Dynamic Reflectivity and Transmissivity Measurements of Black Phosphorus Flakes

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Abstract

We studied the dynamic reflectivity and transmissivity of black phosphorus flakes using a pump/probe laser system. The flakes were excited with femtosecond laser pulses, ~60fs, in order to observe how the optical constants changed with respect to time delay. The relaxation time period of the excited charge carriers was calculated to be ~200-300fs during transmission measurements. Reflectivity measurements had shown longer time periods but could not be calculated due to limitations of the experimental setup. Future improvements to the system’s temporal range will be able to provide more detailed information about the longer lifetimes.

I. Introduction

With the advent of the use of femtosecond laser pulses it has become possible to observe effects which only last on the timescale of $10^{-15}$s. In matter, some processes such as absorption and non-radiative transitions occur on these timescales, $10^{-15}$-$10^{-11}$s. In a pump probe experiment, two laser pulses are used to observe how the optical properties of a material change, which in turn give information about absorption and non-radiative transitions. The “pump” is the laser pulse which excites a sample and the “probe” is the laser pulse which observes a change in the transmissivity or reflectivity of the sample. Multiple different transitions can be determined based off the timeframe of exponential decay of the excited states. This can also give information about how charge carriers move through a material and how quickly a material will dissipate heat.

Black phosphorus is a material which has many interesting optical/electronic properties such as a tunable bandgap, high charge carrier mobility, and anisotropic behavior. These
properties make it a valuable material for electronic devices. Pump probe spectroscopy is a technique which can elucidate more information about the charge carrier dynamics in the material and therefore benefit the design of new devices.

II. Theory

Matter, after being excited by electromagnetic radiation, gives off energy in many different pathways which can be classified as either radiative transitions or non-radiative transitions. Radiative transitions, such as fluorescence or phosphorescence, give off photons and occur on time scales in the range of $10^{-9}$-$10^{-2}$ s.\textsuperscript{1} Non-radiative transitions, such as internal conversion, generally occur much faster on a timescale range of $10^{-14}$-$10^{-11}$s. Internal conversion is a transition where the energy released is put into different vibrational modes and is dissipated as heat.\textsuperscript{2} The Ti-Sapphire laser can produce laser pulses on the femtosecond timescale $10^{-15}$s. This timescale is faster than any vibrational relaxation making it possible to monitor the timeframe of the event and observe the process taking place.

One way this can be achieved is by measuring how the absorption, transmission, or reflectivity changes as a sample is excited. During absorption, charge carriers within the sample gain energy from incoming photons and occupy higher energy states, a process known as linear absorption. This absorption results in a decrease in the transmission and reflectivity of the sample. As the charge carriers in a solid are excited by incoming photons, an excited state may become completely filled. Once this occurs, new incoming photons which would have been absorbed before now pass through the sample since the previous transition is no longer available. This results in a decrease in the absorption and an increase in the transmission or reflectivity. This process is known as saturable absorption (SA).\textsuperscript{3,4} Since the laser pulses can be
approximated as a Gaussian distribution with respect to the intensity, the saturable absorption process can be modeled using the error function where the population of an excited state increases while the pulse is present and will eventually reach a maximum value depending on the time of the excitation.

\[
\text{Erf}\left(\frac{(t - t_0)}{\tau}\right) + 1 = \frac{2}{\sqrt{\pi}} \left[\int_0^t e^{-\left(t - t_0\right)^2 / \tau} \, dt\right] + 1
\]

\(t_0\) is defined as time zero, the point at which the probe and pump pulses are overlapped in the sample, \(t\) represents time delay between the pump and probe pulse, and \(\tau\) represents the length of the pump pulse or the time of excitation.

Another set of processes can occur with pump probe spectroscopy known as non-linear absorption. These processes vary dramatically depending on the intensity of incoming light. The process which we are concerned with is two-photon absorption, (TPA). In this process, the excitation of the pump photons and the probe photons occurs at nearly the exact same time before the charge carriers can relax back down to lower energy states. A charge carrier will jump to an excited state which is equal to the sum of the energies of the two photons involved. More absorption occurs under this process since the excited states are unoccupied which results in a decreased number of photons being either transmitted or reflected by a sample. This process can be approximated by a Gaussian function since two-photon absorption depends on the overlap of the pump/probe pulses. The overlap will increase and decrease as the time delay changes.

\[
A e^{-\left(t - t_0\right)^2 / \tau}
\]

Here \(A\) is a constant which is related to the strength of the TPA process.
In this experiment, any absorption processes occur in a very short time frame due to the nature of the femtosecond pulses. As the more energetic pump pulse passes through a sample, TPA can only be observed when the pump pulse is overlapped with the probe pulse within the sample. After the pump pulse has passed, the only processes that occur are the relaxation of the excited charge carriers back to their initial energy states and the possible absorption of probe photons by excited charge carriers to a higher energy states. These can be modeled as an exponential decay of the transmission or reflectivity with respect to the time delay of the probe pulse to the pump pulse.

\[
e^{-\frac{t-t_0}{\tau}}
\]

Here \(\alpha\) is the lifetime of the charge carrier relaxation.

Using these three processes, we fitted our transmissivity and reflectivity measurements with the following equation.

\[
\text{Fit}(t) = A + Be^{\frac{2\sqrt{\ln(2)(t-t_0)^2}}{1.41\tau_1}} + C\left(\frac{Erf\left(\frac{t-t_0}{\tau_2}\right) + 1}{2}\right)(e^{\frac{-(t-t_0)}{\alpha}})(e^{-\frac{(t-t_0)}{B}} + D)
\]

A represents the relative background signal. The first exponential stands for the TPA process. The error function stands for any other absorption processes. The other exponentials represent any other relaxation transitions of the excited charge carriers with respective lifetimes \(\alpha\) and \(\beta\). The constants B and C represent the relative strengths of the TPA and other absorption processes.

III. Experiment

A. Laser System
In order to observe the ultrafast timescale of charge carrier dynamics, pump probe spectroscopy is necessary. The technique uses an ultrashort laser pulse and splits it into two different components: a stronger pump pulse and a weaker probe pulse. The pump pulse excites the sample and the probe pulse observes the change in optical properties such as reflectivity or transmission. Information about the relaxation time of the excited charge carrier states can be determined by observing how the reflectivity or transmission changes as a function of time delay between the arrival of the pump pulse and the probe pulse.

Figure 1. Laser system schematic.

The laser system within the laser lab at Saint John’s University uses a continuous-wave 532-nm Verdi Laser. The power of the Verdi Laser is set at 4.25W. The pulsing of the laser is achieved by pumping the Verdi Laser through a Ti:Sapphire crystal. The crystal emits light pulses in the red to infrared spectrum. Based on the schematic of the system above, the light emitted by the Ti:Sapphire crystal first passes through one prism pair. This is done to
compensate for the material dispersion in the system. The residual green light emitted from the laser is dumped from the rest of spectrum inside the prism pair. After this path, the light is separated into two beams, the pump and the probe, using a 50/50 beam-splitter. The probe is sent to reflect off a motor-controlled translation stage which can change the path length of the probe with respect of the pump path length. In order to control the power of the probe, a variable linear gradient filter is placed before the probe reaches the sample. Finally, the probe is focused on a sample and can either transmit through or reflect off of the sample toward the detector. The pump beam is sent along a separate path where first it is sent through a 2nd prism pair to compensate for the large amount of material dispersion in the pump beam's path. After this 2nd prism pair, the pump beam is focused into an Acousto-Optic Modulator (AOM). The AOM is used to introduce a modulation frequency of 25kHz, produced from a function generator, onto the probe beam. After passing through the AOM, the polarization of the probe beam is rotated by 90 degrees using a waveplate and a polarizer so that only vertically-polarized pump light passes onto the sample. The rest of the reflected or transmitted probe light is collected and dumped so that it does not arrive at the detector. An additional polarizer, with a horizontal transmission axis, is set up in front of the detector to prevent any possible vertically-polarized light from reaching the detector as well. In order to observe a signal, both the focused pump and the probe spots must overlap with one another on the sample. A CCD camera and lens are used to achieve a 10X magnification image of the sample. Light scattered from imperfections on the sample shows the location of the pump and probe spots.

The electrical signal observed by the detector is sent to a preamplifier for amplification. The DC output of the detector is set to 0.60V so that it does not damage the preamplifier and is
achieved by opening and closing apertures along the probe beam path after reflection or transmission through the sample. After passing through the preamplifier, the signal is sent to a Lock-In Amplifier to block any noise which does not have a frequency of 25kHz. Finally, the signal from the Lock-In Amplifier is sent to a computer which records the lock-in amplifier output voltage signal as the motor-controlled translation stage changes the path length.

B. Optimization

i. Duration of pump/probe pulse

The length/timescale of the pulsed laser is determined using a second-harmonic Frequency-Resolved Optical Gating system. This system creates a small delay between two replica laser pulses in order to monitor the change in intensity of a non-linear signal. A second harmonic generation (SHG) crystal is placed where the two laser pulses focus on one another. If both the laser pulses overlap at the same time, the light from both pulses excite the crystal so quickly that the crystal emits a wavelength of light that is half the wavelength of either pulse before. This light is monitored for intensity changes as a stage-controlled mirror changes the path length of one of the beams. The length of the pulse can be determined from how the spectral intensity changes in the non-linear signal.

As seen in Fig. 2, the BPF were excited using a wavelength of 804nm, pulsed spectral width: 790-818nm, and a pulse duration of 55-60fs. The pulse width of both the pump and the probe are marginally smaller than what has been used in literature for similar measurements which enables faster changes in the sample to be measured.
ii. Laser diameter of pump/probe (Beam waist)

Since the size of the black phosphorus samples are on the order of 100-1000µm², the cross-sectional area of the laser pulses at their focal point must be similar in size in order to observe a signal. One adjustment was made to decrease laser diameter in the experimental setup. For the pump beam, a pair of converging lenses was implemented to increase the beam width before the beam reached the final focusing lens. The diameter could be measured using the Beam’R2 Profiler. This instrument works by mapping out the intensity of the laser across its surface. At the focal point of the probe, the maximum diameter was decreased to a FWHM of 22.1µm. At the focal point of the pump, the maximum diameter was decreased to a FWHM of 60.8µm.

Fig 2. a) Pulse duration of the probe beam, FWHM: 55.4 +/- 0.6 fs b) Pulse duration of the pump beam, FWHM: 59 +/- 3 fs.
Fig 3. Pulse width, beam waist, of the probe beam, FWHM: 22.1 +/- 1.0 µm

Fig 4. Pulse width, beam waist, of the pump beam, FWHM: 60.8 +/- 1.0 µm
C. Procedure

i. Synthesis of BPFs

The black phosphorus samples were obtained from the Koester Nanodevice Laboratory at the University of Minnesota. The samples were assembled within a cleanroom at the Minnesota Nanocenter. First, a single black phosphorus sample was cleaved into smaller pieces using a razor. We then mechanically exfoliated the smaller black phosphorus pieces into flakes using surface protection tape. The adhesion side of the tape, with the black phosphorus attached, is closed in on itself and then opened again in order to separate the layers of black phosphorus from each other. This is done several times in order to create thinner flakes. The flakes are then transferred to a quartz crystal substrate using an adhesive IPad film covering. Quartz crystal was used in order to ensure that the substrate did not interfere with the absorption of the laser pulses. The last step in the synthesis was spin coating a protective layer of Poly(methyl methacrylate), PMMA, on top of the black phosphorus samples to reduce any oxidation reactions from occurring with oxygen gas and water in the atmosphere.

ii. Sample position/initial adjustments

First, the output of the Ti:sapphire laser is set up to a maximum power of 0.7W. The pulsing of the laser can be started by pressing and releasing a prism within the Ti-Sapphire laser. A digital oscilloscope, which is connected to a fast photodiode detector, monitors the scattered light from the Ti:sapphire crystal to identify if the laser is pulsing or not. A spectrometer is used to determine that the bandwidth of the laser is within an appropriate range, 788-819 nm FWHM. Once the laser is pulsing, the frequency generator is set to a $V_{rms}$ value of 5.0 V and a frequency of 25 kHz. The AOM is then turned on to introduce the 25kHz
modulation frequency. Next, the average power of the pump and probe beams are set to a value between 20.0-35.0mW and 0.5-3.0mW respectively. The probe should be kept at a power which is a maximum of 10% of the pump in order to prevent the probe from significantly exciting the sample. Next, the sample is positioned on top of a horizontal translation stage so that the sample is being excited at the focal point of both the pump and probe beams. The surface of the sample should be positioned at an angle so that the reflected pump beam is hitting the beam dump. The camera can confirm that the sample is angled correctly once an image of both the probe and pump beams appears on the camera. If the probe or pump beams are not overlapped, the pump beam can be moved using a mirror mount to position it over the same area as the probe. The sample should be attached to a mirror mount as well so that adjustments can be made to ensure that the surface of the sample is orthonormal to the incoming laser light. In order to know that a signal is being observed, the magnitude of the Lock-In Amplifier should decrease or increase when compared to the background signal. Another way to see this is to block one of the pump or probe beams and see if the signal changes. Once a signal can be seen, it is best to change the batteries of the detector with freshly recharged ones and set the DC output voltage of the detector to 0.60V by opening or closing the shutter aperture on the detector. Also, the Lock-In Amplifier must be set to the phase of the signal and to the correct voltage range so that it does not overload. Once this has all been done, it is time to perform a scan to determine where time zero, the beginning of the excitation, is taking place.

iii. Data Collection
A computer program, developed in LabView 2015, controls the motor-controlled translation stage mirror and records measurements from the Lock-In Amplifier at specified intervals. The step distance of the mirror is correlated to a step in the time delay between the pump and probe pulses. As the mirror progresses, voltage data points are graphed as a function of time delay. The voltage is proportional to the intensity of the laser light reaching the detector. If the mirror is close to time zero, a scan gathering data from -1000fs to 1000fs should observe a relatively large change in voltage. If no signal can be seen, the scan range can be increased. After a signal has been observed, averaging can be done to decrease the noise seen in a single scan.

IV. Analysis

A. Results

i. Varying Pump Intensities

In order to obtain the largest signal from the BPF, the intensity of the pump beam was maximized as much as possible while still preventing degradation of the flakes. As seen in Fig. 5, the maximum pump intensity, 39.75mW, resulted in the largest signal. The max transmission increased approximately linearly with increasing pump intensity. We decided to use a pump intensity of 35mW instead since the power did not vary as much at this level compared to the higher intensity. The constraints of the AOM prevented a stable power output at the highest intensity.

The baseline transmission level increased with increasing intensity of the pump as well. There is a slight change in the baseline transmission level after the excitation seen at 39.75, 35,
30, and 25mW. No change in the lifetime of the excitation/relaxation is seen when varying the excitation intensity.

**Fig 5.** Transmission measurements from flake #2 with varying pump intensities, 39.75-15mW.

**ii. Transmission Measurements**

Reflectivity and transmission measurements were made in order to determine the excitation dynamics of black phosphorus flakes, BPF. We obtained data from two black phosphorus flakes which were large enough in size for the laser system to measure a signal. Both are pictured below in Fig. 6. Flake #1 is slightly thicker than flake #2 since it is less transparent. This may have an effect on the signal during a transmission measurement.
Fig 6. Microscope images of the two black phosphorus flakes. Flake #1 imaged left, flake #2 imaged right. Red circle indicates relative size of focused pump pulse.

Transmission Measurement Flake #1

Fig 7. Average Transmission Measurement from flake #1.
Fig 8. Average Transmission Measurement #1 from flake #2

Fig 9. Average Transmission Measurement #2 from flake #2
All measurements were obtained by averaging 15-30 scans in order to reduce any noise from the measurements. The uncertainty is the SDOM for all of the scans. The timeframe of the absorption, the initial decrease in the transmission to the minimum value is approximately 70-120 fs between the two flakes which is in agreement with double the size of the laser pulses, 55-60 fs. Fig. 8 shows a good example of TPA in the beginning and then switching to SA. The transmission increases after the excited states are all populated. Fig. 7 and Fig. 9 show a decrease in transmission then an increase. This may be due to the fact that the sample does not reach complete SA and therefore photons are still populating the excited states. After the pulse passes through the sample, the energy of the excited charge carriers is dissipated through vibrations/thermal pathways.

In all graphs at later time delays, the signal follows an exponential decay after the excitation takes place. The point at which the decay starts differs between flakes #1 and #2 and so does the decay time. The exponential decay shows the relaxation of excited charge carriers to their initial states. The differences seen in the signals may be due to thickness of the samples or the overall orientation of the samples with respect to the incident pump pulse since absorption can be polarization dependent. It may also depend of the band structure of the black phosphorus since different transitions can be seen taking place in each transmission measurement. Depending on the rate of the exponential decay, one can determine the relative lifetime for a particular transition of the charge carriers from an excited state to a lower equilibrium state.

The uncertainty seen in the Fig. 7 is likely overestimated. The timeframe needed in order to complete multiple scans can be close to 24 hours or more. During this timeframe, the
alignment of the pump/probe on a particular location of a BPF can change from its initial position. It is also possible that alignment can change due to thermal expansion. The outcome of these processes can be seen as a drifting of the entire plot to higher or lower values.

iii. Reflection Measurements

The same conditions were maintained when performing measurements in reflection mode for each flake. The pattern of the signal varied between reflection and transmission modes. The same timeframe was observed for the initial excitation as seen in the transmission measurements.

Fig 10. Average Reflection Measurement from flake #1
For the reflection measurement, the timeframe of the relaxation seems to be much longer compared to the transmission measurement with flake #2. Instead of lasting 200-330fs, it lasts on the order of >10000fs. The relative shape of the signal stayed the same between the two reflection measurements unlike during the transmission measurements. The reflection measurements should be observing what is taking place at the surface of the flakes and therefore should not depend on the thickness of the flakes. An interesting phenomena takes place in the reflection measurements after the excitation of the pump pulse is over. We see the reflectivity increasing to a higher value even though no excitation is taking place in this timeframe.

![Reflection Measurement Flake #2](image-url)
A list of our fit parameters for both reflection and transmission measurements is given below. We could not determine the exact relaxation times for $\alpha$ since we could not scan over a large enough time range.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>$t_0$ (fs)</th>
<th>A (µV)</th>
<th>B (µV)</th>
<th>C (µV)</th>
<th>D (µV)</th>
<th>$\tau_1$ (fs)</th>
<th>$\tau_2$ (fs)</th>
<th>$\alpha$ (fs)</th>
<th>$\beta$ (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Flake 1</td>
<td>70</td>
<td>2.87</td>
<td>-0.055</td>
<td>-0.0135</td>
<td>8.8</td>
<td>57</td>
<td>59</td>
<td>&gt;10000</td>
<td>200</td>
</tr>
<tr>
<td>Transmission #1 Flake 2</td>
<td>70</td>
<td>6.7</td>
<td>-0.59</td>
<td>0.375</td>
<td>-0.03</td>
<td>57</td>
<td>59</td>
<td>-</td>
<td>320</td>
</tr>
<tr>
<td>Transmission #2 Flake 2</td>
<td>115</td>
<td>2.5</td>
<td>-0.2</td>
<td>-1.3</td>
<td>-0.03</td>
<td>57</td>
<td>59</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>Reflection Flake 1</td>
<td>45</td>
<td>22.6</td>
<td>0.98</td>
<td>-3.4</td>
<td>-0.3</td>
<td>57</td>
<td>59</td>
<td>&gt;10000</td>
<td>330</td>
</tr>
<tr>
<td>Reflection Flake 2</td>
<td>53</td>
<td>2.314</td>
<td>0.06</td>
<td>-0.2</td>
<td>-0.3</td>
<td>57</td>
<td>59</td>
<td>&gt;10000</td>
<td>310</td>
</tr>
</tbody>
</table>

**B. Comparisons with literature**

Two faster relaxation times of black phosphorus nanosheets, flakes which consist of only a few layers of atoms, during transmission measurements have been reported to be between 15-32 fs and 320-1360fs depending on the excitation wavelength used.\(^4\) A much longer relaxation time of 150 ps, not dependent on wavelength, has also been reported.\(^3\) Other researchers have used a pump/probe system which produces pulses of approximately 100fs.\(^3,4\) The probe light source can also be different than wavelength of the pump wavelength to elucidate different transitions.\(^3,4\) For our experiment, we split the laser to create the pump and the pulse which had the same wavelength. Some pump wavelengths that have been used in previous experiments include 800, 1300, 1550, 1600, 2000, and 2026nm. As seen in the flake #2 transmission data, the lifetime is approximately around 1000fs or 1ps. This is accordance for
what is seen in literature for the very thin nanosheets.\textsuperscript{4} However, the data which we collected for reflection shows a much longer lifetime than this, \textasciitilde10000fs.

V. Conclusion

The black phosphorus flakes showed responses to photoexcitation for both reflectivity and transmission measurements. For both flakes, a longer relaxation time was seen in the dynamic reflectivity compared to the dynamic transmissivity. One reason for this may have to do with the different band structure of black phosphorus at different parts of the sample therefore affecting the available transitions that are possible between different energy levels. Another reason may that there are a lower number of vibrational modes available at the surface compared to within the sample in bulk resulting in a longer lifetime of the excited states. For the transmission measurement of flake #2, the relaxation time, $\tau$, was calculated to be approximately 240fs using equation (1.3). The transmission measurement of flake #1 did not show a similar signal compared to flake #2. One reason for this may be that the thickness of the flake #1 is different from flake #2 therefore affecting the transmission of photons and the signal. It may also be due to the sample not reaching complete saturable absorption.

The reflection measurements showed similar character with a much larger relaxation time. Due to limitations of the motor translation stage, we could not scan across a significantly long-time period. This prevented us from obtaining an accurate measurement of the relaxation time for the reflection measurements.

Across all measurements we saw an initial decrease in the signal which may be evidence of non-linear absorption such as two-photon absorption spoken about before. This process may be competing with saturable absorption during the excitation of the pulse. It is possible that the
Changing in sign of the signal is due to the orientation of the sample with respect to the linear polarized pump pulse. Defects within the sample and on the surface, may also have an effect on the relative shape of the signal.

Improvements can be made to the laser system in order to make the measurements more precise in the future. For example, the translation stage for the sample holder is only able to make small changes in distance along a horizontal plane. A three-dimensional translation stage would help with making movements along the vertical axis as well. Currently a photodetector is observing the scattered light coming from the sample through a magnifying lens. An imaging system that would illuminate the sample on a background similar to a microscope would help with identifying the position of the laser on a small sample. Adding in a larger range for the motor-controlled translation stage connected for the probe beam path would allow for a larger time scale to be observed during a measurement. Finally, having a sample mount which could rotate the orientation of the sample with respect to the pump pulse would help elucidate how absorption changes with polarization.
VI. References


