Optical Studies of Electron-Phonon Interactions in Two-Dimensional and One-Dimensional Materials

By

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A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate Division of the University of California, Berkeley

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Summer 2019
Abstract

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Reduced-dimensionality nanostructures have long attracted interest in the physics and materials science communities. Zero-dimensional structures such as quantum dots, one-dimensional structures such as carbon nanotubes, and two-dimensional materials such as graphene and transition metal dichalcogenides have all exhibited unique properties as a result of their dimensionality and quantum confinement. Optical spectroscopy has proven to be a versatile tool to study and characterize these materials. Linear optical measurements such as absorption and photoluminescence, scattering measurements such as Raman spectroscopy, nonlinear measurements such as higher harmonic generation, and ultrafast time-resolved measurements have all provided extensive information about the electronic and optical properties and dynamics of nanomaterials.

Many nanomaterials possess strong electron-phonon coupling, which can affect their optical and electronic properties. Here, we employ various optical spectroscopies to investigate electron-phonon interactions in nanomaterials. First, we study the coupling between the electronic valley degree of freedom and Raman scattering in monolayer MoS$_2$, a semiconducting transition metal dichalcogenide. We find that the valley optical selection rules on exciton resonances can affect Raman scattering by modifying the Raman selection rules expected from the symmetry of the material. Second, we study exciton-phonon coupling in semiconducting carbon nanotubes by performing optical Stark spectroscopy. We observe a strong phonon-mediated optical Stark effect in the nanotubes, which enables us to quantify the interactions between phonon-dressed states and exciton states. These studies show that optical spectroscopy is an effective tool to probe electron-phonon interactions in reduced-dimensionality materials.
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Acknowledgements

There are many people who have provided me with invaluable assistance and encouragement over the course of my time in graduate school. First, I would like to thank my advisor, Feng Wang, for his patience, thoughtfulness, kindness, and insightful guidance. His creative ideas and rigorous physical reasoning have served as a model for me for how to effectively conduct and interpret scientific studies. Many current and former students and postdocs in the group have taught me useful experimental techniques and physics concepts, have served as helpful collaborators, and have made my time in the group much more enjoyable. They include Long Ju, Jonghwan Kim, Xiaoping Hong, Jason Horng, Chenhao Jin, Sufei Shi, Bo Zheng, Zhiwen Shi, Hui Ling Han, Hans Kleeman, Ji-Hun Kang, Rai Kou-Takahashi, Hui Shi, Chaw Keong Yong, Chan-Shan Yang, Patrick Gallagher, Halleh Balch, Lili Jiang, Sheng Wang, Yudan Su, Iqbal Utama, Tairu Lyu, Emma Regan, Danqing Wang, Shaoxin Wang, Wenyu Zhao, Sihan Zhao, Guorui Chen, Seok Jae Yoo, Zuocheng Zhang, and Yinchuan Lv. I would also like to thank Ron Shen for always being available as a source of friendly scientific advice and wisdom.

I am grateful to Mike Crommie, Ming Wu, Norm Yao, and Xiang Zhang for serving on my qualifying exam committee or thesis committee.

I would also like to extend my thanks to the staff of the Physics department, who were always available for assistance and made my time at Berkeley go much more smoothly. They include Donna Sakima, Anne Takizawa, Joelle Miles, Eleanor Crump, Anthony Vitan, and Carlos Bustamante.

Lastly, I would like to thank my parents and brother for their continuous support and encouragement on this journey.
1. Introduction

The physics of reduced dimensionality nanostructures has long been a prominent research topic in condensed matter physics and materials science. Quantum effects can have a large impact on the properties of nanostructures. Strong quantum confinement in quantum dots leads to discrete electronic states that are similar to those of single atoms and molecules and are not often found in solid state systems. One-dimensional carbon nanotubes have exhibited many body effects and quantum conductance. Two-dimensional semiconductor quantum wells have led to the discovery of new electronic phases such as two-dimensional electron gasses that can exhibit a variety of quantum Hall effects. More recently, two dimensional materials such as graphene and transition metal dichalcogenides have exhibited relativistic, massless charge carriers, strong many-body effects, and unique valley electronic structures.

Optical spectroscopy is a versatile tool to characterize and understand nanomaterials. A photon is essentially an oscillation of the electromagnetic field at a given frequency. Thus, optical spectroscopy with light of a given energy can be thought of as measuring the electronic conductivity or susceptibility at that frequency. Linear optical measurements like absorption and photoluminescence can give information about the electronic structure of a material and provide information about interband and intraband electronic transitions and excited quasiparticle recombination processes. Light scattering spectroscopy, like Raman spectroscopy, can give insights into the interactions of light and electrons with excitations like phonons that can cause scattering. Nonlinear optical spectroscopy can provide information about higher order susceptibilities and reveal interesting nonlinear effects like higher harmonic generation. Ultrafast time-resolved spectroscopy can study the dynamics of a photoexcited material and provide insight into the processes involved in excitation, thermalization of hot charge carriers, and relaxation back to the initial state through the transfer of energy from the excited carriers to other parts of the system. Controlling the polarization of the incident or measured light in any of the above techniques can reveal information about the selection rules and underlying symmetries of the relevant quantities to a given optical process.

Many nanomaterials possess strong electron-phonon coupling, which can play a large role in determining their electronic and optical properties. In this thesis, we employ both linear and nonlinear, time resolved optical spectroscopy to study electron-phonon interactions in two types of nanomaterials. In Chapter 2, we utilize Raman scattering spectroscopy to investigate interactions between valley excitons and phonons in monolayer MoS$_2$, a transition metal dichalcogenide. We find that the valley optical
selection rules influence Raman scattering for excitations on resonance with the valley excitons and can modify the Raman selection rules expected from the symmetry of the material. In Chapter 3, we carry out optical Stark spectroscopy on semiconducting carbon nanotubes to study coupling between exciton and phonon states. We find that semiconducting carbon nanotubes exhibit a strong phonon-mediated optical Stark effect, which allows us to quantify the coupling between the relevant exciton and phonon states. Overall, we show that optical spectroscopy is a useful tool to study electron-phonon interactions in nanomaterials.

2. Influence of Valley Circular Dichroism on Resonant Raman Scattering in Monolayer MoS$_2$

2.1 - Introduction and Chapter Overview

The discovery of graphene in 2004 instigated a wave of scientific research into layered two-dimensional (2D) materials with novel electronic, optical, thermal, and mechanical properties [1–5]. In the past decade, advances in material preparation techniques, sample identification and characterization, and sample transfer and fabrication have driven continued exploration into additional classes of layered 2D materials, such as transition metal dichalcogenides (TMDC’s) [3–5]. TMDC’s have properties different from and complementary to graphene and are promising for a range of electronic and optoelectronic applications. In a bulk crystal, 2D materials exist as layers of atoms with strong bonding in the plane of the layer and much weaker bonding between layers, allowing for exfoliation down to few-layer and single atomic layer samples [3]. Few-layer and single-layer materials often have electronic bandstructures drastically different from the bulk material. For example, graphene was famously discovered to have a zero-gap, linear electronic bandstructure near the Fermi energy corresponding to massless Dirac quasiparticles [2,6]. In contrast, bulk graphite has a semimetallic bandstructure with ordinary massive charge carriers. In the case of some TMDC’s, the bulk material is an indirect bandgap semiconductor, whereas the monolayer has a direct bandgap [7,8]. Since the properties of a 2D material can depend strongly on
its environment, they also offer numerous potential avenues to control their properties that are not possible with bulk materials. The choice of substrate, the presence of adsorbates, or the presence of an external electric field all provide potential convenient handles for tunability. In graphene, for instance, application of an external electric field can be used to control the conductivity and optical absorption by modifying the charge carrier density [9,10]. 2D materials can also have reduced dielectric screening compared to bulk materials, which increases Coulomb interactions between charge carriers. In some TMDC’s, this leads to the presence of stable many-body charge carriers, such as excitons, trions, and biexcitons [4]. Overall, 2D materials offer a wide range of both new fundamental physics and potential applications.

The novel electronic properties in many 2D materials often gives rise to optical properties that can be drastically different from the bulk material. For example, monolayer graphene can absorb a remarkably high 2.3% of light over a broad range of wavelengths [10]. In certain monolayer TMDC’s, a direct bandgap and the presence of stable, tightly bound quasiparticles like excitons and trions strongly modifies their absorption and photoluminescence compared to bulk samples [7,8]. The electronic structure of monolayer 2D materials can also strongly modify optical processes involving phonons, such as Raman scattering. In this chapter, we will explore the impact of exciton-phonon interactions on optical processes in monolayer TMDC’s. Specifically, we will investigate the influence of the exciton valley structure on Raman scattering in these materials. First, we provide an overview of relevant TMDC materials, including the preparation techniques needed to obtain samples that can be studied with optical measurements and their unique valley electronic structure. We then present an overview of Raman scattering, including non-resonant and resonant cases, and how it has been previously used to study 2D TMDC’s. Finally, we present results showing how the valley electronic structure found in some monolayer TMDC’s effects Raman scattering. Some of the content in this chapter is adopted from a work previously published in the journal Physical Review B, entitled “Apparent Breakdown of Raman Selection Rule at Valley Exciton Resonances in Monolayer MoS$_2$” [11]. It is included here with the permission of the coauthors.

2.2 - Two-Dimensional Transition Metal Dichalcogenides

Transition metal dichalcogenides are materials made up of a transition metal element and a chalcogenide element. Each fundamental layer of the material consists of a plane of transition metal atoms in between two planes of chalcogenide atoms in a trigonal prismatic geometry, as shown in Fig. 2.1 [4]. The chemical formula for these materials
are given by MX$_2$, where M represents a transition metal element, such as molybdenum or tungsten, and X represents a chalcogenide element, such as sulfur or selenium. Each transition metal atom is covalently bonded to six chalcogenide atoms, while each chalcogenide atom is covalently bonded to three transition metal atoms. Stacks of individual layers are held together by Van der Waals forces to form a bulk crystal. Three ways that individual layers can be stacked in a bulk crystal are illustrated in Fig. 2.1: the 2H configuration has hexagonal symmetry, the 3R configuration has rhombohedral symmetry, and the 1T configuration has tetragonal symmetry. Fig. 2.1 also shows that monolayers of an MX$_2$ material have three-fold rotational symmetry and lack inversion symmetry. These symmetry properties have important consequences for the electronic and optical properties of monolayer MX$_2$ materials.

![Figure 2.1](image_url)

**Figure 2.1:** From Ref. [4]. A diagram of the crystal structure of 2D TMDC’s. The dark atoms (M) represent the transition metal element, while the yellow atoms (X) represent the chalcogenide element. The in-plane distance between unit cells in a monolayer is labeled as $a$, while $c$ labels the out-of-plane distance between monolayers that lie directly above and below one another. The three different stacking configurations in a bulk crystal are shown (2H, 3R, and 1T).

Two methods for the production of monolayer TMDC’s that are commonly used to produce samples for optical characterization and electronic device fabrication are mechanical exfoliation and chemical vapor deposition (CVD) [3,4,12,13]. Mechanical exfoliation produces flakes with the highest levels of cleanliness and purity, and so is the
desired method to study the intrinsic electronic or optical properties of the material and fabricate high-quality devices [3,4,13]. In this method, a bulk crystal is repeatedly cleaved with adhesive tape, thinning it down until there are regions of monolayer thickness on the adhesive tape. The tape is then applied to a substrate, such as SiO$_2$, and peeled away to leave the thin flakes of 2D material on the substrate. Investigation of the substrate with an optical microscope is sufficient to find and identify monolayer or few-layer flakes, using the difference in optical contrast for flakes of different thickness. Figure 2.2 shows a bulk crystal of the TMDC MoS$_2$ (a.) as well as an optical microscope image of a monolayer flake (b.) that can clearly be identified with optical contrast [4,12,13].

![Image of bulk crystal and monolayer flake]

**Figure 2.2:** From Ref. [4,12,13]. A bulk crystal of the TMDC MoS$_2$ (a.) and an optical microscope image of a monolayer flake of the same material (b.) produced via mechanical exfoliation. (c.) A diagram of the CVD process, showing the powder precursors, the substrate (labeled “sample”) on which to grow the MoS$_2$ thin films, and the furnace heating elements (red circles). (d.) An optical microscope image of monolayer MoS$_2$ flakes produced with CVD, showing large size and high coverage of the substrate.
The production of monolayer and few-layer TMDC’s has enabled a variety of new experiments characterizing the evolution of their electronic and optical properties with film thickness. The family of MX$_2$ materials consisting of MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ are all semiconducting TMDC’s that have an indirect bandgap in bulk form but have been shown to have a direct bandgap in monolayer form [4,7,8,14]. This has a dramatic effect on the optical properties of monolayers of these TMDC’s and makes them potentially suitable for many applications that graphene is not suited for, such as light detectors or emitters, photovoltaics, transistors, and others [4,5,15].

The emergence of a direct bandgap has been shown to greatly increase the efficiency of photoluminescence from monolayers. Fig. 2.3 shows experimental data establishing the onset of bright photoluminescence in monolayer MoS$_2$ [7]. In Fig. 2.3a, the absorption of monolayer and bilayer MoS$_2$ (shown as black curves) is plotted against the normalized photoluminescence (red curves). In the bilayer MoS$_2$, there are three photoluminescence emission peaks, labeled I, A, and B. The lowest energy peak, I, corresponds to indirect-gap luminescence, while the A and B emission peaks match the A and B excitonic absorption energies and correspond to hot carrier luminescence in the bilayer. The A and B excitons are a result of spin-orbit coupling in TMDC’s. This coupling causes a splitting of the valence band. The exciton formed by a hole in the upper valence band and an electron in the conduction band is the A exciton, and the exciton formed by a hole in the lower valence band and an electron in the conduction band is the B exciton. In the monolayer, the indirect luminescence peak has disappeared, and only an emission peak corresponding to the A excitonic transition is present. Fig. 2.3b contains the unnormalized photoluminescence data, illustrating the drastic increase in magnitude of the emission from a bilayer to a monolayer. The large magnitude of photoluminescence emission from a monolayer at the energy corresponding to the A exciton transition indicates that monolayer MoS$_2$ has a direct bandgap and the A excitonic transition is the lowest energy optical transition. The relatively low magnitude of photoluminescence emission in the bilayer and the presence of the emission peak I indicates that the indirect bandgap at I is the lowest energy optical transition.
Figure 2.3: From Ref. [7]. (a.) The optical absorption (black curves) and normalized photoluminescence (red curves) for monolayer and bilayer MoS$_2$. In the bilayer, there are emission peaks corresponding to the A and B excitonic absorption energies as well as an emission peak I corresponding to indirect bandgap emission. In the monolayer, there is only one prominent peak matching the A exciton energy. (b.) A comparison of the unnormalized photoluminescence from monolayer and bilayer MoS$_2$, showing that the monolayer has drastically higher emission efficiency than the bilayer.

The direct bandgap in monolayer TMDC’s is the result of quantum confinement of the charge carriers in two-dimensions [7,8,14]. This originates from the different character of the electronic states that form the indirect and direct gaps. In bulk MoS$_2$, the states that correspond to the direct exciton transitions have wavevectors at the K point of the Brillouin zone, and are comprised mainly of d orbitals from the Mo atoms. Since these orbitals are strongly localized and each layer of Mo atoms is held in between two layers of sulfur atoms, the d orbitals have weak interlayer coupling, and their energy is not affected very much by the number of layers. On the other hand, the electronic states around the indirect gap have wavevectors near the Γ point of the Brillouin zone, and are comprised of both Mo d orbitals and sulfur p orbitals, which are more extended in space and have much stronger interlayer coupling. Thus, these electronic states are affected strongly by the number of layers. As the layer number is reduced from a bulk crystal down to a monolayer, the energy of the indirect gap at the Γ point gradually increases until, in the monolayer limit, it becomes greater in energy than the direct gap at the K point.
The electronic states at the direct bandgap at the K point have interesting valley properties that arise from the symmetry of a monolayer TMDC such as MoS₂, including the high symmetry K and K’ points at the Brillouin zone corners. Due to the lack of inversion symmetry in a monolayer, the K and K’ valleys have optical selection rules corresponding to photons of opposite helicity.

Figure 2.4: From Ref. [16]. An illustration of the hexagonal Brillouin zone of a monolayer TMDC such as MoS₂, including the high symmetry K and K’ points at the Brillouin zone corners. Due to the lack of inversion symmetry in a monolayer, the K and K’ valleys have optical selection rules corresponding to photons of opposite helicity.

The electronic states at the direct bandgap at the K point have interesting valley properties that arise from the symmetry of a monolayer TMDC [17,18]. TMDC’s have a hexagonal Brillouin zone, with the valence band maximum and conduction band minimum occurring at the high-symmetry K and K’ points, as shown in Fig. 2.4 [16]. In the Brillouin zone, the three K points are equivalent and the three K’ points are equivalent, since the monolayer has three-fold rotational symmetry and a rotation by 120° maps these points onto each other. However, as mentioned above, the monolayer lacks inversion symmetry – it can be seen in Fig. 2.1 that applying an inversion operation through an Mo atom site will map an S atom onto empty space rather than another S atom site. Because of this lack of inversion symmetry, the K and K’ valleys have optical selection rules corresponding to photons of opposite helicity, or valley circular dichroism. A right circularly polarized photon with an energy matching the exciton absorption energy can only excite charge carriers in the K’ valley, while a left circularly polarized photon of the same energy can only excite charge carriers in the K valley. TMDC’s also
have strong spin-orbit coupling arising from the high mass of the Mo atoms and the metal 
$d$ orbital character of the states at the valence band maxima. This causes the valence 
bands at the $K$ and $K'$ points to be split into spin-up and spin-down bands (not shown in 
Fig. 2.4). The higher-energy valence band contributes to the $A$ exciton and the lower-
energy valence band contributes to the $B$ exciton. Due to the lack of inversion symmetry, 
the spin splitting is opposite in the $K$ and $K'$ valleys [17,18]. This means that excitation 
with circularly polarized light will excite charge carriers in a single valley with a single 
spin, and light of the opposite helicity will excite carriers in the alternative valley with 
opposite spin. Graphene, on the other hand, has inversion symmetry and does not have 
strong spin-orbit coupling, so generation and control of carriers in a definite valley and 
with a definite spin is much more challenging in that system. The coupling of spin and 
valley physics makes monolayer TMDC’s possibly uniquely suited for a range of 
applications in spintronics and valleytronics, or even quantum computing applications if 
long enough spin and valley coherence lifetimes can be achieved.

Many experiments have confirmed that the valley physics in monolayer TMDC’s 
can affect their optical properties [16,19–23]. As described above, the emergence of a 
direct bandgap enables bright photoluminescence in monolayer TMDC’s. The valley 
electronic structure has been shown to affect the character of this light emission. Fig. 2.5 
shows the photoluminescence intensity for each helicity following excitation by left ($\sigma$-) 
circularly polarized light and the degree of polarization of the emitted light [19]. As 
described above, excitation by $\sigma$-light at an energy near the valley exciton resonance 
excites carriers in only one valley. As long as the excited carriers don’t scatter to the 
opposite valley, which also requires a flip of their spin, then recombination of the excited 
electron and hole must result in emitted light with the same helicity as the incident light. 
Fig. 2.5a and 2.5c show that for emitted light at the valley exciton resonance energy of 
around 1.92 meV, the light with the same helicity as the incident light is much stronger 
than the emitted light with the opposite helicity. Fig. 2.5a is for MoS$_2$ on an h-BN 
substrate, while (b.) is for MoS$_2$ on an SiO$_2$/Si substrate. Fig. 2.5b and 2.5d show the 
corresponding degree of helicity of the emitted light, with a value of 1 meaning that the 
emitted light is completely circularly polarized, and a value of 0 meaning that the emitted 
light is made up of each helicity equally. We see that as the light energy approaches the 
valley exciton resonance, the helicity of the emitted light increases from near 0 to near 1. 
Taken all together, this shows that light of a given helicity excites only carriers in one 
valley, and that the valley polarization is maintained long enough for the emitted light to 
also be emitted from the same valley.
Figure 2.5: From Ref. [19]. Experimental data showing the photoluminescence intensity for right ($\sigma_+$) and left ($\sigma_-$) circularly polarized emission upon excitation with left ($\sigma_-$) circularly polarized photons (a. and c.), and the corresponding degree of helicity of the emitted light (b. and d.). (a.) and (b.) are for MoS$_2$ on a h-BN substrate and (c.) and (d.) are for MoS$_2$ on an SiO$_2$/Si substrate.

The valley circular dichroism in monolayer TMDC’s can not only affect their linear optical properties, but also their nonlinear optical properties. High intensity, ultrafast pulsed lasers offer a convenient way to probe these materials in the nonlinear regime and allow for ultrafast modulation of their optical and electronic properties. One way to achieve ultrafast modulation of the electronic and optical properties of a semiconductor is through the optical Stark effect. In recent years, experiments have shown that the optical Stark effect can be used to exploit the valley degree of freedom in monolayer TMDC’s to achieve ultrafast, valley selective modulation [21,23]. These results could have implications for quantum computing applications where ultrafast control of the valley degree of freedom may be useful.

In the optical Stark effect, a high intensity, nonresonant pump pulse induces a shift in the energy levels of two electronic states that can be coupled with the light. The shift in the energies of the electronic states occurs only during the duration of the pump laser pulse. When the absorption of the electronic states is measured with a probe pulse, the probe will measure absorption corresponding to one energy when the pump is not present, and a shifted energy when the pump pulse is present at the same time as the probe. In this way, the pump laser can be used to achieve ultrafast modulation of the absorption of the probe.

As described above, monolayer TMDC’s have a valley circular dichroism, where light of one circular polarization can only interact with one valley, and light of the
opposite helicity can only interact with the other valley. This valley circular dichroism causes a valley-selective optical Stark effect when the pump and probe pulses are circularly polarized. Fig. 2.6a illustrates the shift in the energy levels of one valley as a result of a circularly-polarized pump [21]. When a probe of the same circular polarization as the pump is used, a shift in the absorption energy is measured, since the pump and probe interacted with the same valley. When a probe of the opposite circular polarization is used, there is no measured shift in the energy levels, since the probe is measuring the valley that was not affected by the pump. Fig. 2.6b and Fig. 2.6c show the difference in the absorption when the pump is present for a probe of the same and opposite circular polarization as the pump. When the probe has the same circular polarization as the pump, there is a noticeable difference in the absorption, whereas when the probe has the opposite circular polarization, there is no measured change in absorption. This shows that ultrafast, valley-selective modulation is possible in monolayer TMDC’s.

We have established that the valley degree of freedom in monolayer TMDC’s can drastically affect both the linear and nonlinear optical properties of the material. In the next sections of this chapter, we will show that the valley degree of freedom can also affect optical processes involving phonons, such as Raman scattering, when the incident light energy matches the valley exciton resonance.

![Figure 2.6](image_url)

**Figure 2.6:** From Ref. [21]. (a.) shows the shift in energy levels of the K valley upon excitation with light of one helicity, but the energy levels in the K’ valley remain unchanged. (b.) and (c.) show the measured absorption difference with pump on and pump off for probe light of the same circular polarization as the pump, which probes the K valley, and probe light of the opposite circular polarization, which probes the K’ valley. There is a clear signal when the probe has the same circular polarization as the pump (b.), and no signal when the probe has the opposite circular polarization (c.).

### 2.2 –Raman Scattering and Raman Studies on 2D TMDC’s
In this section, we provide an overview of Raman scattering, including the nonresonant and resonant cases, and illustrate how Raman scattering has previously been used to study 2D TMDC’s. Raman scattering is one type of inelastic scattering that can occur when light interacts with a medium [24]. A perfectly homogenous medium will transmit, reflect, or absorb all incident light, but inhomogeneities can cause scattering of the light in all directions. Raman scattering occurs because lattice vibrations dynamically alter the density of a material, leading to dynamic inhomogeneities in the index of refraction that can cause scattering. As with any process, total energy and momentum must be conserved, and symmetry plays a role in determining which types of scattering events are allowed and forbidden.

Raman scattering can be classified as either resonant or non-resonant depending on if the incident or scattered light is resonant with electronic transitions in the material. The vibrational modes of a lattice that can participate in Raman scattering have a well-defined frequency, and the scattered light will be shifted in energy from the incident light by an amount equal to the phonon energy. If the scattering process involves the creation of a phonon in the material and the scattered light is lower in energy than the incident light, the process is called Stokes Raman scattering. If the scattering process involves the annihilation of a phonon in the material and the scattered light is increased in energy, the process is called anti-Stokes Raman scattering. Fig. 2.7 shows a diagrammatic process of Stokes and anti-Stokes scattering and the energy conservation conditions for each. Momentum must also be conserved – the wavevector of a phonon that is created or annihilated cannot be greater than twice the wavevector of the light. Since the light typically used for Raman scattering experiments has a wavevector that is generally orders of magnitude smaller than the size of the Brillouin zone, the phonons that can play a role in Raman scattering must have a momentum close to zero [24]. This has important implications for the symmetry of the phonons that can participate in Raman scattering, and later in this section we will describe how this impacts which Raman processes can be allowed or forbidden.

At normal temperatures, Stokes scattering is much more likely than anti-Stokes scattering, because a phonon can always be created in the material, but anti-Stokes scattering requires the presence of phonons already in the material to be annihilated. Since Stokes scattering is more convenient to measure and provides a lot of the same information about a material as anti-Stokes scattering, most experimental studies of Raman scattering focus on measuring the Stokes scattering, including the measurement that will be presented in the next section of this chapter.

Raman scattering can be understood from either a macroscopic, classical picture or a microscopic, quantum picture [24]. In the macroscopic picture of Raman
scattering, the incident and scattered light and the phonons in the material are treated as classical plane waves.

\[
\text{Stokes: } E_{\text{inc}} = E_{\text{scat}} + E_{\text{phon}} \quad \text{anti-Stokes: } E_{\text{inc}} = E_{\text{scat}} - E_{\text{phon}}
\]

**Figure 2.7:** A diagrammatic description of Stokes and anti-Stokes Raman scattering. In Stokes scattering, the material absorbs a phonon and the scattered light is correspondingly reduced in energy, whereas in anti-Stokes scattering, a phonon in the material is annihilated and the scattered photon is correspondingly increased in energy.

In the general classical theory of a material’s response to electromagnetic radiation, we assume that the incident electromagnetic radiation induces a polarization in the material, and that the relationship between the induced polarization and the incident field can be described by an inherent quantity of the material, the electric susceptibility. In mathematical form, we write

\[
P_{\text{ind}} = \chi E
\]

where \( P_{\text{ind}} \) is the induced polarization, \( E \) is the incident electric field, and \( \chi \) is the electric susceptibility. Here, we are only describing the response of materials to the electric field of incident radiation. This response is generally much greater than effects from the incident magnetic field component of the radiation, which can safely be neglected. In general, the induced polarization and incident electric field are vectors, so the electric susceptibility must be mathematically represented by a tensor. Also, we can easily see that if the incident electric field takes the form of a superposition of plane waves, then the induced polarization will also take the same form.

Now, we will include in this model the dynamic modulations of the material due to phonons that can cause scattering as described above. The electric susceptibility is the only quantity in Eq. 2.1 that depends on the material, so the effect of the material vibrations must be included in \( \chi \). To include them, we assume that the susceptibility can
depend on the atomic displacements associated with a given phonon mode, which we will represent with $Q$:

$$\chi = \chi_0 + \left(\frac{d\chi}{dQ}\right)_0 Q$$  \hspace{1cm} (2.2)

Here, we have just done a Taylor expansion and kept only the term linear in $Q$. In this quasi-static approximation, the response of the material to the incident electric field instantaneously reflects the positions of the atoms due to phonons. This is a good assumption as long as the incident electromagnetic frequencies are much greater than the vibrational frequencies, which is generally a good approximation for visible light. In Eq. 2.2, the total susceptibility is represented as the susceptibility when there are no phonons ($\chi_0$) plus the change in the susceptibility caused by a phonon. Since the susceptibility is a tensor, both terms must be tensors of the same rank, so the derivative quantity is a rank 3 tensor which becomes a rank 2 tensor when contracted with the vector $Q$. It is also convenient to write the atomic displacement for a given phonon mode and the incident electric field as plane waves:

$$Q(r, t) = Q(q)\cos(q \cdot r - \omega_{ph} t);$$
$$E(r, t) = E(q)\cos(k \cdot r - \omega_{inc} t)$$  \hspace{1cm} (2.3)

Here, $r$ represents spatial position, $q$ and $k$ represent the wavevectors of the phonon and incident light, respectively, and $\omega_{ph}$ and $\omega_{inc}$ represent the frequencies of the phonon and incident light, respectively. Combining Eq. 2.1 and 2.2, we see that the total induced polarization will have one component from the static term of the susceptibility and one component from the dynamic term. The dynamic component of the induced polarization that arises from a phonon is given by

$$P_{ph} = \left(\frac{d\chi}{dQ}\right)_0 Q E$$  \hspace{1cm} (2.4)

Combining Eq. 2.3 and Eq. 2.4, we see that the induced polarization from a phonon contains a product of cosines with different frequencies, $\omega_{ph}$ and $\omega_{inc}$. Using standard rules for multiplying trigonometric functions, we can rewrite Eq. 2.4 in the following form:

$$P_{ph} \propto \cos[(k + q) \cdot r - (\omega_{ph} + \omega_{inc})t]$$
$$+ \cos[(k - q) \cdot r - (\omega_{ph} - \omega_{inc})t]$$  \hspace{1cm} (2.5)

In Eq. 2.5, we see that the induced polarization from a phonon has a component that is oscillating with a frequency of $(\omega_{ph} + \omega_{inc})$ and a component oscillating with a
frequency of \((\omega_{ph} - \omega_{inc})\). The higher frequency term corresponds to radiation of anti-Stokes light, where the emitted light gains energy, and the lower frequency term corresponds to the radiation of Stokes light, where the emitted light loses energy.

Now that we have established that phonons in a material can cause radiation at the shifted Stokes and anti-Stokes frequencies, we will discuss how the symmetry of the material and the phonons plays a role. The intensity of the scattered light with a given polarization depends on the overlap of the scattered light polarization with the induced polarization in the material:

\[
I_s \propto |P_{ph} \cdot e_s|^2
\]  

Using Eq. 2.4, we can rewrite Eq. 2.6 as

\[
I_s \propto \left| e_i \cdot \left( \frac{d\chi}{dQ} \right)_0 Q \cdot e_s \right|^2
\]  

In Eq. 2.6 and 2.7, \(e_i\) and \(e_s\) are the unit vectors representing the polarization of the incident and scattered light, respectively. In Eq. 2.7, we see that the scattered light intensity, \(I_s\), depends on the polarization of the incident and scattered light and a tensor in the middle that depends on the material. This tensor is called the Raman tensor \(R\):  

\[
R \equiv \left( \frac{d\chi}{dQ} \right)_0 \hat{Q}
\]

We see from Eq. 2.7 and 2.8 that the intensity of the Raman scattered light depends on the incident and outgoing light polarizations and on the symmetry of the Raman tensor. The incident and scattered light polarizations can be easily and continuously controlled in an experiment, which allows the symmetry of the Raman tensor to be deduced. Above, it was mentioned that due to conservation of momentum and the relatively small wavevector of typical photons compared to the Brillouin zone size, only phonons near the Brillouin zone center can participate in Raman scattering. Phonons at the zone center have zero momentum and infinite wavelength, and their symmetries must reflect the symmetries of the crystal lattice. If the symmetry of the lattice is known, group theory can be used to find the symmetries of the zone-center phonon modes that can exist in that lattice. Put formally, each zero-momentum phonon mode must be an irreducible representation of the point group of the crystal lattice [24–26]. The electric susceptibility \(\chi\) must also have the same symmetry properties as the lattice. The irreducible representation of a given phonon mode determines the form of its Raman tensor. The form of the Raman tensor for the different phonon modes in a lattice can be easily obtained by examining the character table of the point group of that
lattice [25–27]. Eq. 2.7 can then be applied to determine if a particular phonon mode can be Raman active for a certain configuration of incident and scattered polarization. Some phonon modes are required by symmetry to have zero scattered intensity for any polarization configuration of incident and scattered light. These modes are said to be Raman inactive. A phonon mode is Raman active if there is some polarization configuration for which the scattered intensity may be nonzero. Measuring the intensity of the Raman scattered light for different polarization configurations allows the symmetry of the phonon mode causing the scattering to be inferred, and thus the frequency of a given Raman line can be assigned to the proper phonon mode. Clearly, Raman scattering is a powerful tool to measure the energies and symmetries of phonons in a material. Our experimental results in the next section will show how it can also be affected by exciton-phonon interactions and valley polarization in a monolayer TMDC.

We can also understand Raman scattering from a microscopic, quantum picture, which helps illuminate the difference between resonant and non-resonant Raman scattering [24]. In this picture, a Raman scattering event can be broken into three steps. First, an electron-hole pair in the material is excited by a photon from the ground state \( |g\rangle \) to an intermediate state \( |a\rangle \). Then, modulated by the electron-phonon interaction, the electron-hole pair either absorbs or emits a phonon to go from state \( |a\rangle \) to another intermediate state \( |b\rangle \). Finally, the electron recombines with the hole and emits a scattered photon, ending in its final state \( |g\rangle \). In Raman scattering, the initial and final states of the electron-hole pair are both the ground state and are identical. The total scattered light will be the weighted sum over all possible iterations of this process, which means a sum over all possible intermediate states. Quantum mechanically, we can use Fermi’s Golden Rule to write the probability of Raman scattering as a sum of terms that have a form like Eq. 2.9 [24]:

\[
P_s \propto \sum_{a,b} \left| \frac{\langle g|H_{e-r}|b\rangle \langle b|H_{e-ph}|a\rangle \langle a|H_{e-r}|g\rangle}{(E_i - E_a)(E_i - E_{ph} - E_b)} \right|^2
\]

In Eq. 2.9, \( P_s \) is the probability of a Raman scattering event, \( H_{e-r} \) is the electron-radiation interaction Hamiltonian, \( H_{e-ph} \) is the electron-phonon interaction Hamiltonian, and \( E_i \), \( E_a \), \( E_b \), and \( E_{ph} \) are the energies of the incident photon, intermediate electronic states, and phonon, respectively. Generally, \( |a\rangle \) and \( |b\rangle \) represent a continuum of virtual states that must be summed over, making extraction of possibly useful quantities like the electron-phonon interaction or electron-radiation interaction difficult. However, if the incident or scattered light is resonant with a real electronic transition in the material, that term in the sum will dominate the other terms and largely determine the behavior of the Raman
scattering process. In this resonant case, assuming that the only relevant electronic state is a discrete, real state $|c\rangle$, we can approximate Eq. 2.9 as [24]:

$$P_s \approx \frac{2\pi}{\hbar} \left| \frac{\langle g | H_{e-r} | c \rangle \langle c | H_{e-ph} | c \rangle \langle c | H_{e-r} | g \rangle}{(E_c - E_t - i\Gamma_c)(E_c - E_s - i\Gamma_c)} \right|^2 (2.10)$$

In Eq. 2.10, we have added the term $i\Gamma_c$ to the denominators to represent the finite lifetime and energy broadening of $|c\rangle$ and avoid an unphysical divergence when $E_t$ or $E_s$ are equal to $E_c$. If $|c\rangle$ is a bound exciton state, for example, then the scattering probability will depend on the exciton-phonon coupling and the oscillator strength of the exciton. Raman scattering can not only provide information about the energies and symmetries of vibrational modes in the material, but in certain cases it can also help provide information about the coupling of light and phonons with excitons or electronic states.

Since Raman scattering can be a useful source of different kinds of information about a material, it has been used extensively to study 2D materials, including 2D TMDC’s [27–43]. In monolayer MoS$_2$ and other monolayer TMDC’s, the two most prominent phonon modes in Raman scattering are known as the E’ and A’$_1$ modes, which are illustrated in Fig. 2.8. The A’$_1$ consists of vibrations in the direction out of the monolayer plane, while the E’ mode consists of vibrations within the monolayer plane. Since there is only one out-of-plane dimension, which we can label as $z$, the A’$_1$ mode is singly-degenerate. The E’ mode is doubly degenerate due to the freedom of atomic vibrations to occur in the in-plane $x$ and $y$ directions. These modes have analogous phonon modes corresponding to the same vibrational directions in bulk MoS$_2$ that are labeled A$_{1g}$ and E$_{12g}$ – the difference in the labeling of the phonon modes is because the lattices of monolayer and bulk MoS$_2$ belong to different symmetry groups [27,38]. Raman scattering has been used to study the evolution of these phonon modes with the number of layers of the material [28,33,37,42]. In MoS$_2$, as the number of layers approaches one, the A$_{1g}$ mode was found to decrease in frequency, while the E$_{12g}$ mode was found to increase in frequency [28]. For samples with thicknesses greater than five or six layers, the phonon frequencies did not change appreciably. Thus, accurately measuring the positions of the A$_{1g}$ and E$_{12g}$ Raman peaks can be a method to identify layer number for samples of around 1-6 layers.
Since monolayer materials can be strained by an underlying substrate, other Raman studies have looked at the effect of strain on Raman scattering in monolayer TMDC’s or graphene, finding that strain can modify the frequencies of certain Raman modes or lift degeneracies between modes [29,30,43]. 2D materials also provide a convenient platform for studying the thickness dependence of interlayer phonon modes, including modes involving shear (in-plane) and breathing (out-of-plane) atomic motion, which experiments have established can be affected as the number of layers decreases from bulk to a few layers [34–36].

Other experiments have performed resonant Raman scattering, where the incident or scattered light is resonant with exciton transitions, and observed the enhancement of many phonon modes that are not present in nonresonant scattering [28,39,41]. The presence of these additional modes was largely attributed to exciton-phonon coupling and higher-order phonons that can be enhanced on resonance, showing that resonant Raman scattering can be used to learn about exciton-phonon interactions in monolayer TMDC’s. Although there have been many Raman studies on few-layer and monolayer TMDC’s, they do not address the electronic valley degree of freedom or establish how the valley circular dichroism described in the previous section can affect Raman scattering. In the next section, we present experimental results showing that the valley degree of freedom can influence Raman scattering involving valley exciton resonances in a monolayer TMDC.
2.3 – Experimental Results Establishing the Influence of Valley Degree of Freedom on Raman Scattering in Monolayer MoS$_2$

As described above, due to a lack of inversion symmetry in monolayer TMDC’s, the hexagonal Brillouin zone possesses a pair of degenerate but inequivalent valleys at the K and K’ points. This valley index or valley pseudospin serves as an additional electronic degree of freedom in addition to electron spin, and may be useful for a variety of applications, including quantum computing applications. This helicity-selective coupling between light and the valley degree of freedom can affect a variety of optical processes involving the valley excitons. Here, we investigate its effect on Raman scattering. As outlined above, Raman spectroscopy has been used extensively on 2D materials, such as graphene and TMDC’s, for studying thickness-dependent properties and probing strain effects. However, few Raman studies have examined systematically the polarization selection rule for TMDCs with circularly polarized excitation and detection [23]. Here, we present results on polarization-resolved Raman spectroscopy on monolayers of MoS$_2$ with excitation wavelengths both on and off valley exciton resonance. We focus our analysis on the singly degenerate out-of-plane $A'_{1}$ mode and the doubly degenerate in-plane $E'$ mode, which arise from the $A_{1g}$ mode and $E'_{2g}$ mode in bulk MoS$_2$, respectively. Comparing our results to a group theory analysis based on the crystal symmetry, we observe that the $A'_{1}$ mode always obeys the Raman selection rules. The $E'$ mode, however, appears to violate the Raman selection rule at valley exciton resonances: it shows a prominent peak when the incoming and scattered light have the same circular polarization despite being forbidden by the Raman selection rule. We attribute the presence of this peak to a defect-assisted process involving $E'$ phonons slightly away from the $\Gamma$ point, which can be enhanced by the selective coupling of valley excitons to photon helicity at exciton resonances.

Our measurements use MoS$_2$ as the monolayer TMDC, and we also perform some measurements on graphene as a control. To obtain samples for our measurements, monolayers of exfoliated MoS$_2$ and exfoliated graphene were prepared by standard micromechanical exfoliation techniques mentioned earlier in this chapter. They were identified with optical contrast in a microscope. The inset of Fig. 2.9 shows an optical microscope image of the exfoliated MoS$_2$ monolayer flake used for Raman measurements on a Si/SiO$_2$ substrate with 300nm SiO$_2$ thickness. The optical contrast is good enough to easily see and identify monolayers. The scale bar is 15 µm.
Figure 2.9: A diagram of the confocal microscopy/Raman spectroscopy experimental setup used to perform polarization-resolved Raman scattering measurements on monolayer MoS$_2$. The inset is an optical microscope image of the exfoliated monolayer MoS$_2$ flake used for Raman measurements. The scale bar is 15 µm.

We also performed measurements on CVD MoS$_2$ monolayers to test if they show any major differences from the exfoliated flakes [44]. The CVD monolayers were grown onto c-cut sapphire substrates using the ambient pressure vapor transport technique. Sapphire samples were etched in piranha solution for 3 hours at 65°C and washed in DI water multiple times. Growth was performed in a two-zone furnace using semiconductor grade sulphur (access amount ~100mg) and MoO$_3$ powders (4mg). Samples were placed 1 cm directly above MoO$_3$ powders and the sulphur to reaction chamber distance was kept at 20 cm. The sulphur gas (S$_2$(g)) was carried by high-purity N$_2$ gas at a flowrate of 10 sccm. We notice that the temperature at which S$_2$(g) passes is of paramount importance to have ultimate control over domain size, shape, quality, and continuity. Typically, S$_2$(g) was passed above 590°C and the growth was performed at 665°C (at the reaction spot). During growth the flowrate was adjusted down to 3 sccm to improve the overall monolayer quality and improve continuity of monolayers. Growth duration was fixed at 5 minutes and samples were cooled down to 550°C at a rate of 30 C/min and fast cooled between 550-20°C.

In our Raman measurements, we examine four different polarization configurations – the incoming and outgoing light having the same linear polarization,
perpendicular linear polarization, same circular polarization, and opposite circular polarization. We perform all of the Raman scattering measurements with a confocal microscopy setup with the capability to image the sample and perform Raman measurements, as shown in Fig. 2.9. All measurements were done with normally incident laser light, with the backscattered light collected for detection. Immediately after the laser, there is a narrow bandpass filter with the same center wavelength as the output of the laser. This filter narrows the width of the laser in frequency space and filters out any extraneous modes. An excitation laser with a narrow, well-defined wavelength is necessary in Raman scattering to ensure accurate measurement of the Raman shift energy. In addition, Raman active phonon modes can have a relatively low energy, on the order of 100 cm\(^{-1}\) (around 12 meV), and the incident laser must have a narrow enough lineshape to be able to resolve the scattered light that is shifted from the incident light by this amount. Special filters can also be used to measure even lower-energy Raman active phonon modes. In this measurement, the phonon modes we are interested in have energies near 400 cm\(^{-1}\), so normal Raman bandpass filters are sufficient. An initial polarizer sets the linear polarization of the incident light, and a polarizer before the detector controls the linear polarization of the measured light. It is also necessary that the polarizers have a fairly good extinction ratio and that the other optics in the setup don’t distort the polarization drastically, because this will add errors to the measurement of the polarization-resolved Raman scattering and make determining the selection rules more difficult. In our experiments, all of the extinction ratios are on the order of 100 or more, which is sufficient to accurately determine the Raman selection rules.

After the initial bandpass filter and polarizer, the light passes through a beamsplitter, is focused by an objective onto the sample, and the backscattered light is eventually sent to either a spectrometer or an imaging camera. The numerical aperture (NA) of the objective is relevant to the measured Raman signal. Although the incident light generally has a well-defined direction of propagation, Raman scattering is a type of inelastic scattering and the radiation from it will generally be emitted in all directions. A large NA objective is useful for capturing more of this scattered light and boosting the Raman signal. However, if the objective has too large of an NA, then the incident light may be focused tightly enough to damage the sample. The polarizer before the detector is left unchanged for all configurations, ensuring the measured light always has the same polarization. This eliminates possible variation in the measurement due to polarization-dependent efficiency from the spectrometer and detector.

For the linear polarization configurations (incident and outgoing light having the same linear polarization or perpendicular linear polarizations), a half wave plate in the path of the outgoing light controls which linear polarization is detected. There is no quarter waveplate present in these configurations. If the waveplate is rotated so that the polarization of the transmitting light is parallel to the waveplate’s fast or slow axis, the
waveplate will not alter the polarization of the light. If the waveplate is rotated 45 degrees away from this angle, then the light transmitted through the half waveplate will have its polarization rotated by 90 degrees. In this way, both linear polarizations of the Raman scattered light can be measured. For the circular polarization configurations, a quarter waveplate is inserted before the objective. If the linearly polarized incident light is at an angle of 45 degrees to the fast axis of the quarter waveplate, the light will be circularly polarized after transmitting through the waveplate. After the light interacts with the sample and the Raman scattered light is reflected back, it passes through the waveplate again to be converted from circularly polarized back to linearly polarized light. Light that is right circularly polarized will be converted to one linear polarization, whereas light that is left circularly polarized will be converted to the perpendicular linear polarization. In this way, the same detection scheme as above using the half waveplate can be employed to measure the circular polarization configurations.

A long pass filter before the spectrometer filters out the excitation laser light, but transmits the Raman scattered light which has a longer wavelength. This filter must be sharp enough and the incident laser must have a narrow enough frequency linewidth to be completely filtered out from the detector. The intensity of the Raman scattered light may be as weak as $10^{-6}$ of the intensity of the elastically reflected light, so even a small amount of leak from the excitation laser can overwhelm the Raman signal. The spectrometer itself is a monochromator coupled to a liquid-nitrogen cooled CCD camera, which is sensitive enough to detect the weak Raman light. A mirror can also direct the back-reflected light to an imaging CCD camera, where optical images of the sample can be acquired. This allows us to identify particular monolayer flakes and ensure the incident laser is focused on the flake, and monitor the flake to make sure it does not get damaged by the laser during the measurement.

We also performed absorption measurements on monolayer MoS$_2$ samples to characterize them. For the absorption measurement, monolayers of MoS$_2$ were grown with chemical-vapor deposition and transferred onto a sapphire substrate. The measurement was performed with a confocal microscopy setup using a broadband supercontinuum laser as the light source and a spectrometer equipped with a one-dimensional CCD array for detection of the reflected light. The reference spectrum $R_{sb}$ was taken on the sapphire substrate near the sample.

In our Raman measurements, we examine four different polarization configurations – the incoming and outgoing light having the same linear polarization, perpendicular linear polarization, same circular polarization, and opposite circular polarization. Raman data was acquired for two laser excitation wavelengths: a 532 nm solid state laser and a 633 nm HeNe laser. Fig. 2.10 shows the reflection difference spectrum in monolayer MoS$_2$, $(R_{sa} - R_{sb}) / R_{sb}$, where $R_{sa}$ is the reflection from the sample and $R_{sb}$ is the reflection from the sapphire substrate. For a thin film, this reflection difference is directly proportional to the absorption [10,45]. We see that the 633 nm excitation is close to both the A exciton resonance at 655 nm and the B exciton resonance.
at 610 nm [7,8], so it corresponds to on-resonance excitation of the valley excitons. On the other hand, the 532 nm excitation is far away from both the A and B exciton peaks, so it corresponds to off-resonance excitation of the valley excitons. We note that the 532 nm light (2.33 eV) has energy higher than the monolayer MoS\textsubscript{2} exciton transition (1.9 eV), so it will be resonant with some interband transition, just not resonant with the valley excitons [7,8].

![Absorption spectra](image)

**Figure 2.90:** The absorption spectrum of monolayer MoS\textsubscript{2} from a supercontinuum light source. The A and B exciton peaks at 655 nm and 610 nm are clearly visible. The laser excitation wavelengths at 633 nm and 532 nm used for polarization-resolved Raman measurements are labeled. The on-resonance 633 nm excitation is close to both the A and B exciton peaks, while the off-resonance 532 nm excitation is far from both exciton peaks.

We now examine our polarization-resolved Raman data for both laser excitation wavelengths (532 nm and 633 nm) for exfoliated monolayer MoS\textsubscript{2} on a Si/SiO\textsubscript{2} substrate, displayed in Fig. 2.11. Fig. 2.11a shows data for the off-resonance 532 nm excitation, and Fig. 2.11b shows data for the on-resonance 633 nm excitation. The data was acquired at room temperature. The spectral resolution of our Raman setup is around 8 cm\textsuperscript{-1}, limiting the sharpness of the Raman features we observe. We observe the prominent A’\textsubscript{1} phonon mode at 408 rel. cm\textsuperscript{-1} and E’ phonon mode at 388 rel. cm\textsuperscript{-1}, similar to those reported in earlier works [34,36]. As described in the previous section, on-resonance excitation can cause the enhancement of higher-order phonon modes that are not seen in off-resonance measurements. Accordingly, the peak around 424 rel. cm\textsuperscript{-1} for the on-resonance 633 nm excitation is due to a second-order Raman process that is enhanced at exciton resonances and is mediated by exciton-polaritons [40,41]. The broad peak around 455 rel. cm\textsuperscript{-1} off-
resonance is due to the second-order 2LA(M) mode, which involves two longitudinal acoustic phonons at the M-point of the Brillouin zone [40]. Previously, we described how only zone-center phonons with effectively zero momentum are relevant to Raman scattering. Higher order phonon modes can involve multiple phonons whose total momentum is effectively zero, even though the individual phonons have finite momentum. This occurs for the 2LA(M) mode when a resonant excitation is used. The broad peak around 465 rel. cm\(^{-1}\) on-resonance has been previously assigned to a convolution of the 2LA(M) mode and phonons in the A\(_{2\beta}(\Gamma)\) branch [40]. A strong background is also present in the on-resonance Raman spectra due to the tail of the bright photoluminescence peak in MoS\(_2\). We find that additional polarization-resolved Raman measurements of CVD-grown MoS\(_2\) on a sapphire substrate show similar behavior to the exfoliated sample, as shown in Fig. 2.12.

For all polarization configurations and excitation wavelengths, the A’\(_1\) mode appears only when the incident and outgoing light have the same linear or circular polarizations. The behavior of E’ mode, however, appears to be different for the excitations on and off the valley exciton resonances. For the off-resonance excitation, the E’ mode is present when the incident and backscattered photons have opposite circular polarizations, and it is absent when the incident and backscattered photon have the same circular polarization. For the on-resonance excitation, however, the E’ mode shows a prominent Raman peak when the incident and backscattered photons have the same circular polarization. With linearly polarized excitation, the E’ mode always appears for both parallel and perpendicular linear polarization configurations. Additionally, the E’ mode appears to redshift by around 3 rel. cm\(^{-1}\) in the on-resonant excitation compared to the off-resonant excitation, which will be discussed further in the following.

To understand this unusual circular polarization-dependent Raman scattering in MoS\(_2\), we first examine the Raman scattering selection rules arising from the crystal symmetry using a group theory analysis. As described above with Eq. 2.7 and 2.8, the Raman scattering cross section for a given incident and scattered light polarization and a given phonon mode is proportional to \( \langle \hat{e}_i | \hat{R} | \hat{e}_s \rangle^2 \), where \( \hat{e}_i \) and \( \hat{e}_s \) are the polarization vectors of the incoming and outgoing light, and \( \hat{R} \) is the Raman tensor for the phonon mode under consideration. If the Raman cross-section is required to be zero by symmetry, the mode is forbidden, otherwise it is allowed. In a first-order Raman process, an electron can be thought of as absorbing a photon, scattering with a phonon, and emitting a photon to return to its initial state. The Brillouin zone center has the same symmetry as the lattice, so each \( \Gamma \) point phonon mode that plays a role in Raman scattering must transform as one of the irreducible representations of the point group of the lattice. The irreducible representation of a phonon mode determines the form of its Raman tensor, i.e. which elements are required to be zero and which may not be zero. Once the Raman tensor is known, the Raman scattering cross section can be evaluated for a given set of ingoing and outgoing light polarizations.
Figure 2.101: Polarization-resolved Raman spectra for (a.) off-resonance 532 nm excitation and (b.) on-resonance 633 nm excitation of exfoliated monolayer MoS2. The strong background on-resonance is from the tail of the MoS2 photoluminescence peak. The A'1 mode at 408 rel. cm⁻¹ exhibits the same selection rule for both on- and off-resonance excitations. The E' mode at 388 rel. cm⁻¹ is absent for the circular same polarization off-resonance, but seems to appear on-resonance. The additional peaks in the spectra are due to multi-phonon processes and have been identified in previous studies.

The crystal structure of monolayer MoS2 belongs to the symmetry point group D₃h. For this point group and with normally incident light, the only modes that can play a role in first-order Raman scattering are the doubly degenerate E' and singly degenerate A'₁ modes [38]. Therefore, we focus on those phonon modes in our analysis.
We can obtain the Raman tensor for the relevant phonon modes by examining the character table for the symmetry point group D$_{3h}$, shown in Fig. 2.13 [25]. The third column in Fig. 2.13 lists the irreducible representations for this point group, and the first two columns list the functions that transform as those irreducible representations, from which we can read off the form of the Raman tensor for a given phonon mode. Since our monolayer sample is a 2D material, we can define the in-plane directions as $x$ and $y$. For normally incident and backscattered light, the polarization vector will always be in the
plane of the material, so we can neglect the out-of-plane $z$ direction from our analysis and write the Raman tensors as 2x2 matrices with vectors in the $x$-$y$ plane as the basis.

| $D_{3h} = D_3 \otimes \sigma_h$ (6m2) | $E$ | $\sigma_h$ | $2C'_3$ | $2S'_3$ | $3C'_2$ | $3\sigma_v$
|---|---|---|---|---|---|---|
| $x^2 + y^2, z^2$ | $R_z$ | $A'_1$ | 1 | 1 | 1 | 1 | 1 | 1
| (x, y) | $A'_2$ | 1 | 1 | 1 | 1 | -1 | -1 | 1
| (xz, yz) | $A''_2$ | 1 | -1 | 1 | -1 | 1 | -1 | 1
| $(x^2 - y^2, xy)$ | $E'$ | 2 | 2 | -1 | -1 | 0 | 0 | 0
| $E''$ | 2 | -2 | -1 | 1 | 0 | 0 | 0

**Figure 2.123:** From Ref. [25]. The character table for the point group $D_{3h}$. By examining the functions in the first column that transform like the irreducible representations, the matrix form of the Raman tensor can be written down.

Examining the character table, we see that the $A'_1$ mode transforms as the function $x^2 + y^2$. For now, we choose the basis where the $x$ unit vector is (1,0) and the $y$ unit vector is (0,1). In this basis, the matrix form of the Raman tensor for the $A'_1$ mode will have identical, nonzero components in the $xx$ and $yy$ positions, but will be zero in the $xy$ and $yx$ positions. The $A'_1$ mode is singly degenerate, so there is only one matrix corresponding to it. The $E'$ mode is doubly degenerate, and this irreducible representation transforms as $x^2-y^2$ and $xy$, which is equivalent to $yx$. Thus, there will be two matrices for each of the degenerate $E'$ modes, one with nonzero components at the $xx$ and $yy$ positions, and one with nonzero components at the $xy$ and $yx$ positions. Taking all of this information into account, we can write the Raman tensors for all of the modes as

$$R_A = \begin{bmatrix} a & 0 \\ 0 & a \end{bmatrix}; \ R_{E_1} = \begin{bmatrix} b & 0 \\ 0 & -b \end{bmatrix}; \ R_{E_2} = \begin{bmatrix} 0 & b \\ b & 0 \end{bmatrix}$$

(2.11)

In Eq. 2.11, $R_A$ is the Raman tensor for the $A'_1$ phonon mode and $R_{E_1}$ and $R_{E_2}$ are the Raman tensors for the two degenerate $E'$ phonon modes. We can also rewrite the Raman tensors with circularly polarized light as the basis, which is a bit more convenient for our experimental results. In this basis, the polarization vector for right-circularly polarized light is (1,0) and left-circularly polarized light is (0,1). Linearly polarized light in the $x$-direction can be written as $(1/\sqrt{2})*(1,1)$ and linearly polarized light in the $y$-direction can be written as $(1/\sqrt{2})*(1,-1)$. The singly degenerate $A'_1$ mode involves only vibrations in the $z$ direction, so it cannot alter the polarization of light in the $x$ or $y$ directions during
Raman scattering. With our coordinate system, the Raman tensor for the A’\(_1\) mode is 
\[
\begin{bmatrix}
a & 0 \\
0 & a
\end{bmatrix}
\]. On the other hand, the doubly degenerate E’ mode involves in-plane atomic vibrations, which can alter the polarization of light in the \(x\) and \(y\) directions. The Raman tensors for the two degenerate E’ modes can be written as 
\[
\begin{bmatrix}
0 & b \\
0 & 0
\end{bmatrix}
\] and 
\[
\begin{bmatrix}
0 & 0 \\
b & 0
\end{bmatrix}
\],
respectively. We can now calculate which polarization configurations are forbidden and which are allowed for each phonon mode. Fig. 2.14 shows a table of the calculated Raman selection rules for the A’\(_1\) and E’ modes for each polarization configuration, with “O” denoting that a polarization configuration is allowed for a given phonon mode, and “X” denoting that it is forbidden.

<table>
<thead>
<tr>
<th>Polarization Configuration</th>
<th>Linear //</th>
<th>Linear ⊥</th>
<th>Circ. Same</th>
<th>Circ. Opposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>E’ theory</td>
<td>O</td>
<td>O</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>A’(_1) theory</td>
<td>O</td>
<td>X</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>E’ exp.</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>A’(_1) exp.</td>
<td>O</td>
<td>X</td>
<td>O</td>
<td>X</td>
</tr>
</tbody>
</table>

a. **Figure 2.134:** The group theoretical selection rules and the experimental data for the polarization-resolved Raman measurements. “O” indicates that a mode is allowed (theory) or observed (experiment), and “X” indicates that a mode is forbidden (theory) or absent (experiment). The red colored and bolded X and O highlight where the experimental data seems to conflict with the theoretical selection rule.

We can also gain a physical understanding of the Raman selection rules by considering the three-fold rotational symmetry of the lattice. For a crystal potential that is periodic in space, Bloch’s theorem and the crystal boundary conditions lead to discretized values of momentum that are conserved up to a reciprocal lattice vector \(G\), where \(G\) connects two reciprocal lattice points. Analogously, for a lattice with three-fold rotational symmetry, an angular momentum with discretized values can be introduced, and the total angular momentum is conserved up to multiples of \(3\hbar\) since a rotation by
$2\pi / 3$ maps the lattice onto itself. We can consider the angular momentum of the photons and phonons involved in a Raman scattering event, which must conserve total angular momentum. The difference in angular momentum between the scattered and incident photons must be equal to the opposite of the change in angular momentum of the lattice from the phonon being created or destroyed. The $A'$, phonon mode transforms like the function $x^2 + y^2$, which corresponds to zero angular momentum. As a result, it can only couple two photons with the same angular momentum, so it can only participate in Raman scattering processes where the incident and scattered photons have the same polarization. The two $E'$ phonons transform like $(x + iy)^2$ and $(x - iy)^2$, which correspond to an angular momentum of $2h$ and $-2h$, respectively. The $(x \pm iy)^2$ phonons can couple an incident photon with angular momentum $\mp h$ to a scattered photon with angular momentum $\pm h$. However, they cannot couple photons with the same angular momentum. Therefore, the crystal symmetry forbids the $E'$ mode from Raman scattering where the incident and scattered light have the same circular polarization, and allows it when the incident and scattered photons have the opposite circular polarization.

We now compare our data to the selection rules obtained from group theory, which are tabulated in Fig. 2.14. We see that for the $A'$ mode, our data for all polarization configurations and excitation wavelengths agree with the Raman selection rules. For the $E'$ mode, however, the behavior is different. The Raman selection rule is satisfied for the off-resonance excitation, but it is seemingly violated when the excitation is at the valley exciton resonances: the $E'$ mode shows a prominent peak for the same circular ingoing and outgoing configuration even though it should be forbidden.

To understand our result, we need to consider both the phonon bands and the optical properties of valley excitons in monolayer MoS$_2$. First, we examine the phonon band structure to explain the 3 rel. cm$^{-1}$ redshift we observe for the $E'$ mode on-resonance. Examining the calculated energies of the phonons at high-symmetry points in monolayer MoS$_2$, we see that there is no second-order process involving phonons at the $\Gamma$ or $M$ points that has an energy within a few rel. cm$^{-1}$ of the $E'$ phonon mode [39,42]. Additionally, the transverse optical $E'$ branch becomes lower in energy for $k$ values slightly away from the $\Gamma$ point. In a normal first-order Raman process, the phonons involved must have effectively zero momentum. On exciton resonance, however, the real exciton states excited by the incident light can interact with defects, which can provide the additional momentum needed to emit a phonon with a small but finite wavevector. Thus, we believe that the slight redshift we observe for the $E'$ mode on resonance arises from a defect-assisted process involving phonons in the transverse optical $E'$ branch slightly away from the $\Gamma$ point and not a second-order combination of phonons from the $\Gamma$ or $M$ points. Qualitatively similar on-resonance Raman spectra were observed in Ref. [40] for single-layer and few-layer MoS$_2$ without polarization resolution, and the behavior of the $E'$ peak was also attributed to phonons in the $E'$ branch slightly away from $k=0$. We note that the behavior we observe did not seem to appear prominently in the helicity-resolved Raman scattering measurements performed in Ref. [32], which may
be due to a lower concentration of defects in the samples used by Ref. [32]. We also note that the behavior we observe is qualitatively similar for our exfoliated and CVD grown samples, indicating that the relevant defects for the $E'$ Raman mode scattering process are likely present in both samples even though CVD samples are known to be generally lower in quality than exfoliated samples.

Now, we consider the helicity of the valley excitons to address the polarization dependence we observe. Polarization-resolved photoluminescence measurements have shown previously that a given valley preferentially absorbs and emits light of the same circular polarization [16,18,19,22]. Thus, for on-resonance excitation with circularly polarized photons, one valley exciton will be preferentially excited. In first-order Raman processes the momentum of the light and phonon involved is very small compared to the Brillouin zone, so the exciton will remain in the same valley after emitting a phonon and cannot scatter to the other valley. If an exciton does not scatter to the opposite valley, then when it recombines and reemits light, it must emit light with the same circular polarization. The phonons slightly away from the $\Gamma$ point that we believe are responsible for the $E'$ peak we observe in the same-circular polarization configuration do not have a large enough momentum to cause intervalley exciton scattering. The Raman selection rule arising from the crystal symmetry will not be completely strict for phonons with a small but finite momentum, since their symmetry will no longer be required to be exactly the symmetry of the lattice. Therefore, the valley circular polarization selectivity will favor Raman processes with the incident and outgoing photons having the same circular polarization and suppress the circular opposite configuration, in competition with the Raman selection rule that favors the opposite behavior. We believe this causes the drastic difference for the behavior of this Raman mode on and off the valley exciton resonance. We note that the nonresonant contribution to the Raman signal will still be present on-resonance, so it is still expected that we observe the $E'$ for the opposite circular polarization.

To rule out the possibility that our observation of phonons in the $E'$ branch for the same circular polarization case is due to polarization impurity from our polarization optics, we measure the extinction ratio of the total reflected light from the sample in our Raman setup for the linear polarization geometries and the circular polarization geometries. For the 532nm excitation, the extinction ratios we measure ($I_{\text{linear parallel}}/I_{\text{linear perpendicular}}$ and $I_{\text{circular same}}/I_{\text{circular opposite}}$, where $I$ denotes intensity) are 29000 and 145, respectively, and for the 633nm excitation, the same extinction ratios are 7800 and 6000, respectively. This indicates that our observation of the $E'$ mode for the circular parallel configuration for the on-resonance 633nm excitation is not due to an artifact from polarization impurity.

We also perform a control measurement with the 633nm excitation on the G mode in exfoliated monolayer graphene, which has identical Raman selection rules to the $E'$ mode in monolayer MoS$_2$ [43]. This data is shown in Fig. 2.15. The Raman spectra we
observe for the G mode in graphene, a system with no valley polarization, exactly obey these selection rules, indicating that the seeming violation of the E’ mode we observe in MoS₂ is due to an effect in that system that is not present in graphene.

Figure 2.145: Polarization-dependent Raman spectra for the G mode in graphene taken with 633nm excitation. The symmetry-determined Raman selection rules for the G mode in graphene, a system with no selective coupling of valley pseudospin to photon helicity, are identical to those of the E’ mode in monolayer MoS₂. For the 633nm excitation, we see that the G mode obeys these selection rules.

In graphene, it is known that the appearance of the G mode in Raman spectra relies on trigonal warping of the electronic states in the Dirac cone involved in the Raman scattering process [46,47]. Without trigonal warping, the electronic states would be isotropic and lack three-fold rotational symmetry, forbidding the G mode in any polarization configuration. Similarly, in MoS₂, the valley exciton states are isotropic in the absence of trigonal warping. However, trigonal warping in MoS₂ is stronger than that present in graphene, and in graphene it is sufficiently strong that the Raman mode follows the symmetry-determined selection rules [48,49]. Thus, the selection rules
arising from the crystal symmetry should still apply to Raman scattering involving the real valley exciton electronic states excited on-resonance in MoS$_2$.

Figure 2.156: Raman spectra for monolayer exfoliated MoS$_2$ for two different numerical apertures (NAs) for the incident and scattered light having the same circular polarization. Each spectrum is normalized by the maximum of the photoluminescence peak. Reducing the NA does not affect the presence of the E’ mode, indicating that in-plane photon momentum likely does not play a large role in the apparent violation of the Raman selection rule for the E’ phonon mode.

In addition, we test the effect of in-plane photon momentum by measuring Raman spectra of exfoliated MoS$_2$ with different numerical aperture of the laser excitation and light collection, as shown in Fig. 2.16. We used one objective with an NA of 0.6 and another with an NA of 0.2, which varies the in-plane linear momentum of the incident photons. In the case of Fröhlich coupling, it is known that resonance excitation can enhance Raman-forbidden processes through coupling to finite-momentum bulk polar phonons, and the strength of this coupling depends strongly on the in-plane phonon wavenumber [50,51]. We find that the Raman spectra shape does not change significantly for objectives with an NA different by a factor of three, indicating that in-plane photon momentum probably does not play a large role in the violation of the selection rule.

Our analysis shows that on-resonance Raman scattering of phonons in the E’ branch near the Brillouin zone center in atomically thin TMDCs like MoS$_2$ may be
strongly affected by two competing factors. The Raman selection rule from the crystal symmetry favors Raman scattering with opposite incident and scattered circular polarizations, while the valley exciton circular dichroism favors Raman scattering with the same incident and scattered circular polarizations. Our experiment suggests that these two competing factors can have comparable effects on the E’ mode Raman intensity in MoS₂, as we observe E’ phonon peaks of comparable orders of magnitude for the same and opposite circular polarization configurations. Thus, the valley degree of freedom can be important along with the crystal symmetry for determining the Raman spectra for on-resonance excitations.

2.4 Conclusions and Looking Forward

In this chapter, we provided an overview of two-dimensional transition metal dichalcogenides, including their unique properties of having a direct bandgap in the monolayer limit that can greatly affect the optical properties. Monolayers also possess tightly bound, stable excitons that exist at electronic valleys, and inversion symmetry breaking causes these valleys to exhibit circular dichroism in their optical selection rules. We also provided overviews of the theory of Raman scattering and how it relates to the symmetry of a crystal, which we employed in our measurements and analysis. Using techniques that have developed over the past 15 years for exfoliating and growing 2D materials, we obtained samples suitable for optical measurements. Our polarization-resolved Raman scattering measurements and symmetry analysis revealed that the phonon modes do not necessarily follow the symmetry selection rules on valley exciton resonances due to the valley polarization. Thus, our results indicate that the valley physics in 2D TMDC’s can affect optical processes involving interactions between excitons and phonons and that Raman spectroscopy can shed light on these interactions in systems where the electronic structure of the material competes with the symmetry properties.

To add to our results, it might be helpful to perform measurements on other materials in the same MX₂ family. MoSe₂ would be the most promising candidate. In our study we chose to measure MoS₂ because it is the system that can most straightforwardly illustrate the violation of the selection rule for the laser excitation energies we have. For monolayer WSe₂, the A’₁ mode and the E’ mode are coincidentally degenerate, and for monolayer WS₂, the E’ mode is practically degenerate with a 2-phonon mode, the 2LA(M) mode [52]. Thus, it is difficult to draw conclusions about the behavior of the individual A’₁ and E’ modes under different polarization configurations in those materials. For MoSe₂, our 532nm and 633nm lasers do not allow us to have a resonant excitation - both energies are above the energy of the A and B excitons and are off-resonance, but different excitation energies than the lasers we used could possibly allow extending our measurements to this material [53].
To further build on our results, it would be interesting to further test our theory on additional samples of monolayer MoS$_2$ where the defect concentration was very low or tunable. For example, 2D materials that are encapsulated in hBN generally have a lower defect concentration than bare materials on a substrate, so it would be interesting to perform polarization-resolved Raman spectroscopy on encapsulated samples to see if they have the same behavior we have measured [54]. In addition, certain techniques could be used to vary the defect concentration, such as exposing a monolayer to an oxygen plasma. A very high-quality sample could be exposed to a plasma multiple times in controlled doses, and Raman spectroscopy could be performed each time to monitor if it changes as defects are added. This could help confirm our hypothesis or could provide evidence about which kinds of defects are or are not relevant to the Raman scattering mechanism we propose.

3. Phonon-Mediated Optical Stark Effect in Semiconducting Carbon Nanotubes

3.1 - Introduction and Chapter Overview

Since their discovery in 1991, carbon nanotubes (CNTs) have been a prominent research topic in condensed matter physics and materials science. They are a prototypical system to study 1D physics on the nanoscale, and have been singled out for their mechanical, thermal, electrical, and optical properties [55–64]. Electronically, they have attracted interest for applications such as transistors, sensors, and microelectronics [57,64]. Interest has also been shown in both their linear and nonlinear optical properties, and they have been proposed for nonlinear optical applications such as optical limiting and saturable absorption [59,62,65].

In this chapter, we will investigate the nonlinear optical properties of CNTs using optical Stark spectroscopy. Specifically, we will show that optical Stark spectroscopy can be used to probe exciton-phonon coupling in semiconducting CNTs via the phonon-mediated optical Stark effect. First, we will provide an overview of the electronic structure and optical properties of carbon nanotubes, including the effect of excitons and exciton-phonon coupling on their optical properties. Next, we will develop a simple physical model of the optical Stark effect and phonon-mediated optical Stark effect and
illustrate how these effects have been used previously to study semiconducting systems and nanostructures. Finally, we will present our experimental methods and results measuring the phonon-mediated optical Stark effect in semiconducting CNTs. By comparing our experimental results to a simple physical model, we can estimate the coupling parameters between exciton states and phonon-dressed states in CNTs.

3.2 - Optical Properties of Carbon Nanotubes and Effect of Exciton-Phonon Interactions

The 1D physics of carbon nanotubes gives rise to unique optical properties that have attracted interest both in fundamental scientific studies and in the development of applications. Since a CNT is essentially graphene rolled into a cylinder, the electronic bandstructure of a nanotube is derived from that of graphene. However, while graphene is spatially extended in two dimensions, a nanotube is spatially extended in one direction only, along the tube axis. It is confined in the other spatial direction around the tube circumference. This gives rise to additional boundary conditions for the constrained direction. In the unconstrained dimension, the electronic states can be indexed by their wavevector along that direction, and the allowed wavevectors are continuous. In the confined direction, the continuous set of allowed wavevectors becomes a discrete set of allowed wavevectors. Effectively, this means that the electronic bandstructure of a CNT is composed of “slices” of the full graphene bandstructure at discrete values of the electronic wavevector in one of the directions, as shown in Fig. 3.1 [64]. If the slicing captures the center of the Brillouin zone, where the graphene Dirac point is located, then the nanotube will have no bandgap like graphene and it will be a metallic nanotube. If the center of the Brillouin zone is not one of the discrete allowed wavevector values, then the nanotube bandstructure will not contain the Dirac point and the nanotube will be semiconducting.
Figure 3.1: From Ref. [64]. A diagram of the bandstructure of carbon nanotubes in reference to the graphene bandstructure. The additional confinement in one of the spatial dimensions in a nanotube compared to graphene allows only discrete wavevector values in that direction, which corresponds to taking slices of the graphene bandstructure at those values.

This bandstructure in CNTs corresponds to a density of states that diverges at valence band maxima or conduction band minima. The divergences in the density of states are known as Van Hove singularities [64]. In any material, the gradient of the energy with respect to wavevector is always zero at a conduction band minimum or valence band maximum. In three dimensions, this does not lead to a strong divergence of the density of states, but in a 1D system like CNTs, electronic minima and maxima do give rise to Van Hove singularities, as shown in Fig. 3.2 [66].
Fig. 3.2 shows the energy bandstructure and density of states for a metallic (a.) and semiconducting (b.) nanotube. In the metallic nanotube, the density of states never becomes zero, and there are divergences corresponding to band extrema. In the semiconducting tube, there is a band gap where the density of states is zero, and there are also divergences at the band extrema.

Optical absorption is widely described by Fermi’s Golden Rule, which gives the probability per unit time that a lower-energy electronic state \( i \) absorbs a photon and transitions to a higher-energy electronic state \( f \) \cite{67}:

\[
\Gamma_{i-f} = \frac{2\pi}{\hbar} M_{i-f}^2 \rho(E_f)
\]  

(3.1)

In Eq. 3.1, \( \Gamma_{i-f} \) is the transition probability per unit time, \( M_{i-f} \) is the transition matrix element between the initial state and final state under perturbation by a photon, and \( \rho(E_f) \) is the density of electronic states at the final energy \( E_f \). We see that if there is a divergence in the density of states at a given energy, then this can cause sharp peaks in the optical absorption at that energy. In the absence of many-body Coulomb interactions, Fermi’s Golden Rule would predict that the Van Hove singularities in semiconducting CNTs would bring about such sharp peaks at the energies corresponding to transitions between the band extrema. However, similar to 2D TMDCs, the confinement of charge carriers and reduced dielectric screening in 1D semiconducting CNTs leads to tightly bound excitons, which have a large effect on the nanotube’s optical and electronic properties \cite{59–62,65,68–70}.

Excitons have been shown to dominate the optical absorption in semiconducting CNTs \cite{65}. Analogous to a bound electron in a hydrogen atom, a bound exciton consisting of an electron and hole also has a Rydberg series of energy states, e.g. 1s, 2s, 2p, and so on \cite{70–72}. Each allowed optical transition between band extrema in a semiconducting CNT has such a series of excitonic states associated with it. In a
Rydberg series of exciton states, the selection rules for one-photon and two-photon excitation are different for states with different symmetry. Specifically, the $s$ states are singlet states with odd parity and require one-photon excitation, while the $p$ states have even parity and require 2-photon excitation [73]. This was exploited experimentally to selectively probe the one-photon and two-photon transitions in semiconducting CNTs and reveal the presence of energy levels with $s$ and $p$ exciton character [65]. This provided evidence that the resonances in the CNT absorption spectra are due to excitons, not Van Hove singularities corresponding to single-particle behavior, and determined the exciton binding energy to be hundreds of meV, indicating the excitons are easily stable at room temperature.

Figure 3.3: From Ref [74]. Experimentally measured absorption spectra for two species of chiral CNTs, (6,4) and (6,5) tubes. The main absorption peaks $E_{11}$ and $E_{22}$ correspond to $1s$ excitonic transitions. The peaks labeled “PS” correspond to phonon sidebands of the main excitonic peaks.

Fig. 3.3 shows the absorption as a function of wavelength for two different species of chiral CNTs, (6,5) tubes and (6,4) tubes [74]. The largest peak for each tube corresponds to the $1s$ excitonic transition between the highest energy valence band and the lowest energy conduction band, labeled $E_{11}$, and the second largest peak corresponds to the same transition between the second highest valence band and second lowest
conduction band, labeled E_{22}. The optical absorption is relatively flat except for the main absorption peaks and the side peaks labeled “PS,” which stands for “phonon sideband” and will be discussed in the following.

Having established that the optical properties of semiconducting CNTs are largely determined by excitons, we now move on to discuss the influence of phonons on the optical properties. Just as the electronic structure of CNTs could be understood as arising from the electronic structure of graphene with zone-folding caused by the additional confinement in one direction, the phonon bandstructure can be imagined in the same way, with the phonon modes in CNTs originating from corresponding modes in graphene [75–78]. The strong exciton-phonon coupling in CNTs effects the behavior of optical processes and has enabled the study of electron-phonon interactions in CNTs by various optical methods, including normal and ultrafast transient absorption, photoluminescence, and nonresonant and resonant Raman spectroscopy [68,69,79–86].

One of the most prominent ways that electron-phonon interactions effect the optical properties of CNTs is by causing phonon sidebands in absorption and luminescence spectra, as seen above in Fig. 3.3. In the main absorption peaks, an exciton is directly excited by a photon and there are no phonons involved. In the phonon sidebands, the mechanism is more complicated and has been investigated experimentally and theoretically [68,69]. The exciton-phonon coupling mixes the optically bright exciton, which must have a momentum of $q=0$, with phonons of momentum $q$ and other dark excitons of momentum -$q$, ensuring the total momentum remains zero.

Fig. 3.4 shows the theoretical contributions to the absorption in semiconducting CNTs from excitons and phonons [69]. The total absorption is shown in red and is a convolution of the electronic and phonon contributions. The large delta function at E=0 corresponds to the bright E_{11} exciton resonance, and the peak in the red curve around 200meV above the E_{11} transition is the phonon sideband. The phonon contributions are drawn as delta functions due to their narrow linewidth. The main contribution to the phonon sideband comes not from phonons of momentum $q=0$, but from phonons at the K point of the graphene Brillouin zone and dark excitons with an opposite momentum. Experiments have provided additional evidence for this interpretation using a combination of absorption and photoluminescence spectroscopy [68]. Thus, it is well established that exciton-phonon coupling can modify the optical behavior of semiconducting CNTs, and can even be used to gain insight into optically dark excitonic states. In the next sections, we will explore how ultrafast, nonlinear optical spectroscopy, specifically optical Stark spectroscopy, can further be used to investigate exciton-phonon interactions in CNTs.
3.3 - The Optical Stark Effect and Phonon-Mediated Optical Stark Effect

The optical Stark effect is a shifting of the optical transition energies in a system as a result of illumination by intense radiation [87–93]. Fundamentally, it can be understood as originating from interactions between electronic states and photon-dressed electronic states, called Floquet states. Ordinarily, such an effect would be negligible, but the high intensities allowed by ultrafast lasers enable can induce a strong enough response that it can be easily measured. Experimentally, the optical Stark effect is measured as a difference in the absorption spectrum when the perturbing light is present compared to when it is absent. Optical Stark effects have been measured in many semiconducting systems, including semiconducting 2D materials and semiconducting nanostructures like carbon nanotubes [94–99].

Fig. 3.5 is a schematic diagram of the optical Stark effect in a generic two-state excitonic system. Without any light present, the energy eigenstates of the system consist of a ground state and an exciton state. The intense light that induces the optical Stark effect is labeled as the “pump.” As seen in the diagram, the interaction of the electronic states (solid lines in Fig. 3.5) with the strong light gives rise to Floquet states, or photon-dressed states (dashed lines in Fig. 3.5). Before considering any interactions between states, the Floquet states are separated from the electronic states by the pump energy. One Floquet state has an energy equal to the ground state energy plus the pump energy,
and the other has an energy equal to the exciton energy minus the pump energy. The pump light can be thought of as perturbing the Hamiltonian of the original system and inducing interactions between states. The perturbed Hamiltonian will have different energy eigenstates than the original Hamiltonian. The original eigenstates are shown in the left half of Fig. 3.5 and the new energy eigenstates of the perturbed Hamiltonian are shown in the right half of the figure. We see that the photon-dressed ground state and exciton state shift away from each other, as do the photon-dressed exciton state and ground state. This “level repulsion” behavior is typical in quantum systems when a perturbation to the system allows energy states near each other to interact.

For the case when the pump energy is less than the exciton optical transition, we see that the net effect is for the ground state and exciton state to shift away from each other. When the ground state – exciton optical transition is then measured by a “probe” photon, the optical resonance occurs at a higher energy than when the pump light is absent. When the pump energy is greater than the exciton transition, the level repulsion with the Floquet states will cause the exciton and ground states to shift toward each other, and a redshifted optical resonance will be measured by the probe.

**Figure 3.5:** A schematic diagram of the optical Stark effect. Under the influence of pump photons, the ground state and exciton state (solid lines) will interact with the photon-dressed states (dashed lines), which will cause a shift of the energy levels away from each other. The resulting shift in the excitonic optical transition can be measured with a probe photon.

The essential physics of the optical Stark effect in a two-state system can be captured with a simple mathematical model. First, we assume a generic two-state system
with energy levels given by $E_1$ and $E_2$, and that the basis vectors for these energy eigenstates can be written as $(1,0)$ and $(0,1)$, respectively. Under this assumption, the Hamiltonian for the system can be written very simply as

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{3.2}$$

Now, consider the effect of a perturbation which induces interactions between the two states. We can encode interactions between the basis states as off-diagonal matrix elements in the Hamiltonian, and we can write the total Hamiltonian as a sum of the original and perturbing Hamiltonians:

$$H_{tot} = H_0 + H_{int} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix} \tag{3.3}$$

In Eq. 3.3, the interaction between the original energy eigenstates is parametrized by $V$. The total Hamiltonian in Eq. 3.3 will have new energy eigenvalues and eigenvectors. Diagonalizing the total Hamiltonian, we see that the new energy eigenvalues are

$$E_+ = \frac{1}{2}(E_1 + E_2 + \sqrt{(E_1 - E_2)^2 + 4V^2})$$

$$E_- = \frac{1}{2}(E_1 + E_2 - \sqrt{(E_1 - E_2)^2 + 4V^2}) \tag{3.4}$$

Now, we can assume that in the perturbative regime, $V \ll E_1, E_2$, which allows us to do a Taylor expansion for the quantity inside the square root. After Taylor expanding and keeping only the first term that depends on $V$, we see that Eq. 3.4 can be approximated as

$$E_+ = E_1 + \frac{V^2}{E_1 - E_2}$$

$$E_- = E_2 - \frac{V^2}{E_1 - E_2} \tag{3.5}$$

Thus, we see that each of the original energy levels is shifted upward or downward. To second order in $V$, the magnitude of the energy shift is inversely proportional to the energy difference between the levels and directly proportional to the square of the coupling parameter $V$.

We can now add additional details to this model to make it more directly relevant to measurements of the optical Stark effect. In the optical Stark effect, an electronic state, such as the ground state or exciton state, interacts with a photon-dressed state in the
presence of photons. Taking the energy level diagram from Fig. 3.5, we can set $E_1$ as the energy of the exciton state and $E_2$ as the energy of the photon-dressed ground state that interacts with it. Taking the energy of the ground state to be zero, we get $E_2 = \hbar \omega_{pump}$, the energy of a pump photon. Similar to the case of a static field in the static Stark effect, we can write the coupling parameter $V$ as $\mu E_{pump}$, where $\mu$ is the transition dipole moment and $E_{pump}$ is the electric field associated with the pump. Now, we see that Eq. 3.5 contains the well-established result for the optical Stark effect that the shift in energy levels is inversely proportional to the pump detuning, or the difference between the pump energy and the energy level separation, and directly proportional to the pump light intensity [87–93,95].

We also point out that near resonance, where $\hbar \omega_{pump}$ is near the exciton transition energy, the optical Stark effect does not predict a pure shift of the exciton transition.

Examining Eq. 3.4, we see that as the pump energy approaches the exciton energy, i.e. as $E_2$ approaches $E_1$, the Taylor expansion used previously to derive an energy shift becomes invalid. Instead, we see that the energy level previously at $E_1$ will be split into two energy levels above and below it. Thus, it is characteristic of optical Stark spectroscopy to see a shift of the exciton transition energy when the pump energy is away from resonance, and see a splitting of the exciton absorption peak when the pump energy is directly on resonance, with a crossover regime where both effects are present when the pump energy is near the exciton resonance.

The optical Stark effect can be measured experimentally in systems that have well-defined, sharp energy levels. Since excitons have sharp energy levels compared to typical energy bands found in solid state systems, semiconducting solids that can support excitons are good candidates to observe the optical Stark effect. In fact, the first observation of the resonant optical Stark effect in a solid state system was on a crystal of Cu$_2$O, an excitonic system, using a CO$_2$ laser as pump with an optical electric field magnitude of around $10^6$ V/m [95].

Ultrafast lasers are also convenient tools to study optical Stark effects in semiconductors. These lasers have optical pulses on the order of a few hundred femtoseconds in duration, which allows for very high peak powers and correspondingly high optical intensities when the beam is focused. In addition, the optical Stark effect only occurs when the pump laser is present, i.e. when the pump and probe pulses are overlapping on the sample in space and time. Thus, it is helpful evidence in support of the optical Stark effect when time-resolved measurements can show that the signal rises and falls as the probe pulse arrival time is tuned to be synchronous with and offset from the pump pulse. Lock-in detection is also useful to measure the difference in absorbed or transmitted light when the pump is present vs absent. In this scheme, the pump light is modulated at a certain frequency, and the component of the absorbed or transmitted light
that is also changing at that frequency is isolated. This isolates the difference between the pump-present and pump-absent signals by removing any noise or background not being modulated at the right frequency. Fig. 3.6 shows a typical illustration of the measured differential transmission or absorption from the optical Stark effect using lock-in detection [96]. The top panels show the original absorption peak of the sample (dotted line), corresponding to when the pump light is absent, and absorption peak that has been shifted in energy (solid line) from the optical Stark effect when the pump light is present. Subtracting the two curves gives a derivative-shaped feature, shown in the bottom panels, that corresponds to the signal measured with lock-in detection. The sign of the dispersive feature is opposite for opposite Stark shifts.

**Figure 3.6:** From Ref. [96]. A diagram of typical data measured in optical Stark spectroscopy. The upper panels show the normal (pump absent) absorption peak of the sample (dotted line) and the shifted (pump present) absorption peak (solid line). The derivative-like features in the bottom panels are the subtraction of the two curves, which correspond to the differential absorption or transmission signal typically measured in optical Stark spectroscopy.

The optical Stark effect has been used previously to study coupling between different energy levels in nanomaterials, such as 2D TMDC’s and CNTs. As described in the previous chapter, 2D TMDC’s can support tightly bound, stable excitons whose properties can be influenced by their unique valley electronic structure and many-body Coulomb effects due to reduced screening. Both intervalley biexcitonic effects and valley selective effects arising from the valley circular dichroism have been observed.
with optical Stark spectroscopy on monolayer TMDC’s \([21, 23, 96, 97]\). As mentioned earlier in the chapter, semiconducting CNTs are also a good platform to support stable, bound excitons, and Optical Stark effects have also been observed in semiconducting CNTs \([94, 98]\). In our measurements described in the next section, we will extend optical Stark spectroscopy on semiconducting CNTs to probe coupling between phonon-dressed states and excitonic states.

A particular kind of optical Stark effect is the phonon-mediated optical Stark effect (PMOSE), shown diagrammatically in Fig. 3.7.

**Figure 3.7:** A diagram of the phonon-mediated optical Stark effect. Similar to the regular optical Stark effect, pump photons induce interactions between states that shift the energy levels of those states. In the phonon-mediated optical Stark effect, interactions are driven between electronic states and phonon-dressed states. In this diagram, the level labeled “phonon state” is a phonon-dressed ground state and has an energy greater than the ground state by an amount equal to the phonon energy, \(E_{ph}\). Even though the probe is not directly measuring the phonon state, the effect of the phonon state coupling can be seen in the probed ground state – exciton transition.

The PMOSE is the same general effect as the regular Stark effect, only one of the states involved is a phonon-dressed electronic state rather than the effect occurring between pure electronic states. In Fig. 3.7, the phonon-dressed ground state is shown at an energy equal to the phonon energy \(E_{ph}\) above the ground state. The optical Stark effect between the phonon-dressed state and the exciton state causes a shift of each of those states.
When the probe light then measures the transition energy between the ground state and exciton state, there will be an effect measured from the PMOSE. The PMOSE allows coupling between electronic states and phonon states to be investigated through the probing of pump-induced shifts in electronic transitions.

In general, the optical Stark effect and PMOSE will occur together in a 3-level system containing a phonon state as shown in Fig. 3.7. In Fig. 3.7, only the PMOSE effects are displayed, but the pump light will still induce a normal optical Stark effect between the ground state and exciton state. The total effect on the ground state – exciton transition will be the combination of these two effects. As described above, the magnitude of the optical Stark effect depends on the detuning between the pump energy and the difference between the coupled energy levels and on the transition dipole moments of the relevant transitions. Even if the effects of the PMOSE are weak due to a smaller transition dipole moment, by tuning the pump energy to be close to the energy difference between the phonon state and exciton, the PMOSE effect can be increased, while the regular optical Stark effect will not be enhanced too much due to the pump being far away from the ground state – exciton resonance. This allows clear measurement of the PMOSE.

The PMOSE has been measured before in excitonic systems other than CNTs and has been treated theoretically [100–104]. It has been seen in the II-VI direct bandgap semiconductor CdS, which is a polar material that has strong exciton-phonon coupling due to the Frohlich interaction [100]. It has also been seen in the quasi-1D crystalline polymer polydiacetylene-PTS [101,102]. Fig 3.8 shows transient-absorption data from polydiacetylene-PTS that illustrates the PMOSE [101]. The probe light energy is on the horizontal axis and the differential transmission, or change in the transmitted probe light induced by the pump, is on the vertical axis. The different curves correspond to different pump energies. For a pump energy of 1.699 eV, the pump is below the phonon state – exciton transition, and the probe shows a small and mostly negative change in the differential transmission. As the pump increases in energy and moves closer to the phonon state – exciton resonance, the signal becomes dispersive, and then positive when the pump is on the phonon state – exciton resonance around 1.75 eV, corresponding to increased transmission. As the pump is increased further off the resonance, the signal becomes dispersive again, but with the opposite sign as before, as seen for the curve for a 1.78 eV pump. This trend will be investigated and explained in more detail in the next section, where we present data measuring the PMOSE in carbon nanotubes.
Figure 3.8: From Ref. [101]. Representative data showing the PMOSE in polydiacetylene-PTS. The probe energy is on the horizontal axis, the pump-induced change in probe transmission is on the vertical axis, and different curves correspond to different pump energies.

3.4 - Experimental Results Measuring the Phonon-mediated Optical Stark Effect in Semiconducting Carbon Nanotubes

Carbon nanotubes (CNTs) have long attracted attention as an interesting one-dimensional platform to study electronic and optical phenomena. As described above, strong Coulomb interactions in semiconducting CNTs give rise to stable, bound excitons at room temperature that dominate the optical absorption spectra, and electron-phonon coupling can strongly affect optical phenomena in CNTs. As outlined in section 3.2, in semiconducting CNTs, exciton-phonon coupling has been shown to cause prominent
phonon sidebands in linear absorption and luminescence measurements. In this section, we investigate the effect of exciton-phonon coupling on the nonlinear optical properties by performing optical Stark spectroscopy on (6,5) semiconducting CNTs. Optical Stark spectroscopy has been well established as a tool to study ultrafast modulation of optical transitions in many excitonic systems, such as CNTs, polymers, and 2D semiconductors, as outlined in the previous section. In this study, we employ it as a method to quantitatively extract effective transition dipole moments involving phonon-dressed states in a system with strong electron-phonon coupling. In our measurements, we observe an optical Stark effect arising from the ground state – exciton transition and a phonon-mediated optical Stark effect arising from a phonon-dressed state – exciton transition. We identify the phonon-dressed state as a coupling between the ground state and Γ-point G mode phonon. By performing theoretical calculations to compare to our data, we extract effective transition dipole moments for both the ground state – exciton and G phonon-dressed state – exciton transitions. The G phonon-dressed state does not contribute to the sidebands seen in absorption and luminescence measurements, which are instead dominated by K point phonons and K point dark excitons as described in Section 3.2. Thus, our results indicate that optical Stark spectroscopy can be a useful method for investigating optically driven interactions between electronic states and phonon states that are not accessible via linear measurements.

![Figure 3.9](image)

**Figure 3.9:** (a.) The absorption of our solution of (6,5) CNTs in 1% DOC suspension in water. The main E\textsubscript{11} exciton peak is labeled “I” which is from (9,1) tubes that are an impurity in our sample. (b.) A simple diagram of the 3-level system in our CNTs and the pump-induced couplings between the relevant states involved in the optical Stark effect and phonon-mediated optical Stark effect.

Our sample consists of semiconducting (6,5) CNTs in 1% deoxycholate (DOC) suspension in water. Samples were prepared from CoMoCat-generated SG65i carbon nanotubes as source material. The sample was enriched in the (6,5) chirality using an
aqueous two-phase approach [105]. After chirality enrichment, the sample was exchanged into a 1% aqueous solution of sodium deoxycholate (DOC) using ultrafiltration through a cellulose membrane-based Amicon Ultra (100K) 15 mL centrifugal filter.

Our solution is held in a quartz optical cuvette with 2mm path length, allowing all of our optical measurements to be done in a transmission geometry. Fig. 3.9a shows the transmission difference spectrum of our CNT sample as a function of wavelength, \((T_{\text{ref}} - T_{\text{CNT}})/T_{\text{ref}}\), where \(T_{\text{ref}}\) is the transmitted light through a reference sample of pure water and \(T_{\text{CNT}}\) is the transmitted light through our CNT sample. This transmission difference is proportional to the absorption of our sample. We see a prominent peak at 988nm corresponding to the E_{11} exciton absorption of (6,5) CNTs [65]. There is a small impurity presence of (9,1) CNTs in our solution, which gives rise to the small peak around 922nm, labeled “I” in Fig. 3.9a, that corresponds to the (9,1) E_{11} exciton absorption [106]. Since the (9,1) peak is relatively small and well-separated in energy from the main (6,5) absorption peak, its presence will not have a significant effect on our measurements probing the (6,5) exciton.

In a simple semiconducting system with a ground state and exciton state, the optical Stark effect describes how irradiation with pump light will induce an interaction between the ground state and exciton state that will modify the exciton lineshape and position. Specifically, for pump energies below the exciton resonance, the exciton line will blueshift, for pump energies above the exciton resonance, the exciton line will redshift, and for pump energies approximately equal to the exciton resonance, the exciton lineshape will display splitting behavior. In semiconducting CNTs, vibrational states can also become involved in optical Stark effects, giving rise to the phonon-mediated optical Stark effect (PMOSE). The PMOSE has been observed before in other systems with strong electron-phonon coupling, such as in organic molecules and conjugated polymers, but not in inorganic solids [100–102]. Carbon nanotubes provide an interesting intermediate system between organic molecular and crystalline solid materials. Fig. 3.9b shows the electronic and vibrational states involved in the PMOSE for a semiconducting CNT. The phonon-dressed ground state, or vibrational state, has an energy higher than the ground state by an amount equal to the phonon energy.

In our measurements, we optically pump the CNT with photon energies below the E_{11} exciton resonance to avoid any excitation of real charge carriers in the CNTs. This allows us to isolate the coherent response when the pump and probe are overlapped in time. Upon excitation with the below-exciton-resonance pump laser, there will be a blueshift of the ground state – exciton transition from the usual optical Stark effect. In addition, from the PMOSE, the pump light will induce coupling between the vibrational state and the exciton state, which can contribute an additional blueshift, redshift, or splitting behavior to the exciton transition depending on whether the pump light has energy less than, greater than, or approximately equal to the vibrational state – exciton transition. The combination of these two effects illustrated in Fig. 3.9b – coupling
between the ground state and exciton and between the vibrational state and exciton – together determine the ultrafast modulation of the exciton lineshape and position that we measure. As illustrated in Fig. 3.9b, the PMOSE contribution will be most prominent when the sum of the pump photon energy and phonon energy is equal to the probe photon energy.

In our measurements, we perform pump-probe spectroscopy using a pump with wavelength varying from 1080nm to 1300nm and a supercontinuum probe with a wavelength range spanning from 900nm – 1050nm. For our pump, we use the signal pulse from a Light Conversion Orpheus optical parametric amplifier that is pumped by the output of a Pharos regenerative amplifier. The spectrum of our probe is shown in Fig. 3.10. It is generated by focusing fundamental 1020nm light from the regenerative amplifier onto a sapphire crystal. Our supercontinuum probe light spans across a range that includes the (6,5) $E_{11}$ exciton resonance, allowing us to probe the instantaneous changes in the $E_{11}$ exciton absorption induced by the pump. The large difference in intensity in our probe light for wavelengths near 1020nm compared to wavelengths between 900 nm and 950nm means the signal to noise ratio is very different for different wavelengths. To overcome this, we perform one set of measurements with a 1000nm short pass filter, which blocks the strong peak of the probe light and allows us to increase the probe power and acquire data from 920nm to around 980nm with better signal. We then remove the filter and reduce the probe power so the strong peak doesn’t saturate our detector, and acquire data again with a good signal in the regime of around 970nm – 1050nm. We can then combine the two datasets to obtain a transient absorption spectrum with a reasonable signal to noise ratio for the entire wavelength range of 920nm – 1050nm. After passing through our sample, the probe light is directed to a grating and then a linear array CCD detector that allows us to measure the transient probe spectrum for a given pump wavelength and pump-probe time delay.

We perform our pump-probe measurements in a noncollinear transmission geometry, as shown in Fig. 3.11. The spatial separation of the pulses allows us to more easily filter out the pump light from the detector. The angle between the pump and probe determines the volume over which they will be overlapped in the cuvette, which contributes to the strength of our signal. The temporal width of our pulses is around 250 fs. In our cuvette, our CNTs have an isotropic distribution of angles, and only the component of light polarization parallel to the CNT axis interacts with it strongly. Taking this into account, we set the pump and probe to have the same linear polarization to ensure maximum signal. The pump and probe power are controlled with variable ND filters. We focus the pump light to a spot size of around 140µm and the probe to a spot size of around 45µm. The repetition rate of our laser is 150 kHz.
Figure 3.10: The spectrum of the supercontinuum light used for our probe pulse.

Figure 3.11: A diagram of our non-collinear pump-probe geometry and optical cuvette.

Fig. 3.12 shows representative transient probe transmission spectra for two different pump wavelengths of 1130nm and 1220nm. The top panels of Fig. 3.12a and 3.12b show probe wavelength on the horizontal axis and pump-probe delay time on the vertical axis. The change in the transmitted light induced by the pump is represented by
dT, and T represents the total light transmitted through the sample when there is no pump present. Thus, dT/T (represented by color in the top panels) is the pump-induced fractional change in the transmitted probe light, which is proportional to the negative of the change in absorption. The bottom panels of Fig. 3.12a and 3.12b are horizontal cross sections of the corresponding top panel for t0, or zero pump-probe time delay, with probe wavelength again on the horizontal axis and dT/T on the vertical axis. A positive dT/T signal corresponds to increased transmission through the sample, or decreased absorption, and a negative signal corresponds to decreased transmission or increased absorption. In both Fig. 3.12a and 3.12b, we see a strong signal that is only present within ~200fs of t0. For probe wavelengths near the (6,5) E11 exciton resonance at 988nm, we see the coherent signal is positive (decreased absorption) for longer wavelengths, while for shorter probe wavelengths, we see the coherent signal is negative (increased absorption). This general behavior qualitatively corresponds to a blueshift of the exciton line, which we expect to arise from the optical Stark effect since our pump energies are below the exciton resonance.

**Figure 3.12:** Transient transmission spectra for (a.) 1130nm pump and (b.) 1220nm pump. The horizontal axis is the probe wavelength for all plots. dT/T is the fractional change in the probe transmission induced by the pump.
We also point out that the negative component of the dT/T signal for the 1130nm pump in Fig. 3.12a appears to be double-peaked, with one peak near a probe wavelength of 973nm and the other near 957nm. For the 1220nm pump shown in Fig. 3.12b, the spectra is qualitatively different, with the negative component of the signal appearing to have only a single peak around 971nm. The position of the additional negative peak in Fig. 3.12a at 957nm corresponds to a separation of the pump and probe energies of 197meV, which matches the nanotube G+ phonon mode energy [75,76,78,82]. To investigate the curious evolution of the spectra with pump wavelength more carefully, we will systematically study the coherent effects by continuously tuning the pump energy from 1080nm to 1300nm.

We also note that in the top panel of Fig. 3.12a, for a pump wavelength of 1130nm, the transient probe data shows a weak component for probe wavelengths near the exciton resonance at 989nm that persists beyond when the pump and probe pulses are temporally overlapped. Thus, although we are pumping below the exciton resonance, there appears to be some mechanism that allows a small population of real carriers to be excited. In Fig. 3.12b, for a pump wavelength of 1220nm, we see that only the coherent, short lived signal is present. After examining the behavior of this weak, long lived feature as a function of pump wavelength, we observe that it decays over a timescale of several to tens of picoseconds and decreases with the pump energy, eventually vanishing for pump wavelengths greater than 1200nm. To better investigate the optical Stark effect and PMOSE by isolating the coherent signal at t0 for pump wavelengths less than 1200nm, we subtract the signal at t=0.5ps from the signal at t0. Since the coherent signal has totally decayed by t=0.5ps but the weak, long-lived components have hardly decayed, this provides a more accurate measure of the pure coherent signal at t0.

Having established that our measurements are dominated by the coherent signal, we systematically study the coherent effects by continuously tuning the pump energy from 1080nm to 1300nm. Fig. 3.13a displays the 2D transmission spectroscopy data at zero pump-probe delay, with pump wavelength on the vertical axis and probe wavelength on the horizontal axis. The color represents the pump-induced change in the probe transmission. For pump wavelengths shorter than 1200nm, the spectra at t=0.5ps have been subtracted from the t0 spectra as described above. For all pump wavelengths, we observe that the most prominent behavior near the exciton resonance is a negative response for shorter probe wavelengths and a positive response for longer probe wavelengths, qualitatively in agreement with a blueshift of the exciton line arising from the optical Stark effect. We also observe a feature that occurs when the pump and probe are separated by an energy of ~197meV, indicated by the dotted line in Fig. 3.13a. This feature is clearly visible in our data for pump wavelengths ranging from 1110nm to 1200nm. This energy of 197meV matches the G+ mode phonon energy for CNTs, and we attribute it to the PMOSE [100–103].
Figure 3.13: (a. and b.) Experimentally measured (a.) and theoretically calculated (b.) differential transmission spectra at t0 as a function of pump and probe wavelength. The large negative and positive features whose position is independent of pump wavelength is the exciton blueshift from the optical Stark effect, and the diagonal feature marked by a dotted line in (a.) is from the PMOSE. (c. through f.) The differential transmission spectra as a function of probe wavelength for different values of the pump wavelength, showing the evolution of the PMOSE feature with pump wavelength.
To further understand our experimental data and confirm the contributions of the OSE and PMOSE to our measured signal, we can model our experimental data using a simple effective Hamiltonian. Since we always pump with a photon energy well below the exciton resonance, the contribution from the optical Stark effect will be a blueshift of the exciton energy, so that the shifted exciton energy $E'_{11}$ is given by

$$E'_{11} = E_{11} + \frac{V_1^2}{(E_{11} - \hbar\omega)} \quad (3.6)$$

In Eq. 3.6, $V_1$ represents the coupling between the ground state and exciton state and $\hbar\omega$ is the pump photon energy. In our effective Hamiltonian, we can now model the coupling between the vibrational state and exciton state. First, we define the bare exciton-photon states to be used as the basis states to be $|E'_{11}, (n - 1)\hbar\omega\rangle$ and $|g', n\hbar\omega\rangle$. Here, $g'$ represents the phonon-dressed ground state or vibrational state and $E'_{11}$ is the exciton state with the blueshift from the ground state – exciton coupling taken into account. Now, we can write the PMOSE effective Hamiltonian as

$$H_{\text{eff}} = \begin{pmatrix} E_{11} & V_2 \\ V_2 & E_{\text{vib}} + \hbar\omega \end{pmatrix} \quad (3.7)$$

In Eq. 3.7, $E_{\text{vib}}$ is the energy of the vibrational state and $V_2$ represents the coupling between the vibrational state and exciton state. The coupling constants $V_1$ and $V_2$ are related to the effective transition dipole moments $\mu_1$ and $\mu_2$ by $V_{0i} = \mu_i E_{\text{eff}}$, where $i=1,2$ and $E_{\text{eff}}$ is the local optical field strength [87,94,98,107]. Diagonalization of the Hamiltonian allows us to solve for the dressed state energy eigenvalues. Then, we assume a Lorentzian oscillator at the new eigenvalue energies, with a phenomenological inhomogeneous broadening of 8meV. We also assume a homogenous broadening of the exciton of 26 meV which is estimated from the absorption data. This allows us to calculate the absorption of the dressed states. The calculated absorption difference between the dressed states, with pump light present, and initial states, with pump light absent, corresponds to our measured pump-probe signal. From our simulation, we extract a value for $V_1$ of 11.5meV and a value for $V_2$ of 3.2meV to get the best fit of the experimental data.

The simulated pump-probe signal is displayed in Fig 3.13b. We are able to reproduce both the blueshift feature arising from the OSE and the PMOSE feature occurring when the pump and probe photon energies are separated by the G+ phonon energy. The diagonal PMOSE feature is more apparent in the simulated data. To see the comparison between our experimental data and simulation in more detail, Figs. 3.13c-f show the measured and calculated probe spectra for four different pump wavelengths of 1120nm, 1140nm, 1170nm, and 1200nm. The spectra shown in Figs. 3.13c-f show the probe signal, $dT/T$, on the vertical axis vs. probe wavelength on the horizontal axis, and correspond to horizontal cross-sections of the 2D color plot at positions indicated by the
red dots in Fig. 3.13a. In Fig. 3.13c, for a pump wavelength of 1120nm, the PMOSE feature occurs as a dip around a probe wavelength of 950nm, corresponding to a 197meV separation of the pump and probe energies. In Fig. 3.13d, for a pump wavelength of 1140nm, the PMOSE also occurs as a negative dip, but at a probe wavelength of 1165nm. In Fig. 3.13e, for a pump wavelength of 1170nm, the PMOSE feature causes a modification of the measured probe spectra near 985nm, which is close to the exciton resonance and directly on top of the blueshift OSE feature, making the pure PMOSE feature harder to distinguish. For a pump wavelength of 1200nm shown in Fig. 3.13f, the PMOSE feature causes a slight negative dip in the probe spectra around 1008nm.

Although for individual probe spectra the PMOSE feature is only easily visually distinguishable from the OSE behavior for pump wavelengths shorter than ~1150nm (corresponding to the PMOSE feature occurring on the blue side of the main OSE blueshift feature), comparison of Fig. 3.13a and 3.13b shows that the PMOSE feature is clearly present in our measured data for pump wavelengths from 1110nm – 1200nm, beyond which it appears to be too small for us to measure clearly. Using our extracted values for $V_1$ of 11.5meV and $V_2$ of 3.2meV, and combining with our measured pump intensity of $6 \times 10^{12}$ W/m$^2$ (corresponding to a pump power of 8mW), we calculate values of 9.5D and 2.7D for the effective transition dipole moments $\mu_1$ and $\mu_2$.

To better illustrate the contributions from the PMOSE feature, in Fig. 3.14 we plot our experimentally measured and simulated data as a function of pump wavelength for a fixed probe wavelength, with dT/T on the vertical axis and pump wavelength on the horizontal axis. Here, we can see the evolution of the PMOSE feature for different probe wavelengths. In Fig. 3.14a, for a probe wavelength of 950nm, which is on the blue side of the exciton resonance, the PMOSE feature manifests as a negative dip. In Fig. 3.14b, for a probe wavelength of 970nm, the PMOSE feature has a dispersive shape. In Fig. 3.14c, the probe wavelength is 985nm which is very close to the exciton resonance, and the PMOSE feature appears as a positive peak. In Fig. 3.14d, the probe wavelength is 1009nm, which is on the red side of the exciton resonance, and the PMOSE feature takes on a dispersive shape again, but with the opposite sign as in Fig. 3.14b. We see that our simulation is able to capture this behavior for probe wavelengths near the exciton resonance and on the red and blue sides of the exciton resonance. We also note that this behavior is the same qualitative behavior as observed for the PMOSE in polydiacetylene-PTS as shown in the previous section [101,102].
Figure 3.14: Our experimentally measured and theoretically simulated transient transmission spectra as a function of pump wavelength. This is the same data as in Fig. 3.13, with each plot for a fixed probe wavelength corresponding to a vertical cross section of Fig. 3.13a (experimental data) and 3.13b (simulation). Plotting the data in this way more clearly isolates the PMOSE feature and shows its progression from negative, to dispersive, to positive, to dispersive again as the probe wavelength approaches, passes through, and moves away from the exciton resonance.

We note that in addition to the dressed state model provided above, an alternative way to understand our measured PMOSE is through a stimulated inverse Raman scattering picture [108–114]. The general third order nonlinear Raman susceptibility has been calculated to be

\[
\chi^{(3)} = \frac{A}{\omega_{vib} - (\omega_{pr} - \omega_{pu}) - i\Gamma_{vib}}(\omega_{e} - \omega_{pr} - i\Gamma_{e})^2
\]  

(3.8)
In Eq. 3.8, $A$ is an overall constant, $\omega_{vib}$, $\omega_{pr}$, and $\omega_{pu}$ are the phonon, probe, and pump frequencies, respectively, and $\Gamma_{vib}$ and $\Gamma_e$ correspond to the lifetimes of the vibrational and exciton states. The imaginary part of this third order susceptibility describes the pump induced absorption change from the PMOSE, and is equivalent to the PMOSE model outlined above \cite{103,104,108,110,115}. However, it does not include the optical Stark effect from the interaction between the ground state and exciton state that occurs prominently in our measurements and is needed to quantitatively fit our data. This stimulated Raman scattering framework provides a simple way to understand the PMOSE away from the exciton resonance. Since we are describing the PMOSE feature, the pump and probe are separated by the phonon energy although neither is resonant with an electronic transition. In this situation, probe photons are down-converted from the probe energy to the pump energy in the presence of a strong pump field, and the CNT absorbs a phonon as required by energy conservation. Consequently, a negative dip will be observed in the transmitted probe light since some of the probe light is being converted to the pump energy. This matches what we observe in Fig. 3.14a, which corresponds to the above situation. It is harder to gain an intuitive understanding of the behavior close to the exciton resonance with stimulated Raman scattering, where the data show more complicated splitting behavior from the PMOSE that occurs on top of the prominent optical Stark effect feature, as is the case shown in Fig. 3.13e. In contrast, the PMOSE description can intuitively capture both the off-resonance and on-resonance behavior with a relatively simple physical picture.

We have performed optical Stark spectroscopy on (6,5) CNTs in aqueous solution and shown that strong exciton-phonon coupling gives rise to a prominent PMOSE in this system. By comparing our experimental results to a theoretical model, we extract values for the effective transition dipole moments, showing that optical Stark spectroscopy can be a useful tool for investigating optically driven interactions between vibrational states and electronic states.

3.5 - Conclusions and Looking Forward

In this chapter, we provided an overview of the electronic structure of carbon nanotubes, and how it influences their optical properties. Specifically, the optical absorption and luminescence is dominated by excitons. Electron-phonon interactions also play an important role in their optical properties, as they can lead to sidebands in luminescence and absorption peaks. We also outlined the relevant theory of the optical Stark effect and phonon-mediated optical Stark effect and some experimental results in systems similar to carbon nanotubes, such as polyacetylene-PTS. Our results extended optical Stark spectroscopy to carbon nanotubes, where we observe a strong PMOSE for the first time. This provides an example of how strong exciton-phonon coupling can also
effect the nonlinear optical properties in CNTs. By comparing our data to a simple simulation, we were able to estimate the transition dipole moments for the ground state – exciton and phonon-dressed ground state – exciton transitions, showing that optical Stark spectroscopy can be used to gain information about exciton-phonon interactions in systems where it is strong. It might be interesting to extend our measurements to other species of nanotubes with different chirality and different diameter, which could allow a systematic study of the exciton-phonon coupling for different types of nanotubes and provide additional information about the factors that control the strength of electron-phonon interactions.
References


