# Confined Light-matter Interactions in Van der Waals Heterostructures probed by Scanning Near-field Optical Microscopy

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# Abstract

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Heterostructures composed of Van der Waals materials host a variety of sub-diffractional optical phenomena, such as moire patterns [1] and emergent collective modes [2]. In this thesis, we explore three separate phenomena in vdW heterostructures: phonons in moire superlattices, Purcell-enhanced spontaneous emission from excitons, and plasmons at ultrahigh doping. In this thesis, we will describe how the Scanning near-field optical microscopy (SNOM) technnique provides sub-diffractional optical insights into excitons, phonons, and plasmons in vdW heterostructures.

First, we use SNOM to map local phonon resonances in a moire superlattices formed by two twisted bilayers of hexagonal boron nitride. Twisted two-dimensional van der Waals (vdW) heterostructures have unlocked a new means for manipulating the properties of quantum materials. The resulting mesoscopic moiré superlattices are accessible to a wide variety of scanning probes. To date, spatially-resolved techniques have prioritized electronic structure visualization, with lattice response experiments only in their infancy. We therefore investigate lattice dynamics in twisted layers of hexagonal boron nitride (hBN), formed by a minute twist angle between two hBN monolayers assembled on a graphite substrate. Nano-infrared (nano-IR) spectroscopy reveals systematic variations of the in-plane optical phonon frequencies amongst the triangular domains and domain walls in the hBN moiré superlattices. Our first-principles calculations unveil a local and stacking-dependent interaction with the underlying graphite, prompting symmetry-breaking between the otherwise identical neighboring moiré domains of twisted hBN.

Next, we use SNOM to study light emission from excitons into confined waveguide modes

of planar vdW waveguides. Atomically layered vdW materials exhibit remarkable properties, including highly-confined infrared waveguide modes and the capacity for infrared emission in the monolayer limit. In this case, we engineered structures that leverage both of these nano-optical functionalities. Specifically, we encased a photoluminescing atomic sheet of $MoTe_2$ within two bulk crystals of $WSe_2$, forming a vdW waveguide for the embedded light-emitting monolayer. The modified electromagnetic environment offered by the $WSe_2$ waveguide alters $MoTe_2$ spontaneous emission, a phenomenon we directly image with our interferometric nano- photoluminescence technique. We captured spatially-oscillating nanoscale patterns prompted by spontaneous emission from $MoTe_2$ into waveguide modes of $WSe_2$ slabs. We quantify the resulting Purcell-enhanced emission rate within the framework of a waveguide quantum electrodynamics (QED) model, relating the MoTe2 spontaneous emission rate to the measured waveguide dispersion. Our work marks a significant advance in the implementation of all-vdW QED waveguides.

Finally, we investigate phonons and confined plasmonic modes in highly-doped multilayer graphene. Collective modes in multilayer graphene, such as plasmons and phonons, exhibit sensitivity to displacement fields and interlayer coupling, distinguishing them from their counterparts in single-layer graphene. Here, we engineer collective modes in charge-transfer heterostructures composed of multilayer graphene and $U$-$RuCl_3$. In heterostructures with a single $U$-$RuCl_3$ interface, the charge transfer generates displacement fields up to 7 V/nm at the interface between $U$-$RuCl_3$ and the adjacent graphene layer—the highest value achieved through charge transfer methods. As a result of the broken inversion symmetry, we demonstrate enhanced nonlinear optical response and modified phonon selection rules. Conversely, we find that multilayer graphene sandwiched between two $U$-$RuCl_3$ flakes causes displacement fields to cancel. There, we achieve carrier densities as high as $8 \quad 10^{13}$ cm $^{2}$ in multilayer graphene and restore the phonon selection rules to their unperturbed state. The ultrahigh carrier densities deplete multiple valence bands of multilayer graphene, a previously unexplored regime for plasmon propagation. Furthermore, the inverted heterostructure sequence—two multilayer graphene sheets encapsulating $U$-$RuCl_3$—activates significant alteration of the plasmons via interlayer plasmon-plasmon coupling. Hence, multilayer

graphene and $U$-$RuCl_3$ heterostructures offer a gate-free platform for engineering collective modes derived from inversion symmetry and interlayer coupling.

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# Chapter 1: Con ned light-matter interactions in Van der Waals Heterostructures

Van der Waals (vdW) materials are layered compounds held together by weak Van der Waals forces. This weak interlayer bonding allows them to be exfoliated, often with scotch tape, down to atomically thin layers. Stacking thin vdW materials materials can reveal novel phenomena, such as moire patterns [1] and emergent collective modes [2]. In this thesis, we explore three separate phenomena in vdW heterostructures: phonon modulation in moire superlattices, Purcell-enhanced spontaneous emission from excitons in vdW waveguides, and plasmon propgation in highly-doped charge-transfer vdW heterostructures.

To investigate these collective excitations, we leverage light-matter interactions as a versatile probing platform. Phonons, quanta of lattice vibrations, are typically inaccessible via electrical transport but manifest striking optical signatures. Excitons, electron-hole bound states, form upon optical excitation and can ef ciently re-radiate light. By de nition, plasmons are hybrid light-electron excitations, making optical techniques the most straightforward approach to studying them.

Far- eld microscopy provides a straightforward method to probe light-matter interactions in vdW heterostructures. In this technique, light is focused onto the sample through an objective lens and collected after interaction, either at the same or a different wavelength. However, the spatial resolution is constrained by the “diffraction-limit", which prevents resolving spatial features smaller than the free-space wavelength [3]. Thus, conventional microscopy fails to capture the many excitonic, phononic, and plasmonic interactions that occur at sub-diffractional scales [2]. For instance, plasmons in the proto-typical vdW material, graphene, are deeply sub-diffractional, propagating with a wavelength 10-1000 times shorter than free-space light [4]. Likewise, vdW

heterostructures often contain subwavelength spatial inhomogeneities, such as strain, that locally change the collective mode properties. In this thesis, we will describe how the Scanning near- eld optical microscopy (SNOM) technnique provides nano-scale optical insights of excitons, phonons, and plasmons in vdW heterostructures.

## 1.1 Electrodynamics of Van der Waals heterostructures

A quantitative description of light-matter interaction begins with how a material polarizes at frequency $\omega$ in response to an electric eld $\mathbf{E}(\omega)$. The resulting polarization $\mathbf{P}$ de nes the dielectric function $\varepsilon(\omega)$:

$$\mathbf{P}(\omega) = (\varepsilon(\omega) - \varepsilon_\infty)\varepsilon_0 \mathbf{E}(\omega) \tag{1.1}$$

where $\varepsilon_\infty = \lim_{\omega \to \infty} \varepsilon(\omega)$ is the high-frequency dielectric function. Typically, the dielecric function is parameterized by a series $N$ of Lorentz oscillators, each with frequency $\omega_j$, oscillator strength $S_j$, and damping $\gamma_j$ [5]:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{j=1}^{N} \frac{S_j}{\omega_j^2 - \omega^2 - i\gamma_j \omega} \tag{1.2}$$

In general, the polarizability of a medium will also depend on the direction of the incident eld. Therefore, the dielectric function should be written as a rank-2 tensor. This matrix can usually be represeted in a basis where it contains only diagnonal entries (the “principal axes"). Therefore we write

$$\varepsilon(\omega) = \begin{pmatrix} \varepsilon_x(\omega) & 0 & 0 \\ 0 & \varepsilon_y(\omega) & 0 \\ 0 & 0 & \varepsilon_z(\omega) \end{pmatrix} \tag{1.3}$$

In this thesis, we will consider two classes of materials: uniaxial and isotropic materials. The latter involves a material with identical dielectric functions along all directions $\varepsilon_x = \varepsilon_y = \varepsilon_z = \varepsilon(\omega)$. This situation typically describes the dielectric response of noble metals (e.g. gold), silicon, and air. Meanwhile, vdW materials are usually in the former classi cation, a result of the vdW forces

holding layers out-of-plane, and covalent bonds among atoms in-plane. We denote the $z$-axis as the out-of-plane direction, while the $x$-$y$ crystallographic axes lie in the plane of the material. Therefore, $n_{\parallel}(\omega)$ is the dielectric response along the $z$-axis, while $n_{\perp} = n_x = n_y(\omega)$ is the dielectric function in the $x$-$y$ plane.

The vdW heterostructures consist of multiple slabs stacked together, each usually of thickness smaller than the free space wavelength. Consider an electric field with frequency $\omega$ and wavevector $\mathbf{k} = (k_x, k_y, k_z)$ (Fig. 1.1a). Maxwell's Fourier-transformed wave equation reads [6]

$$\mathbf{k} \times (\mathbf{k} \times \mathbf{E}) + \frac{\omega^2}{c^2}\varepsilon(\omega)\mathbf{E} = 0 \tag{1.4}$$

When the incident electric field is polarized in the $x$-$y$ plane ($s$- or TE-polarized), the material dispersion reads

$$\frac{\omega^2}{c^2} = \frac{k_x^2 + k_y^2}{n_{\perp}^2} + \frac{k_z^2}{n_{\parallel}^2} \tag{1.5}$$

where $k_x$ is the in-plane wavevector, and $k_z$ is the out-of-plane wavevector (Fig. 1.1a). For out-of-plane polarization ($p$- or TM-polarized),

$$\frac{\omega^2}{c^2} = \frac{k_x^2 + k_y^2}{n_{\parallel}^2} + \frac{k_z^2}{n_{\perp}^2} \tag{1.6}$$

Consider an electromagnetic field incident from the top of the slab with in-plane momentum $k_x$. In each medium, indexed by $m$, we write the field $\mathbf{E}_m = \mathbf{E}_m^{+} e^{i(k_x x + k_{z,m} z - \omega t)} + \mathbf{E}_m^{-} e^{i(k_x x - k_{z,m} z - \omega t)}$, where $d_m$ is the thickness of layer $m$. For $s$-polarization, denotes the electric field, while for $p$-polarization represents the magnetic field. The field just after exiting the last layer is denoted $\mathbf{E}_{N+1}$. Meanwhile, the incident and reflected fields are denoted $\mathbf{E}_0^{+}$ and $\mathbf{E}_0^{-}$, respectively. Using the well-known transfer-matrix formalism, the fields are related by [7]

$$\begin{pmatrix} \mathbf{E}_0^{+} \\ \mathbf{E}_0^{-} \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \prod_{m=1}^{N} \begin{pmatrix} e^{-i k_{z,m} d_m} & 0 \\ 0 & e^{i k_{z,m} d_m} \end{pmatrix} \begin{pmatrix} \mathbf{E}_{N+1}^{+} \\ 0 \end{pmatrix} \tag{1.7}$$

where

$$\%_{=} = \begin{bmatrix} \cos\left(\frac{:_{I=}3_{=}}{2}\right) & 0 \\ 0 & \cos\left(\frac{:_{I=}3_{=}}{2}\right) \end{bmatrix} \qquad =_{-=1} = \begin{bmatrix} 1 + [_{=-=1} & b_{=-=1} \\ b_{=-=1} & 1 + [_{=-=1} \end{bmatrix} \tag{1.8}$$

and the "+ (-)" in the off-diagonal entries corresponds to $B(?)$ polarization. Likewise, the expressions for $:_{I=}$, $[_{=-=1}$, and $b_{=-=1}$ depend on the incident polarization. For $B$-polarization,

$$:_{I=} = \sqrt{n_{?-=}^{2} - I^{2} \cdot 2^{2}} \qquad @^{2} - \qquad [_{=-=1} = \frac{:_{I-=1}}{:_{I-=}} - \qquad b_{=-=1} = \frac{4cf_{=-=1}I}{:_{I=}2} \tag{1.9}$$

where $f_{=-=1}$ is a 2D sheet conductivity resting at the $= = 1$ interface. For $?$-polarization, we have

$$:_{I=} = \sqrt{n_{?-=}^{1} I^{2} \cdot 2^{2} \qquad @^{2} \cdot n_{I-=}^{o}} - \qquad [_{=-=1} = \frac{n_{?-=}:_{I-=1}}{n_{?-=1}:_{I-=}} - \qquad b_{=-=1} = \frac{4cf_{=-=1}:_{I-=1}2}{n_{?-=1}I} \tag{1.10}$$

Given the transfer matrix de ned by Eqs. 1.7-1.8, the re ection coef cients of the heterostructure may be computed through the de nitions

$$A_{B}^{1}I - @^{0} = \frac{0}{\dot{0}} - \qquad A_{?}^{1}I - @^{0} = \frac{0}{\dot{0}} \tag{1.11}$$

The con ned electromagnetic modes of the heterostructure are complex wavevectors $@$ that satisfy $1 \cdot A_{B}^{1}I - @^{0} = 0$ for TE-polarized modes and $1 \cdot A_{?}^{1}I - @^{0} = 0$ for TM-polarized modes. In other words, the dispersion $@I^{o}$ is understood to be a pole of $A_{?}$ or $A_{B}$.

A common example consists of a planar slab of thickness $3_{=}$ on top of a substrate with permittivity $n_{B}$. It is well known that $1 \cdot A_{?} / 1 \quad A_{01}A_{12}4^{28:_{I6}3}$. Thus, the propagating modes $@I^{o}$ are found to satisfy [8]:

$$:_{I6}3 = \tan^{1}\left(8\frac{:_{I6}}{:_{IB}}\right) + \tan^{1}\left(8\frac{:_{I6}}{:_{I0}}\right) + c - \quad TE \tag{1.12}$$

$$:_{I6}3 = \tan^{1}\left(8\frac{n_{?}:_{I6}}{n_{B}:_{IB}}\right) + \tan^{1}\left(8n_{?}\frac{:_{I6}}{:_{I0}}\right) + c - \quad TM \tag{1.13}$$

where: $l_6$ is the out-of-plane wavevector of the slab, $l_0$ is the vacuum out-of-plane wavevector, and : $l_B$ is the substrate out-of-plane wavevector, each de ned by 1.10. We may consider two limiting cases. When $l \bullet 2 \ddot{Y} @_1 \ddot{Y} n_? l \bullet 2$, the modes are termed “Waveguide Modes", comprising of total internal re ection. On the other hand, $@_1 ¡ n_? l \bullet 2$ is allowed for TM modes when either $n_?$ or $n_l$ is negative (but not both). Such modes are termed "Hyperbolic polaritons", because the isofrequency surface de ned by Eq. 1.6 changes from elliptical to hyperbolic [9].

A simpler dispersion relation is obtained in the limit $3 \to 0$ and $@ \quad l \bullet 2$. This corresponds to an atomically thin plasmonic sheet of conductivity $f^1 l^{\,o}$ (usually graphene) resting on top of a bulk substrate. In this case, $1 \bullet A_? {}^1 l - @^2 = 0$ implies that

$$@^2 l^{\,o} = n_0 {}^1 n_B ¸ 1^o \frac{8 l}{2 f^{\,1} l^{\,o}} - \tag{1.14}$$

where $n_B$ is the substrate permittivity. For a Drude conductivity model, $f^1 l^{\,o} / 1 \bullet {}^1 l ¸ 8 W$, this yields the famous dispersion relation $@ \propto l^{\,2}$ for a 2D plasmon.

Figure 1.1b shows an example polariton dispersion. We plot $A_? {}^1 l - @^2 ¼$, revealing well-de ned poles with momentum $@$ much larger than the vacuum momentum $k_0 = 2c \bullet \_0$. On the other hand, they are still much smaller than the reciprocal lattice vector $2c \bullet 0$, suggesting the need for a nano-scale technique with momentum sensitivity between that of far- eld and atomic probes.

## 1.2 Scanning Near- eld Optical Microscopy: Detection of con ned modes

We overcome the momentum mismatch between free space light and con ned modes with the aid of a scanning nano-optical antenna (Fig. 1.1a), a technique referred to as “Scanning Near- eld Optical Microscopy" [10, 11] (SNOM). In this section, we consider elastically scattered laser light that interacts with the antenna and sample, referred here as “nano-IR”. Figure 1.1c shows how the antenna may be used to detect the con ned modes in real-space, represented by Fig. 1.1a. Light incident on a sharp edge launches the con ned mode, while the antenna outcouples the mode to the far- eld (arrows). The fringes in Fig. 1.1c are detected as the antenna-outcoupled light interferes

with light outcoupled directly from the edge. This interference may be understood simply by considering a plane wave $e^{iq_z z}$ launched from the edge, where $z$ is the tip position. The measured profile is then $\mathrm{Re}\{e^{iq_z z}\} = \cos(q_z z)$ (for now, we are ignoring the smaller phase accumulated along the tip-to-detector path). Another possibile detection scheme occurs when the tip serves to both launch and detect the modes. Here modes accumulate a "round-trip" phase of $2q_z z$ prior to outcoupling light. Since the tip acts as a point source, the form of the propagating field takes on an additional geometric decay factor $1/\sqrt{z}$. Therefore, profiles measured with SNOM $(z, \omega)$, are typically modeled by the form [12]:

$$(z, \omega) = \mathrm{Re}\left\{ e^{iq_z z}, \quad \frac{e^{i2q_z z}}{\sqrt{z^2 + a_{tip}^2}} \right\} \tag{1.15}$$

In the above expression $a_{tip}$ is the radius of the tip at the apex of the antenna, typically less than 20 nm. Thus $2\pi/a_{tip}$ sets the momentum limit for the confined modes, which also defines the spatial resolution limit for imaging real-space nano-structured materials. Moire patterns (Fig. 1.1d) are a quintessential example of naturally-formed nano-structuring. When two atomic layers are twisted by small angle (<1 degree), strain induces the formation of domains with distinct stacking arrangements [1], with the lowest-energy stacking configurations largest in spatial extent. In honeycomb lattices, this results in the formation of a triangular domains, spearated by domain walls of high strain. As a result, variations optical properties across the moire superlattice are expected, making nano-IR an indispensible tool for resolving these features.

## 1.3 Near-field photoluminescence

In Fig. 1.1a, the confined modes are excited by an external laser. These phenomeona are well described by classical electrodynamics, as outlined in section 1.1. In this thesis, we also examine quantum electrodynamical phenomena, particularly spontaneous emission. This is achieved by integrating photoluminescent vdW materials near other vdW materials that host confined modes. A general overview of photoluminesence is presented in Fig. 1.2. We focus on photoluminesence

Figure 1.1: Applications of nano-IR measurements. In panel (a), we show the general setup, consisting of an incident $p$-polarized electric field $E_0$ with frequency $\omega$ and in-plane momentum $q$. The transmitted and reflected fields from the vdW-heterostructure are denoted as $E_C$ and $E_A$, respectively. In order to excite and detect light with momenta $q \gg \omega/c$, a scanning nano-optical antenna with is brought into contact with the sample. (b) The imaginary part of $p$-polarized reflection coefficient, $\mathrm{Im}\, r_p$, is displayed in panel (b) for an example vdW heterostructure. Several dispersing branches in $\mathrm{Im}\, r_p$ are observed for $q \gg \omega/c$ (leftmost black line). The nano-IR mommentum limit, $2\omega/c$, lies between the light line and the atomic reciprocal lattice momentum $2\pi/a_0$. In panel (c), we display the field profile corresponding to the mode indicated by the white arrow in panel (b). In nano-IR experiments, the field profile at the top surface is measured as an interference between incident light scattering from the edge and tip, respectively. In panel (d), we show an example moire superlattice. Following conventional notation, adjacent domains are labeled as “AB" and “BA", respectively. Since the domain size is 100 nm, nano-IR imaging is required to elucidate the inhomogeneous optical properties resulting from such nano-structured media.

(PL) from semiconducting atomically-thin vdW materials with a band gap $\omega_g$. Upon photoexcitation above the gap, electrons and holes relax to the conduction and valence band extrema, respectively, forming bound excitons (X). If residual electrons or holes are present, three-body

bound states called trions (X*) can also form. Over a time $\tau_2$ [3], PL loses coherence due to elastic interactions with the environment, primarily from lattice vibrations (phonons). Over a longer timescale $\tau_1$ [3], the exciton population decays through multiple mechanisms. In a dissipative (lossy) medium, the exciton may lose energy as heat [13], though, idealy the electron and hole recombine via photon emission. The radiative and nonradiative recombination rates $W_{rad}$ and $W_{nrad}$, respectively, both set the population lifetime $\tau_1 = (W_{rad} + W_{nrad})^{-1}$.

For an emitter in vacuum, the spontaneous emission rate follows the Wigner-Weisskopf formula [3]

$$W_0 = \frac{|\mu|^3 \omega^3}{3\pi\varepsilon_0 \hbar c^3} \tag{1.16}$$

This result is determined by the vacuum photonic density of states. A key principle of quantum electrodynamics is that the surrounding electromagnetic environment can enhance the photonic density of states by the Purcell factor $W_{rad}/W_0$. In an isotropic medium with refractive index $n$, Eq. 1.16 increases by the factor $n$ due to modi cations of the speed of light ($c \to c/n$) and permitivity ($\varepsilon_0 \to n^2\varepsilon_0$). In chapter 3, we show that for thin dielectric slabs hosting a con ned mode @ $\omega_0$ with group velocity $v_g$, the Purcell factor scales as $\propto c/v_g$. We will also consider nonradiative quenching that results from losses in surrounding media, i.e. $\tau_2$.

Purcell factor measurements are typically performed with time-resolved photoluminesence (TRPL), where a pulsed laser excites excitons, and a fast detector records photon counts as a function of time delay after the pulse. Strictly speaking, TRPL measures the exciton lifetime $\tau_1$, which includes both radiative and nonradiative contributions, potentially complicating the Purcell factor extraction. Furthermore, con ned modes are dark in the far- eld, so intensity enhancements are not a reliable metric for Purcell enhancement. A rm demonstration of Purcell enhancement via con ned modes may be achieved with near- eld imaging, commonly referred to as nano-PL.

Nano-PL measurements operate similarly to nano-IR, as illustrated in Fig. 1.2c, but with PL as the incident source instead of a laser. A key distinction is that the PL source originates near the con ned medium, allowing it to be tuned via the Purcell effect. Similar to nano-IR, interference arises from two competing emission pathways: propagation to the tip or to the edge. However,

the observed propagation length is also limited by the coherence length $\ell_2 E_6$, such that

$@_2 ! \quad @_2 \, , \, 1 \bullet \ell_2$.

Figure 1.2: Time-domain view of Photoluminesence generation in solid-state materials. Panel (a) shows the initial photoexcitation process, where electrons and holes relax to the valence and conduction band (VB and CB, respectively) extrema, then form an exciton. For our purposes, these processes occur instantaneously ($t = 0$). After the dephasing time $t = \tau_2$ has elapsed, the excitons decohere from one another as a result of interactions with the environment, particularly phonons. After a later time $t = \tau_1$, the excitons have recombined, releasing energy either as heat or electromagnetic radiation. The latter process, termed spontaneous emission, is the fundamental mechanism for generating the observed PL.

## 1.4 Experimental Setup

Having outlined the essential principles behind near- eld microscopy relevant to this thesis, we now describe the experimental setup in greater detail. A 20-nm-radius tip of an atomic force microscope scans across the sample. For nano-IR measurements, an incident, broadly tunable laser is chosen to coincide in frequency with the relevant collective excitations. The laser scatters off of the tip and gets sent to a detector. We consider mid-infrared to near-infrared frequencies in this thesis, roughly 0.1-1 eV, requiring the use of Mercury Cadmium Telluride and InGaAs detector elements. The AFM tip operates in tapping mode so that the near- eld signal may be appropriately separated from far- eld backgrounds via tapping demodulation. We interferometrically detect the demodulated signal at harmonics of the tapping frequency (via the standard interferometric pseudo-

heterodyne technique [10]), we readily obtain background-free signals with amplitude and phase information. The end result is a collection of nanoscale images in the region of interest: AFM topography, near- eld amplitude, and near- eld phase. All nano-IR data were acquired with a Neaspec Gmbh microscope with ARROW-EFM PtIr cantilever tips. Our mid-infrared quantum cascade lasers, from Daylight Solutions, operate in the range 0.1-0.3 eV.

For nano-PL measurements, a tunable CW laser (M-squared, Inc. follows the same path as in nano-IR imaging to excite the sample. For optimal eld enhancement, an App Nano Ag/Au-coated tip is set to contact mode. As Fig. 1.3 indicates, uorescing light is collected in forward scattering, rst with the tip in contact, then with the sample retracted by 150nm. The emission is sent directly to a thermoelectrically cooled InGaAs CCD/spectrometer unit (Andor Instruments, Inc., iDus 9/Kymera). Before reaching the spectrometer, the excitation light is blocked with a Thorlabs, Inc. 1100nm OD5 premium long pass lter. To aid in rejection of far- eld PL, the ltered light is focused through a 75 micron pinhole. Upon entering the spectrometer, the light is dispersed with a 150 lines/mm grating blazed at 1200nm. Integration times of 6 seconds are typically used, and single line pro les are repeated and averaged up to 10 times for further signal-to-noise improvement. To compensate for spatial drift, rows between consecutive measurements may be aligned by tracking the sample edge position in the AFM topography. Each pixel represents the difference in photoluminescence counts measured in- versus out-of-contact.

Fig. 1.1c shows that nano-imaging experiments of con ned modes rely on an interference between two outcoupling channels. We already described in Section 1.2 that the experimentally observed dispersion $\omega_{1B}$ may differ from the correct dispersion $\omega$ by a factor of 2 when intereference occurs between successive tip outcoupling events. Since the edge-to-detector and tip-to-detector paths are in general different, the experimental dispersion for edge-outcoupled modes differs from correct dispersion $\omega$ by a known geometric factor. Let $\theta$ be the angle of incidence with respect to the horizontal, and $\psi$ the angle with respect to sample edge. We then arrive at the relation [14]:

$$\frac{2\omega_{1B}}{l} = \sqrt{\frac{2\omega^2}{l}\left(\cos^2\psi - \cos^2\theta\right)} - \sin\psi\cos\theta \tag{1.17}$$

Note that the azimuthal angle in the Neaspec software is de ned such that $n_{neaspec}$ 2c•3 ¸ \.

Eq. 1.17 is not relevant for polaritonic modes satisfying @g l •2, yielding @= @in this limit.

Figure 1.3: Optical Setup for nano-PL/nano-IR. The excitation laser with energy $\hbar\omega$ split at the Beam splitter (BS). One path focuses the light on the tip. The other path is sent to a reference mirror, which oscillates at frequency $\Omega_{A45}$. The elastically-scattered light is detected back along the same path, interfering with the reference arm at the photodiode position (PD). Photoluminescence at energy l Ÿ , generated at the sample, is collected in the forward path. The emission is separated from the excitation with a long-pass lter and sent to a Thermoelectrically cooled InGaAs CCD/Spectrometer system

## 1.5 Thesis Overview

The remainder of this thesis is organized as follows. First, we explore nano-IR imaging of moire superlattices formed by two twisted bilayers of hexagonal boron nitride. Using nano-spectroscopy, we map the variation of the phonon frequencies across different stacking con g-urations. Next, we investigate near- eld photoluminesence from an $MoTe_2$ monolayer embedded within two bulk $WSe_2$ waveguides. Our nano-PL technique presents a direct visualization of Pur-cell enhancement into waveguide modes through sub-diffractional PL mapping. Finally, we em-ploy nano-IR imaging to study plasmon propagation in charge-transfer heterostructures composed

of multilayer graphene and $\alpha$-$RuCl_3$. Here, plasmons not only reveal key band structure properties but also provide a platform for novel collective excitations such as plasmon-plasmon coupling. This thesis highlights the diverse range of nanoscale light-matter interaction takes place in vdW heterostructures.

# Chapter 2: Nanoscale Lattice Dynamics in Hexagonal Boron Nitride Moire Superlattices

## 2.1 Introduction

Moire superlattices have prompted on-demand control of electronic[15, 16, 17, 18, 19], optical[19], excitonic[19, 20], plasmonic[21], and magnetic[18, 19] properties. A universal attribute of vdW moiré superlattices is that their emergent physics is demonstrably local with the relevant length scales ranging from atomic to mesoscopic. Accordingly, scanning probe measurements are being widely utilized to visualize the electronic structure and elementary excitations across the moire landscapes[15, 21, 22]. Very recently, these efforts have extended to nano-scale studies of lattice dynamics[23, 24]. Twist-angle tunability of phonons is an appealing direction in view of their signi cant role in superconductivity[23], light-matter interaction[25] and thermal transport[26] of vdW heterostructures. Phonons also serve as effective reporters of strain[27] and ferroelectricity[28]. Pursuant to these goals, we report on the lattice dynamics in twisted layers of the prototypical vdW polar insulator hexagonal boron nitride (hBN) [29, 9]. Hyperspectral nano-infrared (nano-IR) imaging reveals systematic variations of the in-plane optical phonon frequencies amongst the triangular domains and domain walls in the moiré superlattices. Our ab-initio calculations implicate the underlying graphite substrate in the stark phonon contrast between the moiré domains, hinting at a role of atomic registry in the dielectric coupling between hBN and graphite.

## 2.2 Multi-channel imaging of twisted hBN moire patterns

We used the standard tear-and-stack method to deterministically produce atomically-thin twisted-hBN (t-hBN) moire superlattices directly on graphite substrates. Nano-imaging data for representative structures are displayed in Fig. 2.1. We investigated parallel-aligned structures formed by

a bilayer on monolayer (“sample 1”) and by a monolayer on a monolayer (“sample 2”). After stacking, the samples are vacuum annealed up to 500°C [30]. Empirically, the high temperature seems to remove more tape and polymer residue in the moiré superlattice than lower temperatures. The exposed graphite regions after this annealing appear to become rougher, whereas the hBN encapsulated regions remain smooth. We nd similar near- eld spectra between samples 1 (Fig. 2.1b–e) and 2 (Fig. 2.1f–l), suggesting the consistency of the sample preparation technique and relative sensitivity and insensitivity to the interface and total layer number, respectively. Note that such parallel- stacking is distinct to natural AA'-stacked bilayers. In a past study[24], the lattice dynamics of naturally-stacked (AA') hBN hexagonal moiré patterns demonstrated a small variation of the phonon linewidth within the 500-nm sized domains. This particular moiré pattern, however, resulted from a happenstance buried interface 15nm under the surface of a bulk ake, complicating the isolation of the interface lattice dynamics. Here, we examine lattice dynamics in the parallel-stacked and atomically-thin limits. The orientations of the Bernal con gurations of t-hBN, also known as AB and BA, are de ned in Figure 2.1a. Unlike AA' alignment, these con gurations host ferroelectric polarization [22, 31, 32]. Common paraelectric AA stacking occurs when the two hBN layers line up directly above each other. All of these stackings, including the saddle point (SP) con guration (not shown), are represented in equal proportion upon twisting two rigid hBN monolayers. Mechanical relaxation [33] then causes our low-twist-angle samples to form triangular AB and BA domains divided by SP stacking lines with vortices of the domains anchored to AA sites.

We proceed with our study of t-hBN superlattices by visualizing domains and domain walls in t-hBN. Piezo-force-microscopy (PFM) imaging in Figure 2.1f captures a representative moiré pattern from sample 2. The triangular domains vary signi cantly in size, a testament to the inhomogeneous twist angle within the eld of view of Fig. 2.1a. PFM contrast is a common reporter of ferroelectric domains [34]. Typically, the contrast reverses between neighboring domains due to a sign-varying ferroelectric polarization. Electrical force microscopy (dc-EFM), also sensitive to the interfacial electrostatic polarization, validates our PFM imaging (inset in Fig. 2.1f), con rming the

ferroelectric nature of the domains [31]. Notably, the curvature of domain walls can be tuned by applying voltages to the tip. Positive (negative) tip-sample voltages create an energetic preference for ferroelectric AB (BA) domains, as conjectured by Yasuda, et al [32]. This enables a well-de ned assignment to AB and BA domains in our data. Figure 2.3 presents dc-EFM imaging of sample 2 at zero and 3.14 V bias, applied such that the tip is biased and the sample's silicon substrate is grounded. Zero bias represents the remnant 2D ferroelectric polarization, where all domain walls appear relatively straight. On the other hand, a nite bias offsets the energy difference between domains, producing pronounced curvature. Since such downward electric elds are expected to create preference for AB stackings, we label the domains accordingly. Such eld-induced domain wall motion has been reported previously in studies of twisted multilayer hBN interfaces [19].

Our phonon imaging experiments utilize the combined nano-optical and atomic force microscope (AFM)-based scattering-type scanning near- eld optical microscopy (s-SNOM), illustrated in Figure 2.1a (see methods). Interferometric detection allows us to investigate both the amplitude ( and phase) of the scattering signal over a broad range of IR frequencies. We focus on the region dominated by the in-plane TO phonon response between 1360 and 1380 cm$^{-1}$. The s-SNOM imaging provides quantitative topographic information and complex nano- IR contrast in the region of interest with spatial resolution down to 10 nm. As can be seen in Figures 2.1b-e, 2.1g-l, each element of the reconstructed superlattice—AB/BA domains, AA sites, and SP domain walls—shows a distinct IR contrast. Nano-IR signals (both amplitude and phase) remain relatively uniform throughout either of the two Bernal triangular domains. Meanwhile, we notice stronger variations amongst the AA sites and SP domain walls. The overall pattern seen in the nano-IR images follows the shape of the domains uncovered by PFM/EFM, while remaining featureless in AFM topography (Figure 2.2 below). Upon tuning the laser frequency, we detect a strong change, even reversal, of the stacking- dependent near- eld amplitude and phase contrast. Such frequency sensitivity suggests systematic spatial variations of the TO resonance between AB/BA domains, SP domain walls and AA sites (Figures 2.1c-e and 2.1g-l and additional images in Supplementary Fig. 6 of Supplementary Note 6). The images presented here demonstrate the utility of nano-IR

measurements in revealing the trends and real space patterns in the lattice dynamics of twisted heterostructures.

Figure 2.1: Nano-imaging of moiré lattice dynamics in t-hBN. (a) Schematic of near- eld imaging of t-hBN sample on a graphite/$SiO_2$/Si substrate. As illustrated by arrows, light scatters off the tip and is sent to a detector. When scanning the tip over the moiré region, we observe a triangular lattice. A schematic of a relaxed superlattice is shown underneath the tip. The possible stacking con gurations are drawn above (AA, AB, BA). All experiments are performed with a laser tuned in the vicinity of the TO-phonon frequency. The eigenmode is illustrated on the left, where atoms oscillate orthogonally to the wavevector $\mathbf{q}_{TO}$. (b,c) Images of the near- eld amplitude taken at two selected frequencies for sample 1 (bilayer-monolayer stacking). (d,e) Images of the near- eld phase taken at two selected

## 2.3 Comparison of Topographic and Near- eld and Imaging

Here we argue that topography is not in uencing the observed near- eld moiré patterns, and that the response observed in Fig. 2.1 is purely optical. While Near- eld imaging shows pronounced contrast in the moiré-patterned region, the topographic signal shows no contrast. This

is not a fundamental expectation: with an AFM of suf cient sensitivity, a moiré pattern can be observed in topography [35]. Typically, topographic height should be largest along domain walls due to relaxation-induced corrugation. In a ferroelectric material like t-hBN, the tip-sample interaction can produce additional topographic responses. The dc-EFM technique then isolates this from standard topographic features. Figure 2.2 compares topography and EFM images, performed without any laser illumination or electrical bias. In this work, none of our topographic images have suf cient  delity to resolve the moiré, even with the ferroelectric interaction. Ultimately, the best con rmation of the reliability of our near- eld imaging is with spectroscopy. As Fig. 2.1 demonstrates, the contrast is strongly sensitive to the laser frequency, whereas a topographic-induced image would be frequency independent.

Figure 2.2: Topography in moiré regions. Comparison of topography and nano-IR channels for samples 1(c-d) and 2(a-b). Tapping-mode height in (a),(c) shows no observable moiré pattern, while being easily distinguished in the dc-EFM images of (b), (d).

Figure 2.3: Sample 2 dc-EFM imaging at various tip bias voltages. The reversal in curvature from $+_{C8?}$ = 3•14 V (a) to $+_{C8?}$ = 3•14 V (c) allow us to identify the AB and BA domains. The contrast at 0 V (b) is attributed to the Ferroelectric remnant polarization.

## 2.4 Nano-IR spectroscopy of lattice dynamics in twisted hbN

A salient feature of data in Fig. 2.1 is a prominent contrast between AB and BA domains. We unambiguously link this contrast to the properties of the TO mode by imaging the domains at a dense set of monochromatic frequencies between 1360-1385 $cm^{1}$. There, subtle but systematic variations in the frequency-dependent nano-optical contrast are well-captured by the amplitude ratio and phase difference for two stackings (e.g. •( (% and q q(% ). This hyper-spectral analysis amounts to three sets of independent amplitude and phase data plotted in Fig. 2.4 for sample 1. Inspecting Figures 2.4a-f, we nd that the AB/AA and AB/SP contrasts are most prominent. The contrast between AB and BA domains is numerically weaker but highly reproducible. All amplitude spectra show two extrema whereas phase spectra reveal a single peak centered around 1370 $cm^{1}$.

Spectra in Figs. 2.4a-f enable quantitative analysis of local lattice dynamics in t-hBN. We describe the optical response by the frequency-dependent in-plane dielectric function $n^{1}I^{o}$. For natural hBN, it is well established that near the TO resonance, $n^{1}I^{o}$ takes the Lorentzian form [36]:

$$n^{1}I^{o} = n_{1} \, , \frac{5}{I^{2}_{)\$} \quad I^{2} \quad 8WI} \tag{2.1}$$

where 5 is the oscillator strength, $\omega_{TO}$ the TO phonon frequency, W the phonon damping rate and $n_1$ the high frequency dielectric constant. Eq. 2.1 holds for both bulk and monolayer hBN, but with varying Lorentzian parameters [37, 38]. With this dielectric function model on hand, we assume that each sub-diffractional stacking con guration conforms with Eq. 2.1. We then use the lightning-rod model [11] to t to our observables: spectra of near- eld amplitude and phase. We take 5, $\omega_{TO}$ and W of each stacking con guration as tting parameters. The results of the tting are shown in the solid lines of Figures 2.4a-f. Here we also plot the extracted dielectric functions $n_1$ '4 »n¼ $n_2$ < »n¼ and Fig. 2.4i tabulates the corresponding Lorentzian parameters. We nd a systematic decrease in the TO-phonon frequency from the BA to AA con gurations by nearly 4 $cm^{-1}$. Similar results are obtained for Sample 2.

## 2.5 Origin of the AA and SP TO-frequency shift: Strain

Next we analyze phonon frequency shifts between domain wall and AA-vortices in Fig. 2.4. The larger AA and SP-stacking frequency shifts documented in Fig. 2.4i admit an interpretation in terms of relaxation-induced strain. Using our ab stacking energies in Fig. 2.6b, we evaluated such a strain pro le. The only required inputs are the coordinates of AA sites [39].

Modeling of the atomic relaxation of twisted bilayer hBN was performed within a continuity model [33] and extended to general real-space geometries [39]. In this model, the total energy of the system is taken as the sum of an elastic energy and a stacking energy term. The total energy was minimized in search for the interlayer real-space displacement eld corresponding to the relaxed structure. The stacking con guration at selected points were imposed as boundary conditions. In the case of a non-uniform strain map as discussed here, such points were chosen to account for the position of AA-stacking con gurations from the experimental image. The generalized stacking fault energy (GSFE) parameters for the AA-type and AA-type twisted bilayer hBN heterostructures were taken from Zhou et al. [40], written in the convention of Carr et al. [33]. Relaxation simulations with domain curvature modify these parameters to accommodate the expected AB/BA energy difference from either ab or ba BN/graphite stackings. The lattice spacing was taken as

Figure 2.4: Stacking-dependent nano-IR spectroscopy of t-hBN. (a-c) Spectra of the scattering amplitude ratios for three independent con gurations averaged over AB, BA and SP regions. The insets are near- eld amplitude images of sample 1 at 1367.9 $cm^{-1}$ marking the regions used to construct spectra in the main panels (scale bars are 200 nm). (d-f) Spectra of nano-IR phase differences for three independent con gurations averaged over AB, BA and SP regions. The error bars in (a-f) equal the standard deviation from averaging amplitude and phase channels across pixels of identical stacking (see methods for more details). All spectra are all simultaneously t to the Lorentz model (Eq. 1). The solid lines show the resulting tting curves described in the text. (g-h) Spectra of the extracted dielectric functions. (i) The tting parameters, with uncertainties on the last digit in parentheses (e.g. 1369.6(5) = 1369.6 ± 0.5), are reported in the table on the bottom right (all in units of wavenumbers). The uncertainties are taken to be the tting parameters' standard deviation upon varying the initial guess parameters.

2.51 Å.

We de ne compressive $\epsilon_2$ and shear $\epsilon_B$ strain in terms of the strain tensor $\epsilon_{ij}$ as:

$$\epsilon_2 = \frac{\epsilon_{GG} - \epsilon_{HH}}{2}; \quad \epsilon_B = \sqrt{\frac{(\epsilon_{GG} - \epsilon_{HH})^2}{4} + \epsilon_{GH}^2} \tag{2.2}$$

We then calibrate the strain with the fractional TO-frequency shift via the well-established

formula [27]

$$\frac{\omega}{\omega^{0}_{)\$-8}} = [\ _{2} \quad [\ _{B} \tag{2.3}$$

where and are constants and $\omega^{0}_{)\$-8}$ is the unperturbed TO frequency in stacking con guration 8 Comparing this formula to our ab-initio calculations of strained AA-type BN frequency shifts, we nd = 0.041 (% strain) $^{1}$ and = 0.0084 (% strain) $^{1}$ (see methods of main text). Note that in addition to a frequency shift, the term predicts a splitting into two orthogonal modes. The high-frequency mode has LO symmetry, while the low-frequency mode contributes to the TO-frequency shift, speci cally $\omega_{)\$} = {}^{1}[\ _{2} \quad [\ _{B}\omega^{0}_{)\$-8}$ and $\omega_{!\$} \quad \omega_{)\$} = 2[\ _{B}\omega_{)\$-8}$. This enables us to plot the relaxation-induced strain map for sample 1 and consequently the predicted TO and LO shifts.

We see from these maps that, within our model of the substrate-modi ed AB/BA stacking energies, the SP domain wall and AA-site surrounding areas are the only strained regions. Strain maps also identify a noticeable domain wall curvature. The magnitude of domain wall curvature depends on the hBN/graphite stacking and strain distribution between the hBN layers. The shear strain (Figure 2.5b), providing the LO-TO splitting (Figure 2.5e), shows a repeating pro le across all domain walls. The compressive strain pro le (Figure 2.5c), providing the TO shift (Figure 2.5d), seems to vary and even switch sign between different domain walls. The smallest twist-angle regions (largest moiré periodicity) show the largest strain. This qualitatively resembles the inhomogeneous domain wall nano-IR response, also displayed in Figure 2.5a. The simulation appears to overestimate this effect, however, partly due to numerical inaccuracies near terminating domain walls and the assumed strain distribution between the layers. However, the remaining inconsistencies in the interior require more systematic investigations of individual domain responses. Meanwhile, Figure 2.5e predicts enhanced LO-TO splitting along the domain walls, which correctly manifests as an increased oscillator strength seen in Fig. 2.4i. Alterative scenarios invoking, for example, a variation of interlayer spacings are not consistent with our data. We therefore conclude that moire-induced strain plays a central role in the AA and SP frequency shifts, oscillator strengths, and inhomogeneous broadening.

Figure 2.5: Strain-induced frequency shifts of Sample 1. Maps of relaxation- induced frequency shifts. (a) near- eld amplitude data taken for sample 1 at 1367.9 $cm^{-1}$. Corresponding incompressive (b) and compressive (c) components of the relaxation-induced strain tensor computed through a relaxation simulation (see methods). Simulated (d) TO and (e) LO frequency-shift maps of the same region (derived from b-c and Equation 2.3).

## 2.6 Origin of the AB/BA TO-frequency shift: Substrate interaction

To understand the AB/BA frequency shift seen in Fig. 2.4, we considered the role of strain and also the impact of the graphite substrate (Figure 2.6). Our analysis in Section 2.5 shows that strain does not extend into the domains themselves and is therefore likely irrelevant to distinctions between $I_{)\$}$ and $I_{)\$}$. We therefore focus on the role of local atomic registry between hBN and the subjacent graphite.

First-principles calculations are performed using density functional theory within the JDFTx code [41]. All calculations are done using ultrasoft pseudopotentials [42] and with the PBEsol exchange-correlation functional [42]. In order to capture the two-dimensional (2D) nature of these systems, we use a Coulomb truncation scheme [43], which successfully removes arti cial interlayer interactions in both the electronic optimization and the phonon calculations. This is particularly important, as it correctly predicts no LO–TO splitting in unstrained 2D hBN [44]. The plane-wave basis set used has a kinetic energy cutoff of 30 Hartrees. Phonons are modeled using

nite differences and throughout the text we consider the zone center longitudinal optical (LO) and TO mode frequencies, speci cally, which are equivalent in the 2D limit. In order to model the vdW interlayer interactions, we use the scheme introduced by Grimme [45]. We use a global scaling factor of 0.15, as this appropriately captures the interlayer spacing of the bilayer hBN, as well as provides good agreement with experiment on optical phonon energies. All calculations use an effective in-plane lattice constant of 2.505Å.

In the case of calculations related to the substrate-modi ed stacking energy in Fig. 2.6, we use a hexagonal unit cell of bilayer hBN stacked on top of graphene. We model the system using a 24×24×1 -centered k-point -mesh and use a 6×6×1 phonon supercell to determine the harmonic phonon properties. In the case of the frequency shifts with strain, we adopt an orthorhombic unit cell of bilayer hBN for ease of use in applying strain along the in-plane cartesian directions. We use a 18×8×1 -centered k-point mesh and a 6×4×1 phonon supercell to capture the shifts in the optical modes with strain. We strain the lattice vectors by up to 0.5% in each direction, in order to t for the C and D constants associated with Eq. 2.3.

Figure 2.6a shows the three possible orientations that the graphene can adopt with the bottom layer of hBN in the limit that the graphene and hBN lattices are commensurate. In the absence of a substrate, AB/BA stackings are identical, but the presence of the graphene causes very small differences between the two con gurations, both in terms of energy and optical phonon frequency, seen in Fig. 2.6c.

In Figure 2.6a we illustrate three possible hBN/graphite commensurate stackings. For clarity, we label hBN/hBN con gurations with the upper case, e.g. AB/BA, while hBN/graphite con g-urations are denoted in the lower case, e.g. ab/ba. In Figure 2.6a, we illustrate the bottom hBN layer on the top graphite layer for the three possible ab, aa, and ba stackings. The corresponding ab-initio stacking energy landscapes are displayed in Fig. 2.6b. We remark that the AB/BA minima share inequivalent energies in the presence of underlying graphite (Fig. 2.6c). Calculations reveal that the that ab alignment is strongly favored over ba and aa alignments by 300 meV nm$^2$. The histogram in Fig. 2.6d shows that graphite's presence also causes a nite frequency shift to the TO

mode between AB and BA arrangements. Beyond the qualitative agreement, we nd that our calculations for the ab stacking arrangement correctly predict the l )$ l )$ phonon frequency shift. This agreement is illustrated in Figs. 2.6e,f where we overlay the raw spectra from Figs. 2.4c,f with the results of nano-IR signal calculations found within the lightning rod model [11]. That frequency shift shows no twist-angle dependence, so long as commensurability is present between the hBN and substrate layers.

## 2.7 Role of Interlayer Spacing on Phonon Frequencies

Next, we examine the interlayer separation between hBN and graphite. We employ the same calculations as above, but with an AB/BA modi ed GSFE. Here, we nd a very slight interlayer-spacing separation difference for ab stacking relative to ba and aa stackings (Figure 2.7). Note that AB and BA stackings have the same separation distance and is therefore not the contributing factor for their frequency shift. We also calculate the dependence of the AB/BA frequency shift on the graphite interlayer separation. These calculations reveal a sensitive inverse relationship between the magnitude of the )$ l )$ frequency shift and the hBN/graphene separation distance. Figures 2.7a-b show that the sensitivity to the commensurate hBN/graphite alignment happens below about 4 Å. Above that point, the stacking energy and frequency shift is nite, decreasing monotonically to zero as the graphite layer separates off to in nity. The squares in Figure 2.7b indicate that the natural (energetically favorable) separations between hBN and graphite are indeed below this critical value.

## 2.8 Effect of Graphite Subsrtate on Ferroeelctricity

While our ab-initio calculations found no direct evidence of ferroelectric coupling to the phonons, we did obtain a stacking-dependent modi cation of the ferroelectric polarization in the presence of graphite. These dipole moments change monotonically with hBN/graphite separation (in a direction dependent on the stacking), but our calculations cannot comment whether they remain equal and opposite.

Figure 2.6: Graphite substrate controls the AB/BA contrast in t-hBN. Upper-case notation (e.g. AB, BA etc) is reserved for hBN-hBN stacking con gurations whereas the lower case is utilized to describe various hBN stacking options on graphite (e.g. aa, ba etc). (a) Schematic of hBN/graphite stacking con gurations. (b) Stacking energy landscapes for all three commensurate hBN/graphene con gurations. Dashed black horizontal lines highlight the subtle energetic preference of AB over BA stackings. (c) Plot of the calculated BA-AB energy difference and (d) TO frequency shift for each commensurate hBN-graphene stacking. (e) Data points reproduce the spectrum of in Fig. 2.4 (with same error bars) plotted using a normalized frequency horizontal axis. Solid line: spectrum of the scattering amplitude calculated with the lightning-rod-model. (f) Similar to (e), data points reproduce the spectrum of q from Fig. 2.4 For consistency with Figure 2.4, the solid line uses the same oscillator strength and damping (not obtainable in this model) extracted from the Fig. 2.4 AB tting parameters.

Figure 2.7: Tuning AB/BA phonons with a graphene substrate. The calculated variation of the BA-AB (a) energy contrast and (b) frequency shifts as a function of bottom BN/graphene separation distance, shown for the three different commensurate graphene stacking con gurations presented in Figure 2.6 The squares in panel (b) correspond to the frequency shifts for the fully-relaxed con gurations, presented in Figure 2.6.

Figure 2.8: Tuning ferroelectricity with a graphene substrate. Difference in polarization calculated in one unit cell of different stacking con gurations of bilayer BN on graphene.

## 2.9 Conclusion

The totality of these observations document that graphite prompts symmetry- breaking between moire domains in hBN. We expect all polar twisted bilayer materials hosting sharp strain-dependent resonances to showcase similar dispersive moire patterns. The AB/BA frequency shift should be  nite in the presence of any symmetry-breaking substrate, with a magnitude dependent on the sample-substrate interaction. Here, the similar lattice constants between hBN and graphite optimize the effect. Investigations of t-hBN lattice dynamics on other substrates are out

of the scope of the present work. The interaction strength between graphene and $p_z$ orbitals of monolayer hBN adds an additional contribution to the harmonic potential landscape and therefore modi es the optical phonon frequency. Similarly, in AB and BA bilayer stacking, the net z dipole of t-hBN interacts with the graphene dependent on the direction of the dipole. This asymmetry is evident from Fig. 2.8, where we calculate the difference in AB/BA dipole moments as a function of graphene separation and local stacking con guration. Thus, while ferroelectricity does not directly soften the phonon, as typical for the out-of-plane modes [46], the ferroelectric dipole's substrate interaction can feasibly translate to modi ed lattice dynamics between AB and BA stackings.

Empowered with subdiffractional nano-IR imaging, we resolved nano-scale TO frequency variations in an hBN moire superlattice. Our rst-principles calculations nd a new TO frequency shift between otherwise identical domains, dependent on the atomic registry between graphite and atomically-thin hBN. Our calculations led us to infer that the directional-dependent interaction of the ferroelectric dipoles with graphite plays a role in the frequency shift of infrared phonons associated with the AB and BA domains. These ndings are reminiscent of plasmon-phonon coupling between proximal atomic layers of vdW materials [47]. Here, the novelty is that the putative plasmon-phonon hybridization is sensitive to the intricacies of the interlayer atomic arrangements of hBN on graphite. To further test and tune this effect, we anticipate exploration of gated t-hBN devices embedded in plasmonic media.

# Chapter 3: Van der Waals waveguide quantum electrodynamics probed by infrared nano- photoluminescence

## 3.1 Introduction

Spontaneous emission of atoms, molecules or solids can be altered by precisely engineering the electromagnetic environment of these emitters with cavities or waveguides. The many roles of the electromagnetic environment in the emission are often categorized by the Purcell effect [48, 49, 50, 51]. The QED description of electromagnetic cavities established that the ef cacy of the Purcell effect is governed by the ratio $\&\bullet+_{<}$, where $\&$ is the cavity quality factor, and $+_{<}$ is its mode volume. Accordingly, the extreme subwavelength con nement ($+_{<}$) enabled, for example, by nano-cavity plasmons produces some of the largest reported Purcell enhancements [52, 53, 54, 55, 56, 57]. However, plasmonically-controlled emission inevitably carries signi cant loss (i.e. low $\&$) inherent to plasmons in metals. Dielectric cavities and waveguides circumvent the loss problem and achieve much larger values of $\&$, enabling con ned light to propagate over considerable distances. However, sophisticated metastructure designs [58, 59, 60, 13, 61] are typically required to achieve notable Purcell enhancements in all-dielectric waveguides. Remarkably, high refractive index van der Waals (vdW) materials seamlessly integrate both superior con nement and low loss [2, 9, 8, 62], effectively serving as natural cavities or waveguides in the infrared frequency range (0.05 – 1 eV). Nevertheless, the ability of natural vdW waveguides to promote Purcell enhanced photoluminescence (PL), especially at technologically important infrared frequencies, remains largely unstudied because of technical limitations associated with probing both spatially and spectrally resolved emission at the nano-scale.

Here we report on waveguide-assisted Purcell effects in the infrared range, harnessing transition metal dichalcogenides (TMDs) as both emitters and waveguides. Because of their high re-

fractive indices, TMDs enable total internally-re ected light to propagate within waveguides with wavelengths 3-5 times smaller than free space light [8, 63]. The dispersion of waveguide modes in TMDs is governed by the slab thickness and can be adjusted in the exfoliation process. Upon thinning down to the monolayer limit, many TMDs, including 2H-$MoTe_2$, exhibit a direct band gap (Fig. 1a,b) and emit PL with high quantum ef ciency [64]. Using the dry-transfer stacking technique (methods), we utilized the two planar slabs of $WSe_2$ with judiciously chosen thicknesses to encase the monolayer of $MoTe_2$ (Fig.1c). This procedure enables deterministic control of the emitting layer vertical placement within the waveguide, thereby optimizing the Purcell enhancement. Losses in TMD materials are relatively low when probed below the optical gap (commonly in the 1 – 2 eV range). However, experimental methods for spatially resolving PL from buried emitting layers in the infrared range presents a technical challenge. Thus, direct imaging of Purcell-enhanced infrared PL reported in Fig. 3.1 remained insofar elusive.

We overcome challenges of nano-PL spectroscopy and imaging of waveguided structures by utilizing experiments outlined in Fig. 3.1c, facilitated by a recently developed antenna-based imaging tool that combines nano-PL and nano-scattering modalities [65]. These antennas nd practical implementation through the sharp tips of atomic force microscopes. To date, antenna-based nano-PL data [65, 66, 67] have been collected from emitters directly underneath the tip, inducing local near- eld PL enhancement. Here, aided by the high-index/low-absorption vdW waveguides, we utilize nano-PL to spatially and spectrally resolve emission from a uniformly-excited buried-layer into con ned waveguide modes of the surrounding TMD slab. In our data, the waveguiding manifests as a dispersing interference pattern, implying coherent light propagation within the examined sample volume. We augmented the nano-PL data with collocated nano-scattering dispersion mapping and analytical Purcell-factor modeling. The totality of the observations and modeling establish the rst nano-scale imaging of Purcell-enhanced emission into coherently propagating waveguide modes. Our experiments set a precedent for the imaging and Purcell analysis of emission in van der Waals waveguide-QED platforms.

## 3.2 Sample Preparation

Monolayer 2H-$MoTe_2$ is chosen as a relatively narrow bandgap emitter, and the larger bandgap material $WSe_2$ is selected for the receiver waveguide. 2H-$MoTe_2$ monolayers are prepared by exfoliating lab-grown crystals inside a glove box onto $O_2$-plasma treated $SiO_2$/Si substrates. Monolayers of adequate size are then fully encapsulated with the dry transfer stacking technique. A polycarbonate (PC) stamp first picks up a top $WSe_2$ flake, which is then used to pick up the $MoTe_2$ monolayer. A second $WSe_2$ flake is then picked up over the $MoTe_2$ region. The transfer slide can then be brought outside of the glovebox without risk of $MoTe_2$ degradation, where the stack is then transferred onto a template-stripped gold substrate. The melted PC is dissolved from the substrate by rinsing in beakers with Chloroform and IPA for 10 seconds each over several iterations.

Adhesive-free template-stripped gold substrates are prepared by cold welding thin films of gold to each other. This was accomplished by first evaporating gold onto two polished $SiO_2$/Si wafers. The "bottom" wafer had a 20 nm Au/5 nm Ti coating, while the "top" had a 100 nm of Au no adhesion layer. Both wafers were diced into 1x1 cm chips, which were then cleaned with $O_2$ plasma prior to use. Top and bottom chips were then stacked together with gold layers touching, clamped in a vice, and placed under vacuum. After >10 minutes, the sample was removed, and a razorblade was used to pry the chips apart. This results in delamination of the top gold film onto the bottom gold surface. The roughness of the newly exposed gold surface mimics that of the polished $SiO_2$, which is significantly smoother than an evaporated metal film.

Fig. 3.1a illustrates that type-I band alignment in our waveguide devices promotes charge transfer from $WSe_2$ to $MoTe_2$, potentially yielding enhanced emission intensity [68, 69]. The dipoles activated in $MoTe_2$ by the excitation laser with energy $\hbar\omega = 1.65$ eV emit 0.8-1.05 eV light into the $WSe_2$ waveguide.

Figure 3.1b displays the room-temperature imaginary (dissipative) part of the dielectric function, $n_2 = \Im\{\tilde{n}\}$, for bulk $WSe_2$ and monolayer $MoTe_2$. A large area (50 x 50 $\mu m^2$) hBN-encapsulated $MoTe_2$ monolayer is transferred onto a fused-silica substrate with several patterned 200 x 200

`$m^2$ gold pads. Similarly, a bulk (125nm) $WSe_2$ flake is transferred onto the same substrate. Reflectance microscopy measurements on these samples are performed with the Bruker Hyperion II system. A tungsten lamp, $CaF_2$ beam-splitter, and Si photodiode are used for the visible range, while a Globar lamp, ZnSe beam-splitter and Mercury-Cadmium Telluride detector are used for the infrared range. A Lorentz multi-oscillator model (in the form of Eq. 1.2) is used to fit to the differential reflectivity data. The data confirm the $MoTe_2$ exciton at $E_{1B}$ = 1.09 eV is well below the $E_{1B}$ = 1.59 eV exciton resonance in $WSe_2$. As testament to the high crystal quality of $MoTe_2$, the 2B exciton at $E_{2B}$ = 1.22 eV is also observed.

## 3.3 Hyperspectral Nano-Photoluminescence Imaging

We display our antenna-based nano-optical setup in Fig. 3.1c, with further details provided in section 1.4. The $WSe_2$/$MoTe_2$/$WSe_2$ structures rest on template-stripped gold (methods), which improves both the PL excitation and the collection of waveguided emission. The excitation laser illuminates the entire sample in the far field, initiating emission from the $MoTe_2$ monolayer. As illustrated in Fig. 3.1c, the $MoTe_2$ may be expected to emit directly into the $WSe_2$ waveguide modes. This waveguided emission then propagates over macroscopic distances in the form of well-defined waveguide modes and eventually reaches the tip or top $WSe_2$ edge. Both the tip and the $WSe_2$ edge outcouple waveguide modes, transforming them into free-space light that is detected by an InGaAs CCD/spectrometer. Each emitting $MoTe_2$ dipole utilizes both tip- and edge-enabled outcoupling channels, producing interference at the detector set by the emission frequency $\omega$ and tip-edge distance $\Delta$. By raster scanning the tip, one maps out the corresponding phase-difference $\varphi(\omega, \Delta)$ at each frequency $\omega$, generating a dispersing interference pattern.

The hyperspectral nano-PL line-profile collected at room-temperature (Fig. 3.1d) reveals dispersing subwavelength oscillations, a direct measure of $\varphi(\omega, \Delta)$. We plot the differential intensity $I(\omega, \Delta)$, defined as the difference between the in-contact PL intensity at tip position $\Delta$ and the PL signal with the sample retracted from the tip by 150 nm. The $I(\omega, \Delta)$ data uncover dispersing oscillating fringes (Fig. 3.1d) that are most prominent near the edge of the top $WSe_2$ layer at