NANOSCALE OPTICAL SPECTROSCOPY OF MONOLAYER WS$_2$ USING PHOTO-INDUCED FORCE

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Abstract

Photo-induced force microscopy is a scanning nearfield optical microscopy technique that was developed within the last decade and has been used to study polymer structures with near 10 nm spatial resolution. We seek to push the boundaries of this technique by extending the working wavelength range into the visible region and use it to study hard materials known as transition metal dichalcogenides (TMDs). TMDs have strong and controllable excitonic effects that has been the subject of many research studies in the past 10 years. However, there has not been much comparable nearfield measurements done. In this work, we were able to measure local absorption spectra of monolayer, bilayer, and encapsulated WS$_2$ all in agreement with that from traditional far field spectroscopic techniques. We also demonstrated 40 nm spatial resolution on WS$_2$ monolayers. Our results show that of photo-induced force microscopy spectroscopy is a promising technique that can be applied to study nanoscale effects in TMDs.
Lay Summary

Traditional optical measurement techniques are all bound by the diffraction limit, where one cannot resolve anything smaller than roughly half the wavelength of the incident light, about 200 nm in the visible region. There are some nearfield optical techniques that can bypass that limit. In this work, we extend the technique of photo-induced force microscopy to the visible wavelengths and apply it to study 2D TMDs. 2D TMDs have robust and controllable optical properties and are an ongoing field of research. We demonstrate the capability of this technique by showing measurements that agree with previous ones on several types of TMD samples. We also demonstrate a high spatial resolution of 40 nm in our measurements. We show that photo-induced force microscopy and spectroscopy is a promising tool for studying 2D TMDs on the nanoscale.
Preface

Initial idea of the project was from Professor Ziliang Ye. Sample fabrication, signal optimization and encapsulated WS$_2$ experiments in sections 4.1, 4.2.1, 4.3.1, 4.4 were done together by me and Quentin Guillet (Summer student from Ecole Polytechnique). Other measurements of monolayer WS$_2$ spectra and spatial resolution analysis were performed by me alone.
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List of Abbreviations

AFM = atomic force microscope
AOTF = Acousto-optic tunable filter
hBN = hexagonal boron nitride
PPC = poly-polycarbonate
PC = polycarbonate
PDMS = Polydimethylsiloxane
TMD = transition metal dichalcogenide
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Chapter 1: Introduction

When thinned down to the single layer limit, transition metal dichalcogenides (TMD) exhibit strong excitonic effects with valley degree of freedom and high controllability that makes it a subject of heavy ongoing research [1] [2] [3]. It has proposed applications from optoelectronics [4] to spintronics [5]. One interesting direction of research is nanoscale control the exciton properties to create nano-emitters. Local control of exciton property can be done through defects, strain [6]. For example, a single point strain has shown to cause a shift in exciton binding energy, and it can be used to potentially create highly localized emitters. More recently, twist angle between two layers of TMD has shown to be another way to control exciton properties. Moiré patterns form when two layers of materials with similar lattice constants are slightly offset, in this case a rotation. Moiré patterns produce a periodic Moiré potential that lead to strongly correlated insulating states and superconductivity in twisted bilayers of graphene [7]. In TMDs, Moiré potential creates Moiré excitons with distinct binding energies that are theorized to be localized at points of the Moiré lattice. The first signatures of these Moiré excitons were recently reported through reflection contrast measurements [8], but the localization of these excitons could not be confirmed.

In optics, the diffraction limit is a lower bound on the size of any focused spot given by
\[ d \geq \frac{\lambda}{2NA} \]
where NA is the numerical aperture of the focusing objective. This limit on spot size means it is impossible to optically resolve features below 200 nm in TMDs using far-field measurement techniques as any signal will be an averaged over the area of the spot size. The period of a Moiré lattice in TMDs is typically 10 nm, so it is not possible to confirm localized
Moiré excitons with far-field reflection contrast measurements in the experiment mentioned above. As we look to further understand nanoscale excitonic properties, we need to rely on nearfield optical measurement techniques to bypass the diffraction limit.

To measure the evanescent waves in the nearfield, a probe needs to be brought within 100 nm of the sample surface. Therefore, it is common to couple to an atomic force microscope (AFM) setup to manipulate the probe. One nearfield measurement method is to pass light through a nanoscale aperture to generate nearfield at the tip. The nearfield is then scattered into far-field and collected [9]. The aperture is usually created by metal coating a highly tapered optical fiber and the aperture size can be as small as 10-20 nm. However, the aperture size is limited to around 10 nm, by the skin depth of the coating metal [10]. A more promising approach is to utilize a sharp metallic tip, such as an AFM probe to scatter the near-field without using an aperture. Scattering scanning nearfield optical microscopy is one realization of this idea, where a modulated laser beam is focused onto the AFM tip and the elastically scattered light carries optical information of the area underneath the tip is collected. In order to separate the nearfield signal from the dominant background, the scattered light is demodulated at a higher harmonic of the AFM cantilever [11].

In our work, we expand on an apertureless nearfield technique called photo-induced force microscopy [12]. In this technique, a modulated laser beam is focused on an AFM tip and the local thermal expansion is measured as a photo-induced force by the cantilever. As a result, no collection optics are needed. Photo-induced force is proportional to the local optical absorption of the sample and sub-100 nm resolution has been demonstrated with infrared light on polymers
[13]. We will expand this technique to the visible region and apply it to TMDs with lower thermal expansion coefficients. We aim to measure nearfield absorption spectra of TMDs and show that this technique is a powerful tool to probe nanoscale properties of TMDs.

Chapter 2 will introduce the principle of photo-induced force and explain some key design points of our set up. Chapter 3 will give a brief overview of some interesting properties of 2D TMDs. Chapter 4 will discuss our experiment results and some features of our photo-induced force signal.
Chapter 2: Measuring photo-induced force

2.1 Principle of Photo-induced Force

When light is focused onto the tip of a gold coated AFM tip, the AFM tip acts as an antenna and creates an enhanced localized nearfield around the apex of the tip. The enhanced nearfield is then absorbed by the TMD creases an increase in local temperature. This temperature increase results in thermal expansion of the sample and underlying substrate. Thermal expansion is then detected by the AFM cantilever and read out as photo-induced force [13].

![Figure 2.1 Schematic of the origin of photo-induced force](image)

If we assume the thermal expansion is fast relative to the pulse width of the incoming laser so thermal expansion is at an equilibrium state, then we have a linear relationship between thermal expansion and sample temperature. Temperature increase is the result of absorbed tip enhanced
nearfield, which is proportional to sample optical absorption. Therefore, our detected photo-induced force is directly proportional to local optical absorption of the sample.

Figure 2.1 is a schematic of the process described above. It also illustrates the role of substrate thermal expansion. In our experiments, the samples we study are nanometers thick so the thermal expansion from the substrate underneath will be much more prominent and contribute to our detected force.

2.2 Separating signal from background

We demodulate our signal at the first and second resonances of the AFM cantilever for simultaneous readout of photo-induced force and topography. We drive the cantilever at the second resonant frequency and read out topography at the second resonant frequency per a standard tapping mode AFM setup. Thermal expansion can be from direct laser heating and tip enhanced nearfield heating, and we must take care to isolate force signal from tip induced thermal expansion. In order to reduce thermal expansion contribution from direct laser heating,
we set the laser frequency to be the sum of the first and second resonant frequencies and utilize sideband coupling to have our photo-induced force read out at the first resonant frequency. A schematic of the frequency setup is shown in Figure 2.2 and the reasoning behind the frequency choices are discussed in Chapter 2.3. Using sideband coupling effectively removes thermal expansion from direct laser heating, and shortened explanation is provided below but more details can be found in Ref [13].

We can model the cantilever tip with an undamped point-mass model and write the equation of motion for the first two resonant frequencies as below

\[
m \dddot{z}_1 + k_1 z_1 = F_1(t, z(t))
\]
\[
m \dddot{z}_2 + k_2 z_2 = F_2(t, z(t))
\]

\(k_i\) and \(z_i\) are the corresponding spring constant and coordinate of the \(i^{th}\) eigenmode. We drive the cantilever at frequency \(\omega_2\) and laser is modulated at frequency \(\omega_m\).

The location of the tip can be described as

\[
z = z_c + z_1(t) + z_m(t) + z_2(t)
\]

\(z_c\) is the equilibrium position of the cantilever. Motion of the 2 resonances are sinusoidal and motion at the modulation frequency depends on the direct thermal expansion \(A_d\) and tip-enhanced thermal expansion \(A_t(z)\).

\[
z_{1,2}(t) \equiv A_{1,2} \sin(\omega_{1,2}t)
\]
\[
z_m \equiv A_t(z)(1 + \sin(\omega_m t)) + A_d(1 + \sin(\omega_m t))
\]

We can expand tip-sample interaction force \(F_{ts}(z)\) about the equilibrium position \(z_c\)
\[ F_{ts}(z) \approx F_{ts}(z_c) + \frac{\partial F_{ts}}{\partial z}|_{z_c}(z - z_c) + \frac{1}{2}\frac{\partial^2 F_{ts}}{\partial z^2}|_{z_c}(z - z_c)^2 + \cdots \]

Photo-induced force \( F_\omega \) at \( \omega_m \) comes from the second term above and can be written down as:

\[ F_\omega(\omega_m) \approx \frac{\partial F_{ts}}{\partial z}|_{z_c} z_m(t) \approx \frac{\partial F_{ts}}{\partial z}|_{z_c} (A_t(z_c) + A_d) \sin(\omega_m t) \]

Sideband coupling force \( F_s \) comes from the second and third terms above to include interaction between the cantilever motion at \( \omega_2 \) and thermal expansion at \( \omega_m \). It can be written down as:

\[ F_s \approx \frac{\partial F_\omega}{\partial z}|_{z_c} z_2(t) \approx \frac{\partial}{\partial z} \left( \frac{\partial F_\omega}{\partial z} A_t(z)|_{z_c} z_2 \right) + \frac{\partial}{\partial z} \left( \frac{\partial F_\omega}{\partial z} A_d|_{z_c} z_2 \right) \]

\[ F_s \approx \left( \frac{\partial F_\omega}{\partial z} \frac{\partial A_t(z)}{\partial z}|_{z_c} + \frac{\partial^2 F_\omega}{\partial z^2} A_t|_{z_c} \right) A_2 \cos(\omega_- t) + \frac{\partial^2 F_\omega}{\partial z^2} A_d |_{z_c} A_2 \cos(\omega_- t) \]

\( \omega_- = \omega_m - \omega_2 \) so if we choose \( \omega_- = \omega_1 \), then we can use the first eigenmode of the cantilever to amplify the sideband coupling signal. Generally, the second derivative is much smaller than the first derivative in the small oscillation limit, so tip enhanced thermal expansion dominates the sideband coupled force.

### 2.3 Force detection setup

A schematic of the essential elements of our setup is shown in Figure 2.2. We collect topography and photo-induced force information simultaneously by demodulating at the first two resonant frequencies of the cantilever. A tunable laser is focused onto the gold coated AFM tip via a parabolic mirror. The parabolic mirror is necessary because it ensures a stable focal point for a wide range of frequencies and allows us to gather spectral information by changing incoming laser wavelength.
Sensitivity of each mode of the cantilever is determined by the thermal noise amplitude at each eigen mode. The minimum detectable force is given by

$$\Delta N_i = \sqrt{\frac{4k_B TB Q_i}{\omega_i k_i}}$$

where Q, ω, and k represent the Q factor, frequency, and spring constant for each eigenmode, $k_B$ is the Boltzmann’s constant, B is the bandwidth of our system, and T is temperature. For our cantilevers at room temperature with a bandwidth of 10 Hz, we get $\Delta F_1 = k_1 \Delta N_1 = 0.09 \text{ pN}$ and $\Delta F_2 = 0.16 \text{ pN}$. As a result, we choose the fundamental frequency for photo-induced force detection.

A diffraction focused spot of a 1 mW laser at 620 nm on WS$_2$ would cause an increase of temperature around 10 K, so we can use this number to get an estimation of our expected photo-induced force if we have a monolayer WS$_2$ on top of a glass substrate. If we only consider the thermal expansion of the top 100 nm of glass substrate, we would get an estimated change of 6 pm which results in an estimate force of 5 pN. Thermal expansion of the monolayer has been omitted and 100 nm is typically the maximum range of an evanescent nearfield. This estimation does not consider any tip enhancement and is only based on far field power measurements, but it is still two orders of magnitude larger than the minimum detectable force by our cantilever. We believe that we should be able to detect photo-induced force signal of a monolayer TMD on a glass substrate.
Figure 2.3 Schematic of the experimental set-up with only key elements included.
2.3.1 Atomic force microscope

We use a modified AFM from Molecular Vista Inc. It is a cantilever-based AFM with a parabolic mirror to focus the incoming laser light over a broad range of wavelengths. There is a 20x objective mounted above for sample and initial laser alignment. The parabolic mirror is mounted on two sets of three piezoelectric motors. One set is for rough positioning and the other set is used to raster scan the mirror while the tip is in contact. Doing so allows us to align the focused laser spot at the tip. The sample is mounted on a motorized stage and is raster scanned during AFM operation. Scanning the sample instead of the tip preserves the alignment between the tip and focused laser spot.

The cantilevers used in our setup are gold coated and purchased through Molecular Vista as well. They have a fundamental mechanical resonance in the range of $\omega_1 = 250$-300 kHz a second order resonance in the range of $\omega_2 = 1700$-1800 kHz. The cantilever is driven at the second resonance with a quality factor in the range of $Q = 900$ in atmosphere.

2.3.2 Light Source

We need a light source that has a tunable repetition rate between 1-2 MHz with tunable output wavelengths in the visible region for our experiment. Our setup uses a supercontinuum laser (YSL SC-OEM) coupled into an acousto-optic tunable filter (AOTF) to meet the above requirements. The supercontinuum laser has a tunable repetition rate from 1 MHz onwards, and the output of the AOTF can be tuned between 450 nm-750 nm or 750 nm to 1400 nm. The operational repetition rate of the laser is set to around 1.8 MHz ($\omega_1 + \omega_2$). The total output of the AOTF is up to 6mW depending on the output wavelength.
Chapter 3: 2D-TMD

3.1 Crystal Structure

Figure 3.1 Crystal structure of a monolayer TMD. Top panel shows the honeycomb lattice and the bottom panel shows the semi-2D nature of the material. The metal atoms are red and chalcogen atoms are blue.

TMDs are a class of materials with the formula MX$_2$, with M being a transition metal and X being a chalcogen atom. The specific class of interest to us have unit cells made up of either Molybdenum or Tungsten atom and two Sulphur or Selenium atoms. TMDs are layered in the bulk, much like graphene, with multiple 2D layers held together by Van der Waals forces. The layered nature means it can be stacked on top of other 2D Van der Waals materials such as graphene, NbSe$_2$, and hexagonal boron nitride. As depicted in the top panel of Figure 3.1, each single layer is a honeycomb lattice with one M(red) and two X(blue) atoms in a unit cell. In each layer, X atoms are offset vertically with regards to the 2D plane of M atoms with a total thickness of roughly 0.7 nm.
3.2 Layer-dependent band gap

Figure 3.2 DFT calculated band structure of bulk(a), four-layer(b), bilayer(c), and monolayer(d) MoS$_2$. Image taken from Ref [14]

TMDs are indirect band gap semiconductors but its band structure changes as it is thinned down to a monolayer [15]. Figure 3.2 shows DFT calculations of band structure of MoS$_2$ as it goes from bulk (a) to four-layers (b), bilayer(b), and monolayer (a). The valence band at the $\Gamma$ point lowers in energy with decreasing layer thickness until the direct band gap at the K point becomes the lowest energy transition. The states at the K point are composed mostly of strongly localized d orbitals at Mo atoms, so the interactions are mostly confined to a single layer. On the other
hand, states at Γ point are a linear combination of Mo d orbitals and p\textsubscript{z} orbitals on S atoms which are much more sensitive to layer thickness [14].

Figure 3.3 below shows photoluminescence spectrum taken from monolayer and bilayer MoS\textsubscript{2}. We can clearly observe the strong signal in monolayers due to the direct band gap. The inset shows the rapid quenching of signal intensity as the number of layers increase.

![Photoluminescence spectrum of monolayer and bilayer MoS\textsubscript{2}. Inset shows rapid quenching of quantum yield as the number of layers increase. Image taken from Ref [15]](image)

Figure 3.3 Photoluminescence spectrum of monolayer and bilayer MoS\textsubscript{2}. Inset shows rapid quenching of quantum yield as the number of layers increase. Image taken from Ref [15]
3.3 Excitons

Excitons are neutral quasi-particles formed by an electron and hole. The Coulomb interaction between an electron in the conduction band and a hole in the valence band creates an energetically favorable state below the band gap energy. This difference in energy is the binding energy of the exciton.

Excitonic effects are prominent in monolayer TMDs. Exciton binding energies are hundreds of meV, which is an order of magnitude larger than conventional 3D semiconductors [16]. Excitons in monolayer TMDs are confined within the 2D plane of atoms and have a Bohr radius of several nanometers. As a result, long range Coulomb interaction determines its binding energy [3]. In a free-standing 2D material, the space above and below the plane of atoms are vacuum which results in drastically reduced Coulomb screening when compared to 3D materials. This reduced screening is the reason of the unnaturally large exciton binding energy in 2D TMDs.

The unnaturally large binding energy makes excitons stable in room temperature with fast radiative lifetimes. As a result, optical response of TMDs is dominated by excitonic properties which makes it very convenient to control. Another consequence of the reduced dimensionality is the exciton becomes very sensitive to the surrounding environment [2]. Different substrates or encapsulation of the monolayer can affect the exciton binding energy, giving another way to manipulate optical property.
3.4 Valley polarization

TMD monolayer is a honeycomb lattice structure with 3-fold rotational symmetry and broken inversion symmetry. Its Brillouin zone is a hexagon with 3 pairs of K and K’ points at the corners with the K, K’ degeneracy lifted via inversion symmetry. As a result, the bottom of conduction bands have an angular momentum of +1 (-1) in the K (K’) valley, and the top of the valence bands have an angular momentum of 0 [17]. Selection rules indicate that an angular momentum change of ±1 must occur during a transition, which can be satisfied with circularly polarized light. σ⁺ polarized light will couple to transitions in the K valley and vice versa. Figure 3.4 is the intensity of σ⁺ polarized and σ⁻ polarized photoluminescence signal after a monolayer MoS₂ is irradiated with σ⁺ polarized light. The black line is the net degree of polarization and reaches near 50% in the experiment done by Cao et al [18]. The degree of polarization shown in experiments over time has increased with increased sample quality.

![Figure 3.4 Circularly polarized PL of monolayer MoS₂ at 83K](image)

Figure 3.4 Circularly polarized PL of monolayer MoS₂ at 83K. Red and blue curves correspond to intensities of σ⁺ and σ⁻ polarizations. The black curve is the total degree of polarization. Image taken from Ref [18]
3.5 Strong spin orbit coupling

![Diagram showing band structure at K and K' valleys in WS\(_2\). Blue and red indicate spin up and down bands respectively.](image)

TMD monolayers also have strong spin orbit coupling due to the heavy elements and contribution of the transition metal d-orbitals [3]. Spin orbit coupling splits the valence bands by 200meV in Mo based TMDs and 400meV in W based TMDs. The conduction bands are also split but only by 10’s of meV. Transitions from the upper valence band are called A excitons and transitions from the lower valence band are called B excitons. Interestingly, spin of the lower conduction band also depends on the transition metal. As a result, spin degeneracy is completely lifted at K and K’ valleys in monolayer TMDs. Transitions between bands of opposite spin are optically forbidden because photons cannot flip spin. Excitons with optically allowed transitions
are called bright excitons and excitons with optically forbidden transitions are called dark excitons. In W based TMDs, the upper valence band to the lower conduction band have different spins so the lowest energy excitons are dark excitons. In the case of Mo based TMDs, the lowest energy transitions are of the same spin, so the lowest energy excitons are bright excitons.
Chapter 4: Photo-induced force in monolayer WS$_2$

4.1 Sample Fabrication

All the TMDs used in our experiments were mechanically exfoliated by tape onto polydimethylsiloxane (PDMS). The technique is very similar to the one in Ref [19]. Monolayers of TMDs were identified via optical contrast under an optical microscope.

4.1.1 Polycarbonate (PC) transfer technique

For heterostructures, we used a dry transfer technique similar to the one described in Ref [20]. A stamp is made by placing a small square of PDMS on a glass slide and laying a thin PC on top. The stamp is lowered until it is in contact with the substrate with the target flake. The contact front between the PDMS and target substrate can be easily seen under an optical microscope. The contact front is brought close to the target flake and the substrate is heated to 90°C. Thermal expansion causes the contact front to move and the PC film is brought in contact with the target flake. After 10 minutes, the substrate temperature is lowered back to room temperature. This moves the contact front back and slowly peels the stamp off the substrate. The flake is now picked up onto the film. The above process is repeated for each flake that needs to be picked up until the whole heterostructure is on the stamp. In order to remove the heterostructure from the stamp, the stamp is brought in contact with the final glass substrate without the contact front crossing the heterostructure. The substrate is then heated to 180°C, past the glass transition temperature of PC. Then, with a sudden lowering of the stamp, the contact front is quickly brought past the flake and the flake is now in contact with the glass substrate. The sudden movement of the contact front serves to squeeze out most of the air and dirt trapped between
layers in the heterostructure. After 10 minutes at 180°C, the area of PC in contact with the substrate melts and detaches completely from the PDMS on the stamp. The remaining PC is then dissolved off the substrate using chloroform.

4.1.2 Poly-polycarbonate (PPC) thin film transfer technique

We can also use PPC thin film instead of PC thin film on the stamp to pick up flakes. There are two main advantages of using PPC instead of PC. We observe significantly fewer surface contaminants when using PPC, whereas PC was leaving polymer residue over large areas of our sample. We are also able to release the flake from the PPC film without melting it off the PDMS. We can then skip the last step of using chloroform to dissolve the remaining film. However, transfer success rate is lower when using PPC and it is difficult to pick up more than three flakes. We suspect the main contributor to the inconsistencies we see during transfer is tied to the substrate temperature during pickup.

4.2 Measurement on WS₂ monolayer

As our first measurement, we measured WS₂ monolayer and bilayers that were exfoliated directly on PDMS. We chose WS₂ as our starting material because it has a strong A exciton absorption peak. We were able to take topographic and photo-induced force images of boundary transitions between monolayer and bilayer WS₂. We also took point spectra on both regions by sweeping our laser wavelength from 450 nm to 750 nm while holding the tip’s xy position. We normalized both spectra by dividing each by a point spectrum we obtained on bare
Figure 4.1 Photo-induced force image (top) of a monolayer to bilayer step edge in WS₂ on PDMS and point spectra (bottom) taken in both regions. The image was taken with 500 nm incident light.
PDMS and the results are shown in Figure 4.1. The photo-induced force image on the top panel was taken at 500 nm laser wavelength. We see clear contrast between monolayer and bilayer regions. The lines in the bilayer region are wrinkles we also observed in topography. The wrinkles were several nanometers high so different thermal expansion response is expected. We did not investigate further at this time because wrinkles are common and often undesirable in TMD samples. Spectra after normalization are plotted on the bottom panel of Figure 4.1. We see a significant A exciton peak at 620 nm and a red-shifted peak at 640 nm in the bilayer. Both peaks values match well with far field measurements results in literature.

4.2.1 Optimization of photo-induced force signal

Before each session of measurement, we raster scan the parabolic mirror with the tip in contact with our sample. A typical image of our spot is shown in Figure 4.2. The spot is in the same area for all visible wavelengths and is stable throughout the day. The center of the spot is on the order of 2um.

![Figure 4.2 Typical image of a focused laser spot after focusing the parabolic mirror.](image)
Strength of detected photo-induced force is also dependent on oscillation amplitude and distance between equilibrium tip position and the sample. To determine the optimal feedback distance, we measured photo-induced force as we gradually lowered our AFM tip until hard contact was made. We can clearly see a region, around 70-85% of free space oscillation corresponding to tip-sample distance near 10 nm where we get the largest photo-induced force signal.

4.2.2 Laser power vs photo-induced force signal

When trying to understand the source of the photo-induced force signal, we assumed that our signal was from a steady state where maximum thermal expansion has been achieved and is proportional to temperature increase. Therefore, our signal was proportional to the optical absorption of our sample. To check the validity of this assumption, we monitored the strength of our photo-induced force signal as we varied laser power. We plotted raw photo-induced force reading against input laser power at several wavelengths across our measurement range and found that the resulting relationship is mostly linear as shown in the top plot of Figure 4.3. The bottom two plots show the raw data for photo-induced force and we see an irregular line shape for each laser power setting. This line shape is related to the absorption properties of the AFM tip and it is slightly different for a different tip. This accounts for the slight non-linearity in the top plot of Figure 4.3. Nevertheless, we conclude that our assumption is valid and that our signal should be proportional to local optical absorption.
Figure 4.3 Top plot is Photo-induced force vs Laser power at different output wavelengths of the AOTF.

Bottom plot is the raw photo-induced force data recorded at each laser power setting.
4.3 Measurement of spatial resolution

One of our main objectives was to explore the kind of spatial resolution we could achieve with this technique. The simplest place for us to do so is a monolayer edge on a hard glass substrate. We transferred a monolayer flake of WS$_2$ onto a piece of BK7 glass. We found a clean edge and took point spectra in a line across the edge. The points were taken with 20 nm spacing along the black line in Figure 4.4 a, with 0 nm being on the left and on the glass substrate. The spectra were then normalized with spectrum from another point near the on the glass. The photo-induced force image was taken at 620 nm and we see in the left half of Figure 4.4 a and b that features in topography can show up as contrast in photo-induced force. Similarly, the step edge in topography could show up as false contrast in the photo-induced force image. We observed the clear emergence of the A exciton peak between the 20 nm and 60 nm scans in Figure 4.4 c. To quantify the exciton peak feature, we fit each spectrum with a Lorentzian and used the amplitude of the fit to represent the oscillator strength of the exciton peak. Error bars were determined by the noise in the 0 nm scan in the region between 600 nm and 650 nm. The results are shown below in Figure 4.5 and we see that there is a significant difference between the 20 nm and 60 nm spectra. Our data is quite noisy and could be improved, but from this we could put 40 nm as a rough upper bound on our spatial resolution.
Figure 4.4 Topography (a) and photo-induce force (b) images of a monolayer WS$_2$ edge on a glass substrate. The series of spectra (c) were taken with 20 nm spacing along the black line. Emergence of the A exciton peak feature can be seen between the 20 nm point and 60 nm point.
4.3.1 Tip heating induced broadband shift

Our normalization process removes the effect of tip and underlying substrate from our spectra so our result should be proportional to the absorption of WS$_2$. We would expect the sub-bandgap region (660 nm onwards) to be flat in an absorption spectrum but we observed a broadband shift in the order of 5% in pretty much all our data as shown in Figure 4.6. As a result, we were able to see a step edge in images obtained while scanning at 700 nm, at laser energies below the exciton band gap. In Figure 4.6, we see that there is also no noticeable trend with respect to laser power.
To further investigate, we took some spectra on different thicknesses of boron nitride. We saw our signal strength scale linearly with the thickness of our sample. We repeated these measurements on different thicknesses of WS$_2$ and saw the same scaling relationship. Each nanometer of WS$_2$ contributes an extra 45 uV of signal, which corresponds to the 2-5% of our signal strength with the same conditions. Although we did not see a trend with laser power, we are confident that the broadband shift we observe here is thermal expansion of our sample due to heat transfer from the AFM tip. There are many other factors other than laser power to this type of heat transfer, so the exact reason is difficult to deduce.
Figure 4.7 Photo-induced force signal with respect to thickness of WS$_2$ (top) and hBN (bottom). Linear fit indicates an extra 45 uV/nm of WS$_2$ and 6 uV/nm of hBN.
4.4 Measurement on encapsulated WS$_2$

Encapsulating monolayer TMD with hexagonal Boron Nitride (hBN) has shown to greatly increase sample quality. Encapsulation increases monolayer flatness and cleanliness. It greatly reduces the number of non-radiative decay pathways usually presented to excitons by surface defects [21]. Some phenomena like Moiré excitons have only been observed in encapsulated samples [8]. Therefore, it is important to test the feasibility of our technique when there is an extra layer of hBN between the AFM tip and our sample.

Figure 4.8 Topography (top left), photo-induced force (top right) of bare (A) and encapsulated (B) monolayer WS$_2$ sample made with PPC transfer process. Point spectra of both regions are on the bottom. Scale bars are 250nm.
For initial measurement, we have fabricated samples of monolayer WS$_2$ encapsulated in hBN with 20 nm thick hBN underneath and 10 nm thick hBN above using the PPC transfer technique. The transfer technique left polymer residue all over our sample surface but we are still able to collect some data from areas between the residue. In Figure 4.7, region A is exposed WS$_2$ and region B is encapsulated WS$_2$ as described earlier. From the spectra in the bottom panel, we observe a slight decrease in linewidth and a red-shift in A-exciton peak energy. These are consistent with trends observed in far field measurements.

Figure 4.9 Photoinduced-force image of a monolayer (A) to hBN (B) transition underneath a top layer of hBN

We also took measurements along an encapsulated monolayer WS$_2$ edge. We were expecting a decrease in spatial resolution because of the top 10 nm layer of hBN. However, in Figure 7.8 we see a long-range gradient over 500 nm across the monolayer edge when scanning at the A
exciton peak energy. This over factor of 10 decrease in resolution is unexpected and we think it may be due to the high lateral thermal conductivity of hBN. The high thermal conductivity increases the area of local heating and thermal expansion thus smearing our measurement resolution. If we decrease the thickness of the top layer of hBN down to 1-2 nm, we expect to recover some our spatial resolution. Being able to conduct high resolution measurements in encapsulated samples is one of our goals and we would like to verify our expectations.
Chapter 5: Conclusion

In this project, we were able to set up a scanning nearfield optical microscopy system that can take local absorption spectra. One of the uncertainties in moving from polymers to 2D TMDs was less thermal expansion due to decrease in thermal expansion coefficient. We were still able to measure tip enhanced thermal expansion of our substrate, and our choice of a transparent substrate ensured that measured expansion was still proportional to the local optical absorption of the WS$_2$. Our spectra on monolayer and bilayer WS$_2$ all show a significant A exciton peak that matches well with far-field measurements. Furthermore, we were able to measure absorption spectra of encapsulated WS$_2$ and observed red shift and slight sharpening of the A exciton peak. We also identified a broadband background in our spectra caused by thermal expansion from tip heating of the sample. Nevertheless, thermal expansion mechanism of the photo-induced force was only adopted recently, and the heating process is complicated. We would like to use our measured force values to compare with our basic model to gain insight about the details of this process. For now, we can only note the correspondence to optical absorption but a more thorough and inclusive modeling of the expansion process in a 2D TMD sample is still needed.

We were also able to demonstrate the spatial resolution of our technique. By taking a series of point spectra across a monolayer edge, we saw the increase in A exciton oscillator strength over 40 nm and came to our conclusion of 20 nm spatial resolution. However, there is still room for improvement in our measurement setup. The shape of the AFM tip is a major factor in determining the size of the local enhanced field. The typical tip radius of curvature is less than 50 nm as specified by the manufacturer, but we have not measured any of ours. A sharper tip
would limit the size of the enhanced nearfield and increase our spatial resolution. We could also change our substrate to gold. Gold substrates are used in tip enhanced Raman spectroscopy to increase electric field enhancement from the tip. We could apply the same idea in our setup to increase our signal strength.

In measuring hBN encapsulated samples, we saw a larger gradient along the monolayer edge that signified a decrease in our spatial resolution. We think that the high thermal conductivity of top layer of hBN along with increased tip-sample distance are both contributors, and that a sample with a mono or bilayer top hBN encapsulation would show better spatial resolution. We would like to verify these predictions and get a resolution limit with encapsulated samples in the near future. Encapsulated samples give higher quality optical measurements and the Moiré excitons have only been observed in encapsulated samples. Being able to work with encapsulated samples with high spatial resolution would be a huge improvement for our technique as we would be able to perform measurements on higher quality samples. With some improvements, we would be able to directly measure Moiré excitons since we are quite close to the 10 nm length scale of Moiré lattices.

Even without relying on encapsulated samples, photo-induced force is still a powerful technique. Excitons in 2D TMDS are sensitive to the nearby dielectric environment. We could measure exciton screening length by spatially mapping the A exciton shift as the substrate beneath a TMD monolayer changes abruptly. Exciton screening length is a fundamental property that has only recently been measured in high magnetic fields [22]. Photo-induced force spectroscopy can also
be used to study TMDs coupled to other fabricated nanostructures that don’t require encapsulation.
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