## Ultrafast Dynamics of 2D Materials The Case of MoS<sub>2</sub> and Black Phosphorus

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#### Abstract

Understanding materials dynamics at the fundamental level requires a thorough investigation of the materials properties along all crystallographic directions and the effect of an external variable on these properties, where an example of these variables can be the applied pressure, the system temperature, or the substrate dielectric constant for a thin film. In the case of van der Waals materials, most thin-film growth techniques and exfoliation techniques lead to a horizontally stacked layers making the study of the transient changes along certain crystallographic orientations challenging or inaccessible even with some of the most advanced probing techniques. Moreover, using van der Waals materials in making or developing a technological device necessitate the evaluation of the effect of the dielectric medium which is in contact with the van der Waals materials.

In this work, ultrafast electron diffraction in reflection geometry is the method of choice to probe the structural dynamics in the out-of-plane direction of MoS<sub>2</sub> and black phosphorus in Chapter 3 and 4, respectively. In the case of MoS<sub>2</sub>, we were able to probe the monolayer dynamics at a low incidence angle and the supporting substrate at a larger incidence angle under similar excitation conditions. We found that the dynamics in the out-of-plane direction of a supported MoS<sub>2</sub> monolayer are comparable to those in-plane and that MoS<sub>2</sub> thermalizes in about 12 ps with a weak thermal boundary conductance at the interface which results in slower dynamics at the MoS<sub>2</sub>-sapphire interface. In Chapter 4, we found that the long-lived carriers in black phosphorus (bp) trigger a lattice contraction at an early time that is concurrent with a coherent lattice movement in the out-of-plane direction and most likely corresponds to a carrier coupling with the A<sub>g</sub> phonon modes that have a large component in the out-of-plane direction. Thermalization in bp is slower comparted to MoS<sub>2</sub> and is reached in about 50 ps evident through the Debye-Waller analysis of several orders of diffraction spots and through the lattice thermal expansion in the out-of-plane direction.

These findings highlight the importance of using ultrafast electron diffraction in reflection geometry to capture a more complete picture of the materials dynamics and relaxation pathways. This work also brings to light the importance of the interlayer coupling in 2D materials and the role of the long-lived carriers in the observed ultrafast dynamics.

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## 1 <u>Chapter 1</u>

### Introduction

#### 1.1 Background

Observing objects in motion is of a great scientific interest; however, this is often met with some challenges. First, depending on the size of the object, an adequate imaging technique is required to resolve the fine structure. For example, to capture a micrometer size object, an optical microscope is sufficient. However, to capture smaller structures, i.e., molecules and crystals that are in the nanometer range (1 nm =  $10^{-9}$ m), we resort to electron microscopy and diffraction techniques. This ability of a technique to resolve the structure of an object is known as the Abbe diffraction limit, where the resolution of a given technique is estimated to scale with  $\lambda/2$ .



Figure 1.1 Length scale of various objects and the appropriate technique to visualize them.

Second, is the time scale of the process of interest. The human eye for example can perceive slow objects movement (a walking person, snail crawling), however, faster objects movement (rotating fan, hummingbird flapping his wings) cannot be clearly resolved and what the human eye perceives is a blurry image which corresponds to the time average movement of the object. The same analogy can be applied for any technique used to capture fast processes. To this end, some fast-imaging techniques for example has been developed that can capture fast events using a shutter (mechanical and/or electronic) that can generate an image with an exposure time of 1  $\mu$ s, all the way down to 70 trillion frames per second [1]. Figure 1.2 summarizes the time scale for many biological, chemical, physical, and fundamental processes. Thus, depending on the process, a temporal resolution is required that represents the fastest process a probing technique can detect.



Figure 1.2 Time scale of biological, chemical, physical, and fundamental processes. Adapted from [2]

A time resolved spectroscopy measurement is broad term that encompasses different techniques that use light to study the progress of an observable as a function of time, that can go down to few femtoseconds and even attosecond resolution. Originally and in the early development stage, the purpose of a time resolved spectroscopy measurement is to study the reactive complex intermediates and their formation mechanism and then it expended to better understand the light-matter interaction in countless systems and the various dynamics and relaxation pathways that system undergoes in the excited state. For example (i) in biological systems, time resolved spectroscopy is used to probe the dynamics of biomolecules such as photoreceptors [3] and photosynthetic systems [4] in order to design artificial molecular devices that can mimic the same biological process; (ii) and in chemistry to understand the bond breaking and bond formation of molecules [5], or to track the charge transport in perovskite solar cells [6, 7] and tracing photocatalytic reactions [8, 9]; (iii) and in physics to study the mechanism of the phase transition in correlated materials [10] and other quantum materials [11-13].

Many variants of time resolved measurements exist, and example of these are pump probe spectroscopy. The concept of pump-probe technique was first introduced by Abraham in 1899 [14] and further developed by Norrish and Porter [15] where they employed flash photolysis to study the free radicals reactions in the gas phase and they achieved a millisecond temporal resolution and even reached a nanosecond flash photolysis a few years later [16]. To achieve his goal, Porter used a photolysis flash lamp, alongside the reaction vessel that is about 1 m in length and 2.5 cm in diameter, which will trigger the photodissociation reaction; and placed a spectro-flash lamp at one end of the vessel and a spectrograph at the other end to measure the changes in the absorption spectra. This setup represents the early version of the transient absorption spectroscopy.

In a pump probe spectroscopy experiment, two laser beams are needed. An optical laser pulse excites the system and brings it into a non-equilibrium state, this is what we call the pump beam. The second optical beam, that is specific to the technique being used, probes the changes in the optical properties of the system. This probe beam has a smaller footprint than the pump beam and a lower fluence as well. Examples include transient reflectivity [17, 18] and transient absorption spanning the whole optical spectrum [19-21], time and angle resolved photoemission spectroscopy [22] where each of the aforementioned probes has their strength and limitation. These spectroscopic techniques offer a plethora of information about the electronic transient changes; however, the structural changes remain hindered or inferred indirectly, although a spatial resolution can be attained when each of these techniques is incorporated into a microscope. For this purpose, and to capture these structural transient changes, diffraction techniques has been developed and implemented and can offer angstrom spatial resolution in addition to the temporal resolution, namely time-resolved X-ray diffraction [23] and time-resolved electron diffraction [24], that in addition to some microscopic techniques that use electrons to image the structural changes [25, 26].

#### 1.2 Benefits of electron diffraction

Gerard Mourou paved the way for the time resolved electron diffraction [27], and led to the development of a time resolved electron diffraction that was expanded by the Zewail group in the early 90s for the study of molecules bond breaking and bond forming in gaseous phase [28]. Since then, major changes occurred to improve the time resolution [29-31], probing a larger momentum space with MeV electron bunch [32-34] and a faster data acquisition. This progress is driven by:

(i) The large electron scattering cross-section that is about 10<sup>6</sup> times larger than X-ray scattering cross-section, allowing, under a similar flux, a higher diffraction image intensity and shorter exposure time with an enhanced signal to noise ratio.

- (ii) De Broglie wavelength  $\lambda_{DB}$  of the electrons is much shorter compared to X-ray. For example, electrons accelerated at 30 keV corresponds to  $\lambda_{DB} = 0.07$  Å and that of X-ray is around few Angstroms. Consequently, the Ewald's sphere radius  $s_0 = 1 / \lambda$  is larger in the case of electron diffraction, thus a greater area of the momentum space can be probed. However, recently, hard X-ray sources have been developed that offer comparable Ewald's sphere radius.
- (iii) Generating a pulsed X-ray beam can be challenging sometimes as it requires a large facility with a cost of few billions to build, in contrast to a tabletop electron gun source. Although some large and complex facilities for MeV electron diffraction do exist.

To obtain a transient molecular movie, in a typical ultrafast electron diffraction (UED) setup, a time delay is created between the pump pulse and the probe electron beam. At each time delay, a diffraction image is recorded from which the 3D transient image of the intermediate state can be inferred.

#### 1.3 <u>Materials of interest</u>

The time scale of relaxation pathways in semiconductors is elucidated in Figure 1.3 and processes can occur from the femtosecond regime all the way to some microseconds. In our lab, we use transient reflectivity to probe processes ranging between 300 fs and up to 2 ns, and ultrafast electron diffraction to probe processes ranging between 700 fs, after implementing a tilted pump beam wave front, and up to 2 ns. This way, we can track the ultrafast electronic and lattice transient changes to build a fuller picture of the materials dynamics in time and in space.

The large scattering cross-section of electrons with matter makes ultrafast electron diffraction ideal to trace the photoinduced ultrafast processes, or more specifically, changes occurring to the crystal lattice. This feature made UED the technique of choice to probe the photoinduced phase-transition mechanism in VO<sub>2</sub> [24, 35-39] to assert the transformation pathways and the intermediate states that are formed before reaching the metallic state. Similarly, to probe the dynamics of the charge density wave [34, 40-44] in quantum materials and in phase change materials used for data storage [45]. Also, using the diffuse scattered electrons, we can probe the phonon population dynamics in each branch and assert the strength of the electron-phonon coupling in materials [46, 47]. In our lab, ultrafast electron diffraction is set up in reflection geometry making this technique surface sensitive due to the small electron-penetration depth at grazing incidence angle. More interestingly, it makes it possible to directly probe the out-of-plane momentum transfer vector (perpendicular to the surface normal), that is not accessible with state-of-the-art microscopic techniques using transmission geometry.



Figure 1.3 Time scale at which various relaxation processes occur. Adapted from [48]
Materials of interest are usually semiconductors exhibiting a photoinduced reversible phase
transition as well as other materials with some remarkable properties. The recent progress on the
application of 2D materials in catalysis, solar cells, nanofabrication and integrated circuits
motivated us to pursue and study the response of these materials following an optical excitation.



Figure 1.4 The number of publications per year portraying the topic "2D materials". From Web of Science.

In his famous lecture in 1959, "There's plenty of room at the bottom." Richard Feynman imagined a world at the atomic level and stressed on how "atoms on a small scale behave like nothing on a large scale" and he saw an opportunity for new field. These speculations by Feynman, came to reality in 2004 when the first single layer of graphene was isolated [49] opening up a new field and the discovery of a new family of materials, which are 2D materials. Indeed, reducing the dimensionality of a system often results in the emergence of new properties of the material, due to the enhanced quantum confinement and the reduced screening effects. The diversity and the richness of these characteristics can be partially presented in Figure 1.5 showing the bandgap of certain 2D materials spanning the whole optical spectrum.



Figure 1.5 The bandgap energy for some 2D materials.

An example of these is transition metal dichalcogenides (TMDs), which have a semiconductor character and a molecular formula of the form MX<sub>2</sub>, where M is a transition metal (Mo, W are the most studied) and X a chalcogenide atom (S, Se, and Te). These materials offer a unique opportunity for novel applications in nanoelectronics and nanophotonic, owing to the ease of engineering their optical and electrical proprieties by tuning the substrate dielectric constant [50-52], the application of an external electric field [53], strain[54-56], layers thickness [57, 58] and interlayer twist angle[59, 60].

Separated by a weak van der Waals force between layers, mechanical exfoliation with a scotch tape from a bulk sample can readily form flakes that can be latter transferred to an adequate wafer. Via tape exfoliation, the flakes size is usually few microns and therefore a microscopy technique would be more adequate to probe the flakes dynamics; to obtain a larger coverage area, many CVD methods have been developed allowing to grow a wafer scale and continuous TMDs monolayer on various substrates [61, 62]. Molybdenum disulfide (MoS<sub>2</sub>) is by far the most common to encounter among TMDs. Upon reducing the dimensionality of bulk MoS<sub>2</sub> down to a single layer, its bandgap increases from 1.2 eV up to 1.85 eV, accompanied by a change from an

indirect bandgap semiconductor to a direct bandgap semiconductor [57, 58] and an enhancement of the photoluminescence quantum yield. Moreover, following light absorption, an exciton is formed (below the Mott density) with a binding energy of some hundreds of meV [63-67], rather than a free electron-hole pair as in conventional semiconductors. Also, because of the lack of an inversion symmetry in monolayer MoS<sub>2</sub>, a strong spin-orbit coupling lifts the degeneracy at the K valley of the valence band.



Figure 1.6 The structure of  $MoS_2$  monolayer. (a) top view and side view of  $MoS_2$  monolayer crystal structure. (b) Brillouin zone of  $MoS_2$  monolayer. (c) Schematic representation of the band structure of  $MoS_2$  at the K valley and the splitting in the valence band.

Another aspect of the TMDs is their crystalline structure. Although some variations may exist, the hexagonal (trigonal prismatic) structure is the most common. A single layer of TMDs is 7 Å thick [68] and is formed by the transition metal atom sandwiched between two chalcogenides atoms. At room temperature,  $MoS_2$  monolayer is a semiconductor and has a trigonal prismatic coordination with a  $D_{3h}$  point group; this phase is the 2H phase (S-Mo-S stacking). At high temperature, the hexagonal lattice is maintained; however,  $MoS_2$  turns into the metallic phase, with an octahedral  $O_h$  point group known as the 1T phase (S-Mo-S' stacking).



Figure 1.7 The structure of bp. (a) the crystal structure of bp with top view (upper panel) and side view along the armchair direction (bottom panel). (b) Schematic representation of the band structure of bulk bp at the Z valley which corresponds to the out-of-plane direction.

Staying within the framework of van der Waals materials, black phosphorus (bp) which is the most thermodynamically stable allotrope of phosphorus is another promising 2D material, with proprieties that are intermediate between the gapless graphene and TMDs [69, 70]. Early work on bp dates to 1914 [71] when Bridgman, Nobel prize laureate for his work on high pressure physics, discovered when applying hydrostatic pressure on white phosphorus; however the research on bp remained stagnant until recently and after the discovery of graphene. Contrary to the case of TMDs, the anisotropy in bp is prominent in the in-plane direction as well as in the out-of-plane direction. bp has an orthorhombic crystal structure, where two perpendicular crystalline directions form the planar layer which are the zigzag and the armchair direction. Similarly to TMDs, the band-gap energy in bp is a function of the number of layers: it increases from 0.3 eV for bulk bp to about 2.0 eV for bp single layer; but unlike TMDs, bulk bp and bp monolayer are both direct band-gap semiconductor [72]. This band gap however is present in the Z-valley which corresponds to the out-of-plane direction in the Brillouin zone, where along this direction exists a strong interlayer coupling that we didn't observe in TMDs. The distinctive anisotropy in bp is prevalent through the differential absorption of a linearly polarized light along the zigzag or the armchair direction [73, 74], the large carrier mobility in the armchair direction reflecting a lighter carrier effective mass [75, 76], the large thermal conductivity along the zigzag direction compared to that in the armchair direction and the out-of-plane direction [77-79].

The technological advancements to achieve an atomic spatial resolution and an attosecond time resolution has led to new discoveries in science that shaped our understanding of some the fundamental aspects in nature. Tracking a system response to an external stimulus and being able to disentangle the various processes which can be occurring, is one of the many applications of a pump-probe scheme that became valuable in elucidating the reaction dynamics in the early stages of the technique development. In this work, a detailed description of the two pump-probe techniques that are being used will be discussed in Chapter 2, namely ultrafast electron diffraction and transient reflectivity, in addition to some theoretical aspects behind the diffraction image formation. The availability of these two techniques in our lab permits to identify the processes that can be occurring in the electronic subsystem and in the lattice subsystem with a sub-angstrom spatial resolution owing to the short De Broglie wavelength of the electron beam. Then in Chapter 3, the ultrafast structural, interfacial, and carrier dynamics of monolayer MoS<sub>2</sub> supported on sapphire are cross-examined by the combination of ultrafast electron diffraction (UED) and transient reflectivity techniques. The out-of-plane motions directly probed by reflection UED suggest a limited anisotropy in the atomic motions of monolayer MoS<sub>2</sub>, which is distinct from that of related materials such as graphene and WSe<sub>2</sub>. Besides thermal diffusion, the MoS<sub>2</sub>-sapphire interface exhibits structural dynamics trailing those of the overlaying  $MoS_2$  and are in stark contrast with the sapphire bulk, which is consistent with the limited thermal boundary

conductance. These structural dynamics provide justification for the determination of carriers being trapped by defects in  $\sim$ 600 fs and releasing energy within a few picoseconds. The rich findings attest to the strength of combining techniques with real-time optical and direct structure probes for a detailed understanding of dynamical processes in functional materials.

In Chapter 4, the dynamics of bulk black phosphorus will be presented, and which exhibits highly anisotropic properties and dynamical behavior that are unique even among two-dimensional and van der Waals-layered materials. Here, we show that an interlayer lattice contraction and concerted, symmetric intralayer vibrations take place concurrently within few picoseconds following the photoinjection and relaxation of carriers, using ultrafast electron diffraction in the reflection geometry to probe the out- of- plane motions. A strong coupling between the photocarriers and bp's puckered structure, with the alignment of the band structure, is at work for such directional atomic motions without a photoinduced phase transition. Three temporal regimes can be identified for the phonon thermalization dynamics where a quasi-equilibrium without anisotropy is reached in about 50 ps, followed by propagation of coherent acoustic phonons and heat diffusion into the bulk.

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# 2 <u>Chapter 2</u>

Theory and Experimental Setup

#### 2.1 <u>Electron energy</u>

Electrons are negatively charged particles and have a particle-wave duality. Therefore, diffraction is a wave propriety just like in the case of X-ray. The corresponding de Broglie wavelength of an electron is given by:

$$\lambda = \frac{h}{p}$$
 2.1

where, *h* is the Planck constant ( $h = 6.626 \times 10^{-34}$  J·s) and *p* is the particle momentum. For an electron accelerated at relativistic speed *v*, the electron momentum is given by the formula:

$$p = \frac{1}{c} \cdot E \sqrt{1 + 2\frac{E_0}{E}}$$
 2.2

where c is the speed of light in vacuum, E is the electron acceleration voltage and  $E_0 = m_0 \cdot c^2$ . For example, in the case where electrons are accelerated at 30 keV and considering an electron rest mass  $m_0 = 9.109 \times 10^{-31}$  kg, this corresponds to a de Broglie wavelength of  $\lambda = 0.0697$  Å. The obtained value of the wavelength can also be approximated using the classical limit for electrons with kinetic energy below 50 keV:

$$\lambda = \sqrt{\frac{h^2}{2 \ m \cdot E}}$$
 2.3

#### 2.2 Bravais lattice and reciprocal space

A crystal is periodic array of atoms. A Bravais lattice is a geometric description of the periodic crystal, regardless of the entity forming the crystal (atoms, molecules...) and it consists of all the position vectors **R** defined by:  $\mathbf{R} = \sum_{i} n_i \mathbf{a}_i$ , where  $n_i$  are integers and  $\mathbf{a}_i$  are a set of non-parallel vectors forming the crystal axes.

The number density n(r) in a periodic crystal can be expressed as a Fourier expansion of the form:  $n(r) = \sum_{G} n_{G} e^{i \mathbf{G} \cdot \mathbf{r}}$ , where **G** is the reciprocal lattice vector, defined as  $\mathbf{G} = \sum_{i} v_{i} \mathbf{b}_{i}$ ,  $v_{i}$ are integers also known as the Miller indices and  $\mathbf{b}_{i}$  are a set of non-parallel vectors forming the reciprocal lattice axes primitive vectors.

To obtain the Fourier coefficient  $n_G$ , we simply multiply by  $e^{-i \mathbf{G} \cdot \mathbf{r}}$  and integrate over the primitive cell volume *V*:

$$n_{\rm G} = \frac{1}{V} \int dV \, n \, (r) \, e^{-i \, \mathbf{G} \cdot \mathbf{r}} \tag{2.4}$$

Under the crystal translation, the number density is invariant then the assumption that  $n(\mathbf{r} + \mathbf{R}) = n(\mathbf{r})$  is true in a periodic crystal.

$$\sum_{\mathbf{G}} n_{\mathbf{G}} e^{i \, \mathbf{G} \cdot \mathbf{r}} e^{i \, \mathbf{G} \cdot \mathbf{R}} = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i \, \mathbf{G} \cdot \mathbf{r}}$$
2.5

Therefore  $e^{i \mathbf{G} \cdot \mathbf{R}} = 1$ , or  $\mathbf{G} \cdot \mathbf{R} = m$ . This later result is known as the definition of the reciprocal lattice.

The reciprocal lattice vectors b<sub>i</sub> can be generated using the Bravais lattice parameters:

$$\mathbf{b}_{1} = \frac{\mathbf{a}_{2} \times \mathbf{a}_{3}}{V}$$
$$\mathbf{b}_{2} = \frac{\mathbf{a}_{3} \times \mathbf{a}_{1}}{V}$$
$$\mathbf{b}_{3} = \frac{\mathbf{a}_{1} \times \mathbf{a}_{2}}{V}$$
2.6

where  $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$  is the volume of the Bravais lattice.

We also define the structure factor as  $S = \int dV n(r) e^{-i \mathbf{G} \cdot \mathbf{r}}$  and since the electrons number density can also be expressed as a superposition of electron density function centered at each atom *j*  shifted by  $r_j$  from the origin of the coordinates, of the form  $n(r) = \sum_j n_j(r - r_j)$  and replacing

it in the equation of the structure factor we obtain:

$$S = \sum_{j} f_{j} e^{-i\mathbf{G}\cdot\mathbf{r}_{j}}$$
2.7

where  $f_j = \int dV n_j(r) e^{-i\mathbf{G}\cdot\mathbf{r}}$  is the atomic form factor. Although the structure factor has an imaginary term, the diffraction peak intensity is real and is given by  $S S^*$ .

#### 2.3 <u>Diffraction theory:</u>

#### 2.3.1 Bragg's law.

Bragg's law is based on the constructive/destructive interference of a coherent light that is reflected from a crystal plane (mirror reflection). In this case, we consider a set of parallel 1D periodic lattice planes separated by an interplanar distance d, an incident beam with a wavelength  $\lambda$  and making an angle  $\theta$  with the crystal plane will be reflected at the same angle  $\theta$ . The path difference  $\Delta$  between the incident and reflected beam is given by:

$$\Delta_1 + \Delta_2$$
  
=  $d \cdot \sin \theta + d \cdot \sin \theta$   
=  $2 d \cdot \sin \theta$   
2.8

For the case of a constructive interference, the path difference is equal to integer multiple of the wavelength  $n \lambda$ . Therefore, the Bragg's law is defined as:

$$n\,\lambda = 2\,d\cdot\sin\theta \qquad \qquad 2.9$$

From the Bragg's law, using a monochromatic light source and for a given set of interplanar distance d, only a discrete set of the diffraction angle  $\theta$  would results in a specular-like reflection spot.



Figure 2.1 Representation of the constructive interference as given by the Bragg diffraction by a set of 2D lattice plane

#### 2.3.2 Laue formulation.

Unlike the Bragg's condition, in the Laue formulation for diffraction there is no assumption of a specular reflection. Instead, each atom in the lattice can scatter the incident beam in all directions and diffraction spots can be observed following a constructive interference. To find the conditions of a constructive interference, we consider the case of two scattering centers separated by a distance *R* (corresponding to a Bravais lattice vector) and an incident beam with a wavevector  $\mathbf{k} = \frac{1}{\lambda}\hat{n}$  propagating along a unit vector  $\hat{n}$  and the scattered light  $\mathbf{k}' = \frac{1}{\lambda}\hat{n}'$  along  $\hat{n}'$ . The path difference  $\Delta$  in this case is given by:

$$\Delta_{1} + \Delta_{2}$$

$$= R \cos \theta_{\text{in}} + R \cos \theta_{\text{out}} \qquad 2.10$$

$$= \mathbf{R} \cdot (\hat{n} - \hat{n}')$$

In the case of the constructive interference, the path difference is an integer multiple of the wavelength, it follows:

$$\mathbf{R} \cdot (\hat{n} - \hat{n}') = m \,\lambda \tag{2.11}$$

Substituting the unit vector  $\hat{n}$  and  $\hat{n}'$  by the corresponding wavevector and rearranging, we obtain:

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = m \qquad 2.12$$

where  $\mathbf{s} = -(\mathbf{k} - \mathbf{k}')$  is the momentum transfer vector with a magnitude  $s = 2\frac{1}{\lambda}\sin\theta$ . Comparing the above result to the definition of the reciprocal lattice:  $\mathbf{R} \cdot \mathbf{G} = m$  where  $\mathbf{G}$  is a reciprocal lattice vector, we obtain the Laue condition for diffraction where constructive interference will occur if the momentum transfer vector  $\mathbf{s}$  matches a vector in the reciprocal lattice  $\mathbf{G}$  ( $G = \frac{1}{d_{(hkl)}}$ ), that is:  $\mathbf{s} = \mathbf{G}$ 



Figure 2.2 Laue diffraction condition. (a) Representation of the constructive interference as given by the Laue formulation of diffraction. (b) Ewald sphere with a radius of k, intercepting a reciprocal space lattice. s is the momentum transfer vector and G is a reciprocal lattice vector. Diffraction conditions are satisfied when both vectors match.

Substituting s and G by the corresponding module and rearranging, we obtain the Bragg's diffraction condition:  $\lambda = 2 d_{(hkl)} \cdot \sin \theta$ 

An easy way to visualize the outcome of the Laue formulation is the Ewald sphere construction as represented in Figure 2.2. The Ewald sphere has a radius of  $k = \frac{1}{\lambda}$  and a diffracted spot will be formed at the intersection of this sphere with a point of the reciprocal lattice. Therefore, the formed reciprocal lattice vector has the origin at the center of the direct beam and the tip is at the surface of the Ewald sphere. This description of the RHEED image formation works great, however, sample surface is not often atomically smooth therefore the recorded image will be modified by the sample surface conditions. Figure 2.3 depicts some surface conditions and what the anticipated RHEED pattern looks like.


Figure 2.3 A schematic representation of the surface condition on the observed RHEED image. Adopted from [1]

# 2.4 <u>Transient changes in electron diffraction.</u>

### 2.4.1 Spectral line profile

The spot intensity profile in a diffraction image reflects the surface disorder and is the Fourier transform of the exponentially decaying height-correlation function [2-4]. Thus, a

Lorentzian line shape is applied to extract information from the diffraction spots. The normalized Lorentzian intensity line shape is given by:

$$I(s) = A \frac{1}{\pi \gamma} \frac{1}{1 + \left(\frac{s - s_0}{\gamma}\right)^2}$$
 2.13

where  $A\frac{1}{\pi\gamma}$  is the peak intensity,  $s_0$  is the peak position and  $\gamma$  is peak half width at half maximum.



Figure 2.4 Line shape of the diffraction spot. A computer-generated diffraction image with a vertical and a horizontal cut are made inside the white area and the fitting the experimental data to a Lorentzian profile.  $S_h$  and  $S_v$  are the horizontal and vertical spot central position. Dashed line

inside the square region (grey for horizontal profile and orange for the vertical profile) represents where the peak profile is extracted from.

### 2.4.2 Intensity change

The diffraction spot intensity given by Equation 2.7 represents the case of a crystal without any thermal motion. By increasing the system thermal energy, the atoms in the crystal experience an increase in their atomic displacement near the equilibrium position  $r_j$  and the atom position changes by u. Therefore, we can write  $\mathbf{r}_j \rightarrow \mathbf{r}_j + \mathbf{u}$ , and the contribution of these effects to the structure factor become:

$$S = f_{j}e^{-i\mathbf{G}\cdot\mathbf{r}_{j}}\langle e^{-i\mathbf{G}\cdot\mathbf{u}}\rangle$$
2.14

where  $\langle e^{-i\mathbf{G}\cdot\mathbf{u}} \rangle$  is the thermal average. The corresponding change in the diffraction spot intensity at a temperature *T* is given by the Debye-Waller effect:

$$I = I_0 e^{-\frac{1}{3}\langle u^2 \rangle \, G^2}$$
 2.15

where  $\langle u^2 \rangle$  is the mean square displacement and according to the Debye model this a function of the system temperature *T* and is defined as:

$$\langle u^2 \rangle = \frac{9\hbar^2}{\overline{m}k_B \Theta_{\rm D}} \left[ \frac{1}{4} + \left(\frac{T}{\Theta_{\rm D}}\right)^2 \int_0^{\frac{\Theta_{\rm D}}{T}} \frac{x dx}{e^x - 1} \right]$$
 2.16

where  $\hbar$  is the reduced Planck constant,  $\overline{m}$  is the average atomic mass,  $\Theta_D$  is the material Debye temperature and  $x = \hbar \omega / k_B T$  with  $\omega$  being the phonon frequency. From this model, it follows that the increase in the system temperature always leads to a drop in the diffraction intensity. Therefore, by measuring the change in the diffraction intensity we can infer the experimental change in the system temperature is a known quantity.

We can also calculate the change in the temperature following an optical excitation by considering a conversion of the photons absorbed energy into heat and in this case the temperature change  $\Delta T$  is defined as:

$$\Delta T = (1-R) f \frac{\alpha}{C}$$
 2.17

where *R* is the material reflectivity, *f* is the laser pump fluence,  $\alpha$  is the absorption coefficient at the pump wavelength and *C* is the heat capacity.

After an optical excitation, a part of the electronic subsystem energy will be transferred to the lattice which will increase the atomic thermal motion via electron-phonon coupling and will result in a drop of the diffraction spot intensity as portrayed by the Debye-Waller analysis. In this case, the temperature extracted from the diffraction intensity change and that calculated from the laser excitation fluence should be comparable. However, this is not always the case especially for materials with an optically induced phase transition where depending on the new atomic rearrangement some diffraction spots intensity would also increase [5, 6].

#### 2.4.3 Peak position change

The obtained diffraction image is a map of the crystal structure that reflects the atomic position in space and the position of the diffraction spot relatively to the direct beam is inversely proportional to the interplanar distance d of the (hkl) plane. An important feature of the ultrafast electron diffraction is the negative change in the peak position corresponding to an increase in the interplanar distance. In the absence of a phase transition, the negative position change is due to the lattice thermal expansion using the relationship:

$$\frac{\Delta s}{s} = -\frac{\Delta d}{d} = -\alpha \,\Delta T \tag{2.18}$$

where  $\alpha$  is the thermal expansion coefficient. For an isotropic crystal  $\alpha$  is constant in all crystallographic directions, but in an anisotropic crystal the thermal expansion coefficient varies across the crystallographic directions and carful projection of the change of the peak position must apply.

## 2.5 <u>Experimental setup</u>

### 2.5.1 Optical setup

A part of the optical setup we use is depicted in Figure 2.5. In our laboratory, we have an ultrafast Yb:KGW laser with central wavelength in the infrared region at 1030 nm and a pulse width at half-maximum of 170 fs. A  $\beta$ -barium borate (BBO1) crystal is placed on the IR path generating the second harmonic at a central wavelength at 515 nm (green); then a dichroic mirror is used to separate the green from the IR. Most of the green beam intensity (90%) is reflected off a beam splitter (BS) and the rest is transmitted (10%) and goes through a second  $\beta$ -barium borate crystal (BBO2) to generate the 4<sup>th</sup> harmonic at 257.5 nm. This latter is focused on the LaB<sub>6</sub> cathode inside the electron gun to generate the photoelectrons and accelerated at 30 keV.



Figure 2.5 Schematic representation of an optical setup we have in the lab. Upper panel is for using a green pump bottom panel for an IR pump. (DM = dichroic mirror, BS = beam splitter, BP=band-pass). The pump beam goes through the mechanical delay line and latter guided to the sample and the UV beam focused on the LaB<sub>6</sub> photocathode.

Just like any pump probe experiment, in an ultrafast electron diffraction experiment a pump beam is needed to trigger the system into the excited state. The choice of the excitation wavelength depends on the materials itself and the purpose we are trying to achieve. For example, an above band gap photon excitation energy is usually required; however, the excess energy above the band gap of the material can affect the observed dynamics. Also, by changing the excitation wavelength, we can generate carriers in different valleys in the material band structure. Therefore, depending on the experimental conditions, either the green beam or the IR beam will serve as a pump pulse (Refer to Figure 2.5). To create a time delay between the arrival of the pump beam and that of the photoelectrons on the sample surface, a mechanical delay line is used.

Alternatively, instead of using an electron beam to probe the dynamics, an optical beam can be used instead (IR or green), and the reflectivity change of the sample surface is subsequently measured with a photodiode coupled to a lock-in amplifier. This will be developed in the next section by performing transient reflectivity measurement.

#### 2.5.2 Transient reflectivity

As light propagates in a dielectric medium with a refractive index  $n_1$  and encounters a discontinuity in the refractive index into another dielectric medium with a refractive index  $n_2$ , a fraction of this incident beam will be transmitted, and another portion will be reflected back (assuming there is no absorption). In a static measurement, the portion of light that is reflected from a flat surface is a function of the media refractive index  $n_1$ ,  $n_2$  and the light incidence angle  $\theta_{in}$ . This is given by the Fresnel equations and is dependent on the light polarization:

$$R_{\rm s} = \left| \frac{n_1 \, \cos \theta_{\rm in} \, - \, n_2 \, \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_{\rm in}\right)^2}}{n_1 \, \cos \theta_{\rm in} \, + \, n_2 \, \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_{\rm in}\right)^2}} \right|^2 \tag{2.19}$$

$$R_{\rm p} = \left| \frac{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_{\rm in}\right)^2} - n_2 \cos \theta_{\rm in}}{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_{\rm in}\right)^2} + n_2 \cos \theta_{\rm in}} \right|^2$$
 2.20

When a laser pulse is absorbed by a material and an electron gets into the conduction band causing a change in the refractive index and subsequently altering the measured reflectivity. Although the refractive index is a characteristic of the material at a given wavelength, however, it is a function of the (i) carriers density and the effect it has on the electron energy distribution and the change on the material band-gap [7] and on the carriers diffusion and mobility, (ii) the electronic sub-system temperature [8, 9], (iii) the lattice temperature, (iv) lattice strain [10, 11]. Therefore, to detect any changes in refractive index we can simply measure the change in the material reflectivity.



Figure 2.6 Schematic representation of a green pump IR probe setup implemented in our lab. (DM = dichroic mirror, BS = beam splitter, LS=lens, CF= color filter). The green beam goes

through the mechanical delay line and is chopped to 1 kHz used to excite the system. The IR probe reflectivity change is measured with a photodiode coupled to a lock-in amplifier.

During transient reflectivity measurement, the laser operates at a repetition rate of 2 kHz. After separating the green beam from the fundamental wavelength, the green goes through the mechanical delay line. A chopper is placed on the pump path and its repetition rate is cut to 1 kHz and the pump beam is loosely focused on the sample surface at a near normal incidence angle. As for the probe, the beam is moderately focused on the same area illuminated with the pump with an angle of incidence of 35° when the measurement is carried in the main chamber, unless otherwise indicated. The change in the reflected beam intensity is measured with as photodiode coupled to a lock-in amplifier locked at 1 kHz to increase the signal to noise ratio. To reduce the effect of the scattered light from the pump, we place a color filter before the photodiode.

Alternative configurations are also possible such as IR pump with green probe and singlecolor transient reflectivity with some minor changes to the optical setup.

#### 2.5.3 Time-resolved electron diffraction

### 2.5.3.1 Electron diffraction setup

An ion pump keeps the main chamber, where electron diffraction images are acquired, at an ultrahigh vacuum level with a base pressure of around  $2 \times 10^{-10}$  torr to maintain a clean sample surface. The sample is placed on a high precision automated omicron style sample stage with five degrees of freedom: three translational motion and two rotational axes. The sample stage is coupled to a programable temperature control allowing cooling with liquid nitrogen down to 95 K and heating up to 450 K. To generate the electron beam, a lanthanum hexaboride (LaB<sub>6</sub>) cathode is used. The electron beam can be generated either via thermionic emission and in this case the continuous electron beam is suitable for a static measurement, or via photoemission with the use of a pulsed laser and in this case the pulsed electron beam is most suitable for dynamics studies.



Figure 2.7 A sideview of the main chamber with the sample placed at the center. The excitation pulse at a near normal incidence angle, the optical probe at a 35° angle and the accelerated electron beam at a grazing incidence angle and the diffraction image formed on the phosphorus screen.

The generated electrons are then accelerated up to 30 keV and directed to the sample surface at a grazing incidence angle, hence the name Reflection High Energy Electron Diffraction (RHEED). The diffraction image is formed on a phosphorus screen coupled to an image intensifier and then re-imaged with a fiber-optic taper on a CMOS camera.

An important feature of carrying electron diffraction in reflection geometry, is the small electron elastic penetration depth at small incidence angle. For a medium with an atomic density N, the electron mean free path is  $l = \frac{1}{\sigma \cdot N}$ , where  $\sigma$  is the total scattering cross section. Values for

 $\sigma$  are a function of the electron acceleration voltage and can be obtained from the NIST database. The estimated electrons penetration depth at an incidence angle  $\theta_{in}$  is therefore  $\delta_e = l \cdot \sin \theta_{in}$ , which corresponds to the probing depth.

Material	Penetration depth (Å)
Si	12
Р	12
Au	2
GaAs	6
MoS <sub>2</sub>	5.6

Table 2.1 The penetration depth of electrons accelerated at 30 keV in certain materials with an incidence angle of  $3^{\circ}$ 

Typical values for the electron penetration depth at a grazing incidence angle at 3°, which is close to the typical incidence angle we use in a RHEED experiment, are portrayed in Table 2.1. On average, the effective electron penetration depth ranges from a couple of Angstroms to some tens of Angstroms which mean it can only probe the upper most part of the surface in a sample This unique feature is what makes RHEED a surface-sensitive-technique.

# 2.5.3.2 UED alignment optimization.

The temporal and spatial overlap of the electron beam with laser beam at the sample surface is the first step in any UED experiment and is based on the coulombic repulsion of the electron beam by the electrons generated on the surface following an intense optical excitation. In the case of a perfect overlap between the pump beam and the direct electron beam, there would be an absence of a sideway deflection of the direct beam. The electrons accelerated at 30 keV propagating along the  $\hat{x}$  direction (Figure 2.8) are near zero incidence angle above the sample surface. After a high-power optical pulse hits the same sample surface, photoelectrons will be generated and they will leave normal to the surface in the  $-\hat{y}$  direction causing a deflection of the direct beam. Experimentally, the landing position of the optical pulse on the sample surface can be adjusted in the  $\hat{z}$  direction until the horizontal deflection of the electron beam is negligeable.



Figure 2.8 Alignment of the electron beam with the excitation pulse. (a) Schematic representation of the overlap between the pump and the probe on the sample surface. (b) Images of the direct beam at negative time-delay (upper panel) and the image difference at a positive time delay (lower panel), without an excitation pulse, with a perfect overlap between the pump and the electron beam (from left to right). (c,d) Deflection angle of the direct beam in the horizontal and the vertical direction, respectively. The shaded blue area represents the mount position where the horizontal deflection is negligible.



Figure 2.9 Experimental setup for the UED measurement. For each position on the translation stage, we record a diffraction image that is specific to a time delay  $\Delta t$ 

Now that we have established a good overlap between the electron beam and the optical pump beam, we can proceed with the UED measurement. Figure 2.9 depicts a schematic description of the experiment performed. To create the time delay between the pump and the probe beam we move the translation stage step wise. For each step position on the translation stage, we record a diffraction image, then we move to a new translation stage position, and we record another diffraction image and then the cycle continue to capture the time window of interest. Thereafter, each captured frame represents a single time-delay point and analysis of the image is carried according to Section 2.4

#### 2.5.3.4 Velocity mismatch

In ultrafast electron diffraction, achieving good time resolution is of a major interest to be able to resolve fast processes. Figure 2.10 represents how the velocity mismatch arises between the pump and the electron beam.



Figure 2.10 Velocity mismatch between the optical pump and the electron pulse wavefront. (a) Schematic representation of the arrival time between the electron beam and the optical pump. (b) Trace of the direct beam intensity change at different needle position along the electron beam propagation direction and (c) the resulting time zero at each needle position.

The optical excitation pulse land on the sample surface at a near normal incidence angle, however the electron beam propagating at 1/3 the speed of light and at grazing incidence angle, experiences a delayed landing time on the sample surface denoted  $\delta t$  depending on the landing position. For example, consider the case of an electron beam with a full width at half maximum of around 20 µm making an angle of 3° with the surface. In this case, the electron beam footprint on the sample surface is about 380  $\mu$ m in the propagation direction, corresponding to  $\delta t = 3.80$  ps. This is equivalent to 10 ps broadening per 1 mm on the sample surface ( $\delta t = 10$  ps/mm).

Experimentally, this can be obtained by measuring the change in the direct beam profile caused by the plasma generated from a sharp needle under intense optical excitation at various time delay and moving the needle along the electron beam propagation direction. With a parallel excitation pulse wavefront, we can clearly see that all normalized traces are similar but shifted in time depending on the needle position. The time zero is then plotted in Figure 2.10c at each needle position and the experimentally obtained slope  $\delta t \sim 10 \text{ ps/mm}$ .

To overcome this additional time delay and therefore improve the time resolution, a tilted excitation pulse setup is implemented [12]. This is accomplished by using a dispersion medium to spread the optical beam angular dispersion and then reimaging it on the sample surface. A representation of the pulse front tilt and the time zero at different needle position is illustrated in Figure 2.11. A clear overlap in time between all of the traces of the direct beam intensity change for a needle spanning a 2 mm range. The temporal resolution can also be confirmed using the VO<sub>2</sub> dynamics as a reference which exhibits a fast drop in the diffraction spot. Shown in Figure 2.12 the dynamics obtained from a thin VO<sub>2</sub> film (~ 70 nm) on c-cut sapphire in the  $(20\overline{1})/(101)$  zone. A fast drop in the diffraction spot is obtained, where the fit to an error function leads to a full width at half maximum of  $520\pm190$  fs

We note that the pulse front tilt setup was implemented the for the study of the dynamics of black phosphorus presented in Chapter 4, and as for the MoS<sub>2</sub> dynamics presented in Chapter 3 a parallel pulse front was used.



Figure 2.11 Pulse front tilt setup. (a) A representation of a perfect temporal overlap between the titled optical pulse and the electron beam. (b) Trace of the direct beam intensity change at different needle position. The convergence of all traces to a single time zero is a direct consequence of the tilted pulse front.



Figure 2.12 Temporal resolution of the instrument. (a) Diffraction image from a thin film of  $VO_2$  on c-cut sapphire. (b) The ultrafast diffraction intensity change of photoinduced phase transition of  $VO_2$  was used for characterization. The fit of the data to an error function yields a full width at half-maximum of  $520\pm190$  fs

# 2.5.3.5 Uncertainty of the zero of time

The zero of time is determined by the spatial and temporal overlap of the footprints of the laser excitation and the electron probe pulses on the specimen surface, whose position is fine-

adjusted by a computer-controlled supporting goniometer. Due to the need of search for a good bp sample region that produces reliable UED dynamics, the actual *Y* position of the surface varies. An illustration of the effect on the footprint overlap is given in Figure 2.13 for two different sample positions,  $Y_1$  and  $Y_2$ ; the corresponding center of the electron landing site is  $X_1$  and  $X_2$ , respectively. Consequently, a path difference of the electron beam exists and is equal to

$$X_1 X_2 = \frac{|Y_1 - Y_2|}{\tan \theta_{\rm in}}$$
 2.21

which corresponds to an additional delay time for the arrival of 30-keV electrons (propagating at 0.32836 times the speed of light *c*) at  $X_2$  versus that at  $X_1$  by

$$\Delta t_{\rm e} = \frac{X_1 X_2}{0.32836 \, c} \tag{2.22}$$



Figure 2.13 Estimate of the uncertainty of the zero of time. Assuming a perfect temporal overlap between the laser and electron pulses at  $X_1$ , a mismatch at  $X_2$  due to the Y difference in the sample position can be estimated to be on the order of 10 fs

For the tilted wavefront of the laser beam, the resulting vertical distance between the pulse centers

landing at  $X_1$  and  $X_2$  is

$$\Delta l = X_1 X_2 \cdot \tan \beta \tag{2.23}$$

where  $\beta = 71.8^{\circ}$  is the pulse front tilt angle by design. The associated delay time is hence

$$\Delta t_1 = \frac{\Delta l}{c} \tag{2.24}$$

In our measurements, the vertical position change  $|Y_1 - Y_2|$  is of the order of 10 µm. Thus, with a typical incidence angle  $\theta_{in}$  of 3°, the mismatch between the arrival times of the laser and electron pulses at  $X_2$  as a result of such a height difference (assuming a perfect temporal match at  $X_1$ ) is

$$|\Delta t_{\rm l} - \Delta t_{\rm e}| = \frac{|Y_1 - Y_2|}{c \cdot \tan \theta_{\rm in}} (0.32836^{-1} - \tan 71.8^{\circ}) = 7.48 \times 10^{-2} \frac{|Y_1 - Y_2|}{c}$$
 2.25

which is no more than few tens of fs. Practically,  $\beta$  may have a residual deviation of a small fraction of a degree from the intended value, which yields a temporal uncertainty of a similar level also. Thus, the zero of time is well defined in our measurements.

# 2.6 **Bibliography**

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# 3 Chapter 3

Cross-Examination of Ultrafast Structural, Interfacial, and Carrier Dynamics of

Supported Monolayer MoS<sub>2</sub>

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Since the experimental discovery of graphene, research of the properties and applications of single- and few-layer two-dimensional (2D) materials and van der Waals solids has been growing exponentially in recent years.[1, 2] Transition metal dichalcogenides (TMDs), in particular, have attracted great attention because of their versatile structures and tunable optical and electronic properties, besides the typical benefits of 2D materials with good mechanical strength and flexibility as well as large electrical and thermal conductivity [3, 4]. Molybdenum disulfide  $(MoS_2)$  is a prototypical example, which exhibits major changes in its electronic structure especially for the evolution from an indirect band gap of 1.3 eV for the bulk to a direct gap of 1.9 eV for a monolayer [5]. Such an electronic modification results in layer-dependent efficiencies in photo- and electroluminescence [5-7], which opens up various potential (opto)electronic applications such as light-emitting diodes, solar cells, and field-effect transistors. Opportunities may also exist when large external stimuli or fields are applied [8]. To further understand lightmatter interactions in 2D and related materials at the fundamental level, studies of ultrafast electronic and structural dynamics following photoexcitation at different levels are therefore needed.

Previously, studies using time-resolved all-optical spectroscopy have suggested a few relaxation mechanisms for carriers photogenerated in monolayer MoS<sub>2</sub> (1L-MoS<sub>2</sub>), including exciton–exciton annihilation below the Mott density [9, 10], defect-assisted electron–hole recombination [11], and carrier–phonon scattering [12, 13]. Measurements of photoluminescence produced from radiative recombination of carriers have often been considered as one of the methods to characterize 1L-MoS<sub>2</sub>, with influence from the formation of excitons and trions [14-16], a supporting dielectric medium [17, 18], applied strain [19, 20], temperature [12], and surface treatment [6]. In these studies, the photoinjection levels were in the range of  $4 \times 10^9$  to  $8 \times 10^{12}$ 

cm<sup>-2</sup> to avoid complex mechanisms that may occur at higher carrier densities. In contrast, only a few reports exist to date about photoinduced structural dynamics of 1L-MoS<sub>2</sub> or TMDs. Ultrafast electron diffraction (UED) in a transmission geometry has been used to examine 1L-MoS<sub>2</sub> transferred onto a copper TEM grid with an amorphous carbon layer, showing in-plane atomic displacements and the inference of induced out-of-plane rippling, at the injection level of ~5 ×  $10^{14}$  cm<sup>-2</sup> [21]. Early time structural dynamics of monolayer and bilayer MoSe<sub>2</sub> probed by transmission UED at ~ $10^{14}$  cm<sup>-2</sup> suggest a softening of vibrational modes in the excited state for an efficient and rapid energy transfer between the electronic and the lattice subsystems [22]. Ultrafast X-ray diffraction in a reflection geometry has been used to investigate the anisotropic inplane and out-of-plane lattice vibrations of WSe<sub>2</sub> supported on sapphire, within a rather small temporal window of 10 ps [23].

A few fundamental issues of 1L-MoS<sub>2</sub> have not been examined in detail. For example, graphene has been found to have different in-plane and out-of-plane atomic motions [24, 25] and Debye temperatures [26, 27], and WSe<sub>2</sub> exhibits prominent anisotropy in lattice vibrations at early times following photoexcitation [23]. The degree of anisotropy of 1L-MoS<sub>2</sub> remains unknown because of the lack of direct probing of out-of-plane dynamics for comparison. Furthermore, structural dynamics at the interface between 2D materials and their supporting substrates have not been resolved to date, whose understanding is relevant to actual devices in that solid supports will likely be present for most applications instead of free-standing films, and an underlying substrate may influence the behavior of supported TMDs [17, 18]. In addition, time-resolved dynamics of photogenerated carriers at higher injection levels require further study, whose results should be consistent with the subsequent lattice dynamics probed by structure-specific methods.

In this report, structural, interfacial, and carrier dynamics of sapphire-supported 1L-MoS<sub>2</sub> are cross-examined using the combination of UED and transient reflectivity measurements, at elevated injection densities ranging from  $5.80 \times 10^{12}$  to  $1.13 \times 10^{14}$  cm<sup>-2</sup>. We note our capability to probe the out-of-plane lattice motions and to differentiate the dynamics of the MoS<sub>2</sub>-sapphire interfacial structure because of the small penetration depth of the 30 keV electrons incident in reflection geometry. It is found that out-of-plane lattice motions of supported 1L-MoS<sub>2</sub> are comparable to the in-plane counterparts reported earlier in a transmission study [21], and hence, a single Debye temperature can be assigned for both in-plane and out-of-plane dimensions. Thermal diffusion via the interface governs the recovery at longer times, whereby the thermal boundary conductance is determined. More significantly, diffractions produced by the MoS<sub>2</sub>-sapphire interface exhibit time-dependent changes trailing those of the 2D material itself, which implies the different behavior of the interfacial structure compared to that of the sapphire bulk. These structural dynamics provide information for a consistent analysis of the results of the optical pump-probe measurements, where the trapping of the photogenerated carriers by defects is found in ~600 fs.

### 3.1 <u>Photoluminescence of MoS<sub>2</sub> monolayer and bulk</u>

Monolayer MoS<sub>2</sub> grown by the CVD method on sapphire (0001) was purchased from 2DLayer. It was found that annealing the specimens in an ultrahigh vacuum at an elevated temperature (above 100 °C) improved the film quality, according to the increase in the intensities of the streak-like diffractions. The change in the band structure of MoS<sub>2</sub> from an indirect-gap semiconductor for the bulk to a direct-gap one for a monolayer, results in a prominent enhancement in photoluminescence (PL) which is evident in Figure 3.1. following an excitation at 532 nm. The PL spectra were acquired from different regions of the specimen used for the time-resolved studies

and no significant change in the intensity was observed. In addition, optical micrographs of the sample used showed no contrast difference that may originate from stacked multilayer MoS<sub>2</sub>. Moreover, no PL peak near 775 nm was observed, which would correspond to indirect-gap PL of bilayer MoS<sub>2</sub>. Hence, we confirm by PL, optical microscopy, and reflection electron diffraction that the specimen used in the experiments was a uniform monolayer



Figure 3.1 Photoluminescence spectra of MoS<sub>2</sub> monolayer (black) and bulk (red). The two peaks labeled as A and B are characteristics of the exciton emissions of monolayer MoS<sub>2</sub>. The peak near 700 nm originates from the c-plane sapphire substrate

### 3.2 Structural dynamics of monolayer MoS<sub>2</sub>

Shown in Figure 3.2a is the diffraction pattern of 1L-MoS<sub>2</sub> acquired at an incidence angle of  $\theta_{in}$ = 3.8° without photoexcitation. The observation of multiple diffraction streaks at all grazing incidence and azimuthal rotational angles confirms the 2D nature of the monolayer, which was grown by chemical vapor deposition (CVD) with azimuthally rotated crystallites. The diffraction streaks (ensemble-probed from an area of 15 × 230 µm<sup>2</sup>) are well indexed with a hexagonal lattice, and a lattice constant of 3.18 Å is obtained [28]. At incidence angles higher than 4.6°, the more apparent diffraction spots and Kikuchi lines indicate the probing of the interfacial structure and the surface region of the supporting substrate underneath the 2D material due to increased electron penetration.



Figure 3.2 Electron diffraction and photoinduced changes of 1L-MoS<sub>2</sub>. (a) Diffraction of 1L-MoS<sub>2</sub> acquired at an incidence angle of  $\theta_{in} = 3.8^{\circ}$  without laser excitation. The 2D Miller indices are given. (b) Diffraction difference image at t = 18 ps referenced to panel a. (c) Diffraction intensity changes along the center streak as a function of  $s_{\perp}^2$  at different laser fluences used. The symbols are the experimental results obtained via intensity curve fits, and the lines are linear fits according to Equation 3.1. (d) Mean-square atomic displacement increments as a function of the maximum temperature reached the respective apparent fluence. The line is a fit by Equation 3.3.

Following an above-gap excitation by 515 nm photons, the intensity of 1L-MoS<sub>2</sub> diffractions decreases within 20 ps (Figure 3.2b). It is crucial first to confirm that the observed diffraction changes originate from structural motions, not from any surface-related field or Coulombic effects. Shown in Figure 3.3b is the lack of any intensity changes near the shadow edge, which signifies the absence of significant surface electric fields that could alter the paths of grazing electron scattering. Given that no apparent structural transition exists at the temperature and

excitation fluences used, the Debye–Waller effect describing the relation between diffraction intensity and the increased motions of ions in 1L-MoS<sub>2</sub> is considered: [29]

$$\ln\left(\frac{I_0}{I(t)}\right) = 2W(t) = \Delta\left\langle \left(\vec{q} \cdot \vec{u}(t)\right)^2 \right\rangle = 4\pi^2 s_{\perp}^2 \cdot \Delta\left\langle u_{\perp}^2(t) \right\rangle$$
 3.1

where the  $I_0$  and I(t) are, respectively, the diffraction intensities of the center diffraction streak before the zero of time and at time t after excitation, W the Debye–Waller factor,  $\vec{u}$  the atomic displacement vector,  $\vec{q} = 2\pi \vec{s}_{\perp}$  the scattering vector of the center diffraction streak, and  $s_{\perp} = 2 \sin (\theta/2)/\lambda$  the vertical momentum transfer perpendicular to the scattering surface, with  $\theta$  being the total scattering angle and  $\lambda = 0.0698$  Å the de Broglie wavelength of 30 keV electrons. Thus, according to Equation 3.1,  $\ln(I_0/I)$  is directly proportional to  $s_{\perp}^2$  at a given time and fluence that correspond to a certain increment value of the out-of-plane mean-square displacement,  $\Delta \langle u_{\perp}^2(t) \rangle$ .



Figure 3.3 Time dependence of structural changes of  $1L-MoS_2$  at  $0.97 \text{ mJ/cm}^2$ . (a) Diffraction intensity change as a function of the delay time. The solid line is a fit according to Equation 3.4. The inset shows the early time dynamics. (b) Absence of intensity changes in the shadow edge region between the diffraction streaks (selected regions of interest are color-coded in the diffraction). (c) Effective temperature derived from the UED data (dots). The solid line gives the simulation result of one-dimensional thermal diffusion. The inset shows the dynamics within 500 ps. (d) Numerically simulated temperatures of  $MoS_2$  and sapphire as a function of the delay time.

This is indeed our observation, which validates the use of reflection UED to probe transient out-of-plane lattice motions. A linear relation is observed between  $\ln(I_0/I)$  and  $s_{\perp}^2$  for all laser fluences used (Figure 3.2c). Furthermore, the consistency with the Debye–Waller effect signifies the thermalization of random atomic motions in 1L-MoS<sub>2</sub> at early times. It is found that the absorption of 44 µJ/cm<sup>2</sup> (3% of the apparent fluence of 1.46 mJ/cm<sup>2</sup> at 515 nm) leads to  $\Delta \langle u_{\perp}^2(t) \rangle \cong 2.5 \times 10^{-3} \text{ Å}^2$ ; in the earlier transmission UED study, the absorption of 220 µJ/cm<sup>2</sup> (6.6% of the

apparent fluence of 3.3 mJ/cm<sup>2</sup> at 400 nm) yields in-plane  $\Delta \langle u_{\parallel}^2(t) \rangle \cong 1.25 \times 10^{-2} \text{ Å}^2$  [21]. Thus, the excellent proportionality between the absorbed energy densities and the induced in-plane and out-of-plane mean-square displacement increments indicates that the thermalized atomic motions after several ps are essentially isotropic, showing limited anisotropy unlike those of graphene and WSe<sub>2</sub>. This shows that dynamical behaviors of different 2D materials vary significantly even though they share the 2D structural motif.

The temperature dependence of mean-square atomic displacements is given by [29]

$$\langle u_{\perp}^{2}(T)\rangle + 2\langle u_{\parallel}^{2}(T)\rangle \cong 3\langle u_{\perp}^{2}(T)\rangle = \frac{9\hbar^{2}}{\overline{m}k_{B}\Theta_{D}} \left[\frac{1}{4} + \left(\frac{T}{\Theta_{D}}\right)^{2} \int_{0}^{\frac{\Theta_{D}}{T}} \frac{xdx}{e^{x} - 1}\right]$$
 3.2

where  $u_{\parallel}(T)$  is the one-dimensional in-plane atomic displacement component,  $\hbar$  the reduced Planck constant,  $\overline{m}$  the average atomic mass,  $k_{\rm B}$  the Boltzmann constant,  $\Theta_{\rm D}$  the Debye temperature, and  $x = \hbar \omega / k_{\rm B} T$  with  $\omega$  being the phonon frequency. The first equal sign is valid here because 1L-MoS<sub>2</sub> exhibits effectively isotropic atomic motions. Hence, the experimentally obtained out-of-plane mean-square atomic displacement has the following temperature dependence:

$$4\pi^{2}\Delta\langle u_{\perp}^{2}(T)\rangle = \frac{3h^{2}}{\overline{m}k_{B}\Theta_{D}} \left[ \left(\frac{T}{\Theta_{D}}\right)^{2} \int_{0}^{\frac{\Theta_{D}}{T}} \frac{xdx}{e^{x}-1} - \left(\frac{T_{0}}{\Theta_{D}}\right)^{2} \int_{0}^{\frac{\Theta_{D}}{T_{0}}} \frac{xdx}{e^{x}-1} \right]$$

$$\approx \frac{3h^{2}(T-T_{0})}{\overline{m}k_{B}\Theta_{D}^{2}} \quad \text{when } T \gtrsim \Theta_{D}$$

$$3.3$$

where *h* is the Planck constant,  $T_0 = 297$  K is the initial temperature and the maximum *T* for each fluence is determined with the specific heat of C = 0.397 J/g·K, the density of  $\rho = 5.00$  g/cm<sup>3</sup>, and a thickness of d = 0.72 nm for 1L-MoS<sub>2</sub> [30], considering that a thermal equilibrium is reached after several ps (see below). A fit of the fluence-dependent results in Figure 3.2d yields  $\Theta_D = 580$ 

K, which agrees well with the theoretical values for both monolayer and bulk MoS<sub>2</sub> at room temperature [31, 32] and the value reported by the transmission UED study for in-plane motions [21].

With regard to the temporal dependence, the diffraction intensity dynamics are fitted to the following function:

$$\ln[I(t)/I_0] = A \cdot (1 - e^{-t/\tau_r}) \cdot e^{-t/\tau_d}$$
 3.4

where A < 0 is a proportionality constant and  $\tau_r$  and  $\tau_d$  are the time constants for the rise and recovery of the observed changes, respectively. A Gaussian function with a full width of ~2.5 ps at half-maximum is used for convolution to account for the instrumental response time (mostly contributed by the velocity mismatch between the optical excitation and the grazing electron probe pulses). A good fit is obtained, with  $\tau_r = 4.0 \pm 2.6$  ps and  $\tau_d = 140 \pm 20$  ps (Figure 3.3a). It is noted that the value of  $\tau_r$  agrees with the typical time for the carrier–phonon and phonon–phonon scattering processes at elevated injection densities. In fact, this is the time scale ( $\tau_r \sim 4$  ps for the out-of-plane motions following the time constant of ~2 ps obtained for the in-plane motions [21]) for phonons to thermalize and establish an effective temperature, which is consistent with the use of the Debye–Waller factor after the first 10 ps for the structural dynamics of 1L-MoS<sub>2</sub>. In what follows, the recovery part of the dynamics is shown to originate from heat diffusion with a single time constant of  $\tau_d$  and, thus, further provides a consistent picture for thermal energy transport via the interface.

#### 3.3 <u>Heat diffusion via the interface</u>

From the diffraction intensity change, a temperature can be assigned at each delay time after 10 ps using Equations 3.1 and 3.3 (Figure 3.3c). A set of equations considering one-dimensional

heat transfer from 1L-MoS<sub>2</sub> to the unexcited supporting sapphire substrate are used in the numerical simulation for time dependence [33] and given by the following coupled equations:

$$C\rho \, d \, \frac{\partial T_f(t)}{dt} = -\sigma \left( T_f(t) - T_s(t) \right) \tag{3.5}$$

$$\left. K \frac{\partial T_s(z,t)}{dz} \right|_{z=0} = \sigma \left( T_f(t) - T_s(t) \right)$$
 3.6

where C and  $\rho$  are the volumetric heat capacity and the density of MoS<sub>2</sub>, respectively, d the thickness of the overlaying film,  $\sigma$  the thermal boundary conductance,  $T_f$  and  $T_s$  the temperatures of the film and the substrate, respectively, K the thermal conductivity of sapphire, and z is along the surface normal direction. In the sapphire substrate, one-dimensional heat diffusion is considered,

$$\frac{\partial^2 T_s(z,t)}{\partial z^2} = \frac{c}{K} \frac{\partial T_s(z,t)}{dt}$$
3.7

with the boundary and initial conditions as follows:

$$T_s(0,t) = T_s(t)$$
  
 $T_s(z,0) = 297 \text{ K}$ 

It becomes clear that the temperature of 1L-MoS<sub>2</sub> should essentially follow a first-order ordinary differential equation because of the large temperature difference between 1L-MoS<sub>2</sub> and sapphire, which results from the relatively slow heat transfer across the interface and the good thermal conductivity of sapphire limiting its temperature increase (Figure 3.3d). Thus, the single exponential decay function in Equation 3.4 is justified, with  $\tau_d^{-1} \cong \sigma/(C\rho d)$  where  $\sigma$  is the thermal boundary conductance of the MoS<sub>2</sub> monolayer on sapphire. It is determined to be 10 MW m<sup>-2</sup> K<sup>-</sup>

<sup>1</sup>, which is similar to the values of 15 MW m<sup>-2</sup> K<sup>-1</sup> for MoS<sub>2</sub> on amorphous carbon [21] and below 20 MW m<sup>-2</sup> K<sup>-1</sup> on a few solid substrates [34].

### 3.4 Structural dynamics at the interface

Further details are found in the structural dynamics at the MoS<sub>2</sub>–sapphire interface beyond the aforementioned thermal diffusion model. At a higher incidence angle of  $\theta_{in} = 4.6^{\circ}$ , electrons are able to probe the interfacial region beneath the 2D layer because of the increased penetration depth. (The elastic mean free path of 30 keV electrons in MoS<sub>2</sub> is calculated to be ~108 Å using the elastic scattering cross sections of Mo and S, which leads to a probe depth of ~7.2 Å at  $\theta_{in}$  = 3.8°, essentially the same as the 2D layer thickness.) Therefore, the observed diffraction spots on the streaks in Figure 3.4a are mainly contributed by the top layers of the sapphire substrate with modulation by 1L-MoS<sub>2</sub>, which is consistent with simulated diffraction patterns using the kinematic scattering theory. Here, both the interfacial region of sapphire and the diffraction modulation by the 2D material are essential for the following reasons. First, without the overlaying MoS<sub>2</sub>, no time-dependent changes are observed from sapphire diffraction spots given that no excitation is made to sapphire by 515 nm photons (see Appendix); hence, its temperature increase as a result of thermal diffusion should be small (Figure 3.3d, inset). Second, the limited penetration of 30 keV electrons at  $\theta_{in} = 4.6^{\circ}$  signifies the probing of only the interfacial layers of sapphire, whose behavior can be different from that of the bulk [35]. We note that effects from a transient surface electric field as a possible cause for our observation can be confidently ruled out, as has been shown earlier in the discussion of the structural dynamics of MoS<sub>2</sub>.



Figure 3.4 Structural dynamics of the  $MoS_2$ -sapphire interface. (a) An electron diffraction image acquired at a high incidence angle of 4.6°, showing weaker streaks from 1L-MoS<sub>2</sub> and a few distinguished spots originated from the interface. (b) Intensity changes of the center diffraction streak and spot as a function of time at 0.97 mJ/cm<sup>2</sup>. The solid curves are fits to Equation 3.4 convoluted with a Gaussian instrumental response function. The inset shows the early time dynamics, where the change of the diffraction spot trailing that of the streak is evident.

Shown in Figure 3.4b are the time-dependent intensity changes of both the center diffraction streak and spot. It is evident that the dynamics of the latter trail those of the former. A fit of the streak data to Equation 3.4 which represents the structural dynamics of the overlaying 1L-MoS<sub>2</sub>, gives  $\tau_r = 2.5$  ps and  $\tau_d = 170$  ps, whose values are consistent with those derived from Figure 3.3a even though the noise level is higher here because of the low intensity at  $\theta_{in} = 4.6^{\circ}$ . In contrast, the diffraction spot intensity change exhibits the time constants of  $\tau_r' = 12$  ps and  $\tau_d' = 240$  ps. The prominent increase in  $\tau_r'$  compared to  $\tau_r$  (with some increase in  $\tau_d'$  compared to  $\tau_d$ ) is thus in good agreement with the kinetics of the enlarged thermal motions of atoms, first initiated and thermalized in 1L-MoS<sub>2</sub> and then coupled to the interfacial layers below for relaxation. It should be noted that atoms at a material's surface experience reduced to no stress along the surface normal direction. Consequently, the atoms in the interfacial layers of sapphire exhibit motions that are greater compared to those in the bulk characterized by the small temperature increase (Figure 3.3d). Moreover, the large difference between  $\tau_r'$  and  $\tau_r$  is an experimental manifestation of the

weak van der Waals coupling and mismatch of phonon density of states between materials, leading to the rather limited value obtained for the thermal boundary conductance [34].

Once the different behavior of the interface and the substrate bulk is confirmed, the observed intensity decrease of  $\ln(I/I_0) \cong -0.15$  at 30–50 ps may be well explained (Figure 3.4b, inset). With the Debye temperature of MoS<sub>2</sub> (580 K) and sapphire (1042 K), temperature increases by ~170 K and ~130 K are deduced, respectively, considering the two extreme cases that the diffraction spot is only contributed by either component. The fact that these values agree with that of the overlaying film, a temperature increase of about 135–155 K from the effective temperature of 435–455 K shown in the inset of Figure 3.3c, indicates a thermal exchange and equilibrium between the film and the interfacial structure, which is reasonable because of their direct contact.

#### 3.5 Carrier dynamics

Determination of the photocarrier dynamics of a material may be better achieved with the knowledge of its structural dynamics, especially for elevated injection densities when other processes, including structural and thermo-optic components, also contribute to the optical pump-probe signals. Shown in Figure 3.5a are the transient reflectivity changes,  $\Delta R/R$ , of sapphire-supported 1L-MoS<sub>2</sub> at room temperature following 515 nm photoexcitation, at various initial carrier densities  $N_0$  ranging from  $5.80 \times 10^{12}$  to  $8.1 \times 10^{13}$  cm<sup>-2</sup>. At each apparent laser fluence used, the reflectivity decreases to a minimum value within the instrumental response time followed by a recovery to the initial state on a ps time scale. The value of the initial decrease may be explained by the mechanisms of free-carrier absorption, band filling, and band gap renormalization, although theoretical modifications are needed to account for the 2D material [36-39].



Figure 3.5 Time-dependent optical pump-probe results of supported 1L-MoS<sub>2</sub>. (a) Transient reflectivity acquired with a 1030 nm probe. The dashed arrow indicates the result of increasing the photogenerated carrier density. Dots represent the experimental data, and the solid lines are fits using the three-exponential model described in the text. The inset shows the longer-time dynamics. (b–d) Time constants ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , respectively) obtained from the fits as a function of the carrier density. The error bars give the standard deviations.

The time-dependent recovery can be described by a three-exponential model,  $A e^{-t/\tau_1} + B e^{-t/\tau_2} + C e^{-t/\tau_3}$  (see below for the justification) convoluted with a Gaussian instrumental response function, where  $\tau_i$ 's ( $\tau_1 < \tau_2 < \tau_3$ ) represent the time constants of three recovery processes and A, B, and C are their respective amplitudes. It is found that, in the range of carrier density used, the fastest process accounts for  $\sim 84 \pm 7\%$  of the recovery of the transient change on the average, whereas  $\sim 14 \pm 6\%$  and  $\sim 2 \pm 2\%$  are for the second and the third components, respectively (the
standard deviation is indicated). In addition, the time constants obtained from the fits do not exhibit a strong dependence on laser fluence (Figure 3.5b–d). The fastest component, with similar  $\tau_1 \sim$ 600 fs, can be attributed to the process of carrier trapping by defects; namely, removal of the free carriers by such a mechanism effectively diminishes the transient change at early times (Figure 3.5b). This is consistent with previous reports for CVD-grown TMDs with a minimal dependence of the sub-ps time constant on the carrier density [10, 40, 41]. The small increase in  $\tau_1$  observed at the highest fluences used may be due to a bottleneck and/or hot-phonon effect that causes elongation of the carrier-trapping process.

It is noted that  $\tau_2 \sim 3.5$  ps and  $\tau_3 \sim 160$  ps (Figure 3.5c,d) are satisfactorily consistent with the time constants ( $\tau_r$  and  $\tau_d$ ) obtained from the UED data (Figure 3.3a). Such an agreement allows the identification of the second and third components in the transient reflectivity results as the phonon thermalization and heat diffusion processes during the recovery, thus justifying the use of the aforementioned three-exponential model. These assignments could be ambiguous if only alloptical pump–probe results are available. Hence, it is crucial to conduct a cross-examination of the photoinduced carrier and structural dynamics, such as presented here for sapphire-supported 1L-MoS<sub>2</sub> using the combination of optical and UED experiments. Moreover, it is concluded that the energy release from the trapped carriers to the lattice in the present fluence range must take place immediately, so to be fully consistent with the phonon thermalization process in a few ps and the success of the Debye–Waller description for the following thermal motions. Such a result also indicates a fast carrier–phonon coupling in MoS<sub>2</sub> via the emission of optical phonons in hundreds of fs [42], instead of a slow process in some tens of ps. [12, 13, 43]

Here, we consider the possibility of a few other carrier relaxation mechanisms to explain the observed transient reflectivity and time dependence. Exciton–exciton annihilation, with a second-order rate equation, is applicable for relatively low injection levels below the Mott density of ~4.3 × 10<sup>12</sup> cm<sup>-2</sup> [39] or ~1 × 10<sup>13</sup> cm<sup>-2</sup> [44]. Auger recombination with a third-order rate equation, on the other hand, may be important at high laser fluences. For these two mechanisms, the effective rate constants should have a clear dependence on the injected carrier densities. However, they may be ruled out based on the fact that the density range used here is above the Mott density, and the obtained time constant  $\tau_1$  remains similar (Figure 3.5b). In fact, the lack of a density dependence for  $\tau_1$  is anticipated for carrier trapping by a given density of defects. We note that, depending on the preparation method for the material, the defect density may greatly differ, which may result in extended carrier lifetimes observed in a large single-crystalline specimen [39]. How the structural dynamics are then affected may be the subject of a further study.

Finally, we would like to address the issue of limited anisotropy in the atomic motions of MoS<sub>2</sub> compared to those of other 2D materials. Before the development of ultrafast diffraction methods, atomic root-mean-square displacements (RMSDs) have been derived via thermal analyses of diffractions obtained in equilibrium. For graphite and WSe<sub>2</sub>, clear anisotropy in the RMSDs has been found, whose ratios between the out-of-plane and in-plane motions are about 5.5 and 4, respectively [45, 46]. For graphene, a corresponding ratio of 6.8 was obtained [47]. In contrast, the anisotropy of MoS<sub>2</sub> is largely reduced, where the out-of-plane to in-plane RSMD ratios are 1.6 and 1.3 for Mo and S, respectively [28]. Although insufficient to provide a direct prediction of the photoinduced dynamical behavior of materials, especially in monolayer cases, the diffraction results in equilibrium appear to be in line with the observations made using ultrafast techniques in terms of the degree of anisotropy in lattice motions. It is well-known that, for photoinjected carriers, the electron–phonon coupling in graphite and graphene is highly anisotropic, first to the in-plane strongly coupled optical phonons followed by phonon–phonon

scattering to induce out-of-plane motions [48]. In the present study, 1L-MoS<sub>2</sub> is found to exhibit comparable out-of-plane and in-plane RSMDs following photoexcitation and hence limited dynamical anisotropy, which is consistent with the former X-ray diffraction results. The microscopic origins could be due to the reduction of the lattice symmetry in TMDs, which would allow additional electron–phonon coupling mechanisms [49] and hence reduce the degree of anisotropy compared to that of graphene. However, this structural symmetry argument may not fully explain the case of WSe<sub>2</sub>, which means that the electronic and phonon structures may also play an important role. Interestingly, the initial coupling to the out-of-plane Ag<sup>1</sup> mode was observed in monolayer WSe<sub>2</sub> by optical transient transmission [50], which is opposite to the observation by femtosecond surface X-ray scattering in the first 10 ps [23]. This disagreement and the less-studied subject to date about the dynamic anisotropy in lattice motions of 2D materials suggest the need for more studies including theoretical investigations. In this regard, reflection UED with surface specificity and an adjustable probe depth may be helpful in providing direct information about the out-of-plane motions.

## 3.6 Conclusion

In summary, the structural, interfacial, and carrier dynamics of monolayer  $MoS_2$  supported on a sapphire substrate were cross-examined at the excitation levels of  $5.80 \times 10^{12}$  to  $1.13 \times 10^{14}$  $cm^{-2}$  above the Mott density threshold, using reflection UED to specifically probe the out-of-plane lattice motions and the interface as well as optical transient reflectivity for electronic and structural processes. A consistent picture was thus obtained to identify the main processes involved. At early times after the above-gap photoexcitation, the injected carriers are trapped by defects in ~600 fs, followed by the release of the carrier energy to phonons via carrier–phonon coupling within a few ps. Phonon scattering and thermalization also occur on a similar time scale, resulting in atomic motions well described by the Debye–Waller factor. Surprisingly, these random atomic motions of a MoS<sub>2</sub> monolayer were found to exhibit little anisotropy, which is in stark contrast with those of other 2D materials such as graphene and WSe<sub>2</sub>. At longer times, heat diffusion across the interface for energy dissipation to the substrate takes place with a time constant of ~140 ps and a thermal boundary conductance of 10 MW m<sup>-2</sup> K<sup>-1</sup>. We further observed the structural dynamics at the MoS<sub>2</sub>–sapphire interface that trails the dynamics of the overlaying 2D film and is evidently different from the nonabsorbing sapphire bulk; such a finding is unique for reflection UED and may not be easily accessed or resolved by other methods. Given the rich observations presented here, the combined use of reflection UED and transient spectroscopy to examine in detail the ultrafast dynamics of other substrate-supported 2D materials and van der Waals solids is anticipated.

#### 3.7 Experimental section

Experimental details about the reflection UED and optical transient reflectivity measurements have been described previously [51, 52]. In short, the 515 nm, 2.41 eV photoexcitation pulses with a repetition rate of 2 kHz were produced by the second harmonic generation of the fundamental output (1030 nm) of a Yb:KGW regenerative amplifier laser system. The photoexcitation beam was loosely focused on the specimen surface at a near-normal incidence angle, resulting in a footprint of ~600  $\mu$ m in the full width at half-maximum (fwhm). A tiny fraction of the remaining fundamental output was used as the optical probe in transient reflectivity, incident at an angle of 35° with a probed range of ~270 × 220  $\mu$ m<sup>2</sup> in fwhm. The electron-generating, 257 nm ultraviolet pulses were produced by another stage of the second harmonic generation of the 515 nm beam. In the UED experiments, the electron probe pulses produced from a lanthanum hexaboride photocathode were accelerated to 30 keV and focused on the specimen

surface for diffraction at a grazing incidence angle. Hence, the convergent electron beam had a footprint of  $\sim 15 \times 230 \ \mu\text{m}^2$  at a grazing angle of 3.8°, which was fully enclosed within the photoexcited region. The number of photoelectrons per pulse was measured to be <250. Finally, the diffraction patterns were recorded by an imaging system composed of a phosphor screen and a gated image intensifier lens coupled to a CMOS camera.

## 3.8 Appendix

The same experimental condition with a laser fluence of 2 mJ/cm<sup>2</sup> was used to measure the diffraction intensity changes from bare sapphire (0001) (Figure 3.6). The absence of time dependent changes is expected because of no absorption of 515-nm photons by sapphire and therefore shows that all photoexcitation was made in 1L-MoS<sub>2</sub>.



Figure 3.6 Diffraction intensity change of a bare sapphire (0001) substrate subject to illumination by 515-nm photon at  $2 \text{ mJ/cm}^2$ 

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# 4 <u>Chapter 4</u>

Ultrafast Carrier-Coupled Interlayer Contraction, Coherent Intralayer Motions, and Phonon Thermalization Dynamics of Black Phosphorus

Besides the spanning of the entire spectrum of electronic properties from gapless graphene to insulating hexagonal boron nitride, two-dimensional (2D) materials and van der Waals (vdW) layered heterostructures have been found to exhibit exceptional quantum and correlated phenomena including superconductivity [1], fractal quantum Hall effects [2, 3], emergent ferromagnetism [4], and valley polarization [5]. Understanding the interplay among the electronic, structural, and spin degrees of freedom and finding additional modulation and control by external stimuli have thus become prominent research endeavors and the foundations to explore the technological potentials of these materials. For black phosphorus (bp), significant attention has been on its highly anisotropic transport, optical, thermal, and mechanical properties [6] as well as the strong dependence of its band structure and correlated behavior on hydrostatic pressure [7], the stacking order [8], and the layer number [9]. The puckered layers and structural anisotropy of bp in ambient conditions show prominent differences than planar graphene, as a result of every P atom having one more valence electron compared to carbon and forming a covalent bond with three neighboring atoms. Electronically, unlike many transition metal dichalcogenides (TMDs), the direct bandgap is maintained for all layer numbers of bp, which is at the  $\Gamma$  point for single to few layers and at the high-symmetry Z valley along the vdW cross-plane direction for the bulk [10]. Such an evolution of the band structure is quite unique, which coincides with the finding of bond-like wavefunction overlaps between bp layers and their important role in an unusually strong interlayer coupling compared to the counterparts in graphene and TMDs [11, 12]. Thus, bp as a layered material shows a profound connection between its structure and various properties in both covalently-bonded in-plane and vdW-separated cross-plane directions.

Dynamically, photoinduced responses of bp have been investigated by various timeresolved measurements, mostly concentrated on the in-plane directions. At low photoinjection densities, exciton-exciton annihilation governed the relaxation of carrier dynamics [13]. Increased photocarriers cause bandgap renormalization as a result of many-body interactions [14, 15] as well as band filling and radiative recombination [16]. Interestingly, a resembling carrier-phonon scattering time was found independent of the photoexcitation and probe polarizations, due to fast randomization of the carriers' distribution in k-space by carrier scattering [17]. Moreover, the coherent phonon modulation observed in optical data has been associated with a breathing mode for few layers of bp and with longitudinal acoustic phonons for thicker specimens [18, 19]. However, direct observations of the photoinduced structural dynamics require techniques such as ultrafast transmission electron microscopy [20] and diffraction [21, 22]. The time-dependent changes of in-plane Bragg diffractions suggest a two-stage relaxation mechanism for fast electronphonon coupling and slower thermalization of phonons; analysis of the in-plane diffuse electron scattering data reveals stronger carrier–phonon coupling along the zigzag direction at early times. Nonetheless, photoinduced structural dynamics and relaxation pathways in the vdW cross-plane direction remain unaddressed, which leaves out the important role of the interlayer coupling in bp in dynamics

In this report, transient reflectivity and ultrafast electron diffraction (UED) in the reflection geometry are used to directly reveal the out-of-plane atomic motions of bulk bp. We show that an above-gap excitation triggers an initial interlayer contraction with a magnitude independent of the optical fluence used, whose lattice change has a strong carrier-coupled origin. More surprisingly, the onset of the diffraction intensity change is delayed by ~3 ps, which has not been observed for Bragg spots of materials with repeated intra-cell lattice changes but no involvement of a phase transition. It is found that such an onset delay can be attributed to the coherent motions of bp layers

that match with the  $A_g$  optical phonons. In the temporal range studied, three temporal regimes may then be identified to describe the carrier–phonon scattering and phonon thermalization processes.

The photoexcitation of bp is achieved by using 2.41-eV photons, where photocarriers are initially injected without particular preferences in the Brillouin zone (Figure 4.1). Carrier scatterings and energy relaxation toward the bandgap in the Z valley lead to the transfer of a significant amount of excess energy to the bp lattice



Figure 4.1 Band structure of bulk black phosphorus. (a) Brillouin zone with high symmetry points. (b) Electronic band structure as adapted from Ref. 22. The green arrow represents the photon energy of 2.41 eV. Blue and red lines denote, respectively, the regions where holes and electrons are initially photogenerated

#### 4.1 <u>Transient reflectivity.</u>

In this section, the optical pump probe for bp is presented. Since bp has an in-plane anisotropy, it would be useful to assert the pump and the and probe polarization effect on the observed dynamics. In the following discussion, a 515 nm photon energy is used as a pump to excite the sample surface, at a near normal incidence angle, and a 1030 nm photon beam is used to probe the surface dynamics by measuring the reflectivity change with a photodiode.



## 4.1.1 Effect of the pump beam

Figure 4.2 Pump polarization change (a) Transient reflectivity measurement at a fixed probe polarization angle and varying the pump polarization. (b) Polar plot of the maximum amplitude change of the reflectivity  $(\Delta R / R_0)_m$  at different pump polarization angle.

First, we assert the effect of the pump beam polarization. The transient reflectivity at a pump polarized in the ZZ and AC direction are presented in Figure 4.2a. After photoexcitation, the reflectivity drops and reaches minimum at 0.6 ps, followed by a fast recovery and a coherent acoustic phonon as it will be shown later. The recovery dynamics are independent of the pump polarization angle, however, the amplitude of the reflectivity change  $(\Delta R / R_0)_m$  is larger in the AC direction compared to that in the ZZ direction. A full range of the pump polarization angle is shown in Figure 4.2b where a periodic modulation of  $(\Delta R / R_0)_m$  is obtained with a period of 180° that reflects the in-plane crystal symmetry in bp. Normally, the absorption coefficient is larger for a light polarized along the AC than that along the ZZ direction, which would explain the larger

 $(\Delta R / R_0)_m$ . To improve the signal to noise ratio, and reduce the acquisition time, the pump polarization is kept along the AC throughout this work.



Figure 4.3 Pump intensity change. (a) Transient reflectivity for an increasing laser fluence at early time delay. (b) A plot showing  $(\Delta R / R_0)_m$  as a function of the pump fluence.

Shown in Figure 4.3a the transient reflectivity at various fluences and since  $(\Delta R / R_0)_m$  is proportional to the laser excitation fluence, we can estimate the photogenerated carrier density  $N_0$  in bp considering a single photon absorption mechanism:

$$N_0 = (1 - R) \frac{\alpha}{E_{\rm ph}} F_{\rm ex}$$

$$4.1$$

where  $E_{\rm ph}$  is the pump photon energy,  $F_{\rm ex}$  is the pump beam fluence, R = 0.44 [23] and  $\alpha = 10^5 \ cm^{-1}$  [24, 25] are the reflectivity and the absorption coefficient, of bp for a pump polarization along the AC direction.

## 4.1.2 Effect of the probe beam polarization



Figure 4.4 Effect of the probe polarization angle. (a) Transient reflectivity for a probe parallel to the ZZ and (b) to the AC direction.

The effect of the probe polarization parallel to the ZZ and to the AC is depicted in Figure 4.4. clear oscillatory signal due to the coherent acoustic phonon propagation is evident in both probe directions; however, the dephasing time is much larger for a probe in the ZZ direction.

Analysis of the coherent acoustic phonon shown in Figure 4.5 and is carried in two steps: first we fit these dynamics to a multiexponential decay function and after subtracting the experimental data from the fitting model, we fit the difference to a decaying sinusoidal function:

$$A_{\rm osc} \cos(2\pi \omega t + \varphi) e^{-t/\tau_{\rm deph}}$$
 4.2

Where  $A_{\rm osc}$ ,  $\omega$  and  $\varphi$  are the amplitude, the frequency, and the phase of the oscillations, respectively, and  $\tau_{\rm deph}$  is the dephasing time.

We found that the oscillation frequency is relatively insensitive to the probe polarization angle and is about 33.47 GHz. According to the strain propagation model, the oscillation frequency is given by:

$$\omega = \frac{2 n v_{\rm s} \cos \theta_{\rm pr}}{\lambda_{\rm pr}} \tag{4.3}$$

where n = 3.8 [23] is the material refractive index at the probe wavelength  $\lambda_{pr} = 1030 nm$ ,  $v_s$  is the longitudinal sound velocity and  $\theta_{pr} = 31^\circ$  is the probe incidence angle. It follows that the estimated sound velocity  $v_s \approx 5300 m/s$ , which matches those obtained earlier [26, 27]. We note that although the refractive index *n* depends on the probe beam polarization angle, however at our probe wavelength  $n_{AC} \approx n_{ZZ}$ .



Figure 4.5 Coherent acoustic phonon. (a) Transient reflectivity with a probe along the ZZ direction. Dotted line represents the experimental data and solid line represents the fitting to the multiexponential decay function convoluted to the instrument response function. Inset depicts the Fast Fourier Transform amplitude with a peak maximum near 33.5 GHz. (b) Oscillation amplitude of the signal difference (dotted line) and the fitting to a decaying sinusoidal function (solid line).

As for the dephasing time and for a probe along the ZZ direction,  $\tau_{deph}^{ZZ} \approx 400 - 450 \, ps$ and for a probe along the AC the dephasing time drops to  $\tau_{deph}^{AC} \approx 45 - 80 \, ps$ . This damping in the acoustic phonon amplitude can be due to either the finite probe penetration depth and in this case the dephasing time is defined as  $\tau_{deph} = \frac{\lambda_{pr}}{4\pi v_s \kappa}$  or to the acoustic phonon decay in the medium. A numerical calculation of the earlier effect with the experimentally obtained longitudinal sound velocity  $v_s$ , we can estimate the imaginary part of the refractive index  $\kappa$  at the probe wavelength; that are  $\kappa_{ZZ} \approx 0.036$  and  $\kappa_{AC} \approx 0.34$ . The fact that these estimates of  $\kappa$  are well within the range of previously reported values [25] suggests that the observed dephasing time is predominantly caused by the probe finite penetration depth [28].



Figure 4.6 Microscopic origin of the coherent acoustic phonon. The linear dependance of the oscillation amplitude with increasing pump fluence indicates the predominance of the deformation potential on the observed dynamics.

Moving now to the microscopic origin of these oscillation which can be due to (i) the deformation potential where the electronic distribution is changed (because of the optical excitation) causing a modification in the interatomic forces between atoms or (ii) to the thermoelasticity of the material caused by the volume change under temperature increase [29]. The linear dependance of the oscillation amplitude on the excitation fluence is shown in Figure 4.6, indicating that the deformation potential is the mechanism behind the strain pulse generation [30] and which implies a relatively long carriers lifetime.

## 4.2 Transient structural change in bp

The time-dependent diffraction changes in bp following excitation are depicted in Figure 4.7. The absence of noticeable intensity change near the shadow edge region indicates the negligible role of interference by surface transient electric field effects, if any. By varying the laser polarization along the in-plane directions (i.e., from the armchair c axis to the zigzag a axis), the magnitude of the diffraction intensity difference changes, whose dependence coincides well with that of photoabsoprtion coefficient (Figure. 4.7D). Thereafter, the polarization is also kept along the armchair direction.



Figure 4.7 Structure and photoinduced diffraction changes of bp. (a) Structure of bp in top (upper) and side (lower) views with the indicated crystal axes. (b) Diffraction image prior to photoexcitation. The profiles obtained along the vertical and horizontal dashed lines are fitted to a

Lorentzian function to extract the intensity and position of the central spot. (c) Diffraction difference image at 50 ps referenced to the negative-time frame. No noticeable time-dependent changes are found in the shadow edge region indicated by the dashed box. (d) Polar plot of the intensity change observed at 50 ps as a function of the polarization varied in the horizontal a–c plane.

#### 4.2.1 Initial interlayer lattice contraction

Instead of the Debye–Waller type of randomized atomic motions typically observed in photoexcited materials without a photoinduced phase transition, we find that bp exhibits unique directional motions along the vdW-stacked cross-plane direction within the duration of a few picoseconds (ps). Shown in Figure. 4.8a is the comparison of the diffraction intensity (*I*) and out-of-plane position (i.e., momentum transfer  $s_{\perp}$ ) changes of the (0 16 0) spot. Two prominent features are worth noting. First, following photoexcitation, an initial positive change  $\Delta s_{\perp}/s_{\perp}$  of  $\sim 8 \times 10^{-4}$  is observed at about 3 ps and precedes the reversed, long-term negative change at later times. Such an observation indicates a lattice contraction  $\Delta b/b$  prior to the dominance of the anticipated thermal expansion after 6 ps, which is reminiscent of the comparable behavior found in layered graphite [31, 32] and TMDs [33]. However, the initial contraction  $\Delta b$  appears to be independent of the photoinjection levels used here, whereas the later interlayer lattice expansion is proportional to the laser fluence (Figure. 4.8b).



Figure 4.8 Photoinduced structural changes of bp. (a) Normalized changes in the intensity and vertical position of the (0 16 0) spot. The solid lines are guides to the eye. The inset shows the early-time dynamics. (b) Corresponding lattice changes in the out-of-plane b axis at two different laser fluences used.

We note that the origin of bp's early-time interlayer contraction has distinct differences from those for graphite and TMDs, with a significant role played by the electronic structure of bp. It is known that bp in equilibrium has strong interlayer coupling due to the lone electron pairs pointing along the cross-plane direction, which results in a prominent wavefunction overlap beyond van der Waals interactions and makes the Z-valley bandgap quite unique among layered materials [9, 11]. Dynamically, after their energy relaxation within one to few ps, the wavefunctions of near-gap photocarriers in the Z-valley have periodic modulations across the vdW-stacked layers. Consequently, the interlayer coupling is expected to be affected due to the presence of these photocarriers. With the out-of-plane elastic constant  $C_{33} = 52.66$  GPa [26, 34] and the ellipsoidal volume of the anisotropic exciton extensions  $V_{ex} \cong 120$  nm<sup>3</sup> [35], we find that the elastic energy induced in the contracted lattice is  $\frac{1}{2}C_{33}(\Delta b/b)^2 V_{ex} \cong 10$  meV, which is comparable to the binding energy of free excitons in bp, about 8 to 9 meV [35, 36]. Such an energy coincidence may be rationalized in the simple framework of a carrier-coupled displaced oscillator, hence implying an important carrier–lattice correlation. Moreover, the bandgap renormalization due to photocarriers' many-body effects can reach tens of meV in the fluence range used [37]. These are in contrast with the limited electronic change predicted in absence of a strong photocarrier–lattice coupling. For example, theoretical results of unexcited bp with an interlayer distance change indicate, proportionally, a decrease of  $\leq 2$  meV in the bandgap for the observed lattice contraction [38]; pure pressure-induced band renormalization via deformation potentials is also insufficient in understanding photoinduced responses of bp (see below).

#### 4.2.2 Early-time coherent intralayer vibration

The second prominent feature of the initial lattice dynamics is a delay of  $\sim$ 3 ps for the onset of the diffraction intensity change, which is entirely unexpected and also significant in the duration, compared with the early-time dynamics of graphite [31]. Certainly, P atoms should acquire additional vertical movements as a result of sub-ps carrier–phonon coupling; a decrease in the diffraction intensity would have been the anticipated observation for bp without a photoinduced phase transition, as a result of the incoherent Debye–Waller randomized atomic motions [21, 31, 39]. Thus, the lack of an intensity change requires the consideration of coherent intra-cell atomic motions at early times. Given the same element in bp, the intensity of the (0*k*0) spot is proportional to the square of the structure factor *F* for a unit cell (omitting the contribution of thermal motions as a Debye–Waller factor at finite temperatures),

$$F = \sum_{j=1}^{8} f_j \ e^{-2\pi i k (z_j + \delta_j)} = f_P \sum_{j=1}^{8} e^{-2\pi i k (z_j + \delta_j)}$$

$$4.4$$

where  $f_{\rm P}$  is the atomic scattering factor of phosphorus and  $z_j$  and  $\delta_j$  are the out-of-plane fractional position and induced displacement of atom *j* in a cell, respectively (Figure. 4.9a).



Figure 4.9 Coherent out-of-plane atomic movements of bp and expected diffraction intensity changes. (a) Schematics of three intra-cell modes (with only the out-of-plane components indicated), which correspond to symmetric  $A_g$ , asymmetric  $A_g$ , and  $B_{1u}$  (respectively from left to right) as examples. The orange arrows indicate the relative signs of the displacements in the *b* (i.e., *z*) axis. (b) Intensity changes of the (0*k*0) diffraction spots as a function of the displacement amplitude corresponding to the symmetric  $A_g$  motions (a, left). Different colors are used for even orders of *k* from 8 to 20. (c) Intensity changes of the (0*k*0) spots for all the other intra-cell modes.

Before photoexcitation with  $\delta_i = 0$ , the structure factor is  $F_{eq} = f_P \cdot 8 \cos(2\pi kz)$  based on

the puckered-layered structure of bp where  $z_1 = z_2 = +z$ ,  $z_3 = z_4 = -z$ ,  $z_5 = z_6 = 1/2 + z$ , and

 $z_7 = z_8 = 1/2 - z$  with z = 0.10168. After photoexcitation, concerted atomic motions following a symmetric A<sub>g</sub> phonon mode will lead to a modified structure factor  $F = f_P \cdot 8 \cos[2\pi k(z + \delta)]$ . For all other motions including the B<sup>2</sup><sub>3g</sub>, B<sub>1u</sub>, asymmetric (across adjacent layers) A<sub>g</sub>, and breathing modes, the modified structure factor is

$$F = f_P \cdot 8\cos(2\pi kz)\cos(2\pi k\delta)$$

$$4.5$$

Shown in Figure. 4.9b and c are the resulting diffraction intensity changes with a small  $\delta$ , where only a symmetric Ag phonon mode gives essentially no intensity change (due to the quasilinear relation between  $\Delta |F|^2 / |F_{eq}|^2$  and  $\delta$ , averaged over an oscillation period of sub-100 fs faster than our temporal resolution) and the rest should result in an intensity decrease (more pronounced for higher diffraction orders). Thus, our observation is consistent with photocarriers' early-time preferential coupling to symmetric Ag phonon modes. Together with the aforementioned compressive strain, the out-of-plane directional, concerted atomic motions add further evidence for the significant coupling of the Z-valley photocarriers to the out-of-plane lattice structure. We further note that the present results are also consistent with the in-plane observations for highly anisotropic transient phonon populations in the first few ps [22]. In such a nonthermalized state, the structure factor analysis for (h00) and (00l) spots show that all intracell normal modes yield an intensity dependence the same as shown in Figure. 4.9c except for only the symmetric  $A_g^2$  mode along the armchair direction for (00l) (Figure 4.15, Appendix). Consequently, the initial population of various in-plane phonons, especially along the zigzag direction, results in an early-time diffraction intensity decrease without a clear onset delay, and hence the conventional Debye–Waller model was still used although phonon thermalization is not reached [21].

## 4.2.3 Three regimes of phonon thermalization

Following the onset delay, the intensity of the (0 16 0) spot decreases to a minimum level corresponding to the fluence used within 50 ps (Figure. 4.10). A biexponential function is more adequate to describe the dynamics compared to the fit of a single exponential function that yields more residual errors (Figure. 4.10b); a fast time constant of 0.9 to 1.0 ps and a slower one of 16±5 ps are obtained, independent of the photoinjected carrier density (the range and the standard deviation are assessed using the early-time data from three samples with eleven different laser fluences in total).



Figure 4.10 Early-time diffraction intensity change. (a) Comparison of the fits with single- (red) and bi-exponential (green) functions. (b) Residuals from the two fit models. Larger systematic deviations are seen from the single-exponential fit.

These characteristic times closely resemble those reported for the in-plane structural dynamics [21, 22]. Hence, the following picture with three major temporal ranges is reached. In the carriercoupled regime for the first 3 ps, the relaxation of energetic photocarriers preferentially produces anisotropic excitation of phonons with momenta along the zigzag direction and the symmetric  $A_g$ modes across the vdW-stacked layers. Concurrently, the resulting excitons and free carriers in the Z valley modulate the cross-plane electronic structure and induce an interlayer contraction as a result of strong photocarrier–lattice coupling. In the second regime up to 50 ps, thermalization of the nonequilibrium phonons becomes a dominant theme of the dynamics, with a transition time of 4–10 ps for still separated intensity and lattice expansion curves and an equilibration period after 10 ps for largely matched dynamics (Figure. 4.8a).



Figure 4.11 Diffraction spot position change. Change of the diffraction spot position along the out-of-plane direction at  $\sim$ 50 ps as function of the laser fluence used and the estimated temperature jump. Results from the same sample are denoted in one color. The solid line is an overall linear fit.

In the final regime after 50 ps, the lattice reached a quasi-equilibrium of thermalized phonons where an effective increase in the lattice temperature  $\Delta T$  can be determined and the Debye–Waller model becomes suitable for the randomized atomic motions. We note that although the photocarriers have a lifetime covering all three regimes, the approximate energy they retain across the bandgap of 0.3 eV is a minor fraction compared to the much larger excess part (2.41 eV minus 0.3 eV per electron–hole pair) transferred earlier to the bp structure. Using the data at 50 ps obtained from 13 bp samples and a linear fit of  $\Delta b/b = -\Delta s_{\perp}/s_{\perp}$  at different fluences, we obtain an out-of-plane lattice expansion coefficient of ~ (5.0±0.4) ×10<sup>-5</sup> K<sup>-1</sup> (Figure. 4.11), which agrees reasonably with the literature value without the influence of photoinjected carriers [40].

Another way to assert the thermal effect is by the amplitude of the relative changes in the diffraction intensity at different fluences near 50 ps based on the Debye–Waller model for several orders of the (0k0) diffraction spot and at various pump fluence above bp's Debye temperature  $\theta_D$ . Based on this model, the diffraction spot intensity is a function of the atomic mean square displacement in the out-of-plane direction  $\Delta \langle u_{\perp}^2(t) \rangle$ :

$$\ln\left(\frac{I(t)}{I_0}\right) = -4\pi \,\mathrm{s}_{\perp}^2 \,\Delta\langle \mathrm{u}_{\perp}^2(t)\rangle \qquad 4.6$$

where I(t) and  $I_0$  are the diffraction intensities of (0k0) at time t and prior to photoexcitation, respectively,  $s_{\perp} = kb^* = k/b$  the vertical momentum transfer derived from the position of the (0k0) spot, and  $\Delta \langle u_{\perp}^2(t) \rangle$  the time-dependent increase in the out-of-plane mean-square displacement. Based on the Debye–Waller model, the experimentally obtained mean-square displacement can be approximated by:

$$4\pi \Delta \langle u_{\perp}^{2}(t) \rangle \approx \frac{3h^{2}\Delta T}{m k_{B} \theta_{D}^{2}}$$
 4.7

if the temperature is close to or larger than the Debye temperature  $\theta_D$ , where *h* is the Planck constant, *m* the mass of a phosphorus atom,  $k_B$  the Boltzmann constant, and  $\Delta T$  the lattice temperature increase. Thus, a linear relation between the changes of the diffraction intensity and the temperature for a given  $s_{\perp}$  is found as follows:

$$\ln\left(\frac{I(t)}{I_0}\right) \approx -\frac{3h^2}{m k_{\rm B} \theta_{\rm D}^2} {\rm s}_{\perp}^2 \cdot \Delta T$$
4.8



Figure 4.12 Linear dependence of out-of-plane diffraction intensity change on photoinduced temperature increase. The diffraction order is denoted in each panel. The solid line is a linear fit to the experimental data, whose slope is equal to  $-3h^2s_{\perp}^2/mk_B\theta_D^2$  according to the Debye–Waller model.

As the carrier lifetime is relatively large in bp, we consider that only the pump photon excess energy  $E_{\text{excess}} = E_{\text{ph}} - E_{\text{g}} \approx 2.1$  eV contributes to the lattice heating and the estimated temperature change is:

$$\Delta T(F_{\rm ex}) = (1 - R) \frac{\alpha}{C} \frac{E_{\rm excess}}{E_{\rm ph}} F_{\rm ex}$$

$$4.9$$

where C=1.87 J.k<sup>-1</sup>.cm<sup>-3</sup> [41] is the specific heat capacity of bulk bp.

The Debye-Waller analysis is carried in two steps: first, we calculate the slope of the linear function  $\ln\left(\frac{I(t)}{l_0}\right)$  at 50 ps (where the temperature is expected to reach maximum) vs. the estimated temperature change for each of the (0 k 0) diffraction spot (k= 8,10,12,14,16,18,20) as shown in Figure 4.12, where the slope at each diffraction order is given by  $-\frac{3h^2s_1^2}{m k_B \theta_D^2}$  and in the second step, we make a second plot of  $-\frac{3h^2s_1^2}{m k_B \theta_D^2}$  as a function of the square of the vertical momentum transfer vector corresponding to the (0k0) spot as indicated in Figure 4.13 and the fit gives an estimate of the Debye temperature in the out-of-plane plane direction  $\theta_D^b \cong 250\pm13$  K



Figure 4.13 Debye–Waller analysis of the diffraction intensity changes. Each data point corresponds to the slope extracted from the fluence-dependent data for the corresponding diffraction order.

In addition to the exciton-coupled elastic energy estimated earlier, a compressive lattice strain of  $8 \times 10^{-4}$  near the bp surface is equivalent to an applied pressure of  $C_{33}(\Delta b/b) \cong 40$  MPa along the surface normal direction. For the comparable observations of TMDs, Mannebach et al. considered an analytical model to explain the dynamic modulation of the interlayer van der Waals interaction [33]. According to the Lifshitz model with a Drude-like electron gas in two charged slabs, an interlayer contraction of  $8 \times 10^{-4}$  generates an effective pressure of ~50 MPa at a nearsurface carrier density of  $2 \times 10^{20}$  cm<sup>-3</sup> in bp; a superlattice model considering the correlations between quantum fluctuations of optically excited electrons and holes yields a low value of around 7 MPa at the same carrier density [33]. All these values are 1.5 orders of magnitude lower than the pressure required for the semiconductor-to-semimetal electronic transition [42], which validates that the observed photoinduced dynamics are perturbative in nature and far from the scenario with large-scale band structure changes. However, we note that the estimates based on the Lifshitz and superlattice models represent the upper bound. While the agreement of the photoinduced pressure suggests the usefulness of the picture given by these models, we caution that the high carrier density may see a significant reduction at 3 ps due to various decay channels (defect-related trapping, bimolecular and/or Auger recombination, exciton-exciton annihilation) as the photocarriers relax toward the narrow Z valley and therefore are not maintained at the initial injection level [37, 43]. With a reduced carrier density (whose value may be highly dependent on the sample quality), the estimated pressure based on a Lifshitz-like model may be much lower and not fully consistent with the experimentally observed compressive strain. Taking the interlayer contraction and intralayer coherent atomic motions together, we consider the important role of bp's band alignment for cross-plane photocarrier-lattice coupling that does not exist in typical **TMDs** 

## 4.3 Heat dissipation at longer times

Due to the large laser footprint compared to the electron-probed region, lateral heat dissipation is hindered and can be neglected. Thus, cross-plane thermal diffusion can be described by an effective one-dimensional model with the volume generation of heat considering the large penetration depth of photoexcitation into the material [44]

$$\Delta T(z,t) = \frac{I_{\rm m}(1-R)\alpha k}{2K} \int_{-\infty}^{t} dt' \exp\left[-\left(\frac{t'}{\tau}\right)^{2}\right] \\ \times \left[\exp\left[-\alpha z + k \,\alpha^{2}(t-t')\right] \operatorname{erfc}\left(\frac{-z+2 \,k \,\alpha \,(t-t')}{2[k \,(t-t')]^{1/2}}\right) + \exp\left[\alpha \,z + k \,\alpha^{2}(t-t')\right] \operatorname{erfc}\left(\frac{z+2 \,k \,\alpha \,(t-t')}{2[k \,(t-t')]^{1/2}}\right)\right]$$

$$4.10$$



Figure 4.14 Heat dissipation at long times. The solid line is a fit using the one-dimensional thermal diffusion model.

where  $I_m$  is the maximum laser irradiance, R,  $\alpha$  and C are as defined earlier,  $k = \frac{K}{\rho c}$  is the thermal diffusivity and K is the thermal conductivity in the out-of-plane direction which is the fitting parameter. A low through plane thermal conductivity is obtained  $K \approx 2 W \text{ m}^{-1} \text{ K}^{-1}$ . Similar values for the out-of-plane thermal conductivity have been reported elsewhere [45]

## 4.4 Conclusion

The current results elucidate early-time photocarrier-driven interlayer lattice contraction and out-of-plane vibrational motions within each puckered layer in a concerted, symmetric fashion, as well as the three major temporal regimes from directional to thermalized atomic motions for the photoinduced dynamics of bp. Its electronic structure with the bandgap at the Z valley aligning with the out-of-plane axis plays a critical role in the strong photocarrier–lattice coupling, which illustrates the significance of probing structural dynamics in the vdW-stacked direction. It will be essential to further examine bp with a reduced thickness to even a monolayer to reveal the impact of the electronic band structure change. As vdW-stacked heterostructures open up new opportunities with engineered phenomena and control, attention for the interlayer dynamic behavior is eminently needed especially when an alignment between the electronic structure and the lattice exists.

#### 4.5 <u>Materials and methods</u>

Crystalline bp samples were obtained from two sources, one from the University of Science and Technology of China (USTC) and the other from HQ graphene commercially. With mechanical exfoliation, the USTC crystals exhibit larger domains whereas the commercial samples produce flakes more of a needle-like shape. However, no major differences were found in their photoinduced dynamics. For each sample, a fresh surface was prepared by exfoliation of the bulk in air and quickly loaded into the ultrahigh vacuum (UHV) assembly with a base pressure of  $2 \times 10^{-10}$ Torr in the main chamber to minimize surface deterioration over time.

Details about the reflection UED apparatus has been described previously [39, 46]. In short, the 515 nm (2.41 eV) photoexcitation pulses were produced by second harmonic generation (SHG) of the fundamental output (1030 nm, 170 fs) of a Yb:KGW regenerative amplifier laser system. Another stage of SHG using a fraction of the 515-nm beam produced the ultraviolet (257 nm) pulses, which were then guided toward and focused on a LaB<sub>6</sub> emitter tip to generate photoelectron pulses accelerated to 30 keV. With the bp specimens mounted on a high precision manipulator with five axes of motion, suitable sample regions for stable stroboscopic measurements were found by fine translational adjustments; different orders of out-of-plane (0*k*0) diffractions were obtained by changing the incidence angle relative to the fixed electron beam. In the present study, the UED measurements were conducted at a repetition rate of 10 kHz. Additionally, a pulse-front tilt setup has been implemented to overcome the temporal mismatch between the arrivals of the nearvertically descending excitation and grazing electron beams [47, 48], which led to the improved instrumental response time of ~500 fs. Moreover, the matching of the laser and photoelectron arrival times has the benefit of a well-defined zero of time which is crucial to confident identification of any onset delays in the dynamics. The laser fluences were estimated using the full width at half maximum of the laser footprint of  $200 \times 1500 \ \mu\text{m}^2$  on the specimen, which is sufficiently larger to cover the tightly focused electron footprint of  $15 \times 230 \ \mu\text{m}^2$  for a uniform photoexcited region. The resulting diffraction images at different delay times were formed on a phosphorus screen and captured by an intensified CMOS camera.

Transient reflectivity measurement was carried in an inert atmosphere inside a chamber purged with nitrogen gas. The 2.41 eV photon excitation pulse and with a repetition rate of 1 kHz lands at a near normal incidence angle on the sample surface with a footprint at FWHM of (880 × 1000)  $\mu$ m. The change in the reflectivity was monitored with photodiode coupled to a lock-in amplifier using a 1.2 eV photon laser beam at a repetition rate of 2 kHz and making an angle of 30° with the surface normal and with a probing area of (240 × 290)  $\mu$ m at FWHM.

#### 4.6 Appendix

4.6.1 Changes of the (00*l*) and (*h*00) diffraction intensities due to in-plane atomic motions Similar to the model described in the main text, the structure factor F for the (00*l*) spot is

$$F = \sum_{j=1}^{8} f_j \ e^{-2\pi i l(x_j + \delta_j)} = f_P \sum_{j=1}^{8} e^{-2\pi i l(x_j + \delta_j)}$$

$$4.11$$

where  $x_j$  and  $\delta_j$  are the fractional position and induced displacement of atom *j* in a cell along the armchair direction, respectively. In thermal equilibrium prior to photoexcitation,  $F_{eq} = f_P \cdot 8 \cos(2\pi lx)$  with  $x_1 = x_5 = +x$ ,  $x_2 = x_6 = 1/2 - x$ ,  $x_3 = x_7 = 1/2 + x$ , and  $x_4 = x_8 = -x$  where x = 0.08060. After photoexcitation, concerted atomic motions following the symmetric  $A_g^2$  phonon mode will lead to a modified structure factor  $F = f_P \cdot 8 \cos[2\pi l(x - \delta)]$  and the resulting change in the diffraction intensity is illustrated in Figure 4.15a. For all the in-plane motions including the  $B_{3g}^2$ ,  $B_{3g}^1$ ,  $B_{2u}$ , and asymmetric (across adjacent layers)  $A_g^2$  [49-51], the modified structure factor is  $F = f_P \cdot 8 \cos(2\pi lx) \cos(2\pi l\delta)$  and the corresponding change in the diffraction intensity is illustrated in Figure 4.15c. Thus, according to Ref. 22, the population of various in-plane phonons at early times should lead to a decrease in the (00*l*) diffraction intensities, whose result may be similar to that considering randomized in-plane atomic motions.



Figure 4.15 Diffraction intensity changes due to in-plane motions. (a) Schematics of three intracell modes (with only the in-plane components indicated), which correspond to symmetric  $A_g^2$ , asymmetric A<sub>g</sub>, in the AC direction and B<sub>1g</sub> in the ZZ direction (respectively from left to right) as examples. (b) Changes of the (00*l*) spot intensity as a function of the in-plane displacement amplitude for the symmetric  $A_g^2$  mode. (c) Changes of the (00*l*) and (*h*00) spot intensity for all the other in-plane phonon modes. The different colors denote the different even orders from 2 to 8.

As for the (h00) spot, the structure factor F is,

$$F = \sum_{j=1}^{8} f_j \ e^{-2\pi i h(y_j + \delta_j)} = f_P \sum_{j=1}^{8} e^{-2\pi i h(y_j + \delta_j)}$$

$$4.12$$

where  $y_j$  and  $\delta_j$  are the fractional position and induced displacement of atom *j* in a cell along the zigzag direction, respectively. Before photoexcitation,  $y_1 = y_2 = +y$ ,  $y_3 = y_4 = 1/2 + y$ ,  $y_5 =$
$y_6 = y$ , and  $y_7 = y_8 = \frac{1}{2} + y$  with y = 0, which leads to the structure factor at equilibrium as  $F_{eq} = 8 \cdot f_P$ . Following photoexcitation, the modified structure factor for all phonon modes (B<sub>1g</sub>, B<sub>2g</sub> and A<sub>u</sub>) is  $F = f_P \cdot 8 \cos(2\pi l\delta)$  and the corresponding change in the diffraction intensity is as shown in Figure 4.15c. Hence, a decrease in the (*h*00) diffraction intensity is expected regardless of the phonon modes involved.

## 4.7 **Bibliography.**

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