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Absolute Raman matrix elements of graphene and graphite

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Using sample substitution [Grimsditch et al., J. Raman Spectrosc. 10, 77 (1981)] we deconvolve the highly wavelength-dependent response of the spectrometer from the Raman spectra of graphene suspended on an SiO2-Si substrate and graphite for the D and G modes in the visible range. We derive a model that considers graphene suspended on an arbitrary stratified medium while sidestepping its problematic ascription as an object of finite thickness and calculate the absolute Raman response of graphene (and graphite) via its explicitly frequency-dependent Raman matrix element [Falicov and Martin, Light Scattering in Solids I: Introductory Concepts (Springer-Verlag, Berlin, 1983), p. 1083] \( K_{2f,10}^2 \) vs laser frequency. For both graphene and graphite the \( K_{2f,10}^2 \) per graphene layer vs laser frequency rises rapidly for the G mode and less so for the D mode over the visible range. Although we find a dispersion of the D mode position with laser frequency for both graphene and graphite of 41 cm\(^{-1}\)/eV and 35 cm\(^{-1}\)/eV, respectively, in good agreement with Narula and Reich [Phys. Rev. B 78, 165422 (2008)] assuming constant matrix elements, the observed intensity dependence is in disagreement. Finally, we show the sensitivity of our calculation to the variation in thickness of the underlying SiO2 layer for graphene. Our findings shall serve as an experimental verification of the behavior of the relevant matrix elements in graphene and its allotropes that may be calculated theoretically in the future.

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I. INTRODUCTION

As a material system graphene1 has enjoyed an unabated surge in popularity as a research subject owing to its novel physics, promise as an interconnect material and sensing abilities.2 The key to understanding the optical properties of graphene and its allotropes lies in knowing the behavior of the matrix elements and resonant denominators that constitute the processes underlying such phenomena. Optical spectroscopies provide access to different combinations of matrix elements. For example, the Raman G mode in graphene and graphite at \( \sim \)1600 cm\(^{-1}\) arises from the interplay of the electron-radiation and electron-phonon interaction matrix elements. Whereas the D mode, a signature of structural disorder and present at \( \sim 1350 \) cm\(^{-1}\) in addition involves the electron-defect scattering matrix element. However, the measured spectra are obscured by the response of the spectrometer and the influence of the underlying substrate via electric field enhancement that needs to be deconvolved to obtain the absolute Raman response of the material. Recently the so-called Raman matrix element3,4 \( K_{2f,10}^2 \) corresponding to the D mode for graphene and graphite based on the double-resonance model of Thomsen and Reich5,6 has been calculated over the entire two-dimensional Brillouin zone of graphene under the assumptions of constant matrix elements and a single value of the broadening parameter for each transition.7 Although the literature is replete with studies of the Raman spectra of different variants of sp\(^2\) carbon detailing their respective peak structure with and without additions such as functional groups or defects,8,9 to our knowledge the absolute Raman response of the D and G modes in graphene and graphite across the visible range has not been experimentally investigated. Such information would be useful while interpreting and validating theoretical work5,7,10 on the component scattering processes in graphene and graphite that give rise to the D mode along with the relevant matrix elements, viz., the electron-phonon coupling and defect scattering. This for instance, has important consequences in determining the phonon dispersion of graphene from Raman experiments. Knowledge of the Raman matrix element \( K_{2f,10}^2 \) would also help to determine which laser excitation frequency and underlying substrate configuration gives the most pronounced Raman response.

We measured the Raman spectra of the D and G modes for graphene and graphite in the visible range and used the method of sample substitution11 with CaF\(_2\) as a reference to deconvolve the highly wavelength dependent response of the charge-coupled device (CCD) detector and spectrometer optics. In this paper we derive a model that considers graphene suspended on an arbitrary stratified medium while sidestepping its problematic ascription as an object of finite thickness and calculate the absolute Raman response of graphene (and graphite) via its explicitly frequency-dependent Raman matrix element squared3 \( |K_{2f,10}^2|^2 \) as a function of laser frequency. For both graphene and graphite the \( |K_{2f,10}^2|^2 \) per graphene layer vs laser frequency rises rapidly for the G mode and less so for the D mode across the visible range. We also find a dispersion of the D mode position with laser frequency for graphene and graphite of 41 cm\(^{-1}\)/eV and 35 cm\(^{-1}\)/eV, respectively, in good agreement with Ref. 7. The paper is organized as follows: in Sec. II we derive an expression that relates the experimentally measured Raman spectra to the \( |K_{2f,10}^2|^2 \), Sec. III provides the experimental details of the measurement setup and sample geometry and Sec. IV gives our results and discussion. Finally, Sec. IV is the summary and outlook for our work.

II. THEORY

In this section we derive an expression that relates the experimentally observed photon count \( R_D \) as measured by
the spectrometer detector with the quantity of interest, the explicitly frequency-independent Raman matrix element squared \( |K_{2f,10}|^2 \) for Sec. II A, an atomically thin graphene layer suspended on a completely general stratified medium and Sec. II B, for the more familiar case of a film of finite thickness relevant for graphite.

A. Raman scattering from a monolayer with an underlying stratified medium

To study Raman scattering in the backscattering configuration we model the graphene sheet as a perfect plane that scatters the incoming laser light of frequency \( \omega_0 \) with an outgoing frequency \( \omega_c \). Clearly, the thickness of a monolayer is ill-defined and our approach contrasts previous (although dissimilar) studies on graphene that ascribe a certain thickness to graphene\(^{12}\) based on atomic force microscopy (AFM) measurements\(^{13}\) or half the out of plane lattice constant \( c \) of Bernal AB graphite \( c/2 \).

We begin by considering the expression for the Raman matrix element\(^3\) \( K_{2f,10} \) per graphene layer. We remove all the explicit laser frequency dependencies by factoring out the contribution of the vector potential \( \vec{A} \) in the electron-radiation interaction Hamiltonian \( \hat{H}_{el} = -\frac{\vec{e}}{2m}\vec{E}\cdot\vec{A} \) which allows \( K_{2f,10} \) to be rewritten in terms of the explicitly frequency-independent term \( K'_{2f,10} \)

\[
K'_{2f,10} = \frac{e^2 \hbar}{2m^2 \epsilon_0^2 \hbar^3} \epsilon(\vec{k}_f - \vec{k}_o) r K^c_{2f,10}.
\]  

To relate the theoretically accessible Raman matrix element \( K_{2f,10} \) to the experimentally obtained \( D \) mode Stokes spectra we invoke Fermi’s golden rule\(^{14}\)

\[
\delta \omega \left[ \omega_o, k_s \right] \equiv \frac{2 \pi}{\hbar} |K_{2f,10}|^2 N(\hbar \omega_{ph}) + 1 \times \rho \left[ \hbar \omega_o - (E_f - E_s), k_s \right],
\]  

where \( \rho \left[ \hbar \omega_o - (E_f - E_s), k_s \right] \) is the transition probability per unit time per unit solid angle for the graphene crystal starting from its initial state and reaching final with a emission of the photon with energy \( \hbar \omega_o \) and wave vector \( k_s \). \( N(\hbar \omega_{ph}) \) is the Bose-Einstein factor corresponding to the phonon frequency \( \omega_{ph} = \omega_o - \omega_c \). For photons in a fictitious cube of length \( L \) we obtain the density of states as \( \rho \left[ \hbar \omega_o - (E_f - E_s), k_s \right] = \frac{2 \pi}{(2\pi)^3} \frac{(\hbar \omega_o)^2}{\hbar \epsilon_0^2 \hbar^3} \).

The differential scattering cross section \( \frac{d\sigma}{d\Omega} \) is obtained by dividing \( \delta \omega \left[ \omega_o, k_s \right] \) by the incident photon flux \( \Phi = \frac{I_0}{\hbar \omega_o} \) giving

\[
\frac{d\sigma}{d\Omega} = \frac{2 \pi}{\hbar} \frac{L^6}{(2\pi)^3} \frac{(\hbar \omega_o)^2}{\hbar \epsilon_0^2 \hbar^3} \times \frac{e^4 \hbar^2}{4m^2 \epsilon_0^2 L^6} |K'_{2f,10}|^2 N(\hbar \omega_{ph}) + 1,
\]  

\[
\frac{d\sigma}{d\Omega} = \frac{2 \pi}{\hbar} \frac{L^6}{(2\pi)^3} \frac{(\hbar \omega_o)^2}{\hbar \epsilon_0^2 \hbar^3} \times \frac{e^4 \hbar^2}{4m^2 \epsilon_0^2 L^6} |K'_{2f,10}|^2 N(\hbar \omega_{ph}) + 1.
\]  

The number of photons \( R \) reaching the detector per unit solid angle \( \Omega \), \( \frac{dR}{d\Omega} \) is given by the product of the differential scattering cross section \( \frac{d\sigma}{d\Omega} \) and the incident photon flux \( \frac{I_0}{\hbar \omega_o} \), where \( I_0 \) is the laser intensity incident normally on the graphene sheet.

\[
\frac{dR}{d\Omega} = \frac{I_0}{\hbar \omega_o} \frac{e^4}{4m^2 \epsilon_0^2 L^6} \frac{|K'_{2f,10}|^2 N(\hbar \omega_{ph}) + 1}{\hbar \omega_c}.
\]  

If the solid angle subtended by the scattered radiation (and subsequently captured by the microscope objective) is \( \Delta \Omega \), the total number of photons \( R \) available to the Raman spectrometer over time \( t \) shall be

\[
R = \frac{I_0}{\hbar \omega_o} \frac{e^4}{4m^2 \epsilon_0^2 L^6} \frac{|K'_{2f,10}|^2 N(\hbar \omega_{ph}) + 1}{\hbar \omega_c} \Delta \Omega.
\]
B. Raman scattering from films with a finite thickness

For samples with finite thickness such as CaF$_2$ and graphite, the backscattered intensity $I_b$ can be written in terms of the incident intensity $I_l$ and native scattering efficiency $\xi$ of the material as

$$I_b = I_l \frac{1 - \text{e}^{-(\xi + \alpha_s + \alpha_t)L}}{\xi + \alpha_t + \alpha_s} T_\text{b}[\omega_s]T_\text{b}[\omega_s],$$

(10)

where $\alpha_t$ and $\alpha_s$ are the absorption coefficients corresponding to the incoming and outgoing radiation, $T_\text{b}[\omega_s]$ and $T_\text{b}[\omega_s]$ are the transmittances of the incoming radiation from the ambient into the sample and from the sample into the ambient, respectively. The transmittances can be calculated from the transfer-matrix method. The expression for $I_b$ in Eq. (10) can be simplified considerably in the regimes of highly transparent and highly absorbing samples. For a highly absorbing sample (for e.g., graphite) we obtain

$$I_{b,\text{absorbing}} = \frac{I_l \xi}{\alpha_t + \alpha_s} T_\text{b}[\omega_s]T_\text{b}[\omega_s],$$

(11)

whereas for highly transparent samples (for e.g., CaF$_2$)

$$I_{b,\text{transparent}} = I_l x L T_\text{b}[\omega_s]T_\text{b}[\omega_s],$$

(12)

where $L$ is the sample length in the $z$ direction or the depth of focus of the microscope objective, whichever is smaller. The relevant expression for graphite now becomes

$$R_D^{\text{graphite}} = S[\omega] \frac{I_l}{\hbar \omega_0} \frac{e^4}{16 \pi^2 \epsilon_0 m_e c^2 \omega_0} K_{2f,10}^2 [N(\hbar \omega_{ph}) + 1] T_\text{b}[\omega_s]T_\text{b}[\omega_s] \Delta \Omega_{\text{graphite}} \left[ \frac{2}{c(\alpha_t + \alpha_s)} \right].$$

(13)

Note that the factor $\frac{2}{c(\alpha_t + \alpha_s)}$ accounts for the number of graphene layers over an effective scattering length $L_{\text{eff}} = \frac{1}{\alpha_t + \alpha_s}$ of the graphite sample. For films of finite thickness such as for the reference crystal CaF$_2$ (where the concept of a primitive unit volume $V_c$ is meaningful) it is convenient to work with an equivalent expression instead of Eq. (13) since the tabulated values of the absolute Raman response are commonly available in the literature in terms of the Raman tensor component $|a|$ giving, us, for example, for CaF$_2$ (Ref. 21)

$$R_D^{\text{CaF}_2} = S[\omega] P_{\text{l}} L \frac{\omega_0 M_{\text{CaF}_2}^2[|a|]}{c^4 V M_{\text{CaF}_2}^2[|a|]} [N(\hbar \omega_{ph}) + 1] \Delta \Omega_{\text{CaF}_2},$$

(14)

where $M_{ph}$ is the reduced mass of the vibrating atoms inside the primitive unit cell of volume $V_c$ and $\omega_{ph}$ is the measured phonon frequency.

III. EXPERIMENTAL DETAILS

A. Graphene

A flake of graphene, prepared by micromechanical exfoliation, was suspended on an Si substrate overlaid with a
thermally grown (293.7 ± 0.5) nm [as measured by a Sen- 
tech SE801 ellipsometer using a deuterium/halogen lamp 
(AvaLight-DHS-Bal)] SiO₂ layer (see Fig. 2). At room 
temperature ~295 K it was subject to a range of visible-range 
laser excitation and analyzed in the micro mode with a 
T64000 Jobin-Yvon Raman spectrometer with a Nikon 
MPlan 100× microscope objective. Although graphene 
prepared by mechanical exfoliation contains defects, their 
density is typically too low to give an appreciable D mode signal 
without exceedingly large exposure times or alternately 
power levels that may lead to heating effects.9 We scanned 
the laser spot perpendicularly across the graphene edge [see 
Fig. 2(b)] which serves as an identifiable and repeatable def-
cent pyrolitic graphite highly oriented pyrolytic graphite 
(HOPG) flake. We therefore decided to average over a larger 
sample area, employing instead the macromode of the spec-
trometer that features a laser spot size that is about 30 times 
larger in diameter compared to the micromode and a depth of 
focus that exceeds a few millimeters. Yet even across this 
graphene obtained for laser excitation wavelengths 632 nm (red), 
514 nm (green), and 472 nm (blue). (b) $|K_{25,10}^{2}|$ for the graphene 
monolayer vs laser energy (eV) for the G (black circles) and D 
(red squares). The corresponding lines are a guide to the eye.

B. Graphite

Due to the very short depth-of-field of the high-
magnification optical microscope objective (~1 μm), 
repeatably isolating a perfect edge proved difficult due to the 
presence of irregular ledges and overhangs in a highly ori-

IV. RESULTS AND DISCUSSION

A. Graphene

For graphene we found a D mode dispersion of 
41 cm⁻¹/eV which is in excellent agreement with our pre-
vious calculations7 and yet further confirms the validity of 
the double-resonant approach in determining the D mode. 
The experimentally determined $|K_{25,10}^{2}|$ for the D and G 
modes of graphene are shown in Fig. 3(b). For the D mode 
the $|K_{25,10}^{2}$ values account for the fact that they are observed 
with the laser spot center imprecisely at the graphene edge 
line. By measuring the G mode in a location far-away from
the edge a correction can be applied as described by Casiraghi et al.\textsuperscript{10} who obtained the D mode at a graphene edge using a piezoelectrically controlled stage. The relative intensity of the D mode achieves a maximum at the edge location whereas the G mode is nominally half its strength at the edge compared to its bulk value.\textsuperscript{10} It is important to keep in mind that the incident intensity employed in the calculation for the D mode $|K_{2f,10}|^2$ is twice the intensity prevailing experimentally. This is because in order to obtain the maximum D mode the graphene sheet only receives half the laser footprint and therefore only half its intensity.

The origin of the increasing D and G mode $|K_{2f,10}|^2$ with laser energy may be due to the approaching Van Hove singularity (and the concomitant increase in the density of states) at the M point of the electronic dispersion of graphene. Since the visible range of laser energies lie on the shoulder of this Van Hove singularity, our results for the intensity of the D mode in Ref. 7 were deemed constant on the scale presented. However, on rescaling our results we again find a nearly linearly increasing D mode in good agreement with the experimentally observed intensity profile.

Our calculation for the $|K_{2f,10}|^2$ of graphene assumes a total enhancement factor $|F[z_{d},\omega_{0}]|^2 |F[z_{d},\omega_{0}]|^2$ which is calculated for an SiO$_2$ thickness of $(293.7\pm0.5)$ nm and changes quite rapidly even with a $\pm 5$ nm variation (see Fig. 4) which needs to be reckoned with for an imperfectly flat sheet of graphene which may be due to the intrinsic ripples in graphene\textsuperscript{23} or sandwiched molecules (e.g., H$_2$O) between the graphene layer and the SiO$_2$ layer. Therefore, our results should be interpreted with care, giving due consideration to their variation as indicated by the vertical solid black lines of Figs. 4(a) and 4(b) for the D and G modes, respectively.

A comparison with previously published data on graphite\textsuperscript{27} and standard scatterers such as diamond\textsuperscript{13,25} and silicon\textsuperscript{24,26} in terms of the conventionally quoted Raman tensor component $|a|$ values based on Eq. (14) is given in Table I together with their absorption coefficients $\alpha_{s}$, as material parameters. The value of $|a|$ for graphene is obtained by using the volume of its unit cell $V_{e,graphene}=0.5 \times V_{e,graphite}$, reduced mass $M_{r,graphene}=2 \times M_{r,graphite}$, and scattering length $L_{z}=0.335$ nm. The transmission coefficients $T_{r}$ are obtained using the transfer matrix formalism for the ambient-graphene-SiO$_2$-Si stack with $L$ as the assumed graphene thickness.

![Diagram](image_url)

**FIG. 4.** (Color online) Variation in the total enhancement factor of Eq. (8), $|F[z_{d},\omega_{0}]|^2 |F[z_{d},\omega_{0}]|^2$ for graphene suspended on a SiO$_2$-Si layer as a function of laser energy for a $(293.7\pm0.5)$ nm variation in SiO$_2$ thickness for (a) the D mode and (b) the G mode. The solid black lines indicate the variation in the total enhancement factor $|F[z_{d},\omega_{0}]|^2$ for the incident laser energies employed.

![Diagram](image_url)

**FIG. 5.** (Color online) (a) Representative Raman spectra of graphite obtained for laser excitation wavelengths 632 nm (red), 514 nm (green), and 472 nm (blue) with indicated D, G, G$, G^+$, and $G^+$ modes. (b) $|K'_{2f,10}|^2$ for graphite per unit area per graphene layer vs laser energy (eV) for the G (solid black circles), D (red squares), $G^-$ (blue diamonds), and the $G^+$ modes (green squares). The corresponding lines are a guide to the eye.
TABLE I. A comparison of the Raman tensor component |a| and material parameters for various materials at the 514.5 nm laser wavelength.

| Material   | Phonon symmetry, wave number (cm⁻¹) | α₁ (m⁻¹) | α₂ (m⁻¹) | Ref. | |a| (Å²) | Ref. |
|------------|-------------------------------------|----------|----------|------|----------|------|
| Diamond    | F₂g, 1332                           | 0        | 0        | 28   | 4.4      | 11   |
|            |                                     |          |          |      | 3.9      | 25   |
| Silicon    | F₂g, 525                            | 1×10⁶    | 0.75×10⁶ | 29   | 66       | 24   |
|            |                                     |          |          |      | 77       | 26   |
| Graphite   | E₂g, 1585 (G mode)                  | 3.72×10⁷ | 3.41×10⁷ | 30   | 88       | 24   |
|            |                                     | 4.18×10⁷ | 3.84×10⁷ | 31   | 104      | 24   |
|            |                                     | 3.35×10⁷ | 3.16×10⁷ | 30   | 131      | This work |
|            | A₁, 1355 (D mode)                   | 3.35×10⁷ | 3.18×10⁷ | 30   | 118      | This work |
| Graphene   | E₂g, 1584 (G mode)                  | 3.35×10⁷ | 3.16×10⁷ | 30   | 92       | This work |
|            | A₁, 1343 (D mode)                   | 3.35×10⁷ | 3.18×10⁷ | 30   | 69       | This work |

G and D modes for graphite are given in Fig. 5(b). The G mode [K'₃/E₁₀]² increases rapidly with increasing laser energy as indicated by the black line of Fig. 5(b). We observe a good agreement with previous experimental results of Wada and Solin[24] for the (albeit single) 514.5 nm excitation frequency [see the black starred points in Fig. 5(b)] calculated from the Raman tensor component |a| for the G mode of HOPG. Also given are the results for the G⁻ and G⁺ modes that can be discerned in our spectra at 1559 and 1624 cm⁻¹ for the 514.5 nm laser line, for instance [see Fig. 5(a)]. Our results show a steady, nearly linearly increasing D mode [K'₃/E₁₀]². The observed rise of the D and G modes with increasing laser frequency may be explained identically to the case of graphene discussed earlier.

A dispersion of the D mode position with laser energy of 35 cm⁻¹/eV was found which is slightly lower than previously reported values on HOPG [44–51 cm⁻¹/eV (Refs. 27, 32, and 33)] and may be due to the smaller grain size of the microcrystallites present in pencil graphite but nevertheless agrees well with our theoretical prediction based on constant matrix elements. 7

V. SUMMARY AND OUTLOOK

We have measured the Raman spectra of graphene and graphite for the D and G modes across the visible range of laser energies. The absolute Raman response of the bare material under consideration was obtained using the method of sample substitution[11] with CaF₂ as a reference[16] that allows the deconvolution of the highly wavelength-dependent response of the spectrometer optics and its CCD detector. The effect of the underlying stratified medium on the Raman response of graphene, via electromagnetic enhancement was modeled by considering the scatterer in the limit of an electric dipole. We derived an expression that relates the experimentally measurable spectra to the absolute Raman response of the bare material as encoded by the explicitly frequency-independent Raman matrix element squared [K'₃/E₁₀]² per unit area per graphene layer considering graphene in the paradigm of a perfect plane scatterer, thus avoiding the problematic ascription of a thickness value for graphene. Our model was further extended to the more familiar case of a scatterer of finite thickness, e.g., graphite.

Our results showed that the [K'₃/E₁₀]² per graphene layer vs laser energy rises rapidly for the G mode and less so for the D mode (see Figs. 3 and 5). This may be due to the approaching Van Hove singularity of the M points in the electronic dispersions of both graphene and graphite. The D mode dispersion for graphene was 41 cm⁻¹/eV in excellent agreement with our earlier theoretical prediction. 7 Whereas a dispersion of 35 cm⁻¹/eV was found for pencil graphite which is somewhat lower than the reported values of HOPG of 44–51 cm⁻¹/eV. 27,32–35 Our results shall aid in the experimental verification of the electron-phonon, electron-defect scattering matrix elements in the visible range of the energy scale that may be obtained using theoretical or ab initio methods and shall be the subject of a future publication.

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Not to be confused with the usual definition of the matrix element: \( \langle \psi | \hat{H} | \psi \rangle \).

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