INVESTIGATION OF THE OPTICAL PROPERTIES IN LOW-DIMENSIONAL MATERIALS AND HETEROSTRUCTURES

by

Jaydeep Dharmendra Joshi A Dissertation Submitted to the Graduate Faculty of George Mason University In Partial fulfillment of The Requirements for the Degree of Doctor of Philosophy Physics

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Date:	Fall Semester 2021 George Mason University Fairfax, VA

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Dedication

I dedicate this work to my family back in India, my parents and grandparents, and my partner of a lifetime. I hope I have made you all proud.

Acknowledgments

I wish to first thank my advisor **Dr. Patrick Vora** for being an amazing mentor, and for his continuous guidance and supervision throughout and beyond my graduate journey at George Mason University. He is one of the brightest and most productive individuals I've had the pleasure of working for and someone I professionally and personally look up to. I feel fortunate when I look back at my experiences working as a graduate student in VoraLab.

My graduate journey would be impossible without the friendships and professional relationships I developed with my colleagues while being a part of Dr. Vora's research team. **Dr. Sean Oliver** and I started our PhD careers around the same time, so we have been through it all. He is a brilliant scientist and an excellent friend, and I have had an incredible time with him traveling to all of our conferences, practicing our presentations a thousand times at the last minute before giving our talks, and eating the same lunches at the cafeteria every day for six years. My graduate years would not be the same without him. I would also like to thank **Sam Yee**, recalling his meticulous ways of conducting research and some of most amazing stories from his days in the U.S. army. I am also grateful to - **Iris Stone**, **Jack Goggin** and **Adam Robinson** and many others who have all played essential roles in my academic and scientific development.

The financial and administrative support I have received from the department of Physics and Astronomy at George Mason University played a huge part during my graduate years, especially being an international immigrant. I would like to specially thank our department chair, **Dr. Paul So**, for the many words of wisdom he shared to a very confused graduate student back in 2014, and secondly for supporting and nominating me for the prestigious **Dean's Award for Graduate Excellence** at the end of my candidacy in 2020. I would also like to thank our department staff, for placing all of my massive and sometimes confusing lab orders, helping me with all of my travel, class and fellowship paperwork and lost lab keys, and being an overall pleasure to work with.

This thesis not only represents my work but also a culmination of all my collaborations with fellow scientists and researchers belonging to some of the finest institutions within the country. I would like to thank **Dr. Albert Davydov**, **Dr. Angela Hight Walker** and **Dr. Francesca Tavazza**, as well their research teams from the National Institute of Standards and Technology, a fellow PhD graduate **Dr. Kehao Zhang** from Penn State University, **Dr. Igor Zutic** and **Dr. Tong Zhou** from University of Buffalo and our very own **Dr. Igor Mazin** for all the insightful and meaningful theoretical discussions. These people have inadvertently left a significant impact on my scientific journey, productivity and outlook. I would also like to thank **Dr. Robert Cressman**, **Dr. Nirmal Ghimire** and **Dr. Angela Hight Walker** for agreeing to be on my dissertation committee.

While writing this and trying to recall the many highlights of my PhD experience, I can't help but think about the people who have always supported me, and are essentially the reason I could dream of coming to the states and achieving something like this. Being

away from my family, my parents **Dipti** and **Dharmendra Joshi**, my then girlfriend and now wife **Ruchika**, and our beloved dog **Courage**, for so many years hasn't really been easy for any of us, but your love, support and trust has made all of this possible and worth something. I am also thankful for all my friends, here and back in India, who can now breathe a sigh of relief as I finally finish up, but have always remained a source of love and encouragement.

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Abstract

INVESTIGATION OF THE OPTICAL PROPERTIES IN LOW-DIMENSIONAL MATERIALS AND HETEROSTRUCTURES

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George Mason University, 2021

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The introduction of layered two-dimensional (2D) materials that offer unconventional pathways to harness and engineer many-body quantum effects have provided new possibilities to develop next-gen optoelectronic and computational applications. In the last decade, the rediscovery of a new-class of 2D materials called the transition metal dichalcogenides (TMDs) have proved to be key-candidates for advanced technology needs, made possible through materials synthesis, growth, and ease of exfoliation. Additionally, TMDs can be easily integrated in stacks, also called heterostructures, tailoring them for emergent phenomena at interfaces between materials with varying structural and electronic properties. Particularly fascinating is their innate polymorphic nature, that offers energetically-inexpensive alternatives to achieve phase-transitions in materials that exhibit multiple crystallographic and electronic characteristics. In this dissertation, we employ fundamental spectroscopy techniques to investigate intriguing properties and quantum phenomena in 2D TMDs. This involves studying atypical materials that exhibit novel structural and electronic phase transitions, understanding the role of defects in the optical properties of synthetically grown materials and proximity effects coupled to interfaces shared between two materials with distinct band-structure, work functions and electron-correlated physics. These results elucidate the importance of quantum correlations in complex low-dimensional materials and heterostructures and highlight some of the challenges that continue to be barriers for the 2D community.

We begin by examining anharmonic contributions to the optical phonon modes in bulk T_d - MoTe₂ through temperature-dependent Raman spectroscopy. At temperatures ranging from 100 K to 200 K, we find that all modes redshift linearly with temperature in agreement with the Grüneisen model. However, below 100 K, we observe nonlinear temperature-dependent frequency shifts in some modes. We demonstrate that this anharmonic behavior is consistent with the decay of an optical phonon into multiple acoustic phonons. Furthermore, the highest frequency Raman modes show large changes in intensity and linewidth near T ≈ 250 K that correlate well with the $T_d \rightleftharpoons$ T' structural phase transition. These results suggest that phonon-phonon interactions can dominate anharmonic contributions at low temperatures in bulk T_d - MoTe₂, an experimental regime that is currently receiving attention in efforts to understand Weyl semimetals.

We then focus our attention to $2H - TaS_2$, a material that undergoes a low-temperature electronic phase transition know as charge density wave (CDW). We explore the CDW transition through a combination of temperature and excitation-dependent Raman spectroscopy, angle resolved photoemission spectroscopy (ARPES), and density functional theory (DFT). Our Raman data reveals the presence of Raman modes related to the CDW phase, that soften and broaden through mechanism not explained by the mean-field theory formalization. Above the phase transition temperature, we observe a strong two-phonon mode that softens substantially upon cooling, suggesting the presence of substantial lattice distortions at temperatures as high as 250 K. Finite-temperature density functional theory (DFT) calculations of the phonon band structure indicate an instability occurring well above the CDW transition temperature, in agreement with our results, as well as the ARPES measurements.

Next, we investigate the largely unexplored optical response of TMD metal-semiconductor junctions, particularly focusing on the NbSe₂ - MoSe₂ heterostructures. We employ a combination of optical characterization tools along with temperature- and power-dependent measurements, to study the interfaces formed between semiconducting-MoSe₂ and metallic-NbSe₂ flakes. We discuss the identification of a new spectral feature, L1, that is present either at the contact or near the edge of the interfacial region. We attribute this feature to recombination of localized excitons trapped by in-plane confinement potentials formed between NbSe₂ - MoSe₂ contact and the pristine MoSe₂ interface. Both our first-principles calculations as well the temperature- and power-dependent PL measurements support this interpretation. We also explain the difference between L1's origin in a variety of samples explored through hyperspectral imaging, by a descriptive illustration of the contact quality for samples fabrication with and without intermediate cleaning procedures.

From our understanding of the optical characteristics in NbSe₂ - MoSe₂ heterostructures, we focus our attention understanding correlations between excitons in semiconducting TMD to the electron-correlated phase transition in layers at close proximity. Continuing from our understanding of the CDW phase, we focus on the electronic properties of TiSe₂, a CDW Mott-Insulator that has attracted considerable interest for years and its interaction with a semiconducting MoSe₂ layer. We employ a combination of optical characterization tools along with temperature- and power-dependent measurements, to study the interfaces formed between semiconducting-MoSe₂ and CDW-TiSe₂ flakes. We discuss the identification of a new spectral feature, H1, that is, spectrally present on the higher energy side of the MoSe₂ exciton, and spatially present only on the TiSe₂ - MoSe₂ contact region. Not only that, the temperature dependence indicates a strong correlation to the TiSe₂ T_{CDW}. We identify three plausible scenarios that may explain the origin of H1, each with their own challenges. These observations are the first identification of a high-energy state (higher than X⁰) in MoSe₂ and demonstrate the surprising mechanism where the CDW superstructure can activate typically forbidden excitons through proximity effects.

This thesis aim to bring together different aspects of quantum correlations in complex low dimensional materials and their heterostructures, while highlighting the scope of physics and challenges offered within this exclusive material system.

Chapter 1: Introduction

1.1 Motivation for materials research

Over the last few decades, developments in silicon-based technologies have attempted to meet an everyrowing demand of reducing device form-factors with a simultaneous increases in its efficiency and performance. Downscaling transistors and integrated circuits to achieve cheap and energy efficient electronics, is subsequently met with limitation in material properties and architecture. Moreover, issues with data retention and scalability due to short-channel effects and quantum-tunneling phenomena in extremely thin transistor interconnects limit the use of silicon microelectronics in the nano regime [3]. To overcome these limitations and advance the progress of both logic and memory devices, a lot of effort has been put in exploring new nanomaterials, with unique optical and electronic properties that may offer a viable substitute to silicon [4–7]. Several carbon-based low-dimensional materials, for e.g. carbon-nanotubes and nanowires [8-10] as well as graphene have been discovered that offer rich physics, with the later being particularly interesting and popular in the scientific community [11-13]. Since its discovery in 2004 [14], graphene has been shown to host fantastic physical and electronic properties: linear dispersion with electrons behaving like massless Dirac fermions [15], half-integer and anomalous quantum-hall effects [16, 17], exceptional mechanical strength [18], ultra-high mobility transport [19, 20], and superconductivity [21, 22] to name a few. This has led to several proposed applications in the field of optical detection and communications, energy conversion and storage, biosensing, etc. [23]. However, its tremendous achievements and superior material properties are overshadowed by the lack of an electronic band-gap making it's use almost impossible in logic devices, especially in low-power memory and data storage applications. Significant efforts have been made to open a finite band-gap in graphene [24-27], however limitations in achieving high-speed switching applications still remain. There have also been numerous other advances to explore new candidates for 2D materials, including but not limited to the layered III-V semiconductors [28], magnetic trihalides [29, 30], transition metal oxides and trioxides [31–34], alloys and intercalated materials as well as heterostructures [35–38] of variety of materials that cater to specific applications.

On the other hand, one of the biggest bottlenecks in miniaturizing devices based on conventional Von Neumann architecture are the energy- and time-expensive memory read/write operations. This has propelled smarter and efficient ways to design memory systems (for e.g., solid-state flash, DRAM, etc.) that improve latency and compute time, while focusing on materials research to develop platforms for non-volatile data storage in reduced dimensional space. The rediscovery of a new class of low-dimensional materials called the transition metal dichalcogenides (TMDs) have proved to be key candidates for this particular technology need [39, 40]. These materials (originally studied in 1970s), like graphene, could be exfoliated in 2D sheets (which wasn't realized till 2010), but unlike graphene, possess a finite direct band-gap, for e.g. the discovery of atomically-flat MoS_2 with a visible direct band-gap of 1.8 eV [41]. The semiconducting nature of their band-gaps and reduced dimensionality have made them more potent for optical and logical electronic applications [39, 40, 42, 43] compared to graphene-based devices. Particularly fascinating is their ability to controllably morph their optical, electronic, and structural properties [42, 44–46]. This can create pathways for unconventional quantum phenomena to exist like non-trivial topological phases [47–52], as well as a multitude of correlated many-body interactions emerging as superconductivity, charge density waves, ferromagnetism, etc. [53–55]. Some of these morphologies offer minimal energy cost for phase conversion between multiple meta-stable structures, meeting a relevant criteria for developing non-volatile phase-change memories and memristive devices [7, 56-58]. In addition to this, circular optical selection rules in monolayer TMDs [59, 60] can create routes to design phase-memories based on selective spin-valley activation, also referred to as *valleytronics* and *spintronics* [61–63]. And lastly but most importantly, the ability to vertically stack TMDs with dissimilar lattice constants and bandstructures allows emergent phenomena to exist at the interface, separate from the individual constituents [64, 65]. This is further complicated through layer-dependent angular control optical properties at the interface, proposing a yet another field of semiconductor *twistronics* using two-dimensional (2D) TMDs [66]. From being used originally as lubricants, potential applications of 2D TMDs are now proposed to be in photodetectors, light-emitting diodes (LEDs), bio-sensing and transistor-IC technologies [42]. While the work discussed in this thesis focuses strictly on 2D TMDs, the field of 2D materials is an evergrowing one, and the discovery of new materials that allow optimal tuning of their inherent quantum properties will subsequently refresh the scope and vision for advancements in next-gen electronics and computing architecture.

The investigations carried out in this dissertation propose to drive numerous advances in understanding some of the fundamental properties of 2D TMDs and the prospects for their application in ultrathin computing and sensing technologies by investigating TMD heterostructures. Explorations of the structural phase transitions in a candidate topological material revealed the crucial nature of non-linear anharmonic interactions in the lowtemperature limit as well as vibrational discontinuities across the transition temperature [67]. These measurements are extremely vital in understanding heat flow as well as higher order interactions of phonons and defects in phase-change materials. Secondly, investigation of the electronic ordering in a candidate CDW material sheds key insight on the presence of quantum fluctuations and the discovery of short-range order that sets in way before the material is believed to undergo an electronic phase change [68]. These results are critical for designing electronic memristive devices that tune between an ON and OFF state via changes in their resistive properties and are highly dependent on the charge order fluctuations. TMDs are also unique in a way that they are layered through weak van der Waals forces that allow for fabrication of vertical stacks (or heterostructure), of materials with unique properties to create exotic interfacial states. Examination of layered heterostacks of materials with dissimilar properties, such as semiconductor-superconductors/semi-metal/insulator junctions, has revealed activation of new, optically-bright interfacial states beyond the conventional emissive properties of the pristine semiconductor [69]. These results are the first of their kind that show proximity coupling between 2D TMDs with unique electronic properties and differing band structures. This also creates exciting possibilities for information storage at the shared-interface, where in addition to the conventional bits 0 and 1, activation of otherwise forbidden states can lead to a new classical bit space. Furthermore, as quantum tunneling effects dominate in the nano regime, interlayer interactions between two TMDs can lead to generation of quantum entangled states, a necessary ingredient to fabricate next generation quantum computers and qubits. These results pave the way for using unconventional and exotic properties of low-dimensional TMDs to harness rich quantum physics and highlight some of the challenges and opportunities for the 2D device community.

1.2 Thesis outline

In this dissertation, we employ a wide range of optical spectroscopy techniques to fundamentally investigate low-dimensional properties and electron-correlated phenomena in 2D TMDs and their heterostructures. This involves studying atypical materials that exhibit novel structural and electronic phase transitions, as well as correlating optical behavior across interfaces shared between two materials with distinct band-structures, work functions and electronic phases through proximity effects. Additionally, as a collaborative project, we investigate the role of defects in synthetically grown materials and their passivation through the means of substitutional doping through a thorough optical examination at cryogenic temperatures. These results elucidate the importance of quantum correlations in complex low-dimensional materials and heterostructures and highlight some of the challenges that continue to be barriers for the 2D community. The thesis outline is as follows:

In Chapter 2, we introduce some basic concepts on semiconductor band-gap theory and the effects of quantum confinement and reduced dimensionality on the electronic properties of 2D materials. We then focus specifically on 2D TMDs, giving an insight into their
polymorphic behavior and many-body interactions that largely govern their physical and optoelectronic properties. We also discuss the nature of band-gaps in 2D TMDs, the selection rules that govern optical transitions and the behavior and origin of excitons quasiparticles in these materials. And lastly, we introduce TMD heterostructures, particularly focusing on semiconductor heterobilayers as well as semiconductor-metal junction, discussing their interfacial behavior and the impact of dissimilar materials on their bandstructures in close proximity. This section serve as an introduction to readers unaware of the optical and electronic nature of 2D TMDs, while setting up a foundation for subsequent chapters that focus on some of these key aspects of TMDs in great detail.

Chapter 3 is desgined to be an introduction to our experimental setups and to get the reader familiar with the scope of optical and electronic toolkits used for materials research. This included the custom transfer station for sample fabrication and assembly, ultra-low frequency Raman, photoluminescence (PL), electroluminescence (EL), reflectance and atomic force microscopy (AFM) setups. The section also briefly covers the fundamental theory for Raman and PL processes, showcasing their strengths in characterizing 2D materials. We also discuss the advantage of using AFM, which is typically a surface characterization tool, to clean interfaces and surfaces of 2D materials that improve both the contact and optical properties of junctions. Lastly, we focus on our hyperspectral imaging capability, and illustrate its ability to spatially and spectrally map a variety of heterostructures to distinguish interfacial physics.

In Chapter 4, we begin by investigating the structural phase transition in the lowtemperature phase of T' - MoTe₂, particularly focusing on the anharmonic changes in its vibrational properties. Understanding the interactions of phonons at low-temperatures is vital, but it becomes pertinent in this case where a structural phase transition changes the vibrational symmetry and lattice dynamics of the crystal structure from its normal phase. We employ temperature-dependent Raman measurements to study the changes in phonon modes between the T' and T_d - MoTe₂ phases and present viable mechanism that explains the behavior of mode frequencies using an anharmonic approach to phonon interactions. In Chapter 5, we focus our attention to $2H - TaS_2$, a material that undergoes a lowtemperature electronic phase transition know as charge density wave (CDW). We explore the CDW transition through a combination of temperature and excitation-dependent Raman spectroscopy, angle resolved photoemission spectroscopy (ARPES), and density functional theory (DFT). We reveal the presence of two CDW amplitude modes that red-shift and broaden with increasing temperature and one zone-folded mode that disappears above T_{CDW} . Above T_{CDW} , we observe a strong two-phonon mode that softens substantially upon cooling, suggesting the presence of substantial lattice distortions at temperatures as high as 250 K. Finite-temperature DFT calculations of the phonon band structure, done in collaboration with the Materials Measurement Laboratory at NIST, Maryland, indicate an instability occurring well above the CDW transition temperature, in agreement with our results, as well as the ARPES measurements carried out by our colleagues at University of Virginia.

In Chapter 6, we investigate the largely unexplored optical response of TMD metalsemiconductor junctions, particularly focusing on the NbSe₂ - MoSe₂ heterostructures. We employ a combination of optical characterization tools along with temperature- and powerdependent measurements, to study the interfaces formed between semiconducting-MoSe₂ and metallic-NbSe₂ flakes. We discuss the identification of a new spectral feature, L1, that is present either at the contact or near the edge of the interfacial region. We attribute this feature to recombination of localized excitons trapped by in-plane confinement potentials formed between NbSe₂ - MoSe₂ contact and the pristine MoSe₂ interface. Both our firstprinciples calculations as well the temperature- and power-dependent PL measurements support this interpretation. We also explain the difference between L1's origin in a variety of samples explored through hyperspectral imaging, by a descriptive illustration of the contact quality for samples fabrication with and without intermediate cleaning procedures.

In Chapter 7, we cover the largely unexplored optical response of excitons in semiconducting TMD to the electron-correlated phase transition in layers at close proximity. Continuing from our understanding of the CDW phase in Chapter 5, we focus on the electronic properties of TiSe₂, a CDW Mott-Insulator that has attracted considerable interest for years and its interaction with a semiconducting MoSe₂ layer. We employ a combination of optical characterization tools along with temperature- and power-dependent measurements, to study the interfaces formed between semiconducting-MoSe₂ and CDW-TiSe₂ flakes. We discuss the identification of a new spectral feature, H1, that is, spectrally present on the higher energy side of the MoSe₂ exciton, and spatially present only on the TiSe₂ - MoSe₂ contact region. Not only that, the temperature dependence indicates a strong correlation to the TiSe₂ T_{CDW} . We identify three plausible scenarios that may explain the origin of H1, each with their own challenges. These observations are the first identification of a high-energy state (higher than X⁰) in MoSe₂ and demonstrate the surprising mechanism where the CDW superstructure can activate typically forbidden excitons through proximity effects.

Chapter 2: Theory of Two dimensional materials: Focus on Transition Metal Dichalcogenides

This section discusses various basic concepts on semiconductor band-gap theory and the effects of quantum confinement and reduced dimensionality on the electronic nature of 2D materials. We then focus specifically on 2D TMDs, giving an insight into their polymorphic behavior and many-body interactions that govern a lot of their physical and electronic properties. We also discuss the nature of band-gaps in 2D TMDs, the selection rules that govern optical transitions and the behavior of excitons in these materials. And lastly, we introduce a brief background on the interfacial physics in vdW heterostructures and the impact of materials in close proximity with varying bandstructures.

2.1 Electronic bandstructures

Electronic bandstructures define the energy-momentum relationship of free and bound electrons in a given material and are an important tool to understand their electronic, optical and magnetic properties. In the simplest case, the energy dispersion of a free electron is given from the Schrödinger equation as,

$$H\Psi_{\vec{k}}(\vec{r}) = \frac{-\hbar^2}{2m} \nabla^2 \Psi_{\vec{k}}(\vec{r}) = \frac{p^2}{2m} \Psi_{\vec{k}}(\vec{r}) = E\Psi_{\vec{k}}(\vec{r})$$
(2.1)

where \vec{k} is the wavevector and m is the mass of an electron. The solution to the above equation is the electron wavefunction $\Psi_{\vec{k}}(\vec{r}) = A \sin(nkx) = e^{i\vec{k}\cdot\vec{r}}$, with $k = n\pi/a$ determined from satisfying the boundary conditions of a confined potential. The eigenvalues are given by $E = \hbar^2 k^2/2m$, where the principal quantum number n denotes the allowed energy levels.



Figure 2.1: (a) Parabolic energy dispersion of a free electron given by **Equation 2.1**. (b) Periodic energy dispersion of an electron bound to a crystal with atoms positioned at specific lattice sites defined by the reciprocal wavevector. The first Brillouin zone is highlighted in yellow. (c) Formation of band-gaps in the reduced BZ picture. (d) Examples of typical bandstructures, for e.g. monolayer 2H-MoSe₂ and the linear dispersion and formation of Dirac cone in graphene.

This is plotted in **Figure 2.1a** for n = 1. In more relevant scenarios, such as in a crystal, periodic positioning of atoms at lattice sites develops a periodic potential $V(\vec{r} + \vec{R}) = V(\vec{r})$, where \vec{R} is the reciprocal lattice vector. This would modify **Equation 2.1**, which now includes a potential energy term given as,

$$H\Psi_{\vec{k}}(\vec{r}) = \frac{-\hbar^2}{2m} \nabla^2 \Psi_{\vec{k}}(\vec{r}) + V(\vec{r})\Psi_{\vec{k}}(\vec{r}) = E\Psi_{\vec{k}}(\vec{r})$$
(2.2)

Since $V(\vec{r})$ is periodic, and one lattice site is no different than any other, the eigenfunctions for the above equation must also be periodic, i.e., $\Psi_{\vec{k}}(\vec{r} + \vec{\mathbf{R}}) = \Psi_{\vec{k}}(\vec{r})$. The electron eigenstates in such a periodic potential are then derived from the Bloch's theorem in the form of Block waves.

$$\Psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$
(2.3)

where $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{\mathbf{R}})$ has the same periodicity as the crystal lattice. The energy dispersion for such a periodic potential is shown in **Figure 2.1b**.

Now, the electron wavefunction described in **Equation 2.3** like all waves would experience Bragg diffraction as it moves around the periodic lattice. In a 1D crystal with a lattice periodicity a, the condition required for Bragg diffraction of wave with wavevector $\vec{k_1}$, reflected into a wave with wavevector $\vec{k_2}$ is given by $\vec{k_1} - \vec{k_2} = \vec{\mathbf{R}}$, where $\mathbf{R} = 2\pi n/a$. In case of an electron, the Bragg condition dictates that the initial electron wavevector must either be half of a reciprocal lattice vector $(\vec{k_1} = \frac{1}{2}\vec{\mathbf{R}} = \pm n\pi/a)$ or the initial electron wavevector must diffract off a Bragg plane such that $\vec{k_1} = -\vec{k_2}$. Therefore, a discontinuity occurs at all values of $k = \pm n\pi/a$ (for n = 0, 1, 2,..) where, the electron wavefunction $e^{i\vec{k}\cdot\vec{r}}$ can be decomposed into travelling waves moving in opposite directions such that it behaves as a standing wave at all $k = \pm n\pi/a$. This region in **k** - space between $+\pi/a$ and $-\pi/a$ is referred to as the first Brillouin zone (BZ) of the crystal lattice. It is also important to note that band-extrema occur at wavevector $\vec{k} = 0$ and is often labelled as Γ point to denote the center of a BZ. In 3D, things get a bit complicated as the reciprocal lattice vectors do not form symmetric structures, and the Brillouin zone can have all kinds of shapes. In that case it is common just to plot the energies along special high-symmetry directions. The energies along these lines represent either maximum or minimum energies for the bands across the whole BZ.

Since the electrostatic potential energy of the two travelling waves differ, an energy gap (E_g) opens at these positions in the reciprocal space, with a magnitude proportional



Figure 2.2: A schematic comparing the simplified electronic band structures of a metal, a semimetal, a semiconductor, and an insulator. The blue shaded areas show the energy states occupied by electrons in the valence band (VB). The dashed line is the Fermi energy E_F above which the states remain unoccupied and is more commonly referred to as a conduction band (CB). A metal has a CB that is partially filled with electrons. A semimetal has a CB and VB that overlap with negligible filling of energy states in the CB. Semiconductors and insulators have a filled VB and an empty CB, which are separated by a band gap E_g .

to the crystalline potential. This is shown in **Figure 2.1c** for the first BZ. Using Fermi-Dirac statistics and Pauli's exclusion principle, one can determine the dynamics of how electrons fill these energy states at 0 K with lowest-energy states getting filled first. We then differentiate in a given material, the continuum of bands that are completely filled, also called valence bands (VB), and the set of bands that remain partially filled or empty, commonly knows as conduction bands (CB). This also allows us to accurately determine the energy below which all states are occupied, known as the Fermi energy (E_F) and the separation between CB and VB as the band-gap or energy gap (E_g) . These quantities together determine the optical and electronic properties of materials as shown in **Figure 2.1d**. We will for much of the work discussed here, focus on semiconducting and metallic systems. In case of semiconductors, $0 \text{ eV} < E_g \leq 4 \text{ eV}$, further sub-classified (not strictly) into narrow-band (0 eV $\langle E_g \leq 0.5 \text{ eV}$), usual (0.5 eV $\langle E_g \leq 2 \text{ eV}$) and wide-band (2 eV $\langle E_g \leq 4 \text{ eV}$) semiconductors. On the other hand, a metal is classified when the conduction band is partially filled and there is no band-gap. An other important classification of semiconductors is based on where the conduction and valence band extrema are located with respect to the **k** space. A direct band-gap semiconductor is when the conduction band minimum (CBM) is aligned with valence band maximum (VBM) in momentum space, while an indirect band-gap semiconductor is when they are located at different points in the **k** space.

2.2 Excitons in semiconductors

In any semiconductor, absorption of photon can excite an electron from the valence band into the conduction band if the energy of the incoming photon is equal or greater than the band-gap. This leaves behind a vacancy in the valence band, commonly referred to as a hole. In a direct band-gap semiconductor, this transition occurs between the VBM and CBM aligned in momentum space. In an indirect band-gap semiconductor, since the VBM and CBM are not lined up along the same momentum vector, momentum conservation demands that finite-momentum processes such as absorption or emission of a phonon is necessary to allow for electron excitation. In any case, the electrons once excited can radiatively or nonradiatively recombine with the holes in the valence band, given the Coulomb interaction between the hole and electron (**Equation 2.4**) is sufficient to create a hydrogen-like quasi particle, we call an exciton.

$$\frac{-e^2}{(4\pi\epsilon_0\epsilon|\mathbf{r}_e-\mathbf{r}_h|)},\tag{2.4}$$

The exciton recombination process results in emission of a photon which can be measured as PL. This technique offers a direct probe to investigate excitons and their recombination lifetimes and provide a wealth of information about the electronic structure within a given semiconductor.



Figure 2.3: (a) Optical vs Electronic band-gaps in semiconductors. The difference between the optical and electron band-gap is due to electron-hole Coulomb interaction, more commonly referred to as exciton binding energy. (b) Direct band-gap recombination process involving excitation and emission of photons for VBM and CBM aligned in momentum space. (c) Indirect band-gap recombination process involving absorption/emission of phonon to conserve momentum difference between the two valleys. Also shown is an Auger recombination process, which is non-radiative and has no PL emission.

Let us dig a little deeper into understanding the basic mathematical formalism of excitons. Depending on the dielectric constant of a given material and the strength of Coulomb interaction, the excitons can be classified into two types: Wannier-Mott excitons and Frenkel excitons [59, 70]. We focus our description of the former as they are more relevant to the type of materials discussed in this dissertation, particularly 2D semiconductors. The energy dispersion of the a typical Wannier-Mott exciton can be given by [70],

$$E_{\rm X}(n, \mathbf{K}) = E_g - E_b + K.E. = E_g - \frac{{\rm Ry}^*}{n^2} + \frac{\hbar^2 \mathbf{K}^2}{2m}.$$
 (2.5)

where E_g is the material band-gap, K.E. is the exciton kinetic energy term and $\mathbf{K} = \vec{k_e} + \vec{k_h}$ makeup the exciton wavevector. The exciton mass $M = m_e + m_h$ is the combined transnational mass of electron and hole. The term E_g is the exciton binding energy calculated from the Coulomb interaction, n is the principal quantum number and Ry^* is the Rydberg energy, which is given as following

$$Ry^* = (13.6 \text{ eV})\frac{\mu}{m_0} \frac{1}{\epsilon^2}.$$
 (2.6)

$$\mu = \frac{m_e m_h}{(m_e + m_h)} \tag{2.7}$$

The above formalism is illustrated in **Figure 2.3** wherein **Figure 2.3b,c** shows the electron excitation and exciton recombination process for direct and indirect band-gap semiconductor. **Figure 2.3a** shows the difference in the electronic and optical band-gap and importance of exciton binding energy in a given semiconductors.

2.3 Quantum Confinement

In semiconductor nanostructures, quantum confinement can lead to fascinating shifts in material properties compared to its behavior in the bulk form, where the electron is free to move in all possible directions. In the theoretical description of particle confined within a potential barrier (V(r) = 0 in the well, $V(r) = \infty$ outside the well), the Hamiltonian is given by **Equation 2.1** where the energy eigenvalues are given as $E = \hbar^2 k^2/2m$, where $k = n\pi/L$, n is the principal quantum number and L is the width of the potential well. This is true for particles confined in one dimension (free to move in the other two dimensions) which in practical scenarios can be visualized by sandwiching a thin layer of material between two other materials with dissimilar band-gaps, also known as a Quantum Well (QW). Similarly, confinement in two-dimensions is commonly known as a quantum wire (QWi) and confinement in all three dimension is referred to as a quantum dot (QD). These confinement models have been practically realized in many 2D materials, including III-V semiconductor systems, where significant dependency of the energy eigenstates to the barrier properties has been seen.



Figure 2.4: Density of states (DOS) representation for quantum confined systems with (a) No confinement (b) Confinement in 1D (c) Confinement in 2D and (d) Confinement in 3D. We can see the DOS change from a continuum of available states in bulk systems to discrete states in a quantum dot which is confined in all three dimensions.

From our previous discussion on semiconductor bandstructures, creating a confined barrier in 1D, 2D or 3D can result in tuning material band-gap, such that the change in the band-gap is given by [71],

$$\Delta E_g = \frac{\hbar^2}{8kd^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \tag{2.8}$$

where d is the non-periodic dimension of the nanostructure and m_e^* , m_h^* are electron and hole masses. Coefficient k is dependent on the dimensionality of the confined structure and can take a variety of values between 1 and 2. It is also important to look at the effect of confinement to the density of states (DOS), which provides information about the number of states available at a given energy level. **Figure 2.4** illustrates the changes in DOS from a typical bulk semiconductor to other confined systems. We can note here that the density of states displays higher quantization as the particles have less freedom of movement, with a QD eventually showing fully discrete energy levels, similar to that of atoms.

Reducing the effective dimensionality an exciton is relevant for any 2D material environment, especially if we are interested in monolayers. So in the 3D case,

$$E_{\rm X}(n, \mathbf{K}) = E_g - \frac{{\rm Ry}^*}{n^2} + \frac{\hbar^2 (K_x^2 + K_y^2 + K_z^2)}{2M},$$
(2.9)

which in the world of 2D materials is reduced to [72]

$$E_{\rm X}(n, \mathbf{K}) = E_g + E_Q - \frac{{\rm Ry}^*}{(n - \frac{1}{2})^2} + \frac{\hbar^2 (K_x^2 + K_y^2)}{2M},$$
(2.10)

where E_Q is the quantization energy as the system is quantum confined in the direction perpendicular to the plane of the material. The reduced dimensionality of the 2D system affects the binding energy and radius of Wannier type excitons.

2.4 Beyond Graphene: 2D Transition Metal Dichalcogenides

The transition metals as characterized by the International Union of Pure and Applied Chemistry (IUPAC) are elements on the periodic table that have an incomplete d subshell. This includes all elements including and within columns 4-10 of the periodic table with the electron configuration ranging from d^0 (Group 4) to d^6 (Group 10) (refer **Figure 2.5**). Chalcogens are identified as elements belonging to Group 16 of the period table, specifically referring to sulphides, selenides and tellurides. These compounds (for e.g. MoS₂, WSe₂, NbSe₂) are referred to as transition metal dichalcogenides (TMDs) and will remain the focus of the work discussed in this dissertation.

Traditionally, TMDs are represented by the chemical formula MX_2 (where M is transition metal and X is chalcogen), where in, each layer of M atoms is sandwiched between two layers of X atoms to form a trilayer covalently-bonded unit. Vertical stacks of such units (each MX_2 trilayer) form a layered structure through weak van der Waals interactions, such that each layer can be individually peeled through the means of mechanical exfoliation, similar to what's been done with Graphene. However, unlike Graphene, because of



Figure 2.5: Periodic table highlighting the transition metals belonging to Groups 4-10 and chalcogens belonging to Group 16, that jointly form the transition metal dichalcogenides (TMDs). This figure is edited from its original version found in Ref.[1]

its three-atom configuration, TMDs can exist in a variety of phases within the same crystal structure providing a richer platform for controlling material properties. Additionally, 2D exfoliated sheets of these compounds can then be controllably stacked to fabricate 2D heterostructures, which will also be detailed in the subsequent sections.

It is also important to note here that TMDs were heavily studied back in 1960s where some of these materials like MoS₂ and WS₂ have already-existing industrial applications in the form of lubricants used in engines, brakes and automotive joints. A tremendous interest has garnered in understanding these materials in the last decade only because of the ability to isolate them in monolayers, which wasn't known back in the day. The discovery of monolayer-MoS₂, a direct band-gap semiconductor has catapulted the 2D materials community into revisiting these materials in their atomically thin form factors and has since uncovered a plethora of quantum rich material properties. This includes some exciting phenomena like superconductivity, magnetism, charge density waves, and entirely new fields of device applications like valleytronics, spintronics and twistronics owing to the 2D nature of these materials.

2.5 Phases and Phase transitions in 2D TMDs

2.5.1 Polymorphism in TMDs

TMDs offer a unique advantage over other layered materials, in that, stable polymorphs (different crystal structures) and polytypes (different stacking sequences) of the same compound are naturally formed or can be easily synthesized. There are at least five kinds of phases that have been observed in TMDs - 2H, 3R, 1T, 1T' and T_d [1] as shown in **Figure 2.6a**, where the number denotes the number of layers. The H and T phase are the most common representing a trigonal prismatic (D_{3h} point group) and octahedral (D_{3d} point group) configuration around the transition metal, respectively. The distorted octahedral (T') and orthorhombic (T_d) phase are variants of the T phase and can be obtained by changing the electron arrangement in the *d*-orbital of transition metal and the relative orientation of the layers in three-atom MX₂ structure. Furthermore, in monolayer H phase, the stacking sequence is AbA (A for chalcogen and b for transition metal) whereas in the T phase, it's AbC where the chalcogen layer C is shifted horizontally relative to the other layers. Additionally, 2H and 3R (rhombohedral) phases have stacking sequence of AbA-BaB and AbA-CaC-BcB respectively [1,73].

It is very common for TMDs to exist in multiple phases within the same chemical arrangement, which makes it vital to understand the phase of a given material for designing applications that cater to specific properties. For example, MoS₂ can exist in three thermodynamically stable phases, wherein 2H and 3R-MoS₂ is a semiconductor widely appropriate for optoelectronics, while 1T-MoS₂ is metallic with applications in electrocatalysis [73]. Let us first understand the reason why TMDs exist in so many different polymorphs and then move forward to controlling phases and transitioning between stable crystal structures.

Polymorphism in TMDs is often a consequence of the rearrangement of electronic structure (except when growth conditions are manipulated to select one phase over the other), specifically pertaining to the *d*-valence orbit of the transition metal [1]. The five orbital of the *d*-shell in a transition metal unperturbed by any EM fields are energy degenerate. It



Figure 2.6: (a) Commonly observed crystal structures in TMDs - H (trigonal prismatic), T (octahedral), T'(monoclinic or distorted octahedral) , T_d (orthorhombic) and 3R (rhombohedral). (b) Comparison of d-orbital spitting due to spin–orbital coupling in 1H and 1T phases, respectively. Filling of electrons in the d sub-shell governs the stability of a phase for a given TMD based on its group location in the periodic table or the *d*-electron count. We see here that group 5 and 6 are stable in both H and T phase, TMDs belonging to group 7 and onward favour the 1T phase.

is then obvious that in any chemical compound, presence of neighbouring atoms can split these energy levels breaking degeneracy. In case of H phase TMDs, the *d*-orbital is split into three levels, two degenerated orbitals of $d_{x^2-y^2}$, d_{xy} , two degenerated orbitals of d_{yz} , d_{zx} and the orbital d_{z^2} [1,73]. In contrast, the octahedral T phase splits into two energy levels with two degenerated orbitals of $d_{x^2-y^2}$, d_{z^2} and three degenerated orbitals of d_{xy} , d_{yz} , d_{zx} [1,73]. With their relative energy differences shown in **Figure 2.6b**, Pauli's exclusion principle dictates that phase stability depends on the d-electron count and how the orbitals are filled. Group 4 TMDs (featuring d^o) are all in 1T phase, while for Group 5 (d^1) and 6 (d^2), filling of d_{z^2} orbital of the 1H phase offers becomes more favourable than the lowest energy orbitals in the 1T phase. Therefore, group 5 TMDs have both H and T stable phases, while group 6 TMDs are typically found in the H phase with a band-gap between d_{z^2} and $d_{x^2-y^2}$. Adding more electrons (d^3 and onward) destabilizes the H phase, favouring the octahedral phase or its variants (T' or T_d) for group - 7, 9 and 10 TMDs.[1].

2.5.2 Phase transitions in TMDs

In TMDs, the relative stability of various material phases can also be controlled via charge, temperature, strain, defects and chemical manipulation [73]. Considering the energy barriers for a structural phase transition in a few commonly known TMDs such as MoS_2 , WS₂, MoSe₂, WSe₂, MoTe₂ and WTe₂, we see that except for WTe₂, the two-lowest energy structural orientations possible are the H and T' phase [46, 74]. In ambient conditions, WTe_2 exists in the T_d phase. It is also seen that the chalcogen Te offers the highest advantage for $H \rightleftharpoons T'$ phase transitions to occur, more specifically the compound MoTe₂ being the best candidate of all [74]. Recent studies have shown that reversible $2H \rightleftharpoons 1T'$ phase transitions can be easily achieved in monolayer MoTe₂ through electrostatically gating [75]. Additionally, MoTe₂ offers yet another possibility for a $T' \rightleftharpoons T_d$ transition which is a function of temperature and layer number [76–79]. Several other mechanism such as ion intercalation, alloying and substitutional doping and applying electrical field have been used to phase convert $2H-MoS_2$ to the IT phase [80]. In addition to structural phase transition, several TMDs (TaS₂, TaSe₂, NbSe₂, etc) undergo an electronic phase transition in the form of charge density waves (CDW). This develops a periodic distortion in the lattice under a certain critical temperature (< 75 K for 2H-TaS₂, < 40 K for 2H-NbSe₂, etc) [68,81] and in some cases, results in a new crystal structure with distinct point group symmetry, for e.g. 2H-TaSe₂. TMDs that host CDW phase often exhibits a competing superconductivity (SC), with unique layer-dependent properties, for e.g. in case of 2H-NbSe₂, where the SC onset temperature increases with increasing thickness, while its the opposite in 2H-TaS₂. Additionally, type-II Weyl semimetal phases are observed in inversion asymmetric T_d -WTe₂ and T_d -MoTe₂ [50, 82, 83].

2.6 Spin-Orbit coupling in 2D TMDs

In semiconducting ML TMDs, the CBM and VBM are both located at the degenerate K and K' points at the corners of the hexagonal Brillouin zone. The energy degenerate K and K' valleys also maintain time reversal symmetry $(E_{\uparrow}(K) = E_{\downarrow}(K'))$ while having broken inversion symmetry $(E_{\uparrow}(K) \neq E_{\uparrow}(-K))$ in the monolayer regime. The conduction (valence) states at these valley mainly consist of transition-metal $d_{z^2}(d_{x^2-y^2}+id_{xy})$ orbitals that contribute towards spin-orbit (SO) coupling. The spin-orbit interaction in the atomic approximation is given the by Hamiltonian [84, 85],

$$\hat{H}_{SO} = \frac{\hbar^2}{4m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$
(2.11)

where m_e is the electron mass, V(r) is the spherical atomic potential, $\hat{\mathbf{L}}$ is the angular momentum operator and $\hat{\mathbf{S}}$ is the vector of spin $\frac{1}{2}$ Pauli matrices, such that the dot product

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_{+} \hat{S}_{-} + \hat{L}_{-} \hat{S}_{+} + \hat{L}_{z} \hat{S}_{z}$$
(2.12)

with $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$ and $\hat{S}_{\pm} = (\hat{S}_x \pm i\hat{S}_y)/2$. The mirror symmetry in the out-of-plane (z) direction dictates that the splitting has to be in the z-direction. Therefore, the out of plane spin projection s_z is a good quantum number and the out of plane spin operator $S_z = \frac{\hbar}{2}\sigma_z$ commutes with the Hamiltonian, giving $[\hat{H}, \hat{S}_z] = 0$. This lets us associate the electronic bands to a given spin projection $s_z = \uparrow, \downarrow$ and the SO Hamiltonian can be approximated to

$$\hat{H}_{SO} = \frac{\hbar^2}{4m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \hat{L}_z \hat{S}_z$$
(2.13)

Since the VB states at the K and K' valleys are composed primarily of the *d* orbitals with magnetic quantum numbers $m_z = \pm 2 \ (d_{x^2-y^2} + id_{xy})$, we see large SO splitting of



Figure 2.7: (a) Schematics of the VB and CB electronic bandstructures at K and K' valleys in (a) Mo-based TMDs (b) W-based TMDs. Also shown are optical selections rules for coupling right handed and left handed circularly polarized light to specific bands at K/K' valleys. (c) Bloch sphere representation of linear (equators of the sphere) and circularly polarized (poles) states that represent the spin orientation of electrons and polarization needed to couple to specific transitions in the K/K' valleys.

the order $\approx 100\text{-}400 \text{ meV}$ in most TMDs. Contrary to this, the CB bands at the K and K' points are composed of metal d orbitals with $m_z = 0$ (d_{z^2}) , leading to negligible SO coupling, of the order of $\approx 10 \text{ meV}$ owing to interactions from transition metal d_{xz} , d_{yz} and the chalcogen p_x and p_y orbitals [84,85]. The large SO coupling in the VB bands at the K and K' valleys therefore leads to spin-valley locking of holes, with both states degenerate in energies but having opposite spin characters, dictated by the time-reversal symmetry and breaking of inversion symmetry in monolayer TMDs. Interestingly, the spin projection of the CB have opposite spin-splitting orders for tungsten (WS₂, WSe₂) and molybdenum (MoS₂, MoSe₂) based TMDs due to competing interaction of chalcogen p and conduction d orbitals. The comparison between CB and VB spin characters is shown in **Figure 2.7**.

2.6.1 Optical selection rules in 2D TMDs

With the electronic bandstructures defined and the valley-selective spin character understood, let's dig into the characterizing the optical selection rules that govern the light-matter interactions in TMD monolayers. A straightforward and rather minimalistic approach here is use gauge theory and define the vector potential of the electromagnetic field, \mathbf{A} , such that momentum can be rewritten as $\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}$, which changes the original Hamiltonian to

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} = \frac{e}{2mc}\hat{\mathbf{p}} \cdot \mathbf{A} = \frac{e}{2mc}(\hat{p}_+A_- + \hat{p}_-A_+)$$
(2.14)

where we define $\hat{\mathbf{p}} = \hat{p}_x \pm i \hat{p}_y$ and $\mathbf{A} = A_x \pm i A_y$. The vector potential A_{\pm} describes a photon with right or left circular polarization, such that the momentum matrix \hat{p}_{\pm} are tied with specific handedness of optical excitation. This shows that the two valleys K/K' are coupled exclusively to the circular polarization, and more importantly with opposite orientation as seen in **Equation 2.14** and required by time-reversal symmetry. This property known as valley circular dichroism is responsible for the valleytronic properties in TMDs, where controllable optical selection and recombination can create new avenues to probe materials for digital electronics. This is shown in **Figure 2.7**. The Hamiltonian in **Equation 2.14** also seems to suggest, that in order to excite both valleys together, one needs a superposition of right and left-handed circular light, and takes the form of a linearly polarized light. This is defined as a coherent valley superposition.

2.6.2 Excitonic states in 2D TMDs

An important conclusion to be made from our previous discussion is that spin-valley locking and SO splitting of the VB and CB bands in W-based TMDs prevents the absorption and emission of charge carrier to the lowest-energy state available, making them optically unfavourable - dark transitions (X^D) . The spin mismatch between the electron and holes spins heavily suppresses their radiative recombination, have long lifetimes (> 100 ps), out-of-plane dipole moment and in-plane light emission. In WSe₂ for e.g., since the dark exciton state is the ground-state, a large accumulation of these exciton can result into observable light emission in PL measurements. Similarly in MoSe₂, the dark transition can be associated with the recombination of electrons from the upper spin-split CB to the hole in the VB. Dark excitons are also classified into two categories - spin-dark and momentumdark excitons. The former is the classic case of optical transition at K/K' valleys in WSe₂ as discussed previously. Momentum-dark excitons are transition between VB and CB bands with opposite spin and not aligned at the same position in momentum space. These can also be defined as indirect dark excitons (IX^D). We must specify here that in monolayer TMDs, the CB minima occurs at four distinguished positions (K, K', Λ , Λ ') with the global minima at K/K'. Similarly in VB, maxima occurs at three valleys (K, K' and Γ) with the global maxima at K/K' valleys. This means there are additional Γ - K transitions possible in both W and Mo-based TMDs that are also optically dark. All of these transition are schematically represented in **Figure 2.8a,b**.

Contrary to this, in Mo-based semiconductors, the optical ground state transition between VB and CB bands have the same spin projections and efficiently emit light. These bright neutral excitons (X^0) have a short lifetime (< 10 ps), an in-plane dipole moment, and an out-of-plane light emission. In case of WSe_2 , for e.g., the bright exciton transition is between the upper spin-split CB and the hole in the VB at K/K' valleys. In addition to the direct bright excitons, contributions from Λ and Γ valleys can result in spin-allowed indirect excitons between K - Λ and K - K' momentum positions. This is shown in **Figure 2.8a**,**b** for Mo and W based TMDs. In addition to the direct and indirect transition between spin allowed and forbidden states, attractive Coulomb interaction can result in excitons acquiring an additional charge, forming a three particle composite, called a trion (X⁻). In PL measurement (Figure 2.8f), the X^- peak appears at energies lower than the X^0 peak, and the energy splitting $(X^0 - X^-)$ is defined as the binding energy of the trion. Also depending on the charge state of the trion, it can be categorised into : Positive trion (e-h-h) (X⁺) and negative trion (e-e-h) (X^{-}) where the additional holes/electrons can belong to either the same valley or different K/K' valleys further classifying them into intravalley or intervalley trions respectively. Depending on the spin character of the exciton itself, a trion can also be dark or bright, all collectively shown in **Figure 2.8c,d**. There have also been reports of



Figure 2.8: Various exciton complexes in (a) MoX₂ and (b) WX₂ TMDs. We see that for valleys K/K' and Λ in the CB and for valleys K/K' and Γ in VB we can have a rich library of excitons features - excitons (X⁰), momentum-forbidden indirect excitons (IX⁰), spinforbidden dark excitons (X^D), and momentum and spin-forbidden indirect dark excitons (IX^D). Moreover due to strong electron-hole Coulomb interactions, formation of additional charge complexes such as - (c) bright inter/intra valley trions (X⁻), as well as (d) dark inter/intra valley trions (X^D_D) are possible. (e) Additionally, replicas of spin-dark excitons have been observed through emission/absorption of chiral phonons. (f) Low-temperature (5 K) PL scans taken on monolayer MoSe₂, WSe₂, MoSe₂ and WS₂ (left to right) showing X⁰, X⁻ and defect-band transitions. We see a prominent defect emission from all other TMDs (except for MoSe₂) indicative of the presence of large number of defects and vacancies, particularly significant in tungsten based compounds. In addition to X⁰ and X⁻, We can also see the B exciton in MoS₂ and the charged biexciton in WSe₂.

virtual trion state, which is formed when a localized electron (bound to impurity or defects) captures a delocalized electrons and emits a phonon. The binding energy of the virtual trion state in this case equals the energy of the optical phonon due to energy conservation and appears to also match the binding energy of a normal trion. Additional exciton complexes charged (XX^0) and neutral bi-excitons (XX^-) have been observed in WSe₂ and MoSe₂ [86–89] as well as other phonon replicas of the dark-exciton states involving emission of a chiral phonon [90,91]. This rich spectrum of single and multi-exciton states as well as the dark and bright nature of electronic bands that couple to specific polarization of EM fields, make these materials vitally important for developing future optoelectronic technologies.

2.7 Interlayer Physics: TMD Heterostructures

TMDs offer unique opportunities to integrate layered stacks of highly disparate materials through the means of weak van der Waals (vdW) interaction. Since the dangling chemical bonds on the surface of TMD MLs are fully saturated (except in case of impurities), absence of direct chemical bonding between subsequent layer also removes the constraint of crystal lattice matching. This means that we can create all sort of material combinations with different crystal structure and electronic properties, commonly referred to as a heterostructure, as long as we can guarantee that the interface between the two is preserved and in contact. A lot of research effort has been put in understanding the properties of these TMD heterostructure as well the application that they cater to, which may be absent in the individual materials. For TMDs in particular, different combination of materials properties and dimensionalities have been investigated, most common being the 2D-2D semiconductor-semiconductor/insulator heterostructure.

2.7.1 Semiconductor-semiconductor heterostructures

The most commonly studied TMD semiconductor heterostructures are fabricated from various combinations of Mo and W-based monolayer, with a stable 2H phase. Their elecronic bandstructure is sensitive to the stacking order as well as to the type of band alignment, which in turn is dependent on their relative band-gaps. The two stacking orders, AA and AB as shown in **Figure 2.9a** have the weakest and strongest interlaver electronic coupling, respectively. Theoretically, the most stable stacking structure is determined by optimizing the interlayer distance between the two materials and their lattice constants and noting which of two (AA or AB) offer unique advantage. Once the stacking structure is decided, the formation of the bandstructures in heterobilayers is understood by Anderson's rule, which requires the vacuum energy levels of the constituent semiconductors be aligned at the same energy. This results into three types of possible band-alignments - Type-I (straddling), Type-II (staggered) and Type-III (broken gap). In type-I heterostructure, the CBM and VBM mainly consists of the orbitals of the semiconductor with the smallest band-gap, in our case the material B as shown in **Figure 2.9a**. A typical examples of this can be WTe₂ -WSe₂ or MoTe₂ - WSe₂ heterostructures. For type-II alignment, the VBM and CBM levels reside in two separate material layers, with the heterostructure acquiring a direct or indirect gap. A classic, most extensively studied example of this is $MoSe_2 - WSe_2$ heterostructure. Finally, a type-III heterostructure is similar to type-II in terms of where the CBM and VBM are located, but there is no band-gap, and is a semi-metal. An example of this is a $WTe_2 - WS_2$ or a $WTe_2 - MoS_2$ heterostructure.

While each semiconducting ML starts with a direct band-gap at K point, the heterostructures formed under Anderson's rule can have - a direct, indirect and zero-band gap and allow new exciton states to appear at the interface. It is also important to note here that for electrons and holes that lie in different layers (type-II and III), recombination of interlayer excitons can only happen if the transition metal orbitals are coupled between the two TMDs. It is seen that for all possible combinations of TMD semiconductor heterostructure, no band-hybridization happens at the K point because of its in-plane orbital character. In contrary, the indirect nature of the bands in some of these heterostructures arrives from the orbital coupling at the Γ/Λ (or Q) valleys, which have an out of plane orbital character. We must also note that the layer separation between the two TMDs, for



Figure 2.9: (a) Atomic structure of AA and AB stacking in vdW heterostructure with various band-alignments allowed under Anderson's rule. (b) Relative misalignment in the Brillouin zone corner of top and bottom layers in TMD heterostructure with small twist or lattice mismatch. For optically bright ILEs, the electron and holes can radiatively recombine if their momentum sum $\mathbf{k} + \mathbf{k}'$ equals the displacement vector between the $\tau \mathbf{K}$ and $\tau' \mathbf{K'}$ valleys of the bottom and top layer. (c) moirépattern emerge at the interface between two TMDs with relative twist angle and lattice mismatch. Three high-symmetry points denoted by A, B and C based on the relative shift and rotational symmetry and govern a set of new optical selections rules that couple to specific circular polarization. In case of points A and B where the hexagon centers in the bottom layer overlaps with the same on top or with a chalcogen, we see circularly σ^+ (σ^-) polarized selection rules, irrespective of the existing optical rules governed by the spin-valley index. Point C, where the metal atom is in top of the hexagonal center, we see no favourable transition, and the ILE has an out of plane polarization.

e.g in $MoSe_2$ - WSe_2 heterostructures is of the order of (≈ 0.7 nm), while the intralayer exciton Bohr radius in ML TMDs is of the order of (1-3 nm) and hence favorable for the formation of an interlayer indirect exciton (ILEs), as seen in this heterostack. Additionally, ultrafast transfer of intralayer charger carrier from one layer to the other has been observed, for e.g. in < 50 fs in MoS₂ - WS₂ heterostructure after photo-excitation. Not only this, PL energy, intensity and magnetic g factors of interlayer excitons

2.7.2 More on ILEs and Moiré patterns

Apart from the case of $MoSe_2 - WSe_2$ heterostructure where the interlayer transition is indirect (K-Q), type-II (and type-I) band-alignment can also lead to a direct gap heterostructure, for e.g. the case of $MoS_2 - WSe_2$. This means that optically active ILEs can be formed from electrons and holes at $\pm K$ and $\pm K'$ valleys that reside in different layers. However, two major challenges emerge in heterostructure TMDs with small lattice mismatch (differences in lattice constants) and rotational misalignment -1) Momentum displaced K and K' band-edges between the two layers 2) Moiré patterns at specific high-symmetry spatial locations that can alter the optical selection rules of ILEs and their interband transitions. Let us focus on each separately.

As shown in **Figure 2.9b**, the rotational and lattice asymmetry between the two layers result in $\tau \mathbf{K}$ and $\tau' \mathbf{K'}$ (τ (τ') are valley indices for electrons and holes) valleys to be misaligned in the momentum space, which would result in an optically dark ILE with momentum-forbidden direct radiative recombination. However, as we can see in **Figure 2.9b**, for an ILE with a certain kinematical momentum (**Q**) range, the mismatch between the relative momenta of electron and holes can be compensated between the two valley. In this range $\mathbf{Q} = \tau \mathbf{K} \cdot \tau' \mathbf{K'}$, the ILE can possess a finite transition dipole and is optically bright. Therefore, we can imagine a case where an electron and hole situated in momentum positions $\tau' \mathbf{K'} + \mathbf{k'}$ and $\tau \mathbf{K} - \mathbf{k}$ respectively, form a direct interlayer exciton $\mathbf{Q} = \mathbf{k} + \mathbf{k'}$, aligned in momentum space. These light cones (these ranges of momenta **Q**) are present at six corner locations of the BZ as shown in **Figure 2.9b**, where \hat{C}_3 denotes the in-plane rotational symmetry of $2\pi/3$ in TMD monolayer with hexagonal BZ. The optical selection rules for ILEs in this case follow the rules determined by the \hat{C}_3 rotational symmetry in each layer. It has also been shown that the transition dipole strength of these light cones decay quickly with increasing magnitude of **Q**, and hence light cones nearest to $\mathbf{Q} = 0$ are optically brightest. This shows that the magnitude of lattice mismatch and rotational misalignment plays a huge factor in the optical observation of ILEs for direct $\tau \mathbf{K} \rightarrow \tau' \mathbf{K}$ ' transitions in type-I,II heterostructures.

An additional effect of this angular mismatch is the formation of moiré patterns with periodic changes in the interlayer atomic registry given by the period $b \approx a/\sqrt{\delta^2 + \theta^2}$, where a is the monolayer lattice constant, δ is the lattice mismatch and θ is the relative twist angle between the two TMDs. We can see form Figure 2.9c that in heterostructures with a moiré superlattice, there exists three high-symmetry sites (points A, B and C), denoted by the relative angular positions of layers that have the same \hat{C}_3 rotational symmetry under common rotation axis between to the two layers. These points are denoted by R_h^h, R_h^X, R_h^M , where X: chalogen site, M: metal site and h: hollow center of the hexagon and R_h^i means that the i site where the CB lies (electron layer) overlaps vertically with the hexagon center (h) of the hole layer. This is also schematically shown in **Figure 2.9c**. These changes in local atomic registry leads to lateral modulation of the interlayer distance and bandgap, producing a spatially dependent moiré potential (similar to lateral quantum wells) at these high symmetry positions. These potentials can then trap ILEs, as well as intralayer excitons, causing modulation in their lifetimes and emission energy. We can also see clearly, that the symmetry points R_h^h, R_h^M have $2\pi/3$ rotational symmetry for both layers with a common axis passing through h. While R_h^M has a $2\pi/3$ symmetry, same as in normal monolayer TMDs. These changes in the \hat{C}_3 symmetry also results in a lateral modulation of the optical selection rules for ILEs along the moiré superlattice, where, at $R_h^h(R_h^M)$ ILEs couple to $\sigma^+(\sigma^-)$ circularly polarized light, with elliptical polarization for all sites between the two. At position R_h^M , ILEs couples to out-of-plane light polarization. This means that at high-symmetry points, ILEs can couple to opposite helicites of circularly polarized light, even though they belong to the same spin-valley index that prefers a certain chirality. Therefore, the optical selection rules in such heterobilayer are determined not only by spin, valley, and orbital quasi-angular momenta (QAM) of the constituent materials, but also the effects of moiré superlattice on the local atomic registries (MQAM), suggesting a new degree of freedom in manipulating optical properties in TMD heterostructures.

2.7.3 Semiconductor-metal heterostructures

For TMD semiconductors to be efficiently integrated in low-power electronics, such as a field effect transistor (FET), their ability to form ideal contacts with bulk metal electrodes become crucial. A low contact-resistance is needed for successful charge migration between the two materials, as well as to obtain large on-current, fast optical response and high frequency switching operations [92]. Similar to the concept of band alignment in semiconductor-semiconductor heterostructure discussed ahead, a key quantity to estimate the interaction in metal-semiconductor heterostructures is the Schottky-barrier height (Φ_{SBH}). According to Schottky theory [93], for a metal to make an intimate contact with a semiconductor, the Fermi level (E_F) between the two materials must be set at equilibrium. This leads to modification of the semiconductor bands leading upto the junction as well as changes in the position of (E_F) relative to the VBM and CBM after contact. As a result, a p(n)-type potential barrier forms at the junction denoted as Φ_{SBH}^{P} (Φ_{SBH}^{n}), where the height of this barrier is set by the metal workfunction (Φ_M), semiconductor workfunction (Φ_{SM}), semiconductor electron affinity (χ) and the ionization potential (E_{ip}), such that,

$$\boldsymbol{\Phi}_{\mathbf{SBH}}^{\mathbf{n}} = \Phi_M - \chi \quad \text{and} \quad \boldsymbol{\Phi}_{\mathbf{SBH}}^{\mathbf{p}} = E_{ip} - \Phi_{SM}$$
(2.15)

Depending on Φ_M and the position of E_F with respect to valence and conduction bands, the charge injection can be on *n*-type or *p*-type as shown in **Figure 2.10**. This also means that we can tune the magnitude of Φ_{SBH} by appropriately choosing materials with specific Φ_M and χ and control the energy required for carrier injection. However, this is not observed experimentally in metal-TMD junctions, where band bending in semiconductors behave independently of the metal-work function. This phenomena, know as Fermi level pinning (FLP) has been attributed to various reasons, such as interface dipoles, impurities



Figure 2.10: Band bending at the interface of metal-semiconductors can create potential barriers, referred to as Schottky barrier height (SBH) for (a) hole injection *p*-type-SBH (b) and electron injection *n*-type SBH. Here, Φ_M represents the metal workfunction, Φ_{SM} is the semiconductor workfunction, χ is the electron affinity, E_g is the semiconductor bandgap and E_F is the Fermi level matched at the junction. (c)In TMD monolayer, in-plane band bending can occur as results of changes in semiconductor workfunction due to vdW interaction from the metal layer. This can create traps for electrons and holes at the inplane boundary between pristine and metal-capped semiconductor layer (more on this in later sections).

and defects at the interface, and existence of metal-induced gap states (MIGS) [94–98]. Significant efforts have been made to improve the contact properties of layered TMDs with metals (mostly noble metals), such as band-gap tuning using few-layer semiconductors, degenerate n-type and p-type doping close to the contact, phase-engineering, inserting buffer layers to mitigate MIG and defect states, using pre-patterned substrates with ultra-clean and flat metal pads, creating edge contacts for stronger orbital hybridization between metals and semiconductors, etc [94,99]. Edge contacts are particularly dangling bonds at the edges of monolayer TMDs offer strong orbital overlap [99], and since the injection is lateral, it eliminates the effect of interlayer resistance present in top contacts. Additionally, scaling down of a 2D devices with lateral edge contact could lead an easier path towards device miniaturization without having the need to crowd contacts vertically.

The 2D nature of metallic TMDs offer unique advantage to mitigate these effects by forming vdW junctions with atomically flat, defect free interfaces. Among 2H-TMDs NbS₂, NbSe₂, TaS₂, TaSe₂ are metallic in nature, with limited 2D DOS, low quantum capacitance and large work functions [44]. Of the various combination of TMD semiconductor-metal interfaces, we see that in most heterostructures, metal bands lie within the band-gap of semiconductor, with little to no offset in the semiconductor valence band [44,87,100]. Further, lack of orbital overlap between transition metal atoms shows that the semiconductor retains its band structure properties at the junction. Despite the tremendous progress in understanding contact properties of metal-TMD junction, their optical properties are rather underexplored. This is largely because excitons tends to disassociate with charge carriers decaying from the semiconductor to the metal in close proximity. This affects their PL properties such as significant drop in PL intensity as well as broadening of linewidth. In addition, there is no band-hybridization between transition metal atoms [69, 87, 100], showing that no new interlayer optical transitions are possible at the interface. Further some of these materials undergo additional electronic transitions such as CDW and superconductivity which massively changes their electronic properties, and can open avenues for optoelectronic interactions between these materials. Studies showing proximity effects in TMD based semiconductor-superconductor junctions with control over proximity length [101], as well as emergence of new optical transition between semiconductor-metal interface due to in-plane band-bending between pristine and metal-capped regions (more on this later!) [69,100].

2.7.4 Excitons and Dielectrics

One crucial aspect that sets 2D TMDs apart is the remarkably strong Coulomb inter

action between charge carriers. This leads to renormalization of the electronic and optical band-gap and hence reflects in changes associated with the binding energy of electron-hole pairs forming the exciton. The strength of the Coulomb interaction is generally dictated by local dielectric screening of the material as well as the environment, and is broadly characterized into - *direct* and *exchange*-contribution with both categories accounting for the effects of long-range and short-range interactions [59]. Coulomb interactions at interparticle distances larger than the bond length in real space are defined as long-range, while the contributions that originate from overlapping of the electron-hole wavefunctions at scales of the order of lattice constants are defined as short-range. The *direct*-contribution comes from the interactions of electrons and holes to the charge distribution in the vicinity, and is a dominant contributor to the exciton binding energy (E_B) as well as sensitive to the material dielectric. The exchange correlation is more descriptive of the Coulomb interaction in terms of electron and hole spin. Since TMDs have bands that are spin-valley locked, the energy of the exciton depends on the mutual spin orientation of electron and holes. Now, in case of electron-hole pairs in close vicinity, the electric-field induced between the two can interact with their individual spin states, and alter the exciton energy which is accounted under long-rane exchange interaction. This interaction is more subtle than the *direct* contribution, but impacts the separation between optically bright and dark states, as well as other multiparticle states such as trion or biexcitons and exciton finestructure. We can describe a Hamiltonian that includes the two categories to give us the total Coulomb interaction as follows [59]:

$$H_{XX'}(\mathbf{k_e}, \mathbf{k_h}, \mathbf{k'_e}, \mathbf{k'_h}) = [H_e(\mathbf{k_e})\delta_{\mathbf{k_e}, \mathbf{k'_e}} + H_h(\mathbf{k_h})\delta_{\mathbf{k_h}, \mathbf{k'_h}} + V_{\mathbf{k_e}, \mathbf{k_h}: \mathbf{k'_e}, \mathbf{k'_h}}]\delta_{XX'} + U_{\mathbf{k_e}, \mathbf{k_h}: \mathbf{k'_e}, \mathbf{k'_h}}(EH : E'H')\delta_{\mathbf{K}, \mathbf{K'}} \quad (2.16)$$

where $H_e(\mathbf{k_e})(H_h(\mathbf{k_h}))$ are the individual electron and hole single particle Hamiltonians, $V_{\mathbf{k_e},\mathbf{k_h}:\mathbf{k'_e},\mathbf{k'_h}}$ is the term that describes the direct Coulomb interaction, particularly at long-



Figure 2.11: (a) Schematic representation of vdW heterostructures with an ideal in-plane boundary (top) and in more realistic scenarios with samples fabricated in air with an air-gap between the two layers (bottom). The electric field lines between the two point charges electrons and holes forming the exciton, is screened by the surrounding dielectric environment. (b) Illustration of the change of the band gap and the bound-state energies due to the different screening environments: freestanding TMD monolayer (left), a TMD monolayer on substrate with no gap between the two causing strong screening reducing both the band gap E_g and the binding energies of X⁰ and X⁻ peaks (middle), and a non-vanishing air-gap between TMD and substrate leading to reduced screening on the right. (c) Comparison of the ML-MoSe₂ PL spectra taken at 5K, when encapsulated in hBN (left), fabricated on a hBN substrate (middle) and fabricated directly on a Si-SiO₂ substrate. Each case represents a unique dielectric environment gradually tuning the X⁻ binding energy.

range, and the term $U_{\mathbf{k}_{e},\mathbf{k}_{h}:\mathbf{k}'_{e},\mathbf{k}'_{h}}$ describes the short and long range electron-hole exchange

interactions. Here, $E = s_e \tau_e$ and $H = s_h \tau_h$ are the spin and valley index of the electron and hole pair respectively.

Now that we have a mathematical structure for Coulomb interaction, let us focus on why it is necessary in TMD heterostructures, at least in the domain of non-local changes in dielectric screening. Due to the in-plane nature of excitons, the electric field between two charged particles permeates both the material layer as well the surrounding environment. This is shown in **Figure 2.11a** for excitons with small and large Bohr radius. As the distance between electron-holes decrease, more field lines lie outside the material and hence, the combined dielectric of the materials above and below the TMD must be considered. In any case, based on **Equation 2.16**, one must find an effective potential that explains the effects of dielectrics for both short and long relative distance (r_{ij}) between electron and hole particles. This is given by Keldysh potential [102],

$$V(r_{ij}) = \frac{q_i q_j \pi}{2\kappa r_*} \left[H_0(\frac{r_{ij}}{r_*}) - Y_0(\frac{r_{ij}}{r_*}) \right]$$
(2.17)

where $q_{i,j}$ is the charge of the particle. The most important quantity here is r_* which is the particle length scale in presence of dielectric environment, further defined by $r_* = 2\pi\chi_{2D}/\kappa$. Here, χ_{2D} is the 2D polarizability of the TMD sheet calculated from its bulk dielectric function and $\kappa = (\epsilon_{top} + \epsilon_{bottom})/2$. Taking in account the dielectric strength of materials in TMD heterostructures, we can use **Equation 2.17** to model the changes in exciton binding energy. Things get a bit more complicated in cases where an interlayer gap between the material and sub(super)strate is present/considered (**Figure 2.11b**), as the Keldysh potential does not completely explain the changes in Coulomb interaction in the short-range limit [103].

Direct experimental observations of changes in the exciton binding energy have been performed for a variety of heterostructure configuration, by either measuring the exciton Rydberg states directly or by observing the change in the exciton Bohr radius as a result of interaction with material dielectric [59,103]. Trions are very sensitive to changes in material electronic properties, as the trion binding energy does not depend on the band-gap, but is directly dependent on the strength of Coulomb interaction and the screening effects. An additional benefit is that trion are easily observed for materials like WSe₂ and MoSe₂, and the effect of trion-binding energy, which is the different between the trion and exciton peak can be measured as a function of different dielectric present around the material in simple PL measurements. We show in **Figure 2.11c**, three separate cases of MoSe₂ PL, with the flake on a Si/SiO₂ substrate (right), a MoSe₂ - HBN heterostructure and finally (middle), an encapsulated HBN - MoSe₂ - HBN heterostack (left). We can see the binding energy of the trion peak decrease gradually as we increase the combined dielectric strength of the MoSe₂ heterostructure (HBN has higher dielectric than air). We also see narrowing of X⁰ and X⁻ linewidths with changes in dielectric environment, which shows an indirect correlation of changes in dielectric screening to exciton and trion lifetimes This has been seen in many 2D TMD semiconductor heterostructure, especially the ones encapsulated in HBN and show the importance of material properties and environment on their optical properties [59,103,104].

Chapter 3: Instrumentation and automation

3.1 Exfoliation, transfer and sample fabrications

Most of the samples discussed in this manuscript are mechanically exfoliated from crystals grown via chemical vapor transport (CVT) method by our colleagues at the national institute for standards and technology (NIST), Maryland, USA. This requires a temperature gradient as well as a transport agent to successfully grow millimeter-size crystals at the end of the quartz tube. The crystals are then mechanically exfoliated by us using a lowtack blue tape, a very common tool to exfoliate 2D materials. After successful exfoliation, the flake are transferred from the tape to a polydimethylsiloxane (PDMS) strip, which is a sticky, transparent polymer, allowing us to visualize the flakes and their optical contrast, particularly for monolayer TMDs. After locating a target flake, we flip the polymer, facing downwards onto a Si-SiO₂ wafer and aligned to be carefully placed anywhere on the substrate. The slow lift-off ensure that the flake has been stamped down successfully. In order to fabricate 2D devices and heterostructures, we repeat this same process, while targeting and aligning each layer on top with layer on the substrate to ensure we have good contact. This method is known as the dry-viscoelastic method [105], and has been characterized as one of the optimum procedures to fabricate TMD heterostructures and devices. A schematic of this transfer process is shown in **Figure 3.1**. A disadvantage of this method is that since PDMS is a sticky polymer, it can sometimes leave residue on the surface of TMDs, causing bubble/gaps to form at the interface between two TMDs. The next section, while focusing on a microscopy technique, will explain how we deal with contaminants.



Figure 3.1: Sample fabrication process involving dry-transfer through PDMS. The identified flake is first stamped on the PDMS strip, and then later stamped on the Si-SiO₂ substrate, using a XYZ micromanipulater stage for lateral alignment. The transfer station used fo making 2D vdW heterostructure is also shown below.

3.2 Atomic Force Microscopy measurements

Atomic Force Microscopy is common tool to characterise materials in addition to the other optical spectroscopy techniques, achieving resolution down to a few manometers and beyond. The basic working principle of an AFM involves the detection of a horizontal cantilever probe trip using a combination of a laser and a photodiode, as the tip deflects over the sample based on the changes in its surface properties. This is schematically shown in **Figure 3.2a**. The sample sits on a vibration free stage, while the tip is attached via a

piezoelectric mount operated through a P.I.D. controller. Any change in the 'Z' deflection of the probe tip registers as a change in the surface of the material, typically its height, and can generate a real-time map of the recorded area. We use the Nanosurf Flex-AFM system which provides a variety of characterization toolkits and imaging modes. We discuss two modes specifically - Tapping mode (or Dynamic mode) and Contact mode (Static mode)



Figure 3.2: (a) A schematic of the basic functionality in a typical atomic force microscope (AFM) system. (b) Examples of two types of AFM functions offered by the Nano-surf system - Tapping mode and Contact mode. We use the contact-mode to remove contaminants lodged between the TMD material and the substrate during the PDMS-based sample fabrication process. This improves the coupling between the two materials as well as the optical properties at the common interface.

as shown in **Figure 3.2b**. In the tapping mode, the probe tip constantly oscillates over the sample and any changes in its amplitude is recorded as a change in surface height, while the tip never makes contact with the sample. However, in the static mode, the tip is in continuous contact with the sample while the probe raster scans the surface. We record the deflection of the tip as a feedback parameter as is set based on how hard the tip is configured to push against the surface of the sample.
We interchangeably use these two modes to characterize monolayer TMDs as well as to methodically clean the interface between two materials of the contaminants lodges during sample fabrication. The use of PDMS to vertically stack TMDs in a heterostructure some times leaves residue on the surface, which can affect the contact properties between these materials. Using the tapping mode, we initially determine the interfacial region where TMDs have made contact with each other and look for sign of residues. Switching to the static mode, we use the probe tip to push the residue off the surface/interface, by appropriately determining the force enough to remove the contaminants but not to damage the material. This method was developed by a group at NRL [106], and name the process 'Nano-Squeegee', where they were effectively able to remove the residue between HBN-TMD interface, simultaneously improving its optical properties. This method is schematically shown in Figure 3.2c. For both the contact and tapping mode, we use a 7 N/m spring constant ACSTGG-10 tip and a contact force in the range of 40 - 140 nN depending on the sample assembly. Additionally, setting P.I.D. gains as well as configuring the *points/line* and *time/line* setting is important for fine-tuning the sweep as well as the efficiency of how well the tip drags the contaminants out.

3.3 Raman measurements

Raman scattering is an electromagnetic phenomena in which light couples to an excitation in a material. The beginning point of all electromagnetic phenomena are the Maxwell's equations, given as

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} ; \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \cdot \mathbf{D} = \rho ; \nabla \cdot \mathbf{B} = 0$$

Under monochromatic excitation, the incident electric field is given by,

$$\mathbf{E}_{\mathbf{I}}(\mathbf{r},t) = \mathbf{E}(\mathbf{q},\omega) e^{(\mathbf{k}_{\mathbf{I}}\cdot\mathbf{r}-i\omega_{I}t)} + \mathbf{E}^{*}(\mathbf{q},\omega) e^{(-\mathbf{k}_{\mathbf{I}}\cdot\mathbf{r}+i\omega_{I}t)}$$
(3.1)

where **E** is the complex amplitude, ω_I is the incident photon frequency and k_I is the incident photon wavevector. The oscillating incident electric field induces an oscillating polarization within the material, given as

$$\mathbf{P}_{\mathbf{j}}(\mathbf{r},t) = \chi_j(\mathbf{r},t) \,\mathbf{E}_{\mathbf{I}}(\mathbf{r},t) \tag{3.2}$$

where χ is the susceptibility vector representing the polarizability of the material independent of the incident electric field and the subscripts denote the polarization axis. In other words, χ denoted the tendency of the material to form induce dipole moments under an external field. The polarizability is time independent if no excitations are induced within the material. In this case, the polarization $\mathbf{P}(\mathbf{r},t)$ oscillates at the same frequency as the incident electric field and the scattering light has the same frequency as the incident light. This is more commonly referred to as elastic Rayleigh scattering. In contrast to this, under inelastic scattering processes, the induced excitations within the material can be modelled as:

$$\left\langle \xi(\mathbf{r},t)\,\xi(0,0)\right\rangle = \int d^3\,\mathbf{q}\,d\omega\,\left[\left\langle \xi\xi\right\rangle_{\mathbf{q},\omega}e^{(\mathbf{q}\cdot\mathbf{r}-i\omega_I t)} + \left\langle \xi\xi\right\rangle_{\mathbf{q},\omega}^*e^{(-\mathbf{q}\cdot\mathbf{r}+i\omega_I t)}\right] \tag{3.3}$$

where $\xi(\mathbf{r}, t)$ represents induced excitations in the form of small rotational or translational displacement of the crystal lattice, charge density or spin orientation from the equilibrium. In this case, the polarizability $\chi_j(\mathbf{r}, t)$ acquires a time-dependent profile similar to the incident electric field. For small displacements around the equilibrium position, we can expand the polarizability $\chi(\mathbf{r}, t) = \chi(\xi(\mathbf{r}, t))$ and subsequently the polarization as a Taylor series, given as



Figure 3.3: Light scattered from a material can be categorized as Rayleigh scattering, Stokes Raman scattering, and/or anti-Stokes Raman scattering. In case of Rayleigh scattering, elastic interactions between the incident photon, with frequency ν_0 and the material results in the emission of a photon with the same frequency. In case of inelastic scattering events, an exchange of energy between the incoming photon and material takes places, resulting into Stokes or anti-Stokes Raman processes. We can further define Stokes Raman when the energy of incident photons is imparted to the material as lattice vibration $(\hbar\nu_{ph})$ such that the scattered light has a lower energy than the excitation. Anti-Stokes Raman happens when the material itself is in a higher order ground state, such that the inelastic interaction leaves a photon with energy higher than the incident photon. For measurements outlined in this dissertation, we focus on Stokes-Raman, referred to as 'Raman', unless otherwise noted.

$$\chi(\mathbf{r},t) = \chi_o + \frac{d\chi_o}{d\xi}\xi(\mathbf{r},t) + \frac{1}{2}\frac{d^2\chi_o}{d\xi^2}\xi^2(\mathbf{r},t) + \dots$$
(3.4)

$$\mathbf{P}(\mathbf{r},t) = \chi_o(\mathbf{r},t) \, \mathbf{E}_{\mathbf{I}}(\mathbf{r},t) + \frac{d\chi_o}{d\xi} \xi(\mathbf{r},t) \, \mathbf{E}_{\mathbf{I}}(\mathbf{r},t) + \frac{1}{2} \frac{d^2 \chi_o}{d\xi^2} \xi^2(\mathbf{r},t) \, \mathbf{E}_{\mathbf{I}}(\mathbf{r},t) + \dots$$
(3.5)

Here, in addition to the first term that explains Rayleigh scattering, Raman processes

involving inelastic scattering of photons are described by the second, linear differential term in the Taylor expansion, giving,

$$\mathbf{P}_{\mathbf{1}}(\mathbf{r},t) = \frac{d\chi_o}{d\xi}\xi(\mathbf{r},t)\,\mathbf{E}_{\mathbf{I}}(\mathbf{r},t) = \mathbf{P}_{\mathbf{S}}(\mathbf{r},t) + \mathbf{P}_{\mathbf{AS}}(\mathbf{r},t)$$
(3.6)

where $\mathbf{P}_{\mathbf{S}}(\mathbf{r}, t)$ denoted the Stokes-Raman polarization, while $\mathbf{P}_{\mathbf{AS}}(\mathbf{r}, t)$ denotes the Anti-Stokes polarization. Moreover, Stokes and anti-Stokes processes are differentiated by the initial vibrational state of the material as well as the energy of the scattered photon with respect to that of the incident. It is important to mention here that probability of elastic Rayleigh scattering is much higher (an intensity of about 0.1% - 0.01% of the excitation) than the inelastic Raman scattering process (≈ 1 in 10 million) and determines the optical threshold in a typical Raman measurement.

A pictorial representation to the above discussed processes is shown in Figure 3.3. We see that an incident photon with energy $E_{exc} = h\nu_0$ is absorbed, exciting molecules of the lattice to a virtual excited state. Upon relaxation, a photon is re-emitted back with certain energy determined by the nature of scattering event. As discussed, no exchange of energy under Rayleigh scattering requires that the emitted photon be of the same energy $h\nu_0$. In case of Stokes Raman scattering, a part of the incident photon energy is transferred to lattice vibrations (quantized as $h\nu_{ph}$), leaving scattered photons with an energy of $h(\nu_0 - \nu_{ph})$. The anti-Stokes scattering occurs when the material is already in a higher order vibrational state, resulting in a scattered photons with energy more than the incident photons given by $h(\nu_0 + \nu_{ph})$. Depending on the type of molecular vibrations allowed under symmetry and optical selection rules that couple to Raman process, we can see new features that appear below (above) the Rayleigh line, and are called anti- Stokes (Stokes) Raman modes. Usually, Raman spectra are plotted as function of the difference ($\Delta\nu$) between the frequency of scattered light to that of the Rayleigh line, in units of cm⁻¹, referred to as wavenumbers. This is mathematically represented by Equation 3.7 where the frequency of Raman peaks (ν_{ph}) determine specific lattice vibrational states, called as phonon modes and are represented in the phonon bandstructure of a given material.

Raman Shift
$$[\mathrm{cm}^{-1}] = -\left(\frac{1}{\lambda \; [\mathrm{nm}]} - \frac{1}{\lambda_0 \; [\mathrm{nm}]}\right) \times 10^7,$$
 (3.7)



Figure 3.4: A schematic of the custom microscope built for temperature-dependent Raman measurements. The entire optical setup rests on a XY translation stage.

Figure 3.4 shows a schematic of the custom confocal Raman microscope setup used for studying the vibration properties of various TMDs discussed in this dissertation. We use a combination of reflective mirrors and lens system to guide the laser beam (532 nm excitation, 2.4 μm spot size) through a 0.42 NA, 50× long working-distance objective onto a sample placed in cryostat under vacuum. An important component of this assembly is the combination of four BragGrate filter (two bandpass filters and two notch filters) employing an inject-reject system to probe Raman modes close to the Rayleigh line at ultra-low frequencies (within 15 $\rm cm^{-1}$). These optical filters are designed exclusively for the 532 nm laser excitation (and specific incidence angle), where the bandpass filters are customized to reflect all light at that wavelength and the notch filters are desgined to reject at the same. Additionally, a sharp rejection at the laser line also allows for simultaneous observation of the Stokes and anti-Stokes Raman modes. We also use a combination of linear polarizers in the excitation and collection path to control the polarity of incident and scattered photons to perform polarized Raman measurements. Finally, the back-scattered light is fibre coupled to a single, 500 mm focal length spectrometer with an 1800 g/mm grating and integrated with a liquid- N_2 cooled CCD detector to resolve observed peaks. An important quality of our Raman setup is that the entire optical assembly rests on a X-Y translation stage (dashed box), designed to move in increments of 50 nm with a load of 20 N. We do this to enable spatially-mapped Raman measurements and record changes in Raman spectra as a function of position on the sample. Temperature-dependent measurements are performed using an external Lake Shore temperature controller coupled to the sample stage in the cryostat and able to alter temperature in the range of 4 K - 300 K.

3.4 Photoluminescence and reflectance measurements

Excitons in 2D TMDs can be directly probed by performing circularly and linearly polarized PL measurements (refer to previous section for more details). This requires exciting a sample with photons resonant to or with energy higher than the band-gap of the material. This creates in most cases and large batch of hot excitons, which can then cool off to available energy states, depending upon the nature of the gap and the optical selections rules that determine their coupling to specific polarization. Additionally, reflectance (RL) measurement is fantastic tools to determine the exciton oscillator strength in semiconducting TMDs, and gives an estimate of the probability for exciton creation/recombination at specific wavelengths. The peaks in the reflection spectra and PL spectra often correlate,



Figure 3.5: A schematic of the custom microscope built for temperature-dependent photoluminescence (PL) and reflectance (RL) spectroscopy. The entire optical setup rests on a XY translation stage.

although higher order excition species remain fairly absent in RL data. A schematic of a custom PL/RL setup is shown in **Figure 3.5**, with option to perform both RL and PL measurements using easily swappable and interchangeable optics. We separate the two paths by colors (yellow and red), where we position the flip mirror to specifically switch between the two measurements.

For PL measurements, we use a 633 nm (1.96 eV) HeNe laser excitation, fixed at vertical linear polarization and attenuated appropriately using a variable neutral density filter. The laser beam is guided by a combination of mirrors, through a long-working distance objective (exactly the same specs as used for Raman) to a sample placed in cryostat. We control our laser polarization using a combination of half $(\lambda/2)$ and quarter $(\lambda/4)$ waveplates. Control over angular positioning of $\lambda/2$ and $\lambda/4$ (excitation polarization w.r.to its fast axis - refer **Figure 3.6**) waveplates enables conversion of linearly polarized light to circularly polarized light, a requirement for probing spin-valley locked transitions in 2D TMDs. The placement of the $\lambda/4$ is crucial to maintain circularly polarized excitation at the sample as any reflection through other optical components in the path can alter the circular properties of the laser line and change it to an elliptical polarization. Similarly, in the collection path, it is important to have the $\lambda/4$ waveplate immediately after the objective to make sure the collected light has the same polarization as was emitted from the sample. The specific angular orientations of the $\lambda/2$ (both collection and excitation) and $\lambda/4$ waveplates are determined by considering the laser polarization at the source as well as any detuning caused due to mirrors and additional optics in the setup. This is mathematical formulated using Jones matrices, Equation 3.8 and experimentally determined by observing the individual polarizing properties of all optics in the setup. $\mathbf{E}'(z,t)$ here represent a polarizing optic that converts the electric field of incident light from its initial polarization to the final polarization upon transmission. Similar to the Raman system, the emitted light is fiber couple to a single spectrometer (switched to a 600 or 150 g/mm grating), with the entire setup resting on a X-Y translation stage allowing for hyperspectral PL measurements.

$$\mathbf{E}'(z,t) = \begin{pmatrix} \sin^2\theta + \xi\cos^2\theta & \sin\theta\cos\theta - \xi\sin\theta\cos\theta\\ \sin\theta\cos\theta - \xi\sin\theta\cos\theta & \xi\sin^2\theta + \cos^2\theta \end{pmatrix} \begin{pmatrix} E_x\\ E_y \end{pmatrix}, \quad (3.8)$$

where the 2 \times 1 matrix on the right is called Jones vector and ξ takes the values

$$\xi = 0$$
 for a linear polarizer with transmission axis at θ (3.9)

$$\xi = e^{i\pi/2} = i$$
 for a quarter-wave plate with its fast axis at θ (3.10)

$$\xi = e^{i\pi} = -1$$
 for a half-wave plate with its fast axis at θ (3.11)

$$\xi = 1$$
 in the limiting case where there is no optic present. (3.12)



Figure 3.6: Relative orientations of linearly polarized (vertical in this case) laser with respect to the fast axis of the $\lambda/4$ waveplate, where in case of (a) a relative 45° shift generates a right circularly polarized light - σ^+ and (b) where a -45° shift produces a left circular polarization - σ^- .

In case of RL measurements, an unpolarized white light source is used for excitation (coupled through a multi-mode fiber), with the rest of polarization optics (linear polarizers and waveplates) removed/flipped out from the setup. We also take out the neutral density filter as well as the laser cut-off filter used for the rejecting the 633 nm Rayleigh line in PL measurements. The spot size of our white light source gets to about 5μ m on the sample, which is twice as large than what we have in PL and Raman measurements. The back-reflected light is coupled to the single spectrometer (switched to a 600 or 150g/mm grating) similar to the other measurement setup.

3.5 Hyperspectral imaging

Hyperspectral imaging is a great technique to map the changes in the optical spectra of a TMD, and correlate that with the spatial geometry of the sample, particularly useful in investigating heterostructures. This can also be a great tool to optically determine the quality of coupling between two TMDs, which as we will see in later sections, can be spatially-dependent. We also use this An extensive amount of work has been done to investigate 2D TMDs as well as other organic compounds and biological materials. In case of TMDs, specific focus has been given to visualizing changes in PL properties, especially near the edges of CVD monolayer flakes. Additionally, a lot of work has been done to observe changes at interface of two TMDs, where new optical signatures emerge, otherwise absent in individual layers. We use the X-Y Microstage from Mad City Labs which is a precision, stepper motor driven, micro-positioning system with long-range (25mm) travel for both X and Y axes. The encoder resolution is of the order of 50 nm with a recommended load of 20 N, which enables ultra-high nanometer resolution for spatially mapping a sample. We have integrated this stage with LabView to perform fully-automated hyperspectral imaging over a region with an pre-determined area size. The LabView interface also simultaneously communicates with the spectrometer for optical readout at each position in the X-Y grid. Since the X-Y stage uses optical encoders to keep track of the actual position, we can also design an interface that generates a grid of randomly selected (x,y) coordinates, and define a global co-ordinate system to accurately and precisely probe each location. Please refer to Chapters 5 and 6 for more details on the applications of this technique to probe interfacial physics.

3.6 Electroluminescence and gate-dependent PL measurements

Electroluminescence (EL) is the property of radiative recombination of electron-hole pairs that form the exciton, as a result of excitation due to applied electric field. In TMDs, extensive amount of research has been conducted to observe EL from excitons and multiparticle charge complexes which exhibit tunable behavior dependent on the electrical pulse parameters [107,108]. Moreover, observation of EL from ILEs in semiconductor heterostructures (p-n junctions) have also been reported under forward bias [109,110]. The EL setup



Figure 3.7: A schematic of the custom microscope built for gate-dependent photoluminescence (PL) and Electroluminescence measurement. The entire optical setup rests on a XY translation stage. Contacts are etched on the sample through e-beam lithography with attached contacts pads (tiny silver blocks) to facilitate easy wire bonding with electrical leads present on the chuck inside the cryostat. These leads are accessible externally and can be directly connected to a source measure unit.

remains fairly similar to the PL setup in way, except for all the optics in the collection path would be flipped out or removed (refer Equation 3.7). Contacts are etched directly on the sample through e-beam lithography with large area pads for ease of wire bonding. We manually wire bond our samples using an ultra-thin Manganese wire, which connects the lead on the cryostat chuck to the electrical pad on the wafer. The sample geometry for electrical connections that determine the source, drain and gate is shown in **Equation 3.7** as well. In case of EL measurements, application of a forward (negative) bias between the source and drain contact results in right (left) circular polarization of emitted EL. This mechanism is different from that of the PL because circularly polarized light in EL is produced not by the valley-dependent carrier populations, but the difference in electronhole overlap between the valleys. This will be discussed in detail in the later sections. Gate-dependent PL measurements are in fact a combination of PL and EL measurement, where in we optically probe our sample similar to PL, but application of a gate-bias changes the carrier concentration in the semiconducting channel, thereby changing the intensity of exciton and charge exciton complexes with increasing gate voltage. We have interfaced our source-measure unit (Keithley) with LabView to continuously change the voltage from negative to forward bias while continuously recording the PL spectrum. Gate-dependent PL measurements are a wonderful tool to determine the nature of exciton complexes, specifically trions and charge biexciton complexes, where change in hole and electron concentration drastically impacts their PL properties.

Chapter 4: Project Aleph (ℵ) - Phase transition and phonon anharmonicity in T'-MoTe₂

4.1 Introduction

Transition metal dichalcogenides (TMDs) exhibit a wide range of layer-dependent phenomena depending on the choice of the transition metal and chalcogen atoms. Most studies of TMDs focus on the trigonal prismatic 2H crystal phase, which is similar to the honeycomb lattice of graphene but has broken sub-lattice symmetry and therefore a large semiconducting bandgap (1-2 eV) and large exciton binding energies. However, unlike graphene and boron nitride, TMDs can exist in multiple structural phases that each exhibit unique electronic properties as discussed in Chapter 2. $MoTe_2$ is one TMD where the barrier between 2H and the alternative inversion-symmetric, monoclinic T' phase is minimal [111, 112]. T'- $MoTe_2$ can be achieved by a modified growth method [113–115], a low-temperature solution phase synthesis procedure [116], through electrostatic doping and by application of strain. This phase is also know to host topological non-trivial electronic bands that host quantum spin Hall states and type-II Weyl Fermions where the later results in anomalous physical phenomena such as Fermi arcs and the "presence" of magnetic monopoles at Weyl nodes. However, an important symmetry condition for the existence of Weyl Fermions in $MoTe_2$ is the breaking of spatial inversion symmetry and is met via another phase transition to the orthorhombic T_d - phase. Bulk T' - MoTe₂ undergoes a temperature-driven, structural phase transition to the T_d phase at ~ 250 K confirmed via temperature-dependent electrical measurements as hysteresis after a warming/cooling cycle [115, 117, 118] and directly observed in X-ray diffraction (XRD) measurements [119,120]. This exciting electronic state has also been predicted in WTe₂ [121] and the alloy $Mo_xW_{1-x}Te_2$ [122], and recent experimental results have confirmed the presence of the Weyl semimetal state in all three systems [123–131].



Figure 4.1: (a) Side and top view of the crystal structure of monolayer T' or T_d - MoTe₂ along with the symmetry elements indicating the inversion centers, 2-fold screw axis along the *x*-direction (C_{2x}) and the horizontal mirror-plane symmetry along the *x*-direction (M_x). (b) Crystal structures for bulk T' - MoTe₂ and the orthorhombic T_d - MoTe₂ phases. We show that in the bulk phase, T_d - MoTe₂ lacks inversion center.

The lattice constants in T_d - MoTe₂ (a = 3.458 Å, b = 6.304 Å, c = 13.859 Å at 100 K) and T' - MoTe₂ (a = 3.493 Å, b = 6.358 Å, c = 14.207 Å) are only slightly different [115, 120, 132], with the stacking angle changing from ~ 93.9° in the T' phase to 90° in the T_d phase. In terms of other symmetry elements, the 1T' phase (point group C_{2h} (2/m)) has a 2-fold screw axis along the x-direction (C_{2x}) and an inversion center resulting from the horizontal mirror plane symmetry (M_x). Contrary to this, the orthorhombic T_d phase

has a 2-fold screw axis along the z direction (C_{2z}) , a diagonal glide plane (M_y) , as well as a vertical mirror plane (M_x) symmetry belong to the point group C_{2v} (mm2). These symmetry representation are are shown in **Figure 4.1** along with the respective crystal structure of the two phases. Changes in crystal structure as well as the symmetry rules that govern the activation of vibrational modes can result in new Raman signatures, and have been observed in a number of temperature-dependent studies carried out in T'- MoTe₂. Subsequently, we must also expect changes in the thermodynamic properties across the phase-transition, as heat transfer and thermal conductivity in semiconductors are largely governed by phonons.

Project \aleph was highly motivated by that largely unexplored (at the time) structural phase transition in the low-temperature phase of T' - MoTe₂, particularly the changes in the overall vibrational properties. Understanding the interactions of phonons at low-temperatures is vital, but it becomes pertinent in this case where a structural phase transition changes the vibrational symmetry and lattice dynamics of the crystal structure in its normal phase. We employ temperature-dependent Raman measurements to study the changes in phonon modes between the T' and T_d - MoTe₂ phases and present viable mechanism that explains the behavior of mode frequencies using an anharmonic approach to phonon interactions.

4.2 Bulk MoTe₂ - Sample growth and exfoliation

MoTe₂ crystals were produced by the chemical vapor transport (CVT) method with iodine as the transport agent. MoTe₂ powder was synthesized by annealing molybdenum (99.999 %) and tellurium (99.9 %) powders mixed in a stoichiometric proportion at 750° for 72 h in an evacuated and sealed quartz ampoule. To obtain MoTe₂ single crystals, approximately 2 g of polycrystalline MoTe₂ powder and a small amount of iodine (99.8%, 4 mg/cm³) were sealed in evacuated 17 cm long quartz ampules. The ampules were placed in a furnace containing a temperature gradient so that the MoTe₂ charge was kept at 1000° and temperature at the opposite end of the ampoule was about 950°. In order to retain the T' phase of MoTe₂, the ampoule was quenched in ice-water after 7 days of growth. Powder XRD patterns at room temperature and pressure confirmed the T' structure of MoTe₂. In addition, MoTe₂ single crystals contained a small amount of the surface oxides comprised of MoO₂ as established by the XRD peaks at $2\theta = 26.08^{\circ}$ and a group of peaks around $2\theta = 37^{\circ}$. Oxides were easily removed from the platelets by mechanical exfoliation. Following structural characterization, the bulk T' - MoTe₂ crystal is mechanically exfoliated using tape and deposited onto Si/SiO₂ substrates with an oxide thickness of 285 nm. Atomic force microscopy (AFM) images indicate that the flake we studied is \approx 120 nm thick and therefore lies well into the bulk regime implying that interactions with the substrate can be neglected. It is notable that both the starting crystal and bulk flake we studied were exposed to atmosphere for prolonged periods of time. This is known to lead to oxidation of defects in 2H - MoTe₂ that can modify exciton dynamics [133], however these effects have not yet been observed in T_d or T'.

4.3 Raman signatures of T' and T_d - MoTe₂

Both 1T' and T_d - MoTe₂ structures contain two layers with 12 atoms in the unit cell and thus have 36 vibrational modes in total. Since these phases differ only in their stacking configuration, the frequencies of the corresponding modes should be similar. However, as per our discussion above, the difference in their respective crystal symmetry should result in different selection rules for the Raman process. The vibrational modes in 1T' phase can be reduced to $\Gamma = 12A_g + 6B_g + 6A_u + 12B_u$, where the A_g and B_g modes are Raman-active, whereas A_u and B_u are classified as Raman-inactive modes. Similarly, in the T_d phase, we can decompose the vibrational modes into $\Gamma = 12A_1 + 6A_2 + 6B_1 + 12B_2$, where all modes are Raman-active, but only A_1 and A_2 modes are observable in the back-scattering geometry. Additionally, Raman selection rules require that the A_g modes of the 1T' phase and A_1 modes of the T_d phase are observed in co-polarized (parallel) configuration, whereas the respective B_g and A_2 modes of the 1T' and T_d phase are observed in the cross-polarized configuration. We mathematically expand on this through Raman tensor calculation for all observed modes in the T' and T_d phase in the Supplementary information section at the end of this chapter.



Figure 4.2: (a) Height profile and (b) AFM image of the MoTe₂ flake on a Si/SiO₂ substrate. The black circle on the flake marks the location where all Raman spectra were acquired. The flake is over 100 nm thick, which corresponds to the bulk regime. (b) Raman spectra of T_d -MoTe₂ acquired a 5 K. The four peaks examined in this study are labeled along with the symmetry assignments.

We present in **Figure B.1**, typical Raman spectra of bulk MoTe₂ in the 1T' and T_d phase observed through temperature-dependent Raman measurements and label their respective mode symmetries. We observe four prominent peaks at $\approx 130 \text{ cm}^{-1}$, 165 cm⁻¹, 254 cm⁻¹, and 264 cm⁻¹, all with A_1 symmetry, that we refer to as Peaks 1-4, respectively. There is also a weak feature at 190 cm⁻¹ that has A_1 symmetry but does not have sufficient signal to resolve its temperature dependence. Under phase transition, the A_g and B_u modes of the 1T' phase become the A_1 or B_2 modes in the T_d phase, similarly, the B_g and A_u modes in the 1T' phase become the A_2 or B_1 modes in the T_d phase. We must reiterate here that selection rules for the back scattering geometry demands at only the A_g and B_g modes be visible in the 1T' phase. The observed vibrational modes highlighted in each spectrum, where in addition to peaks that are common among the two phase, we see several differences - emergence of a low-frequency mode at 13 cm⁻¹ and splitting of the 130 cm⁻¹ and 190 cm⁻¹ peaks in the T_d phase. This splitting is believed to be a result of inversion symmetry breaking in the T_d phase, whereas the new, low-frequency vibrations (sheer and breathing modes) appear due to changes in interlayer coupling and stacking order between the two phases. These results summarize the difference in the Raman signature of the two material phases. We must note here that while we can clearly point of the difference in the Raman modes for a 1T' and T_d phase in bulk-MoTe₂, measurements on few-layer samples remain much more challenging and ambiguous.

4.3.1 The curious case of $T' \rightleftharpoons T_d$ transition in few-layer MoTe₂

The intriguing nature of the phase dynamics between T' and T_d - MoTe₂ phase in thinner samples results from the reported discrepancies in phase transition temperatures for flakes with similar thickness, as well as inconsistent behavior in the Raman peaks in successive warming and cooling runs. In addition to the observation of T' and T_d phase at roomtemperature in few-layer samples (exfoliated from the same bulk crystal), existence of both phases within the same few-layer piece has also been reported. Moreover, splitting of the 130 cm⁻¹ mode shows inconsistent temperature-dependent behavior, where in some studies, the splitting occurs way before the transition temperature, while in other, the emergence of the shear mode at 13 cm⁻¹ does not directly correlate with the splitting of the 130 cm⁻¹ peak. There are also reports on observation of meta-stable phases between the 1T' and T_d phase, where the actual phase transition path seems to depend on a variety of factors, such as local strain or changes in doping levels across different samples. Further, there are reports that claim few-layer samples below ≈ 12 nm exist only in the T_d phase, owing to charge doping induced by layer-dependent quantum confinement effect. In contrary to this, reports on observation of 1T' phase in few-layer samples and CVD grown monolayers seem to suggest the effect of hole doping through air exposure. There are also report that claim to observe unreliable trends in temperature-dependent runs on samples with the same thickness, where an equal probability of successful and unsuccessful $T' \rightleftharpoons T_d$ transition were observed.

The ambiguity in these results can be fairly justified in terms of the difference between the energies of the stable 1T' and T_d phase, which is only of the order of few meV/unit cell. Since the only difference between the two phases involve a horizontal shift, only a small perturbation can cause a shift in the crystal structure. Not only that, transition from one phase to the other becomes even easier in few-layer samples as the energy difference further reduces and the effects of layers shifts are much more significant. Therefore, even a small amount of strain, possibly even during the exfoliation process can a transition to occur which can explain the varying layer-dependent Raman data reported by several studies. Since MoTe₂ is also believed to be sensitive to oxidation, encapsulation of fewlayer MoTe₂ has become a common practice, which only further complicates the strain dependent transition process. In any case, several markers, more importantly the presence of interlayer shear and breathing modes can be unique markers to detect any change in the stacking configuration under phase transition. We will for most of our discussion in this chapter, focus only on the vibrational properties of bulk-MoTe₂.

4.4 Temperature-dependent Raman measurements

We have carried out temperature-dependent measurements on a bulk T' - MoTe₂ flake in the temperature range of 5 K - 320 K. As we increase the sample temperature, all peaks soften although the magnitude of the red shift is different for each peak. In **Figure 4.3a** we present temperature-dependent Raman spectra for Peak 2 along with Lorentzian fits (black curves) and in **Figure 4.3b** we show similar data for Peaks 3 and 4. All spectra in **Figures 4.3a** and **4.3b** have been normalized by the intensity of Peak 2, which remains strong and narrow over the entire temperature range in this study. Peaks 3 and 4 exhibit markedly



Figure 4.3: Temperature dependent Raman measurements of (a) Peak 2 and (b) Peaks 3 and 4. Both spectra are fit to either a single or double Lorentzian function with a linear background. The sample temperature increases from 5 K (bottom) to 320 K (top). In both panels the spectra have been normalized by the intensity of Peak 2. (c) FWHM of Peaks 1(ref. FIG 1) and 2 extracted from fitting a single Lorentzian. (d) FWHM of the Peaks 3 and 4 extracted from the fit in (b). (e) FWHM of the Peaks 2, 3, and 4 versus temperature. Note that the amplitudes are approximately equal near 240 K, which corresponds to the phase transition from the $T_d \rightarrow T'$ phase.

different behavior. As the sample temperature increases, we find that these modes both red-shift and broaden substantially. We quantify these behaviors by fitting Peaks 3 and 4 to a double Lorentzian function plus a linear background, which allows us to extract the center frequency, relative amplitude, and linewidth of each mode. The amplitude of Peak 4 is greater than Peak 3 from 5 K to 240 K at which point they become approximately equal (Figure 4.3c). The linewidths of these two modes also evolves with temperature (Figure 4.3d). At 5 K, Peak 3 is narrower than Peak 4 ($\approx 4 \text{ cm}^{-1}$ versus $\approx 9 \text{ cm}^{-1}$), however the linewidth of Peak 3 steadily increases with temperature until the two modes have similar linewidths, which occurs again at ≈ 240 K. It is notable that observed changes in peak intensity and linewidth correlate well with the $T_d \rightarrow T'$ transition temperature [115,117,118,120,134] suggesting that the relative intensity and width of Peaks 3 and 4 are sensitive to the change in structural phase.

Before we plot the temperature-dependent mode shifts across the $T_d \to T'$ transition, let us dig a little deeper into the theoretical framework that explains the processes responsible for the softening of Raman peaks and relaxation of the phonon bandstructure.

4.4.1 Corrections to the phonon self-energy

An additional effect of external perturbations (such as temperature, pressure, strain, etc.) on the vibrational properties of crystalline solids can be understood via harmonic and anharmonic approximations of the phonon energy. Heat transfer in materials, especially in non-metals, is significantly guided by phonons with finite frequencies $\omega(\mathbf{q})$ and lifetimes $\Gamma(\mathbf{q})$, where \mathbf{q} is the quasi-momentum in the first BZ. At zero temperature, a harmonic or quasi-harmonic treatment leads to non-interacting phonons with infinite lifetime which then results into an infinite thermal conductivity of the material. At finite temperatures, this description no longer remains accurate as thermal properties of solids with infinite conductivity is rather inconceivable. In that regards, a more realistic representation of the changes in vibrational properties of atoms has to be considered, resulting from the anharmonic behaviour of phonons, including the phonon-phonon interaction.

4.4.2 Harmonic and Anharmonic approximations

We can present a canonical from of the total crystalline potential U [135], expanded about the equilibrium lattice configuration as,

$$U = U_{0} + \sum_{lk\alpha} \frac{\partial V}{\partial u_{\alpha}(l,k)} \bigg|_{0} u_{\alpha}(l,k) + \frac{1}{2!} \sum_{lk\alpha} \sum_{l'k'\beta} \frac{\partial^{2}V}{\partial u_{\alpha}(l,k)\partial u_{\beta}(l',k')} \bigg|_{0} u_{\alpha}(l,k)u_{\beta}(l',k') + \frac{1}{3!} \sum_{lk\alpha} \sum_{l'k'\beta} \sum_{l''k''\gamma} \frac{\partial^{3}V}{\partial u_{\alpha}(l,k)\partial u_{\beta}(l',k')\partial u_{\gamma}(l'',k'')} \bigg|_{0} u_{\alpha}(l,k)u_{\beta}(l',k')u_{\gamma}(l'',k'') + \dots$$

$$(4.1)$$

where l = 1,2,... N labels the unit cell, k labels each atom within the unit cell and α denotes the atomic position along the Cartesian coordinates (x,y,z) of each atom in the unit cell. The quantity $u_{\alpha}(l,k)$ determines the displacement vector of the atoms from its equilibrium position.

The first non-vanishing term in this expression is the quadratic term (3^{rd} term) since the first-order derivative (2^{nd} term) goes to zero under equilibrium conditions (minimizing the potential). The quadratic term therefore is associated with the harmonic representation of the potential energy which approximates the interaction between atoms and a significant chunk of the vibrational entropy at low-temperatures. The cubic and all higher orders terms then reflect the anharmonic contributions coming from the phonon scattering process, where a single phonon decays to form two other phonons or vice versa. Similarly, a fourth order process includes a phonon decay into three phonons or two phonons decaying into two new phonons. These additional anharmonic terms extend the description from the limits of zero-temperature harmonic theory to include many-phonon processes and explain thermodynamic properties of crystalline solids at finite temperatures. The renormalization of the non-interacting, harmonic potential by the interacting, anharmonic contribution is accounted in the phonon self-energy (SE) term, mathematically defined as S.E. = $\Delta(\omega_i(\mathbf{q}), T) + i\Gamma(\omega_i(\mathbf{q}), T)$. Here, the real part $\Delta(\omega_i(\mathbf{q}), T)$ determines the temperaturedependent behavior of the phonon frequencies, where as any changes in Raman lifetimes or mode widths are defined by the imaginary part $\Gamma(\omega_i(\mathbf{q}), T)$. We can therefore directly extract these quantities by fitting a Lorentzian to the temperature-dependent Raman data,



Figure 4.4: Anharmonic and quasi-harmonic processes such as (a) volumetric expansion of the lattice (b) mismatch in the thermal expansion coefficients between the substrate and flake (c) Electron-phonon interactions and (d) phonon decay processes where an optical phonon decays into multiple acoustic phonons. The contribution from these process can then be included to explain changes in frequencies and linewidths of phonons across a temperature range.

where the reciprocal of the full-width-half-max (FWHM) - $2\Gamma(\omega_i(\mathbf{q}), T)$ gives the total lifetime. A schematic of the third and fourth order phonon decay process is shown in Figure, where optical phonons (LO) decay into two or three acoustic phonons.

4.4.3 Quasi-anharmonic representation

We must also separately consider the effects of lattice expansion due to changes in temperature and pressure, which are not directly included in the crystalline potential but can be represented by the quasi-harmonic approximations which include two-phonon processes. Here, it is assumed that phonon frequencies depend on volume alone, and that the corrections to the harmonic phonon modes that comes from the thermal expansion of lattice itself. We can define the temperature and pressure-dependent volume $V_o(T, P)$ determined by the minimizing (with respect to volume) the Gibbs free energy, given by the equation,

$$G(T,P) = \min\left(F(T,V) + PV\right)\Big|_{v}$$

$$(4.2)$$

Here, the Helmholtz free energy F(T,V) can be further expressed as,

$$F(T,V) = E_o(V) + \sum_{q,i} \frac{\hbar\omega_i(\mathbf{q},V)}{2} + k_B T \sum_{q,i} \ln\left[1 - exp\left(-\frac{\hbar\omega_i(\mathbf{q},V)}{k_B T}\right)\right]$$
(4.3)

where the term $E_o(V)$ is the ground-state enthalpy of the system, while the second and third terms correspond to the zero-point and vibrational entropy of the system under thermal expansion. For temperature-dependent studies, we can ignore the second term in **Equation 4.2**, while focusing only on the third term in **Equation 4.3** to account for any changes in phonon S.E. due to lattice expansion. Moreover, for few-layer samples, differences in the magnitude and sign of thermal expansion coefficients between the material and substrate can further alter its vibrational entropy, renormalizing the S.E. at low-temperatures. In addition to anharmonic and quasi-anharmonic processes, electron-phonon interactions can also lead renormalization of phonon S.E., as electronic excitation couple directly to the lattice vibrations. We will share more insights on this in our next chapter where we discuss low-energy electronic phase transitions and its effects on vibrational properties in 2D TMDs, however, we neglect these interactions in this chapter assuming the largest anharmonic contribution comes from the phonon-phonon coupling process.

4.4.4 Corrections to phonon mode frequencies

We can now mathematically define the behavior of vibrational mode frequencies observed through temperature-dependent Raman measurements by including all the process discussed ahead, giving us,

$$\omega_i(\mathbf{q}=0,T) = \omega_{0,i}(0)_{harm} + \Delta(\omega_i(0),T)_{anh} + \Delta(\omega_i(0),T)_{therm} + \Delta(\omega_i(0),T)_{sub}$$

$$+ \Delta(\omega_i(0),T)_{e-ph}$$

$$(4.4)$$

Here, the terms $\omega_{0,i}(0)_{harm}$ gives the harmonic contributions at T = 0 K, $\Delta(\omega_i(0), T)_{anh}$ gives the anharmonic phonon-phonon decay probability, $\Delta(\omega_i(0), T)_{therm}$ describes the effects of quasi-harmonic thermal expansion, $\Delta(\omega_i(0), T)_{sub}$ includes any substrate interaction and lastly $\Delta(\omega_i(0), T)_{e-ph}$ accounts for electron-phonon interactions. For the sake of this study, we only consider the first, second and third terms. We can ignore the effects of substrate since our measurements are strictly limited to bulk samples, and we have also ignore the contribution from electron-phonon process assuming that the most prominent anharmonic contribution comes from phonon-phonon scattering processes. This gives us a reduced picture of the temperature-dependent phonon frequencies,

$$\omega_i(\mathbf{q}=0,T) = \omega_{0,i}(0)_{harm} + \Delta(\omega_i(0,T))_{anh} + \Delta(\omega_i(0,T))_{therm}$$
(4.5)

We can now expand each term and represent models that fit each description to the experimentally observed trends in Raman mode frequencies to obtain realistic parameter for anharmonic and quasi-anharmonic corrections. The anharmonic contribution from the phonon-phonon decay processes- $\Delta(\omega_i(0), T)_{anh}$ was formalized by Balkanski et. al. [136], and is given as,

$$\Delta(\omega_i(0), T) = \omega_0 + A\left(1 + \frac{2}{e^x - 1}\right) + B\left(1 + \frac{2}{e^y - 1} + \frac{3}{(e^y - 1)^2}\right)$$
(4.6)

where $x = \frac{\hbar\omega_B}{2k_BT}$ and $y = \frac{\hbar\omega_B}{3k_BT}$. The constants A(B) represent anharmonic contributions to the frequency that involve the decay of an optical phonon into two (three) acoustic phonons. At T = 0, $\omega(0) = \omega_B + A + B$, which implies A and B represent third and fourth order corrections to the phonon self energy. This model has been successfully applied to a variety of nanomaterials to explain nonlinear changes in optical phonon frequencies and linewidths [137–141]. The third term which accounts for the effect of volumetric thermal expansion to the mode frequencies - $\Delta(\omega_i(0), T)_{therm}$ can also be further expanded,

$$\Delta(\omega_i(0), T)_{therm} = \omega_{0,i}(0) \exp\left(-\gamma_i(0) \int_0^T \alpha(T) \, dT\right) - \omega_{0,i}(0) \tag{4.7}$$

where $\alpha(T)$ is the thermal expansion coefficient and γ_i is the Grüneisen parameter, individually described as

$$\alpha(T) = \frac{1}{V} \frac{dV}{dT} \tag{4.8}$$

$$\gamma_i(\mathbf{q}) = -\frac{V_o}{\omega_{0,i}(\mathbf{q})} \frac{d\omega_i(\mathbf{q})}{dV}$$
(4.9)

4.4.5 Temperature-dependent mode frequencies

The frequency of all examined Raman peaks softens with increasing temperature (**Figure 4.5**). Temperature-induced shifts in Raman frequencies are typically fit using the linear Grüneisen model [139, 142–144]:

$$\omega(T) = \omega_o + \chi T. \tag{4.10}$$

 $\omega(T)$ is the temperature-dependent phonon frequency, ω_o is the harmonic phonon frequency at T = 0 K, and χ is the first order temperature coefficient. The Grüneisen model combines the effects of thermal expansion and changes of the phonon self-energy into χ , and is sufficient when $kT \gg \hbar\omega/2 \approx 140$ K. At lower temperatures, $\omega(T)$ becomes nonlinear and can no longer be described by **Equation 4.10**. We illustrate this explicitly in **Figure 4.5** where the extracted phonon frequencies for Peaks 1-4 are plotted versus temperature. The dashed line is a fit of the data with to the Grüneisen model, which agrees well at high



Figure 4.5: Raman frequency versus temperature for (a) Peak 1, (b) Peak 2, (c) Peak 3, and (d) Peak 4. In each panel we fit the data to the Grüneisen model (dashed lines) in **Equation 4.10** and to the Balkanski model (solid lines) in **Equation 7.1**. Error bars correspond to the standard deviation of the fits to our data points.

temperatures but deviates significantly below 100 K. In this regime, thermal expansion makes a negligible contribution to the phonon frequency and instead changes in the phonon self-energy due to anharmonic coupling between different phonon branches are the dominant effect [141]. Theoretical work by Balkanski et al. demonstrated that the temperature dependence of optical phonons can be accounted for by including contributions from optical phonon decays into two or three acoustic phonons [136]. $\omega(T)$ in this formalism is now given

Peak	Ref.	$A(cm^{-1})$	$B(cm^{-1})$	$\omega_B(\mathrm{cm}^{-1})$	$\chi (\rm cm^{-1}/K)$	$\omega_o \ (\mathrm{cm}^{-1})$
1	this work	-0.528	0.016	131.31	-0.0066	130.80
2	this work	-0.903	0.025	167.57	-0.0098	166.94
3	this work	4.165	0.202	259.48	-0.0287	257.21
4	this work	-2.706	0.172	266.95	-0.0171	265.34
MoS_2		-5.687	0.265	-	-0.019	-
	Ref.41	-0.078	-0.04	179.6	-0.01180	-
	Ref.41	-0.41	-0.03	188.84	-0.0129	-

Table 4.1: Measured values of A, B, ω_B , χ , and ω_o , for Peaks 1-4. We also include extracted values of A and B from prior studies of MoS₂, and are included for comparison.

by Equation 7.1. This model has been successfully applied to a variety of nanomaterials to explain nonlinear changes in optical phonon frequencies and linewidths [137–141]. We fit the phonon frequencies of Peaks 1 - 4 (Figures 4.5a - 4.5d) to Equation 7.1 over the entire temperature range. The extracted values of A, B, ω_B , χ , and ω_o are summarized in Table 4.1. We find that Peaks 3 and 4 have much larger A and B parameters compared to Peak 2, suggesting that anharmonic contributions are especially important for these modes. For all three Raman modes A is over an order of magnitude larger than B indicating the decay to two acoustic phonons (third order correction) is the dominant relaxation pathway.

We interpret the difference in behavior between Peak 2 and the higher frequency Peaks 3 and 4 modes to the sensitivity of their atomic displacements to interlayer coupling. As T' transitions to the T_d phase, the *a*, *b*, and *c* lattice parameters decrease by 0.23%, 0.08%, and 0.21%, respectively, which implies the dominant changes are in the directions of the *a* lattice vector and the out of plane *c* lattice vector [115]. Furthermore, the angle between the *b* and *c* lattice vectors also changes from 90 in T' to 93.917 in T_d [115]. These combined structural changes imply phonon modes that are sensitive to interlayer coupling will be most affected by the T' \rightarrow T_d transition. Peak 2 depends only weakly on the number of layers [113] and therefore it is expected to respond minimally to changes in layer alignment and separation. In contrast, Peaks 3 and 4 are highly sensitive to the number of layers [113] and therefore it is reasonable expect that are more sensitive to changes in the spacing and alignment of the layers in the bulk crystal. This is consistent with our observation of larger A and B parameters for Peaks 3 and 4.

4.5 Conclusion

This study was the first ever performed on anharmonic phonon effects in bulk T_d -MoTe₂ for the four most prominent optical phonon modes. Changes in phonon frequency, linewidth, and amplitude are determined and the results correlate well with the $T_d \rightarrow T'$ structural phase transition. $\omega(T)$ is nonlinear, which implies that the dominant contribution originates from the decay of optical phonons into multiple acoustic phonons. Furthermore, we find that modes known to depend sensitively on the number of layers also vary most strongly with temperature as the T_d transitions to T' around ≈ 240 K. This is due to the primary effect of the transition being a change in interlayer separation and alignment. These results highlight the important role of phonon-phonon interactions in T_d - MoTe₂, and an examination of how anharmonic effects in T_d - MoTe₂ vary with the number of layers will give valuable insight regarding the origin and strength of the interlayer coupling.

4.6 Supporting Information

The Raman tensors for the A_g and B_g mode in the 1T' phase can be formulated as

$$R(A_{g}) = \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & |d| \ e^{i\Phi_{d}} \\ 0 & |b| \ e^{i\Phi_{b}} & 0 \\ |d| \ e^{i\Phi_{d}} & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \text{ and } R(B_{g}) = \begin{pmatrix} 0 & |e| \ e^{i\Phi_{e}} & 0 \\ |e| \ e^{i\Phi_{e}} & 0 & |f| \ e^{i\Phi_{f}} \\ 0 & |f| \ e^{i\Phi_{f}} & 0 \end{pmatrix}$$
(4.11)

Considering the case of back-scattering geometry (typical Raman setups are designed for back-scattered collection), the Raman intensity in co-polarized (parallel) configuration can be given by,

$$\mathbf{I}(\mathbf{A}_{\mathbf{g}}) \propto \left(\cos\theta \quad \sin\theta \quad 0 \right) \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & |d| \ e^{i\Phi_{d}} \\ 0 & |b| \ e^{i\Phi_{b}} & 0 \\ |d| \ e^{i\Phi_{d}} & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2}$$
(4.12)

$$\propto |a|^2 \cos^4 \theta + |b|^2 \sin^4 \theta + \frac{|a||b|}{2} \cos(\Phi_a - \Phi_b) \sin^2 (2\theta),$$

$$I(B_{g}) \propto \left| \begin{pmatrix} \cos\theta & \sin\theta & 0 \end{pmatrix} \begin{pmatrix} 0 & |e| e^{i\Phi_{e}} & 0 \\ |e| e^{i\Phi_{e}} & 0 & |f| e^{i\Phi_{f}} \\ 0 & |f| e^{i\Phi_{f}} & 0 \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2}$$
(4.13)
$$\propto |e|^{2} \sin^{2} (2\theta)$$

Similarly in the cross-polarized (perpendicular) configuration, we have,

$$\begin{split} I(A_{g}) \propto \left| \begin{pmatrix} -\sin\theta & \cos\theta & 0 \end{pmatrix} \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & |d| \ e^{i\Phi_{d}} \\ 0 & |b| \ e^{i\Phi_{b}} & 0 \\ |d| \ e^{i\Phi_{d}} & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2} \tag{4.14} \\ \propto \frac{|a|^{2} + |b|^{2} - 2|a||b| \cos(\Phi_{a} - \Phi_{b})}{4} \sin^{2}(2\theta) \\ I(B_{g}) \propto \left| \begin{pmatrix} -\sin\theta & \cos\theta & 0 \end{pmatrix} \begin{pmatrix} 0 & |e| \ e^{i\Phi_{e}} & 0 \\ |e| \ e^{i\Phi_{e}} & 0 & |f| \ e^{i\Phi_{f}} \\ 0 & |f| \ e^{i\Phi_{f}} & 0 \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2} \tag{4.15} \\ \propto |e|^{2} \cos^{2}(2\theta) \end{split}$$

From the above equations, we can see that modes with \mathbf{A}_g symmetry are observed only in

the parallel (co-polarized) configuration while the modes with B_g symmetry are observable only in the perpendicular (cross-polarized) configuration.

We can do a similar analysis in for the bulk T_d -MoTe₂ phase, which has C_{2v} point group. Considering back-scattering geometry, the Raman tensors for the visible A_1 and A_2 mode in the T_d phase can be formulated as

$$R(A_{1}) = \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & 0\\ 0 & |b| \ e^{i\Phi_{b}} & 0\\ 0 & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \text{ and } R(A_{2}) = \begin{pmatrix} 0 & |e| \ e^{i\Phi_{e}} & 0\\ |e| \ e^{i\Phi_{e}} & 0 & 0\\ 0 & 0 & 0 \end{pmatrix}$$
(4.16)

In the back-scattering geometry, the Raman intensity in co-polarized (parallel) configuration can be given by,

$$I(A_{1}) \propto \left| \begin{pmatrix} \cos\theta & \sin\theta & 0 \end{pmatrix} \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & 0 \\ 0 & |b| \ e^{i\Phi_{b}} & 0 \\ 0 & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2}$$
(4.17)

 $\propto |a|^2 \cos^4 \theta + |b|^2 \sin^4 \theta + \frac{|a||b|}{2} \cos(\Phi_a - \Phi_b) \sin^2 (2\theta),$

$$I(A_2) \propto \left| \begin{pmatrix} \cos\theta & \sin\theta & 0 \end{pmatrix} \begin{pmatrix} 0 & |e| e^{i\Phi_e} & 0 \\ |e| e^{i\Phi_e} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^2$$
(4.18)
$$\propto |e|^2 \sin^2 (2\theta)$$

Similarly in the cross-polarized (perpendicular) configuration, we have,

$$I(A_{1}) \propto \left| \begin{pmatrix} -\sin\theta & \cos\theta & 0 \end{pmatrix} \begin{pmatrix} |a| \ e^{i\Phi_{a}} & 0 & 0 \\ 0 & |b| \ e^{i\Phi_{b}} & 0 \\ 0 & 0 & |c| \ e^{i\Phi_{c}} \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2}$$
(4.19)
$$\propto \frac{|a|^{2} + |b|^{2} - 2|a||b| \cos(\Phi_{a} - \Phi_{b})}{4} \sin^{2}(2\theta)$$
$$I(A_{2}) \propto \left| \begin{pmatrix} -\sin\theta & \cos\theta & 0 \end{pmatrix} \begin{pmatrix} 0 & |e| \ e^{i\Phi_{e}} & 0 \\ |e| \ e^{i\Phi_{e}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix} \right|^{2}$$
(4.20)
$$\propto |e|^{2} \cos^{2}(2\theta)$$

From the above equations, we can see that only the modes with A_1 symmetry are observed in the parallel (co-polarized) configuration while the modes with A_2 symmetry are observable only in the perpendicular (cross-polarized) configuration. B_1 and B_2 modes are forbidden in back-scattering geometry.

Chapter 5: Project Phi (Φ) - Charge Density Waves in 2D TMDs

5.1 Introduction

The lowest energy state of an interacting system can become energetically unfavorable by minimizing its free energy. This usually results into breaking of some symmetry, provided that the new configuration has a reduced ground state energy. Fröhlich [145] and Peierls [146] discussed this possibility in a linear, one-dimensional (1D) chain of atoms spaced with uniform periodicity as shown in Figure 5.1a. They proposed that this configuration is energetically unfavourable at low-temperatures, as possibilities to reduce its free energy emerge through distortions in the lattice as well as by modulating the electron density across the 1D chain. In this case, a new stable configuration can occur as long as the energy lost/or spent in distorting the lattice ($\Delta E_{lattice}$) is less than the energy gained from modulating the charge density ($\Delta E_{electron}$), i.e. $\Delta E_{lattice} + \Delta E_{electron} < 0$. The resulting phase as shown in Figure 5.1c has a broken lattice translational symmetry and a periodically modulated electronic distribution. This is described as a charge density wave (CDW) phase, and has been experimentally observed in a variety of 1D, quasi-1D and 2D systems, including TMDs [53,146-152]. It is also sometimes referred to as Peierls instability. The next section is aimed at introducing the background for CDW formation and the phenomena associated to this ordered state on the electronic structure of a compound, particularly 2D TMDs.

5.2 CDW formation: Theoretical background

This section is intended to give a brief theoretical background on the origin and formation of CDW in 1D, quasi-1D and 2D systems. We shall go over some of the more common



Figure 5.1: (a) A 1D periodic chain of non-interacting atoms with uniform charge density represented as a 1D free-electron gas and (b) its expected energy-dispersion. This state is energetically unfavourable below a certain critical temperature T_c (c) A Peierls-like distortion of the 1D lattice modulated the electronic density ($\rho(x)$) with a certain periodicity. This is commonly referred to as a charge density wave (CDW). (d) This opens up a bandgap at the wavevector defined by the reciprocal vector in the CDW Brillouin Zone (BZ) separating the completely filled states from the empty bands.

and extensively discussed mechanisms that are believed to be responsible (or markers) for this instability, however a detailed account, primarily focused on heavy theoretical machinery can be found in Ref. [153]. We will begin with a simple case of Peierls instability.

5.2.1 Peierls transition

In the special case discussed in **Figure 5.1**, the lattice periodicity in the CDW phase is twice as that in the normal phase, which reduces the Brillouin Zone (BZ) from $-\frac{\pi}{a} < k < \frac{\pi}{a}$ to half of its size: $-\frac{\pi}{2a} < k < \frac{\pi}{2a}$. As a result, the half-filled bands in the normal phase fold at the CDW wavevector $q_{CDW} = 2k_F$, creating a completely filled and an empty band separated by a band-gap at the CDW-BZ edge. The opening of a band-gap results in a gain in the electronic energy $\Delta E_{electron}$ where for small lattice distortions δ , $\Delta E_{electron}$ scales as $\delta^2 \ln(\delta)$ [154, 155]. Similarly, the energy lost/spent in distorting the lattice its otherwise equilibrium configuration, $\Delta E_{lattice}$, scales as δ^2 [154, 155]. The resulting ionic/atomic positions can be simply written in terms of δ as,

$$u(x) = u_o + \delta \cos(Q \cdot x + \phi(x)) = u_o + \delta \cos(2k_F \cdot x + \phi(x))$$
(5.1)

where $\phi(x)$ is the local phase of the CDW wave with respect to the lattice and $Q = 2k_F$ is the CDW wavevector defined by the new BZ. Similarly, the electron density can be written as

$$\rho(x) = \rho_o + \rho_1 \cos(2k_F \cdot x + \phi(x)) \tag{5.2}$$

5.2.2 Fermi surface nesting (FSN)

In reduced dimensions, especially 1D systems, the effects of many-body interactions, localized potentials and quantum fluctuations are more profound than in higher phase spaces. For a 1D electron gas as discussed above, the Fermi surface (FS) consists of only two points at $\pm k_F$, and the response of a such an FS to a potential perturbation can be dramatically different than in the 2D case (free electron gas) where the FS is a circle, or in case of 3D systems where it is a sphere. In terms of linear response theory, we can consider a timeindependent potential $V(\vec{q})$ acting on this 1D electron gas, such that the change in electron density $\rho(\vec{q})$ can be given as,

$$\rho(\vec{q}) = \chi(\vec{q})V(\vec{q}) \tag{5.3}$$

where $\chi(\vec{q})$ is the Lindhard response function (also referred to as electronic susceptibility) and is given by [156],

$$\chi(\vec{q}) = \int \frac{d\vec{k}}{2\pi^d} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}}$$
(5.4)

Here, $f_k = f(\epsilon_k)$ is the Fermi distribution function and d is the dimension of the system. For a 1D electron gas at zero temperature, **Equation 5.4** can be simplified to [156, 157],

$$\chi(\vec{q}) = e^2 N(\epsilon_F) \ln \left| \frac{q + 2k_F}{q - 2k_F} \right|$$
(5.5)



Figure 5.2: (a) Behavior of the Lindhard susceptibility $(\chi(q))$ for a free electron gas in 1D, 2D and 3D. The logarithmic divergence for the 1D case becomes a discontinuity for 2D and a continuous transition in the 3D case. Illustration of Fermi surface nesting (FSN) in 1D, 2D and 3D for a free-electron gas showing that in simpler Fermi surfaces (FS), q_{cdw} can map parallel sides of the FS, and ultimately drive the lattice instability as well as the divergence in $\chi(q)$. This may not be true for complex structures.

where $N(\epsilon_F)$ is the density of states are Fermi level. Figure 5.2 shows $\chi(\vec{q})$ plotted as a function of all-q for 1D, 2D and 3D systems where we see divergent behavior of the response function at $q = 2k_F$ in the 1D case, while in 2D a discontinuous first-order derivative at $q = 2k_F$ is seen. In 3D systems, the function (and its first derivative) is continuous
everywhere, showing a dramatic dependence on the dimension of the system in the behavior of $\chi(\vec{q})$. This behavior can also be described in terms of the topology of the FS and whether a single wavevector $q = 2k_F$ pairs all points on either sides of the FS. This phenomena is called Fermi surface nesting and is often considered to be responsible for the origin of CDWs. However, in 3D materials where the FS topology can take up all kinds of weird shapes, presence of a one-to-one nesting vector ($q = 2k_F$) that maps all points between parallel sides of the FS may not be conceivable, while many materials, especially TMDs show CDW transitions without the presence of accurate nesting vectors [149, 158]. This leads us to our next section where we discuss the implications of many-body interactions, especially electron-phonon coupling in the origin of CDWs.

5.2.3 Electron-phonon coupling

Considering that a CDW transitions modulated both the electron density as well as the lattice periodicity, let us formulate a Hamiltonian that includes a term corresponding to electron-lattice coupling, in addition to the Hamiltonians that describe the electron and lattice contributions independently. This can be written as,

$$H = H_{ele} + H_{pho} + H_{ele-pho} \tag{5.6}$$

where the first term H_{el} describes the Hamiltonian of an unperturbed electron gas, the second term describes the Hamiltonian of normal lattice mode vibrations and the last term, represents the electron-phonon interaction. We can expand each term as given by the Frohlich Hamiltonian [145],

$$H = \sum_{k} \epsilon_k a_k^{\dagger} a_k + \sum_{q} \hbar \omega_q b_q^{\dagger} b_q + \sum_{k,q} g_q a_{k+q}^{\dagger} a_k (b_- q^{\dagger} + b_q)$$
(5.7)

Here, a_k^{\dagger} and a_k are the electron creating and annihilation operators respectively and ϵ_k is the energy of the electron state in the first term. In the second term, b_q^{\dagger} and b_q are the phonon creation and annihilation operators characterized by wavevector q, and ω_q represents the harmonic mode frequencies of the ions/atoms. And finally, g_q is the electron-phonon coupling constant in the third term. The CDW instability for a coupled electron-phonon system, has consequence both for the lattice and the electron density. This should result in changes in the material electronic properties as well as a renormalization of the phonon



Figure 5.3: (a) Behavior of the renormalized phonon frequency near the CDW wavevector $(q_{cdw} = 2k_F)$ for temperature approaching the phase transition regime T_{cdw} as well as far from it. We see singularity at q_{cdw} for $T = T_{cdw}$, which is commonly referred to as a Kohn anomaly. (b) The temperature-dependence of the CDW order parameter as described by the Bardeen Cooper Schrieffer (BCS) theory under the mean-field formalism.

vibrational frequencies. Using the total Hamiltonian, we can directly establish the equation of motion of the normal coordinates Q that includes the renormalized phonon frequency, given as,

$$\ddot{Q}_q = -\left[\omega_{ren,q}^2 + \frac{2g^2\omega_g}{M\hbar}\chi(q,T)\right]Q_q$$
(5.8)

where the renormalized phonon frequency $\omega_{ren,q}^2$ can be expanded as,

$$\omega_{ren,q}^2 = \omega_q^2 - \frac{2g^2\omega_q}{\hbar}\chi(q,T)$$
(5.9)

Since in the case of 1D electron gas, the Lindhard susceptibility $\chi(q, T)$ diverges (maximizes) at $q = 2k_F$, we except the renormalized frequency to reduce or soften at the same wavevector, $q = 2k_F = q_{cdw}$. This momentum - dependent softening in the phonon dispersion at the CDW wavevector is referred to as Kohn Anomaly and can be seen as a dip (negative phonon frequencies) in bandstructure calculations. We can rewrite the renormalized frequency at $q = 2k_F$ as [153]

$$\omega_{ren,q}^2 = \omega_{2k_F}^2 - \frac{2g^2 n(\epsilon_F)\omega_{2k_F}}{\hbar} \ln \frac{1.14\epsilon_0}{k_B T}$$
(5.10)

The above equation suggests that as the temperature is reduced, $\omega_{ren,q}$ should soften to zero. The temperature at which $\omega_{ren,q} = 0$ is the CDW transition temperature, which in the mean-field approximation is given by [153],

$$T_c^{MF} = \frac{1.14}{k_B} \epsilon_0 \, e^{-1/\lambda},\tag{5.11}$$

where $\lambda = 2g^2 n(\epsilon_F)/\omega_{2k_F}\hbar$ is the dimensional electron-phonon coupling constant and describe the probability of scattering of an electron by absorbing/emitting a phonon of wavevector $\pm q$ respectively. Additionally, since λ is momentum-dependent, strong or weak coupling close to the CDW-wavevector can further add to the origin of CDW phase transitions in electron-correlated systems. The above equation is also the expression for the mean-field transition temperature for BCS superconductivity. Charge density waves can be described within a BCS framework in which electron-hole pairing is considered instead of electron-electron paring. In addition to **Equation 5.10**, other relevant BCS expressions include $2\Delta = 3.52k_BT_c^{MF}$ relating the mean-field transition temperature to the order parameter Δ . The temperature dependence of the order parameter can be calculated numerically and is shown in **Figure 5.10b**.

5.2.4 Types of CDW orders

From the above description of electron-phonon interactions, we can closely link distortions in the lattice to modulation of the electronic density close to ionic positions and define the CDW to be either commensurate or incommensurate. For a commensurate CDW (CCDW), the ratio of the linear combination of crystal lattice vectors to the CDW lattice vectors is a rational number [159, 160], while this condition is not met for an incommensurate (ICCDW) system. In other words, if we can define a long-range wavelength for electronic density wave, as λ , and the lattice periodicity as a, then a commensurate system guarantees $\lambda/a = n$, where n is an integer. A CCDW is also often associated with an elastic instability, as the relationship with the atomic wavevectors is strong, while an incommensurate one is classically associated with an electronic instability, as the nesting vector is in principle completely unrelated with the symmetry of the crystal. Also, as discussed earlier, for a system to undergo a CDW transition, energetically favorable conditions must arise, where a CDW wavevector, or its wavelength $\lambda = 2\pi/2k_F$ is greatly preferred over an incommensurate superstructure. Therefore, in a weakly-coupled ICCDW, relaxation of the strain due to a mismatch between the charge and atomic registry does often lead to short-range commensurate charge order across smaller domains, whereas the long-range order still largely remains incommensurate. We make a case for this from our measurements on 2H-TaS₂, which undergoes an ICCDW transition.

A peculiar property of Ta-based TMDs is the David-star cluster formation in the commensurate electronic phase, for e.g. in $1T-TaSe_2$ [161] and $1T-TaS_2$ [162, 163]. This is shown in **Figure 5.4b,c** for the case of TaS₂, where we see a star formation of 12 Ta atoms surrounding and approaching a 13^{th} Ta atom in the center. We also show the presence of short-range commensurate domains as it transitions from the ICCDW to the CCDW phase. (a) (b) $\lambda = na$ CCDW R_{i} R_{CDW} 00 00 а λ $\lambda \neq na$ ICCDW R_{Λ} R_{CDW} 00 $\mathbf{0}\mathbf{0}$ $\mathbf{0}$ **⊙⊙** 00 а (c)

It is also important to point out that both TaSe₂ and TaSe₂ undergo a $\sqrt{13}a \times \sqrt{13}b$ CCDW

Figure 5.4: (a) A 1D periodic chain of non-interacting atoms in the CCDW (top) and ICCDW (bottom) phase, along with the comparison of their BZ reciprocal lattice vectors (r.l.c), where R_N and R_{CDW} are the r.l.c is the normal and CDW phase respectively. (b) The top view of the $\sqrt{13} \times \sqrt{13}$ TaS₂ crystal structure showing a David-star formation, where 12 Ta atoms within the layer move toward a 13th central Ta atom. (c) Schematic of network of Ta atoms in the CCDW (left), Nearly-CCDW (middle), and ICCDW (right) phases. The dark blue spheres represent the Ta atoms displaced from their undistorted positions, forming the David-star clusters (shown in red).

Nearly - CCDW

CCDW

ICCDW

transition, which from its nomenclature, can be misunderstood as an incommensurate phase.

However, in both cases, the apparently irrationality in the q_x and q_y components comes from the misorientation of the lattice. On the other hand, 2H-TaS₂, undergoes a $\sqrt{3}a \times \sqrt{3}b$ CCDW transition, where the incommensurability comes from the mismatch between the reciprocal lattice in the CDW and the normal phase.

5.3 Collective excitations of the order parameter

Collective excitations of the CDW mode can be described as position and time-dependent order parameter $\Delta(x, t)$, where its complex nature contains both the amplitude and phase fluctuations. This can be described as $\Delta(x, t) = \delta e^{i\phi}$, where δ and ϕ are the amplitude and



Figure 5.5: (a) Amplitude and Phase fluctuations of the CDW modes that makes up the complex CDW-order parameter. These collective excitations have their own Raman signatures in the form of Amplitude and Phase modes. The former are Raman active, while the later are inactive. However, phasons can become active through inversion symmetry breaking in the CDW phase, which typically requires a phase transition.

phase order-parameter respectively [164]. The electron-phonon interactions in the CDW phase modify the acoustic phonons close to the CDW-BZ edge into pairs of optical and

acoustic modes. These become the amplitude and phase modes, also referred to as amplitudons or phasons. Here, the phase fluctuations (or phasons) involve displacement of electronic condensate relative to the translation of ions/atoms creating a dipole moment. The resulting collective modes are therefore Raman inactive but can become active through breaking of inversion symmetry. This is typically achieved through a complete structural phase transition in the low-temperature CDW regime, as seen in 2H-TaSe₂. Amplitude fluctuations represent changes in the amplitude of the electronic density unrelated to the ionic displacements (and hence no dipole moment), that makes amplitudons Raman active. These are shown in **Figure 5.5**.

5.4 CDW transitions in TMDs

Group V transition metal dichalcogenides (TMDs) belong to a broad class of twodimensional (2D) materials that exhibit CDWs and superconductivity. CDWs are periodic modulations of the electron densities, accompanied by a simultaneous distortion of the crystal lattice where the relative periodicity is governed by the location of the CDW gap in the Brillouin zone. The CDW phase can be incommensurate, nearly commensurate, or commensurate with the underlying lattice which governs the relative mismatch between lattice periodicity and charge modulation. In 2D and quasi-2D systems, strong electron-phonon interactions at low temperatures drive the CDW transition [151,165–167] as opposed to other mechanisms such as Fermi surface nesting [149, 158] exciton-phonon interactions [168–170] and saddle-points near Fermi energy (E_F) [53]. Moreover, recent observations of opposite trends in layer-dependent CDW and superconducting transition temperatures for 2H - $NbSe_2$ [171] and 2H - TaS₂ [172–174] have prompted new questions regarding the CDWs in 2D materials. In addition, the electronic phase diagram of layered CDW materials is highly dependent on the polymorph. TaS_2 serves as an ideal example: $1T - TaS_2$ exhibits transitions between incommensurate, nearly-commensurate, and commensurate CDW phases whereas 2H - TaS_2 only has a single transition from a conventional metallic phase to an incommensurate CDW phase [175]. The more exotic 3R and 2Hb - TaS_2 [176] structural phases reveal additional complexity and illustrate the incredible diversity in the CDW order parameter even with identical chemical composition.

5.5 CDW order in 2H-TaS₂

In this study we explore the incommensurate CDW state in bulk $2H - TaS_2$ which appears below $T_{CDW} \sim 75$ K. While prior examinations of this material focused on CDWs with electrical and structural techniques [172, 177–181] only two studies of CDW phonon modes and their associated temperature-dependence have been reported: One performed nearly four decades ago [182] and a second recent work that focused on the superconducting Higgs mode [183]. By combining temperature and excitation-dependent Raman spectroscopy, DFT calculations, and ARPES data we obtain new insights regarding the nature of the 2H - TaS₂ CDW phase transition. Temperature-dependent DFT calculations of the phonon band structure also indicate the appearance of a lattice instability at 280 K which further validates our interpretation. These results shed new light on layered CDW systems and provide the first correlated experimental-theoretical study of the 2H - TaS₂ system. We anticipate this work will spur further investigations into the intriguing features of CDW phase transitions in various TMDs and find relevance in future efforts to incorporate CDW materials in non-volatile memory technology [184–187].

5.5.1 2H - TaS₂ - Growth, exfoliation and measurement setups

2H - TaS₂ single crystals were grown by chemical vapor transport (CVT) using iodine as the transport gas. Energy-dispersive X-ray spectroscopy (EDX) scans reveal 66 ± 2 % Sulphur to Tantalum composition confirming their 2:1 stoichiometric ratio. Bulk flakes were mechanically exfoliated from these crystals using a low-tack blue semiconductor tape and transferred onto a Si/SiO₂ substrate (285 nm oxide) in air within 1 hour. These bulk samples were subsequently capped with HBN to prevent any further degradation of the sample overtime. High-resolution, polarized Raman measurements were performed from 4 K - 90 K in a back-scattering configuration. The excitation laser was at 476 nm and was focused through a 50 \times objective with 0.82 NA to achieve a 300 nm spot size on the sample. The laser power was $\sim 100 \ \mu W$ before the objective. Scattered light was collected from the sample and directed towards a triple-grating spectrometer with a liquid-N2 cooled Si-CCD detector. To perform polarization dependent measurements, we kept the excitation polarization constant and used a linear polarizer to select the parallel or cross polarization with a half wave plate to rotate the light to the polarization with higher efficiency in the triple grating spectrometer. All spectra are taken in the parallel polarization configuration unless otherwise specified. Raman spectra were taken at 4 K using 458 nm (2.7 eV), 476 nm (2.6 eV), 514 nm (2.41 eV), and 633 nm (1.95 eV) laser lines keeping the power, polarization, and setup constant. The high temperature Raman measurements (90 K- 300 K) were carried out on a home-built confocal microscope setup with 532 nm laser excitation (2 m spot size; 1 mW laser power pre-objective), focused through a 0.5 NA, $50 \times$ long working distance objective. The samples in both setups were kept under an inert environment between measurements. The ARPES measurements were conducted using the 21.2 eV He I line of a discharge lamp combined with a Scienta R3000 analyzer at the University of Virginia. The angular resolution is 0.3° , and the total energy resolution is 8-10 meV. For temperaturedependent studies, ARPES data were collected in a cyclic way to ensure that there were no aging effects in the spectra. All experiments were performed in an ultrahigh vacuum (better than $5 \times 10-11$ Torr).

5.5.2 DFT approach

DFT calculations were carried out using the QUANTUM ESPRESSO (QE) package [188]. The exchange-correlation interaction was described by the local density approximations (LDA) using the Perdew-Wang parametrization of the correlation energy [189]. We used the norm-conserving pseudo-potential [190] and the van der Waals density functional (vdW-DF) method to capture experimental non-local correlations [191]. This combination of exchange-correlation, pseudo-potential and van der Waals correction was chosen as it gave an equilibrium lattice constant in excellent agreement with available experimental data at room temperature (DFT: a = 0.338 nm, c = 1.220 nm, Exp: a = 0.334 nm, c = 1.217 nm) [192]. The kinetic energy cutoff of the plane-wave expansion is taken as 50 Ry. All the geometric structures are fully relaxed until the force on each atom is less than $0.002 \text{ eV}/\text{\AA}$, and the energy-convergence criterion is 1×10 -6 eV. For the unit cell and supercell structure relaxation, we used a $16 \times 16 \times 16$ and $3 \times 3 \times 8$ k-point grid, respectively. Phonon calculations, we used a $4 \times 4 \times 4$ uniform q-grid for unit cell and for the supercell we did only gamma point phonon calculation. While the DFT calculations were performed at 0 K, we modeled the temperature effects behind the formation of the CDW states by varying the electronic temperature, i.e. tuning the smearing factor σ , which describes the Fermi-Dirac distribution. This methodology has been introduced by Refs. [150,153,193–196] and allowed us to qualitatively assess the effect of temperature on the phonon properties of the system. To validate this approach, we computed the lattice parameters at different temperatures for the unit cell and compared it with available experimental results [192]. We found that our predicted lattice constant along the c axis is good agreement with experimental results. No experimental data are available for the dependence of lattice constant a on temperature. A $3 \times 3 \times 1$ supercell was used to investigate the CDW structural transition, to allow for atomic rearrangement, if needed. As it has been experimentally shown that 2H-TaS₂ only CDW phase is incommensurate, we applied a perturbation along the c axis in the form of small compressive stress to computationally model incommensurability using a relatively small cell $(3 \times 3 \times 1)$. This approach was first proposed by Ref. [197].

5.5.3 Raman measurements on bulk 2H - TaS_2 in the Normal phase

Comparison of room temperature and low temperature Raman spectra reveal significant changes originating from the CDW transition. In **Figure 5.6b**, we present 300 K Raman data for 2H - TaS₂ in the normal state (the state at temperatures above T_{CDW}) that was acquired with 532 nm excitation. Four prominent optical phonon modes are observed at 26 cm⁻¹ (E_{2g}), 245 cm⁻¹ (E_{1g}), 290 cm⁻¹ (E_{2g}) and 404 cm⁻¹ (A_{1g}) in agreement with prior studies [181,182]. The two-phonon feature at 180 cm⁻¹ arises from second-order scattering of acoustic and quasi-acoustic modes near the CDW wavevector $q_{CDW} \approx 2/3$ ГM and is commonly observed in other Group V TMDs [81,197–199]. The data in Figure 1(b) can be fit (red curve) using a combination of eight Voigt functions. Two of these Voigt functions are used to account for the Rayleigh background and unassigned spectral weight in the



Figure 5.6: (a) The 2H hexagonal lattice structure of TaS_2 along with a White light image of a bulk TaS_2 flake capped with an insulating layer of hexagonal boron nitride (HBN). (b) Room-temperature Raman spectra of bulk TaS_2 with observed modes and their assignments. The two-phonon mode is shaded brown. Purple and golden shades represent modes with E and A symmetry respectively. Grey areas represent fits to the laser Rayleigh line and other features not predicted to be part of the material's Raman spectrum. Mode displacement for all one-phonon Raman scattering processes included as insets near each mode. Mode displacement diagrams corresponding to modes in the normal and CDW phase are included next to the Raman peaks. (c) Comparison spectra of the measured Raman intensity on bulk flakes with different optical contrast. Our measurements reveal that intensity is function of optical contrast, where flakes colored pink or red have significantly better Raman signal than green colored flakes.

 350 cm^{-1} spectral region. Raman mode symmetry is determined by polarization-resolved measurements and is in agreement with prior studies on 2H - TaS₂ [182,183,200,201]. E and A symmetry modes are shaded in purple and gold, respectively. DFT calculations of the Raman data using the standard 2H - TaS₂ supercell structure reproduce mode frequencies within 15 cm⁻¹ of experimental data and faithfully reproduce the mode symmetries.

5.5.4 Raman measurements on bulk 2H - TaS_2 in the CDW phase

The Raman spectra of 2H - TaS_2 is substantially modified when cooled below T_{CDW} . In Figure 5.7 we present 4 K Raman spectra in the CDW state taken with four different excitation wavelengths. These measurements were performed using a different cryostat that provides access to multiple laser lines used for resonance Raman studies: 458 nm (2.7 eV), 476 nm (2.6 eV), 514 nm (2.14 eV) and 633 nm (1.95 eV). The spectra in Figure 5.7 are normalized by the intensity of the A_{1g} mode at 404 cm⁻¹ to ease comparison. The most obvious change in the data is the appearance of new sharp modes at 48 cm⁻¹ (E_{amp}) and 78 cm⁻¹ (A_{amp}) in all spectra as well as a weak feature at ~ 100 cm⁻¹ that appears when exciting with 476 nm and 514 nm light. Polarization-dependent measurements of the 48 cm⁻¹ and 78 cm⁻¹ modes are included next to the Raman plots **Figure 5.7** and indicate the modes are of E and A symmetry. These new features at low wavenumber are clearly associated with the CDW state and are consistent with observations in Group V TMDs [202–204] and are usually referred to as amplitude modes since they modulate the magnitude of the CDW rather than its phase [182, 183, 201] Lack of inversion symmetry breaking in the incommensurate CDW state of bulk 2H - TaS_2 prevents the observation of phase modes by Raman scattering. The 100 cm^{-1} mode is too weak to be clearly resolved in polarization-dependent data, but likely emerges from zone-folding due to reconstruction of the BZ in the CDW state. DFT calculations predict the CDW modes and their symmetries, along with their atomic displacements shown next to the excitation dependent data (Figure **5.7**). The optical modes observed at 300 K remain at 4 K with only small wavenumber



Figure 5.7: (a) Excitation-dependent Raman measurements performed at 4 K with 458 nm (2.7 eV), 476 nm (2.6 eV), 514 nm (2.4 eV) and 633 nm (1.95 eV) laser wavelength. Peaks E_{amp} , A_{amp} correspond to CDW modes amplitude modes and E_{ZF} is the zone-folded CDW mode. Mode displacement for all one-phonon Raman scattering processes included as insets near each mode.

shifts but with significant changes in intensity. The shear mode at 26 cm⁻¹ (E_{2g}), twophonon mode, and all modes between 180 cm⁻¹ and 350 cm⁻¹ are weakened relative to the mode at 404 cm⁻¹ (A_{1g}) regardless of excitation wavelength. Amplitudons in 2H -TaS₂ appear to have an interesting dependence on excitation wavelength. In **Figure 5.7**, we observe that the relative intensity of the two most prominent CDW modes is roughly the same when excited with 458 nm light. Upon changing wavelength to 476 nm and 514 nm it is the E amplitude mode that dominates, a trend that reverses when using 633 nm excitation. Note that the weak 100 cm^{-1} zone-folded mode also appears in the 514 nm and 476 nm spectra, which when considered in concert with our DFT predictions clearly indicates that it does not arise from laser plasma lines or other spectral artifacts. The origin of these responses is unclear at present since there are no predicted optical transitions in this energy range to which the laser may be quasi-resonant. However, the data shown do provide guidance for us in terms of the optimal laser wavelengths to utilize in our studies.

5.5.5 Temperature dependence of the CDW Raman modes

A key signature of CDW amplitude modes is their softening and broadening when warming across T_{CDW} . We perform temperature-dependent Raman measurements in the range of 4 K to 90 K using 476 nm laser excitation (**Figure 5.8a**) to monitor changes of the modes relevant to the CDW instability. **Figure 5.8a** shows evolution of Raman spectra acquired at different temperatures in and out of the CDW phase with a sample fit shown for the scan taken at 4 K. The shaded gray hatched areas are fits to the Rayleigh background while the E (A) symmetry modes are in purple (gold). The weak 100 ccm⁻¹ zone-folded mode is also shown (in bright green), the fact that it stays static all the way across the CDW phase only to disappear at $T > T_{CDW}$ further validates our assignment that it originates from zone-folding mechanisms. The hallmark softening of CDW amplitude modes is clearly observed as the sample temperature is raised with both modes red-shifting and broadening, finally becoming unresolvable at T > 70 K (**Figure 5.8a**, **5.8b** and **5.8c**). We will elaborate upon the power-law scaling of these modes in the next section.

The CDW amplitude modes are linked to the CDW complex order parameter and therefore are expected to exhibit mean-field like temperature dependence [201],

$$\omega_{CDW}^{i}(T) \propto \sqrt{1 - \frac{T}{T_{CDW}}},\tag{5.12}$$

where $\omega_{CDW}^i(T)$ is the temperature-dependent mode frequency for amplitude mode. We display the temperature-dependent amplitude mode frequencies for the E and A symmetry amplitude modes in **Figure 5.8b** and **5.8c** to illustrate that in 2H - TaS₂ this expectation



Figure 5.8: (a) Temperature-dependent Raman measurements of the CDW modes E_{amp} and A_{amp} using 476 nm excitation with a sample Lorentzian fit shown for the data at 4 K. (b) Frequency of CDW mode E_{amp} extracted from the fits plotted as a function of temperatures. The value of T_{CDW} is fixed at 75 K (c) Frequency of CDW mode A_{amp} extracted from the fits plotted as a function of temperature. The value of T_{CDW} is fixed at 75 K. Dashed magenta line shows a model fit to mean-field theory equation with square-root dependence.

fails dramatically. Mode softening is apparently incomplete, with both amplitude modes

retaining non-zero frequencies immediately before the phase transition. This behavior is frequently observed in CDW materials and is frequently attributed to short-range fluctuations out of phase with local CDW order as in the case of 2H - NbSe₂ [205], 1T-TiSe₂ [206, 207] and other CDW materials [208–210]. The pink dashed curve in each figure is a model fit to the expected mean-field dependence, which clearly cannot capture the observed temperature-dependence. If we instead relax the fitting function to have a varying power β and varying coefficient,

$$\omega_{CDW}^{i}(T) = A\omega_{o}^{i} \left(1 - \frac{T}{T_{CDW}}\right)^{\beta}$$
(5.13)

we find that an excellent fit can be obtained that provides reasonable values for T_{CDW} but unreasonable values for $\beta \approx 0.05$. The departure from square-root-dependence of CDW phonon softening has been observed in other CDW systems such as $TiSe_2$ [206,207] K₂SeO₄ [211], $A_{0.3}MoO_3$ (A = K, Rb) [212] and numerous rare-earth tritelluride compounds [208-210] with values of β ranging from 0.08 to 0.3. A very recent study of amplitude modes in 2H - TaS₂ observes this deviation as well, but fits their data using a modified mean-field fit [183]. While a mean field theory approach is unable to capture the temperature dependence of CDW modes E_{amp} and A_{amp} , finite-temperature DFT is successful at it. Figures 5.9a and $\mathbf{5.9b}$ compare DFT and experimental data for the change in frequency of \mathbf{E}_{amp} and A_{amp} CDW modes as temperature increases. The scale in the figure is much tighter than in Figure 5.8b and 5.8c. The experimental trend is well reproduced for both modes, and an amazing quantitative match is found for A_{amp} . Such excellent agreement supports the modeling strategy we implemented to simulate the incommensurate CDW. It also validates the atomic structure we determined to be the equilibrium configuration in CDW phase. From Figure 5.9c, it is apparent that in-plane movement of Ta - atoms is behind the formation of the CDW phase. This Ta - atoms displacement was observed experimentally [212] The final structure displays a triangular superlattice, much like what has been seen for 2H - NbSe₂ [213]. Lastly, we note that our DFT calculations and experimental data disagree markedly with recent results where the authors claim to observe many more CDW



Figure 5.9: (a) Frequency of the E_{amp} CDW modes at each temperature obtained using DFT and compared with experimental observations. (b) Frequency of the A_{amp} CDW modes at each temperature obtained using DFT and compared with experimental observations. (c) Lattice configuration of bulk 2H-TaS₂ at various temperature in and out of the CDW phase, showing the evolution of a triangular configuration in the CDW regime

modes than we do and assign them as zone-folded phonons [183].

5.5.6 Temperature dependence of the two-phonon mode

In **Figure 5.10a** we focus on a less commonly examined behavior in Group V TMD materials: the two-phonon mode. This Raman feature is associated with the strong wavevectordependent electron-phonon coupling near the CDW wavevector. The two-phonon mode represents a second order process where phonon-assisted scattering of the electrons near the Fermi level leads to the creation of two phonons with equal and opposite wavevectors (i.e. $\vec{q_1} + \vec{q_1} = 0$) [81]. All phonons that satisfy this condition collectively contribute to the two-phonon mode leading to its large width. Usually multi-phonon Raman processes are weaker than their one phonon counterparts, yet in TMDs with CDW transitions such modes tend to be rather strong [214]. The reason being that the Raman scattering amplitudes for this anomalous feature contains a term proportional to the magnitude of the associated electron-phonon coupling constant, which in materials that exhibit CDW and SC phase transitions, is much more dominant [81]. While driving the CDW transition, the ability of the electrons to screen phonons increases, which develops a sharper and deeper Kohn anomaly, but broader and weaker two-phonon mode. Therefore, monitoring the shift of this mode with temperature provides an indirect measure of the phonon branch renormalization, owing to the onset of the CDW phase.

The temperature-dependence of the two-phonon mode at $T > T_{CDW}$ is another curious behavior. We begin with the normal phase where the dominant two-phonon feature at 180 cm⁻¹ in the 300 K spectrum softens and broadens with decreasing temperature in conjunction with the broadening of the in-plane E_{2g} mode at 290 cm⁻¹ (Figure 5.10a). Secondorder scattering processes such as this have contributions form an ensemble of phonons belonging to multiple acoustic branches, with equal and opposite momentum that traces the CDW wavevector q_{CDW} . The softening of the two-phonon feature then from 180 cm⁻¹ at 300 K to 150 cm⁻¹ at 90 K shown in Figure 5.10b (green points) is a response to the renormalization of the phonon frequencies approaching the phase transition temperature and a sign that the instability in the lattice is present at temperatures much higher than T_{CDW} . Interestingly, we also find that the linewidth of the dominant 404 cm⁻¹ mode (Figure 5.10c) follows the same functional form as the two-phonon mode, suggesting that phonon-lifetime of the A_{1g} optical mode might be correlated with structural instability and presence of pseudo-gap indicated by the two-phonon feature. We note that defects provide one mechanism for stabilizing CDW above the critical temperature as has been shown in



Figure 5.10: (a) Temperature-dependent Raman measurements of the higher frequency modes in the metallic phase using 532 nm laser excitation. (b) Evolution of the twophonon mode frequencies with temperature in and out of the CDW phase as a function of temperature. Below T_{CDW} , the mode freezes in response to the CDW modulation while softens at higher temperatures. (c) FWHM of the high wavenumber optical mode at ${}^{1}A_{1g} 404 \, cm^{-1}$ showing similar broadening response at higher temperatures whereas the phonon linewidth remains pretty consisted inside the CDW regime.

scanning tunneling microscopy measurements of NbSe₂ [152].

With regards to the remaining optical modes identified in **Figure 5.7**, the behavior across T_{CDW} is less dramatic. The out-of-plane (A_{1g}) high-wavenumber mode at 404 cm⁻¹ remains prominent upon cooling (**Figure 5.10a**) and survives to 4 K at which point it has slightly blue-shifted and sharpened. Other in-plane modes at 245 cm⁻¹ (E_{1g}) and 290 cm⁻¹ (E_{2g}) show insignificant shifts [215], however, the 290 cm⁻¹ (E_{2g}) mode weakens in concert with the two-phonon mode despite being a Γ -point mode. The interlayer shear-mode at 26 (E_{2g}) in **Figure 5.6b** remains prominent with decreasing temperature, indicating that the formation of a largely 2D CDW mode that eventually is overshadowed by the CDW amplitude modes. The sharpening of the 404 cm⁻¹ (A_{1g}) mode upon cooling to low temperature (**Figure 5.10c**) appears to display the same trend as the frequency of the two-phonon mode which suggests a common origin behind its anharmonicity.

5.5.7 Temperature-dependent APRES data

Finally, we analyze temperature-dependent ARPES data from 2H - TaS_2 in Figure 5.11. To this end, we first focus on energy distribution curves (EDCs) in Figure 5.11a, where an EDC is ARPES intensity as a function of energy at a specific momentum location [216]. These EDCs have been divided by the resolution-broadened Fermi function to approximately de-convolute the effects of energy resolution and Fermi function. Note that the same data set has been used in separate studies by our team in Ref [217]. The inset of Figure 5.11b shows the momentum location of the Fermi function divided EDCs in Fig**ure 5.11a**. It is to be noted that the electronic energy in **Figure 5.11a** is referenced with respect to the chemical potential (μ) the system. The Fermi function divided EDC at the lowest temperature shows that its peak closest to μ is actually located at a negative energy indicating the presence of an energy gap due to CDW instability. In the present case, the exact magnitude of energy gap, however, can't be determined from the ARPES data. This is because the minimum of the Fermi function divided EDC at each temperature is located at a positive energy, which can't be detected unambiguously by ARPES. Such particle-hole asymmetry in energy gap is anticipated for a CDW system like 2H - TaS₂, where the CDW wave vector is not directly connected to Fermi surface nesting. Nevertheless, the presence or absence of an energy gap from ARPES data can be ascertained.

We find that the high-temperature shift of the two-phonon mode correlates with changes in the ARPES data above T_{CDW} . This is illustrated by **Figure 5.11**. A closer look at **Figure 5.11a** highlights that with increasing temperature, the strength of the peaks of the Fermi function divided EDCs get weaker, but the energy locations of the peaks are



Figure 5.11: (a) Fermi function divided EDCs with increasing temperature through T_{CDW} . (b) The green dot on the schematic plot of the Fermi surface in the inset shows the momentum location of the Fermi function divided EDCs in a. Temperature dependence of the spectral weight at the chemical potential. Extrapolation of $L(T) = 1 - (I(T, \omega = 0))/(I(T, \omega = \omega_{peak}))$ to zero provides an estimate of $T^* \sim 240$ K, which is much larger than T_{CDW} .

essentially the same. Even though the spectra at temperatures above T_{CDW} do not possess well-defined peaks, a clear signature of the suppression of low energy spectral weight is always present. This implies the CDW energy gap persists even in the normal state, i.e., for temperatures above T_{CDW} . The survival of CDW energy gap even at ~ 100K (> T_{CDW}), evidences a non-BCS like phase transition at T_{CDW} . This is consistent with the observations in **Figure 5.8b** and **5.8c**. The persistent energy gap above the transition temperature closely resembles the enigmatic pseudo-gap phase in underdoped cuprate high temperature superconductors (HTSC) [218]. It is then natural to speculate that similar to the pseudogap closing temperature in cuprate HTSCs, there would be a temperature T^{*} a 2H - TaS₂ at which the normal state CDW energy gap disappears. We obtain an approximate value of T^{*} by conducting an analysis of the filling up of the energy gap via an accumulation of spectral weight at zero energy (ω) as a function of T. We plot $L(T) = 1 - \frac{(I(T,\omega=0))}{(I(T,\omega=\omega_{peak}))}$ for different values of T in Figure 5.11b, where at a given temperature T, I (T, $\omega = 0$) is the intensity of the Fermi function divided data at $\omega = 0$ and I (T, $\omega = \omega_{peak}$) is the intensity at $\omega = \omega_{peak}$ with ω_{peak} being the energy location of the peak or kink-like structure of the Fermi function divided EDC. Thus, from the extrapolation of L(T) to zero, T* can be estimated. Figure 5.11b shows that the estimated value of T* in the current case is ~ 240K, which is substantially higher than $T_{CDW} \sim 75$ K. Similar analysis has been extensively used in cuprate HTSCs to determine pseudo-gap temperature [219, 220] as well as in ZrTe₃ [221]. It should be noted that such a large value of T* is not unprecedented in 2H polytypes of the TMDs - for instance, ARPES studies on 2H - NbSe₂ suggest CDW order close to room temperatures [222] even though its $T_{CDW} \sim 33$ K. The fact that there is a temperature range in which the structural instability, manifested by softening of the two-phonon mode, coexists with an energy gap above T_{CDW} , suggests that they are connected. This reiterates the significance of electron-phonon coupling in the CDW instability of 2H - TaS₂ and that of incommensurate transition metal dichalcogenides (TMDs), in general.

5.5.8 Temperature-dependent phonon bandstructures

To better understand how temperature affects the vibrational modes of 2H - TaS₂ and at what temperature the first signs of structural instability appear, we calculated the phonon band structure at different temperatures across the CDW transition. The phonon band structures are calculated with the standard 2H - TaS₂ unit cell (6 atoms, 18 bands), instead of our usual $3 \times 3 \times 1$ supercell. While this enabled us to clearly follow the changes of each band it does not allow for a direct modeling of the incommensurate CDW phase as the cell is too small to allow atomic rearrangement. Therefore, we apply the same compressive strain along the c-axis and Fermi surface smearing used in the prior super-cell simulations. We computed the phonon band structure using several k-points meshes ($8 \times 8 \times 8$, $12 \times$ 12×12 , $16 \times 16 \times 16$ and $24 \times 24 \times 24$), to guarantee convergence, and present results obtained using $24 \times 24 \times 24$ k-point mesh. The complete picture of the phonon band structure of 2H - TaS_2 at six different temperatures (T = 300 K, 280 K, 250 K, 150 K, 70 K and 30 K) is presented in Figure 5.12 - 5.14. The three acoustic (red curves) and three quasi-acoustic bands (blue curves) shown in Figure 5.12 and Figure 5.13 respectively are separated from the optical bands in Figure 5.14 by a large (75 cm⁻¹) indirect phonon frequency gap. Approaching the CDW



Figure 5.12: DFT-calculated phonon dispersion curves for the acoustic modes in 2H-TaS₂ at temperatures in and out of the CDW phase (T = 300 K, 280 K, 250 K, 150 K, 100 K, 70 K and 30 K). The conventional unit cell is used for these calculations.

transition temperature, while the optical bands exhibit essentially no temperature dependence close to T_{CDW} Figure 5.14, the story is quite different for the acoustic and quasi acoustic modes. Our calculations of the full acoustic phonon dispersion at different temperatures, indicates that the phonon frequencies remain positive until 280 K. For all temperatures at or below 250 K we observe signs of a lattice instability as negative phonon frequencies appear in the acoustic branches along the M direction. Below 100 K, the same acoustic branches become negative along the ΓK direction as well. The quasi-acoustic branches show a very similar temperature dependence as presented in **Figure 5.13**.



Figure 5.13: DFT-calculated phonon dispersion curves for the quasi-acoustic modes in 2H-TaS₂ at temperatures in and out of the CDW phase (T = 300 K, 280 K, 250 K, 150 K, 100 K, 70 K and 30 K). The conventional unit cell is used for these calculations.

However, we find a curious behavior near the K point where the quasi-acoustic branches increase in energy while the acoustic branches decrease and become negative with decreasing temperature. While investigating unit cell vibrational modes does not allow for the qualitative estimate of the temperature at which the incommensurate CDW phase forms (T_{CDW}) , it reveals that structural instabilities start at temperatures much higher than the expected T_{CDW} . This is, again, in good agreement with our experimental findings.



Figure 5.14: DFT-calculated phonon dispersion curves for the optical modes in 2H-TaS₂ at temperatures in and out of the CDW phase (T = 300 K, 280 K, 250 K, 150 K, 100 K, 70 K and 30 K). The conventional unit cell is used for these calculations.

5.6 Conclusion

We identify the presence of three CDW modes below T_{CDW} , one zone-folded and two amplitude modes. The temperature- dependence of the amplitude modes deviate from the expectations of mean-field theory owing to quantum fluctuations but are captured by finitetemperature DFT calculations. Above T_{CDW} , we observe a strong two-phonon mode that originates from finite momentum phonons near the CDW wavevector. The energy of this feature is highly dependent upon temperature, suggesting that structural instabilities may exist on short length scales at temperatures $T \sim 280$ K. These Raman observations correlate with the CDW gap [217] closing temperature ($T^* \sim 240$ K), estimated from the ARPES data as a function of temperature through T_{CDW} .

In summary, we have carried out the first correlated experimental-theoretical study of CDWs in 2H - TaS₂. These observations confirm the presence of two amplitude modes

and a zone-folded mode below T_{CDW} that exhibit an anomalous temperature dependence. DFT successfully capture this behavior and provide a physical picture regarding the atomic displacements arising from amplitudons. Analysis of the two-phonon mode is correlated with ARPES and DFT data to suggest the presence of short-range CDW order even well above the phase transition temperature. These results show that CDWs in layered systems are more complicated than previously thought and that CDW physics is relevant even at temperatures well-above T_{CDW} .With regards to the remaining optical modes identified in Figure 1(a), the behavior across T_{CDW} is less dramatic. The out-of-plane (A_{1g}) high-wavenumber mode at 404 cm⁻¹ remains prominent upon cooling (Figure 5.10a) and survives to 4 K at which point it has slightly blue-shifted and sharpened. Other in-plane modes at 245 cm⁻¹ (E_{1g}) and 290 cm⁻¹ (E_{2g}).

Chapter 6: Project Sigma (Σ) - Localized excitons in semiconductor-metal heterostructures

6.1 2D Metal-Semiconductor contacts

Semiconductor heterostructures are key to modern technology and devices such as transistors, lasers, solar cells, and light-emitting diodes [223]. However, the growth constraints of lattice matching between different semiconductors significantly limit not only the number of semiconductor heterostructures, but also their ultimate performance and functionality. An important opportunity for vdW heterostructures lies in the potential to interface layered materials with dissimilar properties, dimensionality and lattices, a capability that could enable complex device functionalities impossible with conventional materials [37, 224]. Unfortunately, as we discussed in the earlier sections, TMD-based devices with common metals often lead to highly-resistive contacts [225–228] and a prominent SBH. Furthermore, such metals are typically also responsible for a rapid decay of charge carriers from the semiconductor resulting in significant quenching of PL emission [229–231], constraining their use in TMD-based optoelectronic devices.

A promising direction to solve these obstacles relies on using atomically-thin metals to create low-resistance and highly transparent vdW contacts. Particularly interesting are Nb-based metallic TMDs which offer low, *p*-type Schottky barriers with many 2D semiconductors in addition to exhibiting superconductivity [100, 101, 232–234]. This has enabled further developments in fabricating ultrathin devices, where drastic changes in the electronic landscape of the NbSe₂ contact can modulate the channel carrier properties of the transistor [101, 235–237]. On the other hand, extensive investigations to understand interfacial contact properties and nearby dielectrics in MoSe₂-based metal-semiconductor heterostructures has helped engineer efficient optoelectronic devices [238–241]. However, despite this progress in the studies of 2D metal-semiconductor heterostructures, important uncertainties in their optical properties and the role of excitons remain. Fermi level pinning at metal-semiconductor interfaces can induce mid-gap states in the semiconductor, thereby enabling additional radiative channels for exciton recombination [96,98,242–244]. Semiconducting ML TMDs pose additional challenges with the influence of surrounding dielectric media, where 2D metals can drastically change the exciton dynamics as well as the ability to effectively screen electrons in the semiconductor [245].

Project Σ was motivated by this largely unexplored optical response of TMD metalsemiconductor junction, particularly focusing on the NbSe₂-based contacts. We employ a combination of optical characterization tools along with temperature- and power-dependent measurements, to study the interfaces formed between semiconducting-MoSe₂ and metallic-NbSe₂ flakes.

6.2 NbSe₂ - MoSe₂ heterostructures - Sample fabrication

MLs of 2H-MoSe₂ and bulk- NbSe₂ flakes were obtained through mechanical exfoliation of as-grown crystals and subsequently transferred on O₂ plasma cleaned Si/SiO₂ substrates. This was done using the PDMS-based dry viscoelastic stamping method [105] (outlined in Chapter - 3) in various heterostructure geometries. In Samples 1, 2, 5, 6, 8 and 10, the monolayer is placed directly on the Si/SiO₂ substrate with the bulk-NbSe₂ flake contacted on top as shown in **Figure 7.1a**. In Samples 3 and 4, the NbSe₂ - MoSe₂ heterostructure is encapsulated in HBN as shown schematically in **Figure 7.1b**. Sample 7 is fabricated on bulk-NbSe₂ with ML-MoSe₂ deposited on top and capped with HBN, while Sample 9 is fabricated the same way but capped with bulk-NbSe₂ rather than hBN, resulting in a NbSe₂ - MoSe₂ - NbSe₂ heterostructure, shown in **Figure 7.1c**, d. For samples in panel (a), no intermediate cleaning procedures were employed to get rid of any polymer residue. In case of Sample 3 and 4, we performed the AFM-based 'Nano-squeegee' procedure [106]



Figure 6.1: Fabrication assembly for Samples 1 and 2 (directly stamped on the $Si-SiO_2$ substrate) and Samples 3 and 4 (encapsulated with HBN)

to optimally create clean interfaces also outlined in Chapter - 3. Samples 1, 2, 3, 4, 6, 7 and 8 were annealed later 200 °C for 5 hours under high-vacuum condition. We will for the majority of this chapter focus on Samples 1-5, while measurements done on the remaining samples are included in the supplementary information section at the end.

6.3 $NbSe_2 - MoSe_2$ heterostructures - Optical study

Here, white light images of NbSe₂ - MoSe₂ vdW heterostructures (Samples 1-4) and a Control sample are shown in **Figure 6.2**. The Control sample consists of ML-MoSe₂ fully encapsulated with few-layer hexagonal boron nitride (hBN). Below each image are low-temperature (5 K) PL spectra showing emissions on (black star) and off (red star) the NbSe₂ - MoSe₂ interface shown in the corresponding image. All samples exhibit PL features close to 1.65 eV and 1.62 eV attributed to neutral exciton (X^0) and negatively-charged trion (X^-) emissions in ML-MoSe₂, respectively [246]. The trion is expected to be X^- and not X^+ owing to the formation of Se vacancies and anti-sites during synthesis and the tendency



Figure 6.2: White light images of (a) ML-MoSe₂ Control sample and (b-e) Samples 1, 2, 3 and 4 comprising of NbSe₂ - MoSe₂ van der Waals (vdW) heterostructures. Samples 1 and 2 are fabricated on Si/SiO₂ substrate, whereas Samples 3 and 4 as well as the Control sample are fully encapsulated with few-layer hexagonal boron nitride (hBN). The black dotted line in (d) and (e) outlines the ML-MoSe₂ region. Beneath each image are low-temperature photoluminescence (PL) spectra taken on (black) and off (red) the NbSe₂ - MoSe₂ interface. These locations are denoted by red and black stars in the white light image. The yellow boxes mark the regions scanned in hyperspectral PL maps. In addition to the X⁰ and X⁻ emission observed in Samples 1-4, a PL feature referred to as L1 appears at \approx 1.6 eV in all heterostructures.

of chemical vapor transport (CVT) grown MoSe₂ to be inherently *n*-type [247]. Extrinsic doping effects from polymer residue and the plasma-cleaned Si/SiO₂ substrate likely also contribute to the presence of X⁻. The observed X⁻ binding energy (\approx 27-30 meV) and PL linewidths (\approx 4-6 meV for Samples 3 and 4, \approx 6-9 meV for Samples 1 and 2) are consistent with prior measurements [104, 246, 248–250], and their variation likely due to dielectric tuning of the Coulomb interaction after hBN encapsulation [103, 245, 251].

6.3.1 A new optical feature emerges - L1

The most obvious difference between on (black) and off (red) spectra is the appearance of an additional PL peak close to ≈ 1.6 eV, about 25-30 meV lower than the X⁻ peak. The intensity and linewidth of this peak, hereafter referred to as L1, varies between samples, however, its energy with respect to the X⁻ peak remains unchanged and its emission localized to the NbSe₂ - MoSe₂ interface. L1 is also surprisingly robust to the quality of the interfacial contact between the two TMDs, as demonstrated by its presence in 10 of the 14 heterostructures created in this study (see Supporting Information section for more details) with a variety of stacking configurations (refer **Figure 7.1**) and post-assembly cleaning procedures (discussed in Chapter - 3). The 4 samples where we do not observe L1 have suffered from excessive polymer residue and/or oxidation of NbSe₂.

6.3.2 Hyperspectral imaging of the $NbSe_2$ - $MoSe_2$ heterostructures

To determine whether vdW coupling between NbSe₂ and MoSe₂ contributes to the origin of L1, we performed hyperspectral PL measurements across the interface of Samples 1-10, where for the sake of brevity we focus on two different cases. **Figure 6.3a,b** here show the spatially-mapped integrated PL intensity acquired at 5 K for Sample 2 and Sample 4 (hBN-encapsulated), respectively across area marked by yellow boxes in **Figures 6.2c,e**. The black arrows indicate regions of NbSe₂ - MoSe₂ overlap. We first examine the variation in integrated PL intensity (total sum of X^0 , X⁻ and defect emission), where, compared to the bright emission observed from the uncapped region, a reduction by a factor of five is seen at the overlap between NbSe₂ and MoSe₂ flakes. However, the fact that any PL signals are recorded from the NbSe₂-capped regions suggests that non-radiative relaxation into NbSe₂ is a weaker process than might be expected. The reduction in the total PL intensity at the interface is likely due to the combined reflection of the incoming laser and MoSe₂ PL by the capping NbSe₂ layer, although substrate interference effects may also play a role [252]. **Figure 6.3c,d** show variation in the integrated intensity of L1 measured across the



Figure 6.3: Low-temperature hyperspectral maps of the integrated PL intensity from 1.5 eV - 1.7 eV for (a) Sample 2 and (b) Sample 4, and integrated PL intensity of L1 peak for (c) Samples 2 and (d) Sample 4. The regions scanned correspond to the yellow boxes in Figure 6.2. White arrow in panels (a) and (b) corresponds the path of the linecuts examined in (e) and (f). The magenta dashed outlines in panels (c) and (d) mark pristine ML-MoSe₂. PL spectra extracted along the linecuts in (a) and (b) plotted for (e) Sample 2 and (f) Sample 4. L1 is localized along the NbSe₂ - MoSe₂ perimeter in Sample 4, while it appears across the NbSe₂ - MoSe₂ interface in Sample 2. The black and green dots refer to the start and end positions of the linecuts, respectively.

same area. These maps highlight an important difference between the behavior of L1 in encapsulated and unencapsulated samples. As seen in **Figure 6.3c**, for Sample 2 fabricated without hBN-encapsulation, L1 is present over the majority of the NbSe₂ - MoSe₂ interface. This in contrast to the hBN-encapsulated Sample 4, where L1 is more prominent over the perimeter of the NbSe₂ - MoSe₂ region (**Figure 6.3d**). The impact of interface quality can be made more apparent by examining PL plots of spectra extracted along a linecut, depicted by the white arrow that extends over the interface from the pristine MoSe₂ regions in **Figure 6.3a,b**. The green and black dots represent the starting and ending point of the linecut, respectively. It is clear from **Figure 6.3e** (Sample 2) that as we move from ML-MoSe₂ to the region in contact with NbSe₂, L1 appears at about 30 meV below the X⁻ peak. In contrast to Sample 2, **Figure 6.3f** shows that L1 is more pronounced along the edges surrounding the NbSe₂ - MoSe₂ overlap in Sample 4 than at the interface. Additionally, for both samples, we see clear broadening of the X⁰ and X⁻ PL peaks near the interface compared to the pristine MoSe₂ region. This is typical for metal-semiconductor junctions where rapid decay of charge carriers can result in reduced exciton lifetimes and inhomogeneously broadened PL linewidths. The difference in the spatial distribution of L1 in Sample 2 *versus* Sample 4 over the NbSe₂ - MoSe₂ interface is likely due to variable coupling between the flakes. Sample 4 was processed with a 'nano-squeegeeing' technique [106] (see Chapter - 3) and then annealed in vacuum which produces a clean, uniform interface. Sample 2 was only vacuum annealed which redistributes polymer residue to form larger bubbles and some wellcoupled regions [253–256]. The different spatial distribution of L1 in these samples requires a deeper understanding regarding vdW coupling between NbSe₂ and MoSe₂.

6.3.3 Intralayer moiré excitons in 2D-3D heterostructures

In addition to observing a new, interfacial, low-energy PL emission at 1.6 eV, splitting of the X^0 and X^- PL peaks is observed in the HBN encapsulated samples 3 and 4. Including L1, the resulting spectrum contains five peaks assigned in order of increasing energy: L1, $X^-(2)$, $X^-(1)$, $X^0(2)$ and $X^0(1)$ as shown in **Figure 6.4**. Recalling our discussion on the moiré interfaces between TMDs with mismatched lattice and rotational misalignment, a spatially dependent moirépotential can trap excitons, changing their PL energies, lifetimes and even the optical selection rules. The trapping of excitons is not limited restricted only to the interlayer excitons, as intralayer electron-hole pairs can also succumb to this potential, if present near the high symmetry points. Also, since the X^- transition is really bright and related to an abundance of charge carriers that can couple to the exciton, these moiré potentials could effectively also trap these three particle localized trion composites. As a a result, the PL spectra can include shoulders to the X^0 and X^- energies, emitting



Figure 6.4: (a)-(b) Normalized PL spectrum taken at the edge of $NbSe_2$ - $MoSe_2$ interface (marked by red stars), for samples 3 and 4 with corresponding white light images. Signatures of moiré coupling manifests in two exciton and two trion peaks, which correspond to the respective minima of the moiré potential. L1 is also present, resulting in a five peak structure.

from radiative recombination of e-h pairs trapped in moire potentials. Our PL spectra as well as the energy separation between the X^0 and X^- doublets are consistent with observations of moiré intralayer excitons in MoSe₂ - MoS₂ heterostructures [257] where quantum confinement occurs due to the moiré potential [258]. This behavior has also been predicted in MoS₂ - NbSe₂ heterostructures [259]. Our observations of intralayer moiré exciton in NbSe₂ - MoSe₂ in 2D-3D heterostructure are the first of their kind and pave the way for observing interfacial phenomena in dissimilar material systems with contrasting band properties.

6.3.4 Literature review on MoSe₂ exciton states

In this section, we focus on understanding and distinguishing the origin of the L1 peak from previously studied, low-energy optical pathways in ML-MoSe₂. An extensive amount of work has been done to to engineer MoSe₂ exciton states, multi-exciton MoSe₂ states, and excitons in MoSe₂-based vdW heterostructures, but none of these results are similar or can explain the L1 peak. The controlled application of strain to $ML-MoSe_2$ was found to induce localized quantum emitters with ultrasharp PL linewidths over a wide range of energies below X^0 and $X^-[260]$. While an attractive explanation, L1 exhibits a PL linewidth that is much broader than a strain-induced quantum emitter and a consistent emission energy of ≈ 1.6 eV, disagreeing with discrete quantum-dot picture. On the other hand, a broad low-energy feature (between 1.5 eV and 1.6 eV) appears in gate-dependent PL measurement of pristine ML-MoSe₂, but is associated with impurity trapped excitons with linewidths an order of magnitude larger than X^0 , X^- and L1 [246]. We may also exclude the possibility of NbSe₂-induced activation of dark exciton states based on the recent observation of the $MoSe_2$ dark neutral exciton, which lies 1 meV above X^0 and is therefore spectrally wellseparated from L1 [248]. Strain-dependent measurement on ML-MoSe₂ have revealed a uniform red shift in the X^0 and X^- peak energies, without the appearance of low-energy emission features [261]. Measurements to probe higher-order exciton complexes such as neutral or charged biexcitons have revealed features at energies lower than the X^0 , however their binding energies do not match the spectral position of L1 [262]. Finally, emergence of interlayer valley excitons in MoSe₂-based vdW heterostructures occur at about ≈ 1.4 eV much lower than our observation of L1 [263]. This shows that while $MoSe_2$ has been observed to exhibit a rich platform for excitonic species, the origin of L1 must be tied to its interaction with the neighbouring NbSe₂.

6.4 $NbSe_2$ - $MoSe_2$ contact: First-principles calculations

Recalling our discussion on metal-semiconductor interfaces in Chapter - 3, the interaction between two TMDs in close proximity is dictated by their band-alignment, their workfunctions and electron affinities and their relative positions of the E_F . Moreover, any band-hybridization between their transitional metal orbitals creates new opportunities for interlayer transition, not allowed in individual layers. Therefore, calculations of the electronic bandstructure of each layer, as well as their heterostructure becomes paramount. In collaboration with our colleagues at University of Buffalo, New York, USA we were able to perform first-principles calculation using density functional theory (DFT), one of the most common tools to calculate the electronic properties of monolayer and bulk TMDs.

6.4.1 Electronic Bandstructure calculations

The electronic structure of NbSe₂, MoSe₂ and NbSe₂ - MoSe₂ heterostructure are presented in **Figure 6.5**, calculated for different interlayer separation and scaled to reflect zero energy as the vacuum energy. Here, **Figure 6.5c** illustrates the ML-MoSe₂ bandstructure (red bands) which hosts a direct band gap at the K point in agreement with previous calculations [264, 265]. The calculated electron affinity of ML-MoSe₂ is $\chi_{Mo} = 3.92$ eV, and the Fermi level (E_F) and work function (Φ_{Mo}) are set mid-gap based on the assumption of an undoped monolayer in agreement with recent work [266]. The electronic bandstructure for ML-NbSe₂ is presented in **Figure 6.5b** which is metallic with a calculated workfunction value of $\Phi_{Nb} = 5.56$ eV, in agreement with previous work [267]. Bandstructure calculations for a ML-NbSe₂ - ML-MoSe₂ heterostructure are presented in **Figure 6.5d-f** where the blue (red) bands derive from NbSe₂ (MoSe₂) orbitals, respectively, and qualitatively match prior modeling efforts of this system [100]. We note that although the top NbSe₂ flake is bulk ((60-100) nm) in our case, our use of ML-NbSe₂ in these calculations is sufficient to capture the essential physics of the system as vdW interactions weaken for additional layers. The heterostructure calculations are done using the structure model, which is the


Figure 6.5: (a) Atomic models of the calculated NbSe₂ - MoSe₂ heterostructures, where d denotes the vdW distance between the two materials. (b) The band structure for ML-NbSe₂. (c) The band structure for ML-MoSe₂. (d)-(f) The bands for the NbSe₂-MoSe₂ heterostructure with vdW distance of 9.14 Å, 5.14 Å and 3.14 Å, respectively. The relaxed distance is 3.14 Å. The zero energy in (b)-(e) indicates the vacuum energy.

most stable registry for $NbSe_2$ - $MoSe_2$ heterostructure [100].

Figures 6.5d-f shows the changes in NbSe₂ - MoSe₂ bandstructure with decreasing interlayer vdW distance (d = 9.14 Å, 5.14 Å and 3.14 Å), which is a marker for the coupling between two TMDs. Upon first examination, the MoSe₂ bandstructure is qualitatively unchanged by the presence of NbSe₂ for all interlayer separation considered. The MoSe₂ bandgap (E_g) remains the same and there is no band-hybridization between the MoSe₂ and NbSe₂ orbitals except at the Γ point where there is weak mixing. This mixing originates from the fact that Nb and Mo *d*-bands at the Γ point have an out of-plane (d_{z^2}) orbital character resulting in a weak hybridization, while the high-symmetry K point orbitals are largely in-plane (d_{xy} , $d_{x^2-y^2}$) and therefore less sensitive to the addition of NbSe₂. The lack of Mo-Nb band hybridization at K implies excitonic behaviors in MoSe₂ will remain in the heterostructure. In this case of d = 9.14 Å, the interaction between two materials can be neglected and the bands of the MoSe₂ in the heterostructure remains the same as that of pristine-MoSe₂ (**Figure 6.5c**). Interestingly, the main impact of increasing the coupling between NbSe₂ and MoSe₂, or decreasing layer separation d, is a downwards shift in the conduction and valence band energies by 0.34 eV. This implies that the electron affinity for MoSe₂ in the heterostructure has increased to $\chi_{hetero} = 4.26$ eV. This band offset between pristine MoSe₂ and NbSe₂-capped region is a direct consequence of the vdW interaction, where an attractive potential offered by NbSe₂ relaxes the energy landscape of the semiconductor. These results are consistent with prior examinations of heterostructure where NbSe₂ is stacked upon a semiconductor [100, 232].

6.4.2 In-plane band bending

This seemingly minor change in the electronic affinity χ between the pristine-MoSe₂ and NbSe₂-capped region is critical for understanding the origin of L1 peak. It is important to note here, that while Fermi levels can be tuned arbitrarily within the band-gap of the semiconductor and are pinned by the metal in a metal-semiconductor junction, electron affinities associated with these regions are fixed and determine band alignment. This means, we can use the values of Φ and χ obtained from our first-principles calculations to illustrate an in-plane band schematic as one moves from the pristine MoSe₂ region to the NbSe₂ -MoSe₂ overlap. We do this by directly comparing the bandstructures of ML-MoSe₂ and that of the heterostructure (calculated for d = 3.14 Å) and appropriately marking the respective Φ , χ values for MoSe₂ in both regions, as well as the position of the E_F all relative to their vacuum energy. This is shown in **Figure 6.6a** for when the two regions are spatially separated, i.e. pristine ML-MoSe₂ and NbSe₂ - MoSe₂ heterostructure do not have the same semiconducting channel (or a common MoSe₂ monolayer). We can also see that based on the obtained values of Φ_{hetero} , NbSe₂ makes a *p*-type contact with MoSe₂ and the E_F lies near the valence band. From our discussion in Chapter - 3 and the sample assembly



Figure 6.6: (a) A schematic of changes in the work function (Φ) and electron affinity (χ) between NbSe₂ - MoSe₂ contact and pristine MoSe₂ traced from their respective DFT calculated bandstructures. Red bands derive from MoSe₂, while blue bands derive from NbSe₂. The Y-axis for both bandstructures is scaled such that the zero energy refers to the vacuum energy. (b) Discontinuous band bending allows for formation of potential traps at the in-plane junction as the Fermi Level (E_F) matches between the two region.

shown in Figure 7.1 and 6.2, as a consequence of charge rearrangement to electronically equilibriate the common MoSe₂ layer and to match E_F across the two regions, the MoSe₂ bands in the two regions must bend at the interface. Since E_g does not change, band bending is determined by the differences between Φ and χ at the interface. This is shown in Figure 6.6b where a discontinuous band-bending occurs at the in-plane junction between the pristine and metal-capped region of the common MoSe₂ layer.

6.5 On the origin of L1 - Creating intralyer traps

The dissimilar nature of band-bending leads to a band alignment that can allow formation of pockets at the in-plane boundary as illustrated in **Figure 6.7a**. This allows for trapping of electrons from the NbSe₂ - MoSe₂ overlap region and and holes from the pristine-MoSe₂ region into these potential well from their respective CB and VB levels. The trapped electron-hole pairs can then radiatively recombine to give a low-energy emission, we see at 1.6 eV and result in the L1 peak. This is shown in the zoomed-in view of the trapping potential at the in-plane junction in **Figure 6.7a**. This mechanism of interface trapping and recombination is known to produce an additional PL feature in AlGaAs/GaAs heterostructures referred to as an 'H-band' [268].

The trapping potential created by band bending provides a natural explanation for the hyperspectral PL maps presented in **Figures 6.3c** and **6.3d** which correspond to Sample 2 and Sample 4 (hBN-encapsulated), respectively. Sample 2 was subjected to a vacuum annealing procedure post-assembly that consolidates residual polymer in a vdW heterostructure to form larger bubbles while providing some regions with pristine contact [253–256]. This results in a 'patchy' vertical interface where the interlayer separation varies across the NbSe₂ - MoSe₂ heterostructure. Traps will appear at any boundary between well-coupled and poorly-coupled regions that in turn leads to L1 PL emission that varies over the NbSe₂ - MoSe₂ contact region (Figure 6.3c). In contrast, Sample 4 is fully-encapsulated in hBN and was subjected to the 'nano-squeegee' cleaning technique where the AFM tip was used to physically remove polymer residue from the heterostructure [106]. This results in a more uniform spacing, and therefore coupling, between NbSe₂ and MoSe₂. Thus, the only regions that contribute to the band bending required to create a trapping potential are along the edge of the NbSe₂ - MoSe₂ overlap. The resulting map of the L1 feature therefore should mostly show PL from the edge of $NbSe_2$ which is exactly the case shown in **Figure 6.3d**. These two situations are schematically illustrated in **Figure 6.7b.c**. We observe behavior consistent with this model in 10 of the 14 samples created in this study. In the remaining 4 samples we do not observe L1 which we believe is due to a combination of excessive polymer residue or oxidation of NbSe₂.

We can further justify the band bending model as presented in **Figure 6.7** by performing PL measurements before and after stamping bulk-NbSe₂ to fabricate the contact. This is



Figure 6.7: A zoom in at the junction shows confinement of electrons and holes in the valence band (VB) and conduction band (CB) of capped and uncapped MoSe₂. Emissions from the pristine and capped MoSe₂ regions where in addition to the excitons, possibilities of low-energy emissions from recombination of trapped electrons and holes emerge across the interface (yellow). Spatially-resolved band bending schematics. (a) Samples 1 and 2 have large polymer bubbles between NbSe₂ and MoSe₂ that create numerous in-plane boundaries between well-coupled and poorly-coupled regions. PL from L1 is therefore expected from traps randomly distributed across the NbSe₂ - MoSe₂ overlap. (b) Samples 3 and 4 were subjected to an additional cleaning step, 'nano-squeegeeing', that provides a relatively polymer-free interface. L1 therefore only appears at the edge of NbSe₂ - MoSe₂ overlap.

shown in **Figure 6.8** (for sample 5) where PL linecuts taken across the sample before we deposit bulk-NbSe₂ (panels (d) and (e)), show that only X^0 and X^- features are present. These linecuts also cross torn regions of ML-MoSe₂. After stamping the bulk-NbSe₂ flake we observe the appearance of L1 feature at the boundary of the NbSe₂ - MoSe₂ overlap. This is well-illustrated by examining hyperspectral maps of the integrated PL intensity of L1 across the sample in **Figure 6.8c** and linecuts through this map in **Figure 6.8f**. The lack of L1 over the entirety of the NbSe₂ - MoSe₂ interface despite the lack of 'nano-squeegee' cleaning may be explained by the sample history and stochastic nature of the stamping

process. Sample 5 was cooled to cryogenic temperatures, characterized, and then warmed before NbSe₂ was deposited. This could have driven a migration of the polymer residue during the heating/cooling cycle and the subsequent stamping of the NbSe₂ flake may have led to a largely residue free interface. In this case, the band discontinuity would only appear



Figure 6.8: (a) White light image of sample 5. (b) AFM image of the NbSe₂ - MoSe₂ interface in sample 5. (c) Hyperspectral integrated PL intensity maps for sample 5 before (left) and after (center) stamping NbSe₂. L1 is only present after the addition of NbSe₂ (right). Arrows indicate the paths along which linecuts were. (d)-(f) PL spectra along the linecuts in (c). Before stamping NbSe₂ only X^0 and X^- features are present. L1 only appears after stamping NbSe₂ and is localized to the interface.

at the edges of the NbSe₂ - MoSe₂ overlap. We further exclude the possibility of structural deformations by performing AFM measurements. **Figure 6.8b** clearly shows no structural deformation at the NbSe₂ - MoSe₂ interface, further confirming L1 as having an electronic

rather than structural origin. This also proves that L1 is not a direct product of any surface abnormality in the plane of ML-MoSe₂, and rather originates strictly from manipulations of the electronic landscape by a well-coupled bulk-NbSe₂ flake.

6.6 Localized nature of L1

The present physical model implies that L1 originates from the recombination of excitons, and possibly trions, trapped in a confinement potential created by band bending between MoSe₂ and NbSe₂ - MoSe₂ regions. L1 should therefore exhibit the characteristics of a localized exciton in temperature- and power-dependent PL measurements. Prior observations of localized excitons in 2D materials show they disappear quickly with increasing temperature and exhibit a sublinear power-dependence due to the saturation of all available trap sites [87, 269] This section will focus on temperature and power-dependent measurements at the NbSe₂ - MoSe₂ interface and compare the behavior of L1 with other excitonic species in MoSe₂.

6.6.1 Temperature-dependent measurements

We begin with the temperature-dependent PL measurements done on pristine-MoSe₂sample without the presence of any NbSe₂. We expect to see two transitions here, namely X^0 and X^- associated with the neutral and charged exciton emission in ML-MoSe₂. as seen earlier in **Figure 6.2**. The temperature-dependent profile for the two peaks is shown in **Figure 6.9**, where the main differences lie in the behavior of X^0 and X^- peak past $T \approx$ 100. We see that the trion emission gradually reduces and is no longer observable beyond 100 K, with the X^0 peak being the only dominant feature. The suppression in the intensity of X^- is mainly due to its disassociation as a consequence of the increased electron-phonon interactions at higher temperatures. We can extract the shifts in the emission of the two peaks and plot them as a function of temperature. This is shown in **Figure 6.9** where the extracted peak energies are fit to a standard model that describes temperature-dependence



Figure 6.9: (a) Temperature-dependent PL measurements on pristine-MoSe₂ flake. (b) Temperature-dependent PL intensity map for Sample 3 on the NbSe₂ - MoSe₂ interface. We identify five distinct transitions: L1, $X^{0}(1)$, $X^{0}(2)$, $X^{-}(1)$ and $X^{-}(2)$. Green dots denote the temperatures where spectra were taken. (c) PL scan at 5 K with an example fit to five lorentzians. (d) Energies of all observed PL emission in scans taken (d) at the MoSe₂ - NbSe₂ interface and (e) on bare-MoSe₂region plotted *versus* temperature. 1 sigma error bars are included. Marker colors in (d) match the fill colors for specific lorentzians in (c). The solid black line in panels (d) and (e) is a fit to Eq. (6.1).

of the semiconductor band-gap [246, 270],

$$E_g(T) = E_g(0) - S\langle \hbar \omega \rangle \left[\coth\left(\frac{\langle \hbar \omega \rangle}{2k_B T}\right) - 1 \right], \qquad (6.1)$$

where $E_g(0)$ is the transition energy at T = 0 K, S is a dimensionless constant describing the strength of the electron-phonon coupling and $\langle \hbar \omega \rangle$ represents the average acoustic phonon energy involved in electron-phonon interactions. The values obtained are included in Table 6.1 and are very close to prior work on the same material [246].

Temperature-dependent PL measurements on the NbSe₂ - MoSe₂ interface for Sample 3 are shown in **Figure 6.9b** with an intensity map. We see five distinct transition here. labelled as - L1, $X^{-}(2)$, $X^{-}(2)$, $X^{0}(2)$, $X^{0}(1)$, in ascending order of their PL emission. We straight away observe that L1 is thermally quenched above 60 K in contrast to \mathbf{X}^0 and $\mathbf{X}^$ doublets which are observable very much beyond $T \ge 60K$. This is in agreement with the localized exciton picture, where a thermal energy greater than the trapping potential can eject confined charge carriers through non-radiative mechanisms. Sample 3 has been subjected to an extensive cleaning procedure and is encapsulated in hBN, which results in the observation of five peaks in total compared to samples fabricated on Si/SiO₂ substrates. We fit each spectrum to a combination of lorentzian functions with a constant background from 1.55 - 1.7 eV to extract the emission energy of the observed PL features. This is plotted in Figure 6.9 as a function of temperature for peaks assigned as L1, $X^{0}(1)$, $X^{0}(2)$, $X^{-}(1)$ and $X^{-}(2)$ in keeping with the moiré exciton picture [257] A representative lorentzian fit is shown for the 5 K spectrum in Figure ??b, where the fill color of each peak corresponds to the marker colors in Figure 6.9d. We are able to fit all five observed peaks to this functional form and summarize the fitting parameters in Table 6.1. The obtained values for the dominant X⁰-like and X⁻-like peaks agree reasonably well with previous study of pristing ML-MoSe₂[246]. L1 exhibits the highest value of S, which suggests substantial electron-phonon coupling and is consistent with its rapid thermal quenching.

Temperature-dependence of the integrated PL intensity provides key insight into the localized nature of L1. In TMDs with inherent defects and vacancies, thermal disassociation of trapped exciton can sometimes elevate the number of charge carriers available for radiative recombination, giving a rise in the PL intensity up to a certain thermal threshold. We find that $X^{0}(1)$ exhibits such a non-monotonic temperature-dependent intensity at the interface

Peak ID	E_g (eV)	S	$\langle \hbar \omega \rangle ~(\text{eV})$
-			
$\mathrm{X}^{0}(1)$	1.646	2.41	0.018
$X^{0}(2)$	1.634	2.17	0.017
$X^{-}(1)$	1.628	1.76	0.012
$X^{-}(2)$	1.62	1.66	0.014
L1	1.60	7	0.017

Table 6.1: Best-fit parameters of Equation 6.1 to the temperature-dependent emission energies of Sample 3 (Figure 6.9d).

Table 6.2: Best-fit parameters of the temperature-dependent emission energies in Control sample (Figure 6.9) to Equation 7.2 in the manuscript.

Peak ID	E_g (eV)	S	$\langle \hbar \omega \rangle \ (eV)$
0			
X^0	1.66	2.40	0.019
X^-	1.63	2.02	0.015

as shown in **Figure 6.10b**. For all other peaks, we observe a monotonic behavior that follows the expectation for localized excitons. Temperature-dependence of the integrated PL intensity can be fit with a modified Arrhenius formula [130, 271, 272],

$$I(T) = I(0) \frac{1 + Ae^{-E_{a1}/k_B T}}{1 + Be^{-E_{a2}/k_B T}},$$
(6.2)

where I(0) is the integrated PL intensity at T = 0 K, k_B is the Boltzmann constant, A and B are fitting parameters used to determine the ratio of radiative to non-radiative recombination rates of charge carriers. E_{a1} is the activation energy that increases the number of carriers available for recombination and E_{a2} is the activation energy for the normal thermal quenching process at higher temperatures through non-radiative channels.



Figure 6.10: (a) Temperature-dependent integrated PL intensity of the peaks in (b). The black line is a fit to Eq. (7.2). (d) A zoom-in of the temperature-dependent integrated PL intensity from 30 K to 130 K. A crossover between high and low energy moiré excitons and trions is observed.

 $X^{0}(1)$ is fit extremely well by this model as shown in **Figure 6.10b**. For the remaining peaks in **Figure 6.10b**, all of which lie at lower emission energy, we obtain good fits to **Equation 7.2** when A = 0 implying remaining peaks are not enhanced by the thermal activation of additional carriers. This suggests that it is likely the thermal quenching of L1 that provides the carriers responsible for the rise in the temperature dependent intensity of $X^{0}(1)$. The fitting parameters for the temperature-dependent integrated PL intensity data are summarized in Table 6.3. The values of $E_{a1} = 0.12$ meV and $E_{a2} = 37$ meV for $X^{0}(1)$ and $E_{a2} = 23$ meV for $X^{-}(1)$ obtained from our fits agree with other studies of similar TMDs [130,273,274], whereas for L1, a value of $E_{a2} = 8.58$ meV is extracted. We note that E_{a2} may be interpreted as the binding energy for $X^{-}(1)$, $X^{-}(2)$, $X^{0}(2)$, and L1. For $X^{0}(1)$, the model in **Equation 7.2** is not well constrained over the measured temperature range as the neutral exciton is present well above 300 K. Therefore E_{a2} is only a lower-bound of the expected $X^{0}(1)$ binding energy. Furthermore, the value *B*, which relates to the ratio of non-radiative decay rate in the high-temperature limit to the radiative decay rate is also higher for L1 compared to $X^0(2)$ and $X^-(2)$ peaks indicating a more favourable, nonradiative recombination process for confined states than the intralayer moiré states ($X^0(2)$ and $X^-(2)$) which are strongly protected by the interfacial geometry at the contact region. For $X^0(1)$ and $X^-(1)$, the higher values of *B* are a natural consequence of abundance of free exciton and trion states that undergo non-radiative recombination due to scattering and exciton-exciton annihilation processes. We have included similar analysis for a ML-MoSe₂ sample in **Figure 6.10a**, where we cover a wider temperature range (5 K - 300 K) and observe no anomalous increase in the intensity of X^0 with increasing temperature.

Table 6.3: Best-fit parameters of **Equation 7.2** to the temperature-dependent integrated PL intensity of Sample 3 (**Figure 6.10b**)

Peak ID	$E_{a1} (\mathrm{meV})$	$E_{a2} \ (\mathrm{meV})$	A	В	I(0)
0					
$X^0(1)$	0.12	37.14	0.56	342.47	86209
$X^0(2)$	-	6.14	-	11.11	26461
$X^{-}(1)$	-	23.75	-	171.37	92999
$X^{-}(2)$	-	10	-	9.10	76293
L1	-	8.58	-	64.80	110334

Table 6.4: Best-fit parameters of the temperature-dependent integrated PL intensity in Control sample (Figure 6.10) to Equation 6.1 in the manuscript.

Peak ID	$E_{a1} (\mathrm{meV})$	$E_{a2} (\mathrm{meV})$	A	В	I(0)
\mathbf{X}^{0}	_	23.5	0	54.15	243124
X^-	-	27	0	412.5	1.88147×10^{6}

Finally, we point out an interesting crossover in the intensities of the moiré intralayer excitons. In **Figure 7.3d**, we present the high temperature region (30 K $< T \leq 130$ K) of the temperature-dependent integrated intensity data. At low temperatures we find that X⁰(1) and X⁻(1) dominate the spectrum. However, as temperature is increased, X⁰(2) and X⁻(2) gradually gain spectral weight and replace their higher energy partners. This behavior is consistent with the prior study of moiré intralayer excitons in MoS₂ - MoSe₂ heterobilayers[257] where a similar intensity crossover was observed and attributed to thermallyassisted relaxation of X⁰(1) and X⁻(1) into lower energy regions of the moiré potential. Our measurements are consistent with this mechanism and generally support our assignment of these features as moiré intralayer excitons. It is notable that prior studies have only explored moiré excitons in carefully assembled bilayer vdW heterostructures. The observations presented here indicate that moiré excitons should generally be expected between well-coupled layered materials, even when one is a bulk vdW metal.

6.6.2 Power-dependent measurements

Power-dependent measurements are presented for Samples 1 and 3 in Figure 6.11a,b. We expect for the excitonic species a scaling of $I \propto P^{\alpha}$, where I is the integrated PL intensity and P is the excitation power and $\alpha \approx 1$ for single exciton complexes and < 1 for localized trap-states [87, 269]. For ease of analysis, we plot natural logarithms of the integrated PL intensity and excitation laser power and extract the coefficient (or slope) α for L1, X⁰ and X⁻ peaks. In both cases (Sample 1 and Sample 3), we observe that X⁰ and X⁻ peaks scale linearly with increasing power and the obtained values of α closely approximate to unity. In order to illustrate the sublinear behavior of the L1 peak, we have divided the power axis in two different regimes, and we fit its behavior in each range by a standard linear fit. In case of Figure 6.11, the low-power regime ($0 < P < 50 \ \mu$ W) shows an α value that closely matches that of the X⁰, followed by the high-power regime ($50 \ \mu$ W $\leq P \leq 800 \ \mu$ W) where α is < 1. Similar trends are observed for Sample 1 across the low- and high-temperature ranges. This is typical of a trapped-state, where increased carrier injection saturates the



Figure 6.11: Natural logarithm of the integrated intensity of L1, X⁰ and X⁻ features versus the natural logarithm of the laser power at the NbSe₂ - MoSe₂ interface in (a) Sample 1 and (b) Sample 3. The black solid and dotted lines are power-law fits to the data with the power α indicated for the high power and low power regions. $\alpha < 1$ for L1 at high powers.

trap site and manifests as a change in the behavior of PL intensities at higher laser power, depicting an overall sublinear trend.

6.7 Conclusion

In this study we have identified a spectral feature, L1, in NbSe₂ - MoSe₂ vdW heterostructures. We attribute this feature to recombination of localized excitons trapped by in-plane confinement potentials formed between NbSe₂ - MoSe₂ and MoSe₂. Both our firstprinciples calculations as well the temperature- and power-dependent PL measurements support this interpretation. Surprisingly, even under widely different fabrication procedures of our heterostructures, L1 remains robust and appears consistently at ≈ 1.6 eV. We compare our findings to other low-energy emissions observed in MoSe₂-based vdW heterostructures, and show that L1 is distinctive to the geometry discussed in this manuscript, but may occur in a variety of metal-semiconductor heterostructures depending on the band offset between the pristine and capped semiconducting TMD. Moiré intralayer excitons are observed for hBN-encapsulated nano-squeegeed samples and suggest that moiré excitons should be generally expected in vdW heterostructures, even when one of the constituents is a bulk metal. The consistent PL energy of L1 may solve an outstanding problem of spectral inhomogeneity in 2D single-photon sources, where photon energies vary due to the different strain and defect induced confinement potentials. Since metal-semiconductors interfaces are common building blocks for many optoelectronic devices [275, 276], we also envision extending our findings to systems which would explicitly take into account spin and valley degrees of freedom. For example, preserving similar robust optical properties in ferromagnetic metal-semiconductor heterostructures could be an important step in realizing two-dimensional spin-lasers that in common III-V semiconductors can exceed the performance of the best conventional lasers [277]. Furthermore, with high-quality and tunable interfacial properties, similar heterostructures would be an important platform in designing proximitized.

6.8 Supplementary Information

6.8.1 Additional samples

Here, we present white light images of NbSe₂ - MoSe₂ heterostructure samples along with the respective PL spectra taken on (black star) and off (red star) the interface. Samples in panel (a), (b), (d) and (f) are fabricated directly on Si/SiO₂ substrates. Of these, only samples 6 and 8 are later annealed at 200 °C for 5 hours under vacuum. Sample 7 is fabricated on bulk-NbSe₂ with ML-MoSe₂ deposited on top. The heterostructure is then squeegeed, capped with few-layer hexagonal boron nitride (hBN), and annealed at 200 °C for 5 hours under vacuum. Sample 9 is similar to sample 7, but is capped with bulk-NbSe₂ rather than hBN, resulting in a NbSe₂ - MoSe₂ - NbSe₂ heterostructure. L1 is present in all samples which supports the band-bending model presented in the main text.



Figure 6.12: (a)-(f) White light images of several NbSe₂ - MoSe₂ heterostructures. Next to each image are photoluminescence (PL) spectra taken at positions marked by stars, color coded to match line color. L1 is observed in all samples.

6.8.2 Effect on MoSe₂ PL by AFM 'nano-squeegee'

This section discusses the effect of 'nano-squeegee' procedure on the PL spectra of ML MoSe₂ deposited on hBN. The 'nano-squeegee' cleaning procedure uses an AFM tip to physically remove polymer residue out from between layers in a vdW heterostructure [106].



Figure 6.13: Integrated PL intensity maps for sample 3 (a) before and (b) after 'nano-squeegee' cleaning using the AFM. (c) Individual PL spectra before and after 'nano-squeegee' illustrating the improvement in PL linewidths and the suppression of broad, low-energy defect PL.

We compare hyperspectral maps of the integrated PL intensity for sample 3 before (**Figure 6.13a**) and after (**Figure 6.13b**) this cleaning step. We observe an overall reduction in the integrated PL intensity that is primarily due to the reduction in defect PL emission. This change is most obvious in Figure 6.13c, where X^0 and X^- are brighter and sharper than before the 'nano-squeegee' cleaning indicating a uniform and residue-free interface.

6.8.3 Tears/folds in ML-MoSe₂

Low-energy PL features can appear due to folds and tears in mechanically exfoliated TMD flakes and at the edges of chemical vapor deposition-grown ML TMDs [278–280]. These features are typically either quantum dot - like with ultra-sharp linewidths or extremely broad due to emission from a distribution of defect sites. The structural deformations associated with folds, wrinkles, and tears locally lower the bandgap and therefore



Figure 6.14: (a) Atomic force microscopy (AFM) image of sample 1 showing tears in the lower left region of ML-MoSe₂. (b) Normalized PL spectra from various positions across the sample in (a) showing presence of L1 only at the NbSe₂ - MoSe₂ interface. (c) AFM image ML-MoSe₂ sample with tears and folds. (d) Normalized PL spectra from various positions in (c) showing presence of L1-Like feature at the top tear of ML-MoSe₂ flake, but not at any other tear or fold on this flake.

behave as an exciton trap [281–283]. Here we distinguish these PL features from L1, which arises from electronic modulation at the metal-semiconductor contact. We present PL spectra taken on sample 1 and sample 11 across various locations that have visible tears and folds. We find that for sample 1, L1 only appears at the NbSe₂ - MoSe₂ contact and is absent at all visible regions of $MoSe_2$ with structural deformations. For sample 11, we observe multiple locations where the ML-MoSe₂ has been torn and folded. PL spectra at these locations are unremarkable other than at Position 1 where an L1-like feature is present. The lack of a consistent observation of L1 at these various structural deformations contrasts with our measurements of L1 in 70% of our samples and supports our model of a band-bending induced confinement potential.

6.8.4 Low-temperature reflectance contrast measurements

We present here a comparison of the PL and reflectance contrast (RC) measurements performed at 5 K on the fully hBN-encapsulated heterostructure, sample 3. These measurements were performed after the sample had undergone a 'nano-squeegee' cleaning treatment and vacuum annealing. Figures 7.10(b-d) represent scans taken on, off and at the edge of the interface marked by the positions of the stars in the optical image. For all PL spectra in panels (b-d) we observe X^0 and X^- along with L1 at the NbSe₂ - MoSe₂ interface in **Figure 7.10c**. RC spectra at corresponding positions clearly show features associated with X^0 in ML-MoSe₂. X^- is absent in the RC spectra which is in agreement with other studies of undoped TMDs [246,284,285], however, gate-dependent reflectivity measurement have revealed X^{-} presence with increased *n*-doping as well as in inherently *n*-doped MLs [286, 287]. In case of **Figure 7.10d**, PL scan at the interface shows a more dominant $X^$ emission, for which we observe a weak transition in the RC data as well. The weak signal to noise ratio (SNR) for the scans in (b) is complicated by the reflective nature of the metallic bulk-NbSe₂ capping flake. In panels (e) and (f), we include spatially-mapped PL and RC integrated intensity data across the a wide area of sample 3. We can observe similarity in the spatial homogeneity of PL and RC data across the sample, with differences in the extent attributable to the larger spot size used in RC measurements.



Figure 6.15: (a) White light image of hBN-encapsulated sample 3. (b-d) Reflectance contrast and PL spectra at the locations marked by colored stars in (a). Black and blue colored stars are taken at the NbSe₂ - MoSe₂ interface and its edge, respectively, while the red star is located on ML-MoSe₂. The reflectance contrast spectra in (b) ML-MoSe₂ and (c) the NbSe₂ - MoSe₂ interface edge only show X⁰ while both X⁻ and X⁰ appear (d) on the interface. L1 does not appear in any reflectance spectra implying it is not an intrinsic exciton state. Low-temperature hyperspectral maps of the (e) integrated reflectance contrast and (f) the integrated PL intensity. Discrepancies in the size of the reflectance map *versus* the PL map are due to the larger spot diameter in the reflectance experiment.

Chapter 7: Project Xi (Ξ) - Activation of finite momentum excitons by proximitized charge density waves

7.1 Introduction

Two-dimensional (2D) material interfaces in van der Waals (vdW) heterostructures provide a fascinating playground to explore proximity effects [288]. The relaxation of lattice constraints on heterostructure assembly allows for the arbitrary stacking of 2D materials [289]. These interfaces may, in some cases, support emergent states absent from the parent compounds, with superconductivity in twisted bilayer graphene and moiré excitons in transition metal dichalcogenides (TMDs) serving as remarkable examples [21,258,290,291]. Many studies of vdW heterostructures incorporate semiconducting TMDs as an active component. This commonality is due to the availability of high-quality samples, well-established exfoliation procedures [254,255], and the existence of tightly-bound 2D excitons [59].

The zoology of excitons in monolayer (ML) semiconductors is vast: neutral (X^0) and charged excitons or trions (X^- or X^+) [59, 60, 246, 292], neutral and charged biexcitons [87, 88, 274, 293] and dark exciton states [248, 294–296] have all been observed and exhaustively studied in semiconducting TMDs. The 2D nature of TMD excitons also renders them highly sensitive to the local dielectric environment [103, 297–301] allowing for a remote, contact-free probe of interface characteristics in vdW heterostructures. For instance, semiconductor hetero-bilayer and homo-bilayer heterostructures exhibit new PL emission peaks from interlayer excitons and splitting of exciton peaks due to the moiré potential [109, 257, 263, 291, 302]. Proximity effects between 2D magnets and semiconductors lead to large valley splittings [303, 304], and magnetic manipulation of exciton PL energy, intensity, and selection rules [55, 288, 305, 306]. Exotic correlated insulating states such as Wigner crystals and Mott insulators in twisted TMD semiconductor heterostructures are also observable in PL spectra [307–309]. However, there have been no studies exploring the impact of similar electron correlated phases such as charge density waves (CDWs) on PL in vdW heterostructures.

In Project Ξ , we investigate optical signatures of interlayer coupling between the semiconductor MoSe₂ and the putative excitonic insulator 1T-TiSe₂ [310–314], which hosts a commensurate 2 × 2 × 2 CDW state below 200 K. We find that the CDW alters the manifold of optically-active excitons at the TiSe₂ - MoSe₂ interface, which results in a new PL peak above X⁰. This feature, referred to as H1, appears in the MoSe₂ PL spectrum with a linewidth comparable to X⁰. While lower-energy PL sidebands are relatively common in TMDs due to phonon replicas and exciton localization [90,315–318], these observations are the first such detection of a higher-energy PL sideband. Detailed temperature-, power-, and spatially-resolved PL measurements on multiple heterostructures demonstrate that H1 has an origin consistent with a native exciton state rather than a localized exciton or defect state. However, H1 disappears at the TiSe₂ CDW temperature which suggests these two phenomena are closely linked. We have identified multiple plausible scenarios and discuss them in detail, although none are able to explain all aspects of our observations. Interactions between excitons and CDWs provide a fresh challenge to the theoretical community and a novel method for engineering excitons in 2D materials.

7.2 $TiSe_2$ - $MoSe_2$ heterostructures - Crystal growth and sample fabrication

MoSe₂ crystals were grown by the chemical vapor transport (CVT) method using polycrystalline MoSe₂ powder (≈ 1 g) and SeBr₄ transport agent (≈ 0.1 g). The source and growth zones in a vacuum-sealed 20 cm long quartz ampoule were kept at 980 °C and 890 °C, respectively, for 7 days. The procedure for CVT-grown TiSe₂ crystals is outlined in Ref. 310. Bulk-hBN flakes were mechanically exfoliated and transferred on O₂ plasma cleaned Si/SiO₂ substrates. MLs of 2H-MoSe₂ obtained through mechanical exfoliation were subsequently transferred on an identified hBN flake. For both materials, the transfer process was done using the PDMS-based dry viscoelastic stamping method [105]. This method has been known to leave polymer residue between the interface of two TMDs deposited during the transfer process, but has proven to be optimal for fabricating heterostructures [254]. To create clean interfaces, an AFM-based 'nano-squeegee' procedure was employed [106]. This involves the use of a standard AFM tip to push out polymer residue deposited between the two TMDs in a vertical heterostructure. We were able to use the same method to also remove surface residue present on the ML-MoSe₂ flake, using a 7 N/m spring constant tip and a contact force of 140 nN. Bulk TiSe₂ is then brought into contact with the sample using the same dry-transfer technique as done for ML-MoSe₂. The sample was additionally vacuum annealed at 200 °C for 5 hours to improve coupling.

7.3 $TiSe_2$ - $MoSe_2$ heterostructures - Optical characterization

Optical microscope images of two TiSe₂ - MoSe₂ vdW heterostructures termed Sample 1 and Sample 2, respectively, are presented in **Figures 7.1a** and **7.1c**. These samples are assembled by a modified viscoelastic method [105] that incorporates atomic force microscope (AFM) cleaning [106]. The black dashed line outlines the ML-MoSe₂ flake in each sample. Representative low-temperature (5 K) PL spectra on (black) and off (red) the interface are shown in **Figures 7.1b** and **7.1d** for the two samples respectively. Emission from the MoSe₂ $X^- (\approx 1.62 \text{ eV})$ and $X^0 (\approx 1.65 \text{ eV})$ states agrees with prior observations in both energy and linewidth [104, 246, 248–250].

7.3.1 A new optical feature emerges - H1

The most obvious difference between on (black) and off (red) spectra is the appearance of The interface PL spectra contains a previously unobserved feature, referred to as H1, at ≈ 1.68 eV. H1 is comparable to X⁰ in both intensity and linewidth for Sample 1, while



Figure 7.1: Samples 1 and 2 fabricated with an HBN base on top of a Si-SiO₂ substrate. The interface in Sample 1 and the 2^{nd} interface in Sample 2 have undergone an intermediate AFM 'Nano-squeegee' cleaning procedure. Optical microscope images of TiSe₂ - MoSe₂ vdW heterostructures (a) Sample 1 and (c) Sample 2. The black dotted line outlines ML-MoSe₂ layer. Low-temperature (5 K) photoluminescence (PL) spectra taken on (black) and off (red) the interface for (b) Sample 1 and (d) Sample 2. These locations are denoted by red and black stars in panels (a) and (b), respectively. In addition to the X⁰ and X⁻ emission observed in ML-MoSe₂, the H1 PL peak appears at ≈ 1.68 eV on the interface.

being weaker and broader in Sample 2. Further, its energy with respect to the X^0 peak remains remains spectrally separated by $\approx 24\text{-}32$ meV, and localized to the TiSe₂ - MoSe₂ interface. H1 is also robust to the quality of the interfacial contact between the two TMDs, as demonstrated by its presence in the two heterostructures created in this study, with three interfaces and relatively different angular stacking configurations.

7.3.2 Hyperspectral imaging of the interface

The 5 K PL spectra also show evidence of an anti-correlation between H1 and X^- . Spatially resolved PL maps of the interface allow us to explore this behavior further and connect it to interface quality. We do this by examining the integrated intensity ratios X^-/X^0 (Figures 7.2e and 7.2f) and H1/X⁰ (Figures 7.2g and 7.2h). Additionally, H1 and $X^0 + X^-$ integrated intensities are plotted separately in Figures 7.2a and 7.2b respectively. For Sample 1, the ratio of X^-/X^0 (Figure 7.2e) varies between 1-2 over most of the MoSe₂ flake with a notable jump at the crack on the bottom left quadrant of the map. On the heterostructure itself, this ratio plummets to well below 1 indicating the absence of



Figure 7.2: Spatially-mapped photoluminescence (PL) integrated intensity of the sum of exciton (X^0) and trion (X^-) peaks (1.6 eV - 1. 66 eV) for (a) Sample 1 and (b) Sample 2. Spatially-mapped PL integrated intensity of the H1 peak (1.66 - 1.7 eV) for (c) Sample 1 and (d) Sample 2. Spatially mapped X^-/X^0 integrated intensity ratio across the interface showing variations in the X^- intensity for (e) Sample 1 and (f) Sample 2. Spatially mapped H1/X⁰ integrated intensity ratio across the interface showing changes in H1 intensity in (g) Sample 1 and (h) Sample 2. The ratio X^-/X^0 correlates with changes in H1/X⁰ intensity at the junction.

free charges that can participate in trion formation. The connection of the X^-/X^0 ratio to charge transfer is well established in numerous reports [88, 246, 292, 319] and, since the transfer efficiency is exponentially dependent on distance, can be used as a proxy for interlayer spacing. MoSe₂ tends to be *n*-type as-exfoliated and TiSe₂ band alignment suggests it will act as an electron acceptor [44]. Therefore, the near absence of X⁻ emission on the Sample 1 overlap region suggests good coupling between the TiSe₂ - MoSe₂ flakes. For Sample 2 the X⁻/X⁰ ratio (**Figure 7.2f**) is larger on the MoSe₂ flake, varying between 3-6, which may originate from unintentional doping during the heterostructure fabrication process. On the TiSe₂ - MoSe₂ overlap we observe a reduction in X⁻ intensity co-localized with H1, but smaller than in Sample 1. From this we suggest that interlayer coupling is weaker in Sample 2 which could be due to contaminants or partial oxidation of the TiSe₂ flake. The remaining analyses will therefore focus on Sample 1, unless otherwise noted.

7.3.3 Temperature-dependent measurements at the interface

In this section we discuss temperature- and power-dependent PL measurements on and off the TiSe₂ - MoSe₂ interface. **Figure 7.3a** shows a temperature-dependent PL intensity map from 5 K- 265 K taken on the interface in Sample 1. A similar data set for Sample 2 is included in the Supplementary Information section (**Figure S2**). Here, the 5 K PL emission spectrum is the same as in **Figure 7.1b** with prominent, sharp emission from X⁰ and H1, heavily reduced X⁻ emission and a broad feature originating from defects. With increasing temperature, PL from defect excitons and X⁻ decreases and becomes unobservable for T > 70 K in agreement with prior studies [320–323]. Both X⁰ and H1 are visible at elevated temperatures, but are difficult to distinguish above ≈ 190 K. We obtain a better understanding through analysis of the PL lineshape for ML-MoSe₂ and TiSe₂ - MoSe₂. **Figure 7.3b** compares PL spectra at selected temperatures taken on (red curve) and off (black curve) the TiSe₂ - MoSe₂ interface. The presence of the TiSe₂ capping layer causes X⁰ to blueshift due to the different dielectric constant [300, 301]. To facilitate comparison, we eliminate this shift by adjusting the energy axis of the TiSe₂ - MoSe₂ spectrum so that the X^0 PL peaks overlap. The energy shift amounts to ~ 1-3 meV across the entire temperature range. H1 is visible as a weak shoulder of X^0 between 190 K and 220 K. Above these temperatures, the PL lineshape on and off the interface is identical, indicating the driving mechanism behind H1 has dissipated. We also fit each PL spectrum to a sum of



Figure 7.3: (a) Temperature-dependent PL map on the TiSe₂ - MoSe₂ interface of Sample 1. The dashed lines are guides to the eye and the 5 K PL spectrum beneath the map labels the optical transitions. T_{CDW} for bulk TiSe₂ is indicated by the horizontal white line. (b) Lineshape analysis of PL spectra taken on (red) and off (black) the TiSe₂ - MoSe₂ interface. The interface spectra have been shifted to align the X⁰ emission energies between the two curves. (c) Energy separation between H1 and X⁰ versus temperature for two separate runs (red, blue), each consisting of a warming (W, circles) and cooling (C, squares) curve. $1-\sigma$ error bars from fits to the PL spectra are included. The X⁰-X⁻ is included for ML-MoSe₂ to illustrate the difference from H1. (d) Log-log plot of the PL integrated intensity versus excitation laser power. The solid black lines are power-law fits to the data.

Lorentzian functions and extract the temperature-dependent peak parameters for H1, X⁰, and X⁻. The energy splitting, H1–X⁰, is shown in **Figure 7.3c** over two cooling and warming runs that extend up to 200 K. In both cases the energy separation between H1 and X⁰ decreases with temperature until 200 K after which it is difficult to obtain a reliable fit. The temperature window of 190 K – 220 K is apparently crucial to H1 and is known to be important for TiSe₂. Bulk 1T-TiSe₂ undergoes a 2 × 2 × 2 commensurate-CDW transition in the range of $T_{CDW} \approx 200$ K - 210 K, as observed in a variety of optical and electronic measurements [2, 310, 310, 324, 325]. The CDW transition opens a band gap at the TiSe₂ M point in the Brillouin zone (BZ) with an associated order parameter well described by Bardeen-Cooper-Schrieffer (BCS) model [325]. The observed correlation of H1 with T_{CDW} suggests a close relationship between H1 in MoSe₂ and the CDW in TiSe₂.

7.3.4 Power-dependent measurements at the interface

Power-dependent PL measurements provide further insight into the nature of H1, as presented for Sample 1 in **Figure 7.3d** and for Sample 2 in the Supporting Information (**Figure 7.9**). PL intensity generally scales with power as $I_{PL} \propto P^{\alpha}$, where I_{PL} is the integrated PL intensity and P is the excitation power. The exponent $\alpha \approx 1$ for free excitons and > 1 for multiexcitons [87]. Localized exciton states exhibit a more complicated behavior. At low powers $\alpha \sim 1$ but then becomes sublinear as the localized states are saturated [323]. These behaviors are observed in **Figure 7.3d** where we plot the natural logarithms of I_{PL} and P. Linear fits to this data allow for the extraction of α . We find that both X⁰ and H1 have an $\alpha \approx 1$, with the value for H1 being somewhat lower, suggesting free exciton characteristics. As expected, the defect band first exhibits $\alpha \approx 1$ at low powers and then shows signs of saturation with $\alpha \approx 0.7$. While α for H1 is lower than would be expected for a free exciton, the absence of saturation is more consistent with this interpretation.

7.3.5 Raman measurements of the CDW phase at the interface

Raman spectroscopy can probe the square of the CDW order parameter directly, since the intensity of the symmetry-forbidden modes appears in the second order of the ionic displacements of the high-symmetry positions. Raman measurements performed at the TiSe₂ - MoSe₂ interface in the range of 5 K - 265 K are shown in **Figure 7.4a**. The 5 K Raman spectra show the CDW modes at E_g^{CDW} (70 cm⁻¹) and A_g^{CDW} (108 cm⁻¹), as well as normal TiSe₂ lattice modes at 132 cm⁻¹ and 200 cm⁻¹ of E_g and A_{1g} symmetry, respectively [326, 327]. The MoSe₂ A_{1g} mode is also visible at 245 cm⁻¹ and is related to out-of-plane vibrations [328]. **Figure 7.4b** plots the temperature-dependent shifts of all TiSe₂ modes relative to their frequency at 5 K. The 135 cm⁻¹ mode is largely unaffected by temperature changes, blueshifting slightly as temperature is lowered and then stabilizing. The 200 cm⁻¹ mode is insensitive to the CDW transition and its anharmonicity can be understood by a combination of optical phonon decay and temperature-dependent changes in the lattice constants [136]. This is described by Equation (7.1) (solid black line in **Figure 7.4b**).

$$\Delta(\omega(0), T) = \omega_0 + A\left(1 + \frac{2}{e^x - 1}\right)$$
(7.1)

Here, $x = \hbar \omega_B / 2k_B T$, ω_0 is the 0 K harmonic frequency and A represents the anharmonic contributions to the frequency of 200 cm⁻¹ optical mode as it decays into two acoustic phonons. The obtained value for A = -1.85 cm⁻¹ is within the ballpark of similar phonon anharmonicity studies done on TMDs [67,329] The CDW modes at 70 cm⁻¹ and 109 cm⁻¹ redshift and broaden with increasing temperature. These modes are unresolved above T= 100 K, which is well below T_{CDW} . This behavior is commonly attributed to quantum fluctuations of the density wave [330]. Integrating the Raman intensity over the spectral range encompassing the CDW modes allows us to monitor the CDW up to the transition



Figure 7.4: (a) Temperature-dependent Raman spectra taken on the TiSe₂ - MoSe₂ interface in Sample 1. (b) Shift in the observed TiSe₂ Raman modes relative to the 5 K value. $1-\sigma$ error bars from spectral fitting included. The solid black line is fit to Equation (7.1) that accounts for optical phonon decay processes (c) Normalized integrated Raman intensity of the CDW modes (green diamonds) and lattice modes (blue squares) versus temperature. The dotted magenta line indicates T_{CDW} . The solid black line is a fit to Equation (7.2).(d) Extracted amplitude of the observed Raman modes. (f) Extracted full width half-maximum (FWHM) of the observed features.

temperature (Figure 7.4c). Thermal melting of the CDW is expected to follow a temperature dependence consistent with the BCS treatment where the order parameter $\Delta(T)$ can be given as [331]

$$\frac{\Delta^2(T)}{\Delta^2(0)} \propto \tanh^2 \left(\alpha_{BCS} \sqrt{1 - \frac{T}{T_{CDW}}} \right), \tag{7.2}$$

This model fits the integrated intensity data well up to T_{CDW} as shown in Figure 7.4c.

7.4 On the origin of H1

Investigations into the properties of 2D excitons in TMDs have covered remarkable ground over the past decade [41,59,332,333]. Despite these remarkably comprehensive studies, no observations of vdW heterostructures have shown PL satellites above X^0 . Therefore, we explore here three possible mechanisms that could be responsible for H1.



Figure 7.5: (a) PL integrated intensity ratios $H1/X^0$ (red circles) and X^-/X^0 (blue diamonds) versus temperature. (b) $H1/X^0$ integrated intensity ratio versus the laser power (lin-log scale). (c) Overlay of the energy separation between H1 and X^0 for Sample 1, the integrated Raman intensity of the CDW modes and the TiSe₂-CDW superlattice peak extracted from neutron scattering data in Ref.[2], all as a function of temperature.

Before proceeding with the analysis of potential microscopic interpretations of the new peak, we summarize key experimental observations. First, H1 lies 25–32 meV above X^0 with an intensity that differs between samples (**Figure 7.1**). Second, within a single sample the relative intensity of H1 to X^0 is temperature independent (Figure 7.5(a)). Third,

the energy difference between H1 and X⁰ follows the CDW order parameter Δ^2 . We illustrate this in **Figure 7.5c** by overlaying neutron scattering data from Ref.[2], the energy separation H1–X⁰, and the integrated intensity of the TiSe₂-CDW Raman features. Fourth, the intensity ratio H1/X⁰ decreases with increasing laser power (**Figure 7.5b**). And lastly, H1 and X⁻ are spatially anti-correlated (**Figure 7.1**).

7.4.1 Mechanism I: Activation of Forbidden/Dark Excitons

Semiconducting TMDs host numerous dark exciton states where optical recombination is forbidden by momentum conservation or symmetry. Density functional theory (DFT) calculations of MoSe₂ suggest a finite-momentum dark exciton lies 30 meV above X^0 [334] as shown in **Figure 7.5b**. This indirect exciton is formed from an electron residing at the Q(Q') valley and a hole at the K(K') valley. The indirect exciton has not been observed experimentally in PL, but resonant Raman measurements offers some evidence for dark excitons above X^0 [335]. While the energy of this exciton matches the energy of H1, a viable mechanism is required to provide the missing momentum needed for optical recombination of this dark state. Mechanism I explores how the interface between TiSe₂ and MoSe₂ could potentially activate such dark states by introducing a new spatial periodicity that violates quasimomentum conservation.

MoSe₂ and TiSe₂ form an incommensurate superstructure for most stacking configurations, which, formally, implies a full relaxation of quasimomentum conservation. In order to illustrate this, consider the MoSe₂ Bloch wave functions at the TiSe₂ - MoSe₂ overlap. We assume there is no hybridization between MoSe₂ and TiSe₂ wave functions, which is reasonable due to their large spatial separation. The quasimomentum can then be defined by the MoSe₂ lattice alone and the Bloch functions are $\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{g}} a_{\mathbf{k}+\mathbf{g}} \exp(i(\mathbf{k}+\mathbf{g}) \cdot \mathbf{r})$, where **g** is a MoSe₂ reciprocal lattice (r.l.) vector and $\mathbf{a}_{\mathbf{k}+\mathbf{g}}$ are the Bloch coefficients. The presence of the TiSe₂ lattice and CDW can be thought of as a periodic "defect" for MoSe₂ that enables scattering between the K and Q points. The matrix element of the associated potential for Bloch states is $\langle \psi_{\mathbf{Q}} | V(\mathbf{r}) | \psi_{\mathbf{K}} \rangle$, where **K** is a wavevector for any of the *K*-equivalent points and **Q** is a wavevector for any of the *Q*-equivalent ones (**Figure 7.6a**). $V(\mathbf{r})$ is the effective TiSe₂ defect potential, which can be expanded in the TiSe₂ r.l. vectors **t**. Note that the lattice parameter for TiSe₂ is 7.8% larger than MoSe₂, so that if we measure the reciprocal space in units of $2\pi/a_{\text{MoSe}_2}$, then for Mo the first r.l. vectors will be $\mathbf{g}_{1,2} = \{\sqrt{3}/2, \pm 1/2\}; \mathbf{g}_3 = \mathbf{g}_1 + \mathbf{g}_2$. For TiSe₂, the equivalent r.l. vectors $\mathbf{t}_{1,2,3}$ will be shorter by 7.8%. Using the expansion of $V(\mathbf{r})$ we obtain,

$$\begin{split} \left\langle \psi_{\mathbf{Q}} | V(\mathbf{r}) | \psi_{\mathbf{K}} \right\rangle &= \sum_{\mathbf{t}} \left\langle \psi_{\mathbf{Q}} | v_{\mathbf{t}} e^{i\mathbf{t}\cdot\mathbf{r}} | \psi_{\mathbf{K}} \right\rangle \\ &= \sum_{\mathbf{t}, \mathbf{g}, \mathbf{g}'} \left\langle a_{\mathbf{K}+\mathbf{g}} e^{i(\mathbf{K}+\mathbf{g})\cdot\mathbf{r}} v_{\mathbf{t}} e^{i\mathbf{t}\cdot\mathbf{r}} a_{\mathbf{Q}+\mathbf{g}'}^* e^{-i(\mathbf{Q}+\mathbf{g}')\cdot\mathbf{r}} \right\rangle \\ &= \sum_{\mathbf{t}, \mathbf{K}, \mathbf{Q}} a_{\mathbf{K}} a_{\mathbf{Q}}^* v_{\mathbf{t}} \left\langle e^{i(\mathbf{K}-\mathbf{Q}+\mathbf{t})\cdot\mathbf{r}} \right\rangle \\ &= \sum_{\mathbf{t}, \mathbf{K}, \mathbf{Q}} a_{\mathbf{K}} a_{\mathbf{Q}}^* v_{\mathbf{t}} \delta(\mathbf{K}-\mathbf{Q}+\mathbf{t}). \end{split}$$

In the last line the summation goes over all equivalent K and Q points. While, in principle, in an infinite lattice one can always find a triad $\mathbf{K}, \mathbf{Q}, \mathbf{t}$ wavevectors that closely satisfies the condition $|\mathbf{K} - \mathbf{Q} + \mathbf{t}| = \mathbf{0}$, the coefficients $v_{\mathbf{t}}$, and, to lesser extent, $a_{\mathbf{g}}$, rapidly decay (the form factor effect), and so this scattering process can only be efficient if t is small. This is shown in **Figure 7.6c** by the overlaid BZs of the MoSe₂ and TiSe₂ in the CDW phase.

Determining if the TiSe₂ "defect" potential can enable $K \rightarrow Q$ scattering requires matching $|\mathbf{t}|$ and $|\mathbf{K} - \mathbf{Q}|$. We have carried out DFT calculations of the TiSe₂ - MoSe₂ heterostructure to determine how this position is altered by interlayer coupling. The location of the Q valley is $\kappa = |\mathbf{Q} - \mathbf{\Gamma}|/|\mathbf{K} - \mathbf{\Gamma}|$, which are clustered around 0.55 ± 0.05 for multiple DFT runs. The magnitude of the smallest scattering vectors $\mathbf{K} - \mathbf{Q}$ are: $(1 - \kappa)/\sqrt{3}$, $(1 + \kappa)/\sqrt{3}$, $(\sqrt{1 - \kappa + \kappa^2})/\sqrt{3}$, $(\sqrt{1 + \kappa + \kappa^2})/\sqrt{3}$, $(2 - \kappa)/\sqrt{3}$ and $(\sqrt{4 - 2\kappa + \kappa^2})/\sqrt{3}$, where



Figure 7.6: (a) Brillouin zones (BZ) for the MoSe₂ lattice and the corresponding r.l. unit cell (gray). (b) Exciton dispersion in ML-MoSe₂ showing the direct KK(KK') and indirect KA transitions. (c) BZ of MoSe₂ overlaid on the CDW-TiSe₂ BZ showing the CDW wavevector scattering electrons between $K - \Lambda$ valleys in the MoSe₂ layer. (d) Lengths of the scattering vectors $| \mathbf{K} - \mathbf{Q} |$ in units of the MoSe₂ reciprocal lattice (r.l.) vectors (colored solid lines) compared to the length of the reciprocal lattice vectors of the undistorted (red dot) and CDW (blue dots) TiSe₂. The horizontal dashed lines are guides to the eye. The vertical dashed line is drawn to pass through $\kappa = 0.55$, to facilitate the comparison with the magnitude of the MoSe₂ wavevectors $|\mathbf{K} - \mathbf{Q}|$ and the smallest r.l. vector (dots) in TiSe₂.

the first two values correspond to scattering from Q to K or K', while the next two to scattering from Q' to K or K', and the last two to scattering into the next BZ. For $\kappa = 0.55$, in units of $2\pi/a_{\text{MoSe}_2}$, these are 0.260, 0.895, 0.501, 0.785, 0.832, and 1.033, respectively. At the same time, the smallest vector of the r.l. of TiSe₂ without the CDW is $t_1 = 0.928(2\pi/a_{\text{Mo}})$.

In Figure 7.6d we present the magnitude of the scattering wavevector $|\mathbf{K} - \mathbf{Q}|$ between

different K and Q points versus κ in MoSe₂. These are compared to the r.l. vectors of TiSe₂ in the normal (blue dots) and CDW (red dot) phases. The smallest TiSe₂ r.l. vector can only match one of the $|\mathbf{K} - \mathbf{Q}|$ values if κ is 0.607, which is far outside our DFT predictions. In the 2 × 2 × 2 CDW phase of TiSe₂, the magnitude of the r.l. vectors (τ_i) are shortened to : $\tau_1 = t_1/2$; $\tau_2 = t_1\sqrt{3}/2$; $\tau_3 = t_1$; $\tau_4 = \sqrt{7}/2t_1$. We find that particularly $\tau_2 = 0.804$ is close to the magnitude of one of the $\mathbf{K} - \mathbf{Q}$ vectors. This is shown by the red dot in **Figure 7.6d**. The mismatch is less than $0.019(2\pi/a_{Mo})$ and is reduced to zero for $\kappa = 0.59$, a value within the range of the DFT calculations.

Therefore we conclude that the CDW potential opens a new $K \rightarrow Q$ scattering channel. This would enable optical recombination of an indirect, finite momentum exciton resulting in the appearance of a new PL line at the same energy as H1 [334]. Future calculations taking into account the effect of the CDW-exciton coupling may be able to assess this scenario quantitatively, but such calculations are outside our current capabilities. This result explains the emission energy of H1, its disappearance at T_{CDW} , and its anticorrelation with X^- . However, this mechanism would also imply that H1–X⁰ (barring unrelated phenomena) to be *T*-independent and the H1/X⁰ intensity ratio to follow Δ^2 . Our observations indicate just the opposite (**Figure 7.5a** and **7.5c**). Furthermore, this mechanism cannot explain the decrease in the H1/X⁰ intensity ratio with excitation power in **Figure 7.5b**.

7.4.2 Mechanism II: Interlayer 2D TiSe₂ - MoSe₂ Exciton

Another intriguing possibility is the formation of an interlayer exciton by an electron in MoSe₂ and a hole in TiSe₂ layer as shown in **Figure 7.5a**. This is only possible due to the opening of the CDW band-gap in the low-temperature regime, but is inconceivable in the normal metallic phase. The intensity of such an exciton will be defined by (*T*-independent) interlayer tunneling, and the position will be, roughly, given by $E_c(MoSe_2) - E_F(TiSe_2) - E_{CDW}(TiSe_2)/2$. The energy gap, E_{CDW} , is proportional to the order parameter Δ^2 , and its value is unclear: experiments cite different numbers, most ARPES studies find the top

of the valence band to be separated from the Fermi level (*i.e.*, half the band gap) by 50–75 meV [325, 336], qualitatively consistent with the H1–X⁰ separation, and roughly following Δ^2 .



Figure 7.7: (a) Schematic of the interlayer exciton in $TiSe_2$ - MoSe₂ heterostructures, where in addition to the intralayer exciton in MoSe₂ layer, electrons and holes in separate layers can form bound states and combine radiatively. (b) Band alignment diagram for the same supercell, based on the projected Ti and Mo characters. The state with more Mo characters are depicted on the left hand side, with more Ti characters on the right hand side. (c) A schematic of a type-II band alignment at the $TiSe_2$ - MoSe₂ interface leading to an interlayer indirect transition in the CDW phase.

For this scenario to be realized the top of the Mo valence band (VB) at K should fall inside the CDW gap in $TiSe_2$ (or, equivalently, within a few tens of meV from the $TiSe_2$
Fermi energy, E_F , in the metallic phase). Our standard DFT calculations using a supercell with 2 × 2 periodicity in TiSe₂ and $\sqrt{7} \times \sqrt{39}$ in MoSe₂ (Ti₁₆Mo₁₉) show that E_F is about 230 meV above the MoSe₂ valence band. This is illustrated in **Figure 7.7b** with further details regarding the DOS calculation included in Supporting Information section. In this case, opening of the CDW band-gap as well as the fact that MoSe₂ VB lies below the E_F , satisfies the condition for type-II band-alignment, resulting a high probability for interlayer excitonic transitions to occur. Here, electrons in the K-valley of MoSe₂ can recombine with the holes at the *M* valley in TiSe₂ layer to result in H1 emission. At higher temperatures, as the CDW band-gap closes, no interlayer transition is allowed. This is shown in **Figure 7.7c**. So, while this naturally explains all five experimental observation, it also requires an assumption that the DFT calculations of the band alignment are off by 100–150 meV, which may be reasonable once the electronic correlations that drive CDW formation and the details of the vdW interface are properly included.

7.4.3 Mechanism III: Exciton-Phonon and Exciton-Plasmon Interaction

Exciton formation and recombination can in principle be assisted through coupling to a variety of bosonic excitations. Again focusing on the activation of a dark finite-momentum exciton (**Figure 7.8a**), the lowest energy phonon with the appropriate momentum has an energy of ~ 10 meV [337], so that the corresponding PL energy should be shifted down (phonon-assisted emission) from the momentum-dark exciton energy. This would suggest that H1 is a phonon replica of a higher energy exciton, either symmetry forbidden or momentum-indirect. However, this mechanism is unlikely considering that it is intrinsic to MoSe₂ and cannot explain the role of the TiSe₂ CDW. In principle, interlayer coupling could allow TiSe₂ phonons to create exciton-phonon replicas in MoSe₂. H1 should in this case emerge at higher temperature if TiSe₂ phonons are involved and the replica would show additional temperature dependence compared to X⁰, in contradiction with our observation [130, 271, 272]. An additional possibility regarding the activation of a finite-momentum exciton by coupling to TiSe₂ is the presence of a distinct low-energy plasmon (**Figure 7.8c**).



Figure 7.8: (a) Excitonic relaxation processes in ML-MoSe₂. The photoexcited hot-excitons thermally relax through a series of phonon emission events to the lowest energy states, including transition from the indirect KA valley to the direct KK valley. (b) Exciton-phonon and exciton-plasmon interactions can provide the necessary momentum for the excitons to scatter between K - Λ valley. In case of exciton-phonon interactions, there doesn't exist a low-frequency phonon with sufficient momentum and energy to scatter excitons between the two valleys. In case of exciton-plasmon interactions, we have two mechanisms - one is the renormalization of the exciton Green's function by a virtual process of emission and absorption of a plasmon and two through a real plasmon emission process. Both of these mechanisms have their own flaws which are outlined in the text.

and 7.8d). A curious aspect of the TiSe₂-CDW transition is the presence of a low-energy plasmon, which has been claimed as evidence of the excitonic insulator mechanism [338], although this claim was later disputed [339]. This plasmon was measured to have an energy of $\hbar \omega_{pl}(q) \approx 50$ meV at T = 17 K with q = 0. This excitation was found to soften with temperature, reaching $\hbar \omega_{pl} \approx 35$ meV at T = 185 K. The plasmon is only present in the CDW phase, so it is tempting to associate it with the H1 PL line. Signatures of excitonplasmon interaction in PL have attracted considerable attention recently [340–343]. While these papers consider excitons and plasmons spatially coexisting in the same material, the theory is equally applicable to spatially separated MoSe₂ excitons and TiSe₂ plasmons, as long as they are coupled by Coulomb interaction. In principle, two mechanisms are possible (see Supporting Information section for a detailed discussion): the exciton Green function can be renormalized by a virtual process of emission and absorption of a plasmon **Figure 7.8c** or a process with either emission or absorption of a real plasmon **Figure 7.8d**. The former process shifts the exciton line E_X up by a fixed amount, which in the first approximation can be expressed as $E_X^2 - E_{X0}^2 \approx 4|\mathcal{M}|^2 E_{X0} \hbar \omega_{pl} / (E_{X0}^2 - (\hbar \omega_{pl})^2) \approx$ $4|\mathcal{M}|^2 \hbar \omega_{pl} / E_{X0}$, where E_{X0} is the position of X⁰ in the absence of exciton-plasmon coupling and \mathcal{M} is the exciton-plasmon coupling constant. However, one would expect the coupling constant to vary spatially, so instead of two lines one would observe a broad manifold starting at E_{X0} and ending at around $E_{X0} + 2|\mathcal{M}|^2 \hbar \omega_{pl} / E_{X0}$, in contradiction with the experiment. The other mechanism preserves the main line and adds two satellites, shifted down and up by around ω_{pl} . The intensity of the upper peak is roughly temperature independent, and the intensity of the lower peak is proportional to the population of thermally or extrinsically excited plasmons. We do not observe the lower satellite at all, and the upper satellite, H1, only loses its intensity with temperature (**Figure 7.3b**) and with the laser power (**Figure 7.5b**), in obvious contradiction with the assumed physics.

7.5 Conclusion

We have discovered the presence of a new exciton-like peak in TiSe₂ - MoSe₂ heterostructures using temperature-dependent PL spectroscopy. The H1 emission feature is localized to the heterostructure interface and correlated with T_{CDW} in TiSe₂. We have presented multiple scenarios that could explain the origin of this feature. The most plausible explanations of H1 are, presently, 1) an interlayer TiSe₂ - MoSe₂ exciton and 2) the brightening of momentum dark excitons by the CDW potential. Whichever point of view is favored, we find, experimentally, that the formation of the CDW strongly affects the exciton formation at a TiSe₂ - MoSe₂ interface, opening a new avenue for studying the electronic phenomena in the latter. These results are the first demonstration of exciton engineering via proximitized CDWs and provide the 2D theoretical community with a fresh challenge to understand the microscopic mechanisms underlying CDW-exciton interactions.

7.6 Supporting Information

7.7 Temperature- and power-dependent PL in Sample 2



Figure 7.9: (a) Temperature-dependent PL plots taken at the TiSe₂ - MoSe₂ interface (Sample 2) in the range of 5 K - 200 K. We observe three distinct transitions: X^- , X^0 and H1. (b) Energy of the H1 peak with respect to X^0 showing a BCS type temperaturedependence. The solid black line is fit to an empirical model described by Eq. (2) in the main manuscript. (c) Power-dependent data showing linearity of X^0 peak, where the solid black line is a power-law fit ($I \propto P^{\alpha}$) with α approaching 1 for H1, while a sublinear behavior of the X^0 and X^- peaks is observed. These results are similar to our observations of Sample 1 discussed in the manuscript.

Temperature and power-dependent measurements on sample 2, showing the CDW dependence of H1 peak. We see similar trends as in Sample 1 discussed in the previous section.

7.7.1 Reflectance measurements on Sample 1

We present here a comparison of the PL data with reflectance and reflectance contrast (RC) measurements performed at 5 K on and off the TiSe₂ - MoSe₂ junction in Sample 1. All measurements were performed after the sample had undergone a 'nano-squeegee' cleaning treatment and vacuum annealing. In **Figure 7.10b**, PL and reflectance scans are color coded to differentiate between data taken at on (black stars/spectra) and off (red stars/spectra) the interface and are appropriately scaled and shifted for the purpose of overlaying. In case of ML-MoSe₂ reflectance, we see a singular absorptive feature that corresponds to the X⁰ transition, in line with the X⁰ emission in the PL scan. For the data taken at the interface, we see a weak absorptive feature at ≈ 1.683 eV, matching the H1 transition in the PL scan. We do not see any other absorptive features related to X⁰ or X⁻ transition at the junction.

In Figure 7.10c, we calculate reflectance contrast for the data shown in panel (b), using the following equation:

$$\% reflectance contrast (RC) = \frac{R_{data} - R_{reference}}{R_{reference}} = \frac{\Delta R}{R}$$
(7.3)

Here, R_{data} is the dark-subtracted reflectance taken either on ML-MoSe₂ (black scan) or the TiSe₂ - MoSe₂ junction (red scan), and $R_{reference}$ is the dark-subtracted scan taken on the HBN substrate. We see similar results as in panel (b) where a high-energy feature is present for scans taken at the interface, but is absent on the pristine MoSe₂. The RC data here is filtered with appropriate background subtraction to flatten the curve and improve the signal to noise ratio. We can further improve the ease of identification of the observed



Figure 7.10: (a) White light image of the $TiSe_2 - MoSe_2$ heterostructure sample 1. (b) Overlay of the raw reflectance and PL spectra at the locations marked by colored stars in (a) - black spectra/star are taken at the $TiSe_2 - MoSe_2$ interface and the red spectra/star is taken on ML-MoSe₂. (c) Overlay of the reflectance contrast (calculated from (b)) and PL spectra taken at the same position as in (a) and (b). (d) Derivative of the reflectance contrast calculated from scans in (c) plotted in the energy range of 1.55 eV - 1.8 eV focusing on the features observed within that energy range in (c). All spectra derived from reflectance measurements have been filtered to improve signal to noise. PL spectra is panels (b) and (c) are appropriate scaled and offset to overlay over reflectance data.

features by calculating the derivative of reflectance contrast, $d(\Delta R/R)/d\omega$. This is plotted in **Figure 7.10d**, where we clearly see the peak at 1.683 eV rise above the noise only in the black curve, lining up with the PL emission energy of the H1 peak at the interface. The emergence of a new absorption channel at the same energy further validates our observation of the H1 peak being related to interactions between TiSe₂ and MoSe₂ layer.

7.7.2 General Model for exciton - plasmon interaction

The close proximity of the $MoSe_2$ and $TiSe_2$ layers also allows for the possibility of the $MoSe_2$ excitons to interact with plasmons excited in $TiSe_2$. To treat the interaction between the excitons and plasmons, we employ the methods developed in Ref. [344] for exciton-phonon coupling and in Refs. [340, 341, 343, 345] for exciton-intervalley plasmon coupling and adjust them to account for $MoSe_2$ excitons and $TiSe_2$ plasmons instead.

In the following, we consider only one species of (bright) excitons in $MoSe_2$ for simplicity and assume that these excitons originate from electron-hole excitations between a single conduction band and a single valence band. Then the corresponding $MoSe_2$ electrons are described by the Hamiltonian

$$H_{e-h} = \sum_{k} \left[\epsilon_c(k) \hat{a}_{c,k}^{\dagger} \hat{a}_{c,k} + \epsilon_v(k) \hat{a}_{v,k}^{\dagger} \hat{a}_{v,k} \right] + \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} V_{k_1 k_2, k_3 k_4} \hat{a}_{v,k_1}^{\dagger} \hat{a}_{c,k_2}^{\dagger} \hat{a}_{c,k_3} \hat{a}_{v,k_4}, \quad (7.4)$$

where $\hat{a}_{c,k}^{\dagger}$ ($\hat{a}_{c,k}$) and $\hat{a}_{v,k}^{\dagger}$ ($\hat{a}_{v,k}$) are creation (annihilation) operators for electrons in the conduction and valence bands, respectively. Here the relative crystal momentum k is measured from the conduction band edge, $\epsilon_c(k)$ and $\epsilon_v(k)$ describe the electron dispersions of the conduction and valence bands, and $V_{k_1k_2,k_3k_4}$ is the matrix element of the electron-electron interaction.

Within the Tamm-Dancoff approximation, excitons X with momentum q arising from Equation 7.4 are given by $|X,q\rangle = \prod_k \mathcal{A}_{vck}^{X,q} \hat{a}_{c,k+q}^{\dagger} \hat{a}_{v,k} |\text{GS}\rangle$, where $|\text{GS}\rangle$ is the ground state with fully occupied valence bands. The coefficients $\mathcal{A}_{vck}^{X,q}$ can be determined by diagonalizing an eigenvalue equation corresponding to a Bethe-Salpeter equation [346]. The corresponding free exciton Green function acquires the form [340, 341, 345, 347, 348]

$$G_0(\Omega, q) = \frac{1}{\Omega - E_X(q)},\tag{7.5}$$

where Ω is a bosonic Matsubara frequency, q the exciton momentum and $E_X(q)$ its energy. The energy of the exciton is given by $E_X(q) = E_{X0} + \hbar^2 q^2/2M$, where E_{X0} is the position of the MoSe₂ exciton with q = 0 and the exciton mass $M = m_c + m_v$ consists of the effective masses of the conduction and valence bands from which the exciton is formed.

Furthermore, we assume that the conduction-band electrons that participate in the formation of the $MoSe_2$ excitons are coupled to plasmons in the adjacent $TiSe_2$ layer by

$$H_{e-pl} = \sum_{q,k} \mathcal{M}_q \left(\hat{b}_{-q} + \hat{b}_q^{\dagger} \right) \hat{a}_{c,k-q}^{\dagger} \hat{a}_{c,k}, \tag{7.6}$$

where $\hat{a}_{c,k}^{\dagger}$ and $\hat{a}_{c,k}$ have been defined above in **Equation 7.4** and \hat{b}_q^{\dagger} and \hat{b}_q are creation and annihilation operators for plasmons in TiSe₂. The electron-plasmon coupling strength is given by \mathcal{M}_q and q denotes the plasmon momentum here. In **Equation 7.6** we have assumed momentum conservation and only on type of plasmons for simplicity.

The TiSe₂ plasmons are described by the free plasmon propagator

$$D(\Omega,q) = \frac{2\hbar\omega_q}{\Omega^2 - \hbar^2\omega_q^2},\tag{7.7}$$

where Ω is again a bosonic Matsubara frequency and ω_q the TiSe₂ plasmon dispersion. Exciton-plasmon coupling then leads to a dressed MoSe₂ exciton Green function,

$$G(\Omega, q) = \frac{G_0(\Omega, q)}{1 - G_0(\Omega, q)\Sigma(\Omega, q)}.$$
(7.8)

Here the self-energy $\Sigma(\Omega, q)$ due to TiSe₂ plasmons is given—to lowest order—by

$$\Sigma(\Omega, q) = -k_{\rm B}T \sum_{q',\Omega'} \left| \mathcal{M}_{q'} \right|^2 D(\Omega - \Omega', q') G_0(q + q', \Omega')$$

$$= -\sum_{q'} \left| \mathcal{M}_{q'} \right|^2 \left[\frac{g(E_X(q + q')) - g(\hbar\omega_{q'})}{\Omega + \hbar\omega_{q'} - E_X(q' + q)} - \frac{g(E_X(q' + q)) - g(-\hbar\omega_{q'})}{\Omega - \hbar\omega_{q'} - E_X(q' + q)} \right]$$

$$= \sum_{q'} \left| \mathcal{M}_{q'} \right|^2 \left[\frac{g(\hbar\omega_{q'}) - g(E_X(q + q'))}{\Omega + \hbar\omega_{q'} - E_X(q' + q)} + \frac{g(\hbar\omega_{q'}) + 1 + g(E_X(q' + q))}{\Omega - \hbar\omega_{q'} - E_X(q' + q)} \right]$$
(7.9)

with the Boltzmann constant $k_{\rm B}$, the temperature T, and the Bose-Einstein distribution function

$$g(\epsilon) = \frac{1}{\exp\left[\epsilon/(k_B T)\right] - 1}.$$
(7.10)

The self-energy contribution from Equation 7.9 corresponds to the propagation of an exciton which temporarily transitions into a different exciton state by absorbing or emitting a plasmon. In the second step in Equation 7.9 we have performed the sum over bosonic Matsubara frequencies and in the third step we have used that $g(-\epsilon) = -1 - g(\epsilon)$. To arrive at Equation 7.9, we have assumed that exciton-plasmon coupling arises from electron-plasmon coupling (with the valence-band electrons acting as spectators) [340, 341, 345].

Typically, one is mostly interested in excitons with q = 0 and we consider this case in the following. Then the absorption, which is proportional to the imaginary part of the exciton Green function, is given by

$$\alpha(\omega) \propto -\mathrm{Im}\left[G(\Omega \to \hbar\omega + \Gamma, 0)\right] \tag{7.11}$$

after analytical continuation of Ω , where $\hbar\omega$ denotes photon energies and Γ a phenomeno-

logical broadening. Likewise, PL can be related to the Green function via [348]

$$\mathcal{L}(\omega) \propto -\mathrm{Im}\left[G(\Omega \to \hbar\omega + \Gamma, 0)\right] g(\hbar\omega - \mu),$$
(7.12)

where g is again the Bose-Einstein distribution and μ is the quasichemical potential of the electron-hole pairs. We are only interested in the dilute limit, $\mu \ll E_{X0}$, and can therefore approximate **Equation 7.12** by

$$\mathcal{L}(\omega) \propto -\mathrm{Im} \left[G(\Omega \to \hbar \omega + \Gamma, 0) \right] g(\hbar \omega)$$
 (7.13)

in the following.

7.7.3 Simplified Model

Since we cannot assume momentum conservation between the MoSe₂ excitons and the TiSe₂ plasmons, we use a simplified model and assume that \mathcal{M} is momentum-independent. Moreover, we assume that the exciton momentum is completely independent of the plasmon momentum, that is, we use $E_X(q)$ instead of $E_X(q+q')$. With these simplifications, **Equation 7.9** becomes

$$\Sigma(\Omega, q=0) = |\mathcal{M}|^2 \sum_{q'} \left[\frac{g(\hbar\omega_{q'}) - g(E_X(0))}{\Omega + \hbar\omega_{q'} - E_X(0)} + \frac{g(\hbar\omega_{q'}) + 1 + g(E_X(0))}{\Omega - \hbar\omega_{q'} - E_X(0)} \right]$$
(7.14)

for q = 0.

To further simplify our discussion, we from now on neglect the momentum dependence of the excitons and assume the plasmon does not have a dispersion and has just one plasmon energy $\hbar \omega_{pl}$. Then **Equation 7.14** becomes

$$\Sigma(\Omega) = |\mathcal{M}|^2 \left[\frac{g(\hbar\omega_{pl}) - g(E_{X0})}{\Omega + \hbar\omega_{pl} - E_{X0}} + \frac{g(\hbar\omega_{pl}) + 1 + g(E_{X0})}{\Omega - \hbar\omega_{pl} - E_{X0}} \right],\tag{7.15}$$

where E_{X0} is the zero-momentum exciton energy.

Adjusting the dressed exciton Green function given by **Equation 7.8** to our simplified model yields

$$G(\Omega) = \frac{1}{\Omega - E_{X0} - \Sigma(\Omega)}.$$
(7.16)

It proves instructive to study the poles of the dressed Green function at T = 0 more closely. At T = 0, the self-energy is simply

$$\Sigma(\Omega) = \frac{|\mathcal{M}|^2}{\Omega - E_{X0} - \hbar\omega_{pl}},\tag{7.17}$$

which has a pole at $\Omega = E_{X0} + \hbar \omega_{pl}$. The Green function (in **Equation 7.16**) then



Figure 7.11: Imaginary part of the dressed exciton Green function computed from Eqs. (7.15) and (7.16) as a function of the photon energy $\hbar\omega$ for (a) different excitonplasmon coupling strengths \mathcal{M} and (b) for different temperatures T. In panel (a) the temperature is fixed at T = 10 K and in panel (b) $\mathcal{M} = 20$ meV. In all plots, $E_{X0} = 1.7$ eV, $\hbar\omega_{pl} = 50$ meV, and $\Gamma = 5$ meV. To evaluate $\Sigma(\Omega \to \hbar\omega + \Gamma_{\Sigma})$ a separate broadening of $\Gamma_{\Sigma} = 1$ meV has been taken.

becomes

$$G(\Omega) = \frac{\Omega - E_{X0} - \hbar\omega_{pl}}{(\Omega - E_{X0})(\Omega - E_{X0} - \hbar\omega_{pl}) - |\mathcal{M}|^2},$$
(7.18)

which has poles at

$$\Omega = E_{X0} + \frac{\hbar\omega_{pl} \pm \sqrt{(\hbar\omega_{pl})^2 + |\mathcal{M}|^2}}{2}.$$
(7.19)

Hence, at low T the dressed exciton Green function exhibits one pole close to the original exciton peak position at $\hbar\omega \approx E_{X0}$ and another one close to $\hbar\omega \approx E_{X0} + \hbar\omega_{pl}$. If the plasmon population $g(\hbar\omega_{pl})$ increases, either by raising T or by otherwise exciting plasmons in the TiSe₂ layer, a third peak, which is located in the vicinity of $\hbar\omega \approx E_{X0} - \hbar\omega_{pl}$, arises.

7.7.4 Results

These statements are corroborated by **Figure 7.11**, which shows $-\text{Im} [G(\Omega \rightarrow \hbar \omega + \Gamma, 0)]$ as a function of the photon energy for different exciton-plasmon coupling strengths (**Figure 7.11a**) and for different temperatures (**Figure 7.11b**). At low temperatures, one can clearly see that in addition to the exciton peak at $\hbar \omega \approx E_{X0}$, a side peak emerges at photon energies above E_{X0} due to exciton-plasmon coupling. With increasing coupling strength \mathcal{M} , more spectral weight is transferred to this side peak, as illustrated by **Figure 7.11a**. **Figure 7.11a**, moreover, shows that exciton-plasmon coupling also leads to a renormalization of the position of the exciton, as described by **Equation 7.19**.

Increasing the temperature leads to an increased TiSe₂ plasmon population, which in turn results in the appearance of a second side peak due to exciton-plasmon coupling, as can be discerned from **Figure 7.11b**. This second side peak is located below the exciton peak at $\hbar\omega \approx E_{X0}$ and its spectral weight increases with increasing temperature. Since $-\text{Im} \left[G(\Omega \rightarrow \hbar\omega + \Gamma, 0)\right]$ enters both the absorption and PL via **Equations 7.11** and **7.12**, one can conclude that those also exhibit an additional side peak at $\hbar\omega \approx E_{X0} + \hbar\omega_{pl}$ at low temperatures if the exciton-plasmon coupling is sufficiently strong.

7.7.5 Density functional calculations of the band alignment

DFT calculations for semiconductors always have to be taken with a grain of salt because of the infamous derivative discontinuity problem affecting the band gap. Furthermore, the large lattice mismatch between the TiSe₂ and MoSe₂ makes it necessary to use large supercells to restore the lateral periodicity. With these reservations, we have attempted an estimate of the band alignment using a just a MoSe₂ - TiSe₂ bilayer. One can construct a supercell [349] consisting of 2×2 TiSe₂ unit cells and $\sqrt{7} \times \sqrt{29}$ MoSe₂ unit cells, rotated by $\approx 36^{\circ}$ and expanded by $\approx 1.3\%$.

With this unit cell, we have optimized the internal coordinates and the interlayer distance using the Vienna Ab-initio Simulation Package (VASP) [350] with the PBE-GGA approximation to the exchange correlation potential [351] and PAW pseudo-potentials [352], including the van der Waals correction from Ref. [353]. After that, we have listed all oneelectron states according to whether their main character is Mo (left on **Figure 7.7b**), or Ti (right). Since most states are either predominantly Mo or predominantly Ti, we can clearly see the top of the MoSe₂ valence band is about 230 meV below the Fermi level (which is set to zero). As **Figure 7.7b** shows, the TiSe₂ in this DFT calculations is metallic, as usual in the uncorrected DFT, but opening a small gap around E = 0 in **Figure 7.7b** will not change the main conclusion.

Chapter A: Defects and its passivation in CVD-grown MoS_2 thin films

A.1 Introduction

Intrinsic defects in TMDs, generally due to volatile chalcogen vacancies or surface oxidation, tend to create new states within the bandgap commonly referred to as traps. These defect states can degrade the optical and electronic properties of these materials and are bottlenecks prohibiting any realistic integration of 2D TMDs into modern devices. An additional challenge in synthesizing defect-free 2D materials comes in the form of lateral heterogeneity, which are largely dependent on the choice of substrate during the growth process. where non-uniform strain, composition and defect density make it harder to passivate defect states without causing permanent changes in the intrinsic properties of the material. In the work that follows, we investigate the origin of the widely observed lateral heterogeneities in synthetic monolayer MoS_2 and the effects of controlled substitutional doping to mitigate trapped states that result from inherent defects.

Heterogeneity depends on substrate choice. This is evident when comparing as-grown monolayer WS₂ single crystalline domains to transferred domains to a new SiO₂substrate, where a 50 meV shift of ground state exciton and ~ 0.25 % reduction of tensile strain is identified [22], indicating the film-substrate coupling during the growth may play an important role in the heterogeneity. Indeed, the film-substrate interaction is stronger than the ideal van der Waals, especially in epitaxy [6, 17]. To date, most heterogeneity studies on synthetic 2D materials are on SiO₂[15, 20, 22], with few on 'epi-ready' substrates such as sapphire [6]. As epitaxy is one of the most important techniques to achieve the industrially compatible 2D materials, it is critical to understand the origin of heterogeneities resulting from epitaxial growth.

A.2 Optical measurements on the CVD-grown ML - MoS_2

A PL emission spectra from an MoS₂ flake (30-35 μ m; in black) and c-sapphire substrate (in blue) is as shown in **Figure A.1a**, measured at 5 K. Highlighted region indicate broad features in the range of 2 - 2.4 eV and a sharp emission line close to 1.77 eV that are present



Figure A.1: (a) Raw PL spectrum from L-MoS₂ domains at 5 K (blue) on c-sapphire substrate. We see three distinct signatures: a low-energy but significantly brighter peak at 1.6 eV correlated with the defect emission in ML-MoS₂; a standard neutral exciton (X^0) emission at 1.8 eV; and higher energy broad emission form the substrate/N-grease as seen from the black curve. In order to filter the background emission, we appropriately scale and subtract the black curve from the blue curve. The resulting red curve represents PL emission just from the MoS₂ domain.

both on and off the flake. We believe these correspond to Raman generated form the csapphire substrate and PL from the N-grease beneath the substrate used to mount the sample to the cryostat. In order to reveal features present just on the flake, we scale the substrate PL to match the PL from the flake at the highlighted regions and then subtract it from the same. A typical spectra after subtraction is shown by the red curve in **Figure A.1a**, where the features above 2 eV as well as the sharp emission around 1.77 eV have been appropriately subtracted revealing features pertaining only to a ML-MoS₂ flake. This leaves us with two distinct emission, the feature at 1.82 eV, corresponding to the neutral exciton (X^0) emission in monolayer MoS₂, and a broad, but significantly intense low-energy emission at 1.6 eV, corresponding to PL from defect states. Intrinsic defects in monolayer TMDs, generally due to volatile chalcogen vacancies or surface oxidation, tend to create new states within the bandgap commonly referred to as traps or defect states. On excitation, in addition to the higher energy state available at the conduction band minima, electrons can excite to these mid-gap states, and later recombine via radiative pathways resulting in low-energy emission such as the one we see at 1.6 eV. This defect-band represents an entire ensemble of gap states available as a result of defects and vacancies inherent to the TMD (either during growth or later) which explains the broadness of this peak. This is shown in **Figure A.1b** along with the interband exciton recombination process in ML-MoS₂.

In addition to this, we were able to confirm the presence of defect-luminescence at the center of relatively large (> 20 μ m, L - MoS₂) domains, where the intensity of defect emission correlates directly with the domain size (**Figure A.2c**). Further, using hyperspectral PL measurements, we observe an intriguing spatial response in the PL spectra, where the magnitude of defect emission reduces as we move from the center to the edges of the domain (**Figure A.2a**). For small epitaxial domains (< 10 μ m, S - MoS₂) however, a more homogeneous response of the PL is observed, exhibiting uniformity in inherent defect population across the entirety of the surface as shown in **Figure A.2b**. Domain size is a key indicator of epitaxial MoS₂ orientation, strain, and electron concentration heterogeneities. The origin of observed lateral heterogeneity in epitaxial monolayer MoS₂ on sapphire is a result of oxygen rich defects in single crystalline domains. Small domains (~ 10 μ m, S - MoS₂) exhibit aligned crystal orientation, and uniform PL emission and strain, while large domains (> 20 μ m, L - MoS₂) lose orientation alignment and exhibit a sharp lateral



Figure A.2: Low-temperature (5 K) spatial map of the integrated defect intensity (bottom) and X^0 intensity (top) in (a) L-MoS₂ and (b) S-MoS₂. The defect emission is negligible in S-MoS₂, while the defect emission is concentrated at the center platelet of L-MoS₂ (c) Size-dependent PL spectra from the center of MoS₂ domains taken at 5 K. The defect emission increases with the domain size

transition under optical probes. Our PL measurements reveal almost doubled PL intensity (**Figure A.2**) correlated with a 0.3% - 0.4% released tensile strain at the center region of L - MoS₂. We also observe an overall increase in the defect emission across this region that aligns well with the presence of vacancies and oxygen-defects in non-epitaxial domains of larger spatial dimension. Moreover, based on all the experimental and computational results, it is proposed that two distinct growth mechanisms respectively dominate the earlier growth cycle of L - MoS₂ and the later growth of S - MoS₂, explaining their difference in defect such as MoO_x density and orientation uniformity. L - MoS₂ nucleates earlier and is grown under a solid-solid mechanism, where MoO_x is condensed on the substrate and

subsequently sulfurized, resulting in an O-defective center region. On the other hand, S - MoS_2 nucleates later, after which both S - MoS_2 and the edge region of L - MoS_2 are grown under a vapor-solid mechanism, where MoS_2 is formed in vapor-phase and condensed onto the substrate.

A.3 Passivating defects through substitutional doping

Passivating inherent defects in the form of vacancies either at the surface or edges of asgrown TMDs is currently under investigation. Recently, substitutional doping has provided an efficient route to not only tune the carrier concentration but also to suppress defect based trapped states, curb vacancies and prohibit external absorbates to form any unintentional covalent bonds. In our study, we aimed to observe the optical response of in-situ rhenium (Re) doped-MoS₂ monolayers. Our low-temperature photoluminescence measurements indicate a significant quench of the defect-bound emission when Re is introduced, which is attributed to the passivation of sulphur vacancies and reduction in defect-induced gap states due to the presence of Re atoms.

Most notable effect is the suppression of sub-gap states arising from sulfur vacancies with Re substitution. To illustrate the presence and elimination of these mid-gap defect states, we performed temperature-dependent PL measurements on pristine (**Figure A.3a**) and Re-doped monolayer MoS₂ (**Figure A.3b**). At 5 K, pristine MoS₂ (red curve in **Figure A.3a**) exhibits the well-documented neutral exciton emission feature at 1.82 eV, but also a substantial asymmetric emission feature centered at 1.6 eV. This feature strongly resembles observations of defect emission in ML - MoS₂ domains discussed in the prior section. The asymmetric nature of the feature also suggests a wide variation in defect state energies rather than a well-resolved intrinsic exciton state. As discussed in the prior section, the dominance of the defect emission over the X⁰ at 5 K suggests a large density of defects in as-grown MoS₂ on r-sapphire. As the temperature is increased from 5 to 300 K, we observe an initial blue shift and sharpening of the defect emission at 100 K followed by a gradual



Figure A.3: Defect passivation by Re-doped MoSe₂. Temperature-dependent PL from (a) pristine MoS₂ and b) Re-MoS₂. Defect-activated emission is significantly brighter in pristine-MoS₂ at lower energy, while it is completely quenched after Re doping.

reduction in defect PL and its disappearance at 300 K. Note that the sharp features in **Figure A.3a** appearing at 1.80 eV are artifacts arising from the subtraction of background PL from the r-sapphire substrate, as shown in Figure. The PL and temperature dependence of Re - MoS_2 (**Figure A.3b**) exhibits strikingly different behavior. While the overall PL emission intensity is lower in Re - MoS_2 , the defect PL is highly suppressed at 5 K and the A-exciton emission is sharper, which suggests that Re - MoS_2 either exhibits a lower defect density or shallower defect states with PL energy much lower than the spectral range of our camera. Note that the low signal-to-noise ratio in **Figure A.3b** is due to the r-sapphire background PL subtraction and the overall lower emission intensity of Re - MoS_2 .

The temperature dependence of the defect emission in Re - MoS_2 seems to follow the same general trend as seen in the pristine sample.

Chapter B: Spin reorientation in anti-ferromagnetic Dy_2FeCoO_6 double perovskite

B.1 Introduction

Scientific interest in double perovskites stem from the technical possibilities of realizing applications ranging from multiferroics [354, 355] to strongly correlated magnets [356] to solid oxide fuel cells [357] to room temperature magnetoresistive oxides [358]. There is immense interest in obtaining an alternating (ordered) arrangement of 3d and 5d cations as a route to combine strong electronic correlations of 3d ions with the spin-orbit coupling of 5d whereby exotic magnetism and spin-orbit-assisted Mott insulating state was can be observed. The perovskite Dy₂FeO₃ belongs to the family of orthoferrites that crystallize in the orthorhombic P_{nma} structure and has attracted attention in recent times due to the discovery of a magnetic field induced ferroelectric state at $T_N = 3.5$ K [359]. On the other hand, the orthoperovskite compound Dy₂CoO₃ adopts Dy₂CoO₃ structure but orders magnetically at very low temperature, $T_N = 3.6$ K. Solid solutions of RFeO₃ and RCoO₃ (R is a rare earth) were studied in the case of R = La [360], however, detailed studies on solid solutions of RFeO₃ and RCoO₃ forming double perovskite structures are limited.

This study was done in collaboration with our colleague at the University of Texas. The published paper compiles the results of magnetic measurements, crystal and magnetic structure determined through neutron diffraction and DFT studies of electronic and magnetic properties of Dy_2FeCoO_66 [361]. In this chapter, we will explore the vibrational properties of the double perovskite Dy_2FeCoO_6 using temperature-dependent Raman measurements.

B.2 Sample fabrication and experimental setup

Polycrystalline powders of Dy_2FeCoO_6 used in the present study were prepared by citrate based sol-gel method. Details of the synthesis can be found elsewhere in Ref p. Low and high-temperature Raman measurements were carried out on a home-built confocal microscope setup with 532 nm (2.4 μ m spot size; <500 W laser power measured preobjective) and 50x long working distance objective. The light is collected in a back-scattering geometry, with the collection fiber-coupled to a 500 mm focal length single spectrometer integrated with a liquid-N2 cooled CCD detector. The sample was placed under vacuum and cooled in a closed-cycle He cryostat with a variable temperature range from 5 K to 300 K. Excitation laser polarization is kept constant for all measurements unless otherwise noted.

B.3 Low-temperature Raman on Dy₂FeCoO₆

Since both the rare-earth perovskites Dy₂CoO₃ and Dy₂FeO₃ ferrites crystallize in the orthorhombic P_{nma} structure, we expect the double perovskite to retain the same crystal symmetry and space group. The orthorhombic P_{nma} structure gives rise to a total of 24 Raman active vibrational modes: $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ [362]. Here, the modes < 200 cm⁻¹ - $3A_g + 3B_{1g} + B_{2g} + B_{3g}$ represent the mode displacements for rare-earth ions (Dy). In the high wavenumber range of > 300 cm⁻¹, modes $4A_g + 2B_{1g} + 4B_{2g} + 4B_{3g}$ are characterized by the movement of the oxygen (O) as well as the iron (Fe) and cobolt (Co) ions. Note that iron ions occupy centers of inversion in the P_{nma} structure and, therefore, vibrations involving Fe³⁺ ions need inversion symmetry breaking to become Raman active. Here, in addition to the involvement of ions, we expect to see variation in mode displacements where a total of 10 modes - $A_g + 2B_{2g} + B_{3g}$ and $2A_g + B_{1g} + 2B_{2g} + B_{3g}$ are related to rotation and tilt of the octahedral cage, respectively, where as modes $A_g + B_{1g}$ and $2B_{2g} + 2B_{3g}$ represent the symmetric and antisymmetric stretching movements of Fe - O chain [363].



Figure B.1: Dy_2FeCoO_6 Raman spectrum taken at 5 K in the back-scattering geometry with labelled vibrational modes.

Of the expected 24 modes, we observe a total of 12 distinct Raman features, with their positions marked in **Figure B.1**. The observed Raman signature at 5 K is consistent with the assigned P_{nma} orthorhombic crystal symmetry based on prior studies on perovskite systems. The Raman scan is dominated by two prominent modes appearing at ~ 630 and ~ 650 cm⁻¹. These features are common in double perovskites and are thought to originate from oxygen breathing and stretching modes of the B-site octahedra [362–365]. The observed modes can be assigned an origin in Co or Fe compounds based on prior studies of the perovskites DyFeO₃ [362] and DyCoO3 [364]. The weak intensity of modes below 600 cm⁻¹ is curious as perovskites typically exhibit strong, sharp modes in this range [362–365]. In contrast, double perovskites often exhibit suppressed intensity in this range [365, 366]. Studies on Ho and La based compounds have attributed the enhancement of the $\sim 650 \text{ cm}^{-1}$ modes to charge transfer between the B site atoms that in turn activates oxygen breathing modes [364, 367] although octahedral tilt and structural changes also likely contribute [365, 367]. We also outline the mode symmetry (based on prior studies of single perovskites) and atomic motions a for each vibrational frequency in **Table B.1**.

Table B.1: Symmetry mode assignments, mode vibrations and atomic displacements for the observed Raman signature in Dy_2FeCoO_6 at 5 K.

Mode symmetry	Mode frequency $\rm cm^{-1}$ (meV)	Mode displacements
A_g	103	Dy(x), $Dy(z)$ - in - phase in xz, of phase in y
A_g	137	Dy(z) - out-of-phase
B_{2g}	157	Dy(x) - out-of-phase
A_g	270	FeO_6 rotation, in-phase
A_g	329	O(1) x-z plane
A_g	399	Fe/Co - $O(2)$ stretching in-phase
B_{3g}	473	O(2) - Fe - $O(2)$ scissor like bending, out of phase
B_{2g}	514	O(2) - Fe/Co - $O(2)$ scissor like bending, in phase
B_{2g}	541	O(2) - Co - $O(2)$ scissor like bending, in phase
B_{2g} (?)	567	-
B_{2g}	619	Fe/Co - $O(2)$ stretching, in-phase
B_{3g}	645	$\rm Fe/CoO_6$, breathing

B.4 Temperature-dependent Raman measurements

Temperature-dependent Raman spectra of Dy_2FeCoO_6 is presented in Figure B.2. Mode frequencies are extracted from the 5 K data by fitting with a sum of 13 Lorentzians (red curves in the figure). With increasing temperature we observe only minimal changes to the spectra, which implies that the system remains in the P_{nma} structural phase. Temperaturedependent magnetic measurements have revealed a spin reorientation and the antiferromagnetic transitions at $T_{SR} = 86$ K and $T_N = 248$ K occurring in the Fe/Co sub-lattice [361]. We do not observe any signatures of these magnetic transition in Raman measurements.



Figure B.2: The Raman intensity of Dy_2FeCoO_6 as a function of wavenumbers at different temperatures. The red curves are the Lorentzians used to identify vibrational modes. Spectra are normalized by maximum intensity.

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Curriculum Vitae

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CANDIDATE PROFILE

Condensed matter Ph.D. candidate specialized in experimental and theoretical techniques that explore optical and electronic properties of low-dimensional quantum materials at cryogenic temperatures. Proficiency in the following areas:

- Designing high-resolution optical spectroscopy setups
- Lasers, quantum optics, Cryogenics
- 2D semiconductor devices and nanofabrication
- Creative problem solver, team-player, mentor, machine-learning enthusiast.

EDUCATION

Ph.D. Candidate, Condensed Matter Physics, GPA: 3.9/ 4.0 George Mason University, VA Adviser: Dr. Patrick Vora Expected August 2021

- Exploring optical properties of nano-fabricated quantum devices based on semiconductor superconductor junctions for use in quantum circuits and qubit technologies.
- Recipient of the 2020 Dean's Award for Graduate Excellence awarded to a single graduate student nominee from College of Science, George Mason University.
- Recipient of the 2017, 2019 and 2020 Summer Research Fellowship awards granted by the Department of Physics and Astronomy, College of Science, George Mason University.

M.S., Applied Physics, GPA: 3.87/4.0

Adviser: Dr. Patrick Vora

• Specialized in building high-resolution spectroscopy and metrology setups to perform linear and non-linear quantum optical measurements at cryogenic temperatures. These are automated to simultaneously interface with LabView and Python for hyperspectral data acquisition and post-processing.

B.E., Electrical Engineering, GPA: 3.7/4.0

Adviser: Prof. Nitin Adroja

• Designed a power distribution system which transmits electrical power from generating stations to distant substations via a wireless local area network. Contributed to design and fabrication of waveguide components, antenna and the electrical framework for magnetron microwave generators.

LAB EXPERTISE AND RESEARCH SKILLS

C Measurement Setups

- Raman, Photo/Electroluminescence, Reflectance, Absorption and Atomic Force Microscopy techniques.
- Fully automated, nanometer-precision hyperspectral imaging
- 4-Probe electrical transport measurements
 - A Material Science
- Low-dimensional materials and thin films
- Electronic and topologically ordered material systems

A Supplementary skills

- Proficiency in LabView and Python for data acquisition & analysis Experience with MatLab and C
- Automation across various platforms and peripherals

• Experience with nanofabrication techniques

• 2D devices and device physics

• Machine-shop fabrication, 3D printing

• Quantum materials beyond graphene

Gujarat Technological University, India Aug 2009 - August 2013

• VIS-NIR Optical monochromator

George Mason University, VA

Aug 2014 - May 2016

• Hyperspectral imaging

• Data analysis & automation

• Materials characterization

Proximity Effects in 2D Heterostructure for Quantum Computing Applications

George Mason University

- Discovery of optically activates robust emissive states at 2D semiconductor superconductor and semiconductor CDW junctions.
- Discovery of proximity coupling between two materials with distinct electron correlated physics.
- Propositions made to optically harness entangled photon pairs in this material system using quantum tunneling of electron Cooper pairs.
- -> **Published work**: Activation of Forbidden Excitons by Proximitized Charge Density Waves (2021-reviewing)
- -> **Published work**: Localized excitons in NbSe₂ MoSe₂ heterostructures (2020)

Phase Transitions in 2D materials for Phase-Change Memory Applications

George Mason University & NIST

- Investigation of atypical systems that exhibit novel structural and electronic phase transitions at cryogenic temperatures using high resolution optical spectroscopy.
- First observations of non-linear anharmonic changes in a low-dimensional, topological material MoTe₂, at cryogenic temperatures.
- First observations of short-range electronic order in 2H-TaS₂, a material that exhibits CDW and superconductivity transitions using multiple spectroscopy techniques with theoretical interpretations.
- -> **Published work**: Phonon anharmonicity in bulk T_d -MoTe₂ (2016)
- -> Published work: Short Range Charge Density Wave Order in 2H-TaS₂ (2019)

Defects and Its Passivation in Epitaxial 2D Films for Advanced Optoelectronics

George Mason University & PSU

- Understanding the role of defects in the optical properties of CVD-grown materials and the effect of substitutional doping on mitigating them.
- Evidence of defect luminescence in epitaxially grown samples at cryogenic temperatures and correlated that with domain size.
- Observed significant changes in the magnitude of optical response across individual domains through high resolution, hyperspectral mapping.
- -> **Published work**: Probing the origin of lateral heterogeneities in synthetic monolayer molybdenum disulfide (2019)
- -> Published work: Tuning the electronic and photonic properties of monolayer MoS₂ via in situ rhenium substitutional doping (2018)

Relevant Leadership & Collaborative Initiatives

- Participant Member (Technical Lead) National Science Foundation (NSF) Innovation-Corps (2021)
- Guest Researcher Laboratory of Physical Sciences (LPS) (2020 2021)
- Guest Researcher Penn State University (PSU) (2019)
- Guest Researcher National Institute of Standards and Technology (NIST) (2017 2019)

Mentored and assisted several senior undergraduates to enable independent research Graduate Research Assistant, George Mason University

2017- Present

• Trained students in the physics of semiconductors, exfoliation and fabrication of low-dimensional sample structures as well as in instrumentation of highly sensitive optics and deliver routes for complete automation of the optical setup with LabView.

SELECTED TALKS/PRESENTATIONS

- Joshi, J. et al. 2D heterostructures for entangled photon generation. 2020 QED-C Student e-session
- Joshi, J. et al. Excitonic behavior at metal-semiconductor interfaces. 2019 APS March Meeting, MA
- Joshi, J. et al. Raman Signatures of the Charge Density Waves in 2H-TaS₂. 2018 APS March Meeting, CA
- Joshi, J. et al. Phonon anharmonicity in bulk Td-MoTe₂. 2016 MRS Fall meeting, MA

2018 - Present

2016 - 2018

2017 - 2018

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