_F as shown by red dots of Fig. 2(a)[Fig. 2(b)][Phys. Rev. Lett. **109**, 046801 (2012)]. However, for the case of the G' band, peak position and linewidth show opposite behavior from that of the G band as shown by red dots of Figs. 2(c) and (d). The change of peak position and linewidth originates from phonon self-energy correction due to the electron-phonon interaction, known as the Kohn anomaly (KA) effect. Previous works calculated phonon self-energy [Phys. Rev. B **86**, 201403 (2012)], nevertheless Raman intensity calculation was not performed, therefore theoretical confirmation to the experimental problem is still missing. We calculated phonon self-energy based on sec-

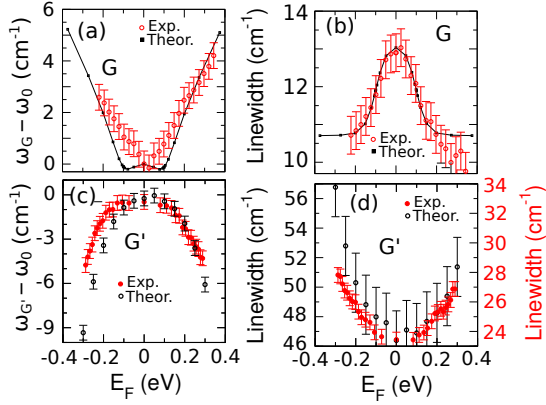


Figure 2: (a) Peak positions and (b) linewidth of the G band as a function of E_F . (c) Peak positions and (d) linewidth of the G' band as a function of E_F . Calculated results (black dots) are this work and the experimental results are taken from Araujo et al. [Phys. Rev. Lett. **109**, 046801 (2012)].

ond order-perturbation of phonon energy through the electron-phonon interactions. The value of renormalized phonon energy ω is generally a complex number where $\text{Re}(\omega)$ [$-\text{Im}(\omega)$] gives phonon energy shift (phonon linewidth). Calculated results show that the opposite KA effect between the first- and second order Raman spectra appears because the KA effect of the first-order Raman spectra comes from interband electron-hole excitation, while in the second-order Raman spectra, the intraband electron-hole excitation dominates over the KA effect. After Raman intensity calculation, we compare the peak position and linewidth for the G band [G' band] as shown by black dots in Fig. 2(a) and (b) [Fig. 2(c) and (d)], respectively.

E_F dependence of intensity. In Raman process, each electronic \mathbf{k} state interferes with each other. This quantum interference effect can be probed by observing the change of Raman intensity as a function of E_F . The first-order Raman spectra are found to have destructive interference between their two resonant conditions, known as the incident and scattered resonance [Chen, Nature 471, 617 (2011)]. When the scattered resonant condition can be suppressed while keeping the incident resonance, the G band intensity enhancement can be achieved at $2|E_F| = E_L - \hbar\omega_G/2$, where E_L is the laser energy and ω_G is the frequency of the G band $\sim 1600 \text{ cm}^{-1}$ [Fig. 3(a)]. Present calculated results found that not only the resonance conditions are important, but also the explicit consideration of the electron-phonon matrix elements are essential to determine the quantum interference effect of general

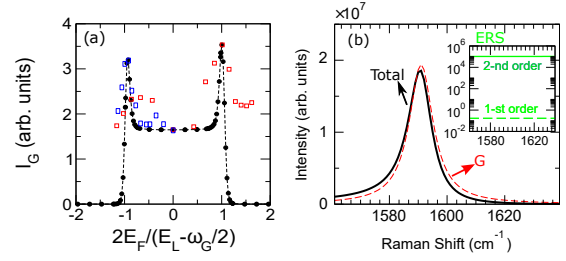


Figure 3: (a) G band intensity as a function of E_F . Black dots are calculation results, red squares and blue squares are experimental results from [Nature **471**, 617 (2011)] and [Nano Letters **13**, 6170 (2013)], respectively. (b) Calculated total Raman intensity (black), the G band intensity (red), and ERS intensity (green) at $E_F = 0$.

bands in Raman spectra [see. Fig. 3(a)].

E_F dependence of lineshape. For long years it was believed that the G band shows symmetric lineshape. However, Yoon et al. [Carbon **61**, 373 (2013)] found that the G band of undoped (doped) graphene shows asymmetric (symmetric) lineshape. According to Fano, the asymmetric lineshape comes from interference effect between the continuous and discrete phonon spectra [PR **124**, 1866 (1961)]. We assign the continuous spectra as the electronic Raman spectra (ERS) originates from the Coulomb interaction between the photo-excited electron with electrons near the Fermi energy. In this calculation, we found that intensity of the first-order ERS process is 6-order of magnitude smaller than that of the second-order because the direct Coulomb interaction vanishes at $\mathbf{q} = 0$ due to the symmetry of electron wavefunctions [inset of Fig. 3(b)]. Considering the second-order Raman process for the ERS spectra, we were able to reproduce the asymmetric lineshape of the G band [Fig. 3(b)].

Summary

Based on the calculation of Raman intensity, phonon self-energy, and electron-electron interaction, we explained the origin of changes of Raman spectral properties (peak position, linewidth, intensity, and lineshape) as a function of E_F . Our calculation results have been compared with the experiments with good agreement.

Publications

- (1) **E. H. Hasdeo**, et al. Phys. Rev. B **88**, 115107 (2013).
- (2) **E. H. Hasdeo**, et al. Phys. Rev. B **90**, 245140 (2014).
- (3) **E. H. Hasdeo**, et al. Phys. Rev. B in Press

There are 13 number of publications unrelated to the thesis

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論文審査の結果の要旨

光の非弾性散乱であるラマン散乱は、1原子層物質であるグラフェンの評価に幅広く使われている。ラマン・スペクトルを測定する際に、グラフェンにゲート電極をつけフェルミエネルギーを変化させてスペクトルを測定する実験的技術を、ゲート変調ラマン分光と呼ぶ。本博士論文は、グラフェンのゲート変調ラマン分光に関する理論的研究であり、5章からなる。

第1章では、本博士論文の背景となるグラフェンの紹介と、ゲート変調ラマン分光に関する3つの実験結果が述べられている。具体的には、(1) ラマン分光で観察される格子振動の振動数がフェルミエネルギーの関数として変化すること（コーン異常）、(2) ラマン強度がフェルミエネルギーの関数として変化すること（量子干渉効果）、(3) ラマンスペクトルの形状が振動数の関数として非対称になりフェルミエネルギーの関数として変化すること（ファノ効果）である。第2章では、この3つの実験結果を理論的に説明するために必要な、定式化と計算方法について説明している。第3章と第4章では、本論文の計算によって得られた新しい知見について説明されている。第3章ではGバンドと呼ばれるグラフェンとグラファイトのラマンスペクトルに対する、上記の3つの効果に対する計算結果が報告され、実験事実を再現することに成功している。特に量子干渉効果における非対称的な増強効果がエネルギーバンドの形状によること、またファノ効果で電子ラマンスペクトルのフォノンスペクトルに対する相対的位置がスペクトルの非対称性を決めることなどを新たな知見として見出した。第4章では、G'バンド、G*バンドと呼ばれるラマンスペクトルに対する上記の3つの効果に関する計算結果が報告され実験事実を再現した。特にG'やG*バンドのコーン異常の起源として、異なるバレー間かつ同じエネルギーバンド内の電子格子相互作用が重要な役割であることを新しい知見として示した。第5章では、本博士論文で得られた主な成果のまとめと展望について述べられている。

本論文は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、エッドウイ・ヘスキ・ハスデオ提出の博士論文は、博士（理学）の学位論文として合格と認める。