Optical Properties of Carbon Conjugated Systems

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Optical Properties of Carbon Conjugated Systems

A dissertation presented
by
Yuan Yang
to
The Department of Chemistry and Chemical Biology
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Chemistry

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Optical Properties of Carbon Conjugated Systems

Abstract

Conjugated carbon systems have played an important role historically in the theoretical study of physical phenomena and are finding many modern-day applications in electronic devices. Raman spectroscopy is a powerful tool in calibrating the structure of conjugated carbon systems and in studying their carrier dynamics, both of which are important to their potential applications. In Chapter 1 and 2, I provide a comprehensive understanding of the Raman spectrum of polyacetylene and graphene under the framework of the Kramers-Heisenberg-Dirac theory.

Graphene is made up of $sp^2$-hybridized two-dimensional carbon lattice consisting of conjugated hexagonal cells. It shows extraordinary optical properties because of its low-dimensionality and unique electronic band structure. Graphene has found use in transparent electrodes, optical display materials and opto-electronics such as photodetectors, optical modulators, among many more. A proper understanding of the carrier dynamics in graphene is key to realizing its potential application in high-speed photonics and optoelectronics. In Chapter 3, we present a new paradigm for understanding optical absorption and hot electron dynamics experiments in graphene. In Chapter 4, we focus on the unique terahertz property of graphene, which has attracted a lot of recent attention due to its novel optoelectronic applications. We show that it is the coherence length of electrons that produces the peculiar terahertz properties in graphene.
Single-wall carbon nanotubes (SWNTs) are nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a tube. There has been a lot of recent activity exploring the electrical properties of SWNTs and their potential applications in electronics since their discovery in the early 1990s. In Chapter 5, I extend the methods used to understand polyacetylene and graphene Raman spectrum to explain various Raman spectrum features of SWNTs.

Phonon-assisted light absorption in materials is an important optical process both from a fundamental and a technological point of view. Silicon is a commercially successful photovoltaic material because of the indirect optical transitions that enable photon capture in the spectral region between the indirect (1.1 eV) and direct (3.4 eV) band gaps. Despite its importance, only a very limited number of first-principles studies of phonon-assisted optical absorption spectra exist. In Chapter 6, we provide a new paradigm based on the Born-Oppenheimer approximation with light-matter interaction to calculate silicon’s phonon-assisted absorption spectrum.
Contents

0 Introduction 1

1 Raman Scattering in Carbon Nanosystems: Solving Polyacetylene 7
  1.1 Abstract ................................................................. 7
  1.2 Introduction .......................................................... 8
  1.3 Theoretical Background ............................................. 11
  1.4 Results and Discussion ............................................. 17
  1.5 Implications and Conclusion ....................................... 34

2 Theory of Graphene Raman Scattering 35
  2.1 Abstract ................................................................. 35
  2.2 Introduction .......................................................... 36
  2.3 Results and Discussion ............................................. 38
  2.4 Conclusion ............................................................ 77
  2.5 Method ................................................................. 79
  2.6 Acknowledgements .................................................. 81
  2.7 Supporting Information ............................................ 82

3 Reassessing Graphene Absorption and Emission Spectroscopy 92
  3.1 Abstract ................................................................. 92
  3.2 Introduction .......................................................... 94
  3.3 Absorption Spectrum ................................................ 98
  3.4 Ultrafast Hot Electronic Dynamics Upon Absorption ............. 102
  3.5 Conclusion ............................................................ 107
  3.6 Acknowledgement .................................................... 109
  3.7 Supplementary Material ............................................ 109

4 Graphene Terahertz Absorption 114
  4.1 Abstract ................................................................. 114
  4.2 Introduction .......................................................... 115
  4.3 Results and Discussion ............................................. 118
  4.4 Conclusion ............................................................ 123
## 5 Raman Spectrum of Isolated Single-Wall Carbon Nanotubes

5.1 Abstract .................................................. 125
5.2 Introduction ............................................ 126
5.3 Results and Discussion ................................. 127
5.4 Conclusion ............................................. 141

## 6 Phonon-Assisted Transition in Silicon

6.1 Introduction ............................................ 142
6.2 Silicon Electronic and Phonon Properties ............ 143
6.3 Phonon-Assisted Absorption Calculation Method .... 146
6.4 Preliminary Results ................................... 153

References ................................................. 167
To my parents, Ping Yuan and Jianyong Yang.
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Publications


Introduction

Conjugated carbon systems have played an important role historically in the theoretical study of physical phenomena and are finding many modern-day applications in electronic devices.

The polyacetylene molecule once played an outsized role, first as a promising organic conducting polymer \textsuperscript{26,5}, then the focus of the Su-Schrieffer-Heeger \textsuperscript{119,48,19} model for soliton behavior of the Peierls distortion of the chain. Around the same time, intensive work on its spectroscopy, especially
Raman spectroscopy, was begun. Heeger, MacDiarmid, and Shirakawa shared the Nobel Prize in Chemistry in 2000 “for the discovery and development of conductive polymers”, notably polyacetylene.

The polyacetylene spectroscopy boom trailed off inconclusively. Unusual spectral features were assigned to polydisperse or inhomogeneous samples, unconventional vibrational patterns together with inhomogeneity, and coexistence of ordered and disordered phases (another kind of polydisperse sample). Solitons, important as they were for other reasons, were also cited as a cause of the signature Raman scattering effects.

In Chapter 1, under the framework of Kramers-Heisenberg-Dirac (KHD) theory, we show that the enigmatic spectral features of polyacetylene, across a wide range of experiments, are in fact attributable to monodisperse samples and Born-Oppenheimer quantum dynamics, especially the transition moments and their coordinate dependence (i.e., no Condon approximation). Molecular ends and internal defects do play a role in the intensity and bandwidth of Raman sidebands, but not their frequencies. The molecule and methods here strongly inform the burgeoning field of Raman spectroscopy of conjugated carbon systems including nanotubes and graphene.

Today, graphene is the new polyacetylene, so to speak. Strong scientific, programmatic, and historical analogies exist between the two systems, including an enigmatic Raman spectrum and hopes for new devices based on conjugated conducting organic crystals.

Graphene, with its $sp^2$-hybridized honeycomb two-dimensional carbon lattice consisting of conjugated hexagonal cells, shows extraordinary optical properties because of its dimensionality and unique electronic band structure. As an atomically thin two-dimensional carbon material,
Graphene is used for transparent electrodes and optical display materials. Graphene also provides a unique material system to study Dirac fermion physics in two dimensions. Researchers have demonstrated in graphene exotic Dirac fermion phenomena ranging from anomalous quantum Hall effects to Klein tunneling in low-frequency (DC) electrical transport. They also observed an optical conductance defined by the fine-structure constant and gate-tunable infrared (IR) absorption in Dirac fermion interband transitions. Situated between DC electrical transport and interband optical excitation is the spectral range dominated by intraband transitions. This intraband dynamics response has attracted much recent attention and is expected to play a key role in the future development of ultrahigh-speed electronics at terahertz (THz) frequencies and THz-to-mid-IR optoelectronic devices. A proper understanding of the carrier dynamics in graphene is key to its potential applications in high-speed photonics and optoelectronics. Many theoretical works concern the electron dynamics in graphene.

Raman scattering plays a key role in unraveling the quantum dynamics of graphene. It is crucial to correctly interpret the meaning of the spectra. It is therefore very surprising that the widely accepted understanding of Raman scattering, i.e., KHD theory, has never been applied to graphene. In Chapter 2, we study graphene Raman spectrum based on KHD theory. Doing so here, a remarkable mechanism we term “transition sliding” is uncovered, explaining the uncommon brightness of overtones in graphene. Graphene’s dispersive and fixed Raman bands, missing bands, defect density and laser frequency dependence of band intensities, widths of overtone bands, Stokes, anti-Stokes anomalies, and other known properties emerge simply and directly.

In Chapter 3, we present a new paradigm for understanding optical absorption and hot electron
dynamics experiments in graphene. Our analysis pivots on assigning proper importance to phonon assisted indirect processes and bleaching of direct processes. We show indirect processes figure in the excess absorption in the UV region. Experiments which were thought to indicate ultrafast relaxation of electrons and holes, reaching a thermal distribution from an extremely non-thermal one in under $5-10$ fs, instead are explained by the nascent electron and hole distributions produced by indirect transitions. These need no relaxation or ad-hoc energy removal to agree with the observed emission spectra and fast pulsed absorption spectra. The fast emission following pulsed absorption is dominated by phonon assisted processes, which vastly outnumber direct ones and are always available, connecting any electron with any hole any time. Calculations are given, including explicitly calculating the magnitude of indirect processes, supporting these views.

The unique terahertz properties of graphene has been identified for novel optoelectronic applications very recently\textsuperscript{61,78,113,56,87,44,81,120,133}. In a graphene sample with bias voltage added, there is an enhanced absorption in the far infrared region and a diminished absorption in the infrared region. The strength of enhancement(diminishment) increases with the gate voltage, and the enhancement compensates the diminishment. In Chapter 4, we show that it is the coherence length of electrons in graphene that allows pure electronic transitions between states differing by small momentums and makes intraband transition possible, is responsible for the far infrared enhancement. Phonon assisted processes are not necessary and would not in any case contribute to a sum rule. This naturally leads to results obeying the general sum-rule in optical absorptions. Our prediction of the strength of enhancement(diminishment) in terms of the bias agrees with experiments. This is the first direct calculation we are aware of, since the prior phonon assisted model for indirect transition should not
Single-Wall Carbon Nanotubes (SWNTs) are nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a tube. There has been intense activity exploring the electrical properties of these systems and their potential applications in electronics since their discovery in the early 1990s\textsuperscript{55,56}. SWNTs with different structures display different electric properties. Raman Spectroscopy is the most promising technique which calibrates the structure of SWNTs\textsuperscript{16}.

In Chapter 5, methods developed to understand polyacetylene and graphene Raman spectrum are applied to explain various Raman features of SWNTs. We show that the transition moment of individual SWNT is always along the tube longitudinal direction regardless of vibrational modes, and this explains the dependence of Raman spectrum on incident and scattered light polarization directions. We also explain the difference between Raman spectrum of metallic SWNTs and that of semiconducting SWNTs, the length dependence of sideband Raman peaks, etc.

The phonon-assisted light absorption in materials is an important optical process both from a fundamental and from a technological point of view. For indirect-band-gap semiconductors phonon-assisted processes determine the onset of absorption. For example in silicon, the value of the direct band gap (3.4 eV) is large and precludes optical absorption in the visible. However, silicon is commercially successful photovoltaic material because of the indirect optical transitions that enable photon capture in the spectral region between the indirect (1.1 eV) and direct band gaps.

Despite their importance, at present, only a very limited number of first-principles studies of phonon-assisted optical absorption spectra exist. Ab initio calculations of direct optical absorption spectra including excitonic effects have already been performed for Si and other bulk semiconduc-
tors and the underlying methodology is presently well established. However, Phonon-assisted absorption studies are more involved, and the associated computational cost is much higher than the direct case. The traditional calculation of the indirect absorption coefficient involves a double sum over $k$ points in the first Brillouin zone (BZ) to account for all initial and final electron states. In addition, these sums must be performed with a very fine sampling of the zone to get an adequate spectral resolution. The computational cost associated with these BZ sums is in fact prohibitive with the usual methods.

In Chapter 6, we provide a new paradigm based on Born-Oppenheimer approximation and light-matter interaction to calculate the phonon-assisted absorption spectra. Under the paradigm, we reduce the phonon-assisted absorption calculation from a second order process to a first order process calculation.
1.1 Abstract

Polyacetylene has been a paradigm conjugated organic conductor since well before other conjugated carbon systems such as nanotubes and graphene became front and center. It is widely acknowledged
that Raman spectroscopy of these systems is extremely important to characterize them and understand their internal quantum behavior. Here we show, for the first time, what information the Raman spectrum of polyacetylene contains, by solving the 35-year-old mystery of its spectrum. Our methods have immediate and clear implications for other conjugated carbon systems. By relaxing the nearly universal approximation of ignoring the nuclear coordinate dependence of the transition moment (Condon approximation), we find the reasons for its unusual spectroscopic features. When the Kramers-Heisenberg-Dirac Raman scattering theory is fully applied, incorporating this nuclear coordinate dependence, and also the energy and momentum dependence of the electronic and phonon band structure, then unusual line shapes, growth, and dispersion of the bands are explained and very well matched by theory.

1.2 Introduction

The polyacetylene molecule (Figure 1.1) once played an outsized role, first as a promising organic conducting polymer, then the focus of the Su-Schrieffer-Heeger model for soliton behavior of the Peierls distortion of the chain. Around the same time, intensive work on its spectroscopy, especially Raman spectroscopy, was begun. Heeger, MacDiarmid, and Shirakawa shared the Nobel Prize in Chemistry in 2000 “for the discovery and development of conductive polymers”, notably polyacetylene.

The polyacetylene spectroscopy boom trailed off inconclusively. Unusual spectral features were assigned to polydisperse or inhomogeneous samples, unconventional vibrational patterns together with inhomogeneity, and coexistence of ordered and disordered phases (another kind of
polydisperse sample)\textsuperscript{72}. Solitons\textsuperscript{40,72}, important as they were for other reasons, were also cited as a cause of the signature Raman scattering effects.

Here, we show that the enigmatic spectral features of polyacetylene, across a wide range of experiments, are in fact attributable to monodisperse samples and Born-Oppenheimer quantum dynamics, especially the transition moments and their coordinate dependence (i.e., no Condon approximation). Molecular ends and internal defects do play a role in the intensity and bandwidth of Raman sidebands, but not their frequencies. The molecule and methods here strongly inform the burgeoning field of Raman spectroscopy of conjugated carbon systems including nanotubes and graphene.

Today, graphene is the new polyacetylene, so to speak. Strong scientific, programmatic, and historical analogies exist between the two systems, including an enigmatic Raman spectrum and hopes for new devices based on conjugated conducting organic crystals. It therefore struck us as odd that polyacetylene’s Raman spectrum still remained mysterious, while graphene has enjoyed a well established narrative, for the past 12 years\textsuperscript{123,38}.

In Figure 1.1 we provide an overview of the systems and properties to be understood. As the incident laser energy increases starting from the deep red, the polyacetylene Raman bands evolve gradually from narrow, slightly asymmetric single peaks into a two-peak band consisting of an unshifted sharp peak at lower Raman displacement, tailing off to higher displacement, and a partially overlapping upward shifted sideband peak that becomes dominant in several circumstances.
Figure 1.1: Overview of all-trans polyacetylene and its unusual spectroscopy. (Top left) The structure of polyacetylene, with alternating single and double bonds, the result of a Peierls instability. The double bonds are shorter (1.345 Å against 1.415 Å) for the single bonds, although the π electrons are delocalized over the whole molecule. (Middle left) Absorption spectrum of polyacetylene in the region investigated for resonance Raman scattering. (Bottom left) Off-resonance Raman spectrum of polyacetylene from Gussoni et al. (Copyright 1991 Wiley). (Right column) Some of the major features and changes as incident wavelength decreases, needing an explanation, from 576.4, 524.5, and 457.8 nm. Red and green arrows point to sharp, nearly one-sided bands (shaded pink, tailing off to the right) that show no dispersion (see vertical lines) or growth with incident λ. Blue arrows point to dispersive bands growing in strength and also developing increasing frequency displacement from neighboring k = 0 fixed bands (dispersion) with increasing photon energy. Spectral data on the right and middle left are redrawn from Lefrant (Copyright 1983 EDP Sciences).
1.3 Theoretical Background

Making Full Use of the Transition Moment. The key to decoding this rather strange polyacetylene Raman spectrum relies on closely adhering to the well established Kramers-Heisenberg-Dirac (KHD) theory, including the long neglected (in condensed matter theory) nuclear coordinate dependence of the transition moment $\mu(\xi)$, where $\xi$ represents phonon coordinates. The transition moment $\mu(\xi)$ controls the amplitude to absorb a photon as a function of nuclear geometry, i.e., atomic positions defined by the phonon coordinates $\xi$, and is an integral part of KHD theory (see below). Neglecting the coordinate dependence (called the Condon approximation) is common almost to the point of universal, but we now believe this is quite dangerous, at least in systems consisting of large networks of conjugated carbon. This was recently emphasized by Duque et al., who found that transition moment coordinate dependence was needed to explain spectroscopic data for carbon nanotubes.\(^{38}\)

No Change in Potential upon Photo Absorption. Because of the dilution of the delocalized $\pi$ orbital amplitude over the infinite chain, it is almost obvious that the Born-Oppenheimer potential energy surface is unchanged after a lone electron-hole pair excitation in a large system with a huge number of delocalized orbitals. ( Longer times, too long to matter to Raman scattering, can lead to spontaneous localization taking place.\(^{117}\).) The stability of the Born-Oppenheimer potential against electron-hole pair formation was discussed by Zade et al.\(^{131}\), where the reorganization energy (the potential energy available in the excited state starting at the ground state geometry) vanished in long linear oligothiophenes with polymer length $N$. This implies phonons can be created only through
the transition moment coordinate dependence \( \mu(\xi) \), since no change happens in the potential energy surface. Transition moments and their coordinate dependence are the only active mechanism for phonon production in such systems, within Born-Oppenheimer theory. Transition moment coordinate dependence is a certainty: without it, the polarizability of the system would vanish within Born-Oppenheimer theory.

Of course, in a finite length molecule with defects it is expected that some displacements will occur in the excited states relative to the ground state, even at short times. (We are not interested in longer times beyond where Raman scattering is important.) It is worth noting that intensities created by excited state coordinate displacements are instantaneous in the same sense as the transition moment effects, and are also far from being electron-phonon “scattering”. In other words, the populations of the phonons are instantly created, whether it is a transition moment or wave function displacement in the excited state that causes it.

Arriving at Kramers-Heisenberg-Dirac Theory. The underpinnings of the KHD expression for Raman scattering, which we use here, are becoming somewhat ragged in the literature. It is not understood in all quarters that the Condon approximation is optional, and in others there is confusion between it and "Franck-Condon theory". Another factor is the popular "double resonance" (DR) Raman theory, associated with a large literature and applied singularly to conjugated carbon compounds like graphene (although not to polyacetylene to our knowledge). DR bears no stated relation to KHD. We could not find the otherwise universally employed KHD Raman theory mentioned anywhere in the extensive double resonance Raman literature, so to clarify matters we derive KHD in a few steps from the same starting point as DR, namely, the Martin and Falicov many-body
The 1925 Kramers-Heisenberg theory for Raman scattering \(^6\) predated quantum mechanics and was based on the Correspondence Principle. Dirac gave the quantum derivation in 1927 \(^3\). The paper by Born and Oppenheimer forming the basis for an intuitive and practical (if approximate) molecular and solid state quantum mechanics came just a bit later (1927) \(^4\). It justified the Franck-Condon principle in terms of the large mass difference between nuclei and electrons. As we will presently see, the KHD expression is fully derivable from the Born-Oppenheimer approximation and light-matter perturbation theory, as is the modern quantum implementation of the Franck-Condon principle.

The Martin and Falicov (MF) many-body expression for general two-photon processes \(^5\) reads

\[
\alpha_{sf,ui} = \sum_k \frac{\langle \omega_2, f | H_{MR} | 0, k \rangle \langle 0, k | H_{MR} | \omega, i \rangle}{\hbar \omega - E_k} \tag{1.1}
\]

where \(\alpha_{sf,uf}\) is an amplitude whose absolute square is proportional to the Raman scattering cross section, with \(\omega_2\) the emitted light frequency, \(\omega\) the incident frequency. The symbols \(i, k,\) and \(f\) represent initial, intermediate (excited, with energies \(E_k\)), and final system eigenfunctions of the full many-body Hamiltonian. \(H_{MR}\) is the operator controlling the first-order perturbative matter-radiation coupling. The symbol \(0\) in the intermediate states implies the absence of a photon. We have dropped a second term in the MF expression that corresponds to emission of the photon \(\omega_2\) before absorption of the incident photon \(\omega\). Unfortunately the full many-body evaluation of the MF expression is far out of reach for systems of interest, and even if it were available, it would be oddly
unsatisfying as a pure number lacking physical interpretation or intuition.

It is straightforward to derive the KHD expression by making Born-Oppenheimer approximations to the quantities in the Martin and Falicov expression. We suppress the photon labels since they are implied by the energy differences of the initial and final states; however, the incident frequency still appears in the denominator.

\[
|\omega, i\rangle \xrightarrow{\text{Born-Oppenheimer}} |\psi_i(\xi; r)\chi_{i,n}(\xi)\rangle \tag{1.2}
\]

\[
H \xrightarrow{\text{Born-Oppenheimer}} H^{\text{B.O.}} \tag{1.3}
\]

\(H^{\text{B.O.}}\) regards the Born-Oppenheimer wave functions \(\psi_i(\xi; r)\chi_{i,n}(\xi)\) as eigenstates with energies \(E_{i,n}\). The coordinates \(\xi\) represent all the nuclear position or phonon displacements, and \(\psi_i(\xi; r)\) is the usual adiabatic Born-Oppenheimer solution of the \(i\)th electronic state, a function of the electron coordinates \(r\) for fixed nuclear position \(\xi\). The wave function \(\chi_{i,n}(\xi)\) is the \(n\)th vibrational (phonon) state in the \(i\)th electronic state. The MF expression becomes

\[
\alpha_{fm,io}^{\xi,\sigma} = \sum_{j,n} \frac{\langle \psi_j(\xi; r)\chi_{j,m}(\xi) | \hat{e}_\xi \cdot r | \psi_j(\xi; r)\chi_{j,n}(\xi) \rangle \langle \psi_j(\xi; r)\chi_{j,n}(\xi) | \hat{e}_\xi \cdot r | \psi_i(\xi; r)\chi_{i,0}(\xi) \rangle}{\hbar\omega + E_{i,\sigma} - E_{j,n}} \tag{1.4}
\]

where \(\xi, \sigma\) indicate initial and final polarizations of the light. Introducing the transition dipole operator \(\mu_{ji}^{\xi}(\xi)\),

\[
\mu_{ji}^{\xi}(\xi) = \langle \psi_j(\xi; r) | \hat{e}_\xi \cdot r | \psi_j(\xi; r) \rangle , \tag{1.5}
\]
where the subscript \( r \) reminds us that only the electron coordinates are integrated over, we have

\[
\alpha_{\sigma, \rho} = \sum_{j, n} \left\langle \chi_{f, m}(\xi) \right| \mu_{ji}^\sigma \left| \chi_{j, n}(\xi) \right\rangle \left\langle \chi_{j, n}(\xi) \right| \mu_{ji}^\rho \left| \chi_{i, o}(\xi) \right\rangle \frac{\hbar \omega + E_{i, o} - E_{j, n}}{\hbar \omega + E_{i, o} - E_{j, n}}
\] (1.6)

This is the KHD expression, shown here to be purely the Born-Oppenheimer approximation plus ordinary light-matter perturbation theory. There is a subtle point which needs to be made now: the KHD expression, although a result of light matter perturbation theory, is to be evaluated to give “the answer”. That is, it is summed and a number is obtained and that is the Raman amplitude seen in the experiment in a very many cases. Although it is clear that some terms with the vanishing denominators are in a sense “more important” than others, they all count, and they are all to be summed up to get the answer.

The same is true for what can be called the Franck-Condon expression (the quantum embodiment of the Franck-Condon Principle), which is also purely the Born-Oppenheimer approximation plus ordinary light-matter perturbation theory for one photon absorption and emission. It predicts spectral intensities proportional to

\[
P_{\sigma, \epsilon} = \propto \left| \left\langle \chi_{f, m}(\xi) \right| \mu_{ji}^\epsilon \left| \chi_{i, n}(\xi) \right\rangle \right|^2
\] (1.7)

In both the Franck-Condon and KHD expressions, the Condon approximation means neglect of the coordinate dependence of \( \mu_{ji}^\epsilon(\xi) \).

Off Resonance: Polarizability and Transition Moments. It is well-known that off-resonance Ra-
man scattering depends primarily on the nuclear derivatives of the Placzek polarizability\textsuperscript{81}. Coordinate dependence of the transition moments are responsible for the Placzek polarizability\textsuperscript{11}, which would be unacceptably zero in the Condon approximation. Off resonance Raman scattering is necessarily a short time process (due to time-energy restrictions - tuning $\Delta E$ below resonance implies at most time $t = \hbar / \Delta E$ allowed in the excited state before re-emission\textsuperscript{1}). This gives precious little time for excited state wave function evolution, Born-Oppenheimer or not. Even if atomic displacements were significant (and we have argued that they are not), or if electron-phonon scattering was thought to be important on resonance, phonon production depends increasingly on the static coordinate dependence of the transition moment for Raman intensities as one goes further off resonance. It is an “instant” phonon production process which does not get erased on re-emission, explaining why it dominates off resonance. Coordinate displacements in the excited state can be “erased” upon fast re-emission because there has been insufficient time for wave packet motion under the new regime of excited state forces, implying a return to the initial phonon state upon reemission, with high probability.
1.4 Results and Discussion

Figure 1.2: Schematic of the $\pi$ orbitals in an infinite polyacetylene chain. Each colored dot represents the top half of a carbon $p_z$ orbital, with color giving the sign of that lobe of the orbital. The hidden lobe of each orbital in this top down view is below the plane of the molecule and of opposite sign to the visible part. Transparency depicts wave function amplitude. In the valence band, all double bonds are of bonding character (same sign on adjacent carbons). In the conduction band, all double bonds are of antibonding character. Every carbon-carbon double bond is "anti-bonding," in the conduction band. As energy increases, more single bonds acquire anti-bonding character.
Figure 1.3: Schematic of transition moment calculation and implications. A photon (blue vertical arrow) creates an electron-hole pair, promoting an electron in a valence orbital to a conduction orbital, here of the same $q$, conserving crystal momentum (or of opposite $q$, also conserving crystal momentum and having the same energy, if the birth is accompanied by a creation of a phonon of wave vector $2q$ via coordinate dependence of the transition moment). The phonon energy is prepaid so to speak by reducing the energy of the electronic transition, leaving an energy matched electron and hole from the beginning, $\hbar \omega = \Delta E_{\text{electron transition}} + \Delta E_{\text{phonon creation}}$. The local moments are summed to give the total transition moment and are seen on the right to be modulated at twice the wavevector of the electronic $q$, along the backbone of the molecule. The $2q$ modulation in the transition moment, shown with short blue arrows, going like $M \cos^2(qx) = M/2[1 + \cos(2qx)]$ is caused by the oscillation in orbital occupation with Bloch vector $q$. The strength of $M$ depends on carbon-carbon distances through phonon derivatives $\partial^2 \mu_{q-q}/\partial \xi_{2q}$; this $k = 2q$ phonon oscillates in phase with the transition moment, enhancing it at its maxima and doing less diminishment at its minima. Since $q$ changes with photon $\hbar \omega$ according to the electronic band structure, the resulting Raman $k = 2q$ sidebands will show dispersion with incident light frequency. There is also seen to be a constant or "DC" component, corresponding to the $q$-independent term in the expansion of $\cos^2(qx)$: this creates a $\Gamma$-point $k = 0$ phonon and band, independent of the excitation frequency or $q$, i.e., with no dispersion.

Accounting for Energy and Pseudomomentum. The electron energy adjustment due to instantaneous phonon production is evident in eq (1.6) since the largest terms correspond to a vanishing $\hbar \omega + E_{i,o} - E_{j,n}$, i.e., when the excited electronic energy plus the phonon energy, $E_{j,n}$, equals the initial energy in the system $E_{i,o}$ plus the photon energy $\hbar \omega$. We remark here that normally a small imaginary part is added to the dominator, so that a range of terms, not one term, dominates. This imaginary part represents spontaneous radiation rates, for example, but it can effectively be quite
a bit larger if there are missing degrees of freedom not accounted for, such as a bath of particles interacting with the system. Therefore, in spite of the appearance of the sum, it is not normal for one term to dominate it even at special frequencies $\omega$. The exception to this is small molecules, with discrete levels in the excited state; we are not concerned with this here. Nonetheless, with a small imaginary part, the most important terms still have very nearly perfect energy compensation built-in; that is, the electronic transition energy is adjusted downward at the get-go to compensate for the creation of phonons. It is also adjusted upward for annihilation of phonons, which can result in anti-Stokes scattering.

![Figure 1.4: Dispersion and growth of the 1064 and 1456 cm$^{-1}$ sidebands of trans-polyacetylene taken by Mulazzi et al. at the laser frequencies shown, redrawn from ref 96 (Copyright 1983 Elsevier). Our prediction of sideband position, using the phonon bands in the inset, right, is shown by the red arrows. (We have not found a well established, ?most reliable? phonon dispersion for polyacetylene.) One can alternately say we have here established the phonon dispersion in the early part of the bands for the first time, through interpretation of the experiments. The overall line shape is the sum of the constant $k = 0$ band and the moving and growing $k = 2q$ sideband. The inset (upper left) shows the $k = 0$ band fit to an exponential falloff on the right for the 1064 cm$^{-1}$ band. Inset, right: Polyacetylene phonon dispersion curves according to Jumaeu et.al. 60, used here.](image)
Tight Binding Model. We present a polyacetylene tight binding model using out of plane carbon $p_z$ orbitals. The model provides the basis for the derivations to follow. Figures 1.2 and 1.3 show a top-down representation of a portion of an infinite length quasi-1D polyacetylene crystal. The lowest and highest extremal $q = 0$ (crystal momentum zero) $\Gamma$ point states and representative intermediate states for the valence and conduction bands are shown. The valence band electronic states exclusively consist of bonding $\pi$ orbitals (same sign on both carbon atoms) on the double bonded carbons, and the conduction bands exclusively consist of antibonding $\pi$ orbitals (opposite sign) on the double bonded carbons.

The figures and their captions make clear that $k = 0$ fixed and $k = 2q$ oscillating transition moment densities result, where $q$ is the Bloch wave vector of the conduction band electronic orbital created by the incoming photon. The tendency for the transition moment to change with phonon Bloch vector $k$ will depend on whether it is in-phase with the transition momentum oscillations. It will clearly have a maximum at the $2q$ transition density oscillation wave vector, causing phonons to be produced at $k = 2q$, and more to be produced at $k = 0$, caused by the constant part of the transition density. The $k = 0$ phonon creation involves no momentum change for the electron. The transition will have been made at lower energy to account for the phonon energy as described above and therefore produces a perfectly matched electron and hole. The $k = 2q$ phonon on the other hand will have given a backward kick to the electron, taking it from $q$ to $-q$, so the electron needs elastic backscattering $k = 2q$ to realign it with the hole, allowing Raman emission and thereby sideband intensity.

The cause of the sideband dispersion is already clear, namely, the electronic band structure, with
changing as photon and thus electron energy changes, and the $2q$ phonon reacting with an appropriate photonic band structure energy shift (see Figure 1.4, right). It is clear that sources of backscattering such as defects and molecular termination will facilitate electron-hole annihilation and increase sideband intensity. Already this simple model reveals the essence of striking sideband variations in frequency and intensity as laser frequency changes, and as backscattering is made more or less prevalent.

The valence band Born-Oppenheimer electronic orbital $\psi_{q_v}(\xi, r)$ possesses Bloch vector $q_v$ (reducing to one dimensional notation in the pseudo 1D crystal). It depends on phonon coordinates $\xi$, and electron coordinates $r$. The available conduction band state $\psi_{q_c}(\xi, r)$ has the same Bloch vector (in the case of the $k = 0$ band, or a reversed Bloch vector $-q$ if a term in the transition moment creates a phonon of wavevector $k = 2q$). We will see why these processes turn up as Raman scattering below. We say right now that according to our model, there are plenty of other processes going on starting in the excited state that do not show up as Raman scattering.

Specializing eq (1.5) to the present case of a linear periodic system, the transition moment for polarization $\hat{e}_x$ and electron pseudomomentum $q_v$ and $q_c$ in the valence and conduction bands, respectively, is written according to eq (1.5) above

$$\mu_{\sigma q_v q_c}(\xi) = \langle \psi_{q_c}(\xi; r) | \hat{e}_x \cdot r | \psi_{q_v}(\xi; r) \rangle_r$$

We proceed to make this more specific to see how the "suggestive" tight binding model given earlier can be used explicitly to give the selection rules observed in the experimental spectrum. The
tight-binding wave functions can be expanded

\[ \psi_{q^v}(\xi; r) = \sum_n e^{iq^v \cdot R_n(\xi)} \varphi(r - R_n(\xi)) \]  

(1.9)

where \( \varphi \) is a \( p_z \) orbital and where the atomic coordinates \( R_n(\xi) \) depend here explicitly on the phonon coordinates \( \xi \). After this tight binding form (and one like it for the conduction band) is inserted into the expression eq (1.8) for the dipole transition moment, using the velocity (derivative) form of the dipole operator, noting the vanishing diagonal terms

\[ \int dr \varphi(r - R_n(\xi))(d/dr)\varphi(r - R_n(\xi)) = 0, \]

and keeping only the nearest neighbor off diagonal terms, we obtain

\[ \mu_{q^q^v}(\xi) \propto \sum_n e^{-i(q^c - q^v) \cdot R_n(\xi)} D_{n-1,n}^x(\Delta_{n-1,n}(\xi) | \Delta_{n-1,n}(\xi) \rangle) + e^{-i(q^c \cdot \Delta_{n,n+1}(\xi)} D_{n,n+1}(\Delta_{n,n+1}(\xi) | \Delta_{n,n+1}(\xi) \rangle) \]  

(1.10)

where

\[ \Delta_{n-1,n}(\xi) = R_{n-1}(\xi) - R_n(\xi) \]  

(1.11)

\[ \Delta_{n,n+1}(\xi) = R_n(\xi) - R_{n+1}(\xi) \]

The factor \( D_{n-1,n}^x(\Delta_{n-1,n}(\xi) \rangle \) and its partner\( D_{n,n+1}(\Delta_{n,n+1}(\xi) \rangle \) one site away are the dipole matrix elements

\[ D_{n-1,n}^x(\Delta_{n-1,n}(\xi) \rangle) \]  

(1.12)

\[ = \int dr \varphi(r - R_{n-1}(\xi))e_x \cdot (d/dr)\varphi(r - R_n(\xi)) \]
between neighboring $\pi$ orbitals; these are quite clearly dependent on the distance between the adjacent carbon atoms.

It is crucial that unless atom-atom distance derivatives like $\partial \Delta_{n-1,n}(\xi)/\partial \xi_k$ for certain $\xi_k$ vary in a synchronized way with the Bloch factor $e^{i(q_c - q_v) \cdot R_n(\xi)}$, the dipole moment derivatives like

$$\frac{\partial \Delta_{n-1,n}(\xi)}{\partial \xi_k}$$

will vanish, along with any chance of creating a phonon in coordinate $\xi_k$ of momentum $k$. But the phonons have a variety of pseudomomenta, and for many combinations of $q_c$ and $q_v$ several may be available to "neutralize" the phase drift of the term $e^{i(q_c - q_v) \cdot R_n(\xi)}$. The exponent acquires a net term

$$e^{i(q_c - q_v - k) \cdot R_n(\xi)}$$

and the sum over $n$ along an infinite chain will vanish as promised unless $q_c - q_v - k = 0$.

The first nonvanishing possibilities that present themselves are $q_c = q_v$ and $k = 0$ (associated with a $\Gamma$ point phonon $\xi_{k=0}$), and $-q_c = q_v$ together with $k = 2q$ (dropping the valence-conduction labels). This is associated with a sideband phonon $k = 2q$. Whereas the $\Gamma$ point phonon is immediately able to recombine with its hole emptied in the valence band (the electron and hole are exactly matched), the sideband electron can reunite with the hole only after elastic backscattering, when again it becomes perfectly matched, and if it emits it reveals the presence of the phonon, which is present in any case.
However, many other phonons can be produced with a variety of electron valence and conduction pseudomomenta such that \( q' - q'' - k = 0 \), which sounds like a problem: too many phonons! However, there is an efficient gatekeeper normally preventing Raman emission from such phonons, even though they are present: Pauli blocking prevents such unmatched electrons and holes, \( |q'| \neq |q''| \) from recombining even after elastic backscattering. What makes the gatekeeper so strict is that time is very short, and there is no time to get "sloppy" about electron-hole matching: e-e scattering is utterly destroying the memory of conditions of the conduction electron on a time scale of femtoseconds.

Given the requirements of pseudomomentum matching upon photo absorption in infinite periodic systems, both the hole and the particle equally share the adjustment of their energy to "pay" for the birth of the phonon. Suppose the ground state electron pseudomomentum is \( q \) with a quiescent phonon bath. In the excited state, phonons with a range of \( k \)'s are born; the transition moment is indiscriminate about this. Among these are phonons with momentum \( 2q \), causing the electron to be born at \(-q\) instead of \( q\) by momentum conservation. Elastic backscattering \( k = 2q\) then perfectly realigns the electron with its hole. Phonons born instead at arbitrary \( k \) can be backscattered or not, but unless \( k = 2q\) a moment's thought reveals the result is a stillborn, i.e., a Pauli blocked electron. This implies many unused incoming photons generate phonons not seen in Raman spectra. Let us remind ourselves that the total yield of Raman photons is often on the order of one in 10 million incoming photons, much less in a given band. This explains the special appearance of pseudomomentum \( 2q \). It is characteristic of the sideband dispersion and permitted (free of) Pauli blocking.

The Kramers-Heisenberg-Dirac expression, eq (1.6), with minor notational adjustment appro-
appropriate to polyacetylene, scattering from the initial valence electronic state with Blochvector $q$ with no phonons present, i.e., $|\chi_0(\xi)\rangle$, to conduction states at $q$ (or $-q$ if a phonon with pseudomomentum $2q$ has been created in the $j$th phonon band), finally (after backscattering if necessary) emitting back to the ground electronic state into phonon wave function $|\chi_{j,2q}(\xi)\rangle$ following electron-hole recombination, reads

$$
\rho_{c,j,k,v,0}^{\sigma} = \sum_{c,j',k'} \left( \frac{\langle \chi_{j',2q}(\xi) | \mu_{c,j',q}(\xi) | \chi_{j',k'}(\xi) \rangle \langle \chi_{j,k'}(\xi) | \mu_{c,j,q}(\xi) | \chi_0(\xi) \rangle}{\hbar \omega + E_{c,j,k} - E_{c,j,k'}} \right)
$$

(1.15)

where $E_{c,j,k}$ is the energy of the phonon of wave vector $k$ in band $j$ and electronic conduction band $c$.

The initial state $|\chi_0(\xi)\rangle$ is multiplied by the transition moment $\mu_{c,j,q}(\xi)$, producing

$$
\mu_{c,j,q}(\xi) |\chi_0(\xi)\rangle = (\mu_{c,j,q}(\xi_0) + \sum_{j,k} \frac{\partial \mu_{c,j,q}(\xi)}{\partial \xi_{j,k}} |\xi_0 \cdot \xi_{j,k} + \ldots \rangle |\chi_0(\xi)\rangle
$$

(1.16)

where the subscripts $j$, $k$ on $\xi$ refer to wave vector $k$th in the $j$th phonon band. This implies instant phonon creation, since

$$
\mu_{c,j,q}(\xi) |\chi_0(\xi)\rangle = \mu_{c,j,q}(\xi_0) |\chi_0(\xi)\rangle + \sum_{j,k} \frac{\partial \mu_{c,j,q}(\xi)}{\partial \xi_{j,k}} |\xi_0 \cdot \xi_{j,k} |\chi_0(\xi)\rangle + \frac{1}{2} \sum_{j,\xi,j',\xi'} \frac{\partial^2 \mu_{c,j,q}(\xi)}{\partial \xi_{j,k} \partial \xi_{j',k'}} |\xi_0 \cdot \xi_{j,k} \xi_{j',k'} |\chi_0(\xi)\rangle + \ldots
$$

$$
= a_0^\sigma |0\rangle + \sum_{j,k} b_{j,k}^\sigma |j\rangle + \sum_{j,k,j',k'} c_{j,k,j',k'}^\sigma |j,k\rangle + \ldots
$$

(1.17)

after rewriting the polynomials multiplying the ground state in terms of the equivalent set of excited
phonon modes. This is a sum over the ground and excited conduction band phonon modes with Bloch wavevectors $|k_j⟩$, $|k_j', k_j'⟩$, ..., including possible multiple occupation different bands $j$ and $j'$ of different or the same wavevector $k_j$ and $k_j'$ in the electronic band $q$, of which here we consider two, the $\pi$ valence and conduction bands.

![Molecular size dependence of sideband intensity](image)

![Defect density dependence of sideband intensity](image)

**Figure 1.5:** Dispersion and growth of Raman sidebands with length and defects. (A) As the polyacetylene length becomes shorter in a monodisperse sample, the ends of the molecule become accessible to a higher fraction of the electrons, increasing the backscattering efficiency. The $k = 2d$ intensity falls like the inverse length of the molecule. The figure was redrawn and the dashed $k = 0$ band contribution added, from ref.\(^{115}\). (B) As the density of defects increases, the $k = 2q$ dispersive sideband accounts for an increasing fraction of the Raman scattering in the 1054 cm\(^{-1}\) band. Other sideband features in different bands show the same behavior. The figure was redrawn and the dashed $k = 0$ band contribution added, starting from Schafer-Siebert et al.\(^{114}\). Important details: (1) the sideband increases intensity but does not broaden in fwhm after 4.5% defects. The sideband width and line shape are not determined by the time it takes to backscatter. (2) The $k = 0$ band is added to the sideband to give the total intensity, making a break in slope of the total to the right of the $k = 0$ band peak in both A and B panels (and verified in the numerical calculations, Figure 1.6).

Transition Moment Estimates. There is indeed a strong dependence of the propensity to make a $\pi$ to $\pi^*$ transition depending on carbon-carbon interatomic distance, in a single bond. However, does this survive the transformation to a finite derivative with respect to phonon coordinates in
the long molecule limit? Detailed arguments given in the Supporting Information show this is the case, but there is a very quick and convincing shortcut to the conclusion: if the phonon coordinate derivatives vanished, the off resonance Raman scattering the phonon modes in question would too. This is obviously not the case (see Figure 1.1). The Placzek polarizability derivatives \(^8\) used for calculating off-resonant Raman scattering \(^8\) depend on these derivatives.

A simple estimate of the transition moments and their coordinate dependence for polyacetylene along, for example, the \(\text{C} = \text{C}\) double bond direction may be had using tight binding and Gaussian orbitals. In arbitrary units, we find transition moments (constant term) near 25, and the first derivative along a \(\text{C} = \text{C}\) stretch 1456 cm\(^{-1}\) phonon mode of about 16 per angstrom of double bond stretch. The individual \(\text{C} = \text{C}\) dimer stretch is however diluted roughly by \(1/N^{1/2}\) in a phonon mode, where \(N\) is the number of dimer units along the chain. The Raman intensity to the phonon goes as the square of this, or \(1/N\). There is another factor of \(1/N\) diluting the transition moment, coming from the average \(1/N^{1/2}\) reduction of the orbital amplitude on each bond, keeping the delocalized electronic orbitals of a given \(q\) normalized. The transition moment involves multiplication of two such orbitals on each dimer, but the integral involves integrating over all \(N\) dimers. The orbital dilution is thus canceled in the transition moment integral. There still remains the \(1/N\) phonon dilution in Raman intensity. However, the full KHD expression involves a sum over all electronic states, resonant or not. It is easily shown, after summing over nearly resonant terms, that the total Raman intensity to a given phonon mode, given a small damping, e.g., including spontaneous radiation), becomes constant as \(N \rightarrow \infty\). This makes sense, since one electron is making a transition over the whole polymer.
Figure 1.6: Numerical results from a simple phonon simulation as input to the Raman theory presented in this paper. The calculations involve a 450 unit cell long sample with alternating "bonds" and two or four randomly placed defect impurities. The defective phonons we found by diagonalizing the Hessian matrix of a linear chain of 900 atoms (450 unit cells). About 3000 placements of the random impurities were averaged here for each result shown. The electronic orbitals were assumed to ignore the impurities and span the sample. The $k = 0$ and $k = 2q$ components can be computed separately (see their contribution to the total in the top row), and their ratio varied by hand. It would be difficult in the extreme to get the backscattering intensity ab initio, because a quantitative theory giving the number of defects of all sorts, and their backscattering propensities, would be required for samples produced in a given lab. The line shapes nonetheless emerge naturally from the simulation; these are not put in by hand so to speak. They are due to the partial vibrational confinement between ends and defects, seen at the bottom in another simulation (a Gaussian 09 density functional calculation on polyacetylene with four Si atoms in place of carbon). Four low lying vibrational modes are seen, with darkness of the atoms representing vibration amplitude. The vibrational modes have a near linear dispersion in this low $k$ regime and are driven by the constant and sinusoidal terms in the transition moment, as in the tight binding model presented above in Figures 1.2 and 1.3. See text and Supporting Information for more details on the calculation.

Sideband Dispersion, Backscattering. The Taylor expansions of the coordinate dependence of
the transition moment is sometimes called a Herzberg-Teller expansion; it is not a perturbation expansion but merely a way to organize its coordinate dependence. Electronic structure calculations can yield the full coordinate dependence at an ab initio level, boding well for future quantitative prediction of Γ point band strengths. Prediction of sideband strength depends on total backscattering, which requires sophisticated understanding of kinks, environment, other defects, and their backscattering amplitudes. This is beyond our current capabilities, but we later show revealing trends with changes that can only increase or decrease backscattering, such as proximity to molecular ends, introduction of defects, etc.

The presence of $k = 2q$ phonons could in principle also backscatter electrons elastically, but experiments (see below) show the $k = 2q$ sideband intensity effectively vanishing if artificial sources of backscattering are absent, so such backscattering is evidently not important. A $k = 2q$ sideband should be attached to every high symmetry point, subject to selection rules, again because of the transition moment undulations, which produce a DC component populating the high symmetry point and another component at $k = 2q$.

If a phonon of wave vector $k = 2q$ is created instantaneously upon excitation, the energy devoted to the electronic transition is adjusted by the phonon energy, according to the total energy in the photon: $\hbar \omega = E_{\text{electron transition}} + E_{\text{phonon}}$. The phonon’s energy dispersion is thus written into the photon’s Raman sideband dispersion.

The $k = 2q$ phonon sidebands diminish in strength (and move toward the $k = 0$ line as $q$ diminishes) with redder incoming light and are missing altogether below resonance. If the phonons are reliably produced as a byproduct of the transition moment, why do corresponding Raman side-
bands diminish in intensity this way? Off resonance, there is insufficient time to backscatter the conduction band recoiling electrons, so they remain very unlikely to find their way back to the hole they left behind. There is no such problem for the $k = 0$ band, since the electron did not change crystal momentum in the first place. These facts contribute to the large change in the ratio of $k = 0$ and $k = 2q$ Raman band intensities with incident frequency. In summary, phonons of both types, sidebands and main peak, are reliably created, but the fraction of sideband that gives rise to Raman shifted emission depends on backscattering conditions.

Absorption vs Emission. The question arises whether the phonon production must occur only in absorption, since the transition moment acts twice, once absorbing a photon and once emitting one. Indeed the $k = 0$ band may be generated in either step or both. The story for the sidebands is different. A sudden exchange $-q$ for $q$ producing a phonon $2q$ upon emission would make recombination unlikely.

Defects and Finite-Sized Molecules. What makes the features of the polyacetylene Raman band shapes peculiar, beyond the dispersion of $k = 2q$ Raman bands, is the strongly variable strength of the (broadened) sidebands depending on conditions, and the width and shape of the band. These are not Gaussian or Lorenzian lineshapes obeying a sum rule! The band shapes and their evolution with incident wavelength can be explained in terms of the different responses of the $k = 0$ peak and the $k = 2q$ peak to the effects of backscattering.

The $k = 0$ Γ point bands are always present for Raman allowed transitions, induced by the constant component of transition moment; these do not require backscattering in order to be produced. The exponential tail to the right of the sharp $k = 0$ feature at $1164 \text{ cm}^{-1}$ is found not to depend
strongly on backscattering strength (pink and tan shaded regions, Figures 1.4 and 1.5).

With modest concentrations of defects and presence of ends, $k$ and $q$ are no longer perfectly good quantum numbers, effectively making $k$’s close to 0 allowed. Defects also play a dual role in the $k = 2q$ sideband, making nearby $k$’s available and backscattering electrons so they can fill the holes they created. The degeneracy of left and right traveling plane waves is broken, both electronically and vibrationally.

The phonons associated with the $k = 0$ line carry no pseudomomentum even as they carry energy above that of the $k = 0$ line. The energies do not lie below the $k = 0$ line because no phonon states exist there, since even with defects present, it is difficult to generate vibrations of lower frequency than the $\Gamma$ point of each band. Confining the vibrations tends to produce higher, not lower, frequencies if the band dispersion slope is positive, as it is here. Thus, the abrupt falloff to the left of the $\Gamma$ point line.

Experimental Tests. It is remarkable that three critical experimental tests were performed supporting the transition moment/backscattering model given here: varying the incident wavelength that we have already mentioned, varying the length of the molecule in a controlled way, and varying the defect density in a controlled way.

In ref, three samples of nearly monodisperse polyacetylene with lengths of about 200, 400, and 3800 unit cells were synthesized and their Raman spectra were obtained. The sidebands remained, and many of the earlier “polydisperse” explanations for the line shape quickly evaporated.

A shorter polyacetylene molecule has ends available to backscatter to a larger fraction of electrons. The prediction is that the $k = 2q$ sideband intensity falls like the inverse length of the molecule,
assuming no defect scattering. The \((k = 0)/(k = 2q)\) ratio in the three parts of Figure 1.5A using the same \(k = 0\) band shape (dashed line) as in Figure 1.4 changes by a factor of \(1 : 7.5\). Assuming a (crude guess) 50 unit cell proximity rule in order to reach the end intact to backscatter, the ratio should have been roughly \(1 : 10\). In any case, the experiment clearly shows that accessible ends dramatically enhance the \(k = 2q\) band, according to both the model and the experiment (see Figure 1.5A).

Another key measurement involved controlled oxidation of the polyacetylene (see Figure 1.5B), resulting in a knowable additional defect density (over the nascent density) of 0%, 5%, 7%, or 13%, see Figure 5. The ratio of the larger to smallest \((k = 0)/(k = 2q)\) sideband intensity is about \(1 : 6\) going from 0% to 13% new defects, meaning six times as many electrons relax by backscattering, emitting, and filling their holes with the highest defect density compared to nascent density plus end effects.

Finally, we discuss the trends with laser frequency, as seen in Figure 1.4. We have already mentioned that being off resonance eliminates the sidebands, due to a cutoff in the time allowed to backscatter (see Figure 1.1). Preliminary calculations using 20 unit cells (40 carbon atoms) polyacetylene molecules with defects caused by Si replacing C, or oxidation giving a carbonyl in place of a normal chain carbon, both show a general trend toward increased localization, some of it very severe, of the hole especially as the hole energy is reduced (as happens at higher photon frequency). This trend would support the growth of the sideband area with shorter laser wavelengths, but should be viewed as tentative pending more extensive structure calculations. Another trend may be the growth in the number of possible sideband transitions as dispersion opens a larger gap (on the order
of $50 \text{cm}^{-1}$) between the $k = 0$ and $k = 2q$ peaks. More states become available to be populated with phonons. Rayleigh scattering is still by far the dominant process, so there is much leeway for phonon production to become a larger fraction of events following photoabsorption.

Numerical Check. As a check on the mechanisms for line shape evolution, we constructed a tight binding model with the molecular backbone represented by alternating bonds, of length 450 unit cells, including two or four randomly placed 10% mass defects. The spectra were calculated for each case by assuming constant and sinusoidal "driving terms" coming from transition moments of the electronic transitions. The spectrum was computed by calculating the excitability of each phonon mode of the chain at the given driving $q$'s (with impurities in place), and adding its contribution to the Raman shift spectrum at the mode's frequency. The overall sideband backscattering intensity (but not its frequency or line shape or line width) was adjusted to match weak, moderate, and strong backscattering limits. Various limits of high and low impurity, long and short molecules, etc. were investigated this way. The results for various combinations are shown in Figure 6, which should be compared with Figures 1.4, 1.5, and 1.1. It takes about 3000 random realizations of the impurity positions before the average (shown) settles down. More details on the calculation, including Mathematica code, can be found in the Supporting Information.

METHODS

The use of standard quantum chemistry package Gaussian 09 in places was mentioned in the text, and the code for the sideband simulation is available on request in Mathematica format.
1.5 Implications and Conclusion

The spectrum of polyacetylene has been explained, in terms of Kramer-Heisenberg-Dirac Raman scattering theory, without using the Condon approximation to KHD that treats transition moments as a constant. The key is indeed the transition moment and its coordinate dependence, leading to immediate phonon production upon electron-hole pair formation. This means the phonon energies are subtracted from the electron at birth in the excited state, yielding a q matched electron and hole. In an infinite crystal with delocalized orbitals there is no structural change nor new forces in the excited states, making the transition moment solely responsible for the Raman signal. Electron-phonon scattering plays no role, except to knock out candidate emitters, helping to keep the time scale allowed for Raman emission very short; e-e scattering is thought to be much faster, however.

It is important, if difficult perhaps, to experimentally check for the predicted instant presence of phonons after photoabsorption. Raman emission in the sidebands is delayed waiting for backscattering, but in the $k = 0$ bands is immediate. This means there should be an evolution of the sidebands with time, in a pulsed experiment.

The implications of this work for other conjugated carbon systems, including nanotubes and graphene, are clear: The ideas put forth here carry over immediately and promise new insight into the information that Raman spectroscopy can provide on the “quantum clockwork” of many carbon nanosystems.
2.1 Abstract

Raman scattering plays a key role in unraveling the quantum dynamics of graphene, perhaps the most promising material of recent times. It is crucial to correctly interpret the meaning of the spectra. It is therefore very surprising that the widely accepted understanding of Raman scattering, i.e., Kramers-Heisenberg-Dirac theory, has never been applied to graphene. Doing so here, a remark-
able mechanism we term “transition sliding” is uncovered, explaining the uncommon brightness of overtones in graphene. Graphene’s dispersive and fixed Raman bands, missing bands, defect density and laser frequency dependence of band intensities, widths of overtone bands, Stokes, anti-Stokes anomalies, and other known properties emerge simply and directly.

2.2 Introduction

The unique properties of graphene and related systems have propelled it to a high level of interest for more than a decade. Raman scattering is perhaps the key window on graphene’s quantum properties, yet the crucial aspects of the spectrum of graphene, carbon nanotubes, and graphite Raman spectra have been a subject of much controversy, in some cases for decades.

The delay in applying Kramers-Heisenberg-Dirac theory (KHD) to graphene is attributable to the rise of a nontraditional, fourth-order perturbative Raman model (KHD is second order) called "double resonance" (DR), which appeared 15 or so years ago¹²⁴, rapidly gaining wide acceptance exclusively in the conjugated carbon Raman community. DR is not a variant of KHD tuned to graphene, but rather it is incompatible with KHD. DR relies on inelastic electronic scattering to create phonons, requiring introduction of two additional orders of electron-phonon perturbation theory, making it overall fourth order. These inelastic processes make no appearance in KHD, which cleanly produces phonons free of Pauli blocking by two other mechanisms, overall in second order perturbation theory.

Search engines quickly reveal that none of the 3000+ published contributions developing DR or using it to interpret experiments has mentioned the much older and more established KHD Raman
formalism, in the last 15 years. No rationale was ever given as to why a radically different, non-KHD formalism was needed. On the face of it, even without regard to the theory given in this paper, these facts leave the DR approach seriously unexamined and exposed. It is our opinion that DR was a wrong turn on the way to understanding graphene quantum dynamics and Raman spectroscopy.

When KHD is applied to graphene, phonons are produced exclusively and instantly at the moments of photoabsorption or photoemission by the explicit nuclear coordinate dependence of the transition moment. The transition moment in DR fourth-order perturbation theory expression is taken to be a constant. It has already been noted that a nonconstant transition moment is needed to understand some aspects of nanotube spectroscopy.

The present graphene study has a strong precedent in another conjugated conducting polymer. In a recent study, the long-standing mysteries of the dispersive polyacetylene Raman spectrum yielded to KHD theory, extended to include 1-D crystal structure, defects, and electron and phonon dispersion relations. All these arise from within Born-Oppenheimer theory and KHD Raman scattering theory. The coordinate dependence of the transition moment plays a key role, since geometry does not change when the electron-hole pairs are created in the extended conjugated system.

These principles are the starting point for surprising new insights that graphene has in store. For example, “transition sliding”, not possible in a DR picture, is responsible for the brightness of overtone bands, and explains their impurity and doping dependence, as well as their disappearance in the deep UV. Transition sliding does not apply to polyacetylene because there are no Dirac cones and no linear dispersion; indeed polyacetylene overtones are correspondingly weak.
2.3 Results and Discussion

Does the Born-Oppenheimer Approximation “Break Down” for Graphene? KHD relies heavily on the Born-Oppenheimer approximation, as does much of condensed matter physics. Recently, the “headlines” in a highly cited paper left the impression that the ABO fails particularly in graphene. The excellent article has the provocative title “Breakdown of the adiabatic Born-Oppenheimer approximation in graphene” 108. Published in Nature Materials with over 800 citations, we find the statements “... ABO has proved effective for the accurate determination of chemical reactions, molecular dynamics and phonon frequencies in a wide range of metallic systems. Here, we show that ABO fails in graphene.” and later “Quite remarkably, the ABO fails in graphene” 108, see also ref 41.

Born-Oppenheimer is an approximation and fails in specific regimes and situations. Reference 108 claims nothing very drastic once one reads deeper. Instead it makes important points about a stiffening of the $G$ mode with electron density near the Dirac point involving the Kohn anomaly, missed by ABO. By their nature, Kohn anomalies involve rapid changes of electronic structure with small nuclear configuration changes, a warning sign of potential ABO breakdown. In this paper, we do not attempt to correct for the Kohn anomalies and their effect on phonon modes and mode frequencies. Electron-hole pairs created in Raman studies are normally well away from the Dirac point and orbitals affected by Kohn anomalies.

The ABO succeeds in the large, that is, the point. Recall that within ABO, if the nuclei return to a prior configuration, the electrons do also. This is strictly incompatible with inelastic electron-
phonon scattering having taken place in the meantime. Inelastic electron-phonon scattering is nonetheless a valid nonadiabatic correction to ABO. However, electron-phonon scattering would appear to Pauli block the affected electrons, immediately rendering them silent in Raman scattering.

We have been given a late opportunity to use KHD theory the first time in graphene. KHD is vastly more established than DR, and astonishingly accurate most of the time. It much simpler to execute, and lower order in perturbation theory.

Kramers-Heisenberg-Dirac Theory. We provide a review of KHD here; facilitating the developments in succeeding sections. Just before the dawn of quantum mechanics, in 1925 Kramers and Heisenberg published a correspondence principle account of Raman scattering, which Dirac translated into quantum form in 1927. The Kramers-Heisenberg-Dirac Theory of Raman scattering has been used ever since to explain more than half a million Raman spectra in a very wide range of systems, including very large conjugated hydrocarbons. There is no reason that removing hydrogens from carbon materials should cause KHD to catastrophically fail and require replacement by a theory based on different physics.

The KHD formula for the total Raman cross section $\Sigma$, for incident frequency $\omega_I$ and polarization $\rho$, scattered frequency $\omega_s$ and polarization $\sigma$, between initial Born-Oppenheimer state $|i\rangle$ and final Born-Oppenheimer state $|f\rangle$ via intermediate Born-Oppenheimer states $|n\rangle$ reads

$$\Sigma^{\rho,\sigma}_{i\rightarrow f} = \frac{8\pi e^4 \omega_I}{9c^4} |\alpha^{\rho,\sigma}_{i\rightarrow f}|^2,$$

$$\alpha^{\rho,\sigma}_{i\rightarrow f} = \frac{1}{\hbar} \sum_n \frac{\langle f| D^{\dagger,\sigma} |n\rangle \langle n| D^{\rho} |i\rangle}{E_i - E_n + \hbar \omega_I - i\Gamma_n} + \frac{\langle f| D^{\dagger,\sigma} |n\rangle \langle n| D^{\rho} |i\rangle}{E_i + E_n + \hbar \omega_I + i\Gamma_n}$$ (2.1)

39
where $\Gamma_n$ is the damping factor for the excited state, accounting for events and degrees of freedom not explicitly represented. The transition moment operator $D$ controls the first-order perturbative matter-radiation coupling. Usually the second, nonresonant term inside the square in eq 2.1 is neglected, for simplicity.

Making this more explicit, suppose with phonon coordinates $\xi$ and electron coordinates $r$, we write

$$|f\rangle = |\Psi_{B,O}^{B,O}(\xi, r)\rangle = |\phi(\xi; r)\rangle |\chi_{mf}(\xi)\rangle,$$

$$|i\rangle = |\Psi_{m_i}^{B,O}(\xi, r)\rangle = |\phi(\xi; r)\rangle |\chi_{mi}(\xi)\rangle, \text{ and}$$

$$|n\rangle = |\Psi_{q_v,q_c,m}^{B,O}(\xi, r)\rangle = |\phi_{q_v,q_c}(\xi; r)\rangle |\chi_{mv}(\xi)\rangle.$$

$|\phi(\xi; r)\rangle$ is the approximation to the Born-Oppenheimer $\pi$ electron ground state (we suppress the other electrons) based on a Slater determinant of valence electron spin orbitals; $|\phi_{q_v,q_c}(\xi; r)\rangle$ is an electron-hole pair relative to the ground state, with an electron in the conduction band orbital $|\phi_{q_v}(\xi; r)\rangle$ and a hole in the valence band orbital $|\phi_{q_c}(\xi; r)\rangle$. $|\phi_{q_v,q_c}(\xi; r)\rangle$ is a complete intermediate state, including the phonon wave function. $q_v, q_c$ and $m_v$ may range quite freely, with the following remarks: (1) almost all $q_v, q_c, m_v$ will give vanishing matrix elements with the dipole operator, due to momentum nonconservation (including the momentum of the phonons). (2) Some pairs $q_v,q_c$ with unmatched momentum $q_v \neq q_c$ give nonvanishing matrix elements nonetheless because they are associated with newly created or destroyed phonons contained in $|\chi_{mv}(\xi)\rangle$ relative to the initial state, conserving momentum. Such states are the electron-hole-phonon triplets. (3) Mo-
mentum is conserved when elastic backscattering is required to realign the hole and particle (because of the kick given to the conduction electron by newly formed or destroyed phonons) through the recoil of the whole sample, or laboratory, as is familiar in Mössbauer scattering or elastic neutron scattering for example. This feature is embedded in eq 2.2 since the electronic orbitals include the presence of impurities, edges, etc., which are part and parcel of ABO. Even though the eigenfunction orbitals thus include the elastic backscattering as a boundary condition entirely within ABO, and thus opposite momenta are populated, we may decompose the process of promotion into opposite traveling components. Promoting one propagation direction, the electron is kicked to the opposite by the phonon production at $2q^-$. But the opposite direction is already occupied, in the valence state. Therefore, elastic backscattering is still required in spite of the mixed nature of the orbitals. Time is required for this to happen. In the energy domain, being off resonance in effect shortens the time and nearly removes the effects of the backscattering.

Due to dilution of the delocalized π orbital amplitude over the infinite graphene sheet, it is almost obvious that the Born-Oppenheimer potential energy surface is unchanged after a single electron-hole pair excitation from the ground electronic state. No new forces on the nuclei arise upon a single electron-hole pair formation and no geometry changes take place, thus, the independence of $\langle \chi_{m,v}(\xi) \rangle$ on the electron?hole state denoted by $q_v q_c$ (the occupations indicated by $v c$ may vary, but the phonon wave functions themselves do not depend on the electron-hole pair created).

The Transition Moment Operator. We may write

$$\langle n \mid D^f \mid i \rangle = \langle \chi_{m,v}(\xi) \mid \left\langle \varphi_{q_v q_c}(\xi; r) \right\rangle D_{q} \mid \varphi(\xi; r) \rangle \left| \chi_m(\xi) \right\rangle$$

(2.3)
as

\[ \langle n | D^\xi | i \rangle = \left\langle \chi_{m_i}(\xi) \right| \mu_{q_i,q_v}^\xi(\xi) \right| \chi_m(\xi) \right\rangle \] (2.4)

with

\[ \mu_{q_i,q_v}^\xi(\xi) = \left\langle \phi_{q_v,q_i}(\xi; r) \right| D_{\xi} \left| \phi(\xi; r) \right\rangle \] (2.5)

The matrix elements of the dipole operator \( D \) between two Born-Oppenheimer electronic states is the transition moment \( \mu_{q_i,q_v}^\xi(\xi) \) connecting valence level \( q_v \) and conduction band electronic levels \( q_i \); \( \mu_{q_i,q_v}^\xi(\xi) \) is written for light polarization \( \rho \); the subscript \( r \) indicates that only the electron coordinates are integrated. Note that \( \mu_{q_i,q_v}^\xi(\xi) \), if it does not vanish, is explicitly a function of phonon coordinates \( \xi \).

In terms of the transition moments, the Raman amplitude reads (using only the resonant term of the two)

\[
\alpha_{m_i,m_f}^{q_i,q_v} = \frac{1}{\hbar} \sum_{v,c,m} \frac{\left\langle \chi_{m_i}(\xi) \right| \mu_{q_i,q_v}^\xi(\xi)^\dagger \left| \chi_m(\xi) \right\rangle \left\langle \chi_m(\xi) \right| \mu_{q_i,q_v}^\xi(\xi) \left| \chi_{m_i}(\xi) \right\rangle}{E_{m_i} - E_{v,c,m} + \hbar \omega_l - i \Gamma_{f,m}} \] (2.6)

The sum over the intermediate states with energy denominators is of course the energy Green function, i.e., the Fourier transform of the time Green function propagator. Although we do not write out the time dependent expression here (see Supporting Information), we see that the valence state phonon wave function \( \left| \chi_{m_i}(\xi) \right\rangle \) arrives in the conduction band multiplied and thus modified by
the transition moment $\mu_{q,c}$, including its phonon coordinate dependence, before any time propagation takes place. Moreover, that propagation does not further change the phonon populations.

The product of the transition moment and the phonon wave function is called $\phi_{q,c,m}(\tilde{\xi})$ above. When $\phi_{q,c,m}(\tilde{\xi})$ is reexpanded in all the phonon modes $|\chi_m(\tilde{\xi})\rangle$ in all the conduction bands, some $m$ will differ in the occupation numbers compared to the unmodified initial lattice occupation $m_i$ (recall that because there is no geometry or force constant change, the phonons are the same in all valence and conduction bands). Every electron-hole pair production event carries some amplitude for no phonon change, plus simultaneously a finite amplitude for phonon creation or destruction relative to the initial phonon wave function. The transition moment’s dependence on nuclear separation or equivalently phonon displacements is unquestionable, not only on direct physical grounds and explicit calculations, but also because there would be no off-resonant Raman scattering without it. The derivative of the polarizability with nuclear coordinates, i.e., the Placzek polarizability, would vanish without coordinate dependence of the transition moment. If the transition moment is (unjustifiably) set to a constant independent of phonon coordinates, no Raman scattering occurs at all in KHD theory for graphene.

The intermediate, typically conduction band (assuming no doping) Born-Oppenheimer states $\Psi^{B.O.}_{q,v,c,m}(\tilde{\xi}, r)$ with energy $E_{v,c,m}$ range over resonant and nonresonant (very small or not so small denominators, respectively) states including all with nonvanishing matrix elements in the numerator. Only those with Pauli and momentum matched electron-hole pairs and electron-hole-phonon triplets can be nonvanishing; it is not necessary that they be “resonant”, i.e., minimize the denominator, in order to contribute importantly (however, see caveats below to modes like D requiring
backscattering). Rather, a range of states is collectively important, the range depending on $\Gamma$. Although not relevant to undoped graphene, even when none of the denominators reach resonance, there is still sufficient Raman amplitude to be quite visible as off resonance Raman scattering. The final Born-Oppenheimer state $\chi_{m_f}(\xi)$ with energy $E_{m_f}$ conserves total system plus incident and emitted photon energy, and may differ from the initial state only by $0, 1, 2, \ldots$ phonons. The electron has filled the hole and the initial electronic state is restored.

An exception to this notation is the filling of an empty level created by doping, leaving the hole created by the photon unfilled. All the electronic states reside exactly on the electronic band surface, here on the Dirac cone near the Dirac point.

It is good to keep in mind that the vast majority of states $|\varphi_{q,v,q,c}(\xi; r)\rangle \chi_{m,v,c}(\xi)\rangle$ (violating momentum conservation with respect to the initial state for example) in the KHD sum have vanishing matrix elements and do not lead to Raman (or even Rayleigh) scattering. Some terms (or really a small group of terms, see discussion in section “Kramers-Heisenberg-Dirac Theory” about backscattering) give nonvanishing matrix elements, and if they include phonons, they are usually still incapable of Raman emission. An example is a D phonon produced in absorption in a clean sample, unable to emit a Raman photon due to the Pauli blocking effect of the electron recoil. Such states eventually relax and thermalize by a cascade of e-e and e-ph inelastic processes. Sliding transitions (see the section “Sliding Phonon Production”) do not help because even elastic backscattering by defects does not alleviate the Pauli blocking for the majority D phonons produced. These “orphan” phonons, not appearing in the Raman spectrum, are always in the majority compared to phonons seen in Raman emission. It is not the phonons themselves that fail (they live on quite well), but
rather their associated, Pauli-blocked conduction electrons than cannot emit to signify the phonon via a Stokes shift for example.

Even if no phonon is produced at the time of absorption, the chances of achieving Rayleigh emission are small, or phonon production upon emission even smaller, given the withering removal of electrons from eligibility by inelastic e-e scattering, raising the near certain specter of Pauli blocking. This occurs on a femtosecond time scale (see refs. 6, 84, 18, 15, 85).

Phonon Adjusted Electronic Transitions. A fraction of resonant conduction band eigenstates \( \langle \phi_{q,v}^{\xi,r} | \chi_{m,v}^{\xi} \rangle \) giving nonvanishing matrix elements differ by one or more phonons relative to the valence band state. The energy of the Born-Oppenheimer eigenstates is a sum of phonon and electronic components, so the largest, resonant terms in the KHD sum eq 2.2 necessarily arrive with the electronic transition energy correspondingly lowered if a phonon is activated in the conduction band eigenstate relative to the valence state or raised if a phonon is deactivated in the conduction band eigenstate relative to the valence phonon wave function. This key fact automatically alters electronic transition energies and phonon frequencies for dispersive bands. For phonon creation, the valence energy of the hole is raised, and the conduction band energy lowered, keeping \( q \) the same in both, thus creating momentum matched (possible except needing elastic backscattering) holes and particles free of Pauli blocking. We term this prepayment a “diminished” electronic transition in the case of phonon creation (leading to Stokes scattering), and an “augmented” electronic transition in the case of phonon annihilation (leading to anti-Stokes scattering). It is important to note (see also the section “Virtual Processes and Backscattering”) that it is very difficult to produce an electron-hole triplet (i.e., with a phonon change) off-resonance in a mode requiring backscatter-
ing. Thus, the dispersive modes are locked into a given diminishment or enhancement depending on the laser energy.

![Figure 2.1:](image)

Near resonance, the pseudomomentum $q^-$ is determined by the requirement that the energy cost of creating the electron-hole-phonon triplet is just the laser photon energy. Typically, most of the energy needed is electronic, on the order of $1.5 \text{eV}$ or more with the phonon energy on the order of several $0.1 \text{eV}$, which is not ignorable. The electronic transition energy is given by $E_e = E'(q^-) - E'(q^-) = \hbar \nu_I - E_{\text{phonon}}(2q^-)$, where superscripts $c, v$ refer to conduction and valence bands. As $\hbar \nu_I$ is changed, $q^-$ of the phonon changes according to the valence and conduction band dispersion, which ideally is a Dirac cone structure with light-like linear dispersion of both bands. As $q^-$ changes, the phonon energy $E_{\text{phonon}}(2q^-)$ changes according to the well-known positive disper-
sion of about $50 \text{ cm}^{-1}/eV$ for the D band, see Figure 2.1A. For simplicity, we usually use intravalley diagrams even when (in some cases) the process is intervalley. If in a single phonon transition the phonon is created or destroyed at the time of emission, the electron-hole pair formation is not diminished or enhanced. All the initial photon’s energy goes into the electronic transition, as in DR, and no phonon change is yet present. The momenta of electron and hole are created in a matched pair (again, near resonance) with pseudomomentum $q^-$. The conduction band electron may then elastically backscatter $q \rightarrow -q$, in the presence of defects. This allows recombination with the hole of momentum $q$, provided it creates a phonon at $-2q$ at that precise moment of emission (due to coordinate dependence of the transition moment). The emitted light must be of the proper Raman shifted frequency to conserve energy. The processes described are shown in Figure 2.1B. Since in this case $q$ did not suffer diminishment in absorption, it will produce a phonon with slightly larger magnitude $−2q$ (no “−” on the $q$ is present) than if produced in absorption with its diminished transition. The Raman shifts are thus slightly different depending on whether the phonon was created at the time of emission or absorption, since given dispersion the phonon will have a slightly different energy with a different $q$.

This means that all entries in phonon dispersion diagrams made based on the DR model needs a small correction, because absorption electron-hole-phonon triplet transitions are not at the $q$ DR supposes, differing instead by a phonon energy and the effect of dispersion. Reich remarks: “To find the double resonant $q$ we assume that the $q = 2k_e$ rule is strictly valid.” The correction we think is needed is small, and contributes to the broadening (the addition of for example $q$ and $q^-$ peaks) as well as slight shift of the center frequency.
The terms in the KHD sum constructively and destructively interfere with one another before the square is taken. The sum includes many different momentum conserving electron-hole pairs and electron-hole-phonon triplets leading to the same final states of the graphene system. Processes leading to different final states (e.g., a different final phonon type or energy) appear in separate, non-interfering terms.

Avoiding Pauli Blocking. An important pathway that avoids Pauli blocking begins with \( q^-_c = -q^-_e \), associated with a phonon of pseudomomentum \( k = 2q^-_e \), where the superscript “-” refers to a diminishment of the electronic transition energy by the simultaneous creation of a \( 2q^- \) phonon (in the case of Stokes scattering); see below. The conduction electron suffers a \( q^-_e \rightarrow -q^-_e \) kick to conserve momentum, and is Pauli-blocked. However, in this case, subsequent defect elastic backscattering can realign it with the hole, allowing recombination. A photon is emitted at a frequency revealing the diminished Stokes shift of the \( 2q^- \) phonon production. Since the diminished \( q^- \) depends also on the incoming laser energy, the phonon dispersion will be revealed by changing that energy. A \( 2q^- \) modulation of the \( G \) mode for example will become Raman allowed by this mechanism. The modest dispersion of that mode will give rise to a sideband to \( G \), which we call \( G' \), visible only in the presence of defects. This is exactly what is observed, see Figure 2.3.
Figure 2.2: (Left panels) The extended tight binding results for the $G$ and $G'$ modes. The valence states are at the far left. The middle panel (on the left) depicts the conduction band state in each case, and at the top right of the left set of panels is shown the derivative of the transition moment with respect to the $k = 0$ $G$ phonon coordinate, and the $k = 2q G'$ (formerly called $D'$; see below) phonon coordinate (bottom right of the left set of panels). (Middle panel) The first derivative of the transition moment in the $D$ sideband mode direction at $K + q$, $K = 2\pi \left( \frac{1}{3a}, \frac{1}{3\sqrt{3}a} \right)$, and $q = 2\pi \left( 0, \frac{1}{2\sqrt{3}a} \right)$. The transition moments and their derivatives are integrals over the data in these figures. The first derivative of the transition moment has amplitude of $1.2$ in arbitrary units. (Right panel) The second derivative of the transition moment, which has amplitude $0.01$.

Another important case is $q^- = -q^+$, i.e., $k = 0$, which was discussed in the section "The Transition Moment for Graphene". This corresponds to creating a $\Gamma$ point $G$ phonon that carries no momentum, but it still carries energy. Some of the photon’s energy is channeled directly into the $G$ phonon energy, diminishing the (in the case of Stokes scattering) electron-hole transition energy, including shifting the $|q|$ of the transition nearer to the Dirac cone $K$ point, as if lower energy light had been used: $0.185\text{eV}$ lower for a $1500\text{cm}^{-1}$ phonon. Raman emission is active because the electron and hole are born matched in $q$ and ready to recombine. Fast e-e scattering is the enemy of Raman emission, since if it occurs, the change in electron momentum makes Pauli blocking a near certainty. (Studies point to a time scale of a few femtoseconds before irreversible relaxation of conduction band electrons by e-e scattering. Definitive experimental results affirm the extremely rapid relaxation
of photo excited electrons due to e-e scattering\textsuperscript{6,8,15,85,86}. The G band is indeed bright, and benefits too from off resonant contributions (unlike D), but the fact that a normally weak overtone, 2D, is perhaps 10 times brighter than G follows from a fascinating process; see section “Sliding Phonon Production” below on sliding transitions.

Tight Binding and Density Functional Realization of Graphene KHD. The simplest model Hamiltonian for the single-layer graphene involves only nearest-neighbor interactions. However, in the presence of crystal distortions, the hopping strength should vary with the pair distance. This is especially important to incorporate here, since this will contribute to the dependence of transition moments on geometry changes, needed in our KHD theory.

On the basis of the DFT band structure and Bloch waves, the Kohn-Sham Hamiltonian can be transformed into a basis of maximally localized Wannier functions (MLWF) using the Wannier90 code\textsuperscript{95}. The initial projections for Wannier functions are the atomic $p_z$ orbitals and the transformed Hamiltonian is the ab initio tight-binding Hamiltonian. By varying the positions of the basis atoms, the hopping strength $t$ for different pair distances $r$ can be extracted and its empirical formula at the linear order reads:

$$t(r) = t(r_0) + f_1(r - r_0)$$ \hspace{1cm} (2.7)

where $r_0 = 1.42\text{Å}$, $t(r_0) = -2.808eV$ and $f_1 = 5.058eV/\text{Å}$. Figure 2.2 gives the extended tight binding results for the G and G' modes at the left, in two three-panel strips, one above the other. The middle panels of each strip depict the conduction band states, and the rightmost panels show the derivative of the transition moment with respect to the $k = 0$ G and the $k = 2q$ G' phonon.
coordinate, shown by the small arrows within the images (notice the undulations in the atomic displacements). The middle and right panels show the first and second derivatives of the transition moments for the $D$ mode at $K + q$, where $K = 2\pi \left( \frac{1}{3a}, \frac{1}{3\sqrt{3}a} \right)$, $q = 2\pi \left( \frac{1}{12\sqrt{3}a}, \frac{1}{12\sqrt{3}a} \right)$.

Consider a transition from $K + q^-$ (valence) to $K - q^-$ (conduction), with $K = 2\pi \left( \frac{1}{3a}, \frac{1}{3\sqrt{3}a} \right)$, $q^- = 2\pi \left( \frac{1}{12\sqrt{3}a}, \frac{1}{12\sqrt{3}a} \right)$ is exactly at the Dirac cone, $q$ gives a small displacement from the cone center, $a$ is the carbon-carbon bond length at equilibrium. In this case, the electron has a momentum change of $-2q^-$, and the phonon has momentum $2q^-$. (For comparison, using the graphene sheet only partly depicted in Figure 2.2, the constant part of the transition moment has amplitude about 60 in arbitrary units). With displaced atoms of amplitude 0.01Å (adjusted according to $2q$ modulation), the first derivative of the transition moment has amplitude of 1.2; the second derivative has amplitude 0.01.

We find that the electronic transition moment has a robust first derivative along any choice of the independent and degenerate $G$ mode phonon coordinates, and this accounts for their presence in the Raman spectrum. Figure 2.2 shows the local transition moment along one of those choices. It is seen to be perfectly repetitive with the unit cell translation vector as befits a $k = 0$ optical mode. Integration of this $2D$ local transition moment over space yields the transition moment at the given nuclear positions, and repeating this after a phonon distortion reveals the phonon coordinate dependence of the transition moment.

Thus, $D$ should be robust (with sufficient elastic backscattering), but simultaneous production of $2D$ seems in doubt. Since $2D$ is the brightest band, an explanation is needed, and is given below in the section labeled "Sliding Phonon Production"; see also the evidence for them, "Hole Doping
Evidence of Sliding D Absorption”.

Figure 2.3: (Left) Averaged defective graphene $^{12}$C Raman spectrum on a Si substrate, adapted with permission from ref.7. (Right) Placement of phonon dispersion points found and assigned through Raman spectroscopy by Hilke et al.9, reproduced with permission. $D'$ symbol replaced by $G'$, appropriate to a sideband of $G$.

Analysis of Graphene Raman Band Structure with KHD. We now go through a few prominent characteristics of graphene Raman spectrum discovered and discussed over the years. All can now be explained (very directly) by the KHD theory. In Figure 2.3 a Raman spectrum obtained by the Hilke group is an average of 60 different samples, each with defects, in order to bring out weak bands forbidden in clean, perfect graphene crystals. The $D$ band is one such case, while $2D$ is allowed and bright in pure samples.

Origin of $G$ Band Intensity. The constant part of the electronic transition moment for arbitrary electronic $q$ is nonvanishing and responsible for most of the light absorption in graphene. It delivers electrons to the conduction band without creating a phonon. A phonon’s creation (or annihilation) is the result of a changing electronic transition moment as its coordinate is displaced from equilib-
rium. The more rapid the change in transition moment as a function of phonon coordinate, the more likely is the phonon’s creation.

The $G$ modes have no dispersion; the same $q = 0$ mode is produced independent of laser frequency. The $G$ mode may also be produced in emission. The KHD expression has the same transition moment promoting either event. The production of the $G$ by either means is a small minority of events in any case, as is any phonon producing a successful Raman emission. (It is often stated that typically only about $1$ in $10^4$ or $10^5$ incident photons causes a Raman emission.) The mechanism based on KHD for $G$ mode production in absorption is given in Figure 2.4.

In the section “$G$ Mode Brightening”, we discuss the brightening of the $G$ mode band due to hole doping and off resonant scattering. For the $G$-mode, the phonon production off resonance occurs by the same mechanisms familiar in KHD that populate vibrational modes in smaller systems off resonance.
Virtual Processes and Backscattering. The $G$ mode does not require backscattering to be produced. The electron is ready to fill the hole the moment it appears. Not so the $D$ mode. To produce a $D$ mode, a momentum-conserving recoil of the conduction electron is required. For that mode to be visible in Raman emission, the Pauli-blocked electron must be elastically backscattered. Off-energy shell virtual processes are by nature short-lived; forcing the conduction electron to fill the hole quickly and emit a Raman shifted photon. This leaves insufficient time for off-shell elastic backscattering. Any off-resonant electron and hole cannot remain long, since after some time the energy imparted becomes more certain; off-resonance, the energy is not sufficient to support this.

The difficulty is seen in the $\text{eq} \ 2.6$. If an off-resonance state is created with a phonon and $q_v = \hbar \omega_s$.
\(-q_o\) in a pure sample without subsequent backscattering this situation arrives Pauli-blocked at the second transition moment operator, and the numerator vanishes, which should be taken as evidence that no virtual process will intervene. However, the Born-Oppenheimer approximation is comfortable with boundary conditions like walls and scatterers and if they are present, the Born-Oppenheimer propagation will time evolve some of say a right-trending electron wave into a left-trending one. Even for an embedded impurity, some of the scattering built into the Born-Oppenheimer propagation will be elastic backscattering. This amplitude arrives at the second transition moment operator and matrix element survives, i.e., it is not Pauli-blocked.

Absence of 2G Overtone. Given the robust strength of the G band, at least a small overtone at 2G would be expected, yet the 2G band did not make any appearance in the spectra of Hilke et al.\(^9\), where other weak bands were seen for the first time. We have been touting the uncommon strength of the overtones in graphene, so this absence must be regarded as one of its mysteries and must be explained. There is no group theoretical ban on its existence, and like G, it is a \(\Gamma\) point mode, requiring no backscattering. Why is it missing?

DFT-tight binding calculations of the transition moment show that the second derivative along the G phonon mode is about 2 orders of magnitude smaller than the first derivative. Since the intensity goes as the square of the transition moment, this would wash out 2G if it were the only scenario for a 2G.

However, there is another possibility to consider: The robust linear slope in the transition moment along the G mode could be used twice, once in absorption and the second time in emission. Although not a simultaneous production of the phonons, two G mode phonons will have been pro-
duced, and a Raman band would appear at $2G$. The phonons together would be pseudomomentum $k = 0$. It is easy to see however that the intensity for this process must be extremely low: If there is an amplitude of 0.025 (probably much too high an estimate, but conservative for this purpose) for producing a single $G$ mode in absorption, the amplitude for two $G$ phonons, one in absorption and one in emission, is 0.000625. This corresponds to a probability of two $G$ phonons produced this way some 1600 times smaller than the probability of a single $G$ phonon production. “One up, one down” does not lead to a visible signal.

Paradoxically, we will see that this “one up, one down” mechanism is the key to the brightness of the 2D band, and other overtone bands. The $2G$ mode is unable to increase its brightness by one up, one down “transition sliding” (see the section “Sliding Phonon Production”), because sliding requires a $k = 2q$ phonon be produced. Sliding greatly amplifies the chance of producing a phonon, for example in the case of $2D$, or $2Gs$ (formerly called $2D'$) since many simultaneous amplitudes are summed. Transition sliding is a key principle made possible by linear Dirac cone dispersion (see the section “Sliding Phonon Production”), and a key Raman mechanism revealed here.

The $G'$ [Former $D'$] and $2G'$ [Former $2D'$] Bands. Nearby the $\Gamma$ point $k = 0$ phonon, the transition moment can also give rise to $k = 2q^-$ phonons, giving a momentum kick $2q^-$ to the conduction band electron. Elastic backscattering makes recombination possible, revealing the existence of the sideband to $G$ formerly known as $D'$, now $G'$.

The healthy $2G'$ band, present without impurities, is the overtone of defect-hungry $G'$ band. Published spectra are often cut off before its ca. 3200 cm$^{-1}$ displacement is reached. Its frequency is very close to twice that of $G'$. It seems the $2G'$ band owes its unexpectedly large intensity in the
absence of defects to the same transition sliding mechanism that benefits 2D; see the next section.

Sliding Phonon Production. The brightness of the 2D overtone mode (and of other \( k = 2q \) overtone bands like 2G) is a consequence of continuously many simultaneous transition amplitudes, all producing the same D phonon in absorption and one of opposite pseudomomentum in emission. Amplitude for electron-hole and electron-hole-phonon production appears simultaneously up and down the Dirac cone, vastly extending the nominal symmetrical \( K - q \) to \( K + q \) transition (giving a \(-2q\) kick to a new phonon). That is, a continuum of \( K - q^- + \delta q \) to \( K + q^- + \delta q \) transitions is available, all generating the same \(-2q^-\) phonon. This is possible due to the linear dispersion of the Dirac cone. Since the \( 2q^- \) phonons are the same, the sliding transition amplitudes all share the initial state \(|i\rangle\) and final state \(|f\rangle\) and add coherently, before the square is taken. The energy \( E_{v,c,m} \) in the sum over electron-hole-phonon triplets \( \left| \phi_{q,v} (\xi; r) \right| \chi_{m_u} (\xi) \right\rangle \) is not changed by sliding: the same photon is absorbed, and always put into making the same \(-2q^-\) phonon with the balance put into the electronic part of the transition; thus, \( E_{v,c,m} \) is highly degenerate.

The initial state is the ground electronic state with no hole, no conduction electron, and no phonon change; the final state also has no hole, no conduction electron, but if it has given a Raman shift, it has phonons (usually one or two) added or subtracted from the initial state. The initial and final state remain the same for all the sliding intermediate states, which therefore interfere with each other. The sliding diagram in fact describes the intermediate state, including the hole that is created, the conduction electron, and the phonon. Even though we think of the electron as being promoted from valence to conduction band, this happens as a change to the fixed initial state; the hole does not define the initial state, rather it is part of what defines the intermediate state.
The sliding transitions are already built into the KHD eq 2.2; one has only to examine the possible intermediate states to see that they are present. Their ultimate limitation will be a topic for future study: trigonal warping and distortion away from linear dispersion at energies farther from the Dirac point will cause slightly different energy phonons to be produced; these will add to the intensity noncoherently, only after the square. They will broaden the transition but are intrinsically less bright due to diminishing constructive interference. Also limiting the sliding is the density of states, diminishing to 0 as the band edges are reached.

We have checked the transition moments for sliding transitions with our tight binding model. For example, we examined the transition from an occupied conduction band level at \( K + q \) to an empty conduction band at \( K + 3q \). The transition moment first derivative is not significantly smaller than a transition from an occupied valence band at \( K - q \) to an empty conduction band at \( K + q \).

Sliding adds to the transition amplitude for production of the first \( 2q^- \) phonon, but electrons produced by such sliding transitions do not match the holes they leave behind and are thus Pauli-blocked in emission. Elastic backscattering does not rescue these phonons from obscurity; \( (K + q^- + \delta q, \text{backscattered elastically, gives } K - q^- - \delta q), \) which does not match the original hole at \( K - q^- + \delta q \). Below, we note hole doping creates empty valence bands, that can, if conditions are right, accept emission from such conduction band states, giving rise to a spectacular broadband “electronic Raman” emission as seen in reference 25; see “Hole Doping Evidence of Sliding D Absorption”. (These authors provided a different interpretation involving “hotband” emission following electron-phonon scattering.)

Reversing the Path. The Raman-silent single phonon sliding can become Raman active if the con-
duction band electron, produced by a sliding transition along with a \( k = 2q^- \) phonon, emits (without first backscattering) to the valence band along the reverse path used in absorption (see Figure 2.5). A second, oppositely propagating phonon is released. The electron is automatically matched to the hole and recombines, without Pauli blocking of any sort, and in the case of \( D \) phonons, a proper matched \( 2D \) phonon pair has been produced. The cumulative effect of constructively interfering such amplitudes over a continuous sliding range of terms in the KHD sum (the numerator is absolute value squared of the sum of all sliding terms producing the same pair of phonons,). This produces a large enhancement of the \( 2D \) Raman band intensity. In graphite whiskers, the intensity of the \( 2D \) overtone is found to be about 10 times stronger than the single phonon \( G \) mode, normally expected to be much stronger than an overtone band. As mentioned above, the \( G \) or \( 2G \) modes are not amenable to sliding transitions.

![Figure 2.5: Transition sliding on a Dirac cone. (Left) The nominal, symmetric “Double D” (2D) transition with energies equal above and below the Dirac point. Absorption is followed, without any backscattering, by emission along the reverse path, producing a second phonon of opposite momentum. (Right) By moving the rectangle up, not changing any dimension, we find it still fits absorption and emission transitions (it could also slide downward) along the Dirac cone. The reference transition is shown as a dashed rectangle. Sliding the rectangle up or down leaves the phonon \( 2q^- \) unchanged.](image-url)
Figure 2.5 shows the sliding scenario. A large range of sliding $\Delta E^v = \Delta E^c$, i.e., equal shifts in valence and conduction bands, are available; all of these are resonant, not virtual, transitions. Compared to the reference, nonsliding symmetric case, in up-sliding the valence wave vector has been shortened by $\delta q$, and the conduction wave vector has been lengthened by the same amount, so it remains a $2q^-$ transition and gives a $2q^-$ phonon production, just as when $\delta q = 0$. All the sliding transitions are independent amplitudes at the same photon energy simultaneously present, and together, they vastly enhance the probability of producing a pair of $D$ phonons. The density of states for both the initial and final electronic states will have a major effect on the propensity to slide various amounts.

The sliding mechanism explains many known facts of Raman scattering in graphene. First and foremost, the brightness of the $2D$ and other overtone bands (mixed transitions can also occur, i.e., two phonons each from a different band, as long as the pseudomomentum of both is the same). As just explained, this results from addition of a continuous range of sliding amplitudes, before the square is taken to give Raman intensity.

The fact that the $2D$ peak strongly decreases with increasing doping or disorder is now explained easily: Doping can provide much faster phonon-less emission pathways emptying conduction band levels and diminishing the population producing emission of another $D$ phonon. Moreover, scattering of the conduction electron (it does not have to be elastic backscattering) by defects will also quench the $D$ emission probability by Pauli blocking. The $D$ phonons produced in absorption are present nonetheless; the electron is hung up in the conduction band and must relax by means other than Raman emission.
**D Band Stokes, Anti-Stokes Anomaly.** The Stokes versus anti-Stokes frequencies in the $D$ and $2D$ bands are graphene Raman anomalies, discussed first in pyrolytic carbon and graphite whiskers$^{121,21,42}$. There are two striking experimental results to explain: (1) A difference between $D$ band Stokes and anti-Stokes frequencies. In a small molecule, the Stokes and anti-Stokes bands measure the same vibrational state, and there cannot be any difference between the two: they are symmetrically spaced across the Rayleigh line, i.e., 0 asymmetry. For the graphene $D$ band, the asymmetry is instead about 8 or 9 cm$^{-1}$. (2) As shown in the next section, the $2D$ band Stokes, anti-Stokes asymmetry is not twice the $D$ band asymmetry, which would be expected because two $D$ phonons are produced, but close to 4 times the $D$ band shift, or 34 cm$^{-1}$. These numbers emerge simply from our KHD theory, without invoking any virtual processes.

![Figure 2.6: Predictions of Stokes and anti-Stokes Raman spectra of the $D$ and $2D$ band positions and their anomalies, in KHD theory. The horizontal scale of the $2D$-band spectra (upper right) spans twice the range of the $D$ scale. Anti-Stokes processes were brought across the origin of the Rayleigh line and are shown dotted. See text for details.](image)
The D mode Stokes band is an average of emission and absorption production, with emission production unshifted. Production in absorption is shifted down $8 \text{cm}^{-1}$ by the dispersion of $D$ and the diminishment cause by energy conservation. The average of the two is $4 \text{cm}^{-1}$ closer to the Rayleigh line than the undiminished emission production alone would be (see Figure 2.6). Similarly, the D mode anti-Stokes production in absorption also consists of two bands, overall $4 \text{cm}^{-1}$ higher.
in energy and farther from the Rayleigh band. At $3.5eV$ and $1350\text{cm}^{-1}$, the Stokes vs the anti-Stokes D phonons (reflected about the Rayleigh line for comparison) will differ by about $8.4\text{cm}^{-1}$. This is an anomalous Stokes, anti-Stokes asymmetry of about $8.4$ wave numbers, in excellent agreement with experiment. Thus, the anomaly has a simple explanation in terms of phonon production in absorption vs emission.

The 2$D$ Band. The 2$D$ overtone band in pure graphene is the strongest line in the spectrum, even much stronger than the fundamental G band. The Kohn anomaly has been proposed as a contributor to the strength of 2$D$, and indeed it may be, but then G is weaker, also born at a Kohn anomaly, and is a fundamental, not a normally weak overtone.

It is important to note that if two counter-propagating D phonons were actually produced simultaneously in absorption, there would be a doubling (two phonons) of a double diminishment of the electronic energy (since twice the energy is needed from the photon to produce both phonons at once). This implies a shift of $32\text{cm}^{-1}$ relative to the presumably equally important simultaneous emission production of two counter-propagating phonons, a transition that is not diminished in energy or q. This would imply that the 2$D$ band would either be double or a single peak considerably broader than $32\text{cm}^{-1}$. This would not be consistent with experiments revealing a slightly asymmetric line about $25\text{cm}^{-1}$ fwhm$^8$.

But there is another possibility, just described, that of producing a D phonon in absorption and another in a mirror image emission. There are a continuum of such amplitudes which can slide up and down the cone, part of the KHD sum, each contributing an imaginary part with the same sign to the total 2$D$ amplitude and each producing phonons at the same 2$q^-$ pseudomomentum (see
Figure 2.5). The simultaneous 2D production in emission or absorption with its 32 cm\(^{-1}\) problem is thus alleviated (not to mention it is very weak compared to what sliding produces). The sliding mechanism also predicts the experimentally measured Stokes-anti-Stokes anomaly for 2D (see below). The density of states for both the initial and final electronic states will have a major effect on the propensity to slide various amounts.

2D Band Stokes, Anti-Stokes Anomaly. The 2D Stokes, anti-Stokes anomaly is simple to explain. In the sliding mechanism, both phonons share the same energy and diminishment, or augmentation (in anti-Stokes). Each Stokes 2D (one in absorption, one in emission) suffers an 8.4 cm\(^{-1}\) diminishment, or 17 cm\(^{-1}\) total, and each anti-Stokes 2D enjoys an 8.4 cm\(^{-1}\) augmentation, or 17 cm\(^{-1}\) altogether, for an overall 34 cm\(^{-1}\) asymmetry, four times greater, not the expected two times greater, than the 8.4 cm\(^{-1}\) 2D band asymmetry. Again, this is in agreement with experiment (see Figure 2.6).

The D and 2D Stokes, anti-Stokes anomalies are thus directly and simply explainable using KHD theory, unlike the very elaborate rationales used to coax the DR model to agree\(^{21}\).

D and 2D Bandwidths; 2D Intensity with Laser Frequency. The D-mode band must be broader than the band centers spaced by 8 or 8.4 cm\(^{-1}\) that comprise it. We find it to be ca. 20 – 25 cm\(^{-1}\) fwhm in the literature, about twice the fwhm of the G mode, or 13 cm\(^{-1}\)\(^{41}\). The G has no dispersion and no issues of Stokes, anti-Stokes anomalies. A D line much broader than 13 cm\(^{-1}\) supports the idea that the Stokes D mode is really the superposition of two displaced peaks, one coming from production in absorption, another in emission. Not only are the Stokes and anti-Stokes peaks shifted by 8.4 cm\(^{-1}\); they also must be overlapping when brought to the same side of the Rayleigh peak, exactly as seen in experiment; see also Figure 2.6.
The 2D bandwidth is only somewhat larger than D, approximately $30\text{cm}^{-1}$. It is not a double
peak, at least not until the symmetry is broken (as revealed by tensioning the sample in some direction). It seems likely that 2D earns its width in a different manner than D, perhaps a result of the
sliding process on slightly nonlinear or trigonally warped Dirac cones.

Intensity Changes with Frequency in 2D and G. The decrease in 2D intensity with increase laser
energy, and broadening of 2D, leading to near complete absence of 2D at 266 nm in the ultraviolet
is easy to explain based on the KHD and sliding transition picture. The graphene electronic disper-
sion suffers significant bending (as distinct from trigonal warping) as the ultraviolet is approached,
degrading the linearity essential to the coherent sliding 2D mechanism and its interference enhance-
ment. It is easy to show the sliding is nowhere linear at 266 nm.

On the other hand, the G mode frequency is insensitive to the laser energy increase, since it does
not depend on transition sliding for its intensity. It has been reported to increase intensity at the
fourth power of the laser frequency\textsuperscript{79}, which fits the $\omega I^3$ classic KHD dependence, eq 2.1. G is
ready to emit a Raman shifted photon immediately upon photoabsorption, and benefits from off-
resonance contributions.

Defect and Laser Frequency Trends. Several interesting trends develop in the Raman spectra as
density of defects or laser frequency changes. We begin with the fascinating similarity of sidebands
in polyacetylene and graphene. High symmetry $k = 0$ dispersionless bands can be parents of disper-
sive sidebands carrying momentum $2q^-$, coming from the production of a phonon in absorption,
where $q^-$ is slightly less than $q$, the higher electronic pseudomomentum when no phonon is pro-
duced. The conduction band electron gets kicked to $-q^-$ as it generates a $2q^-$ phonon. If $-q^-$ is
populated initially, that is not the hole waiting to be filled; rather $q^-$ is. Therefore, elastic backscattering is required to appear in the Raman signal. In emission, the sideband phonons carry momentum $2q$.

The trends in the $G'$ band are quite parallel to sidebands in polyacetylene: fixed $k = 0$ peaks with nearby dispersive sidebands, growing in intensity with increasing sources of elastic backscattering, and moving in frequency according to the band dispersion and phonon $q$. The $G'$ band (formerly called $D'$) has nothing to do with the $D$ band, and is simply the sideband to $G$, as Hilke and others have known for some time

Sideband Growth with Impurity Density. The growth in sideband intensity with increasing sources of impurity backscattering is seen on the left of Figure 2.7. We explained these trends entirely within a KHD context applied to the one-dimensional polyacetylene crystal with defects.

The sideband growth shown in the $1054 \text{ cm}^{-1}$ polyacetylene band as elastic backscattering defects are added is seen at the upper left in Figure 2.7. The figure was adapted and the $k = 0$ band contribution colored, using Schäfer-Siebert et al. The sideband is present at 0% added defects because of pre-existing defects (including molecular ends). The total intensity consists of the $k = 0$ band and the overlapping sideband, making a break in slope to the right of the $k = 0$ band peak. At the top right, an important graphene Raman study taken from Childres et.al. is shown, with permission, with similar sideband growth ($G'$, sideband to $G$).

Trends with laser frequency in sideband growth and dispersion as a function of incident laser frequency are shown at the lower left for polyacetylene and graphene (red arrows in the case of polyacetylene, giving band frequency predictions based on electron and phonon dispersion and
backscattering trends with laser frequency). The trend is opposite in the two cases. In graphene, the conductance trend is toward increased sideband strength with decreasing laser energy, as seen in Figure 2.7. In polyacetylene, the trend is reversed. One obvious effect causing this difference is that a propagating electron wave cannot fail to collide with a defect in one-dimensional polyacetylene.

We have undertaken density functional calculations on polyacetylene distorted by kinks and other geometrical defects, which show that higher energy electronic states backscatter more readily from such defects than do lower energy ones, in the conduction band.

In Figure 2.7, both polyacetylene and graphene show increased sideband intensity as edges or ends grow closer to the interior, increasing the efficiency of elastic backscattering.

The $D$ and $2D$ Bands Are Sidebands to $“D^K,”$ a Forbidden $k = 0$ K Point Vibration. In a definable sense, the $D$ and $2D$ bands are dispersive sidebands in a classic way to a nondispersive, but forbidden Dirac $K$ point band we call $D^K$, living at the vibrational $K$-point. In another classic case, the dispersive bands $G'$ [$D'$] and $2G'$ [$2D'$] are sidebands to the nondispersive $G$ band, see Figure 2.7. In still another classic case, dispersive sidebands in polyacetylene are partner to visible nondispersive bands belonging to $\Gamma$ point vibrations. The band edge $K$ point vibration $D^K$ is of course not a $\Gamma$ point vibration; one consequence is that it has a vanishing transition moment and Raman intensity, as is required by symmetry. This however does not disqualify the $D$ and $2D$ bands from being labeled as dispersive sidebands to the silent and dispersion-less $D^K$ parent band; $D^K$ would lie typically $8cm^{-1}$ to the left of $D$ and not require backscattering.

Defects and $2D$ Intensity. There is a well-known dramatic decrease in the $2D$ band intensity with increased defect density (Figure 2.7, upper right). This is easily understood in terms of the sliding
production of the two $D$ phonons. The amplitude for production of the first $D$ phonon in absorption is relatively insensitive to defect density. Transitions with no sliding contribute to $D$ Raman intensity if they are elastically backscattered, and indeed the $D$ intensity increases with added impurities. Sliding $D$ transitions are Pauli-blocked, even if backscattered, since their wave-vector mismatch with the hole persists. Sliding transitioned electrons are equally prone to defect elastic backscattering or more often, general scattering, making it extremely unlikely they can produce another $D$ in emission, being unable to reverse absorption path. Defect scattering of the conduction electron thus quenches the source of $D$ phonon production in emission, and the $2D$ Raman band intensity diminishes as defects are added. This is just what is seen in Figure 2.7. The reverse trends of $D$ and $2D$ intensity with added defects therefore follow from the sliding, “up and back down along a reversed path” mechanism for $2D$ Raman emission.

Anomalous Spacing of $D$ and $2D$. A prediction can be made about the $D$, $2D$ spacing seen in experiments at any frequency. This has been discussed within the DR model also $^{21,32}$. The frequency of $2D$ is smaller than twice $D$, by amounts depending on experimental conditions. The ideal “bare”, unstrained, low temperature, and fairly clean (but dirty enough to see $D$) graphene experiment has not been done to our knowledge. However, quoting Ding et.al. $^{32}$, ”The results show that the $D$ peak is composed of two peaks, unambiguously revealing that the $2D$ peak frequency ($\omega_{2D}$) is not exactly twice that of the $D$ peak ($\omega_D$). This finding is confirmed by varying the biaxial strain of the graphene, from which we observe that the shift of $\omega_{2D}/2$ and $\omega_D$ are different.”

According to our application of KHD to graphene, a $1335 cm^{-1}$ $D$ phonon produced in absorption is diminished owing to the $50 cm^{-1}/eV$ phonon dispersion, by $1335/806550 = 8.28 cm^{-1}$. A $D$
phonon produced in emission is undiminished. The two bands will overlap to make a broader feature than either component. Assuming the two bands are equally intense, as KHD predicts, there should be a combined band with an average $4\text{cm}^{-1}$ displacement to the left in the Stokes spectrum. The idea that $D$ is composed of two bands with an $8\text{cm}^{-1}$ splitting was also suggested within the DR model, with a very different justification, “depending on which of the intermediate states is virtual.” The reason for the two bands is actually much less exotic (absorption vs emission production) and on a firmer foundation in KHD (both real, resonant processes) than the virtual processes supposed in DR.

The $2D$ band consists of two separately produced, diminished $D$ phonons. There is an $8\text{cm}^{-1}$ diminishment in absorption, and a matched $8\text{cm}^{-1}$ diminishment in emission according to the sliding scenario, totaling a $16\text{cm}^{-1}$ shift. As just discussed, the $D$ band is displaced by $4\text{cm}^{-1}$, thus twice the frequency of $D$ is predicted to be $8\text{cm}^{-1}$ shifted as opposed to the $16\text{cm}^{-1}$ shift of $2D$, or a $-8\text{cm}^{-1}$ difference between $2 \times D$ and $2D$. Review of many published spectra under different conditions shows $E(2D) - 2E(D) \sim -2 \text{ to } -10\text{cm}^{-1}$. However, samples were suspended on different substrates by a variety of methods; measured shifts depend on these conditions. Reference shows that any source of stretching or compression can affect the $D, 2D$ distance. The $D, 2D$ shift deserves more investigation using suspended, gently pinned graphene.

Mixed Bands and Bandwidth Trends. Does the sliding mechanism enhancing the $2D$ band brightness also contribute to the strength of other bands? We have already noted that sliding does not help the $D$ band gain intensity, since the electron is Pauli-blocked even with elastic backscattering (however, see the last section for the changed situation when the sample is hole doped). The $G$
band transition cannot slide since the $\Gamma$ point produces a $k = 0$ phonon. The same applies to $2G$, which does not appear in the Raman spectrum regardless of defects.

The sliding mechanism for mixed transitions is a different story than for homogeneous ones, especially for bandwidth. The momentum conservation requirements on the production of a pair of phonons requires that they are matched in $q$. They do not need to be matched in type; e.g., a Raman band for $G'$ (old $D'$) and $D^i$ (Hilke’s notation) could be produced by the sliding mechanism. This fact allows us to explain many of the disparate bandwidths seen in the Hilke et.al. data\(^9\), since differences in dispersion and frequency of the two components contributes to the bandwidths, as we presently see.

Most of the mixed transitions are weak (and certainly would be invisible without transition sliding), as Figure 2.3 shows. The weakness may reflect small transition matrix elements or the possibility of destructive interference between terms in the sum in eq 2.1. The strength of homogeneous two phonon transitions, like $2D$ or $2G'$, is expected to be high since they are produced by mirror image processes with in-phase numerators.
Figure 2.8: Calculated (blue) and experimental (data from ref\textsuperscript{9}, red) bandwidths for mostly mixed combination bands. The calculations were as follows: The wavenumber difference for \( G^s \) (old \( D' \)) up first and \( D_4 \) down versus \( D_4 \) up first and \( G^s \) down was calculated using the mode frequencies and dispersion slopes from ref\textsuperscript{9}. The Raman shift (and phonon energies) depend on which transition is first, and this difference is widening the bands. For modes \( a \) and \( b \), the formula is \( W = (|S_a - S_b|)(\hbar \omega_a + \hbar \omega_b) \) where \( W \) is the component of the width coming from which mode is created first, \( S_i \) is the dispersion slope in \( \text{cm}^{-1} / \text{eV} \), and \( \hbar \omega_i \) is the energy of the phonon in \( \text{eV} \). The theoretical results are compared to widths found in the data from ref\textsuperscript{9} after adding 16 \( \text{cm}^{-1} \) for the "intrinsic" width. Except for the \( G^s + 2D \) (assignment and data taken from ref\textsuperscript{109}) and \( G^s + D \), the agreement is good, and it lends confidence to the KHD approach and the one up, one down scenario double phonon. See text for discussion of bands labeled by a red star. See Supporting Information for a discussion of the "outliers" in the sense of a poor fit, indicated by black stars.
Figure 2.9: Continuum emission in graphene from normally Pauli-blocked sliding transitions at some laser energies and hole dopings. Horizontal bands are spaced by $0.1eV$. At the top, four scenarios for doping levels and sliding transitions at $1.58eV$ laser energy are shown, together with their relation to the data of ref 25. For a $D$ phonon, the diminished electronic part of the transition is at $1.44eV - 1.58eV$ (laser energy) $- 0.166eV$ (phonon energy). Scenario 1 at $|E_F| = 1.58eV$ is Pauli-blocked without defect backscattering; sliding does not help; and is therefore invisible in Raman. Scenario 2 at $|E_F| = 1.1eV$ is shown sliding down $0.15eV$, thus matching a hole opened by doping and avoiding Pauli blocking. However, it produces a minimum $3765cm^{-1}$ electronic Stokes shift (lower dashed line). Scenario 3 at $|E_F| = 1.4eV$ is within the bright continuum electronic Stokes emission starting at ca. $1340cm^{-1}$ and going higher, but cut off at higher Stokes shifts by (1) declining density of states as the relevant conduction and valence bands approach the Dirac point, and (2) the emission factor $\omega_s$ (see eq 2.1). Scenario 4 (upper dashed line) needs to slide down to reach occupied levels that can be promoted to the conduction band, but this again causes large Stokes shifts. Scenario 5 applies to a hypothetical $2.18eV$ laser energy (not used in the hole doping experiment of ref 25); it shows that at any available hole doping, the D + electronic Raman shift continuum emission would not appear anywhere near the low energy regime seen in the current experiment. The complete fading out of the $2D$ band at the onset of the continuum emission (lower right) as $|E_F|$ is increased is explained in the text. The panel at lower right is adapted with permission from ref 25. Copyright 2011 Nature Publishing Group.

For mixed transitions, sliding applies but leads to slightly different Raman band frequencies depending on which phonon is produced first, in absorption. The bandwidth will reflect this (see Figure 2.8). Using data from Hilke 109 at $288nm$, we arrive at Figure 2.8. The reasons for the bandwidths...
of the $D + G'$ and $2D + G'$ are discussed below. Red stars on $D + D''$ and $G' + D''$: We have used ref$^{91}$ to help understand the skewed line at about $2450 \text{cm}^{-1}$ with the nominal assignment $D + D''$.

This study decomposed it into two bands, one of which is $D + D''$ with a width of $20 \text{cm}^{-1}$, and the overlapping higher energy LO $G'$ band near the $\Gamma$ point, but now near the $K$ point, a less intense band, with a fwhm of $29 \text{cm}^{-1}$.

Some mixed sliding transitions, such as $G' + D^1$, $G' + D^4$, and even some hint of $D + D^5$ (Hilke’s notation, except $D' \rightarrow G'$) do not require defect backscattering and are seen weakly in high quality spectra of clean graphene, for example in Childres et al$^{17}$.

Consider a mixed overtone band involving phonon modes A and B. If A is created in absorption, the $q_A$ of the transition will be different than if B is created first, giving an electron pseudomomentum $q_B$. If A is a higher frequency phonon than B, the electronic transition energy diminishment is larger if A appears in absorption, and $q_A$ will be smaller. The emission B phonon must follow with the opposite pseudomomentum $2q_A$. This allows for matched electron-hole recombination, but the B phonon is required to adjust its energy to arrive at the right $q_A$. This energy correction depends on its momentum dispersion. Thus, the total phonon energy (and thus the Raman shift) is slightly different if A is created in absorption than if B is. This fact contributes to a small uncertainly in frequency and contributes to the bandwidth. We calculated the bandwiths for each mixed transition and added $16 \text{cm}^{-1}$ to allow for the intrinsic broadening seen in narrow bands, due presumably to phonon decay??. Using data mostly from Hilke$^9$ at $288 \text{nm}$, we arrive at Figure 2.8.

Hole Doping Evidence of Sliding $D$ Absorption. Chen and co-workers$^{25}$ hole doped the valence band by as much as $0.8eV$ and saw abundant continuum emission, in a certain range of depletion...
and Raman shift. We now show this emission, that as ref\textsuperscript{25} points out, integrates to more than 100 times the strength of the G band that it overlaps, can be explained by sliding D phonon transitions that are normally Pauli-blocked or could have been the first step in making a 2D pair by reversing the sliding transition, coupled with an electronic Raman component.

With hole doping, D phonons produced in a sliding transition and the associated electronic conduction band level are normally orphaned by Pauli blocking (unless the electron returns by the sliding 2D mechanism along the reverse path). With deep doping the electron has a new option: to emit to a valence orbital emptied by doping without creating another phonon. The original hole remains unfilled, and the valence orbital emptied by doping is filled instead. This leads to a continuum of potentially large electronic Stokes shifts. (Electronic Stokes because the valence electron has been promoted, not a phonon in the final step.) This phononless emission step is far more likely than creating another phonon, and thus, the “feedstock” of the 2D band is depleted, quenching the 2D band. The 2D band should fade out in the experiment as the continuum emission appears, just as seen in the experiment (see lower dotted white line, Figure 2.9). Before that happens, we note that deeper hole doping lessens the sliding up distance available before the last populated initial valence level is reached. This progressively removes sliding 2D transitions, weakening the 2D band as $2 | E_F |$ increases. The consistent, progressive weakening of the 2D starting as low as $2 | E_F | = 0$ is evident in the lower right experimental data.

G Mode Brightening. In the paper by Wang and his group\textsuperscript{25}, a brightening of the G band is noted as hole doping is increased. It can be seen as a gradual waxing of G intensity in Figure 2.9, even after the continuum band is exceeded in the upper left corner of the plot on the lower right.
The authors attributed this to removal by doping of destructively interfering paths. We agree: this also happens within the KHD picture. The sum over nonresonant states $|n\rangle$ of energy $E_n$ normally extends above and below resonance, which causes cancellations in the real part of the sum. Doping eliminates part of the sum on the high side of resonance, enhancing the real part. The relevant states $|n\rangle$ all contain matched electron-hole $G$ phonon triplets and matched electron-hole pairs (if $G$ is to be produced in emission, with slightly different energy denominator) even if $E_n$ is quite nonresonant.

Figure 2.10: Mostly nonresonant electronic processes contributing to $G$ mode creation, including under hole doping. See text.

In Figure 2.10, case A, a given laser frequency causes below (1) and above (3) resonant transitions capable of instant production of a $G$ mode, and a resonant one (2). Emission energy is reduced by the same energy in each case by the same $G$ phonon produced, so the cases (1), (2), (3) add coherently.
In the below resonance Raman transition (i), virtual promotion occurs from the lower blue solid to the upper blue dashed line. Due to momentum conservation, no other states are available (they give zeros in the numerator of the KHD sum) starting at the blue valence level. The upper blue dashed state is an electron-hole-phonon triplet. Since the phonon is produced instantly, there is no time-energy roadblock to forming a $G$ mode. All three cases apply to the same incident photon. (B) With hole doping, some transitions are no longer possible with their valence levels “missing”. This eliminates some coherent destructive interference of terms in the KHD sum. (C) The $G$ mode phonon coordinate is displayed as the abscissa, and energy in the ordinate. Filled bands are solid; empty bands are dashed. The density of states is indicated qualitatively using the level spacing. The restriction red-to-red, blue-to-blue is due to $q$-conservation (small energy differences due to phonon production not shown). A continuum of off-resonant transitions apply for the same laser energy (arrows are the same lengths) and the same phonon. The sum over such states is truncated with hole doping and the above resonance missing terms have the opposite sign in their real part with below resonance terms still present. Thus, some of the cancellation present without hole doping is lifted, enhancing $G$ intensity, in agreement with ref 25.

When present, real (not virtual) processes play a dominant role in KHD, and apart from hole or particle doping scenarios, real pathways are always available in graphene. Virtual processes (such as those present in ordinary off-resonant Raman scattering) do not normally play a center stage role, living in the shadows of the real, resonant processes, contributing mostly near resonance, in accordance with damping factors.

Off-resonant (pre- or post-resonant) Raman scattering still contributes in parallel with resonant
transitions in graphene, just as it does in molecular systems. For hole doped graphene, off-resonant transitions may dominate when the resonant initial valence states are depleted of population. For example, starting on the lower Dirac cone below a hole doped, lowered $E_F$, a laser may be too low in energy to reach resonant levels on the upper cone (see Figure 2.10, B); yet, electron-hole excitation and recombination with no Pauli blocking quickly follow upon virtual absorption, within a time scale $\Delta t$ given by the detuning $\Delta E$ from resonance, where $\Delta t\Delta E \sim \hbar/2$. A $G$ phonon, for example, may thus be created or destroyed, off resonance. Time can become too short for electron-phonon scattering or any nuclear motion to develop; these go no faster than $t^1$ (time after absorption), but Raman intensity comes instead from an instantaneous, $t^0$ phonon creation/annihilation process, which KHD provides through the transition moment coordinate dependence.

2.4 Conclusion

The universally used (except in the conjugated carbon community), 90 year old KHD Raman scattering theory has been applied for the first time in graphene Raman scattering. The results are in excellent agreement with experiment, and new insights (and predictions about new hole doping experiments) have resulted. The most important of these may be the sliding transitions, explaining the brightness of overtone transitions in graphene.

KHD includes nuclear coordinate dependent transition moments as a central part of the theory. The coordinate dependence becomes crucial when nuclear forces do not change in making an electronic, photoinduced transition. DR keeps transition moments constant; in fact, DR bypasses KHD completely. Instead, ad hoc, one or two orders of perturbatively treated, Born-Oppenheimer
violating electron-phonon scattering are inserted. Virtual processes are finally needed to create phonons in the conduction band. The result is a fourth-order perturbation theory, two orders beyond KHD.

If we take photoabsorption and electron-hole formation to be real, and suppose that electron-phonon scattering takes time, then conduction electron energy and momentum is well established before inelastic scattering. This all-resonant picture leads straight to severe Pauli blocking after the kick and energy reduction the electron receives in inelastic electron-phonon scattering. The fact that Raman scattering is in fact robust in graphene leads the DR model to suppose instead that non-resonant virtual processes must have lead to a final “double resonance” and provided the Raman photons. But now that we know the transition moment coordinate dependence, combined with all-resonant processes free of Pauli blocking provide the Raman photons, the appeal to virtual processes and inelastic electron phonon scattering becomes unnecessary. Ockham’s razor would strongly suggest taking the simpler, resonant, real, lower order in perturbation theory, long established KHD theory seriously.

We believe KHD is the correct theoretical basis for understanding Raman scattering in graphene. Using KHD, in one contribution we have been able to explain the major effects discovered in 15 and more years of experimental effort on graphene and graphite, including the behavior of fixed and dispersive Raman bands, their dependence on laser frequency, their sensitivity to defect and doping densities, anomalies in Stokes, anti-Stokes positions and widths, hole doping experiments, brightness of $2D$ and absence of $2G$, widths of different overtone features, and more.

We have exposed the sliding mechanism, a direct result coordinate dependence of the transition
moment and linear Dirac cone dispersion. A key spectroscopic agent in graphene, sliding is plain to see in the KHD formula. Sliding explains graphene’s extremely bright overtone bands.

2.5 Method

The Transition Moment for Graphene. Consider the integral involving transition between a valence Bloch orbital at pseudomomentum \( q_v \), described in terms of Wannier functions \( \alpha_{q_v}(r - R_{q_v}(\xi)) \), and a conduction Bloch orbital at pseudomomentum \( q_c \), assuming only nearest neighbor (\( A \) with nearest \( B \) ) interactions. The transition moment becomes

\[
\mu_{\xi_{q_v}, q_c}(\xi) = \sum_{A,B} \int dr e^{-i q_v \cdot R_A(\xi)} \alpha_A(r - R_A(\xi)) \hat{D}^\rho e^{i q_c \cdot R_B(\xi)} \alpha_B(r - R_B(\xi))
\]

\[
= \sum_{A} e^{-i(q_v - q_c) \cdot R_A(\xi)} \sum_{j=1}^{A} \delta_{\xi}(\xi) D^\rho_{A,B_j}(\xi)
\]

\[
= \sum_{A} e^{-i(q_v - q_c) \cdot R_A(\xi)} F^\rho(q_c, A, \xi)
\]

\[ (2.8) \]

\( \hat{\delta}_j(\xi) \) is a nearest neighbor vector, i.e., \( B_j = A + \hat{\delta}_j(\xi) \). \( q_v, q_c \) are Bloch pseudomomenta in the valence and conduction band, respectively. Here we have given only the simplest form of the transition moment; in fact, in our calculations, we use density functional theory modified Wannier wave functions as a function of nuclear coordinate; see the section ”Tight Binding and Density Functional Realization of Graphene KHD”.

The sum and therefore the transition moment vanishes at the equilibrium position of the lattice \( \xi_0 \) unless \( q_v = q_c \) or \( q_v - q_c = K \), a reciprocal lattice vector, since \( F^\rho(q_c, A, \xi) \) is the same func-
tion of \( q_c \) for all \( A \). However, it is not the transition moment at a single configuration of the nuclei that is required, but rather the integral over phonon matrix elements, i.e., eq ??.

Suppose \( q_v = q_c \), so we are considering a \( \Gamma \) point vibration. Clearly the exponential is unity. But it is easily seen that

\[
\frac{\partial P(q_v, A, \xi)}{\partial \xi_G} \neq 0 \text{ at } \xi = \xi_0, \text{ i.e., } P(q_v, A, \xi) \text{ is odd at } \xi_0 \text{ about either } G \text{ mode.}
\]

(Moving the \( A \) lattice up slightly and the B lattice down by the same amount is a distortion along a \( G \) mode \( \Gamma \) point vibration.) Thus, the transition moment can induce changes by one quantum (and also more, we do not analyze that here) in the \( G \) modes, at the \( \Gamma \) point.

A phonon of pseudomomentum \( k = q_v - q_c \) can be induced by lattice distortion \( \xi_k \neq \xi_0 \) and the transition moment if \( \mu _{q_v,q_c} (\xi) = \sum A e^{-i(q_v - q_c) \cdot R_A(\xi)} P(q_v, A, \xi) \) becomes nonvanishing for \( q_v - q_c = k \) or \( q_v - q_c = k \pm K \). This happens due to periodic undulations in \( P(q_v, A, \xi) \) arising from displacement of the lattice \( R_A(\xi_k) \) and \( R_B(\xi_k) \) according to a phonon with wave vector \( k \). However, unless strict conditions are met, such phonons, though present, are associated with a conduction band electronic level that is Pauli-blocked, keeping the phonon silent in the Raman spectrum. Elastic backscattering will not help, except for special cases, as described next. If hole doping is present, matters can be changed in a fascinating way; see "Hole Doping Evidence of Sliding D Absorption".

Ab Initio Procedure. A two-step ab initio procedure is used to model realistic hopping parameters, computing transition moments and their coordinate dependence. First, the density functional theory (DFT) calculations are performed using the Vienna ab initio Simulation Package (VASP)\(^{68,69}\), with the exchange-correlation energy of electrons treated within the generalized gradient approximation (GGA) as parametrized by Perdew, Burke, and Ernzerhof (PBE)\(^{106}\). To model the single layer
graphene, a slab geometry is employed with a 20Å spacing between periodic images to minimize the interaction between slabs, a 450eV cutoff for the plane-wave basis and a reciprocal space grid of size $19 \times 19 \times 1$ for the $1 \times 1$ unit cell.

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2.7 Supporting Information

2.7.1 Time domain KHD

According to the time dependent form of KHD theory, the amplitude to scatter from phonon state $m_i$ is

$$
\frac{\delta \sigma}{\delta \epsilon_m}(t) = \int_{-\infty}^{t'} dt' \int_{-\infty}^{t} dt'' \left\langle \psi^\text{B.O.}_{m_f} \left| G^\text{+}_{0}^\text{+}(t - t')V(t')G^\text{+}_{0}^\text{+}(t' - t'')V(t'')G^\text{+}_{0}^\text{+}(t'') \right| \psi^\text{B.O.}_{m_i} \right\rangle 
$$

$$
= \int_{-\infty}^{t} dt' \int_{-\infty}^{t} dt'' \left\langle \psi^\text{B.O.}_{m_f} \right| e^{i E^\text{B.O.}_{m_f}(t - t')/\hbar} D^\epsilon e^{-iH^\text{B.O.}_{m_f}(t - t')/\hbar - \Gamma(t' - t'')/\hbar} \beta(t'') D^\epsilon e^{-iE\epsilon_{m_i} t''/\hbar} \psi^\text{B.O.}_{m_i} \right\rangle 
$$

where $D^\epsilon$ is the dipole operator polarization $e$. We have incorporated a damping factor $\Gamma$ to account for the environmental factors not explicitly included in the Hamiltonian. $G^\text{+}_{0}^\text{+}(t' - t'') = e^{-iH^\text{B.O.}_{m_f}(t - t')/\hbar}$, $t > t'$; $G^\text{+}_{0}^\text{+}(t' - t'') = 0$, $t' < t''$ is a retarded Born-Oppenheimer Green function (one that propagates Born-Oppenheimer eigenstates unchanged except for a phase factor) and $V(t'')$ is the light-matter perturbation with arbitrary time dependence governed by $\beta(t'')$, which we take normally to be $\exp[i\omega_\text{L} t'']$ corresponding to a cw laser.

The expression 2.9 shows clearly that the propagation on the conduction band Born-Oppenheimer potential surface takes place after the transition moment $D^\epsilon$ has acted at time $t''$ on the initial valence wave function. The transition moment changes the functional form of that wave function and the Born-Oppenheimer Hamiltonian is presented at time $t''$ with newly created or destroyed phonons relative to the valence state, before any excited state propagation has taken place. This is
also clear below after we insert a complete set of Born-Oppenheimer eigenstates to resolve the propagator. The excited state propagator acts until time $t'$, when the electron fills the hole, giving the transition moment another chance to act. No phonons are created or destroyed during the time evolution in the conduction band, according to KHD, nor are they needed to produce the Raman signal.

$$\phi_{B.O.}^{m_i}(\xi; r) = |\phi(\xi; r)\rangle |\chi_{m_i}(\xi)\rangle$$

is the Born-Oppenheimer state before the photon interacts. The electronic state $\phi(\xi; r)$ is a function of all electrons at $r$, depending parametrically on all the phonon coordinates $\xi$. The dipole moment connecting the initial electronic state $i$ and the electron-hole pair state $q_c, q_v, \mu_{q_c, q_v}^{s} (\xi)$, is a function of the phonon coordinates $\xi$, defined as

$$\mu_{q_c, q_v}^{s} (\xi) = \langle \phi_{q_c}^{s} (\xi; r) | D^{s} | \phi_{q_v}^{s} (\xi; r) \rangle_r$$

where the subscript $r$ reminds us that only the electronic coordinates are integrated. We insert a complete set of Born-Oppenheimer eigenstates (they are complete, even if not exact eigenstates of the full Hamiltonian) in front of the Born-Oppenheimer propagator in equation 2.9:

$$1 = \sum_{c,v,m} |\phi_{q_c, q_v}^{s} (\xi; r)\rangle |\chi_{m_c}(\xi)\rangle \langle \chi_{m_v}(\xi) | \langle \phi_{q_c, q_v}^{s} (\xi; r) |$$

where we have acknowledged by absence of a subscripts on the phonon wave function $\chi_{m_i}(\xi)$ that the phonon modes do not change upon electron-hole pair formation (in extended systems like...
graphene). Since $H^{B,O} \left| \phi_{q,ξ} (ξ; r) \right\rangle = \sum_{i,v,m} \left| \chi_{m_i}(ξ) \right\rangle \left| \chi_{m_v}(ξ) \right\rangle$, we have

$$d_{m/m} (t) = \sum_{c,v,m} \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' e^{iE_{c,v,m}(t-t')/\hbar} e^{-iE_{c,v,m}(t'-t'')/\hbar} e^{-\Gamma(t'-t'')/\hbar} e^{i\omega I t''/\hbar}$$

(2.12)

Apart from pre-factors, equation 2.9 with the insertion equation 2.11 can be easily converted (ignoring the second, off-resonant term as usual and gently damping the laser field at infinite positive and negative times) to the Raman scattering amplitude for the $m_i \rightarrow m_f$ process starting and finishing on electronic state $i$ with incoming light of frequency $\omega_I$, incoming polarization $\rho$, and outgoing $\sigma$, i.e. equation 2.12. The final state is designated, apart from initial and final polarization, by the initial (and final) ground, valence electronic state labeled by $i$ and the final phonon occupations labeled by $m_f$. The sum labeled by $c, v$ and $m$ is over all electron-hole states and phonon occupations that connect both initial and final states via the transition dipole $D$. Here reside some surprising and important terms, including the sliding transitions (see main text).

It is illustrative to incorporate the transition moment into the phonon wave function $\phi_{q,ξ} (ξ) = \mu_{q,ξ} (ξ) \chi_m (ξ)$. Phonon excitations are included in $\phi_{q,ξ} (ξ)$ (the electron-hole-phonon triplets?) but may be much less common than the pure electron-hole pair amplitude. Equation 2.12 can be
returned usefully to a new time domain expression\textsuperscript{76},

\[ \frac{i}{\hbar} \sum_{c,v} \int_{0}^{\infty} e^{i(\omega_{f} + E_{v,m}) t / \hbar - \Gamma t / \hbar} \left| \langle \phi_{q_i,q_f,m_j}^{c,v} | e^{-iH_{\text{B}^{\text{O}}} t / \hbar} | \phi_{q_i,q_f,m_i}^{c,v} \rangle \right| \left( \frac{\Delta m}{\hbar} \right) dt \]

It is important to note that the KHD Raman amplitude is overall 2nd order, involving only perturbation in the matter-radiation interaction. One could go to higher order by adding well known non-adiabatic correction terms to Born-Oppenheimer theory, but we do not do that here. Even better, degenerate perturbation theory involving the same correction terms might be used to account for Kohn anomalies and possibly other effects.

The sum labeled by \( j \) is over all electron-hole states that connect both initial and final states via the two transition dipoles \( D \). Here reside some surprising and important terms, including the sliding transitions described in the main text. Equation 2.13 is useful for many things, including understanding the effect of \( \omega_{f} \) on the Raman amplitude, if something is understood about the time dependence of the amplitude \( \langle \phi_{q_i,q_f,m_j}^{c,v} | e^{-iH_{\text{B}^{\text{O}}} t / \hbar} | \phi_{q_i,q_f,m_i}^{c,v} \rangle \), especially for early times. The faster the amplitude grows in time, the more robust it will be against \( \omega_{f} \) lying far from resonance for a given electron-hole state \( p \). This is due to the half Fourier transform aspect of the time integral and transient behavior near \( t = 0 \). Transition moment coordinate dependence permits, at time \( t = 0 \), \( \langle \phi_{q_i,q_f,m_j}^{c,v} | e^{-iH_{\text{B}^{\text{O}}} t / \hbar} | \phi_{q_i,q_f,m_i}^{c,v} \rangle \neq 0 \), i.e. immediate finite amplitude at \( t = 0 \). Returning to the en-
ergy domain, we probe the effect of setting the transition moments constant in phonon coordinates:

\[
\delta_{m_i m_f}(\omega I) = \sum_{c,v,m} \frac{\mu^{x}_{q_i,q_m} \mu^{x}_{q_i,q_m} \langle \chi_{m_f}(\xi) | \chi_{m_i}(\xi) \rangle \langle \chi_{m_i}(\xi) | \chi_{m_f}(\xi) \rangle}{\hbar \omega_I + E_{i,v,m} - E_{c,v,m} + i\Gamma} \\
= 0, \ m_f \neq m_i \\
= \sum_{c,v,m} \frac{\mu^{x}_{q_i,q_m} \mu^{x}_{q_i,q_m}}{\hbar \omega_I + E_{i,v,m} - E_{c,v,m} + i\Gamma}, \ m_f = m_i \\
(2.14)
\]

This is still 2nd order, but barren of Raman scattering. Something has to be done to create phonons. Here we allowed the transition moments to vary, as they were always meant to, and are often allowed to do in other contexts, these past 90 years. The DR model left them frozen and went deeper into perturbation theory to generate phonons, which we believe are given a Pauli blocked still-birth with no path of the electron to return to the hole.

### 2.7.2 Off-resonant Raman scattering

Off-resonance, the effective lifetime in the virtual excited conduction band states is \(\frac{\hbar}{\Delta E}\) over twice photon energy gap \(\Delta E\) of the laser promotion to electronic resonance\(^{49,74}\). For very short times well off-resonance, the transition moment is applied twice to the initial state as the electron is promoted and then fills the hole; nothing more happens. There is not time for nuclear wave packet motion in cases where equilibrium geometry changes in the excited state. In the time domain picture of KHD, wave packet motion takes place along Born-Oppenheimer potentials mostly in steepest descent directions\(^{49}\), electrons are interacting with phonons but most decidedly not inelastically. The
displaced phonon wave packets are instantly registered as phonons as the excited state is reached, but the corresponding Raman intensity develops slowly - first order in time - as the wave packet develops velocity. In contrast, the transition moment coordinate dependence means instant excited state phonon population and Raman intensity. This time dependance is more robust to off-resonant detuning, and starts to dominate far enough off-resonance. Thus the off-resonant $D$ mode contribution suffers even with impurities present since there is not sufficient time to backscatter, but $G$ and $2D$ do well off-resonance since no backscattering is required.

### 2.7.3 Bandwidth outliers in figure 2.8

We now discuss the outliers marked by an asterisk seen in figure 2.8. The biggest deviations from the estimates are the $D + G'$ band, just above $2D$, about $50 \text{ cm}^{-1}$ broad as opposed to an estimate done with our assumptions of about $25 \text{ cm}^{-1}$, and the $2D + G'$, rarely reported experimentally at $4280 \text{ cm}^{-1}$ and about $80 \text{ cm}^{-1}$ broad. Unlike the other combination bands, the $D + G'$ band requires impurities and elastic backscattering to be seen, allowing it to grow strong (and broad). $2D + G'$ does not require impurities. Presumably, different mechanisms are at work in each case, explaining why the bands do not fit the assumptions going into the bandwidth estimate and why $D + G'$ needs backscattering.

Intervalley backscattering is necessary for an electron that produces a $D(G')$ phonon upon excitation before it can emit a $G'(D)$ phonon on the way down (see figure 2.1). This is because the $G$ phonon occupies a third of the unit cell of the $D$ phonon, or equivalently, the $D$ phonon is at the $K$ point with respect to the $G$ phonon. We further speculate that the nature of the scattering (figure
2.1) allows the $D + G$ band to be composed of both $D + G$ and $G'$ in the following way: $G$ does not participate in sliding, but it can ?slant? (the analog of sliding, but for transitions near the vertical).

The $G$ becomes a $G'$ transition by becoming nonvertical (keeping the electronic energy fixed); this requires the creation of low $k G'$ phonons, to keep momentum conserved; a small $k'$ deviation from the electronic $K + k$ is created, which with elastic backscattering of the electron becomes a small $-k'$ deviation from the $K - k$. The next step, involving emission creating a $D$ phonon, varies in energy according to $-k'$ and the $D$ mode dispersion.

If $G'$ is produced first, and slides, it is the $D$ emission that must slant on emission, causing a range of $k$ values for this dispersive band (although $k = 0$ is forbidden by symmetry). Between these two possibilities, there is easily a sufficient energy range of phonons thus produced by slanting, accounting for both the enhancement of the "$D + G$" band intensity with backscattering defects (due to slanting) and the breadth of the band.
Figure 2.11: Genesis of the 2950 cm$^{-1}$ band labeled, variously $D + G$ (sometimes) or $D + G'$ (usually). It requires impurities to become visible. If $D$ is produced by a sliding intervalley transition, then after elastic backscattering the $G'$ transition slants to reach the hole, generating a (generally) low $q G'$ phonon to preserve momentum. The slanting transitions have somewhat larger Raman shift than pure $G$; the totality of such transitions explains the width of the 2950 cm$^{-1}$ band. The required backscattering explains why impurities are required to make the $D + G'$ combination overtone appear, unlike the other combination overtones, which can be faintly seen in a relatively pure sample at the top right of figure 2.6 of the main text, $N_e = 0$, but are suppressed as impurities are added. (The $2D + G'$ does not require impurities to be robust.)

The same slanting transitions can occur when producing lone $G$ phonons in absorption, so why is the $G$ band not correspondingly broadened? The reason is that the resulting low $k G'$ phonons are Pauli blocked, and elastic backscattering only blocks them further. The $G$ bandwidth may however reflect the intrinsic "Pauli blocking tolerance" for very small $k'$.

The only three phonon band we discuss in this paper is $G + 2D$ (or $G' + 2D$), which is rarely reported experimentally at ca. 4270 cm$^{-1}$ Raman shift. It is broad, with roughly an 80 cm$^{-1}$ line width, and does not require impurity backscattering. The reason for its existence and its linewidth have a plausible scenario from our KHD based approach, including transition sliding.
The band may be produced by first creating a $G'$ phonon in parallel with a $D$ in absorption, with a $2q$ momentum kick to the electron, followed by a $-2q$ emission along the reverse $D$ path creating a second $D$ phonon. The new twist here is that the first $2q$ kick can be shared in any proportion as $2q = 2q_{G'} + 2q_D$. Again, even without a detailed calculation of intensity distribution and fall-off, it is clear that there is more than 80 cm$^{-1}$ energy difference available depending on the ratio of $G'$ to $D$ in the first step. The emission is through a normal $D$ at momentum $2q$. The $2q = 2q_{G'} + 2q_D$ process can also happen in emission.

2.7.4 The “molecular approach”

An important prior and non-DR perspective on Raman scattering in graphene has been termed the ”molecular approach”. A molecular polarizability context of the type familiar from off-resonance Raman scattering was used. Electron-phonon ”scattering” plays no role. The off-resonance Placzek polarizability derivatives for computing Raman intensities, like the experimental Raman bands, are often quite similar to on-resonance spectra for the conjugated hydrocarbons, except for overall intensity. A finite Placzek polarizability derivative requires non-constant transition moments. However, an approach restricted to off-resonance polarizability cannot be regarded as a complete theory for resonance Raman scattering in graphene, but it is a step in the right direction away from DR.

Consistent with its off-resonant character, the polarizability approach is a near instantaneous picture, leaving little to no time for electron-phonon scattering in the excited state. The $D$ mode requires elastic backscattering (and some time) to become visible in the Raman spectrum, and indeed
the polarizability picture is most successful it seems with the $G$ and $2D$ modes, which require no backscattering. The molecular polarizability picture is a big step in the right direction, quite distinct from DR methods.

Another interesting and instructive contribution to the molecular approach is found in Tommasini et.al.\textsuperscript{155}, attempting a more general electronic resonance formulation. It was based on a KHD foundation but still resorted to the Condon approximation, i.e. constant transition moments.
Reassessing Graphene Absorption and Emission Spectroscopy

3.1 Abstract

We present a new paradigm for understanding optical absorption and hot electron dynamics experiments in graphene. Our analysis pivots on assigning proper importance to phonon assisted indirect...
processes and bleaching of direct processes. We show indirect processes figure in the excess absorption in the UV region. Experiments which were thought to indicate ultrafast relaxation of electrons and holes, reaching a thermal distribution from an extremely non-thermal one in under $5 - 10$ fs, instead are explained by the nascent electron and hole distributions produced by indirect transitions. These need no relaxation or ad-hoc energy removal to agree with the observed emission spectra and fast pulsed absorption spectra. The fast emission following pulsed absorption is dominated by phonon assisted processes, which vastly outnumber direct ones and are always available, connecting any electron with any hole any time. Calculations are given, including explicitly calculating the magnitude of indirect processes, supporting these views.
Figure 3.1: An illustration of mostly indirect optical absorption and emission processes in graphene: The left image shows two absorption mechanisms. The green arrow linking two green circles is a direct phononless absorption process from $-\hbar\omega/2$ in the valence band to $\hbar\omega/2$ in the conduction band, and the black arrows linking holes and electrons are phonon assisted indirect absorption processes at the same vertical $\hbar\omega$. The right image shows the emission mechanism. Any electron in the conduction band is ready for emission to any hole in the valence band by a phonon assisted transition. It does not need to await perfect momentum alignment of randomly distributed electrons and holes. This is not the reverse of absorption, where a vacant conduction band state awaits every valence state. Conduction electrons are almost always Pauli blocked for direct emission (red arrow with X).

3.2 Introduction

Graphene, with its $sp^2$-hybridized honeycomb two-dimensional carbon lattice consisting of conjugated hexagonal cells, shows extraordinary optical properties because of its dimensionality and unique electronic band structure\textsuperscript{104}. As an atomically thin two-dimensional carbon material, graphene is used for transparent electrodes and optical display materials. It has also been applied in opto-
electronics such as photodetectors, optical modulators, and so on. A proper understanding of the carrier dynamics in graphene is key to its potential applications in high-speed photonics and optoelectronics. Many theoretical works concern the electron dynamics in graphene.

In condensed matter theory, the electronic transition moments connecting valence and conduction band states are traditionally taken to be constant, independent of phonon displacement. However, we have found most of graphene spectroscopy falls into place only when transition moments are freed to depend on phonon coordinates, as they must do. (For example, the polarizability of a material would remain constant under arbitrary lattice distortion if the electronic transition moments remain unchanged under those distortions). Recently, it was shown that indirect transitions induced by coordinate dependence of the transition moment are responsible for the great intensity of some Raman overtones. This puts Raman scattering in graphene in line with traditional 2nd order Kramers-Heisenberg-Dirac Raman scattering, in use since 1925-27. In the present paper, coordinate dependence of the transition moment and indirect processes again play a central role for femtosecond pulse-probe absorption and femtosecond pulsed emission experiments, as well as traditional absorption spectroscopy. We show that no ultrafast relaxation is necessary or implied by a variety of experiments.

A significant body of work claims or assumes that ultrafast (5-10 fs) electron-electron relaxation follows ultrashort pulsed excitation. This seemed to be an obvious inference: in a variety of experiments, one looked within femtoseconds after (one supposed) creating an extremely non-equilibrium initial population, only to find the electrons behaving relaxed and even thermalized. For example, upon short pulsed excitation, graphene samples produce fast, readily observable light emission, ap-
 appearing to be coming from a relaxed or even thermal distribution as soon as it can be seen, on the 7-20 fs time scale\(^{82,87,88}\). Ultrafast pump-probe absorption experiments similarly see spectra that appear to have no resemblance to the assumed narrow ranges of populated electrons and holes\(^{16}\).

Nonetheless there have long been clouds on the horizon of the ultrafast landscape. No experiment has ever caught a system in the act of the supposed ultrafast relaxation, nor any vestige of the putative ultrafast component. The fastest relaxation times directly measured in experiments have been in the 100-300 fs range, often attributed in the ultrafast literature to fast, but not ultrafast electron-phonon inelastic events. However saturable absorption (SA) experiments reveal unambiguously that the fastest timescale for electronic relaxation is 100-200 fs, which agrees with earlier femtosecond pump-probe measurement on pyrolytic graphite\(^{93,70^2}\). The timescale for relaxation from an extremely nonequilibrium, saturated narrow band of energies to full thermalization could not be 10-20 fs or shorter, if saturation recovery takes 100-300 fs.

Another cloud threatening the ultrafast narrative could be called the missing energy conundrum. In Lui et. al.\(^{86}\), it is mentioned that the vertical energy per conduction electron at 1.5 eV (0.75 eV for the conduction band electrons) corresponds to an electron temperature of 9000 Kelvin. Once the assumption is made that the electrons and their emission are thermal just a few femtoseconds after the pulse, one is forced to arbitrarily remove 2/3 of the energy that has just been supplied to the electrons and use 3000 Kelvin electron temperature instead of 9000 to fit the emission. This is a serious defect, since the fastest process and the only one effective on the few femtosecond timescale, namely e-e scattering, cannot change the average energy per electron. The temperature becomes an adjustable fitting parameter, even though it should have been non-adjustable. Carrier multiplication might
be suspected, and was indirectly inferred and modeled as the only plausible explanation for what seemed to be 10 fs relaxation\textsuperscript{17}. However when carrier multiplication was actually measured, it wasn’t found to be present\textsuperscript{45}.

Seemingly in favor of the ultrafast relaxation idea are the beautiful experiments measuring electron coherence as seen by D-mode Raman scattering from a localized source, made visible after elastic backscattering from edges\textsuperscript{17}. If the source of the conduction band electron was more than 8 nm round trip from the edge, or about 8 fs, the D mode lost intensity due to lack of coherence with the hole. However, this was properly viewed as a coherence length and dephasing issue, and not a measurement of the complete electronic relaxation time by any means.

Experimental results of disparate types fall into one unified picture if the “thermal” electron and hole distribution is produced not by any relaxation, but nascently at $t = 0$ by a dominance of indirect transitions which, although present even for weak radiation, take over from the easily bleached direct transitions in a bright pulse\textsuperscript{3}. To state it plainly, the electron-hole distribution is born pre-"relaxed" in bright pulsed absorption. This new narrative is competed by careful consideration of how emission takes place, which is also by phonon assisted channels that vastly outnumber elastic processes (figure 3.1). Though individually weaker than the elastic channels, the inelastic pathways are available from any electron to any hole at any moment. Direct emission on the other hand requires waiting for perfect momentum coincidence of randomly distributed electrons and holes. See figure 3.1. Following the lead of indirect absorption plus indirect emission gives excellent agreement with experiments, without the need for arbitrary excited state energy removal, or any excited state relaxation at all on the femtosecond timescale. Although this is a long way from the prevailing con-
sensus, it agrees with direct measurements of electron-electron relaxation rates from saturation experiments, mentioned above, and is free from the clouds and conundrums that the prevailing views are laboring under.

Regarding ordinary CW light absorption, excess absorption over the “universal” value develops in the UV region \(^{98, 88, 117, 78}\). We show here by explicit calculations that phonon-assisted transitions play an increasingly important role as the laser frequency enters the UV region, contributing to the excess absorption in the UV.

In what follows, by new results for graphene UV absorption are discussed first, where phonon assisted processes are key. Then, we address the subject of fast spontaneous emission following bright pulsed excitation, showing that phonon assisted processes explain the spectra without any relaxation. Finally we show that seemingly ultra-rapid relaxation seen in pump-probe absorption experiments are instead the result of nascently produced electron and hole distributions via phonon assisted processes.

3.3 Absorption Spectrum

3.3.1 Theoretical Background

In the Supplemental Material, an expression is derived for the absorption cross section from an initial state \(|i\rangle\) to a final state \(|n\rangle\) as

\[
\frac{\text{(Energy/unit time) absorbed by the lattice}(i\rightarrow n)}{\text{Energy flux of the radiation field}}
\] (3.1)
The absorption cross section from an initial state $|i\rangle$ to a final state $|n\rangle$ can be written in terms of the transition moment as

$$
\sigma_{i,n} = \frac{4\pi^2 \hbar^2}{m_c^2 \omega} \left| \left\langle \chi_{m_i}(\xi) \left| \mu_{\eta_i,\eta_n}^{\epsilon}(\xi) \right| \chi_{m_n}(\xi) \right\rangle \right|^2 \delta(E_n - E_i - \hbar\omega)
$$

with the phonon coordinate dependent transition moment $\mu_{\eta_i,\eta_n}^{\epsilon}(\xi) = \left\langle \phi_{\eta_i,\eta_n}(\xi; r) \right| D^{\epsilon} \left| \phi(\xi; r) \right\rangle$, connecting the Born-Oppenheimer valence and conduction band electronic states, some with different phonon occupations, given by a matrix element of the dipole operator $D^{\epsilon}$ over the electronic states at the given nuclear positions. The wavefunction $|\chi_{m_i}(\xi)\rangle$ is a particular nuclear wavefunction with phonons labeled by $m_i$.

### 3.3.2 Computational Methods

We use SIESTA to perform DFT calculations to get vertical phononless absorption and phonon-assisted absorption. To get meaningful physical quantities, we need wavefunctions having complete periods in our finite lattice, an 80 by 80 graphene supercell. Γ point wavefunctions in the supercell to calculate both absorptions.

For direct, vertical absorption, we consider all electronic transitions from valence band to conduction band at the Γ point of the supercell Brillouin zone, and with electronic wavefunctions we can compute $\mu_{\eta_i,\eta_n}^{\epsilon}(\xi_{0})$. For indirect phonon-assisted absorption, we calculate $\frac{\partial \mu_{\eta_i,\eta_n}^{\epsilon}(\xi)}{\partial \xi_j} \mid_{\xi = \xi_{0}}$, i.e. the change of transition moment under lattice distortion, by a finite difference method.
The numerator in Eq. (3.3) reads as the change of transition moment from an electronic state \( q_v \) to \( q_c \) when lattice is distorted from \(-\delta \xi\) configuration by \(+2\delta \xi\) to \(\delta \xi\). We use a diabatic approximation to the electronic states when the lattice is distorted by \(+2\delta \xi\) from \(-\delta \xi\), connecting the maximally overlapping adiabatic states, which have been re-computed after the change in nuclear displacements. (Recall that some lattice symmetry has been broken to make the displacements, so the old set of good quantum numbers do not otherwise make the connection obvious).

### 3.3.3 Absorption in the Near-IR-to-UV Spectral Region

Graphene displays universal absorption in the near-IR region of \(0.5 - 1.5\, eV\), and a slow, at first quadratic rise above the universal absorption \(\pi e^2 / 2h\), starting in the visible spectral region. There is a pronounced peak at \( E = 4.62\, eV\), dropping in the far UV region as in Figure 3.2. Our calculations as described above and in the Supplementary Materials, with coordinate dependence of the transition moment included, show that in the near-IR region, phononless direct absorption still dominates. Starting in the visible, phonon-assisted absorption starts to play an increasingly important role, and is responsible for the quadratic rise in the near UV, with its influence increasing into the UV. The early rise starting in the visible is not justified by nonlinearities in the Dirac cones, but nonlinearities do play a role at higher energies.

Assuming linear electronic dispersion, the density of electronic states for graphene is propor-
tional to energy. For vertical phononless direct transitions, at a laser frequency \(h\omega\), an electron at 
\(h\omega/2\) below the Fermi level is excited to an empty state at \(h\omega/2\) above the Fermi level. There is a lone 
eligible conduction band electronic state for each occupied valence state, and the total number of 
vertical transitions is proportional to \(\omega\).

For phonon assisted indirect transitions, given a laser frequency \(h\omega\), the conduction band state 
can lie anywhere with \(0 < e < h\omega\), and the hole can lie anywhere with energy \(h\omega - e > 0\) below 
the Fermi level, as long as the vertical energy gap between any given e-h pair is \(h\omega\) minus the energy 
to create the associated phonon. The total number of phonon assisted processes is proportional to 
\(\int_0^{h\omega} e(h\omega - e)de \propto \omega^3\). Even though the matrix element for each indirect process is small compared 
to that of a direct one, the cubic growth of the number of indirect processes with energy makes the 
phonon assisted contribution significant at higher laser frequency. The two processes are shown in 
Figure 3.1, left. In the absorption calculation, there is a \(1/\omega\) factor, making the contribution of direct 
processes constant linear Dirac cone dispersion region. The contribution of the phonon-assisted 
processes is seen rising at first as \(\omega^2\). The nonlinearity of the Dirac cone in the UV region enlarges 
the electronic density of states, contribute significantly to the UV excess absorption above 3 eV.

The calculations are based on a supercell with periodic boundary conditions, giving a uniform 
sampling in the Brillouin zone. There are sampling errors especially in the low energy region, where 
the number of states is insufficient to compensate the \(1/\omega\) factor accurately, as seen in figure 3.2. There 
is also a small error compared to the known universal optical absorption in the low energy region in 
Figure 3.2, but the fit is good enough to give us confidence in the numerics.
3.4 Ultrafast Hot Electronic Dynamics Upon Absorption

3.4.1 Phonon-Assisted Emission Spectrum

It is found in several experiments that "relaxed" photoluminescence takes place in the time scale of 10 femtoseconds. These experiments were interpreted assuming both the absorption process and the emission process are purely phononless direct transitions. Thus the excited electron and hole distribution is extremely non-thermal. To fit the experimental results, the argument that ultrafast relaxation of electrons and holes, reaching a thermal distribution from an extremely non-
thermal one in $5 - 10$ femtoseconds, is used. Unfortunately, the thermalization argument is compromised in that $2/3$ of the electron energy has to be arbitrarily removed.

The time scale for an electron-electron scattering process is in the order of several femtoseconds, and that for an electron-phonon scattering is in the order of picoseconds. Both time scales are too long to make the excited electrons and holes to reach full thermalization in the order of $10$ femtoseconds. To fit the experimental emission spectrum, a temperature much lower than the temperature of the excited electrons should reach is used, otherwise there is a ludicrous $9000$ Kelvin fit to the data. This shedding of electronic energy is not explained. Under the thermalization argument, the temperature should only depend on the incident laser fluence and not the laser frequency. Instead the data shows the higher the frequency, the higher the temperature.

In our theory the "thermal" electron and hole distribution is produced nascently at $t = 0$ by a dominance of indirect transitions which, although present for weak radiation, take over from the easily bleached direct transitions in a bright pulse. No relaxation is required of the nascent distribution to give the observed emission spectrum. To state it plainly, the electron-hole distribution is "born" pre-"relaxed". Furthermore, the emission thereafter is almost certainly via vastly predominant inelastic indirect channels, which are always available from any electron to any hole, and do not need to wait perfect momentum coincidence of randomly distributed electrons and holes.

The linear dispersion is assumed in our model. Assuming holes in the valence band and electrons in the conduction band are generated by phonon-assisted absorption and we ignore the matrix element for each transition for simplicity. Then the probability of a conduction band state located at $e$
above Fermi level occupied by an electron is proportional to the density of electronic states at $E_i - e$:

$$f(e) \propto (E_i - e) H(E_i - e) H(e)$$ (3.4)

where $E_i$ is the incident light energy, and $H(x)$ is the Heaviside function. Similarly, the probability of a valence band state located at $e$ below Fermi level occupied by a hole is proportional to the density of states at $E_i - e$:

$$b(e) \propto (E_i - e) H(E_i - e) H(e)$$ (3.5)

Similarly, we ignore the matrix element variation for different transitions, simulating the emission by simple process counting. Then the phonon-assisted emission intensity at $E_e$ when incident energy is $E_i$ by processes counting is:

$$\sigma(E_e) \propto \int_0^{E_i} \int_0^{E_i} \delta(E_e - (e_1 + e_2)) de_1 de_2$$ (3.6)

where the total number of excited electrons at $e$ above the fermi level is $\propto e f(e)$ and the total number of holes at $e$ below the fermi level is $\propto e h(e)$. We plot Eq (3.6) for different $E_i$'s, and a fit of the curve to experimental data is as Figure 3.3.
Figure 3.3: Emission Spectrum with Different Incident Laser Frequencies: Solid lines are experiment results of ultrafast photoluminescence from graphene under different excitation photon energies adapted from Liu. Dashed lines are emission curves obtained from equation 3.6. No relaxation of the nascent electron-hole distribution or arbitrary energy removal is needed. Indirect absorption and emission, as in figure 3.1, was used to calculate the emission spectrum, without adjustable parameters (save for the vertical scale, which was arbitrary in the experiment). Note two important features not explained by the ultrafast thermalization model, but predicted by the indirect transition model: (1) The emission does not extend beyond energy $2\hbar\omega$ (because that is the maximum indirect process separation of electrons and holes). (2) There is movement of the high energy tail toward the UV as incident frequency is raised in the indirect mechanism, but the tail should be only fluence dependent, not frequency dependent, in the nearly instant thermalization model.

The expected laser fluence $A$ dependence of the emission rate, assuming a purely indirectly produced e-h pump population and indirect emission, goes as $A^2$, exactly as seen in the experiments at higher fluences. (Any electron able to emit to any hole with both populations proportional to
A). The experiments show an \( \sim A^{-5} \) dependence at lower fluences. This may be due to the onset of indirect process dominance as saturation becomes important. The indirect processes are too numerous to get saturated, but if the source of the electrons and holes is a direct process, saturation would cut off the quadratic \( A^2 \) rise at larger pump fluences. This fact alone weighs heavily against the "direct transitions followed by ultrafast relaxation" model.

3.4.2 Pump-probe spectra

In pump-probe experiments by Breusing et. al., a starkly different probe absorption spectrum from that expected from the presumed pump e-h population leads to the understandable conclusion that ultrafast relaxation must have taken place in the femtoseconds between pump and probe. There is a totally different explanation involving indirect transitions that fits the data extremely well.

The scenario is shown in figure 3.4. Even a narrow bandwidth pump gives a probe absorption spectrum looking very much like the broad and dispersed experimental one (panel b in the figure), without any relaxation required.

There is no doubt that direct transitions are present, and we now address their impact. Because we have questioned the existence of ultrafast relaxation of the 10 fs variety, we assume the direct transitions are not much relaxed in the fastest experiments. For practical reasons, pump-spontaneous emission experiments must block emission at the incident laser wavelength, so they are not revealing about any direct emission from unrelaxed direct absorption. Pump-probe absorption is free of this problem, and indeed if direct probe absorption followed unrelaxed direct pump absorption then there should be an imprint of the pump profile on the probe. However if 20% of the absorption is
direct, and 20% of the probe is also direct, then only 4% of the probe absorption is direct-direct. The indirect signature of a direct component is a very diffuse transparency spectrum. Of greatest importance in this discussion is that the femtosecond pump and pump-probe experiments appear to be run deep in the saturated absorption regime (see, for example,\(^3\)).

An earlier pump-probe experiment on graphite, not privy to the relaxed-appearing spectral distribution, found a strongly bi-exponential decay, associating the faster decay with e-e relaxation, stating “the electronic system approaches an internal equilibrium with a characteristic time constant of 250 \(\pm 50\) fs”\(^93\). The slower ps and longer decay was associated with e-ph scattering. In fact it needs stating that the more recent experiments also see these two timescales. They are therefore stating there are three relaxation times scales, a sub 5-20 fs timescale, a 100-250 fs timescale, and a 1+ ps timescale. Here, we are maintaining the sub 5-20 fs timescale does not exist, and is an erroneous but very understandable inference from the deceptive indirect nascent e-h distribution.

3.5 Conclusion

There are two major goals of this work. The first is to provide evidence that there is no ultrafast carrier relaxation in graphene implied by several important experiments, in spite of appearances. This is a matter of interpretation backed by the theory and calculations presented here, not a criticism of the experiments. Second, we seek to release the electronic transition moment from its traditional bondage (a principle that also drove re-casting the theory of Raman scattering in graphene\(^{52}\)). If the electronic transition moment depends on phonon displacements (as it must), then phonons are produced (or destroyed) the instant a photon is absorbed, within first order light matter perturbation...
Figure 3.4: Explaining Breusing et al. results without the need for relaxation. a) (Top row) Production of the nascent e-h distribution by indirect processes in the pump stage. The dashed lines give the upper and lower bounds for the creation of electrons and holes at photon energy $\hbar \omega$, respectively. Transitions at $\hbar \omega$ (the total difference energy including created or destroyed phonons) connect the red and blue lines as they slide over the Dirac cones. The middle row shows the range of probe transitions at higher energy $\hbar \Omega > \hbar \omega$; all the pump-produced electrons and holes separately induce missing processes in the probe pulse, inducing $\Delta T/T_0 \propto \omega^3/\Omega^3$. In the bottom row, a lower energy probe photon $\hbar \Omega < \hbar \omega$ picks up only some of the electrons and holes produced by the pump as missing processes resulting in $\Delta T/T_0 \propto 3\omega/\Omega - 2$. In b), the predicted probe absorption spectrum given a narrow band pump laser at $\hbar \omega$ is shown as a black line; there is no vestige of the pump profile even with no relaxation after the pump. c) A red dashed line shows the predicted probe spectrum assuming the first pulse had the spectral distribution of the thin dashed line; the experimental distribution is the grey dotted line. The experimental probe absorption spectrum is shown as dashed at 0 fs and solid at 30 fs.
Although the traditional frozen transition moment is badly misleading in graphene. It is surely a reasonable approximation in many other situations, but they might profitably be re-examined with the electronic transition moment set free. A prime example are the indirect gapped transitions so important in many solids: it is known of course that a phonon is required to make these transitions allowed. Nearly every source we have checked leaves the matter there, as if a necessity or a momentum conservation law is an explanation of mechanism, which it is not. It is likely that an explanation is the phonon coordinate dependence of the electronic transition moment.

### 3.6 Acknowledgement

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### 3.7 Supplementary Material

The formula for the total absorption cross section $\sigma$, for incident frequency $\omega$ and polarization $\hat{\varepsilon}$, between initial Born-Oppenheimer state $|i\rangle$ and final Born-Oppenheimer state $|n\rangle$ reads

$$
\sigma_{i,n}^{\hat{\varepsilon}} = \frac{4\pi^2 \hbar^2}{m^2 \omega \hbar c} \left| \langle n | e^{i(\omega/\epsilon)(\xi \cdot x)} \hat{\varepsilon} \cdot p | i \rangle \right|^2 \delta(E_n - E_i - \hbar \omega) \quad (3.7)
$$

Making it more explicit, suppose with phonon coordinates $\xi$ and electron coordinates $r$, we write
\begin{align}
|\ell\rangle &= |\varphi(\xi, r)\rangle \chi_{m_\ell}(\xi) \\
|n\rangle &= |\varphi_{q_v q_c}(\xi, r)\rangle \chi_{m_n}(\xi) \tag{3.8}
\end{align}

$|\varphi(\xi, r)\rangle$ is the approximation to the Born-Oppenheimer electron ground state based on a Slater determinant of valence electron spin orbitals; $|\varphi_{q_v q_c}(\xi, r)\rangle$ is an electron-hole pair relative to the ground state, with an electron in the conduction band orbital $|\varphi_{q_v}(\xi, r)\rangle$ with momentum $h q_v$ and a hole in the valence band orbital $|\varphi_{q_c}(\xi, r)\rangle$ with momentum $h q_c$. $\chi_{m_n}(\xi)$ and $\chi_{m_\ell}(\xi)$ are phonon wavefunctions in the initial and final state, respectively. In the case of a lattice, each phonon coordinate is independent of each other. The potential of each phonon could be well approximated by a harmonic potential, and the wavefunction for each phonon coordinate takes the form of a Gaussian multiplied by an Hermite polynomial. $m_n$ and $m_\ell$ are series of quantum numbers indicating which phonon is excited. In the initial state, we treat phonons are in ground states, then $m_\ell = (0, 0, \ldots, 0)$. Under electric dipole approximation and with the Born-Oppenheimer approximation, the matrix element in Eq (3.7) can be expressed as

\begin{align}
\langle n | e^{i(\omega/c)(\hat{\omega} \cdot \hat{x} \cdot \hat{p})} | \ell \rangle &= \langle n | D^\dagger | \ell \rangle \\
&\approx \langle n | D^\dagger | \ell \rangle = \left< \chi_{m_n}(\xi) \right| \left< \varphi_{q_v q_c}(\xi, r) \right| D^\dagger \left| \varphi(\xi, r) \right| \chi_{m_\ell}(\xi) \tag{3.9}
\end{align}

Rewrite $\langle n | D^\dagger | \ell \rangle$ as
\begin{align}
\langle n | D^\varepsilon | i \rangle &= \langle \chi_m(\xi) | \mu^\varepsilon_{q_v,q_c}(\xi) | \chi_m(\xi) \rangle \\
\end{align}

with

\begin{align}
\mu^\varepsilon_{q_v,q_c}(\xi) &= \left\langle \varphi_{q_v,q_c}(\xi; r) \right| D^\varepsilon \left| \varphi(\xi; r) \right\rangle_r
\end{align}

The matrix elements of the dipole operator $D^\varepsilon$ between two Born-Oppenheimer electronic states is the transition moment $\mu^\varepsilon_{q_v,q_c}(\xi)$ connecting valence level $q_v$ and conduction band electronic levels $q_c$. The subscript $r$ indicates that only the electron coordinates are integrated. Note that $\mu^\varepsilon_{q_v,q_c}(\xi)$ is a function of phonon coordinates $\xi$. If we perform Taylor expansion of the transition moment around the equilibrium geometry of the lattice till the first order term of lattice distortion, we have

\begin{align}
\mu^\varepsilon_{q_v,q_c}(\xi) &= \mu^\varepsilon_{q_v,q_c}(\xi_0) + \sum_j \frac{\partial \mu^\varepsilon_{q_v,q_c}(\xi)}{\partial \xi_j} |_{\xi = \xi_0} \xi_j - \xi_0 | + O(|\xi_j - \xi_0|^2)
\end{align}

### 3.7.1 Vertical Phononless Absorption (Direct Processes)

We first consider only the constant part of the transition moment $\mu^\varepsilon_{q_v,q_c}(\xi_0)$ Eq (3.12), i.e.

\begin{align}
\sigma^\varepsilon_{i,n} = \frac{4\pi^2 \hbar}{m^2_c \omega} \left| \langle \chi_m(\xi) | \mu^\varepsilon_{q_v,q_c}(\xi_0) | \chi_m(\xi) \rangle \right|^2 \delta(E_n - E_i - \hbar \omega)
\end{align}

Promoting a small minority of the valence electrons to the conduction band leaves the lattice constants almost unchanged. The vast majority of terms in Eq (3.13), vanish, due to zero phonon wavefunction overlap and momentum mismatch. Of all the possible excited states, only a few will
have the right energy and fewer still have the right momentum. So we can further simplify Eq (3.13).

For simplicity we suppose that the lattice is initially in the phononless ground state, namely
\[ \chi_m(\xi) = \chi_{(0,0,...,0)}(\xi). \] Since there are no geometry changes involved in the process (constant transition moment), there would be no phonons generated in the final state, and the transition is purely electronic transition. Since there are no phonons involved, and the momentum of light is ignored under dipole approximation, the transition between electronic state must conserve momentum. So in Eq (3.13), we have
\[ \chi_m(\xi) = \chi_{(0,0,...,0)}(\xi) \text{ and } q_c = q_v, \] which gives vertical phononless transition, namely
\[
\sigma_{i,n}^{\text{direct}} = \frac{4\pi^2 \hbar c^2}{m_e^2 \omega} | \left\langle \chi_{(0,0,...,0)}(\xi) \left| \mu_{q_c,q_v}^{ij}(\xi) \right| \chi_{(0,0,...,0)}(\xi) \right\rangle |^2 \delta(q_c - q_v) \delta(E_n - E_i - \hbar \omega) \quad (3.14)
\]

So we can reduce the summing over all possible states (including phonon excitation) to summing over states with electron momentum and energy matched, and phonon in the ground state to get the total vertical phononless absorption. Similar arguments can also be applied to emission formula.

### 3.7.2 Phonon-Assisted Absorption (Indirect Processes)

We consider the first order terms in Eq (3.12), and these terms give phonon-assisted transition. Similarly we assume that there is no phonon in the initial state, namely \( \chi_m(\xi) = \chi_{(0,0,...,0)}(\xi). \) The first order term of the transition moment implies the dependence of the transition moment on the \( j \)th phonon coordinate, which means a type \( j \) phonon could be generated in the process. So in the final state we have phonon wavefunction \( \left\langle \chi_{(0,0,...,1,...,0)}(\xi) \right\rangle, \) where \( (0,0,...,1,...,0) \) means the \( j \)th phonon is
excited to the first excited state. The transition to higher vibrational states could be ignored because their transition matrix elements are much smaller. So we have

\[
\sigma_{i,n}^{\text{indirect}} = \frac{4\pi^2 \hbar c^2}{m^2 \omega} \left| \left\langle \chi_{i(0,0,...,0)}(\xi) \left| \frac{\partial \mu_{q_c q_v}}{\partial \xi_j} \right| \chi_{(0,0,...,0)}(\xi) \right\rangle \right|^2 \delta(E_n - E_i - \hbar \omega)
\]

(3.15)

Let \( k_j \) be the wave vector of the \( j \)th phonon. So under electric dipole approximation, we need \( q_c = q_v + k_j \) to conserve momentum, namely

\[
\sigma_{i,n}^{\text{indirect}} = \frac{4\pi^2 \hbar c^2}{m^2 \omega} \left| \left\langle \chi_{i(0,0,...,0)}(\xi) \left| \frac{\partial \mu_{q_c q_v}}{\partial \xi_j} \right| \chi_{(0,0,...,0)}(\xi) \right\rangle \right|^2 \delta(E_n - E_i - \hbar \omega) \delta(q_c - q_v - k_j)
\]

(3.16)

The sum over all possible states is reduced to those states with one phonon excited, with electronic to states making up for the momentum and energy of the phonon, leaving energy and momentum conserved. Similar arguments can also be applied to emission formula.

In support of the importance of phonon-assisted processes, reference 4 reports a nonsaturable absorption component in graphene of about 34% for 2-4 layers of graphene. The indirect transitions are extremely difficult to saturate, given their huge variety and number, and very likely the cause of the nonsaturable component, there being no other transitions in this relevant frequency range.
4.1 Abstract

The unique terahertz properties of graphene has been identified for novel optoelectronic applications. In a graphene sample with bias voltage added, there is an enhanced absorption in the far infrared region and a diminished absorption in the infrared region. The strength of enhancement(diminishment) increases with the gate voltage, and the enhancement compensates the diminishment. We find that
it is the coherence length of electrons in graphene that allows pure electronic transitions between 
states differing by small momentums and makes intraband transition possible, is responsible for the 
far infrared enhancement. Phonon assisted processes are not necessary and would not in any case 
contribute to a sum rule. This naturally leads to results obeying the general sum-rule in optical ab-
sorptions. Our prediction of the strength of enhancement(diminishment) in terms of the bias agrees 
with experiments. This is the first direct calculation we are aware of, since the prior phonon assisted 
model for indirect transition should not obey a sum rule.

4.2 Introduction

Graphene provides a unique material system to study Dirac fermion physics in two dimensions. 
Researchers have demonstrated exotic Dirac fermion phenomena in graphene, ranging from anom-
alous quantum Hall effects\textsuperscript{103,114} to Klein tunneling in low-frequency (DC) electrical transport\textsuperscript{62}. 
They also observed an optical conductance defined by the fine-structure constant\textsuperscript{88,98} and gate-
tunable infrared (IR) absorption in Dirac fermion interband transitions\textsuperscript{78,127}. Situated between DC 
electrical transport and interband optical excitation is the spectral range dominated by intraband 
transitions. This intraband dynamics response has attracted much recent attention and is expected 
to play a key role in the future development of ultrahigh-speed electronics at terahertz (THz) fre-
quencies and THz-to-mid-IR optoelectronic devices\textsuperscript{61,78,113,66,87,44,81,110,133}.

In a tunable carrier concentration graphene sample, intraband absorption increases as the Fermi 
energy, $E_F$, moves away from the Dirac point in either direction(p-type or n-type). On the other 
hand, interband absorption is possible only when the photon energy is larger than $2E_F$, see fig-
ure 4.1(a)(b)(c). In the absorption curve, the rise in the far infrared region compared to the universal absorption compensates the dip in the infrared region, figure 4.1(d) \(^{53,63}\). The capability of tuning the type and concentrations of charge carriers and conductivity in graphene is desired for many electronic and optoelectronic applications. It is essential to understand the true mechanism of the far-infrared and infrared transitions in order to make use of them in tuning the electronic properties in graphene devices.

The Drude model is used to understand the optical conductivity of graphene \(^{47,53,107,63}\). In the Drude model, electrons are treated as classical charged particles moving under an electric field. It neglects any long-range interaction between the electron and the ions or between the electrons. The only possible interaction of a free electron with its environment is via instantaneous collisions. The quantum dynamics under the model is blurred. In this work, we develop a quantum description of both intraband and interband transitions. We show that it is the coherence length of electron that makes the intraband transition in a doped graphene sample possible. Both intraband and interband transitions are due to the electronic excitations between quantum states. This naturally leads that the enhancement in the far-infrared region compensates the diminishment in the infrared region, which gives the result obeying the sum-rule.

Phonon assisted processes have been invoked to account for the intraband component \(^{87}\). Phonons seem necessary when thinking of strict momentum conservation for a non-vertical intraband transition (figure 4.1(a)). However phonon assisted processed cannot in any case contribute to the desired sum rule, since the other, compensating direct interband transitions do not involve a phonon. A sum rule cannot involve physically different processes with unrelated terms in their matrix ele-
ments. Since Bloch wave momentum is less than perfectly definite due to finite coherence lengths, momentum conservation is only approximately enforced by Bloch waves. Slightly momentum non-conserving processes may be drawn in the usual band structure diagrams.

\[ \text{Figure 4.1: Graphene far infrared and infrared region absorption: (a) is an illustration of intraband (solid arrow) and interband (dash arrow) transitions in hole-doped graphene. (b) is an illustration of the corresponding absorption spectrum for the doped (yellow) and undoped (green) case. When graphene is doped, the absorption strength below } \frac{1}{2} |E_F| \text{ is transferred to lower energy (black arrow). (c) shows the experimental gate-induced change of IR transmittance } \Delta T / T \text{ through graphene at } V_g = -70 \text{ V (hole doped) compared to transmittance at the charge neutral graphene. The spectrum shows an increase of absorption at low wave numbers in the far infrared region and a reduction of absorption at higher wave numbers in the infrared region. (d) shows the experimental integrated value of the enhancement and diminishment in optical absorption as a function of gating voltage. The change of the interband contribution is equal to that of the intraband parts. Intraband absorption increases with carrier doping, while interband transitions up to } \frac{1}{2} |E_F| \text{ become forbidden due to empty initial states. Figures (a), (c) and (d) are adapted from the work of Hornig etc.}^{53} \text{ and figure (b) is adapted from the work of Kim etc.}^{63} \]
4.3 Results and Discussion

The optical absorption of graphene in the far-infrared and infrared regions arises from two types of contributions, those from intraband and those from interband optical transitions. In the far-infrared region, the optical response is dominated by the intraband transition \(47,107\). In the mid- to near-infrared region, the optical absorbance is attributable primarily to interband transitions. This response is nearly frequency independent and is equal to a universal value determined by the fine-structure constant \(e^2/\hbar c\) in pristine graphene \(47,98\). However, the optical absorption in graphene can be controlled through electrostatic gating, which shifts the Fermi energy and induces Pauli blocking of the optical transitions \(127,78\).

When the Fermi level of graphene is shifted away from the charge neutral point, the absorption in the far-infrared region gets enhanced (compared to the universal absorption) and gets diminished in the infrared region as in figure 4.1(c). The amount of enhancement (yellow part in figure 4.1(b)) equals to the amount of diminishment (green part in figure 4.1(b)). A common argument is that the rise in the far-infrared region is due to phonon-assisted intraband processes made possible by the empty levels made available by doping, and the dip in the infrared region is due to the missing phononless vertical interband processes caused by the doping \(53\). The equivalence of the area of the far infrared rise and infrared dip is attributed to a sum rule. There are several problems however: If phonon-assisted absorption played an important role in the far-infrared region, it should make an important contribution in the infrared region. The sum rule applies to similar physical processes, and should not be used to explain the intensities of two different processes.
Figure 4.1(d) shows both the rise in the far-infrared region and the compensating dip in the infrared region as the bias voltage changes. The mild asymmetry between the hole response and electron response on either side of 0 bias is due to asymmetric carrier response when the bias is applied in different directions, even though the Dirac cone is quite symmetric in the region we are interested in. The absorption enhancement equals the absorption diminishment suggests a sum rule which should be sought relating to the same physical process. The infrared dip is clearly due to missing phononless interband electronic transitions when the Fermi level is shifted, and we must look to the far-infrared region for added phononless electronic transitions.

Are momentum conserving phononless intraband electronic absorption transitions possible? A sketch on a band diagram would suggest not (figure 4.1(a)). The intraband process lies at very low energy absorption region, which means that the transition is between two electronic states with very close wavevectors, if we consider the Bloch state in the graphene band structure. The overlap between electronic states with different wavevectors would be zero if the electron had infinite coherence length and the sample was infinitely large. However, the coherence length of electron could not be infinite in practice, and is on the order of ten nanometers. This makes the overlap between electronic states with different wavevectors not exactly zero. When two wavevectors are very close to each other, the overlap becomes significant. The major difference between two Bloch states with close momentums lies in the Bloch modulation, which is essentially plane waves with different momentum \( k_1, k_2 \). Figure 4.2(a) shows the overlap integral of two plane waves with momentum different by \( \Delta k \). The blue line is the real part of the integral, the green line is the imaginary part, and the red line is the amplitude of the integral. The light blue line is a Gaussian function fitting to the
amplitude curve. Figure 4.2(b) shows the standard deviation of the Gaussian function goes down as the coherence length goes up.

Figure 4.2: (a) Overlap integral of two plane waves with momentum different by $\Delta k$: Assuming the coherence length $l$ is 20nm, and the integral is in the range of 0 to 20nm. A $\sin(\frac{x}{l})$ decay is added to the plane wave, which guarantees the wave function goes to 0 at the boundary smoothly. The blue line is the real part of the integral, the green line is the imaginary part, and the red line is the amplitude of the integral. We fit the amplitude by a Gaussian function (light blue line), and the Gaussian is centered at 0 and has standard deviation $0.25\mu m^{-1}$. (b) Fit the overlap integral amplitude with a Gaussian function, the standard deviation of the gaussian goes down as the coherence length goes up.

The Gaussian-like behavior of the overlap of two Bloch states implies that pure electronic transition could take place even though two Bloch states have slightly different momenta. The slightly nonvertical or “wobbling” effect of the electronic transitions is enabled by the finite coherence length of the electrons, causing a coupling and broadening of the Bloch waves, which are now imperfect enforcers of momentum conservation. The momentum conservation constraint in the Bloch basis becomes a Gaussian instead of a Dirac delta function, given as Eq (4.1).

$$g(\Delta k_x, \Delta k_y) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(\Delta k_x)^2 + (\Delta k_y)^2}{2\sigma^2}},$$  \hspace{1cm} (4.1)
implying that both vertical or close to vertical processes are allowed to happen in phononless absorption. $\sigma$ controls the strictness of the momentum conservation, becoming a Dirac delta function at infinite electron coherence length $\sigma \rightarrow 0$. According to figure 4.2, we choose the standard deviation for momentum as $0.2nm^{-1}$. The electronic dispersion around the Dirac cone follows $E(q) = 3/2at |q|, t = 2.7eV, a = 0.142nm^2$. The standard deviation for momentum tolerance in terms of energy becomes $0.11eV^{-1}$.

Except for the Bloch modulation, the pure electronic transition matrix elements change only slightly at different energies. Thus we model the transition intensity between two states by considering their Bloch modulation overlap, approximated by a Gaussian function as we see qualitatively in figure 4.2. In the relevant region the electronic dispersion is quite linear, as was used used in the model. Assuming the Fermi level is shifted down from the Dirac cone by $E_f$, then the absorption at incident light energy $E$ can be expressed as

$$
\sigma(E) = \frac{1}{E} \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^E \int_0^E dE_F \int_0^E dE_e \left| E_F - (E - e) \right|
$$

\begin{equation}
g((E_F + e) \cos \phi_1 - \left| E_F - (E - e) \right| \cos \phi_2)
\end{equation}

\begin{equation}
(E_F + e) \sin \phi_1 - \left| E_F - (E - e) \right| \sin \phi_2)
\end{equation}

We set the energy of the center of Dirac cone to 0. The excited electron has energy $-(E_F + e)$, and the density of electronic states at energy $-(E_F + e)$ is proportional to $E_F + e$. The final state has energy $-(E_F - (E - e))$, and the density of states at the final state with energy is proportional to
$|E_F - (E - e)|$. The initial state has momentum proportional to $(E_F + e) \cos \delta_1, (E_F + e) \sin \delta_1)$, and the final state has momentum proportional $(|E_F - (E - e)| \cos \delta_2, |E_F - (E - e)| \sin \delta_2)$. This formula holds if the Fermi level is shifted up by $E_F$.

Figure 4.3 shows results calculated based on Eq(4.2). Figures 4.3(a) reveal the rise of absorption in the far infrared region and the dip in the infrared region when the Fermi level is shifted away from the cone center by different amounts. Figure 4.3(c) shows the corresponding area, revealing the sum rule. These areas linearly increase with the Fermi level shift, because the number of phononless electronic transition processes is proportional to the density of states of electron. The area of the rise is proportional to the number of extra processes and the area of the dip is proportional to the number of lost processes due to the applied bias.

The amount that the Fermi level shift is roughly the square root of the bias voltage. Using a simple capacitor model, $|E_F(\Delta V_g)| = \hbar v_F \sqrt{\pi |\alpha_0(\Delta V_g)|}$, where $v_F = 1 \times 10^6 m/s$ is the Fermi velocity of Dirac fermions in graphene, and $\alpha_0 \approx 7 \times 10^{10} cm^{-2} V^{-1}$ is the gate capacitance in electron charge. Figure 4.3(d) shows the integrated values of the enhanced absorption in the far-infrared region and the diminishment absorption in the infrared region as a function of the gating voltage. The trend agrees well with the experimental result in figure 4.1(d).

Figure 4.3(b) shows the changes of the absorption curve as different $\sigma$'s are used for a fixed Fermi level shift 0.5eV. The far infrared absorption gets a sharper raise and the infrared absorption gets a more significant drop when a smaller $\sigma$ is used. The sum rule implied in the model is not affected by the exact value of $\sigma$.

It is clear from our model that the rise in the far-infrared region is due to extra intraband pure
electronic transitions when the Fermi level is shifted and the dip in the infrared region is due to the lack of initial electronic state which reduces some electronic transitions. This should not be a special phenomenon in graphene, we should also be able to observe similar effects in materials such as doped semiconductors with small enough band gaps.

Low temperature transport experiments have shown that the coherence length of charge carriers in graphene is proportional to $\frac{1}{T^{\frac{1}{2}}}$ \(^{94}\). A lower temperature implies a longer electron coherence length and thus a smaller momentum tolerance according to our model. So we expect to observe a sharper far infrared absorption enhancement at a lower temperature as implied in figure 4.3(b).

4.4 Conclusion

We developed a quantum description for the intraband absorption and interband absorption in graphene. Under the framework both absorption processes are caused by the same physical mechanism, pure electronic transition between quantum states. Thus they can obey a sum rule. We have explained the rise of far infrared absorption and the dip of infrared absorption in a doped graphene, and their dependence on the gate bias. Our model naturally lead to results obeying the sum rule.

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Figure 4.3: Graphene far infrared and infrared region absorption: (a) is the simulated absorption results according to Eq (4.2) when the Fermi level is shifted away from cone center by 0.1, 0.2, 0.3, 0.4 and 0.5 eV. The plot shows the dip of absorption in the infrared region and the rise in the far infrared region. The universal absorption is also shown. (b) shows how the absorption curve changes as we choose different σ's, assuming the Fermi level is shifted away from the cone center by 0.5 eV. (c) shows the integrated values of the enhanced absorption in the far-infrared region and the diminished absorption in the infrared region as a function of the amount that the Fermi level shifted by. The enhancement compensates the diminishment. The integrated area almost increase linearly in terms of the shift amount of the Fermi level. (d) shows the integrated values of the enhanced absorption in the far-infrared region and the diminished absorption in the infrared region as a function of the gating voltage. The trend agrees well with the experiment result in figure 4.1(d).
5.1 Abstract

Intense researches exploring the electrical properties of single-wall carbon nanotubes (SWNTs) and their potential applications in electronics have been carried out since their discovery in the early
1990s. Raman spectroscopy is the most powerful tool to calibrate structures of SWNTs, which is key to their applications. In this work, Kramer-Heisenberg-Dirac (KHD) theory is applied to understand the resonant Raman spectrum of SWNTs. We find that the transition moment of SWNTs is always along the tube longitudinal direction, and this explains the dependence of Raman spectrum on incident and scattered light polarization directions. We also explain several other Raman features of SWNTs, including the difference between Raman spectrum of metallic SWNTs and that of semiconducting SWNTs, the length dependence of sideband Raman peaks, etc.

5.2 Introduction

Single-Wall Carbon Nanotubes (SWNTs) are nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a tube. There has been intense activity exploring the electrical properties of these systems and their potential applications in electronics since their discovery in the early 1990s. SWNTs with different structures display different electric properties. Raman Spectroscopy is the most promising technique which calibrates the structure of SWNTs.

SWNT Raman spectrum intensity depends on light polarization directions (direction of electric field component of light). The early polarization dependent Raman spectrum of spatially separated thin ropes composed of SWNTs were performed by Duesberg et al. and Gommans et al. The maximum signal is always observed when the polarization of the incident light is parallel to the nanotube axis regardless of scatter light polarization for all SWNT vibrational modes. This result is different from later experimental results, which measure the polarization dependence Raman in individual SWNTs by Jorio et al. and Judek et al., and this difference is due to the bundle
effect, meaning the polarization dependent Raman spectrum for single SWNT and bundle SWNTs are different. We focus on explaining the polarization dependence of individual SWNT Raman spectrum.

Several efforts have been tried to explain the polarization dependence of individual SWNT Raman spectrum. The current dominating Raman scattering theory consider the Raman process is composed of sequential electron-photon interaction and electron-phonon interaction processes, which lead to third or fourth order Raman scattering perturbation theory. The use of such a high order perturbation theory blurs the underlying physics and makes it not easy to figure out its dependence on incident light and scatter light polarizations. Under the KHD theory with Born-Oppenheimer approximation to the electron and nuclei wavefunction, the Raman process is always a second order process. The dependence on incident and scatter light polarization become very clear as we will show below.

We also show that the tube length effect on different Raman peaks and how the tube conductivity affect its Raman features.

5.3 Results and Discussion

5.3.1 Outline

We first introduce the Kramer-Heisenberg-Dirac (KHD) theory and we point out the role of transition moment in the theory, which is key to understand several SWNT Raman features. Then We display typical vibration modes in SWNTs. We then show typical Raman spectrum for metallic and
semiconducting SWNTs and explain how the tube conductivity affects Raman features. Then we show the dependence of SWNT Raman spectrum on light polarizations and explanations to such dependence come out naturally from KHD theory. Lastly, we show how the tube length affect in SWNT Raman spectrum.

5.3.2 KHD theory

KHD formula is a theory describes the cross section for scattering of a photon by quantum states.\textsuperscript{65-35} It has been successfully used in molecular systems to understand their Raman Features.\textsuperscript{122} KHD theory is also nicely used to explain extended systems such as graphene, which could be treated as the origin of SWNT, and another one-dimensional carbon conjugated system polyacetylene\textsuperscript{50}.

The KHD formula for the total Raman cross section $\Sigma$, for incident frequency $w_I$ and polarization $\rho$, scattered frequency $w_S$ and polarization $\sigma$, between initial Born-Oppenheimer electron-phonon state $|i\rangle$ and final Born-Oppenheimer electron-phonon state $|f\rangle$ via intermediate Born-Oppenheimer electron-phonon state $|n\rangle$ reads

$$
\Sigma_{\rho,\sigma}^{\rho,\sigma} = 8\pi e^4 w_I^3 w_I \frac{\alpha_{i,f}^{\rho,\sigma} \alpha_{i,f}^{\rho,\sigma}}{9\epsilon^4} \sum_n \left[ \frac{\langle f | D^{\dagger,\sigma} | n \rangle \langle n | D^{\rho} | i \rangle}{E_i - E_n + i\hbar w_I + i\Gamma_n} \right] + \left[ \frac{\langle f | D^{\dagger,\sigma} | n \rangle \langle n | D^{\rho} | i \rangle}{E_i + E_n + i\hbar w_I + i\Gamma_n} \right]$$

(5.1)

where $\Gamma_n$ is the damping factor for the excited state $|n\rangle$, accounting for events and degrees of freedom not explicitly represented. The transition moment operator $D$ controls the first order perturbative light-matter interaction. Usually the second, non-resonant term inside the square in equation
is neglected, for simplicity.

Under Born-Oppenheimer approximation, the electron-phonon states have the form of $\psi_{BO}(\xi; r) = \phi_l(\xi; r) \chi_l(\xi)$, where $r$ is electron coordinates and $\xi$ is phonon coordinates (nuclei coordinates). $\phi_l(\xi; r)$ is the approximation to the Born-Oppenheimer electron wavefunction, $\chi_l(\xi)$ is the approximation to the nuclei wavefunction. Explicitly, $|i\rangle = \phi_i(\xi; r) \chi_i(\xi)$, $|f\rangle = \phi_f(\xi; r) \chi_f(\xi)$, $|n\rangle = \phi_n(\xi; r) \chi_n(\xi)$. Then the expectation of transition moment operator in equation 5.1 could be written as: $\langle n| D^\rho |i\rangle = \langle \chi_n(\xi) \phi_n(\xi; r) | E^\xi \cdot r | \phi_i(\xi; r) \chi_i(\xi) \rangle$, and we define transition moment as $\mu^\rho_{i,n}(\xi) = \langle \chi_i(\xi) \phi_i(\xi; r) | E^\xi \cdot r | \phi_n(\xi; r) \chi_n(\xi) \rangle$. Then $\langle n| D^\sigma |i\rangle = \langle \chi_n(\xi) \mu^\sigma_{i,n}(\xi) \chi_i(\xi) \rangle$. Similarly, $\langle f| D^{\dagger \sigma} |n\rangle = \langle \chi_f(\xi) \mu^{\dagger \sigma}_{n,f}(\xi) \chi_n(\xi) \rangle$.

To have a sound transition intensity from an initial state $|i\rangle$ to a final state $|f\rangle$ via intermediate state $|n\rangle$, we need the numerator components in equation 5.1 $\langle n| D^\rho |i\rangle$ and $\langle f| D^{\dagger \sigma} |n\rangle$ be non-zero, which requires the total momentum of electron and phonon be conserved, and the real part of denominator be close to zero, which requires the energies of electron, phonon and photon be conserved.

For transition moment $\mu^\rho_{i,n}(\xi)$, the subscript $r$ means the braket is integrated over electronic coordinates, and thus the transition moment is a function of nuclei coordinates $\xi$. The phonon wavefunctions are orthogonal to each other, namely $\langle \chi_i(\xi) | \chi_n(\xi) \rangle = \delta_{i,n}$. Thus for phonon states with different number of phonons, their inner product is zero. To have valid transition between phonon states involving phonon generation or phonon annihilation, for example, generating a phonon $\xi$, we need the transition moment $\mu^\rho_{i,n}(\xi)$ has dependence on phonon coordinates $\xi$. This requires the total momentum of phonon and electron is conserved. Raman intensity is positively
related to the intensity of this dependence. We will show that for carbon nanotubes, the transition
dipole has the strongest dependence on phonon coordinates when the light is polarized along the
tube longitudinal direction and the weakest dependence on phonon coordinates when light is polar-
ized perpendicular to the tube longitudinal direction.

5.3.3 Typical vibration modes and SWNT Raman features

Typical vibrational modes include radial breathing modes (RBM), two types of G modes (one vi-
bration is along the tube longitudinal direction and another is along the perimetric direction), D
breathing mode and its overtone (usually called as G'). We choose (10,0) SWNT (semiconducting
nanotube) for the demonstration of vibrational modes and transition moments accompanied by
these modes. The typical vibrational modes of (10,0) SWNT are shown in Figure 5.1.
Figure 5.1: SWNT typical vibration modes: 4 types of non-modulation k=0 typical vibration modes in (10,0) carbon nanotube. Radial breathing mode (a), D breathing mode (b), 2 types of G modes (c) and (d).

Ideally, for each vibration mode, it contributes to two peaks in the Raman spectrum. One is the fundamental $k = 0$ peak and another is the sideband $k = 2q$ peak. The $k = 0$ peak is generated by vertical electronic transition process from an initial electronic state $k = q$ to an intermediate state $k = q$. The $k = 2q$ vibrational mode is generated by electronic transition from $k = q$ to $k = -q$. Both processes guarantee the total pseudo momentum of electron and phonon is conserved, and the value of $q$ is determined by the energy conservation of phonon, electron and photon. The $k = 2q$
peak is usually forbidden for an infinite system because of Pauli blocking, but the end of carbon nanotube always provide as a source for electron back scattering and thus we don’t need to worry about this forbidden for SWNT. It happens that one of the two peaks is missing and only one exists, but that is due to other reasons instead of lacking of electron back scattering. We give a brief analysis for these typical modes here. The typical Raman spectrum of SWNT is shown in Figure 5.2.

Figure 5.2: Typical SWNT Raman spectrum: Raman spectra from a metallic (top) and a semiconducting (bottom) SWNT at the single nanotube level. The spectra show the radial breathing modes (RBM), D-band, G-band and G’ band features, in addition to some weak features. The isolated carbon nanotubes are sitting on an oxidized silicon substrate which provides contributions to the Raman spectra denoted by ***, and these Si features are used for calibration purposes. This is reproduced from the work of Dresselhaus etc. in 2005.
For RBM, only \( k = 2q \) peak exists and the fundamental \( k = 0 \) peak is missing. This is because for \( k = 0 \) mode, all atoms stretch from and shrink towards the longitudinal axis in the tube center, and there are no other electron wavefunction redistributions accompanied with the vibration except for its move with nuclei. This leads to 0 transition moment change. For \( k = 2q \) vibration, some atoms stretch from the tube axis and some shrink towards the tube axis, and this leads to electron redistribution along longitudinal direction of the tube, and gives non-zero transition moment change in the longitudinal axis direction.

For both types of G modes, each of them has \( k = 0 \) and \( k = 2q \) peaks, four peaks in total. Each vibration mode will lead to electron wavefunction redistribution in the tube longitudinal direction, thus all of the four vibrations have nonzero transition moment change in the tube longitudinal direction.

For D breathing mode, the \( k = 0 \) peak is missing and only \( k = 2q \) peak survives. The missing of \( k = 0 \) peak is due to the three equivalent sets of D breathers which together give zero nuclei motion as the case in graphene\(^5\). The \( k = 2q \) mode breaks the equivalence of three breathers and its nuclei motion leads to nonzero transition moment change in the tube longitudinal direction.

For the overtone of D, the overtone of \( k = 0 \) D breathing mode is forbidden and \( k = 2q \) breathing mode, usually called as G', exists. The forbidden of \( k = 0 \) D breathing mode overtone and the allowance of G’ is due to the same reason as that in D breathing mode. The overtone is caused by a two-phonon process, one phonon generated in excitation, one generated in de-excitation\(^5\).

We can also tell the difference between Raman spectrum of metallic SWNTs and that of semiconducting SWNTs from Figure 5.2. One typical feature is that the relative intensity of breathing mode
overtone peak $G'$ to $G$ is bigger for metallic SWNTs than semiconducting SWNTs. We can apply the “Sliding” mechanism we discovered in graphene to understand the difference. The electronic structure of SWNTs could be derived from that of graphene. The graphene electronic dispersion takes the form of $E(k_x, k_y) \propto \sqrt{k_x^2 + k_y^2}$. For metallic SWNTs, they have states going through the Dirac cone center. Assuming the nanotube is rolled in the $y$ direction, then we can set $k_y = 0$, and we get the electronic dispersion $E(k_x) \propto |k_x|$. This gives a linear dispersion for electronic states. The linear electronic dispersion allows electronic transition could slide along the linear region, which contribute to the strong $G'$ peak in metallic SWNTs. For semiconducting SWNTs, there are no electronic states going through the cone center, and so the electronic dispersion takes the form of $E(k_x) \propto \sqrt{k_x^2 + k_0^2}$, which is nonlinear in terms of the distance from the cone center. Then “Sliding” mechanism could not be applied to semiconducting SWNTs, and thus the overtone $G'$ has a smaller intensity.
5.3.4 Transition moment in real space

Figure 5.3: SWNT typical vibrational modes transition moment in real space: the change of transition moment in the tube longitudinal direction (horizontal direction in the plots) for (10,0) nanotube led by typical vibrational modes of SWNT. To show the change of transition moment at each atom site more clearly, the nanotube is unfolded along tube longitudinal direction. The bloch modulation for vibrational modes and electronic wavefunction is along the tube longitudinal direction. For (a) RBM (atoms shrink towards tube center are plotted bigger, and stretch from tube center are plotted smaller), (b) breathing D mode, (d) $G^+$ sideband mode, (f) $G^-$ sideband mode, the electron is excited from valence band with wavevector $K + q$ to conduction band with wavevector $K - q$, and phonon modes have modulation $\pm q$. For (c) $G^+$ fundamental mode, (e) $G^-$ fundamental mode, the electron is vertically excited from $K + q$ in valence band to $K + q$ in conduction band, and phonon modes have wavevector $\alpha$.
Figure 5.3 shows tube axial direction transition moment change of a (10,0) SWNT for RBM \( k = 2q \) mode, four types of G modes and \( k = 2q \) D breathing mode. The transition moment is calculated by a nearest neighbour tight binding approach with hopping parameters depending on bond length. The basis function at each atom site is \( 2p_z \) orbital, and the hopping parameter describes the interaction between two nearest neighbour \( 2p_z \) orbitals.

For the change of transition moment to have a significant value, it requires the phonon modulation pattern matches with the modulation pattern of electronic wavefunctions in the excited state and ground state. Explicitly, if the electron is vertically excited, then the phonon accompanies the process should have \( k = 0 \) momentum, and if the electron is excited from state with momentum \( q \) to state with momentum \(-q\), then the phonon in the process should have \( k = 2q \) momentum. This gives the momentum conservation requirement.

For these vibrational modes we describe, they have circular symmetry in the tube perimetric direction. Thus there won’t be transition moment change accompanying these vibrations when light is polarized in any direction perpendicular to the tube longitudinal direction. Only when the light electric field direction has component in the tube longitudinal direction, then there is change of transition moment, and when light is polarized along the tube longitudinal direction, it has the largest transition moment change.
5.3.5 Experimental results and explanation

**Figure 5.4**: SWNT light polarization dependence Raman Spectrum: Normalized intensity $I(\varphi)/I(\alpha)$ angular $\varphi$ dependence of seven selected Raman modes (from bottom to top: RBM, G, G’, D, M, 823+867 cm$^{-1}$, 1042 cm$^{-1}$) from one light spot on the isolated semiconducting SWNT sample in two configurations: VV (a) and VH (b). The continuous lines show a fit of data points with the functions $\cos^4(\varphi)$ (a) and $\cos^2(\varphi)\sin^2(\varphi)$ (b). (c) Raman spectra for selected configurations. This is reproduced from the work of Judek et al. in 2009$^{59}$.

Judek et al. showed the light polarization dependence Raman spectrum in 2009$^{59}$. In Figure 5.4(a), the incident light electric field direction and scatter light electric field direction are parallel, and have an angle $\varphi$ with tube longitudinal direction, called as VV configuration. In Figure 5.4(b), the incident light electric field direction and scatter light electric field direction are perpendicular, and incident light polarization direction has an angle $\varphi$ with tube longitudinal direction, scatter light polarization direction has an angle $\varphi + \frac{\pi}{2}$, called as VH configuration. From top to bottom are the
relative intensities of RBM, G, G', D, M, 823 + 867 cm⁻¹, 1042 cm⁻¹ mode depending on \( \phi \). In VV configuration, it shows for all the modes, the Raman intensity is proportional to \( \cos^4 \phi \) and in VH configuration, the Raman intensity is proportional to \( \cos^3 \phi \sin^2 \phi \).

The explanation of the light polarization angle dependence is very natural from the transition moment in KHD expression. Ignoring the non-resonant term in equation 5.1, the probability of going from an initial state \(|i\rangle\) to a final state \(|f\rangle\) is:

\[
\alpha_{i,f}^{\sigma} = \frac{1}{\hbar} \sum_n \left[ \frac{\langle f | D^{\dagger} \sigma | n \rangle \langle n | D^{\dagger} | i \rangle}{E_i - E_n + \hbar \omega_f - i\Gamma_n} \right] 
\]

\[
= \frac{1}{\hbar} \sum_n \left[ \frac{\langle \chi_f (\xi) \sigma | n \rangle_{n,f}^{\dagger} \langle \chi_n (\xi) \rangle_{i,n} \langle \chi_n (\xi) \rangle_{i,n}}{E_i - E_n + \hbar \omega_f - i\Gamma_n} \right] 
\]

As we’ve pointed out, due to the circular symmetry of SWNT in the perimetric direction, the transition moment is almost 0 when light is polarized perpendicular to the longitudinal direction of SWNT, and the transition moment is biggest when light is polarized along the longitudinal direction of SWNT for all vibrations. The phonon in SWNT system has bloch modulation along the longitudinal direction. When a phonon is generated, there would be electron wavefunction redistribution along the longitudinal direction, and the major change of transition moment is also along the longitudinal direction of SWNT. The transition moment, also the probability of going from an initial state \(|i\rangle\) to a final state \(|f\rangle\) is proportional to the electric field projected to the tube axial direction. \( u_{n,f}^{i\sigma} = \cos \varphi^\sigma u_{n,f}^{i} \), where \( \varphi^\sigma \) is the angle between transition moment
change direction (tube axial direction for SWNT) and incident light polarization direction, and $\phi^\rho$ is the angle between transition moment change direction and scatter light polarization direction. $u^\dagger_{n,f}$ and $u^\rho_{i,n}$ don’t depend on light polarization. So

$$\alpha^{\rho,\sigma}_{i,f} = \cos \phi^\sigma \cos \phi^\rho \sum_n \frac{\langle \chi_f (\xi) | u^\dagger_{n,f} (\xi) | \chi_n (\xi) \rangle \langle \chi_n (\xi) | u_{i,n} (\xi) | \chi_i (\xi) \rangle}{E_i - E_n + \hbar \omega_f - i \Gamma_n}$$

$\propto \cos \phi^\sigma \cos \phi^\rho$$

Then for VV configuration, $\phi^\sigma = \phi^\rho = \phi$, and $\alpha^{\rho,\sigma}_{i,f} \propto \cos \phi^\sigma \cos \phi^\rho = \cos^2 \phi$. For VH configuration, $\phi^\sigma = \phi$, $\phi^\rho = \phi + \pi$, and $\alpha^{\rho,\sigma}_{i,f} \propto \cos \phi^\sigma \cos \phi^\rho = \cos \phi \sin \phi$. Then Raman intensity is proportional to the square of $\alpha^{\rho,\sigma}_{i,f}$, namely $\Sigma^{\rho,\sigma}_{i,f} \propto \cos^4 \phi$ for VV configuration and $\Sigma^{\rho,\sigma}_{i,f} \propto \cos^2 \phi \sin^2 \phi$ for VH configuration. This is in good agreement with experimental results.

According to KHD theory and transition moment analysis, we could also expect antenna effect of Raman spectrum in other one dimensional systems. For a one dimension system, from the perspective of a phonon, nuclei have the same vibration pattern from one unit cell to another, and the pattern is modulated by bloch wave function. So the vibration direction is the same from unit cell to unit cell, and the vibrations are different only by the intensity. Then in the transition moment $u^\dagger_{i,n} (\xi) = \langle \phi_n (\xi; r) | E^\sigma \cdot r \phi_i (\xi; r) \rangle$ and $u^\rho_{n,f} (\xi) = \langle \phi_f (\xi; r) | E^\sigma \cdot r \phi_n (\xi; r) \rangle$, the change of $\langle \phi_n (\xi; r) | r \phi_j (\xi; r) \rangle$ and $\langle \phi_j (\xi; r) | r \phi_n (\xi; r) \rangle$ have the same direction for all unit cells. Thus for the whole one dimensional system, the change of transition moment has the biggest value when the light is polarized in this particular direction. We define $\phi^\sigma$ as the angle between transition
moment change direction and incident light polarization direction, and \( \phi^c \) as the angle between transition moment change direction and scatter light polarization direction, the Raman intensity is always proportional to \( \cos^2 \phi^c \cos^2 \phi^\rho \).

5.3.6 SWNT Length Dependent Raman Spectrum

Simpson and Chou show that ratio between the disorder-induced D peak intensity to G’ Raman peak intensity or G peak intensity decays as a function of the nanotube length \( L \), proportional to \( 1/L \). As the carbon nanotube length becomes shorter, the ends of the molecule become acces-

Figure 5.5: Length dependence of the D/G’ ratio for the DNA (red circles) and sodium deoxycholate (blue squares) dispersed SWCNTs. The D/G’ (and D/G) ratio for both decreases with increasing SWCNT length. Equivalent length fraction pairs A and B are indicated. Inset: D/G’ ratio on a log-log scale.

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29
118, 29
sible to a higher fraction of the electrons, increasing the backscattering efficiency. The $k = 2\theta D$ intensity falls like the inverse length of the tube length. This agrees with result we discovered in polyacetylene\textsuperscript{50}.

5.4 Conclusion

We apply the KHD theory to understand SWNTs Raman spectrum. The transition moment plays a key role in the understanding of light polarization dependence of SWNTs Raman spectrum. The intensity of Raman spectrum is proportional to the change of transition moment, and the change of transition moment is proportional to the amplitude of tube longitudinal component of light electric field for SWNT. “Sliding” mechanism discovered in the graphene applies to understand the difference between Raman spectrum of metallic and that of semiconducting nanotubes. The length dependence relationship for sideband Raman peaks discovered in polyacetylene applies to nanotubes.
6.1 Introduction

The phonon-assisted light absorption in materials is an important optical process both from a fundamental and from a technological point of view. For indirect-band-gap semiconductors phonon-assisted processes determine the onset of absorption. For example in silicon, the value of the direct band gap (3.4 eV) is large and precludes optical absorption in the visible. However, silicon is com-
mercially successful photovoltaic material because of the indirect optical transitions that enable photon capture in the spectral region between the indirect (1.1 eV) and direct band gaps.

Despite their importance, at present, only a very limited number of first-principles studies of phonon-assisted optical absorption spectra exist. Ab initio calculations of direct optical absorption spectra including excitonic effects have already been performed for Si and other bulk semiconductors and the underlying methodology is presently well established\textsuperscript{105}. However, Phonon-assisted absorption studies are more involved, and the associated computational cost is much higher than the direct case. The traditional calculation of the indirect absorption coefficient involves a double sum over $k$ points in the first Brillouin zone (BZ) to account for all initial and final electron states. In addition, these sums must be performed with a very fine sampling of the zone to get an adequate spectral resolution. The computational cost associated with these BZ sums is in fact prohibitive with the usual methods.

In this chapter, we provide a new paradigm based on Born-Oppenheimer approximation and light-matter interaction to calculate the phonon-assisted absorption process. Under the paradigm, we reduce the phonon-assisted absorption from a second order process to a first order process.

### 6.2 Silicon Electronic and Phonon Properties

Silicon crystallizes in the same pattern as diamond, in a cubic structure which is usually called “two interpenetrating face-center cubic” primitive lattices. The unit cell is shown as in Figure 6.1(a). Lines between silicon atoms in the lattice illustrate nearest-neighbor bond, and the bond length is 0.235nm. The first Brillouin zone of the lattice has a truncated octahedron shape as shown in Fig-
ure 6.1(b). Silicon is an indirect band gap semiconductor as shown in Figure 6.1(c). The top of the valence band locates at $\Gamma$ point and the bottom of its valence band locates around $X$ point. The indirect band gap is about $1.1eV$ as indicated by the red arrow and the direct band gap is about $4.3eV$ as indicated by the blue arrow.

Figure 6.1: Silicon Structure and Electronic Properties: (a) Silicon unit cell. Lines between silicon atoms in the cell illustrate nearest-neighbor bond, and the bond length is $0.235nm$. (b) The first Brillouin zone of silicon has a truncated octahedron shape. (c) Silicon electronic band structure and density of electronic states (DOS). The top of the valence band locates at $\Gamma$ point and the bottom of its valence band locates around $X$ point. The red arrow indicates the indirect band gap which is about $1.1eV$ and the blue arrow indicates the direct band gap which is about $4.3eV$. The right panel shows the density of electronic states.$^{102}$
Figure 6.2(a) is the phonon dispersion relation of silicon. Silicon unit cell has two atoms and so there are six phonon branches in the dispersion relation, three acoustic branches and three optical branches. The large direct band gap of silicon implies there are no pure electronic transitions in the visible frequency, but phonon-assisted indirect transitions. In 1973, Nishino etc. performed a low-temperature experiment and estimated the relative contributions to indirect absorption by different phonons as shown in Figure 6.2(b). They estimated that the transition matrix element for TO phonon assisted indirect absorption was 0.110ℏ/Å, 0.0367ℏ/Å for LO phonon and 0.0178ℏ/Å for TA phonon.

Figure 6.2: Silicon Phonon Properties: (a) Silicon phonon dispersion. Silicon unit cell has two atoms and so there are six phonon branches in the dispersion relation, three acoustic branches and three optical branches. Solid lines are calculated results and empty circles and stars are experimental results. (b) Phonon-assist transition intensities caused by transverse acoustic(TA) vibrational mode, transverse optical(TO) vibrational mode and longitudinal optical(LO) vibrational mode in silicon at 1.8K.
6.3 Phonon-Assisted Absorption Calculation Method

Direct electronic transitions calculation methods are well established, but phonon-assisted absorption studies are more involved due to that the associated computational cost is much higher than the direct case. We provide a new paradigm based on Born-Oppenheimer approximation and light-matter interaction to calculate the phonon-assisted absorption process. Under the paradigm, we reduce the phonon-assisted absorption from a second order process to a first order process.

The full Hamiltonian of a lattice could be written as:

$$ H = \sum_{nuc} -\frac{p_{nuc}^2}{2M_{nuc}} + \sum_{ele} -\frac{p_{ele}^2}{2m_e} + V_{nuc} + V_{ele} + V_{ele-nuc} $$  (6.1)

We apply the formalism of time-dependent perturbation theory to the interactions of lattice system with the classical radiation field. By a classical radiation field we mean the electric or magnetic field derivable from a classical radiation field. The light matter interaction reads

$$ H_{int} = \sum_{ele} -\frac{e}{2m_e c} \left( p_{ele} \cdot A + A \cdot p_{ele} \right) + \frac{e^2}{2m_e c^2} A \cdot A $$  (6.2)

$$ + \sum_{nuc} \frac{Q_{nuc}}{2M_{nuc} c} \left( p_{nuc} \cdot A + A \cdot p_{nuc} \right) + \frac{Q_{nuc}^2}{2M_{nuc} c^2} A \cdot A $$

where $A$ is the vector potential of the light satisfying $\nabla \cdot A = 0$. The second order term $A \cdot A$ could be omitted. The second sum over nuclei could also be ignored for absorption because it gives zero matrix elements. The interaction Hamiltonian reduces to
\[ H_{\text{int}} = \sum_{\text{ele}} -\frac{e}{2m_e c} (p_{\text{ele}} \cdot A + A \cdot p_{\text{ele}}) \]  

(6.3)

Then the formula for the total absorption cross section \( \sigma \), for incident frequency \( \omega \) and polarization \( \epsilon \), between initial Born-Oppenheimer state \( |i\rangle \) and final Born-Oppenheimer state \( |n\rangle \) could be derived as

\[
\sigma_{\epsilon,i,n} = \frac{4\pi^3 \hbar^3 \epsilon^2}{m_e^2 \omega \hbar c} \left| \langle n | e^{i(\omega/\epsilon)(\hat{r} \cdot \hat{x})} \hat{r} \cdot p | i \rangle \right|^2 \delta(E_n - E_i - \hbar \omega)
\]  

(6.4)

Making it more explicit, suppose with phonon coordinates \( \xi \) and electron coordinates \( r \), we write

\[
|i\rangle = \left| \varphi(\xi; r) \right\rangle \chi_{m_i}(\xi)
\]

\[
|n\rangle = \left| \varphi_{q_c q_v}(\xi; r) \right\rangle \chi_{m_n}(\xi)
\]  

(6.5)

\( \left| \varphi(\xi; r) \right\rangle \) is the approximation to the Born-Oppenheimer electron ground state based on a Slater determinant of valence electron spin orbitals; \( \left| \varphi_{q_c q_v}(\xi; r) \right\rangle \) is an electron-hole pair relative to the ground state, with an electron in the conduction band orbital \( \left| \varphi_{q_c}(\xi; r) \right\rangle \) with momentum \( \hbar q_c \) and a hole in the valence band orbital \( \left| \varphi_{q_v}(\xi; r) \right\rangle \) with momentum \( \hbar q_v \). \( \chi_{m_i}(\xi) \) and \( \chi_{m_n}(\xi) \) are phonon wavefunctions in the initial state and final state respectively. In the case of a lattice, each phonon coordinate is independent of each other. The potential of each phonon could be well approximated by a harmonic potential, and the wavefunction for each phonon coordinate takes the form of a gaussian multiplied by an Hermite polynomial. \( m_n \) and \( m_i \) are series of quantum numbers.
indicating which phonon is excited. In the initial state, we treat phonons are in ground states, then
\[ m_i = (0, 0, \ldots, 0). \]
Under electric dipole approximation and with the Born-Oppenheimer approximation, the matrix element in Eq (3.7) can be expressed as

\[
\langle n | e^{i(\omega/c)(\hat{n} \cdot \mathbf{p})} | i \rangle \approx \langle n | D^\xi | i \rangle = \left\langle \chi_{m_i}(\xi) \left| \sum_{j} \frac{\partial \mu_{q, q_v}}{\partial \xi_j} \bigg|_{\xi = \xi_0} \right| | \chi_{m_i}(\xi) \right\rangle.
\]

Rewrite \( \langle n | D^\xi | i \rangle \) as

\[
\langle n | D^\xi | i \rangle = \left\langle \chi_{m_i}(\xi) \right| \mu_{q, q_v}^\xi(\xi) \left| \chi_{m_i}(\xi) \right\rangle
\]
with

\[
\mu_{q, q_v}^\xi(\xi) = \left\langle \phi_{q, q_v}(\xi; r) \right| D^\xi \left| \phi_{q, q_v}(\xi; r) \right\rangle.
\]

The matrix elements of the dipole operator \( D^\xi \) between two Born-Oppenheimer electronic states is the transition moment \( \mu_{q, q_v}^\xi(\xi) \) connecting valence level \( q_v \) and conduction band electronic levels \( q_c \). The subscript \( r \) indicates that only the electron coordinates are integrated. Note that \( \mu_{q, q_v}^\xi(\xi) \) is a function of phonon coordinates \( \xi \). If we perform Taylor expansion of the transition moment around the equilibrium geometry of the lattice till the first order term of lattice distortion, we have

\[
\mu_{q, q_v}^\xi(\xi) = \mu_{q, q_v}^\xi(\xi_0) + \sum_j \frac{\partial \mu_{q, q_v}^\xi(\xi)}{\partial \xi_j} \bigg|_{\xi = \xi_0} \xi_j - \xi_0 | + O(|\xi_j - \xi_0|^2)
\]
The constant part of the transition moment $\mu^i_{q_c,q_v}(\xi_0)$ Eq (6.9) is responsible for vertical phononless absorption and first and higher order terms contributes to phonon-assisted absorption.

Here we consider the contribution of first order terms in Eq (6.9) to phonon-assisted transition. We assume that there is no phonon in the initial state, namely $\chi_m(\xi) = \chi(0,0,...,0)(\xi)$. The first order term of the transition moment implies the dependence of the transition moment on the $j$th phonon coordinate, which means a type $j$ phonon could be generated in the process. So in the final state we have phonon wavefunction $\langle \chi(0,0,...,1,...,0)(\xi) \rangle$, where $(0,0,...,1,...,0)$ means the $j$th phonon is excited to the first excited state. The transition to higher vibrational states could be ignored because their transition matrix elements are much smaller. So we have

$$\sigma_{i,n} \propto 4\pi^2 \frac{e^2}{m^2 \omega} \frac{\hbar}{c} \left| \left\langle \chi_{(0,0,...,1,0)}(\xi) \right| \frac{\partial \mu^i_{q_c,q_v}(\xi)}{\partial \xi_j} \right|_{\xi=\xi_0} \left| \chi_{(0,0,...,0)}(\xi) \right\rangle \right|^2 \delta(E_n - E_i - \hbar \omega)$$

(6.10)

Let $k_j$ be the wave vector of the $j$th phonon. So under electric dipole approximation, we need $q_c = q_v + k_j$ to conserve momentum, namely

$$\sigma_{i,n} \propto 4\pi^2 \frac{e^2}{m^2 \omega} \frac{\hbar}{c} \left| \left\langle \chi_{(0,0,...,1,0)}(\xi) \right| \frac{\partial \mu^i_{q_c,q_v}(\xi)}{\partial \xi_j} \right|_{\xi=\xi_0} \left| \chi_{(0,0,...,0)}(\xi) \right\rangle \right|^2 \delta(E_n - E_i - \hbar \omega) \delta(q_c - q_v - k_j)$$

(6.11)

The sum over all possible states is reduced to those states with one phonon excited, with electronic
to states making up for the momentum and energy of the phonon, leaving energy and momentum conserved. Similar arguments can also be applied to emission formula.

For indirect phonon-assisted absorption, we need calculate \( \frac{\partial \mu^{\xi}_{q, q_v}}{\partial \xi_j} \bigg|_{\xi = \xi_0} \), i.e. the change of transition moment under lattice distortion, by a finite difference method.

\[
\frac{\partial \mu^{\xi}_{q, q_v}(\xi)}{\partial \xi_j} \bigg|_{\xi = \xi_0} = \frac{\mu^{\xi}_{q, q_v}(\xi + \delta \xi) - \mu^{\xi}_{q, q_v}(\xi - \delta \xi)}{2 \mid \delta \xi \mid}
\]  \hspace{1cm} (6.12)

The numerator in Eq (6.12) reads as the change of transition moment from an electronic state \( q_v \) to \( q_e \) when lattice is distorted from \(-\delta \xi\) configuration by \(+2\delta \xi\) to \(\delta \xi\). We use a diabatic approximation (figure 6.3(a)) to the electronic states when the lattice is distorted by \(+2\delta \xi\) from \(-\delta \xi\), connecting the maximally overlapping adiabatic states, which have been re-computed after the change in nuclear displacements. (Recall that some lattice symmetry has been broken to make the displacements, so the old set of good quantum numbers do not otherwise make the connection obvious).
Figure 6.3: Silicon Electronic Structure Change Under Lattice Distortion: (a) An illustration of diabatic path and adiabatic path. (b) A longitudinal optical vibrational mode in silicon. (c) Silicon electronic band structure changes under lattice distortion by the vibrational mode in (b). The amplitude of each atom displacement is small such that the total displacement is normalized to 1Å.

Figure 6.3 illustrates the necessity of using the diabatic path to calculate the transition moment derivative. Figure 6.3(b) shows a typical longitudinal optical phonon mode in a $3 \times 3 \times 3$ silicon supercell. Figure 6.3(c) left is the electronic band structure calculated based on a $3 \times 3 \times 3$ supercell in the equilibrium geometry and the right plot is the electronic band structure when the lattice is distorted according to the phonon mode in (b). The amplitude of each atom displacement is small such that the total displacement is normalized to 1Å. Under the distortion, the recalculated elec-
tronic band structure changes significantly compared to electronic structure in the equilibrium lattice geometry. The significant change of the band structure implies that the electronic structure had to change drastically to follow the lattice vibrations, if adiabatic path was the correct picture. Degenerate states are quite common at the Γ point as in figure 6.3(c) left. The drastic change is even worse when a lattice vibrational mode splits the degeneracy of an electronic state. A more physically correct picture should be that when lattice vibrates, electrons follow the diabatic path, which connects the maximally overlapping adiabatic states. This agrees with the validity of using equilibrium electronic band structure to do analysis even when the temperature is usually nonzero and nuclei are vibrating. When lattice vibrates around its equilibrium geometry, electron usually couldn’t follow the abrupt change to reach the new adiabatic states, and electrons tend to stay around states in the equilibrium lattice geometry. That’s why the equilibrium electronic structure largely gives the correct picture even though the lattice is usually not frozen at 0 K.
6.4 Preliminary Results

Figure 6.4: (a) Phonon density of states at the $\Gamma$ point: There are 750 phonon modes in the $5 \times 5 \times 5$ supercell. Top: histogram of the energy distribution of 750 phonon modes. Bottom: smoothed density of phonon modes energies. (b) Density of the electronic of states at $\Gamma$ point in the $5 \times 5 \times 5$ supercell. Left: histogram of the energy distribution of $\Gamma$ point electronic states. Right: Electronic band structure of the supercell. The vertical blue line indicates the Brillouin zone $\Gamma$ point. Horizontal blue lines indicate the band gap.

We use a $5 \times 5 \times 5$ silicon supercell to do the calculation. There are 250 silicon atoms in the supercell. Each atom has 3 degrees of freedom for translational motion, and so there are 750 vibrational modes in the supercell. The energy distribution of the 750 vibrational mode is as Figure 6.4(a). The energy distribution largely agrees with the phonon density of states in Figure 6.2(a). Figure 6.4(b) is the electronic band structure of the supercell. Left panel shows the energy distribution of $\Gamma$ electronic
states, which largely agrees with the pattern in Figure 6.1(c). The discreteness of the phonon energies and Γ electronic states energies indicate that sampling points in the original unit cell Brillouin zone are not dense enough to get the accurate density of states. We haven’t been able to use a bigger supercell for denser sampling points due to the limit of our calculation ability. Figure 6.5 shows when the supercell size gets $20 \times 20 \times 20$, the density of Γ point electronic states converge to the exact density of states.

Figure 6.5: (a) Electronic density of states at the Γ point: Left: result by Noffsinger\textsuperscript{102}. Middle: density of Γ point electronic states from a $10 \times 10 \times 10$ supercell calculation. Right: density of Γ point electronic states from a $20 \times 20 \times 20$ supercell calculation.

For a $5 \times 5 \times 5$ silicon supercell, we calculate the phonon assisted absorption. Figure 6.6(a) shows the calculated phonon assisted absorption spectra. The trend of phonon-assisted absorption goes
up as light frequency goes up. However, the absorption curve is not smoothed due to the sampling points in the original Brillouin zone is not dense enough. We can expect smoother curve as we go to bigger supercells. Figure 6.6(b) shows the contribution of each phonon mode to indirect transitions. Except for low energy acoustic modes, most phonon modes contribute similarly to indirect transitions.

Figure 6.6: Silicon Phonon Assisted Absorption: (a) Phonon assisted absorption calculated from the $5 \times 5 \times 5$ supercell. The curved is not smooth due to the Brillouin sampling is not dense enough. (b) Contribution to the indirect phonon-assisted transition of each phonon: The plot shows the contribution of each phonon mode in the $5 \times 5 \times 5$ supercell to indirect transitions below energy $2.5 eV$. 

References


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