Title
Study of the Transition Metal Dichalcogenide and its Direct Organic Intercalation Chemistry

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Author
Halim, Udayabagya

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A Study of the Transition Metal Dichalcogenide and its Direct Organic Intercalation Chemistry

A dissertation submitted in partial satisfaction
of the requirement for the degree of
Doctor of Philosophy in Chemistry

by

Udayabagya Halim

2017
The development of graphene and the nanotechnology revolution brought new interest in Layered transition metal dichalcogenides (TMDs). First explored in the 1960s, these TMDs are a subject of interest due to their wide range of material properties form semiconductor, metals, to superconductor. Through intercalation chemistry, there is additional flexibility to tune the materials’ parameters to the desired property. Naturally semiconducting, Group 6 TMDs (i.e. MoS$_2$) have the most potential for future electronic application. Yet these Group 6 TMDs are also the most chemically inert. While over 240 organic-TMD complexes have been made
reported for Group 4 (i.e. TiS$_2$) and Group 5 (i.e. TaS$_2$) TMDs, for 50 years, organic complexes of Group 6 TMDs remained unexplored.

With the goal of tailoring the properties of Group 6 TMDs, we followed three different experimental approaches. We begin by pursuing liquid phase exfoliation to produce few/mono layer products and use contact angle measurement to infer the thermodynamic of the exfoliated materials in mixed solvents. We expanded a pen-paper vibrational model of 2H-MoS$_2$ to analyze the vibrational spectra of WS$_{2-x}$Se$_x$ alloy with a tunable optical gap. Inspired by Lithium based intercalation methods, we propose a new and direct electrochemical intercalation route to produce Organic-MoS$_2$ complexes using quaternary ammonium compounds. We use the same electrochemical concept and show that the theory is sufficiently robust, allowing intercalation onto Layered Black Phosphorus (BP).
The dissertation of Udayabagya Halim is approved.

Paul S. Weiss

Seth J. Putterman

Xiangfeng Duan, Committee Chair

University of California, Los Angeles

2017
To my parents,

Who taught me to read,

Encouraged me to think

And believed I’d succeed
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Chapter 4 is a version of: Xidong Duan, Chen Wang, Zheng Fan, Guolin Hao, Liangzhi Kou, Udayabagya Halim, Honglai Li, Xueping Wu, Yicheng Wang, Jianhui Jiang, Anlian Pan, Yu Huang, Ruqin Yu, and Xiangfeng Duan. “Synthesis of WS2xSe2–2x alloy nanosheets with composition-tunable electronic properties”. Nano Lett. 16, 264 (2016) The work is predominantly done by Xiong Duan and Chen Wang. They both synthesis, characterized, and wrote the manuscript under the help of Dr. Xiangfeng Duan and Dr Yu Huang. I helped developed the vibrational model and analyze the emergence of an alloy peak around 385 cm\(^{-1}\). Chapter 4 is predominantly the development of the model.
Chapter 6 is a version of Chen Wang, Udayabagya Halim, Enbo Zhu, Qiyuan He, Ziying Feng, Yuanyue Liu, Rui Cheng, Nathan O. Weiss, Guojun Ye, Yun-Chiao Huang, Hao Wu, Hung-Chieh Cheng, Xianhui Chen, William A. Goddard III, Yu Huang, Xiangfeng Duan. “Monolayer phosphorene molecular superlattice’. Chen Wang was instrumental in the development and measurement of the in situ electro-chemical-optical measurement platform. He is involved in the final experimental data displayed in the manuscript, including the Raman, photoluminescence, TEM, and electrical measurements. Without him, this work would not have happened. Yuanyue Liu from the Goddard Group in California Technical Institute of Technology is responsible for the final simulation data, including crystal and band structure calculation. I was involved in the theoretical and development of the understanding of the chemical synthesis. In addition, Chen and I analyze the first round of structural analysis and Raman shift analysis. Chen Wang, Yuanyue Liu and I contributed in the writing of the manuscript. Dr. Xiangfeng Duan, Dr. William A. Goddard III, and Dr. Yu Huang contributed to the manuscript editing. Manuscript is currently under review in Nature Nanotechnology.
BIOGRAPHICAL SCETCH

Teaching Experience

Upcoming Fall 2017

*California State University – Channel Island / Adjunct*

CHEM 250  Quantitative Analysis  
Analytical chemistry theory, techniques, and statistical relevance of measurements.  
F 2017  

*University of California – Los Angeles – Extension School / Instructor*

CHEM XL14A  Atomic and Molecular Structure, Equilibria, Acids, and Bases  
Intro. to Chemistry for Life Science Major #1  
F 2017  

Mar – June 2017  
*University of California – Los Angeles – Extension School / Instructor*

CHEM XL14A  Atomic and Molecular Structure, Equilibria, Acids, and Bases  
Intro. to Chemistry for Life Science Major #1  
S 2017  

2011 – Present  
*University of California – Los Angeles / Teaching Assistant*

List of Courses:

- CHEM 14A  Atomic and Molecular Structure, Equilibria, Acids, and Bases  
  Intro. to Chemistry for Life Science Major #1  
  F 2016  

- CHEM 14B  Thermodynamic, Electrochemistry, Kinetics, and Organic Chemistry  
  Intro. to Chemistry for Life Science Major #2  
  W 2015  

- CHEM 14BL  General and Organic Chemistry Laboratory I  
  Laboratory Intro. to Chemistry for Life Science Major #1  

- CHEM 14CL  General and Organic Chemistry Laboratory II  
  Laboratory Intro. to Chemistry for Life Science Major #2  
  Su. A 2012  

- CHEM 20A  Chemical Structure  
  Intro. to Chemistry for Physical Science Major #1  
  F 2012, W 2013, F 2014  

- CHEM 20B  Chemical Energetics and Change  
  Intro. to Chemistry for Physical Science Major #1  
  W 2016  

- CHEM 110A  Physical Chemistry: Chemical Thermodynamics  
  Upper Division Thermodynamics  

- CHEM 114  Physical Chemistry Laboratory  
  Upper Division Physical Chemistry Laboratory  
  Sp 2012, Sp 2013  

Jan – Mar 2016  
*University of California – Los Angeles*

PEERS Facilitator:  
Facilitate CHEM 20A, General Chemistry for STEM majors.
Education
Ph.D Candidate, Physical Chemistry, Advisor: Xiangfeng Duan

2015  University of California – Los Angeles  M.S. in Physical Chemistry

2009 – 2011  University of California – Los Angeles  B.S. in Physical Chemistry

Research Experience
2011 – Present  Graduate Research
Dr. Xiangfeng Duan; Dept. of Chem. & Biochem., UCLA
- Pen-and-paper theoretical calculation of vibrational modes to understand the vibrational spectroscopy of Transition Metal Dichalcogenides.
- Uses of electrochemistry to explore the reactivity and intercalation of Layered Materials in solution
- Wetting properties of 2-D materials and its relation to the thermodynamic dispersibility of its nano-sheets in mixed-solvent environment.

2010 – 2011  Undergraduate Research
Dr. Sarah Tolbert; Dept. of Chem. & Biochem., UCLA
- Investigate the effect of temperature and vapor of organic compounds to control the Self-assembly of Block Co-polymer morphology.

Award & Internship
2013  Excellence in Second Year Academics and Research Award
May – Sep 2009  Internship – Lawrence Berkeley national Laboratory
Dr. John B. Kerr/ Dr. John Chmiola
Ionic Liquid applications as supercapacitor electrolyte

Publication & Presentation
“Monolayer phosphorene molecular superlattice”, Science, Submitted


2013  Presentation  Probing liquid-solid interacting for Co-Solvent Exfoliation of Layered Materials Nanoscience Future Conference, University of Bristol
CHAPTER 1. Introductions

The development of graphene and the nanotechnology revolution brought new interest in Layered transition metal dichalcogenides (TMDs). In the 1960s-1980s, TMDs were a subject of interest due to their wide range of material properties from semiconductor, metals, to superconductor. In earlier studies, these materials were predominantly studied in bulk and powder form. With the realization that monolayer of an atomic crystal can be stable at the standard condition, an interest in mapping the properties of few- / monolayer TMDs and its applications began.

The interest in layered materials such as TMDs and other layered materials remains at large today because of the ability insert various organic/inorganic molecules in between these layered compounds through intercalation chemistry. Through the insertion of these foreign molecules, various additional properties can be added and various parameters can be tailored to some specific needs. Insertion of metallocene into TaS$_2$, for example, can induce both superconductivity and magnetism.

Naturally semiconducting, Group 6 TMDs (i.e. MoS$_2$) have the most potential for future electronic application. Yet it was found that these Group 6 TMDs are also chemically inert. Only alkali metals, strontium, and calcium can form direct intercalation with these Group 6 TMDs. While over 240 organic-TMD complexes have been made reported for Group 4 (i.e. TiS$_2$) and Group 5 (i.e. TaS$_2$) TMDs, for 50 years, organic complexes of Group 6 TMDs remained unexplored.
We decided to focus our effort in this Group 6 TMDs precisely because its chemistry is unexplored. The discovery of direct insertion chemistry of organic molecules onto these Group 6 TMDs can further expand the application of these semiconducting materials.

With the goal of tailoring the properties of Group 6 TMDs, we followed three different experimental approaches. We begin by pursuing liquid phase exfoliation to produce few/mono layer products and use contact angle measurement to infer the thermodynamic of the exfoliated materials in mixed solvents (Chapter 3). We expanded a pen-paper vibrational model of 2H-MoS$_2$ to analyze the vibrational spectra of WS$_{2-x}$Se$_x$ alloy with a tunable optical gap (Chapter 4). Inspired by Lithium based intercalation methods, we propose a new and direct electrochemical intercalation route to produce Organic-MoS$_2$ complexes using quaternary ammonium compounds. We use the same electrochemical concept and show that the theory is sufficiently robust, allowing intercalation onto Layered Black Phosphorus (BP) (Chapter 6).

In the first part of this dissertation (Chapter 2), the structural aspect and reactivity of group 4, 5, and 6 TMDs are reviewed. Two of the most common crystallographic structure of TMDs (trigonal prism and octahedral) are discussed. We will explore on how coulomb interaction appears to be one of the best determining factors that affect the preferential crystallographic state. Intercalation mechanism of these TMDs is further discussed, particularly involving alkali metals and organic compounds. It was found that intercalated TMDs forms an intermediate structure as a function of alkali metal loading. The discussion will focus on electrochemical detection method to determine the existence of these intermediate states. With the understanding of Alkali-metal intercalation, we will build a Charge Transfer model and apply the same fundamental to understand the nature of Organic-TMD intercalation.
The following portion of this dissertation, (Chapter 3) will discuss the Liquid Phase Exfoliation of graphite, MoS$_2$, and other layered materials. It was found that through simple sonication of powdered layered material in a solvent, a large amount of exfoliated compound can be formed. In its fundamental, we argue that thermodynamic interaction between the solvent molecules and the layered materials should affect the stability of the dispersion of these layered compounds. Layered materials are particularly interesting as the surface area of the basal plane is much larger compared to that of its sides. Simple contact angle measurement can then be used to measure the relative interfacial energy difference when a material is in contact with different solvents. We found that, in addition to interfacial energy, solvent molecular size has an additional kinetic effect in the stability of the dispersion—not unlike the behavior of a surfactant.

We applied and developed a monolayer model (1L-Model) for a trigonal prismatic crystal (Chapter 4) to understand the vibration modes of MoS$_2$ and WS$_2$. Following the work by Bromley, using a simplifying assumption of harmonic oscillator as well as only nearest-neighbor interaction, the 1L-Model calculate the vibrational spectroscopy of MoS$_2$ both intuitively and accurately. It is intuitive because the vibrations can be expressed in a simple mathematical expression involving spring constants. It is accurate with an error of 4%, comparable with other more complicated models. We expand this model and apply on a WS$_{2-x}$Se alloy that exhibits a large optical band gap tunability. We found that this alloy exhibit a new vibration at ~385 cm$^{-1}$ that can be not observed in the pure WS$_2$ and WSe$_2$ compound. We found that it can be explained by the changing mass of S/Se.

Drawing conclusion from a Lithium intercalation, we proposed a new organic intercalation chemistry (Chapter 5) on MoS$_2$ (Group 6 TMD). It came from a simple postulate: Lithium intercalates into MoS$_2$, and thus other cations that are as electrochemically stable should also
intercalate into MoS2. This leads us to a series of quaternary alkyl ammonium compound which degrades at approximately -3 V vs. SHE. These quaternary alkyl ammonium compounds are as stable as alkali metals (redox potential of -2.7 to -3.1 vs. SHE). We further explored the structure and stability of these intercalated compounds as a function of alkane carbon chain length.

Last, introduce similar organic intercalation method onto Layered Black Phosphorus (BP). This exploration started because MoS2 undergoes a metallic transition upon intercalation due to a 2H-to a 1T- structural transformation. Unlike MoS2, BP does not undergo crystallographic changes upon intercalation. Crystallographic, vibrational, luminescence and electrical properties of the new structure is explored further in the chapter.
CHAPTER 2. Crystal Structure and the Charge Transfer Model of Intercalation

Structural Aspect of TMDs

The building blocks of transition metal dichalcogenides (TMDs) are sandwich-like structures consisting of a layer of transition metal atoms (T) between two layers of chalcogen atoms (X). These sandwiches are only loosely bound to each other, as is demonstrated by the fact that the crystals can be easily cleaved\textsuperscript{1,2,3}. The weakness of the forces keeping the TX\textsubscript{2} units together is also the reason the ease with which a large variety of electron donors can be inserted in between the structure.

![Atomic arrangement in TMDs. Trigonal prismatic and Octahedral are two of the most common crystal structure found for TMDs. Group IV and V are found in Octahedral structure, while Group VI are found as Trigonal Prism.](image)

**Figure 2.1** Atomic arrangement in TMDs. Trigonal prismatic and Octahedral are two of the most common crystal structure found for TMDs. Group IV and V are found in Octahedral structure, while Group VI are found as Trigonal Prism.
Majority of these TMDs have a trigonal prism or an octahedral symmetry around its metal center (Fig 2.1). Different TMDs generally prefer one configuration over another. Generally, Group IV TMDs, such as TiS$_2$, are found as octahedral. Group V TMDs, such as TaS$_2$, are found in both trigonal prism as well as octahedral. Lastly Group VI TMDs, such as MoS$_2$ and WS$_2$, are found predominantly in a trigonal prismatic structure.

It is best to first simplify the understanding of the TMD structure as a simple transition metal with a charge +4 ($T^{+4}$) and chalcogenide with a charge of -2 ($X^{-2}$). For example, the atomic distances of MoS$_2$ can be understood by thinking of the structure as Mo$^{+4}$ and S$^{-2}$. Consider that the radius of pure S$^{-2}$ anion is known to be 1.84 Å and an Mo$^{+4}$ have a hard sphere radius of 0.79 Å. XRD study of MoS$_2$ shown that the intralayer S-S bond to be 3.16 Å, and the Mo-S bond to be 2.42 Å. This is comparable with radius of S$^{-2}$ ion ($\frac{1}{2} \times 3.16 \, Å = 1.58 \, Å$) and radius of Mo$^{+4}$+S$^{-2}$ ($0.79 \, Å + 1.84 \, Å = 2.63 \, Å$). It is immediately clear the sulfur radius is less than a pure -2 charge. This difference is expected, as the electronegativity difference of Mo and S is small – hence their bond are not purely ionic.

The determining factor that effect the preferential structure of a trigonal prismatic symmetry v.s. octahedral symmetry is still a matter of debate. Two competing factors seems to contribute to the difference in energy between these two structure: atomic size, and degree of ionic character.

It is always the case in crystallography that ionic charges as well as hard sphere radius must be balanced to produce the most stable crystal structure. Gamble et all have proposed an intuitive method to compare the iconicity of the material with its geometrical constraint. By dividing the in-plane chalcogenide bond (parameter “$a_1$”) with twice of its pure ionic charge ($2R_{X^{-2}}$), one can
estimate the iconicity of the bond \((a_H/2R_X)\). This division allows a normalization between the different radii of S,Se and into a unitless parameter. Unlike Gamble et al. in which he determines the transition metal radius by subtraction, here we will simply divide twice the metal chalcogenide bond distance \((2d_{TX})\) with \(a_H\) to create a new parameter \((2d_{TX}/a_H)\). While the physical meaning remains the same this simplification allows the crystallographic information to remain intact.

\[
\frac{a_H}{2R_X} \approx \frac{R_X^{-\delta}}{R_X^{2\delta}}
\]

\[
\frac{2d_{TX}}{a_H} \approx \left( \frac{2R_T^+ + 2R_X^{-\delta}}{2R_X^{-\delta}} \right) = \left( \frac{R_T^+}{R_X^{-\delta}} \right) + 1
\]

The logic behind the two variable \((a_H/2R_X)\) and \((2d_{TX}/a_H)\) is to compare the iconicity of the T-X bond as well as the radius ratio through crystallographic data. Structurally, the crystallographic parameter \(a_H\) represents the intralayer distance between two chalcogenide (X-X bond distance).

If the chalcogenides are purely ionic, the parameter \(a_H/2R_X\) should be equal to 1 (Equation 2.1). The less ionic the nature of the chalcogenide, the less the value of \(a_H/2R_X\) becomes. Secondly, the parameter \(2d_{TX}/a_H\) provides an information of the radius-ratio-plus-one (Equation 2.2). For example, the optimal radius ratio of octahedral is 0.414. If a TMD have an optimum octahedral geometry, the parameter \(2d_{TX}/a_H\) will be equal to 1.414. Similarly, if a TMD have an optimum trigonal prismatic geometry, the parameter \(2d_{TX}/a_H\) will be equal to 1.527. Using the crystallographic data of 26 different TMD crystals used by Gable et al., a graph of \((a_H/2R_X)\) vs. \((2d_{TX}/a_H)\) are plotted in Figure 2.2.
Figure 2.2 Relationship between radius ratio and ionic nature of the T-X bond derived through crystallographic parameters. Group IV TMDs are Octahedral, Group V contains mixture of octahedral and trigonal prism geometry, and Group VI are exclusively trigonal prismatic. Octahedral structure are preferred for more ionic crystal and tend to have a small radius ratio. Trigonal prism are preferred when the radius ratio is larger and crystal less ionic in nature.
Let us first discussed the effect of radius ratio. The figure of $a_H/2R_x$ vs. $2d_{TX}/a_H$ shows an interesting divide. All structure with $2d_{TX}/a_H$ less than ~1.495 are all octahedral, while anything beyond it are Trigonal Prismatic. Structurally it is not surprising. Octahedral symmetry is a closed pack structure; hence the size of the transition metal cation must be quite small compared to the size of the anion. Trigonal prismatic structure is not a closed pack structure, thus is allows larger cation to be placed in between the anions. When the radius ratio is small, one should expect that the octahedral geometry is preferred to optimize the coulombic interaction.

![Image of undistorted and distorted Trigonal prismatic TMD](image)

**Figure 2.3. Visual representation of undistorted and distorted Trigonal prismatic TMD.**

Top view of undistorted trigonal prism (a) commonly found in Group VI TMDs and typical distorted trigonal prism (b) found in Group V TMDs. The distortion occurred due to the metal center being too small compared to the available gap between the chalcogenide anions. Distortion are usually small. Image taken from ref. 7

However, the divide of 1.495 is much smaller compared to the optimum trigonal prism value of 1.527. It appears that radius ratio is insufficient explanation of why a TMDs adopts a particular structure. Note that majority of the TMDs with a radius ratio less than 0.527 is in Group V. This
explain the peculiar distorted-trigonal prismatic structure that is common in Group V. A more detailed diffraction studies have shown that NbSe$_2$, for example have a slight distortion in its crystal structure (Figure 2.3)$^{1,6,7}$. This is a result of having a cation that is “too small” compared to the size of the chalcogenide.

Figure 2.2 clearly shows that chalcogenides in Group IV (predominantly Oh) have a larger ionic property compared to Group V, and that chalcogenides in Group V are more ionic than Group VI (iconicity Group IV > Group V > Group VI). In addition, if one were to compare only octahedral structure, structures with more ionic chalcogens also have a smaller radius ratio. Similar conclusion can also be made when looking only at crystals with trigonal prismatic symmetry. The conclusion is that TMDs with larger ionic characteristic have smaller radius ratio.

The relationship between radius ratio an ionic character is straight forward. A more ionic chalcogenide must also indicate that the transition metal is also more cationic in nature. A more negatively charged anion is larger in size and a more positively charge cation is smaller in smaller. For the same crystal structure, whichever TMDs are more ionic must also have a smaller ionic radius.

Combining the effect of both radius ratio rule and iconicity of the structure shows that structure that are more ionic in nature have a smaller radius ratio and therefore prefer an octahedral structure. It is important to understand that these structural data does not explain why, for example, MoS$_2$ is less ionic in nature compared to ZrS$_2$.  

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Staging Mechanism in 2D-intercalation

Intercalation reaction refer to the insertion of a guest species into a one-, two-, or three-dimensional structure. It is a general term use for a wide variety of host materials from insulators, semiconductor, and metals. Whittingham, in his book entitled Intercalation Chemistry, described best the significant interest in intercalation chemistry: “The essential feature of intercalation reaction, and what makes its study so exciting and profitable, is that the guest and host experience some degree, along a spectrum from subtle to extreme, of perturbation in their geometric, chemical, electronic, and optical properties. There is considerable latitude available to the worker for controlling many of the parameter in order to tailor the behavior desired.”

Figure 2.4. Staging mechanism model of intercalation reaction. Generally, the Daumus-Herold model is accepted as the most probable mechanism. Image taken from ref. 10
Multiple studies, such as Inaba eta al (Li-Graphite intercalation)\textsuperscript{8} and Hooley (Br2-Graphite)\textsuperscript{9}, demonstrated that an intercalation reaction in a 2D material occurred through a staging intercalation mechanism. Rather than an intercalation occurred everywhere simultaneously, intercalant species form periodic sequence of one fully intercalated layer every “n\textsuperscript{th}” empty host layers (Figure 2.3)\textsuperscript{1,2,6,8-12}. More recent studies have shown that Daumus-Herold model of intercalation is preferred in a Li-Graphite system as the host species are generally sufficiently flexible to distort around the intercalant\textsuperscript{10}. However, disorder phases, in which all planes have nearly equal concentrations of foreign atoms, also exist at high temperatures and phase transition between staged and disordered phases have been observed. Depending on the intercalants, certain stages might be especially prominent or completely missing.

**Support of Staging Mechanism through Electrochemical data**

The most convincing support of staging mechanism comes from electrochemical intercalation data\textsuperscript{2}. Insertion of foreign species into a host material, when a charge transfer occurred, cause a change of the host’s electronic structure. This is due to the difference of the electronic structure of a bulk material in comparison to mono- or few- layers. It is well documented, for example, that the electronic properties of mono, bi, and few layers graphite and MoS\textsubscript{2} change significantly\textsuperscript{11}. For example, the optical band gap of MoS\textsubscript{2} changes from ~1.3 eV of bulk to 1.9 eV for monolayer\textsuperscript{11}. This difference would mean that an electron transfer onto bulk MoS\textsubscript{2} should be easier compared to an electron transfer onto a monolayer MoS\textsubscript{2}. Electrochemical measurement changing MoS\textsubscript{2} from an unintercalated bulk structure onto a stage-1 intercalated compound reflects this change in energetic.
Let us first consider the typical electrochemical signal that we should expect to see in a system with multiple equilibrium species (Figure 2.5)\textsuperscript{12,13}. Staging mechanism is predicated in the existence of an intermediary state with a locally minimum energetic state. Whether measured through voltammetry or coulometry, these different stages should exhibit some differing electrochemical signature.

In a typical cyclic voltammetry data with a single product/reactant species, a single cathodic peak current and a single anodic peak current will be observed. Alternatively, when there are multiple species with differing redox properties, multiple cathodic/anodic peak current will be observed. For example, the cyclic voltammetry of iron-diazenyl pyridine complex shows four different redox potentials. This shows that there are at least 5 different detectable distinct species involved in the chemical reaction\textsuperscript{12,13}. Note that the when the redox potential are close to one another, it can be hard distinguishing one redox species from one another.

Similar observation should be found in a coulometry data, whether it is a charging/discharging curve or a molar ratio/loading data. The constant current discharge curve of a chemical reaction of a single product/reactant species should be a smooth and gradual change upto a stoichiometric equivalence point in which the cell potential will drop quickly (similar to a titration) which then plateau. If 5 species/stages are involved when the reaction progresses from an initial to a final stage, coulorometry data should also indicate 5 different plateau.
Figure 2.5. Typical electrochemical signature of chemical compound undergoing a single transition or multiple chemical reaction as a function of applied potential. When there is a single transition from one product to one reactant, voltammetry will show one anodic and cathodic peak. If “n” number of transition exist, voltammetry will show “n” number of peaks.
Figure 2.6. Li-Graphite intercalation shows staging behavior as observed through \textbf{coulorometry and collaborated with Raman shift}. Charging and discharging curve of Li-Graphite intercalation (a) with a corresponding Raman shift (b). Numerical labels in (a) refer to the same number in (b). Charging and discharging curve shows multiple equilibrium species correspond to the different staged intermediates. Image taken from ref. 10.

Figure 2.6 shows a a typical constant-current discharge curve of Li-Graphite system. In that particular work, Sole et al combine vibrational as well as electrochemical data. Raman spectroscopy are taken during a charging and discharging of a HOPG to show the effect of
lithium loading on the Raman signature of the Carbon-Carbon bond. The potential of Li-Graphite system shows multiple shoulder/plateau around 0.7V, 0.2V, 0.1V, 0.075V vs. Li/Li⁺. It shows at the very least that there are 4 distinct intercalated graphite compounds with its own individual redox signature.

Similar charging and discharge curve can be observed in Li-MoS₂ intercalated system. Work by Wang et al. in particular is interesting as the author combined electrochemical, x ray diffraction and SAED, as well as cross section TEM. Form the charging/discharge curve (Fig2.7) shows a multiple peak/plateau indicating multiple different electrochemical species. Unlike Sole et al, Wang et al combined diffraction data and found 4 distinct phases denoted as P1, P2, P3, and P4 (Figure 2.7)¹⁴. The initial MoS₂ is in 2H phase is labeled as P1. Upon sufficient Na intercalation, the structure expands creating a new structure with different diffraction pattern (P2, P3). Crystallography shows that several phase changes can happen as a function of varying degree of intercalation, and peak shift on the diffraction pattern can determine the intercalation stage
Figure 2.7. Intercalated Li-MoS2 shows similar staging behavior as Graphite. Charge/discharge curve (a) shows multiple electrochemical species as denoted in the change in crystal structure seen in XRD. Four different phases are observed (b) labeled P1 to P4. P1=2H-Na0.5MoS2, P2= 1T-Na0.5MoS2, P3=1T-Na0.5MoS2, P4=NaxS Image taken from ref. 14
It should be cautioned that interpretation XRD pattern is harder compared to electrochemical data. Selection rules, for example, means that some peaks are unobservable. While XRD is a powerful technique by comparing the product to a tabulated value, back-calculation of the structure solely from the diffraction pattern is generally complicated.

**SAED, Electron diffraction, and TEM support**

The work by Wang et al is particularly interesting because SAED, electron diffraction and TEM cross section are taken alongside the electrochemical and XRD data. Figure 2.8 a-d as well as figure e-h shows that in addition to the staging mechanism, a phase transition occurred during MoS$_2$ intercalation. It is observed that the position of the S-atoms, in particular, shift from a trigonal prismatic structure into a closed-packed octahedral structure (a, c). Electron diffraction pattern after further loading of sodium atom shows a complete 1T/Octahedral phase (h) from its initial 2H / Trigonal Prismatic structure.

The TEM cross section is particularly illuminating because it shows that indeed, sodium atom intercalates through staging mechanism. In figure 2.8 i-k shows different stages of Na-MoS$_2$ at various sodium loading density.

The intercalation reaction of TMDs with alkali metals are driven by charge transfer from the alkali metal into the host structure. It is understood that, upon intercalation, the alkali metals acts predominantly as a positive charge, while the electron transferred in shared between the transition metal and the chalcogenides atoms. Therefore, one should expect upon intercalation with alkali metals that significant change in the electron binding energy should be observed.
Figure 2.8. High resolution TEM and electron diffraction shows the phase transition of MoS$_2$ as it is intercalated with Sodium atom of differing sodium content. Cross section TEM shows a support of staging mechanism, where only a few layer of MoS$_2$ are intercalated (j). Image taken from ref. 14

In earlier structural analysis, we discussed the degree of iconicity with the propensity of Octahedral / Trigonal Prism structure. It appears that the radius ratio rule plays a significant role in the structural preference of Octahedral vs. Trigonal Prism. A more ionically charged TMDs generally have a larger radius of chalcogenide due to the increased electron density. This in turn,
decreases the radius ratio between the transition metal and chalcogenide, induces a preference for Octahedral structure.

**Figure 2.9.** Electron transfer from Na to MoS$_2$ decreases binding energy and changes Raman signature. Binding energy of Na-MoS$_2$ intercalated compound obtained through XPS (a) and its corresponding Raman shift (b). Intercalated MoS$_2$ have lower binding energy compared to unreacted MoS$_2$ due to charge transfer from the alkali metal. Raman shift intensity weakens due to changes in selection rule. Image taken from ref. 14

In the case of intercalation of MoS$_2$, based on the binding energy of the Mo atom that electron transfer indeed took place between the Na and MoS$_2$. Upon intercalation, it becomes easier to
remove electrons from the Mo atom. This is a clear indication that the sodium atom donates its electron density to the Mo host. Upon sufficient Na insertion (ration of 1.5 Na per Mo atom), the original Mo binding energy peak disappear and replaced by a new metallic Mo3d peak. XRD and the disappearance of the E$_{2g}$ and A$_{1g}$ peak indicates that the result after excessive intercalation is Mo$^0$ and Na$_2$S, increasing the ionic character of the MoS$_2$ host. The increased iconicity induces a decrease in radius ratio, which resulted in a transition between Trigonal Prism and Octahedral structure.

**Conclusion on Staging Mechanism of TMDs**

Staging behavior does not necessarily occur for all TMDs. Whittingham et al. found that staging compounds are more likely to occur, in the case of alkali metals, for intercalant of a larger size (Figure 2.10$^2$). In a study of TiS$_2$- and ZrS$_2$- Alkali metal intercalated compounds, Lithium intercalation only show a stage 1 compound. On the other hand, Na, K, Rb and Cs intercalated compound shows multiple staged structure.
Figure 2.10. Staging behavior of other TMDs and the effect of cation size. (a) Staging behavior of TiS$_2$- and ZrS$_2$- intercalated with alkali metals. Smaller alkali metal tend to not form a staging compound. (b) Electrochemical potential of Na-TiS$_2$ as a function of Na loading. When staging occurred, electrochemical measurement shows multiple equilibrium species. (c) Electrochemical potential of Li-TiS$_2$ as a function of Li loading (no staging) shows a single curve corresponding to single species equilibrium. Roman numerals I, II, IV indicate the staging. Image taken from ref. 2.
Evaluating whether staging or any intermediate structure exist can easily be done through electrochemical means. Consistent with Figure 2.5, a staging compound (Na-TiS$_2$) shows multiple slopes in its electrochemical potential. On the other hand, when it only forms a single final product (Li-TiS$_2$), there is only a single slope observed.

Electrochemical signal must be collaborated with some additional experiments. Typically, XRD, Raman shift, and other experiments are needed to collaborate the nature of the intermediate and final products. These additional experiments can determine the structure and other properties of the products.

**Organic intercalation of TMDs**

At this time, over 240 organic intercalation compounds have been reported in literature$^{1,2,17,18,19}$. Nearly all nitrogen containing organic molecules, ammonia and hydrazine will intercalate with the transition metal dichalcogenide$^{1,2,3}$. Albeit rarely reported, due to its similar chemistry to nitrogen, phosphine based organic molecules are also found to intercalate into TMDs$^{20}$.

In general, the metallic dichalcogenides such as TaS$_2$ and TiSe$_2$ will intercalate more easily, but with the group VI semiconductors such as MoS$_2$ it is more difficult to form organic intercalate complexes$^{18}$. Multiple works in the 1960s-1980s almost exclusively reported on Group IV and Group V organic intercalation$^{1,2,17,18,19,20}$. For almost 50 years, no new chemistry regarding MoS$_2$ and other Group VI TMDs have been discover.

The simplest way to intercalate organic compounds is to immerse the crystal in the liquid or vapor at a suitable temperature. In TaS$_2$ intercalation, Gable et al found that ammonia, aliphatic
amines, pyridine and similar compounds readily reacts to produce a stable product\textsuperscript{18}. In general, submerging powdered TaS\textsubscript{2} into a solution containing stoichiometric/excess amine in benzene at 25°C produce the intended products in matter of hours. Experimental procedure by Gable et al found it necessary to leave the reaction to proceed for upto 30 days to achieve satisfactory completion\textsuperscript{1,2,18}. Other larger intercalants such as pyridine requires immersion for 30 days of reaction in 200°C. Anecdotally Gable et al noted that, “the rate of intercalation, which was satisfactorily rapid even at room temperature, was always faster for amines with an even number of carbons than for amines with an odd number of carbons.”\textsuperscript{18}

Our work primarily focuses on the reactivity of MoS\textsubscript{2} precisely because group VI TMDs hardly reacts with anything. However, we will begin the introduction to organic intercalation based on the reactivity of metallic TMDs such as TaS\textsubscript{2} and NbS\textsubscript{2} (Group V). It is important to take ideas and observation in these well studied materials and apply them to have a better understanding why MoS\textsubscript{2} (Group VI) are much less reactive and what strategies can be applied to find a new and different chemistry in TMD intercalation.

Analysis of the structure of the intercalant are generally done through XRD, TGA and elemental analysis\textsuperscript{1,2,18,21}. In general, identification of newly created crystal structure is done first through XRD to obtain the interlayer separation distance. Second, if possible, TGA was used to determine the molecular ratio between TMD and the intercalated species. After knowing the molecular ratio and separation distance, several possible structures are proposed that satisfied both the separation distance and the mole ratio.
Figure 2.11. Structure estimation of Organic-TaS2 intercalated compound. The increase in interlayer distance is equivalent to the sum of the length of the amine. Given that the bond distances are commonly known and are highly robust, a first approximation can quickly be made.

Given that bond length and vdw radius is especially uniform, the structure of intercalate species can be estimated to a great accuracy. In most cases, adding the host interlayer distance ($d_0$) with the total length of the alkylamine intercalated into the structure can accurately estimate the interlayer distance produced. In general, the equation of separation distance, following Schollhorn’s equation, can be expressed as:\(^20\):

**Mono-layer intercalation**

$$d_{mono} = d_0 + \left[ \sin \left( \frac{109.5^\circ}{2} \right) \left( n_{CC}L_{CC} + n_{CN}L_{CN} + n_{CH}L_{CH} \right) \right] \sin \theta + 2r_H$$
Bi-layer intercalation

\[ d_{bi} = d_o + 2 \left[ \sin \left( \frac{109.5^\circ}{2} \right) \left( n_{CC}L_{CC} + n_{CN}L_{CN} + n_{CH}L_{CH} \right) \right] \sin \theta + 2r_H \]

d\(_o\) is the hosts unintercalated interlayer distance. \( n_{CC}, n_{CN}, n_{CH} \) are the number carbon-carbon, carbon-nitrogen, and carbon-hydrogen bonds. \( L_{CC}, L_{CN}, L_{CH} \) are the bond length between carbon-carbon, carbon-nitrogen, and carbon-hydrogen. The \( \sin \left( 109.5^\circ/2 \right) \) term is multiplied onto the total bond lengths of the alkylamine to account for the sp3 hybridization. Two the radius of a hydrogen atom \( (r_H) \) are then added to express the total length of the alkylamine. Lastly the length of the molecule is multiplied by \( \sin\theta \) to account for angle \( \theta \) that the alkylamine chain is oriented against the basal plane of the host structure. A graphical representation can be seen in figure 2.11.

Two assumptions come into play in the structural proposition. First, the nitrogen head are oriented towards the basal plane of the host TMDs \(^{18-21}\). This assumption comes from the inert nature of the alkane chains. In order for reaction to occur the amine group, which is more reactive, must be interacting with the host structure. Secondly, it is assumed that the carbon chain of the alkylamine to extend linearly without bending. Having the carbon chain extend linearly will reduce the rotational and translational entropy of the alkane—which is generally true for a crystalized organic molecule.

Result by Schollrn et al.\(^{21}\) and Gable et al.\(^{18}\) have differing conclusion on the nature of the intercalation. Both researcher intercalated TaS\(_2\) with alkylamine of differing carbon chain length from 1 – 20 and analyze its crystal structure (Figure 2.12). For carbon chain length greater than 12, both Schollhon and gable have the same conclusion: the carbon chain makes a 90 degree angle with respect to the basal plane of the host structure / standing straight up, and the structure
consist of a bilayer alkylammonium. Both researcher found that TaS$_2$ crystal structure can expand by ~50Å upon intercalation. However, for carbon chain between 0-12, the two authors are in disagreement with the nature of the intercalation. Schollhorn interpret that shorter alkylamines forms a structure with an approximately 56° angle from the basal plane. On the other hand, Gable et al found that the shorter alkyamines lay flat / 0° to the basal plane of the host lattice.

Figure 2.12. Experimental result of alkylamine intercalated TaS$_2$ by Gable et al. and Schöllhorn et al shows expanded structure. Both author found that the alkyl chain are oriented perpendicularly to the basal plane of the host when the carbon chain length is 12 or greater. For shorter chains, Gamble suggest that the alkane chain is parallel to the basal plane whereas Scholhorn suggest a 56° angle. Image taken from reference 18,21.

Two factors can cause the differing conclusion on the nature of short alkylamine intercalation. The first is experimental difference that may cause differing crystal structure. In the same experimental work, Scholhorn demonstrated that annealing Oleylamine and Octadecylamine can
cause a structural conversion as measured through interlayer distance. Heating the material cause some evaporation of intercalated amines. The reduced molecular ratio rearrange itself into a more compact structure. Upon heating to approximately 60°C, Oleylamine-NbS$_2$ undergoes a large change of interlayer distance from ~58 Angstrom to ~46 Angstrom, and Octadecylamine change from ~55 Angstrom to 50 Angstrom. It may be the case that slight difference in experimental procedure cause a smaller loading density of amine in the work of Gamble et al in comparison to Schollhorn.

Figure 2.13. Temperature annealing changes crystal structure of intercalated compounds. Crystal structure change as a function of temperature of Octadecylamine (circle) and Oleyamine (triangle) intercalated NbS$_2$. It indicates that different reaction condition and treatment can produce different product. It may explain the discrepancy in Figure 2.12 for short alkane chain. Image taken from reference 21.
Figure 2.14. Typical early XRD of intercalated TMDs. XRD changes between unintercalated TaS$_2$ (a) and ethylamine intercalated TaS$_2$ (b) measured between $2\theta$ of 25° to 65°. Multiple peaks are observed that can complicate structural interpretation. Early study in TMD intercalated compound lacks low-angle XRD data.

A second and more disturbing difference might be due to a different the interpretation of the XRD data. Due to selection rule, the observed interlayer distance can differ by a factor of 2. For a carbon chain of 12 or less, Gable interpret the interlayer spacing as ~10 Angstrom, whereas Schollhorn interpret the interlayer distance as ~20 Angstrom. Unfortunately, both author failed to provide exact procedure, XRD data as well as the TGA data of their experiments. It may be
due to the fact that both published their work in the 1970s (Schollhorn) and 1980 (Gabble) where publicists do not support supporting information capability.

The earliest raw XRD data for TaS$_2$ intercalated compound that can be found was by Meyer et al$^{22}$. This particular work analyzed the xrd data from $\sim$25° to 65° and using the data to extrapolate the structure. Note that in the intercalated structure, the relevant facets are (00 24), (00 20) and (00 16). The selection rules cause only a few of these peaks to be visible. Interpreting a structure with an expansion larger than 20 Å may require a low angle x ray diffraction.

However, qualitative conclusion can be drawn. Both author came to the same conclusion that shorter alkylamine are less stable because it does not provide sufficient stabilization through vdw interaction$^{18,21}$. Similar experiment was done on NbS$_2$ showing similar result: longer carbon chain forms a 90° angle with respect to the basal plane.

Through NMR spectroscopy, it was found that the nitrogen center is positively charged$^{1,23-26}$. A charge transfer of approximately 0.2 electrons from the lone pairs of pyridine onto TaS$_2$. Similar conclusion can be found for intercalation of TMDs with Cobaltocene and Chromatocene$^{27,28}$. It is best to equate the organic intercalation as a similar process to the alkali-metal intercalation: the driving force of crystallization is electrostatic in nature.

MoS$_2$ Organic Intercalation, understanding

Semiconductor TMDs, especially MoS$_2$ and WS$_2$ are especially unreactive$^{1,218}$. Earlier discussion revolves the intercalation of metallic TaS$_2$, which is among the easiest TMD to intercalate. While simply mixing amine with TaS$_2$ produce intercalated compounds, MoS$_2$ will
not react with amines at all. Even after 50 years after the research in TMDs started, there has been no new chemistry relating to the intercalation of MoS$_2$ that has been discovered. This research on MoS$_2$ was started precisely due to the challenge of finding a new reaction mechanism.

The first question was “why are group VI unreactive?” The charge transfer model seems to explain the chemistry of TMDs quite well. The basics of electrochemistry requires that for a charge transfer/redox to occur the reducing agent must donate an electron density towards the oxidizing agent. That means that the HOMO of the reducing agent must be higher in energy compared to the LUMO of the oxidizing agent.

The band energy diagram of Group IV to VI can explain the difference in reactivity. Due to the metallic nature of group V TMDs (I.E. TaS$_2$), it is easy to donate an electron density to the LUMO because there is a semi-filled conduction band that can accept a large amount of electrons. Group VI (i.e. MoS$_2$), however, is a semiconductor. Electron donated must go into the empty conduction band which is much higher in energy compared to the valence band.
Figure 2.15. Schematic representation of the band structure of the layered Group IVB, VB and VIB transition metal dichalcogenides. Group VI are the least likely to accept electron due to the highly energetic LUMO.

Suppose an amine have an electrochemical potential/LUMO of somewhere between the Valence and Conduction band of MoS$_2$. No reaction will occur because the Lumo of Amines are less than the conduction band of MoS$_2$ and the valence band of MoS$_2$ is already completely filled. Alternatively, TaS$_2$ is metallic and there are large amount of empty band available for the electron from an amine to donate into the TaS$_2$. Overall, the energy of the electron will decrease, and thus a chemical reaction occurred. In order to stabilize the now negatively charged TaS$_2$, the
positively charge amine(ammonium) have sufficient driving force to overcome the TaS$_2$ interlayer bond.

Figure 2.16. Reactivity difference between TaS2 and MoS2 due to band structure

difference. TaS$_2$ reacts with amine (a) because the electrochemical potential of amine is higher and it can fill into the conduction band of TaS$_2$. MoS$_2$ being a semiconductor (b) have a filled valence band, and most amines are insufficiently energetic to fill in the conduction band of MoS$_2$. However, highly reducing amines such as hydrazine does react because its electrochemical potential is higher than the conduction band of MoS$_2$.

Is there electron donating N-based organic compound that will react with MoS$_2$ and other Group VI TMDs? To date, only one examples are found: hydrazine$^{29,30}$, a known strongly reducing agent$^{31}$. It was found, however, though electron transfer was observed, it appears it is insufficient to produce chemical intercalation, although it assists exfoliation$^{29}$. Treated with
hydrazine, p-type WSe₂ turns into a strongly n-type semiconductor with enhanced conductivity\textsuperscript{30}. These reactions further support the charge transfer model of the reactivity of these TMDs.

**Current method of MoS\textsubscript{2} organic intercalation**

Several organic-MoS\textsubscript{2} complexes have been reported in literature\textsuperscript{32-34}. Several alkanes, ferrocene and polymers were successfully intercalated in between the layers of MoS\textsubscript{2}. XRD shows that interlayer distance between the layers increased by 3.4 Å up to 50 Å. The author found that small alkanes and solvents such as hexane, benzene and n-butylacohol are unstable and does no perform intercalated material, whereas larger molecules are stable. This is expected and consistent with the work by Schöllhorn and Gamble. The work, however, did not contain detail stoichiometric amount nor thermodynamic argument—which is unsurprising as will be explained below.

The method is generally described as intercalation through flocculation. A litigated MoS\textsubscript{2} (either through electrochemical reaction or organo-lithium) is exfoliated by exposure to ultra pure water and ultrasonication. The water reacted with the lithium to form H\textsubscript{2} gas. As gas is being produced, few/moно layer MoS\textsubscript{2} are separated creating a dissolved MoS\textsubscript{2} suspended in water. Ultrapure water is needed as various works have indicated that the presence of salt will quickly cause flocculation and an unstable dispersal.
Figure 2.17. MoS$_2$ organic complexes obtained through flocculation. (a) Ferrocene-MoS$_2$, and (b) Ferrocene-MoS$_2$ heated at 80°C and (c) MoS$_2$ powder. List of other flocculated organic-MoS$_2$ complexes are listed in (d). Organic molecule are trapped in between MoS$_2$ layers due to rapid flocculation of water-dispersed MoS$_2$. In order to make the water-dispersed MoS$_2$, it is first treated with organo-lithium. The true driving force is Li-MoS$_2$ reaction.

The inclusion material is produced by dripping a supersaturated solution of -say- ferrocene in hexane/highly volatile solvents on the surface of aqueous MoS$_2$. Due to the hydrophobic nature of the MoS$_2$, it forms a film on the water-hexane interface and flocculate. By chance, due to the
concentrated ferrocene in the solution, some will be trapped in between the layers. Other author recommends vigorous shaking in order for inclusion compound to form.

This method does not require that any chemical bond to exist between the layer, only that the inclusion material to be sufficiently large as to prevent the layers to recombined. However, the by-chance nature of its inclusion is fickle and is unsuitable to produce consistent and single phased result. Hence it is of no use trying to further find the stoichiometric amount.

In conclusion, to date, there is no good method to produce MoS$_2$ – Organic complex materials. In almost all cases, the inclusion of organic compounds into MoS$_2$ are done through by-chance trapping of organic molecule from a water-dispersed Li-MoS$_2$. Because there is no driving force to the reaction, the quality of the resulting product are inconsistent and unsuitable for large scale usage. A different chemical pathway is needed to produce a better product.

**Conclusion and the Charge Transfer model of TMD intercalation.**

The structure of TMDs is generally separated into two structures: Octahedral and Trigonal Prismatic. Based on the analysis of group IV, V, and VI TMDs it appears that that the radius-ratio argument is one of the best predictor of the preferred crystal structure. Crystals with a radius ratio of less than 0.49 adopt the Octahedral structure and anything with greater prefers Trigonal Prismatic structure.

Upon intercalation with alkali metals, the crystal structure of TMDs may change. Some host materials, such as MoS$_2$ and other group VI undergoes Trigonal Prismatic to Octahedral. This transition is partly due to the electron transfer between alkali metal with the host structure,
causing changes in the radius ratio. It should be noted that some, such as TaS$_2$ that exits in both Octahedral and Trigonal Prismatic structure remains unchanged upon intercalation.

Study of a wide variety of intercalation compound of TMDs, whether organic molecules or metals induce it, indicates that charge transfer is the driving force for the reaction. Consistently, it was found that the host structure has an increased electron density, or the intercalant having a decrease in electron density. The intercalated structure can then be understood as a negatively charged host TMDs with positively charge intercalant, creating an overall neutrally charged species.

Figure 2.18. Electronic Structure of TMDs shows the relative electrochemical energy. ZrS$_2$ and TaS$_2$ can easily accept electrons because the LUMO is lower compared to MoS$_2$.

Direct organic intercalation only occurs for Group IV and Group V TMDs such as TiS$_2$ and TaS$_2$, while group VI TMDs are largely inert. This can be understood by evaluating the Band Structure of these different TMDs. Both Group IV and V TMDs have lower fermi
energy/electrochemical potential compared to Group VI. Hence electron transfer from organic molecule is possible because there are other available/empty bands that can accept an electron. The LUMO of Group VI, however, is filled. Only sufficiently strong reducing agent can undergo electron transfer with MoS$_2$ and other Group VI TMDs.

For close to 50 years, no new organic intercalation was discovered for Group VI TMDs. With understanding of the basic of intercalation, we will attempt, in this work to describe a newly realized intercalation for MoS$_2$, other Group VI TMDs, and other layered compounds (Chapter 5).
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CHAPTER 3. Interfacial Energy and Liquid Exfoliation of Layered Materials

Two-dimensional (2D) layered materials (LMs) are characterized by their strong in-plane bonds and weak van der Waals (vdW)-like coupling between the layers. Since the discovery of graphene, there has been a growing interest in single or few layers of exfoliated LMs. These materials can form a natural 2D crystal structure and offer promising opportunities for both fundamental studies and technological applications. Graphene has been explored for a wide variety of usage as transparent conductors, transistors and biological sensors\textsuperscript{1-4}. Transition metal dichalcogenides (TMDs) such as MoS\textsubscript{2} and WS\textsubscript{2} are semiconducting and have shown significant potential for use in electronic devices, energy storage, and catalytic purposes\textsuperscript{5-7}. Other TMDs such as NbSe\textsubscript{2} are metallic, and have been shown to be superconducting at low temperatures\textsuperscript{8}.

While the bulk syntheses of these materials have been successful, ways of producing large-scale mono/few layers are still limited. Currently, the highest yielding exfoliation process from a bulk starting material is restricted to chemical modification through intercalation, oxidation, or functionalization\textsuperscript{9-14}. However, the chemical reactions involved in the aforementioned processes can often introduce a large number of defects in the crystal structure and severely alter or degrade the intrinsic properties of the resulting materials\textsuperscript{9-16}. Exfoliation methods without a chemical reaction are preferred in order to maintain the integrity of the material.

Recent studies have shown that LMs can be directly exfoliated by sonication in a suitable solvent\textsuperscript{17-21}. If the yield can be improved, the solvent exfoliation method is largely preferred because, unlike the common lithium intercalation method, liquid exfoliation is not an air
sensitive process and does not involve chemical reactions. These factors improve the processability while maintain the intrinsic properties of LMs. However, there is not yet a good method to evaluate the suitability of a solvent for the effective exfoliation of LMs. The exploration of this subject is largely being developed through a trial-and-error process by testing a large number of solvents. So far, Coleman et al. have shown that N-methyl-2-pyrrolidone (NMP) and other pyrrolidone-based solvents are found to be the more effective exfoliating solvents for both graphite and MoS$_2$\textsuperscript{17,18}. However, these pyrrolidone-based solvents are generally toxic and have a high boiling point. Classified as a reproductive toxin, industrial scale use of such solvent may pose a significant negative environmental effect\textsuperscript{22,23}.

On the other hand, it has been demonstrated that drugs and polymers show a co-solvency effect in which the solubility of a material can be greatly improved by using a mixture of solvents while showing low or no solubility in either of the individual components of the mixture\textsuperscript{24,27}. The nature of plane-plane vdW-like interaction of LMs is fundamentally similar enough to that of polymers. Demonstrated by the isolation of monolayers of graphene and MoS$_2$ with scotch tape\textsuperscript{1,7,28}, the basal plane of both graphite and MoS$_2$ displays a strong vdW-like interaction. Given the right solvent mixture, similar co-solvency effect observed in polymer materials can also occur in these LMs\textsuperscript{20,21}. Indeed, Zhou et al. have recently shown that LMs can be exfoliated using a mixture solvent of water and ethanol\textsuperscript{21}.

To rationalize the experimental data observed, recent studies have used the Hansen solubility parameters (HSP) as an explanation\textsuperscript{17,18,21}. The HSP works by assigning values on the extent of a materials’ ability to form dispersion, polar and H-bonding interactions (H-bond does not mean exclusively Hydrogen bonding, but rather everything else not accounted for by dispersion and polar). The HSP of a material are extracted by testing its solubility on a large number of solvents.
of known solubility parameters and finding the best fit\textsuperscript{35}. However, it is usually a challenge to obtain all three solubility parameters due to the large test pool needed. In addition, the HSP intrinsically assumes that solvents only engage in three distinct interactions, and neglect other possible interactions. As a result, it can causes uncertainty that makes it difficult to determine the best exfoliation solvent in a predictable manner.

In this study we explore the fundamental factors governing the liquid exfoliation process through a rational design of a co-solvency approach for the exfoliation of graphite and MoS\textsubscript{2} in a simple water-alcohol mixture. We demonstrate by directly determining the liquid-solid interfacial energy through contact angle measurement, it is possible to predict the optimum co-solvent concentrations for the effective exfoliation of LMs without the need to make any assumption on the material’s solubility parameters or the exact nature of the material-solvent interactions. Moreover, we found that molecular size of the co-solvent system can play an important role in the exfoliation yield.

**Directly probing the solvent-solid interaction**

Equilibrium contact angle of water-solvent mixture was measured on highly ordered pyrolytic graphite (HOPG) and large single crystal MoS\textsubscript{2}. As an experimental control, we chose methanol (MET), ethanol (ETA), isopropanol (IPA), and t-butyl alcohol (TBA) as co-solvents. These solvents were chosen because their chemical structures differ only by the substitution of –H group with –CH\textsubscript{3} bounded to the central carbon atom. Due to the similar nature of the alcohols, we expect that a greater clarity in exfoliation trends would emerge through the use of these selected solvents rather than through the use of a wide range of randomly chosen solvents.
To predict thermodynamic stability, we used Young’s Equation by evaluating the change in interfacial energy:\(^29,30\):

\[
\gamma_{sl} = \gamma_{sg} - \gamma_{lg}\cos\theta_c \tag{1}
\]

Where \(\gamma_{sl}\), \(\gamma_{sg}\) and \(\gamma_{lg}\) are the solid-liquid, solid-gas, and liquid-gas interfacial energy respectively, and \(\theta_c\) is the equilibrium contact angle. For a liquid, \(\gamma_{lg}\) is equal to its surface tension, and its value is usually well known from published sources or can be measured by using a goniometer\(^31,32\). \(\gamma_{sg}\) represents interfacial energy between solid and atmosphere and does not change regardless of the solvent used, it therefore simply acts as a constant in the equation and can be readily subtracted out of the equation when comparing two different solvents. This is beneficial because the \(\gamma_{sg}\) value varies substantially for graphite in literature (100-200 mJ/m\(^2\))\(^33,34\) and is largely unreported for MoS\(_2\). Calculating the solid-liquid interfacial energy (\(\gamma_{sl}\)) directly would produce large uncertainty. Thermodynamically, the most stable interaction should occur when the value of \(\gamma_{sl}\) is minimized or, equivalently, when \(\gamma_{lg}\cos\theta_c\) is maximized by considering \(\gamma_{sg}\) as a constant for a given LMs. Therefore, when comparing the interfacial energy between a given LMs with two different solvents, the only factors needed are the surface tension of the solvent (\(\gamma_{lg}\)) and the solid-liquid contact angle (\(\theta_c\)). Both of these parameters can be readily measured experimentally for any solvent system (Fig. 1a-d). Therefore, this approach can be used for evaluating essentially an arbitrary solvent mixture.

The maximum value of \(\gamma_{lg}\cos\theta_c\) for the tested solvent mixtures are found to be \(~24\) mJ/m\(^2\) for both graphite and MoS\(_2\) and are clustered around a surface tension of 30-35mJ/m\(^2\) (Fig. 1e,f). In contrast, the \(\gamma_{lg}\cos\theta_c\) value for pure water is much smaller (~5 mJ/m\(^2\)). Because the maximum \(\gamma_{lg}\cos\theta_c\) indicates the most thermodynamically preferred solvent composition, we predict that the
maximum exfoliation would occur for alcohol-water mixtures that have surface tension around the maximum point of 30-35 mJ/m².

![Graph showing surface tension and contact angle measurements for different Alcohol-water mixtures and various solvents.](image)

**Figure 3.1.** The prediction of minimum solid-liquid interface energy based on Young’s equation. ( ■ Methanol, ○ Ethanol, ▲ Isopropanol, ▼ T-butyl alcohol). (a) Surface tension of water-alcohol mixture at various weight fraction at 25 °C³¹,³². (b,c) Contact angle of various co-solvent (alcohol - water) mixture on highly oriented paralytic graphite (HOPG) and MoS₂. (d) Contact angle measurements of IPA/water co-solvent at various concentrations on graphite. (e,f) The calculated decrease in interfacial solid-liquid energy ($\gamma_{lg}\cos\theta_c$) shows a thermodynamic minimum occurring at surface tension of 30-35 mJ/m² for both HOPG and MoS₂.
Materials characterizations

In order to test our predictions, we proceeded to use the mixed solvents for the exfoliation of LMs. The powder LMs and the solvent mixtures described above were placed in small vials and exfoliated in a sonication bath. The colloidal suspension was then centrifuged to remove larger non-exfoliated materials. We used absorbance to characterize the degree of exfoliation using $A=eLC$. Tapping mode atomic force microscopy (AFM), high resolution transmission electron microscope (HRTEM) and electron diffraction (ED) was used to characterize the exfoliated flakes.

An absorption spectrum of the exfoliated graphite (Fig. 2a) shows a peak at 260 nm, which is consistent with reported values for graphene\textsuperscript{16}. The peak position also indicates that there is not significant modification in structure or oxidation that is usually seen in graphene oxide samples with a shifted absorption peak around ~230 nm depending on the degree of oxidation\textsuperscript{16}. A typical absorption spectrum of MoS\textsubscript{2} shows three peaks on 657, 602 and 385 nm (Fig. 2f). Based on the spectra, the exfoliated MoS\textsubscript{2} showed a band gap of ~ 1.77 eV, consistent with previous studies\textsuperscript{7}.
**Figure 3.2. Characterization of the exfoliated LMs.** (a,f) Typical absorption spectra of the exfoliated graphite with a peak absorbance at 260 nm and the exfoliated MoS\(_2\) with absorbance peaks at 657, 602 and 385 nm. (b,g) AFM images and section height profiles of the exfoliated graphene and MoS\(_2\). (c,h) Sheet thickness distribution of exfoliated graphite and exfoliated MoS\(_2\). d,i. TEM image and electron diffraction pattern of few layer graphene and MoS\(_2\). (e,j) HRTEM image of the exfoliated graphene with a lattice spacing of 0.265 nm and MoS\(_2\) with a lattice spacing of 0.317 nm. Scale bar, 200 nm (b,g), 500 nm (d), 1 nm (e,f) 100 nm (i).

AFM studies of the exfoliated graphite and MoS\(_2\) samples on substrate show flakes with the thickness ranging from 1-6 nm are present in graphite and MoS\(_2\) samples (Fig. 2b,c,g,h),
indicating the presence of mono-layers in the solvent, as well as other thicker materials. Scanning electron microscopy (SEM) images shows both the exfoliated graphene and MoS$_2$ flakes have a relatively large lateral size distribution varying from 100 nm to 1 µm (Supplementary information Fig. S1). Electron diffraction and HRTEM studies demonstrate that both the exfoliated graphite and MoS$_2$ show a hexagonal structure with lattice spacing of 0.265 nm and 0.317 nm (Fig. 2d,e,i,j) respectively, indicating no distortion in structure$^{14,15}$. Together, these characterizations demonstrate that the exfoliated LMs maintain their crystal structure during the exfoliation process with size distribution similar to previous studies, and maintain their typical crystallographic characteristics$^{17,18}$.

**Co-solvent and concentration effect**

We next investigate the effect of various solvent mixtures. We began by exploring the exfoliation rate of LMs in different water-IPA mixtures (Fig. 3a,d). As expected, no appreciable absorption was detected for both LMs in pure water due to the hydrophobic nature of the materials. Similarly, little exfoliation was observed in pure IPA after sonication. Upon mixing water with IPA in an appropriate ratio, obvious exfoliation can be observed. It appears that the exfoliation rate first increases up to a critical concentration of IPA and then decreases for both graphite and MoS$_2$. Indeed, the UV-vis studies show that the exfoliation rate for both graphite and MoS$_2$ was not linear or monotonic with the concentration of IPA. For both graphite and MoS$_2$, it appears that the exfoliation is most effective with an IPA concentration around 30 w%. Decrease or increase IPA concentration could lead to a less effective exfoliation results (Fig. 3a,d). Photographs of the solutions of exfoliated graphene and MoS$_2$ also clearly demonstrate this trend (Fig. 3b,e).
Keeping a constant sonication time of 3 hours, we also compared the final concentration of exfoliated materials in MET, ETA, IPA and TBA-water mixtures. As expected from the exfoliation rate study, we saw a peak in exfoliation yield at certain co-solvent concentrations. It is noted that the alcohol concentration can vary over the 3-hour sonication exfoliation process due to a solvent (alcohol) evaporation effect (Supplementary information Fig. S2). After correcting the solvent evaporation effect, we plotted the exfoliation yield (represented by absorbance) against the surface tension, in which a peak exfoliation yield is observed at surface tension ~ 25-30 mN/m² for both graphite and MoS₂ (Fig. 3c,f). Co-solvent exfoliation studies on other LMs such NbSe₂ and MoO₃ show qualitatively similar trends (Supplementary information Fig. S3), demonstrating the general applicability of this co-solvent approach for diverse materials.
Figure 3.3. The effect of co-solvent concentration on exfoliation. (a,d) Absorbance of exfoliated graphite and MoS$_2$ in various concentration of co-solvent system as a function of sonication time. (b,e) Photographs of the exfoliated graphite in 5, 10, 30, 60, 100 w% IPA and MoS$_2$ in 20, 30, 40, 60, 80 w% IPA obtained after 3 hour sonication time. (c,f) Absorbance of exfoliated graphite and MoS$_2$ in various co-solvent mixture plotted against surface tension ($\gamma_{lg}$), showing a peak around 25-30 mJ/m$^2$ for graphite MoS$_2$. The relation of $\gamma_{lg}\cos\theta_c$ vs. surface tension ($\gamma_{lg}$) is also plotted in the graph with the dotted line representing a fitting curve of $\gamma_{lg}\cos\theta_c$ as a line guide to the eye.
It should also be noted that a consistent trend is observed that, at its most effective concentration, the exfoliation yield was higher for co-solvent with more –CH$_3$ groups for both the graphite and MoS$_2$. Here we used the co-solvent molecular weight (MW of the alcohol) as a rough measure of the co-solvent molecular size due to the non-spherical shape of the molecules. When plotted against co-solvent molecular weight, the exfoliation yield increases with increasing co-solvent molecular weight (MW) (Fig. 4a,b). That is, the exfoliation yield follows the trend: MET<ETA<IPA<TBA.

**Figure 3.4. Trend of maximum absorbance (exfoliation) plotted against co-solvent molecular weight (MW), for (a) graphite and (b) MoS$_2$ (■ Methanol, ● Ethanol, ▲ Isopropanol, ▼ T-butyl alcohol). Both LMs shows an increased exfoliation yield for larger co-solvent molecules.**

**Discussions**

The presence of maximum peak based on Young’s Equation clearly indicates that the interaction of graphite with solvent mixture is thermodynamically preferred compared to its pure water or alcohol constituents. Contact angle measurement predicts that for all tested solvents, the minimum of $\gamma_M$ occurs when the solvent-mixture surface tension is around 30-35 mJ/m$^2$. We
would like to emphasize that, as seen on Fig. 1, the solid-liquid interaction energy ($\gamma_{sl}$) is not necessarily minimized when the contact angle is zero. Contact angle is a competition between liquids at the interface whether to bond with the solid or with other liquid molecules. If the liquid-liquid interaction is weak, as measured from its surface tension, it is then more likely to form a smaller contact angle with most solid. Therefore, a smaller contact angle alone does not necessarily indicate stronger solid-liquid interaction and lower solid-liquid interface energy ($\gamma_{sl}$). As expressed in the Young’s equation, the value of $\gamma_{sl}$ depends on both liquid surface tension and its contact angle with the solid surface. More generally, the equation predicts that a higher surface tension solvent with the smallest contact angle will provide higher thermodynamic stability for the liquid exfoliation of LMs.

The experimental studies shows a peak exfoliation occurs at a co-solvent system with a surface tension value around 25-30 mJ/m$^2$ for both graphite and MoS$_2$ (Fig. 3c,f), which is smaller than the predicted optimal co-solvent surface tension (~ 30-35 mJ/m$^2$) based on the contact angle measurements and interface energy considerations (Fig. 1e,f) This difference can be largely attributed to the error in the contact angle measurements caused by the evaporation loss of alcohol. Due to the relatively small liquid droplets used in the contact angle measurement and the large surface to volume ratio, this evaporation can be quite significant especially for the higher alcohol concentration solvents. Overall, this evaporation suppresses $\gamma_{lg} \cos \theta_c$ most prominently on the higher alcohol concentration end and shifts the predicted peak exfoliation position to the right (higher surface tension values). With a correction of this evaporation effect, the predicted surface energy peak can shift left-wards to better overlap with the experimentally observed peak exfoliation position (Supplementary information Fig. S4).
The minimization of interfacial energy and observation of a peak exfoliation at certain co-solvent concentration (Fig. 1e,f) is somewhat counter-intuitive. It is not trivial to quantitatively explain why the interfacial energy is minimized at a certain co-solvent concentration. Qualitatively, however, the observation of the minimum interfacial energy may be explained by postulating that the co-solvent alcohol molecules behave similarly to surfactant molecules due to their tendency to aggregate in water\(^{39-42}\). While macroscopically alcohol mixes well with water in all proportion, microscopically the alcohol molecules can form aggregates to hide their hydrophobic group\(^{39-42}\). These aggregates are believed to be highly mobile and readily fluctuate. In the case of water-TBA system, these aggregates were found vary with concentration and can be as large as 40Å\(^{41}\). This aggregate formation is analogous to micelle formation in surfactants. The main difference of alcohols from normal surfactant is their degree of hydrophobicity. While highly hydrophobic surfactant can have critical micelle concentrations in the \(~1\) wt% concentration, alcohol requires a much higher concentration to form their aggregate (\(~10s\) wt%).

With the hypothesis that the co-solvent behaves analogously to a surfactant, we may explain the observed increase-then-decrease in the interfacial energy. It has been shown for the case of carbon nanotubes in water-surfactant system, if the surfactant concentration is above its critical micelle concentration, the dispersion decreases\(^{43}\). The decrease in dispersion is true for most surfactant system\(^{44}\). Adding too much surfactant causes a competition between micelle formation and particle stabilization\(^{43,44}\). This competition reduces the effective concentration of surfactant available to absorb on the particle surface. By adding too much, the surfactant would prefer to form micelles than being absorbed on the particle surface. As a result, the overall dispersion decreases. This means that the most effective surfactant concentration is right below the critical
micelle concentration, which can explain the minimum interfacial energy at certain co-solvent concentration. It would also roughly explain why more methanol is needed to reach a critical concentration (less \(-\text{CH}_3\) substituents, so less hydrophobic) compared to t-butyl alcohol (exfoliation peak occurs at \(~80\%\) for MET, \(50\%\) for ETA, \(30\%\) for IPA, \(10\%\) for TBA).

Nonetheless, we recognize that the argument is speculative at this point. It will require detailed scattering experiments and molecular dynamic simulations to confirm our hypothesis, which will certainly be a fundamentally interesting problem to investigate in future studies.

In addition, while the contact angle measurements on HOPG predicts that the degree of exfoliation would be very similar based on the magnitude of \(\gamma_{lg}\cos\theta_c\), our experimental results clearly show that the peak height differs greatly from one co-solvent mixture to another (MET< ACT<IPA<TBA). This difference suggests that there are other factors contributing to the exfoliation process in addition to the interfacial energy. As plotted on Fig. 4, maximum exfoliation varies linearly with solvents’ molecular weight for both graphite and MoS\(_2\). The difference may be explained by the larger steric repulsion (Leonard-Jones (L-J) potential) provided by larger co-solvent molecules. Recent simulation studies suggest that the size of solvents (e.g., NMP, DMF, and several other solvents known to exfoliate graphite were examined) trapped in between graphene layers plays an important role in the exfoliation process\(^36,37\). When the two graphene sheets are less than a critical separation distance of approximately 6.4 Å, the L-J attraction force of the sheets dominates and expels the solvent molecules in between the sheets, favouring restacking\(^36,37\). If the sheet separation is increased beyond the critical distance, the L-J attraction force between sheets is no longer significant, creating a metastable separation. It was found that the stability of the exfoliation process largely depends on steric repulsion, with some contribution by electrostatic and vdW interactions. Due
to the difficulty of expelling the trapped molecules, larger solvent molecules provide a greater steric hindrance and stabilize the separation of the graphene sheets. Experiment studies have shown similar oscillatory force that occurred due to solvent molecular sizes. Although these studies did not explore properties of mixed solvents, we suggest that the same steric repulsion effect may be responsible for preventing recombination of both graphite and MoS$_2$ (Fig. 5).

**Figure 3.5. Solvent size effect on stability of exfoliation.** (a) Large solvent molecules preventing graphene-graphene Leonard-Jones potential interaction to stabilize the exfoliation. (b) Small solvent molecules are expelled due to overlapping Leonard-Jones potential.

Because of the hydrophobicity of the tested LMs (Fig. 1b,c,d), we believe that the non-polar end of the alcohols acts as the main protective group to interact with surface of LMs and to prevent recombination. The -CH$_3$ region of the alcohol molecules is absorbed on the LM surface, with its hydrophilic (-OH) group sticking out interacting with water to help solvate the entire system.
Consistent with experiment result, a larger co-solvent molecule (e.g. TBA vs. MET) would then provide a larger steric repulsion to promote the exfoliation.

We conclude that Young’s equation along with contact angle measurements can be used to evaluate the solid-liquid interfacial energy and predict the optimal exfoliation co-solvent concentration. We have shown that the interfacial energy in conjunction with steric repulsion can qualitatively predict the exfoliation efficiency of mixed solvent system. Our study provides the critical insight into the exfoliation of LMs, and defines a rational strategy for the design of an environmentally friendly pathway to high yield exfoliation of LMs. In particular, it is important to note that the addition of 10-30 w% of t-butyl alcohol or isopropanol into water can greatly increase the exfoliation yield of both graphite and MoS$_2$. The low concentration of co-solvent presented here is relevant for large scale industrial applications as the majority of our solvent is water. This reduces both the cost and many safety hazards. In addition, these solvents have a much lower boiling point compared to other commonly used liquid exfoliation solvents such as NMP (bp. 300 °C). Processing the material after exfoliation would be easier as it is possible to evaporate the solvents through gentler heating compared to the high boiling point solvents.

Methods

**Solvent mixture.** Methanol (≥99.5 %), Ethanol (≥99.9 %), Isopropanol (≥99.5 %) and T-butylalcohol (≥99 %) was mixed with de-ionized water. Surface tension of the solvent-mixture was obtained from CRC Handbook 83rd ed[23] and ref. 24 at 25°C.

**Contact angle measurement.** HOPG graphite purchased from nanosurf and natural single crystal MoS$_2$ was purchased Wolfrrn Camp Mine, Australia. Layered material was used after rinsing with acetone and isopropanol, and vacuum dried at 100 °C. Contact angle measurement was measured at 20 °C. Data was averaged over 5 data points.
Exfoliation. 10 mg of powder graphite (>99 %) or MoS$_2$ (> 99 %) sample was added to a 2 dram (1/4 oz) glass vial. Then 5 mL of water/alcohol mixtures with weight fraction of 0 to 100 w% was added as dispersion solvent. Samples were batch sonicated for 3 hours with each sample placed in different position in the sonic bath every ½ hour cycle to give uniform power distribution. In call cases, solution was sonicated in VWR B2500A-DTH model sonic bath at high setting. The resulting dispersion was centrifuged using Eppendorf MiniSpin Plus centrifuge at 14,500 rpm for 5 minutes. The supernatant was decanted by pipette followed by another centrifugation at 14,500rpm for 15 minutes to further remove non-exfoliated materials and the absorbance of graphite and MoS$_2$ was taken at 260 nm and 385 nm, respectively. Data was averaged over 5 experiments.

Materials characterization. Absorbance spectrum of the exfoliated materials was obtained using DU800 UV-vis spectrometer in a quartz cuvette (path length 1cm) purchased from Starna Cell Inc. AFM samples were prepared on Si substrate. A solution of exfoliated LMs was mixed with isopropanol and 1-butanol which was then added drop wise onto a distilled water surface. Free-standing film of dispersed exfoliated LMs on water surface was then scooped onto the Si-wafer surface. TEM images were carried out on an FEI CM120 transmission electron microscope operating at 120 kV. HRTEM images were taken on an FEI Titan transmission electron microscope operated at 300 kV.
Supporting Information

1. SEM image of the exfoliated graphite and MoS$_2$

![SEM image of exfoliated graphite and MoS$_2$](image)

**Figure S11** a. SEM image of the exfoliated graphene flakes and b. MoS$_2$ flakes. Scale bar 500 nm.

2. Solvent concentration change during sonication exfoliation

![Graph of solvent concentration change](image)
**Figure S2I a.** Absorbance calibration curve (at 1200 nm) of IPA-Water mixture normalized with pure water. **b.** Concentration change of 70, 50 and 30 w% IPA solutions over time. We observed that after 3 hours of sonication, concentration decreased from 67 w% to 56 w%, 52 w% to 44 w% and 29 w% to 21 w%. **c,d.** Absorbance of exfoliated graphite and MoS$_2$ before solvent evaporation correction. Using the evaporation profile above, surface tension was re-calculated. The corrected graphs are shown in Fig. 3c,f.

3. Co-solvent exfoliation of MoO$_3$ and NbSe$_2$.

**Figure S3I** Absorbance of 3-hour exfoliated MoO$_3$ (675 nm) and NbSe$_2$ (400 nm) in water-IPA co-solvent system. Absorbance of the exfoliated materials is plotted against surface tension, exhibiting a similar trend to that of graphite and MoS$_2$. Absorption peaks around 25-33 mJ/m$^2$ for MoO$_3$ and around 22-28 mJ/m$^2$ for NbSe$_2$ were found.
4. Evaporation effect on contact angle measurements and surface energy determination

**Figure S4**

(a) Droplet volume change over time for various IPA-water mixtures. The corresponding labelled number is the IPA concentration. The contact angle measurement was typically taken around 10-15 sec. Solid lines are guide to the eye. 

(b) Concentration profile of IPA-water mixture after a similar evaporation loss in a Petri dish.

(c) The corrected $\gamma_{lg}\cos\theta_c$ vs. $\gamma_{lg}$ plot after considering the evaporation loss shows a shift of the peak toward left ("negative shift").

It is noted that the peak exfoliation position shift to the left compared to the peak surface energy plot. This difference might be largely attributed to the solvent evaporation effect during the contact angle measurements. Due to the relatively small liquid droplets and large surface to volume ratio, this evaporation can be quite significant especially for the higher alcohol concentration solvents. In general, this evaporation causes the lowering of alcohol concentration and an overestimation of the expected contact angle for a nominal solvent composition. In the other words, for a contact angle determined for a given nominal solvent composition, the actual solvent composition would have less alcohol than the nominal composition.
To evaluate the impact of the solvent evaporation during the contact angle measurement, we have used IPA/water systems as one example, and measured the liquid droplet volume change over a 1 minute period of contact angle measurement, in which an evaporation loss as a large as ~60% was observed for high alcohol concentration solvents (Fig. S4a). For a typical contact angle measurement takes ~10-15 s, there is a volume loss of ~10-20% for high alcohol concentration solvent.

Since it is difficult to determine the exact solvent composition in such a small droplet (~1 mm diameter) during the contact angle measurement, we have tried to replicate the evaporation profile in a petri dish with larger amount of solvents, and determined the solvent compositions after the evaporation loss of a similar volume percentage (Fig. S4b). Based on the corrected solvent composition, we can re-calculate $\gamma_{lg}$ and $\gamma_{lg}\cos\theta_c$ to produce a corrected plot of $\gamma_{lg}\cos\theta_c$ vs. $\gamma_{lg}$, which shows a left shift of the peak position (Fig. S4c). The initial peak position at ~32 mJ/m$^2$ shifts to ~29 mJ/m$^2$, which is closer to the observed exfoliation peak (Fig. S4c, blue line).
References


5. Yu, W., et al., Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters, *Nat. Mater. advance online publication*, 16-12-2012 (DOI: 10.1038/NMAT3518)


In this chapter, we will discuss the lattice dynamics of MoS$_2$ and similar structures through a simple-minded approach to the theory of lattice vibration. A full treatment of the lattice dynamics would demand he comparatively sophisticated methods comparable to the work of Livneh and Spanier$^1$. However, the complexity of the method can mask our basic understanding of the vibration modes.

The general theory presented below follow very closely to the work by Bromley et al$^2$ with a few substitutions to improve its accuracy in respect to MoS$_2$. Bromley et al, through certain simplifying assumptions, follow the elementary approach of the Born-von Karman method (Born and Huang 1954)$^3$. Using well documented crystallographic data$^{4,5}$ as well as simplification of consider only nearest-neighbor interaction, we can reconstruct an intuitive picture of the vibration modes of MoS$_2$ with surprising accuracy. Later, we will apply this simplified model on the vibration of WS$_{2-x}$Se$_x$ and draw conclusion on its structure.

**General Theory, 1L-Model**

We shall consider a single layer of the crystal structure (1L-Model)$^2$, which is of hexagonal symmetry. The monolayer assumption is reasonable, as the intralayer bonding is considerably weaker compared to the interlayer bonding. This assumption is justified by various experimental result of the vibration modes of MoS$_2$ where the intralayer vibration is almost 10x smaller (30 cm$^{-1}$ and 50 cm$^{-1}$) compared to the natural vibration modes (~400 cm$^{-1}$)$^6$. Although the lattice
itself must be described by reference to its (non-orthogonal) crystallographic axis, the lattice dynamics will be treated in a Cartesian coordinate system.

**Figure 4.1 Cartesian coordinate (i,j,k) and crystallographic axis of MoS2 (x,y,z).** Position of the metal atoms can be expressed as $i(2n-m)a/2 - j\sqrt{3}ma/2$ and the position of the Sulfur atom can be expressed as $i(2n-m+1)a/2 - j\sqrt{3}(3m-1)a/6 \pm k u$. $a$ represent the latteral Mo-Mo and S-S distance, $u$ represent the half of the vertical S-S bond distance. Through crystallographic analysis, it was found that the Mo-S-S angle ($\theta$) is equal to 48.56°.

Thus the unit cell $(m, n)$, referred to the crystallographic axes, contains atoms whose mean positions in Cartesian coordinates are $i(2n-m)a/2 - j\sqrt{3}ma/2$ for the metal and $i(2n-m+1)a/2 - j\sqrt{3}(3m-1)a/6 \pm k u$ for the non-metal atoms. The depth of the layer is $2u$, the vertical separation of the non-metal pair; hence the angle $\theta$ between the metal-ligand bond and the z direction is
such that \( \tan \theta = \frac{a}{\sqrt{3}u} \) (fig. 2). Through crystallographic data, we can calculate with great accuracy that the angle \( \theta \) to be 48.56\(^\circ\).

We may set up an expression for the elastic potential energy, \( V \), of the structure in an instantaneous configuration. Three force constants are involved in this expression: they are \( \alpha \) for the metal-metal bonds, \( \beta \) for the ligand-ligand bonds, and \( \gamma \) for the metal-ligand bonds. It is convenient to decompose \( \gamma \) into \( \gamma' = \sin^2 \theta \) and \( \gamma'' = \cos^2 \theta \). Differentiation of \( V \) with respect to a given instantaneous displacement gives the corresponding component of the restoring force acting on the relevant atom. We may thus obtain the equation of motion for small atomic displacement; in the coordinate system we are using, these equations occur in three sets, one for each (orthogonal) axis. Since we seek a harmonic solution of these equations we substitute for the coordinate of the atom \( l \) in the cell \((m,n)\) of the lattice the harmonic function:

\[
\psi^l(m, n) = \frac{A^l_i}{\sqrt{m_i}} e^{i(wt - \vec{k} \cdot \vec{r}_l(m, n, u))}
\]

Where

\[
(\psi^1, \psi^2, \psi^3) = (x, y, z)
\]

\[
A^l_i = (A_l, B_l, C_l)
\]

And \( l=1 \) for the Mo, \( l=2 \) for the S at +u and \( l=3 \) for the S at -u; \( m_i \) is the mass of the \( l \)th atom. In the exponential term, the cartesian coordinate \( \vec{r}_l(m, n, u) \) is Fourie transformed into the lattice coordinate by the dot product around the \( \Gamma, K, M \) point (\( \vec{k} \)) as seen in figure 3. For simplicity we separate the xyz axis.
By further algebra, we find that the equations of motion in the $x,y,z$ direction around the most intense vibration (Γ) are expressed in Table 1. Because both of the ligands are identical, we simplify $m_2=m_3$. A more general list of the equation of motion have been derived by Bromley et al are expressed in Table 2. The various $E_i$ are the moduli originated from the various phase factors in the brillouin zone. Majority of these terms are complex exponential resulting from the fourier transform, and only the moduli are expressed.

![Figure 4.2. Brillouin zone of a hexagonal lattice.](image)

<table>
<thead>
<tr>
<th>Symmetry points $(u,v,w)$</th>
<th>$[k_x,k_y,k_z]$</th>
<th>Point group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ: (0,0,0)</td>
<td>[0,0,0]</td>
<td>6/mmm</td>
</tr>
<tr>
<td>A: (0,0,1/2)</td>
<td>[0,0,π/u]</td>
<td>6/mmm</td>
</tr>
<tr>
<td>K: (2/3,1/3,0)</td>
<td>[4π/3a,0,0]</td>
<td>62m</td>
</tr>
<tr>
<td>H: (2/3,1/3,1/2)</td>
<td>[4π/3a,0,π/u]</td>
<td>62m</td>
</tr>
<tr>
<td>M: (1/2,0,0)</td>
<td>[π/a,−π/√3a,0]</td>
<td>mmm</td>
</tr>
<tr>
<td>L: (1/2,0,1/2)</td>
<td>[π/a,−π/√3a,π/u]</td>
<td>mmm</td>
</tr>
</tbody>
</table>

![Figure 4.3. Different vibrational mode associated with the MoS$_2$ vibration.](image)
Given that each axis is a 3x3 matrix, hand-calculation is possible to find the eigen value of each of the solution. Given that there are 3 symmetry point (Γ, K, M) and each consist of three (x,y,z) 3x3 matrix, 27 solutions of the eigenvalues are expressed below in Table 3. Symbol A,D,H correspond to the acoustic dipolar, and homopolar modes. We choose the ADH labeling system, because the proper symmetrical assignment of the 1L model is different than that of a bulk 2H-MoS$_2$. 
Table 4.1. Solution for the equation of motion for the first order vibration modes derived through the Born-von Kramer method. \( \alpha, \beta, \gamma \) are the bond force constants associated with Metal-Metal bond, Ligand-Ligand bond, and Metal-Ligand bond. \( \gamma' = \gamma \sin^2 \theta \), \( \gamma'' = \gamma \cos^2 \theta \). Label 1,2,3 refer to metal (1) and the two dichalcogenide atoms (2,3).
General solution, equation of motion

<table>
<thead>
<tr>
<th>X</th>
<th>( w^2 A_1 = \left( \frac{E_3 \alpha + 3 \gamma'}{m_1} \right) A_1 - \frac{3}{4} \frac{E_1 \gamma'}{\sqrt{m_1 m_2}} A_2 - \frac{3}{4} \frac{E_1 \gamma'}{\sqrt{m_1 m_2}} A_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>w^2 A_2 = -\frac{3}{4} \frac{E_1 \gamma'}{\sqrt{m_1 m_2}} A_1 + \left( \frac{E_3 \beta + \frac{3}{2} \gamma'}{m_2} \right) A_2</td>
<td>0</td>
</tr>
<tr>
<td>w^2 A_3 = -\frac{3}{4} \frac{E_1 \gamma'}{\sqrt{m_1 m_2}} A_1</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Y</th>
<th>( w^2 B_1 = \left( \frac{E_4 \alpha + 3 \gamma'}{m_1} \right) B_1 - \frac{1}{4} \frac{E_2 \gamma'}{\sqrt{m_1 m_2}} B_2 - \frac{1}{4} \frac{E_2 \gamma'}{\sqrt{m_1 m_2}} B_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>w^2 B_2 = -\frac{1}{4} \frac{E_2 \gamma'}{\sqrt{m_1 m_2}} B_1 + \left( \frac{E_4 \beta + \frac{3}{2} \gamma'}{m_2} \right) B_2</td>
<td>0</td>
</tr>
<tr>
<td>w^2 B_3 = -\frac{1}{4} \frac{E_2 \gamma'}{\sqrt{m_1 m_2}} B_1</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Z</th>
<th>( w^2 C_1 = \frac{6 \gamma''}{m_1} C_1 - \frac{E_5 \gamma''}{\sqrt{m_1 m_2}} C_2 - \frac{E_5 \gamma''}{\sqrt{m_1 m_2}} C_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>w^2 C_2 = -\frac{E_5 \gamma''}{\sqrt{m_1 m_2}} C_1 + \left( \frac{\beta + 3 \gamma''}{m_2} \right) C_2 - \frac{\beta}{m_2} C_3</td>
<td></td>
</tr>
<tr>
<td>w^2 C_3 = -\frac{E_5 \gamma''}{\sqrt{m_1 m_2}} C_1 - \frac{\beta}{m_2} C_2 + \frac{\beta + 3 \gamma''}{m_2} C_3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E</th>
<th>( E_1 = 2 \cos \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_2 = 2(4 + 4 \cos \xi \cos \eta + \cos^2 \xi) \frac{1}{2} )</td>
<td></td>
</tr>
<tr>
<td>( E_3 = 5 - \cos \xi \cos \eta - 4 \cos^2 \xi )</td>
<td></td>
</tr>
<tr>
<td>( E_4 = 3 - 3 \cos \xi \cos \eta )</td>
<td></td>
</tr>
<tr>
<td>( E_5 = (1 + \cos \xi \cos \eta + 4 \cos^2 \xi) \frac{1}{2} )</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2. General solution for the equation of motion for the first order vibration modes.

Term \( k_x \) and \( k_y \) refers to the symmetry points given in Figure 2.
Table 4.3. Eigen values obtained from the equation of motion for different Brillouin Zone.
Result and Analysis

Figure 4.4. Atomic motion corresponding to the E\textsubscript{12g} and A\textsubscript{1g} vibration modes and the corresponding mathematical description of its vibration. The angular frequency squared is expressed in term of its bond force constant and effective mass. The equation provides an intuitive picture of the nature of its vibration.

Consider the vibrational frequency observed for phonon mode E\textsubscript{12g} and A\textsubscript{1g} (Figure 4). The equation appropriately expresses motion of the metal and ligand. E\textsubscript{12g} phonon is caused by six equivalents of the x-component of the Mo-S bonds (\(\gamma'\)). Because 4 of the Mo-S bond forms 60° angle with the direction of motion, these bonds have to be multiplied by a factor of ¼, resulting in a factor of 3\(\gamma'\). The effective mass \(\mu\) for the E\textsubscript{12g} motion can be simplified as one mass of Mo connected with symmetrically vibrating S atoms. Thus \(1/\mu\) can be written as the sum as \(1/m_{Mo} + 1/2m_S\). Similarly, the A\textsubscript{1g} motion equation is also reasonable. The total force constant for A\textsubscript{1g} mode must be an addition of the z-component of the Mo-S bond as well as the vertical S-S bond. The entire bond force constant is then divided by the effective mass of 2m\(_S\).
Due to its intensity, $\gamma$ can be extracted from the E$_{2g}^1$ peak and $\beta$ can be extracted from the A$_{1g}$ peak using the equation:

$$\gamma = \frac{\left(w_{E_{2g}^1}\right)^2 \mu}{3 \cos^2 \theta} = 196.75 \frac{N}{m}$$

$$\beta = \left(\left(w_{A_{1g}}\right)^2 m_2\right) - 3\gamma \sin^2 \theta = 27.52 \frac{N}{m}$$

Based on this simple model, we can estimate that the Mo-S bond is approximately 197 N/m and the S-S bond is considerably weaker at 27.5 N/m. In comparison, other calculations have shown that the shear intralayer bond force constant is 2.7 N/m and the compression intralayer bond force constant is 7.4$^{6,10}$. 

From the magnitude of forces, we can see where the 1L-Model will have the greatest error compare to bulk. The Mo-S bond force constant is more than 1 order of magnitude greater than the shear or compression intralayer bond force constant. This indicate these vibration is largely unaffected between bulk and 1L. However, the S-S bond is sufficiently weak that we should expect at it may show the largest variation/error when compared with bulk.

In earlier structural analysis, we estimated that the Mo-S bond is partially ionic in nature, given that the S radius in MoS$_2$ is approximately 85.95% the radius of purely S$^2-$ ion$^{4,11}$. Using coulombic interaction, we can further estimate the ionic nature of the Mo-S bond

$$\frac{dF}{dr} = -2keqMoqS \frac{q_S^2}{r^3} = 4keqS \frac{q_S^2}{r_0^3} \approx -\gamma$$

Estimation of the effective ionic characteristic can be done given for very small displacement. For a small displacement, we will be concern with dF/dr where r is equal to the Mo-S bond
length of 2.41 Å. We also know that the charge of Mo ($q_1$) and charge of S ($q_2$) must have the relation of $q_1 + 2q_2 = 0$ to make a neutrally charged crystal. Using these number, we can then estimate that the effective charge of the S anion in MoS$_2$ to be -1.73. Dividing this effective charge with -2, the full ionic charge of S, shows that the sulfur is 86.4% purely ionic. This number is surprisingly close to the observed radius ratio of 85.95%.

![Figure 4.5. Relationship of bond length and bond force constant for disulfide bonds using Badger's empirical relationship](image)

**Figure 4.5. Relationship of bond length and bond force constant for disulfide bonds using Badger’s empirical relationship** (see Supporting information). Data for various disulfides bonds (black) are taken from ref. 7. MoS$_2$ data (red) follows the trend observed. The weak disulfide bonds observed in MoS$_2$ of ~27.5N/m is due to the increase in bond length.

It is useful to recall the work by Steudel$^{7,8}$ and Badger$^9$. Steudel summarize the S-S bond force constant with respect to its bond length for a variety of disulfide bonds. Using Badger’s
empirical relation between bond length and bond force constant and data by Steudel, the relationship between the two parameters can be expressed as (Figure 5):

$$\log(r_{SS} - 1.180) = 0.23\pm 0.01 - 2.76\pm 0.08 \log(f_{SS})$$

Where $r_{SS}$ is the disulfide bonds (Å) and $f_{SS}$ is the disulfide bond force constant (mdyne/Å).

It is known that the bond force constant in S₈ is roughly 220 N/m⁸,⁹, a much larger number compared to the calculated bond force constant of 27.5 N/m in MoS₂. At first glance, it appears that the bond is incredibly weak. Using the Badger’s relation, however, we can see that the decrease in the bond force constant appears to originate solely due to the increase between the S-S distance. This relationship will be useful to approximate changes in the bond length due to chemical reaction.

**Comparison to Experiment and Other Model**

All of the vibration modes are calculated, using the bond force constant derived through the A₁g and E₂g vibration modes. Specifically, we used $\alpha=0$ N/m, $\beta=27.5$ N/m and $\gamma=196.75$ N/m. We chose the value of 0 for $\alpha$, because the two Mo atoms are not in contact with one another (Figure 1). Considering that the hard sphere radius of the Mo atoms are roughly 0.8 Å and are separated by a distance of 3.16 Å⁴, we hypothesize that they don’t make a significant bond with one another. The result of the calculation is shown in Table 4.
<table>
<thead>
<tr>
<th>Point</th>
<th>Branch</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ</td>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>382.7</td>
<td></td>
<td>477.8</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>296.3</td>
<td></td>
<td>407.4</td>
</tr>
<tr>
<td>K</td>
<td>A</td>
<td>595.8</td>
<td></td>
<td>302.4</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>159.1</td>
<td></td>
<td>369.9</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>391.6</td>
<td></td>
<td>407.4</td>
</tr>
<tr>
<td>M</td>
<td>A</td>
<td>170.7</td>
<td>Complex number</td>
<td>Complex number</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>382.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>341.9</td>
<td>418.5</td>
<td>407.4</td>
</tr>
</tbody>
</table>

Table 4.4. Vibrational frequency calculated from the equations in Table 3, units are in cm\(^{-1}\).

Bond force constants $\beta$ and $\gamma$ was derived from the $A_{1g}$ and $E_{2g}$ peaks. $\alpha$ was assumed to be zero. $\alpha=0$ N/m, $\beta=27.5$ N/m and $\gamma=196.75$ N/m.

We then compare the different vibration modes with experimental result of the Raman vibration of MoS\(_2\) using 514nm laser at room temperature (Figure 6). We then label each of the observed vibration modes with the calculated value using the 1L-Model. We then compare the result with the more sophisticated method derived by Lyneh & Spanier\(^1\). Whenever possible, we will attach the appropriate possible vibration modes with its proper symmetry assignment by comparing it with the result of Lyneh & Spanier\(^1\) (Table 5). In several second order processes, we use the value of $B_{2g}^2$ (58 cm\(^{-1}\)) and $E_{2u}^2$ (35 cm\(^{-1}\)) and combined it with the result obtained from the 1L-model.
Figure 4.6. Vibration mode of MoS2 at room temperature using 514nm laser. Graph is presented in Log-intensity to enhance visibility of low-intensity peaks. Tabulated data of observed peaks are given in Table 5.
<table>
<thead>
<tr>
<th>MEASURED DATA</th>
<th>1L-MODEL</th>
<th>LABEL</th>
<th>LIVNEH &amp; SPANIER</th>
<th>LABEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>156.2</td>
<td>159.1</td>
<td>MD&lt;sub&gt;xy&lt;/sub&gt;</td>
<td>156</td>
<td>E&lt;sup&gt;2&lt;/sup&gt;&lt;sub&gt;1uM&lt;/sub&gt;2</td>
</tr>
<tr>
<td>177.20</td>
<td>170.7</td>
<td>KA&lt;sub&gt;xy&lt;/sub&gt;</td>
<td>174, 184</td>
<td>B&lt;sup&gt;2gM&lt;/sup&gt;, B&lt;sup&gt;2gK&lt;/sup&gt;</td>
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<tr>
<td>189.26</td>
<td></td>
<td></td>
<td>190, 188,</td>
<td>E&lt;sup&gt;2&lt;/sup&gt;&lt;sub&gt;1uK&lt;/sub&gt;1, E&lt;sup&gt;2&lt;/sup&gt;&lt;sub&gt;2gK&lt;/sub&gt;1</td>
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<tr>
<td>(?)207.62</td>
<td></td>
<td></td>
<td>286</td>
<td>E&lt;sub&gt;1g&lt;/sub&gt;</td>
</tr>
<tr>
<td>285.66</td>
<td></td>
<td>296.3 (silent)</td>
<td>297 (silent)</td>
<td>E&lt;sub&gt;2u&lt;/sub&gt;</td>
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<tr>
<td>(?)320.64</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>382.72</td>
<td>382.7</td>
<td>ΓD&lt;sub&gt;xy&lt;/sub&gt;, KD&lt;sub&gt;x&lt;/sub&gt;</td>
<td>383, 384, 385</td>
<td>E&lt;sup&gt;2g&lt;/sup&gt;, E&lt;sub&gt;1u, E&lt;sup&gt;1g&lt;/sup&gt;K&lt;/sub&gt;2</td>
</tr>
<tr>
<td>407.40</td>
<td>407.4</td>
<td>ΓH&lt;sub&gt;x&lt;/sub&gt;, KH&lt;sub&gt;z&lt;/sub&gt;, MH&lt;sub&gt;z&lt;/sub&gt;</td>
<td>(475-58) =417,</td>
<td>B&lt;sup&gt;1g&lt;/sup&gt;-B&lt;sup&gt;2g&lt;/sup&gt;</td>
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<tr>
<td>422.79</td>
<td>418.5</td>
<td>KH&lt;sub&gt;y&lt;/sub&gt;</td>
<td>(383+35) =418</td>
<td>E&lt;sup&gt;2g&lt;/sup&gt;+E&lt;sup&gt;1g&lt;/sup&gt;</td>
</tr>
<tr>
<td>451.64</td>
<td>(407.4+35) =442</td>
<td>ΓH&lt;sub&gt;x&lt;/sub&gt;+E&lt;sup&gt;2g&lt;/sup&gt;</td>
<td>(35+409) =444,</td>
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<td>ΓD&lt;sub&gt;z&lt;/sub&gt;</td>
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<td>E&lt;sup&gt;1g&lt;/sup&gt;+B&lt;sup&gt;2g&lt;/sup&gt;</td>
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<tr>
<td>(?)531.45</td>
<td>(477.8+58) =535.8</td>
<td>ΓD&lt;sub&gt;z&lt;/sub&gt;+B&lt;sup&gt;1g&lt;/sup&gt;</td>
<td>(58+475) =533</td>
<td>B&lt;sup&gt;2g&lt;/sup&gt;-B&lt;sup&gt;1g&lt;/sup&gt;</td>
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<td>(?)560.48</td>
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<td>569.53</td>
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<td>(286+286) =572</td>
<td>E&lt;sub&gt;1g&lt;/sub&gt;+E&lt;sub&gt;1g&lt;/sub&gt;</td>
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<td>(?)588.79</td>
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<td>599.61</td>
<td>(296.3+296.3) =592.6</td>
<td>ΓH&lt;sub&gt;xy&lt;/sub&gt;+ΓH&lt;sub&gt;xy&lt;/sub&gt;</td>
<td>(297+297) =594</td>
<td>E&lt;sub&gt;2u&lt;/sub&gt;+E&lt;sub&gt;2u&lt;/sub&gt;</td>
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<td>(?)616.40</td>
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<td>654.03</td>
<td></td>
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<tr>
<td>674.86</td>
<td>(296.3+382.7) =679</td>
<td>ΓH&lt;sub&gt;xy&lt;/sub&gt;+ΓD&lt;sub&gt;xy&lt;/sub&gt;</td>
<td>(286+383) =669</td>
<td>E&lt;sub&gt;1g&lt;/sub&gt;+E&lt;sub&gt;1g&lt;/sub&gt;</td>
</tr>
<tr>
<td>705.10</td>
<td>(296.3+407.4) =703.7</td>
<td>ΓH&lt;sub&gt;xy&lt;/sub&gt;+ΓH&lt;sub&gt;xy&lt;/sub&gt;</td>
<td>(286+409) =695</td>
<td>E&lt;sub&gt;1g&lt;/sub&gt;-A&lt;sub&gt;1g&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Table 4.5. Raman shift of MoS2 and calculation result of the 1T-Model. Calculation result of the 1L-Model is compared to the observed values and result from reference ___. Whenever appropriate, possible symmetry assignment is given. 1T-Model shows ~0-4% error compared to measured result, while more sophisticated method by Livneh & Spanier show ~0-3% error.
The result of the 1L-Model shows a remarkable accuracy comparable to that by Livneh & Spanier from the value of 200 to 700 cm\(^{-1}\). The major error is located between \(E_{1g}\) and \(E_{2u}\) which correspond to 285 cm\(^{-1}\) and 296 cm\(^{-1}\). In this particular vibration mode, the 1L-Model does not distinguish between the two symmetries. As a result, only \(E_{2u}\) mode can be calculated in the 1L-Model. Other common splitting due to multi-layer interaction are provided in supporting information.

In general, the error between the model with the actual calculated value close to 2-4\%, which is comparable to Livneh & Spanier of 1-3\%. This show that the 1L-Model can serve as a good starting point to understand the nature of the vibration, and more importantly, how it will change upon additional stress, chemical substitution, or reaction.

**Conclusion**

The 1L-Model is an intuitive and accurate model to understand the vibration modes of MoS\(_2\). By simplifying the system, it is possible to reduce the vibration into simple interconnecting bond force constants. By doing so, we can understand the nature of the vibration by evaluating the changes in its Raman spectrum. We found that it is also comparably accurate with respect to other more complicated models, with a deviation of 0-4\% from measured values,

The model is also highly flexible and can be applied to any hexagonally symmetrical crystals such as graphite or hexagonal boron nitride. We can also use this model and expand it to intuitively evaluate TMDs with S/Se alloy as shown later in this chapter.
Vibration mode of WS$_{2-x}$Se$_x$ alloy and application of the 1L-Model

![Diagram of WS/Se2 model](Image)

**Figure 4.7. Expanded model of WS/Se2.** The model involves three unit cells A,B,C each involves 1 Metal atom and 2 Ligands. The model of equation of motion is based on the Crystallographic coordinate (x,y,z) instead of the Cartesian coordinate (i,j,k). ● represents metal atoms and ○ represents the ligands.

We shall consider a single layer of the crystal structure, which is of hexagonal symmetry. In this model, we assume that the inter-layer bonding is due to weak van der Walls forces that may be neglected. This approximation is reasonable because raman spectroscopy in MoS$_2$ shows that the interlayer vibration mode have an energy of $\sim 30 \text{cm}^{-1}$ and $50 \text{cm}^{-1}$ which yields to $\sim 2.5 \text{N/m}$ and $7.8 \text{N/m}$ of effective force constant$^{6,10}$. This value is roughly 1 order of magnitude lower than the interlayer forces.
Solving the equation of motion, we obtain three 9x9 matrices (Supporting info Table 5), which refers to the motion in the x,y,z directions. Three force constants are involved in this expression: they are α for the metal-metal bonds, β for the ligand-ligand bonds and γ for the metal-ligand bonds. In order to account both the crystallographic change and bond strength change between pure WS2 and WSe2, we approximate that the force constant varies linearly as a function of composition, with the exception of α, which we set the value to 0 N/m. The force constant of the non-metal bond used are \( \beta_{\text{pure WS2}} = 35.1 \text{N/m} \) and \( \beta_{\text{pure WSe2}} = 29.4 \text{ N/m} \). The force constant for the metal-ligand bond used are \( \gamma_{\text{pure WS2}} = 206 \text{ N/m} \) and \( \gamma_{\text{pure WSe2}} = 182 \text{ N/m} \). These values are calculated based on the \( E_{2g} \) peaks (356 cm\(^{-1}\) and 248 cm\(^{-1}\)) and \( A_{1g} \) peaks (420 cm\(^{-1}\) and 252 cm\(^{-1}\)) following Bromley et al. calculation, and data from reference 12\(^{12}\). It is convenient to express the γ movement in the x and y direction as \( \gamma' = \gamma \sin^2 \theta \), and in the z direction as \( \gamma'' = \gamma \cos^2 \theta \). These values are the average force constant of WS\(_2\) and WSe\(_2\) obtained from analyzing the vibrational frequencies of pure WS\(_2\) and WSe\(_2\) using the same treatment done with MoS\(_2\) (Figure 8). We set the value of α to zero because the metal-metal distance are very large \( \sim 3 \text{ Å} \), and they do not have direct contact. We take account only the nearest neighbor interaction/force constants.
Figure 4.8. Raman shift of WS\textsubscript{2} and WSe\textsubscript{2} from bulk to mono layer. From the 1T-Model the bond force constant $\beta$, $\gamma$ of WS\textsubscript{2} are found to be 29.34 N/m and 195.4 N/m respectively. Bond force constants $\beta$, $\gamma$ of WSe\textsubscript{2} are found to be 29.34 N/m and 182.3 N/m. These numbers will be used for further calculation. Image taken from ref. 12

This model of WS\textsubscript{2}-WSe\textsubscript{2} model follows closely works by Bromley\textsuperscript{2} as explained in earlier section. The exact detail and derivation is very closely follow their work. In this we will only expand on the modification to their model: instead of solving a 3x3 equation of motion, which consists of 1 metal atom and 2 non-metals, we use a 9x9 matrix to account for the substitution of Sulfur / Selenium which consists of 3 metals and 6 non-metal atoms.
There are 7 masses in this matrices, where \( m_1 \) refers to the mass of the metal atoms, and \( m_2 \) refers to the masses of the ligands. We can then substitute \( m_2 \) with the mass of either Sulfur or Selenium, and apply the appropriate bond force constant of metal-ligand bond. The construct of S/Se composition around the transition metal can be seen in Figure 2.

Mathematically, we can then construct an equation of motion such as:

\[
\omega^2 A_1 - \lambda = 0 = \frac{3\alpha + 3\gamma'}{\sqrt{m_1 m_3}} A_1 + \frac{-3\gamma'}{\sqrt{m_1 m_2}} A_2 + \frac{-3\gamma'}{\sqrt{m_1 m_3}} A_3 + \frac{-3\alpha}{\sqrt{m_1 m_4}} B_1 + \frac{-3\gamma'}{\sqrt{m_1 m_5}} B_2 + \frac{-3\gamma'}{\sqrt{m_1 m_5}} B_3 + \frac{-3\alpha}{\sqrt{m_1 m_5}} C_1
\]

A full list of the 9x9 matrices for the equation of motion of WS-Se substituted compounds are given in supporting information.

---

**Figure 4.9. Model of substitution of S/Se involving three unit cells A,B,C.**
There are only 1 possible combination for both pure S and Se, 1 combination for 1 substitution, 3 combinations for 2 and 3 substitution. In total, there are 13 configurations.
Given that there are 6 positions that can be filled with either S or Se, we should then expect that there are 64 different possible combinations. To simplify the calculation we considered the various equivalent structures for removal. For example, because all of the sites are identical, there is only 1 distinct structure associated with 1 substitution of S/Se. We found that the possible and distinct variations are: 1,1,3,3 for 0, 1, 2, 3 substitution (Figure 9).

Removing the degenerate states, we found that there are in total 13 different configurations corresponding to pure Sulfur to pure Selenium compounds. We solved for the eigenvalues of these matrices. We then calculated the wave number $\bar{v}$ from the eigenvalues, where it correspond to the vibrational peaks in the relation $\lambda = \omega^2 = (2\pi\bar{v}c)^2$.

**Results of Simulation**

Table 6 shows the calculated solution of the frequencies. This data does not, however, take into account the selection rules associated with Raman/IR spectroscopy, nor its relative intensity. The highlighted part of the table shows the $E_{2g}$ peak transition (355 – 248 cm$^{-1}$), and $A_{1g}$ peak transition (420 – 253 cm$^{-1}$). We found that the frequency does not necessarily varies gradually with concentration, but rather split into some separate distinct frequencies. That is, the frequency observed are very atomistic in nature. The different possible configuration will produce its own vibrational frequency albeit small in intensity, and are also highly degenerate between different configurations.

In general, we found that frequency of WSe$_2$ peak will increase as the sulfur content increase, and the frequency of the WS$_2$ peak will decrease as the selenium content increase. Our calculation show that upon mixing, the solution to the eigenvalue / frequency becomes an imaginary number. This indicates that the mismatch in the natural frequency of S vs Se caused a dampening effect. The faster vibration of the S atoms, cause the Se atom to vibrate slightly
faster. On the other hand, because the Se atoms are slower, it decreases the movement of the S atoms.

In the case of $A_{1g}$ peak, our model shows that the frequency changes very gradually from pure WSe$_2$ at a frequency $\sim 248$ cm$^{-1}$ for 100%Se to 268 cm$^{-1}$ for a composition of 33% Se. During this decrease in Se composition, the intensity of this peak also quickly decreases at 33% composition. On the other hand, the frequency of the $A_{1g}$ peak decrease from 421 cm$^{-1}$ for pure WS$_2$, to a value of 376 cm$^{-1}$ at 13% sulfur. However, the intensity of the WS$_2$ $A_{1g}$ peak persist even at low sulfur content. This may be due to the inherently more intense signal of this peak compared to other. Similar observation can be made for the KA$_x$ vibration mode (see Table 3) where it gradually increases as a function of sulfur content. Interestingly, however, our model shows that the $E_{2g}$ peak position of WS$_2$ remains relatively constant at 355 cm$^{-1}$.

### Table 4.6. Full result of Raman Shift calculated from model.

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<th>X, Y</th>
<th>6S-0Se</th>
<th>5S-1Se</th>
<th>4S-2Se</th>
<th>4S-2Se</th>
<th>3S-3Se</th>
<th>3S-3Se</th>
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<th>4S-2Se</th>
<th>3S-3Se</th>
<th>3S-3Se</th>
<th>3S-3Se</th>
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**Experimental synthesis and Analysis of WS$_{2-x}$Se$_x$**

Synthesis of WS$_{2-x}$Se$_x$ was carried out through chemical vapor deposition$^{13}$. Two quartz boat with 0.8 g WS$_2$ powder (Alfa Aesar, 99.8%) and 0.6 g WSe$_2$ powder (Alfa Aesar, 99.98%) were loaded at variable locations inside a 1-inch quartz tube in a horizontal tube furnace. A clean Si/SiO$_2$ substrate (~1 cm × 5 cm) was placed at downstream end of the furnace as the growth substrate. The system was purged with ultra-high purity argon (Ar) gas (Rizhen, ~99.999%) and then raised to the desired growth temperature.

**Figure 4.9. Characteristics of synthesis WS$_{2-x}$Se$_x$.** (a) optical microscope shows triangular geometry with a color associated to monolayer. (b,e) Photoluminesce change as a function as S/Se. (c,d) Uniformity of samples measured through photoluminescence. (f) AFM of a monolayer of WS$_{2-x}$Se$_x$. image taken from ref. 13.
The WS2 source and WSe2 source were placed at different locations in the quartz tube with an intrinsic temperature gradient inside the tube furnace. The ultra-high purity Ar gas is used as the carrier gas and the overall pressure inside the growth chamber is kept at 1 bar. To grow WS$_{2-x}$Se$_x$ nanosheets with increasing S atomic ratio, the temperature of WS2 source is gradually increased from 1155°C to 1194°C, while WSe2 source is reduced from 1194°C to 1100°C by controlling their exact locations inside the tube furnace, producing systematically tunable vapor pressure of WS2 and WSe2 and their relative ratio. Monolayer or few layer WS$_{2-x}$Se$_x$ alloy nanosheets with different compositions can thus be synthesized by controlling the equilibrium partial pressure ratio of WS2 and WSe2 (Figure 10).
The resulting alloy nanosheets are typically monolayers with a well-defined triangular shape, as identified by optical contrast and atomic force microscopy studies (Figure 1a and Figure S2). AFM shows that the triangular nanoparticles are sub-nanometer in height, consistent monolayer dichalcogenides. In addition, the highly intense photoluminescence shows that the particles are monolayer, as even bilayer will have a substantially quenched photoluminescence. The chemical composition of S/Se are determined using dispersive X-ray spectroscopy (EDS) elemental analysis (Figure 11). The uniform intensity obtained by EDS shows that composition of S/Se are quite uniform. The PL and raman spectroscopy of particles of known composition are then analyzed in order to find the trend and effect of S/Se substitution (Figure 12).
**Figure 4.12. Summary of Raman Shift of WS$_2$-xSex.** (a-d) Raman shift data that shows various peaks and its relative intensity. (d) Measured Raman shift position as a function of $\%\text{S/(S+Se)}$.

Image taken from ref. 13.

**Comparison of Model with WS$_2$-$x$Se$_x$.**

Observational data support the 1L-Model well. The 1L-Model successfully predict that the WS$_2$ $A_{1g}$ persist as a function of S/Se substitution and its raman shift gradually red shift as a function of increasing Se loading. Similar observation was found with the blue shift of the WSe$_2$ $A_{1g}$ peak with increasing S loading. Consistent with model, the WS$_2$ $E_{2g}$ peak also does not change much thoughout large composition change. In addition, the 1L-Model also predict that the KA$_x$ shift gradually change as a composition of S/Se changes.
The largest error / uncertainty in the model is the prediction of peaks around 200 cm$^{-1}$. These peaks were not observed experimentally. It should be noted that these peaks are very weak even for pure WS$_2$/WSe$_2$. Figure 8 shows, for example, that there are no observed peak in WSe$_2$ around these region.
Figure 4.13. Combination of 1L-Model with experimentally observed result. Clustering of model (grey) is an indication of highly probable observed peak. Note Emerging peak around 385 cm^{-1} that is not observed in either WS2 nor WSe2. Merging peak was expected around 175-225 cm^{-1}, but was too weak to detect. KAx vibration changes gradually from pure WS2 to WSe2 with no emerging peak, consistent with experimental observation.
These emergent peaks can be explained roughly by the expression of $A_{1g}$ by Bromley et al. The simple understanding of the origin of this expression is a combination of three M-L bond ($\gamma$) and a linear bond between two ligands ($\beta$). The combination of $m_2$ and $m_3$ correspond to the combination of the mass of S and Se. These will produce 3 separate frequencies depending on mass of ligands ($m_2$ and $m_3$) used in the equation. In Table 3, we present the calculated emergent Raman shifts. For the emergent peaks, we use the average of $\gamma''$ and $\beta$ of WS$_2$ and WSe$_2$.

$$\omega_{A_{1g}}^2 = \frac{3\gamma''}{m_2} + \beta\left(\frac{1}{m_2} + \frac{1}{m_3}\right)$$

**Figure 4.14. Vibrational expression of WS1S1 alloy.** $m_1$ represent the Metal atom and $m_2, m_3$ represents the Ligands. Solution to the frequencies of $E_{2g}$ and $A_{1g}$ peak by Bromley et al. which only involves 1 unit cell are shown. In our expanded model, there are three unit cells to express atomic substitution of S and Se atoms.
Table 4.7. Calculated Emergent Raman peak due to S/Se substitution.

<table>
<thead>
<tr>
<th>Combination</th>
<th>m2</th>
<th>m3</th>
<th>$\gamma''$ (N/m)</th>
<th>$\beta$ (N/m)</th>
<th>$\tilde{v}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure WS$_2$</td>
<td>S</td>
<td>S</td>
<td>118.21</td>
<td>35.11</td>
<td>420.21</td>
</tr>
<tr>
<td>Prediction</td>
<td>S</td>
<td>Se</td>
<td>110.41</td>
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<td>385.23</td>
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<tr>
<td>Pure WSe$_2$</td>
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<td>Se</td>
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</tbody>
</table>

It is clear from the model and experiment that the $A_{1g}$ peak will not shift continuously from the peak of pure WS$_2$(420cm$^{-1}$) to WSe$_2$(253cm$^{-1}$). Instead the peak will split into an emergent peak around 385cm$^{-1}$. These emergent peaks are due to the local condition of the mixing of S and Se. The intensity of these emergent peaks can be very weak is maximum at around 50% concentration where the probability of mixing is the highest. As expected, figure 4.12 shows that this Raman shift quickly emerge and then disappear.

**Conclusion.**

The vibrational frequency of WS/Se$_2$ substitution will not change continuously based on mixing composition. Instead the local composition will produce its own individual Raman spectrum. For example, a Metal atom surrounded by 1 S and 5 Se atom will have slightly different spectrum involving 3 S and 3 Se atoms. Our model shows that the $E_{2g}$ peak is highly affected by the presence of Se, and drops dramatically even with small presence of Se to a much lower frequency close to the frequency of pure WSe$_2$. The $A_{1g}$ peak, on the other hand, splits
into 4 peaks that is determined by the local environment. Two peaks should emerge around 385 cm$^{-1}$ and 280 cm$^{-1}$. 
Badger’s Empirical rule

Badger found that for a variety of diatomic atoms, the bond force constant \( f_0 \) and bond length \( r_e \) are found to have the relationship:

\[
f_0 \left( r_e - d_{ij} \right)^3 = C = 1.86 \times 10^5
\]

Where \( f_0 \) is expressed in dyn/cm, and \( r_e \) is expressed in Å. \( d_{ij} \) is a constant characteristic of all the diatomic molecules made up of one element in the \( i^{\text{th}} \) row and one in the \( j^{\text{th}} \) row of the periodic table. Very roughly speaking \( d_{ij} \) is the closest possible distance of a bond between two species, where \( r_e - d_{ij} \) is the dislocation from this initial condition. Given this we are attempting to evaluate a S-S bond, the relevant \( d_{ij} \) in this case is 1.180 as both sulfur atoms are of element in row 2.

<table>
<thead>
<tr>
<th>Type of Molecule</th>
<th>Atom ( i )</th>
<th>Atom ( j )</th>
<th>Examples</th>
<th>( d_{ij} )(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>( \text{H}_2 ), LiH, BeH(^+)</td>
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</tr>
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<td>H</td>
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**Supporting info Table 1.** List of \( d_{ii} \) for various 1st and second row elements.

To simplify the relationship, we modify the equation slightly. We will use \( r_e \) in Å, and \( f_{ss} \) in term of mdyne/Å (1 mdyne/Å=100 N/m). Constants \( C_1 \) and \( C_2 \) are empirically calculated:

\[
\log(r_{ss} - 1.180) = C_1 + C_2 \log(f_{ss})
\]
The data of S-S bonds are taken from the work of Steudel. Where $\nu_{SS}$ is the vibration S-S bond, $f_{\text{exp}}$ is experimentally derived from vibration mode, and $d_{SS}$ is the disulfide bond. We will add, in this case that the S-S bond force constant is calculated to be 0.275 mdyne/Å, and the bond length to be 3.16 Å.

<table>
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<th>$\nu_{SS}$ [cm$^{-1}$]</th>
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<th>$d_{SS}$ [Å]</th>
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<td>$\text{BaS}_2$</td>
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<tr>
<td>$S_2(^1\Lambda_u)$</td>
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<td>1.72</td>
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<td>$S_2(^3\Sigma_u^-)$</td>
<td>423</td>
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<td>$S_2O$</td>
<td>320</td>
<td>1.45</td>
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Supporting info Table 2. List of disulfide bonds and its bond force constants.

An empirical relation with MoS$_2$ is found to be:

$$\log(r_{SS} - 1.180) = 0.2304\pm 0.01 - 2.7624\pm 0.08 \log(f_{SS})$$

If MoS$_2$ is removed, the relationship can be expressed as:

$$\log(r_{SS} - 1.180) = 0.22\pm 0.01 - 2.93\pm 0.13 \log(f_{SS})$$

Percent difference between C$_1$ and C$_2$ are 4.4% and 6.0% respectively. This is comparable to the natural uncertainty of C$_1$ and C$_2$ which are both 4.4%. We conclude that the linear relationship is sufficiently robust and unchanged by the introduction of MoS$_2$. 

99
Math vibration modes with its appropriate symmetry assignment.

The vibration modes are selected based on the closest value to work by \( \text{___} \). We match the observed and calculated vibrational frequencies, and whenever possible, that also lies in the same Brillouin zone. Several possible matches modes may be given. Frequencies below 475 cm\(^{-1}\) are matched with Supporting info Table 3. Matching second order raman mode are compared with the data provided in table Supporting info Table 4. For example, the second order mode of \( E_{2u} + E_{2u} = 297 + 297 = 594 \text{ cm}^{-1} \). Similar result can be calculated using \( E_{2u} \) of our model.
<table>
<thead>
<tr>
<th>Band</th>
<th>Γ/D₃h</th>
<th>ν(cm⁻¹)*</th>
<th>Band</th>
<th>M/D₃h</th>
<th>ν(cm⁻¹)#</th>
<th>Band</th>
<th>K/D₃h</th>
<th>ν(cm⁻¹)#</th>
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<td>B₃₈</td>
<td>393</td>
<td>a</td>
<td>B¹₂₅ K</td>
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<td>A¹₂₀ M</td>
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<td>c</td>
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<td>B₁₈ M</td>
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<td>235</td>
<td>r</td>
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<td>E¹₀ M₂ (TA)</td>
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Supporting info Table 3. A list of phonons of 2H-MoS₂, their symmetry assignments and frequencies for high-symmetry point of Γ, M, K in the Brillouin zone. Obtained from ref. 1.
Supporting info Table 4. Raman (colored) and IR (white) active combinations for second-order processes from phonons at $\Gamma$ in 2H-MoS$_2$ measured at 300 K. The x sign denotes an inactive combination. Obtained from reference 1

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<th>Combination</th>
<th>A$_{1g}$ 409</th>
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<th>B$_{1g}$ 475</th>
<th>B$_{2g}$ 58</th>
<th>B$_{1u}$ 403</th>
<th>B$_{2u}$ 383</th>
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<th>E$_{1g}$ 384</th>
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<td>E$_{2g}$ 297</td>
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Graphical representation differences between Bulk vs. 1L MoS$_2$

The 1L-Model disregard the intralayer interaction. In real cases, these vibration modes will separate into at least 2 modes. One mode accounts for symmetric vibration between the top and bottom layer. The other mode accounts for asymmetrical vibration between the top and bottom layer. The symmetrical cases tend to be lower in frequencies compared to the asymmetrical cases.
Supporting info Figure 1. Comparison of the vibrational splitting of the 1L-Model vs. Bulk due to intralayer interaction. Image taken from ref 6.

Supporting info Table 5. Full list of 9x9 matrices of WS-Se mixture equation of motion

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<th>A_2</th>
<th>A_3</th>
<th>B_1</th>
<th>B_2</th>
<th>B_3</th>
<th>C_1</th>
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<td>ω^2A_3</td>
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References


5. Friend, R.H., Yoffee, A.D., Electronic properties of intercalation complexes of the transition


CHAPTER 5. Reactivity and Intercalation

In general, the metallic dichalcogenides such as TaS$_2$ and TiSe$_2$ will intercalate more easily, but with the group VI semiconductors such as MoS$_2$ it is more difficult to form organic intercalate complexes$^{18}$. Multiple works in the 1960s-1980s almost exclusively reported on Group IV and Group V organic intercalation$^{1-17}$. For almost 50 years, no new chemistry regarding MoS$_2$ and other Group VI TMDs have been discovered. With understanding of the basics of intercalation, we will attempt, in this work to describe a newly realized intercalation for MoS$_2$, other Group VI TMDs, and other layered compounds.

This work is predicated on the assumption that the intercalation reaction of TMDs follows the Charge Transfer Model, earlier presented in chapter 2. It was found that in TaS$_2$, whether the intercalated materials are alkali metals (Li, Na), transition metals (Ag, Cu) or nitrogen-based organic compounds (amine, pyridine), a redox reaction seems to be a driving force between the intercalation$^{1-17}$. The intercalants (Li or Amine) donates an electron density to the host TMDs creating a negatively charged layer (TaS$_2$$^{x-}$). A counter charged ion, such as Li$^+$ or R-NH$_3^+$ then inserts in between the layer to stabilize the entire structure. Due to the large size of the organic molecule, a large change in intralayer distance greatly increase.

The idea behind the organic electrochemical intercalation of MoS$_2$ was inspired by the work by Whiteside et al$^{18}$. The publication argued that gaseous ammonium radical (NH$_4^0$) behaves as a “pseudo alkali metal”. The gaseous ammonium radical shares several similar properties to gaseous alkali metals. These include its ionization energy, electronegativity, and its effective
charge, which roughly place ammonium radical somewhere between sodium (Na) and potassium (K).

That gave us the idea that, if ammonium radical is sufficiently stable, it will behave similarly to alkali metal and intercalate into TMDs. Upon reading this work, we attempted an electrochemical intercalation of MoS$_2$ with CTAB (cetyl trimethyl ammonium bromide), a quaternary ammonium compound frequently used as a surfactant. To our surprise, CTAB does form intercalation material with MoS$_2$, expanding its interlayer distance by ~ 9 Å, as observed through the visible expansion of the material, and later through XRD. We then began synthesis of a large variety of organic ammonium cations and tests its electrochemical properties as well as XRD properties.

We will begin this chapter by a review of what is currently known, electrochemically, of the charge transfer reaction of Li-MoS$_2$. It will then follow the experimental result and analysis, predominantly on the intercalation of CTAB-MoS$_2$. The carbon substituents used in this work are simple alkane (methyl- and hexadecyl-). However, the substituents are not necessarily limited to just simple alkanes. It is possible to attach an electronically active substituent onto the alkane chain (for example polycyclic aromatic hydrocarbons) and use the quaternary ammonium reaction as a driving force for intercalation.

**Review of Li-MoS$_2$ intercalation**

Mulhener et al$^{19}$ in 1989 combine chronopotentiometry and XRD study of MoS$_2$ intercalation and attempt to correlate the structure at a given applied potential and lithium loading. During the intercalation process, a small amount of Li is intercalated into MoS$_2$ until it reaches ~ +2 V (vs
Li/Li\(^+\)). Upto this point, the MoS\(_2\) still adopts a 2H- (trigonal prismatic) structure. Upon sufficient Li insertion at a potential of < 2 V (vs Li/Li\(^+\)), the MoS\(_2\) undergo a phase change into 1T- (octahedral) geometry (Fig 5.1). During the de-intercalation process, the crystal structure re-converts into a 2H- structure. However, the structural change occurred at ~ +2.5 V (vs Li/Li\(^+\)); a 0.5 V shift from the intercalation process.

The cyclic voltammetry of Li-MoS\(_2\) intercalation does not seems to change much after the first cycle. Work by Fang et al.\(^{20}\) shows that even after the 92\(^{\text{nd}}\) cycle, the cyclic voltammetry is not much different compared to the 2\(^{\text{nd}}\) onward. The first intercalation cycle, appears to be harder than the subsequent intercalation. The first intercalation occurred at ~+1V (vs. Li/Li\(^+\)). In comparison, the second cycle shows an intercalation peak at +2 and +1.25 V (vs. Li/Li\(^+\)). It is not too surprising that the first cycle requires more energy: the first intercalation requires a large energy barrier in separating the layers as well as a first nucleation point for 2H to 1T structural changes.

In all studies introduced\(^{19-21}\), as well as vibrational study\(^{22}\), there are multiple intercalation peaks found at 2.2, 1.9, 1.1, and 0.4 V (vs. Li/Li\(^+\)). As discussed earlier in Chapter 2, these distinct peaks occurred due to changes in redox potential of the Li-MoS\(_2\) complex that is caused by with the electrochemical potential changes of the host structure as it turns fr0m bulk into a Lithiated monolayers.
Figure 5.1. Electrochemical signature of Li-intercalation of MoS$_2$. Cyclic voltammetry of Li-MoS$_2$ (a) 1$^{st}$ to 5$^{th}$ cycle and (b) 91$^{st}$ and 92$^{nd}$ cycle are similar in shape, with the exception of the 1$^{st}$ cycle require a more negative potential for intercalation. Chronopotentiometry of Li-MoS$_2$ system with annotated crystal structure and amount of Lithium loading (c). Charge and discharge curve of Lithium into exfoliated MoS$_2$ nanosheet shows a step wise behavior indicating multiple electrochemical equilibrium potential. (a,d) was taken from ref. 21, (b) ref. 20, (c) ref. 19.

Reaction that occurred around 2 – 3 V (vs. Li/Li$^+$) have a large resemblance as a reaction between Lithium and Polysulfide (Fig. 5.2)$^{23,24}$. By comparing the intercalation reaction to reaction of Li-Sulfide battery we found that the redox reaction occurred at a very similar
potential of 2 – 2.5 V (vs. Li/Li⁺). One can then imagine that the reaction within this region is dominated by the charge transfer from Lithium into Sulfur. Chapter 3 discuss briefly that the effective charge of S in MoS₂ is roughly -1.7. The first portion of the reaction involves an electron transfer to create a full -2 charged S atoms. Observation have shown that the polysulfide-like reaction seems to stop at ~ 0.3 Li per MoS₂¹,¹⁹⁻²¹. This strongly suggest that during a reaction with lithium, electrons are first transferred into the orbitals of the S-atoms, causing it to be more ionic.

Figure 5.2. Comparison of Li-MoS₂ with Li-Polysulfide reaction. Large similarity of cyclic voltammetry of Li-MoS₂ intercalation with Li-polysulfide reaction between 1.6-3.0 V vs. Li/Li⁺. It indicates that the first reaction between Li & MoS₂ involves electron transfer to the S atoms. Figure (a) taken from ref. 21, (b) ref. 24

The first sets of redox potentials at 2.2 V (vs. Li/Li⁺) is not related to the intercalation reaction and is predominantly dominated by the Li and Sulfur reaction. True intercalation occurs at 1.1V
(vs. Li/Li\(^+\)), and lastly further applied potential is related to the reduction of the Molybdenum centers.

In conclusion, one can separate the reaction of Li-MoS\(_2\) into 3 general steps. First, the reaction is predominantly between Li and S at ~2.2V vs. Li/Li\(^+\). Further loading of Lithium would cause a true intercalation reaction that require a potential around ~1.1V vs. Li/Li\(^+\). Lastly, a full electron transfer from Mo\(^{4+}\) to Mo\(^0\) further progressed upon more Lithium loading at a potential ~0.6 V vs. Li/Li\(^+\). It can be expressed as:

\[
\begin{align*}
S & + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2S & \text{(approx. 2.2 V vs. Li/Li}^+) \\
\text{MoS}_2 & + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2 & \text{(approx. 1.1 V vs. Li/Li}^+) \\
\text{Li}_x\text{MoS}_2 & + (4-x)\text{Li}^+ + (4-x)e^- \rightarrow \text{Mo} + 2\text{Li}_2S & \text{(approx. 0.6 V vs. Li/Li}^+)
\end{align*}
\]

**Definition**

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**Figure 5.3. Labeling method for quaternary ammonium.** Number indicates the number of alkane chain, subscript indicate the quantity of the organic group.
Due to the number of tested ammonium compound, we will use the labeling system provided in figure 5.3. In general, the number of carbon in the “n”-alkyl chains will be represented by a number “n”, and the amount of that particular alkyl chain will be described as a subscript. For example, trimethyl hexadecyl ammonium bromide is labeled as $1_3N16Br$; triethyl ammonium hydrobromide is labeled as $2_3NHBr$; tetrabutylammonium bromide will be labeled as $4_3N4Br$.

**Experimental set up**

Experimental set up for an organic-MoS$_2$ intercalation follows a typical electrochemical set up. Quaternary ammonium bromides are dissolved in aprotic polar solvent, such as Acetonitrile and N-methyly pyrroldione. Typically, a large MoS$_2$ crystal is connected directly with a clamp and used as a working electrode. Graphite rod is used as a counter electrode. In general, Br$_2$/Br$^-$ redox reaction or Ag/Ag$^+$ are used as an internal reference. Conversion between Li/Li$^+$: SHE: Ag/Ag$^+$: Br/Br$^-$ is approximately -3V : 0.0 : +0.2 : +1.0. For example, +1V vs. Li/Li$^+$ observed for the intercalation of Li-MoS$_2$ is approximately equal to -2 V vs. SHE, -1.8 V vs. Ag/Ag$^+$, and -3 V vs. Br$_2$/Br$^-$.

The choice of solvent is crucial. We found that most typical solvents used in Lithium battery to work well, except for propylene carbonate. We found that polar protic solvents, such as alcohol, does not work as it degrades under the applied potential. Propylene carbonate was also unsuitable because it polymerizes when exposed to amines.
Figure 5.4. Typical electrochemical set up in MoS2 organic intercalation reaction (a).

Starting material of bulk intercalation are highly crystalline single crystal MoS2 (b). MoS2 layer visibly undergo a physical expansion before (c) and after (d) reaction, concurrent with Br2 production indicated by the orange/yellow solution.

Primary and tertiary ammonium was synthesized by mixing a primary alkylamine (H2NR) and tertiary alkylamine (NR3) with HBr. SN2 reaction of the concentrated strong acid with amine quickly produce heat and a white precipitate. After re-crystallization in acetonitrile, the purified compound is used in the electrochemical reaction. Specifically, hexadecylammonium bromide (13N16Br) and trimethylammonium bromide (13NHBr) was tested.

Quaternary ammonium bromides are synthesized using similar method. A stoichiometric amount of bromoalkene is mixed with a solution of trialkylamine dissolved in acetonitrile. We found that trimethylamine react reasonably fast within bromoalkene. Most compounds can be produced with 24 hours of heating at 70°C. Reaction involving triethylamine and triallylamine is
as expected, much slower. Depending on the length of the alkane chain a reaction at 70°C for several days are needed produce the final product. We found that trihexylamine would not react with bromoalkene, presumably due to the significantly higher steric repulsion.

We found that there are several notable observations that can be made. We observe that upon applied potential of ~3V or higher, a yellow liquid was formed on the graphite counter electrode. This is due to the Br₂ production on the cathode, given the choice of quaternary ammonium bromide. After prolonged reaction, the solution becomes yellow/orange in color. On the anode side, we observed that the silver/reflective MoS₂ surface quickly tarnish and darken. This tarnishing process, we found, are significantly faster for ammonium compound that produce intercalation compound. The MoS₂ also visibly thickens, indicating an intercalation process with significant lattice expansion. With a higher applied potential or higher temperature, we found that bubble formation can also be observed on the MoS₂ surface and the part of the alligator clip that are submerged into the solution. It appears that this gas formation is independent of the MoS₂ intercalation reaction. Lastly, with a long intercalation time involving CTAB and other long chained carbon, we found that the MoS₂ surface can be covered with a clear-gel substance.

X-ray diffraction and TGA data are collected from the bulk product of reacted MoS₂. Reaction of the bulk MoS₂ was generally allowed to proceed under constant potential for at least 4 hours before measurement was taken. The reacted product is then rinsed with acetonitrile and dried with compressed air.

PL and Raman spectroscopy are collected through reaction of mechanically peeled MoS₂. In general, mechanically peeled MoS₂ on gold coated SiO₂ are reacted by electrically connecting and submerging the SiO₂-Gold-MoS₂ into the reaction vessel. We found that the reaction
reached completion within seconds of applied potential. Excessive reaction time typically cause the gold/metal conductor coating to degrade/detach from the surface of the SiO$_2$ wafer.

**Physical Changes in Intercalation**

**Figure 5.5. Visible physical expansion of quaternary ammonium intercalated MoS$_2$.**

Before reaction, MoS$_2$ crystal is thin (a); it went a large expansion after reaction (b).

Intercalation reaction on mechanically peeled MoS$_2$ shows a similar thickness change (c,d).

SEM suggest that the intercalated material are somewhat porous and rough.

Successfully intercalated MoS$_2$ shows a large increase in thickness. Figure 5.5 shows an MoS$_2$ sample clamped in a vernier caliper shows a significant change in thickness before and after reaction. SEM shows that the edge of the MoS$_2$ crystal becomes porous and large gaps can be seen in between the layers. When a reaction was done on mechanically peeled MoS$_2$ on gold coated SiO$_2$, we also see that the surface of MoS$_2$ after reaction becomes rough and the thickness
increase. The thin film interference of indicates this thickness change. For example (Fig. 5.5) turquoise colored flakes turns yellow, which signifies a large change in thickness. We believe this increase in roughness caused the silver/reflective appearance of MoS$_2$ to tarnish and blackened due to black body effect.

Figure 5.6. AFM of MoS$_2$ flakes before and after intercalation. 10 nm MoS$_2$ flakes thicken to 30 nm after reaction (a) and 150 nm flake expanded into 800 nm. Significant increase in roughness was observed, consistent with SEM image.
We quantified the change in physical thickness of MoS$_2$ through AFM for a 10 nm and 150 nm thick flakes. We found that the thickness of the 10 nm flakes increased to ~32 nm and the 150 nm flakes increased to ~800 nm. That represent at 3x and 5x increased in thickness. It should be noted that the thickness changes also include the significant change in roughness, as observed in figure 5.6. We believe that the true increase in lattice parameter should be less than these observed physical changes. The exaggerated increased in thickness is a result of increased roughness.

**Electrochemical Signature of Intercalation.**

**Intercalation of 1$_3$N16Br**

Voltammetry data of MoS$_2$ in supersaturated 1$_3$N16Br are typically shows similar peaks as figure 5.7. Three anodic peaks are observed at approximately -1.5 V, -2.4 V, and 3.7 V vs. Br$_2$/Br$^-$. Two reverse reaction peaks are also observed at -2.0 V and -0.8 V. The deintercalation peak at -2.0 V continuously shift up to 1V between cycles as seen in Figure 5.7b. It indicates that the reaction is becoming less and less reversible. This is probably due to the accompanying gas-forming reaction that is observed during the intercalation.
Figure 5.7 Cyclic voltammetry of 13N16-MoS2. The anodic peaks observed at -1.5 V, -2.4 V and -3.7 V vs. Br₂/Br⁻ are highly similar as Li-MoS₂ intercalation (a). The reaction shows a highly irreversible behavior, most probably due to the gas forming reaction that accompanies the intercalation (b).

Earlier we discussed the intercalation reaction of Li-MoS₂ and, based on its anodic peaks, proposed three different equilibrium reactions. We can then use these numbers Shifting the number to Br₂/Br⁻, the values are as follow:

\[
\begin{align*}
S & \quad + \quad 2\text{Li}^+ \quad + \quad 2\text{e}^- \quad \rightarrow \quad \text{Li}_2\text{S} \quad \text{(approx. -1.8 V vs. Br}_2/\text{Br}) \\
\text{MoS}_2 & \quad + \quad x\text{Li}^+ \quad + \quad xe^- \quad \rightarrow \quad \text{Li}_x\text{MoS}_2 \quad \text{(approx. -2.9 V vs. Br}_2/\text{Br}) \\
\text{Li}_x\text{MoS}_2 & \quad + \quad (4 - x)\text{Li}^+ \quad + \quad (4 - x)e^- \quad \rightarrow \quad \text{Mo} \quad + \quad 2\text{Li}_2\text{S} \quad \text{(approx. -3.4 V vs. Br}_2/\text{Br})
\end{align*}
\]
These electrochemical potentials appears to be similar as the ones observed for 13N16Br-MoS$_2$ reaction$^{19-22}$. We will propose the reaction is as follow:

(approximate)

$$S + 2 \text{13N16}^+ + 2e^- \rightarrow (\text{13N16}^+)_{2}S \quad (-1.5 \text{ V vs. Br}_2/\text{Br}^-)$$

$$\text{MoS}_2 + x \text{13N16}^+ + xe^- \rightarrow (\text{13N16}^+)_{x}\text{MoS}_2 \quad (-2.4 \text{ V vs. Br}_2/\text{Br}^-)$$

$$(\text{13N16}^+)_{x}\text{MoS}_2 + (4-x) \text{13N16}^+ + (4-x)e^- \rightarrow \text{Mo} + 2 (\text{13N16}^+)_{2}S \quad (-3.7 \text{ V vs. Br}_2/\text{Br}^-)$$

While there’s a large shift between the different the intercalation compound, it is predominantly due to the highly irreversible nature of the 13N16Br intercalation, and the uncertainty of having two different reference electrodes. However, the similarity indicates that the reaction is highly similar.

**MoS$_2$ vs. Copper wire, determine the electrochemical signature of intercalation**

The cyclic voltammetry of a typical quaternary ammonium bromide with MoS$_2$ is compared with the cyclic voltammetry of quaternary ammonium bromide with copper wire (Fig 5.8). We use this comparison to establish that indeed the electrochemical reaction involving MoS$_2$ is indeed different with that of copper metal that is certainly known to not form an intercalation compound.

There are several cathodic peaks observed for both Cu wire and MoS$_2$ observed. An important feature in the degradation of quaternary ammonium appears at -2.8 V (vs. Br$_2$/Br$^-$) based on the Cu wire, whereas the same feature is observed at -3.0 V(vs. Br$_2$/Br$^-$).

It appears that the degradation potential for quaternary ammonium compound occurs at a smaller potential compared to the intercalation reaction of MoS$_2$. This is an important feature, as it suggests that the quaternary ammonium degradation and the intercalation process occurs at a
very similar potential. It may be difficult to untangle the effect of intercalation with respect to
gas formation as both occur at very similar potential.

Figure 5.8. Cyclic voltammetry signature of non-intercalating (a) and intercalating (b)
working electrode. Cyclic voltammetry of copper wire shows an electrochemical breakdown of
quaternary ammonium around -2.77 V vs. Br₂/Br⁻ occurred at a very similar intercalating
potential in MoS₂ around -3.00 V vs. Br₂/Br⁻. Intercalation reaction in MoS₂ occurred at a
similar potential as observed in Li-MoS₂.

Effect of -H substituent in Ammonium

Upon successful intercalation with CTAB, we then started our investigation by evaluating the
electrochemical property of ammonium cations. The goal is simple, we tried to evaluate whether
intercalation occurs for primary, secondary, tertiary, and quaternary alkylammonium.
Figure 5.9. Ammonium with hydrogen substituent does not form intercalation. Tertiary ammonium bromide (a,b) shows no intercalation reaction, whereas quaternary ammonium (1$_3$N16) shows intercalation (c). The presence of hydrogen substituent prevents intercalation reaction from occurring.

We found that voltammetry signature of primary and tertiary ammonium is similar to one another (Fig. 5.9). We observed that a gaseous product was visibly produced at an applied potential of -1.8V vs. Ag/Ag$^+$ (equivalent to -3.0 V vs. Br$_2$/Br$^-$. Upon further applied potential, the gas production becomes more rapid causing a fluctuation in measured current. The fluctuation is clearly visible around -3 to -4 V vs. Ag/Ag$^+$ applied potential. As the sweep direction is reversed, no de-intercalation peak was observed.

In comparison, quaternary ammonium compound shows a distinct deintercalation peak. Initially the de-intercalation peak occurs at -1.4V vs. Ag/Ag$^+$. Subsequent cycle shifts the de-intercalation peak to -1.23V vs. Br$_2$/Br$^-$. In addition, a deintercalation peak around -0.6 V and
+0.33 V was also observed. Figure 7 shows that multiple cycle will merge these deintercalation peaks into a single curve around -0.6 V vs. Ag/Ag⁺.

We believe that this distinct de-intercalation reaction peak is the best feature that indicate the presence or lack of intercalation. For the remaining of this discussion, will use this de-intercalation signal as a primary method to determine whether an intercalation reaction occurred.

**Symmetrical vs. Asymmetrical quaternary ammonium**

We explored the electrochemical signature effect of symmetric or asymmetric alkyl chain length of MoS₂ quaternary ammonium compounds. The cyclic voltammetry of the following compounds are presented in figure 5.10: 1₃N16Br , 1₃N12Br, 2₃N12Br, 4₃N4Br, 7₃N7Br, and 12₃N12Br. It appears that there is no difference in the electrochemical signature between a long/short alkyl carbon chain. That indicates that these quaternary ammonium forms intercalation compound with MoS₂.

The size difference of the deintercalation peak is predominantly due to the different MoS₂ counter electrode used. We found that similar sized/shaped MoS₂ crystals used in the intercalation process shows a differing rate of intercalation. We are still unsure of the nature of such difference. However, upon prolonged cycles, all the MoS₂ crystal will show a deintercalation peak. We conclude that chemically there are no difference in the reactivity of quaternary alkylammonium compounds.
Figure 5.10. Symmetrical and Asymmetrical quaternary ammonium shows no difference in electrochemical reactivity. All shows a de-intercalation peak. It indicates that electrochemically, alkyl substituent does not affect the electrochemical reaction. Unlike the rest, we observe that 73N7Br and 123N12Br intercalated MoS2 shows an large expansion such that pieces of intercalated MoS2 breaks apart. While the chemical reaction is identical, the physical stability of the product may differ.
Physically, however, we found that 7₃N7 and 12₃N12 does not produce a crystalline product. The visually observed product of these quaternary ammonium compounds undergoes a very large expansion, are highly porous, and create a hard-foam like material. During the reaction, typically chunks of MoS₂ will break off the main pieces and fall on the bottom of the reaction vial. We believe that the large expansion and porosity observe will cause a break in the electrical contact and stop the reaction progress.

While the intercalation reaction involving quaternary ammonium shows similar chemistry, the physical stability of the product may differ depending on the length of the alkyl chain.

**XRD Data and Structural Analysis**

**XRD**

The XRD shows that the organic intercalation expands the interlayer distance of MoS₂. The pristine MoS₂ shows the dominant peak at 2θ = 14.36°, corresponding to an interlayer distance of 6.1 Å. The fully intercalated MoS₂ with 1₃N16 shows clean (00l) peak at 5.83°, corresponding to an increased interlayer distance of 15.1 Å (Fig. 5.11). We did not observe any other peak corresponding the organic compound. This indicate that while the separation distance is uniform, the orientation of the organic compound in between the layer are not entirely crystalline.
Figure 5.11. Intercalation product XRD shows no change in interlayer spacing with respect to carbon chain length. XRD of MoS$_2$ intercalated with $1_3$N12Br, $1_3$N16Br, and $1_3$N18Br shows a similar product with an interlayer distance of 15.1 Å (a). Proposed structure of shows an organic molecule that lays parallel with the basal plane of MoS$_2$ (b).

To determine the configuration of the inserted organic molecules, alkyl ammonium with different carbon chain length (12, 16, and 18) is used as intercalates. All alkyl ammonium intercalation shows similar XRD results with an interlayer distance of ~ 15 Å, regardless of the length of the carbon chain.
Figure 5.12. Thermogravimetric Analysis (TGA) of 13N16Br-MoS2 intercalated compound. Disregarding the solvent weight, the mass content is 37% 13N16Br and 63% MoS2. This is equivalent to 0.25 : 1 ratio or 13N16Br to MoS2.

We can evaluate the molecular ratio of organic/MoS2 by TGA (Fig. 5.12). We found that around 80°C there is a sharp decrease in mass. We believe that this drop is due to trapped solvents in between the layers. IT then follow by another large drop mass that we attribute to CTAB weight. There appear to be a second phase of intercalated material formed at 200°C that we were unable to identify. The mass continues to decrease slowly until 600°C. We estimated that the organic weight is ~2.5 mg and the MoS2 weight is ~ 4.4 mg. This correspond to a 0.25 to 1 mole ratio of CTAB vs. MoS2.

In addition, we can also see that the material has low temperature stability. Almost all of the organic mass were removed at 150°C. the large slope also indicates that the material will
deintercalated easily even at 100°C, showing a similar behavior as fig. 2.12. Our own experiment result shows that heating the material to 100°C for ~24 hours will revert the structure into the original 2H- structure.

**Proposed Structure**

There are several possible configurations of the quaternary ammonium compounds. The alkyl chain could have a straighten configuration and form anywhere between an angle(θ) of 0° (laying down) all the way to forming a 90° angle (standing up) with respect to the basal plane of MoS₂ or it could also form a random and complex structure (Fig. 5.13). In addition, one, two, or more layers of organic compound can exist in between the layer.

Using a process of elimination, we can estimate the structure of the organic intercalant in between the MoS₂. If the chains are straightened, an alkyl chain with “n” number of carbon will produce an “n x cosθ” dependence in the increased in the interlayer distance (Fig. 5.11). We found that the interlayer distance is independent of the longest carbon chain length. First, we can eliminate the “random” formation. It is unlikely all of these carbon chain arranges randomly but accidentally form the same interlayer expansion. This indicate that the alkyl chain must form a zero-degree angle (θ=0) with respect the basal plane. Having the carbon chain laying down will produce an interlayer expansion that is independent of alkyl chain length. This is different from previous result or TaS₂-amine intercalation (Chapter 2).
Figure 5.13. Possible orientation of organic molecule inside the MoS2 layer. Organic molecule with perpendicular orientation (a) and tilted (b) will have an interlayer distance that is linearly dependence on the length of the carbon chain. Parallely oriented organic molecule will provide a constant interlayer distance (c). If the organic molecules form a complex structure, the interlayer distance will have a random/unpredictable orientation (d). By process of elimination, the most likely structure is (c), as it follows the observed XRD trend.

The result suggests that the interlayer distance is determined by the CH$_3$-N-CH$_3$ axis of tertiary ammonium. We can estimate the layer expansion by having a bilayer structure of organic compound using the equation in Chapter 2$^{1,25}$ and received an approximate bond length of 15.16Å (Fig. 5.14). This is in line with the observed 15.14Å separation distance.

We can further approximate the packing density by considering the crystallographic parameter of a pure CTAB crystal. It is known that the crystallographic unit cell of CTAB is 5.60 x 7.16 x 25.90 Å (a x b x c). Suppose that we attempt to pack two unit cells of CTAB crystal on a basal plane of MoS$_2$ such that the b-c plane is laying perpendicular to the surface. We can then use this structure to attempt to estimate the packing density of bilayer CTAB-MoS$_2$. Given that
MoS$_2$ surface area per mole is ~26 Å$^2$ and the surface area of CTAB is ~186 Å$^2$, we can estimate that the maximum molar ratio of CTAB to MoS$_2$ is approximately 0.28 to 1.

Figure 5.14. Unit cell of 13N16. The crystallographic parameter a x b x c are 5.6 Å x 7.16 Å x 25.9 Å. Molecular ration with MoS$_2$ can be estimated by placing the a-c plane is parallel with the basal pane of MoS$_2$. For a bilayer structure, the mole ratio of 13N16Br to MoS$_2$ is approximately 0.28 to 1.

The molar ratio obtained from this purely crystallographic analysis matches well with the TGA ratio obtained of 0.25 to 1. In a bulk structure, the ratio is lower possibly due to incomplete reaction or a slightly different packing density compared to a pure CTAB structure. We believe that overall, the mole ratio supports our model of MoS$_2$.

Therefore, we conclude that the hydrocarbon chain follows the orientation parallel to the interlayers. XRD shows that the change in interlayer distance is independent of alkyl chain length, which indicate a most probable parallel orientation of the alkyl chains. Estimation of the increase of interlayer distance follows very well the equation used in previous TMD-Organic
intercalation, supporting a bilayer model. Lastly the TGA analysis indicates that the mole ratio of organic intercalation match well with the expected value of a parallel bilayer formation.

**Stability of intercalation material**

Electrochemical data indicates that all quaternary alkylammonium bromide reacts the same way with MoS\(_2\) to form an intercalated compound. However, that is not observation found of the products. We found that intercalated product only form when: 1) the alkyl longest chain is 12 or longer; 2) at most, the longest alkyl chain is 4.

![Graph](image)

**Figure 5.15. Room temperature stability of organic intercalated MoS\(_2\).** Experiment suggest that when the longest alkyl chain is less than 12, the intercalant is unstable (a). Stable product are noted in (black) and unstable products are noted in (red). XRD of \(1_3\)N6Br-MoS\(_2\) intercalation at -20°C shows a quick evaporation of intercalant as it heat up to room temperature within 15 minutes (b).
Reason 2) is easy to explain. Earlier, we discussed was due to an extremely large physical expansion observed, chunks of MoS$_2$ pieces detached from the reaction and falls down. This cause an incomplete reaction which in turn shows no visible intercalation.

Observation 1) was harder to understand. The discrepancy between the XRD data and observed electrochemical signature was a puzzle. One would expect that all the alkylammonium product to form an intercalation compound. However only when the carbon chain length is greater than 12 that the product was stable.

It is only when a low-temperature intercalation was performed the picture becomes clear. We found, through intercalation of 1$_3$N6Br at -20°C, that the intercalated product was highly unstable. Figure 5.15 shows a measurement of the same sample of 1$_3$N6Br in the span of ~15 minutes after removed from the -20°C reaction chamber. The samples are removed from the reaction chamber and was loaded into the diffractometer within approximately 5 minutes. Each scan took approximately 5 minutes.

The result shows that intercalated compound with separation distance of 15 Å quickly revert back to form a compound with separation distance of 6 Å. It seems that the intercalant are unstable at room temperature, and cause a rapid evaporation. We believe that while the electrochemical reaction is similar, the final product is not thermally stable and quickly degrade. We found that the interlayer separation was seen when at least the number of carbon chains is 4. Tested tetramethylammonium bromide and tetraethylammonium bromide shows no changes in interlayer distance.
**Reaction in molten salt**

TGA shows that significant amount of solvent are trapped in the MoS\(_2\) that may change the mobility of the alkyl chain, causing them to adopt a parallel orientation. We expect that we may be able to obtain a different product if there are no solvent, and when the alkyl chain quickly re-crystalizes at room temperature.

While majority of quaternary ammonium bromide tend to degrade before they melt (around 200\(^\circ\)C), we found that tetrabutylammonium bromide (4\(_3\)N4Br) to have a relatively low melting point (103\(^\circ\)C). We intercalated bulk MoS\(_2\) in the molten 4\(_3\)N4Br to see what the effect would be when there is no solvent present.

In a typical experiment, 1 gram of 4\(_3\)N4Br are melted at 120\(^\circ\)C and was used as both solvent and ion source. Electrochemical set up was done for 4 hours in a similar matter as other intercalated compound in figure 5.16. We observed that once the reacted MoS\(_2\) was removed the molten salt quickly froze, covering the MoS\(_2\) with a thick layer of unreacted 4\(_3\)N4Br. These layers was removed by rinsing the MoS\(_2\) in acetonitrile several times.

We observed through XRD that the intercalation products have an interlayer distance of 18.69Å, is highly crystalline. This is different from the 15.Å expanded structure observed in majority of the 1\(_3\)N16Br and other solvated alkylammonium. We estimated, based on the monolayer equation presented in Chapter 2, that the expansion observed is consistent with a monolayer of 4\(_3\)N4. We caution the validity of this particular structure estimation as we were able to consistently create intercalation product of only molten 4\(_3\)N4Br.
Given that the stability of final product is temperature dependent, using molten salt as both solvent and reactant can produce a thermodynamically trapped structure. We believe that further exploration in the reaction of molten salt.

Figure 5.16. Proposed structure (a) of MoS2 intercalated in molten/solvent less 43N4Br. Intercalated product is highly crystalline and shows a separation distance of 18.7 Å. It shows that changing experimental condition can produce intercalated compounds with varying lattice expansion.
Raman and PL

We found that the intercalated MoS$_2$ shows a significant increase in photoluminescence (Fig. 5.17). Here we chose a few-layer MoS$_2$ as a comparison. However, we also do see a particle that initially have no photoluminescence will have a large and intense PL. We found that the peak intensity is 712 nm or equivalent to 1.74 eV. This optical gap is smaller than a typical monolayer of 1.88 eV$^{26}$.

Figure 5.17. Raman shift of various points of intercalated few-layer-MoS2 (a) and its corresponding photoluminescence (b). Raman spectroscopy shows a consistent E$_{2g}$ peak and a red shifted A$_{1g}$ peak. PL shows a significantly enhanced intensity, indicating a mono-layer like behavior. PL peak is found at 712 nm. Spectrum taken with 514 nm Laser.
We also observed, there is a significant red-shift in the Raman shift of the $A_{1g}$ peak (Table 1). Unreacted MoS$_2$ have an observe $A_{1g}$ peak of 404.8 cm$^{-1}$, whereas the intercalated MoS$_2$ shows an $A_{1g}$ Raman shift of 393.1 cm$^{-1}$. We found, however, that the $E_{2g}$ peak shows a relatively unchanged shit that fluctuates between 382 cm$^{-1}$ to 380 cm$^{-1}$. We calculated that the Mo-S bond force constant remains relatively unchanged of 194-196 N/m, whereas the S-S bond force constant underwent a by 37% decrease from 27 N/m to 17 N/m.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{2g}$</th>
<th>$\gamma$ (Mo-S bond)</th>
<th>$A_{1g}$</th>
<th>$\beta$ (S-S bond)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>N/m</td>
<td>cm$^{-1}$</td>
<td>N/m</td>
</tr>
<tr>
<td>Unreacted</td>
<td>380.2</td>
<td>194.2</td>
<td>404.8</td>
<td>27.2</td>
</tr>
<tr>
<td>Intermediate 3</td>
<td>380.8</td>
<td>194.8</td>
<td>405.4</td>
<td>27.3</td>
</tr>
<tr>
<td>Intermediate 2</td>
<td>381.4</td>
<td>195.4</td>
<td>405.4</td>
<td>26.9</td>
</tr>
<tr>
<td>Intermediate 1</td>
<td>380.8</td>
<td>194.8</td>
<td>403.6</td>
<td>25.9</td>
</tr>
<tr>
<td>Intercalated</td>
<td>382.0</td>
<td>196.0</td>
<td>393.1</td>
<td>17.2</td>
</tr>
</tbody>
</table>

Table 5.1. Observed $E_{2g}$ and $A_{1g}$ Raman shift and the calculated bond force constant.

Intercalated product shows a significantly weakened S-S bond.
Side reaction of Quaternary Ammonium Degradation

Figure 5.18. Gas chromatography result shows the observed gas formation was found to be methane. (a, b) shows an increased in Methane signal as measured through Gas Chromatography (GC). Methane production originated from the trimethyl- group (c).

The gas formation observed during can be explained by the formation of methane gas production. Gas chromatography (GC) supports this observation. In order to measure the gas species, we intercalated a bulk MoS$_2$ in a sealed container. Every half hour, a portion of the gas was syringed out for GC measurement. The source of the hydrogen required is unclear. We believe that any source of water is sufficient to complete the reaction.
Study on the electrochemical break down of quaternary ammonium shows that it produces an amine and an alkane\textsuperscript{27-30}. When there are several different side groups associated with the quaternary ammonium, it was found that the side group with the more stable radical have a slightly higher likelihood to detach. It indicates that both methane and hexadecane can be produced. Simply due to the fact that there are three methyl group and one hexadecyl group, the methane gaseous product is more prominent.

We would like to note that the observed anodic breakdown of the quaternary ammonium occurred at a potential 1V lower than expected in multiple studies (Fig. 5.8). Cyclic voltammetry shows that the quaternary ammonium break down at approximately -2V vs. SHE, whereas most study shows a breakdown at -3V vs. SHE.

We believe that the electrochemical breakdown of our samples are affected greatly by the presence of water\textsuperscript{28}. Most sources cited deals with hydrophobic ionic liquids which naturally have low water content. In our case, the quaternary ammonium and the solvents used are highly hygroscopic. The presence of water can significantly shift the electrochemical breakdown window of the solvent.

**Conclusion**

Drawing conclusion from a Lithium intercalation, we proposed a new organic intercalation chemistry on MoS\textsubscript{2} (Group VI TMD). It came from a simple postulate: Lithium intercalates into MoS\textsubscript{2}, and thus other cations that are as electrochemically stable should also intercalate into MoS\textsubscript{2}. This leads us to a series of quaternary alkyl ammonium compound which degrades at approximately -3 V vs. SHE. These quaternary alkyl ammonium compounds are as stable as
alkali metals (redox potential of -2.7 to -3.1 vs. SHE). We should expect that these quaternary ammonium compounds can be electrochemically intercalated into MoS$_2$.

With the understanding that intercalation of MoS$_2$ intercalates at ~+1 V (v.s. Li/Li$^+$), there is a simple guideline that can predict whether a material may perform intercalation with MoS$_2$: whatever cation it may be, its’ cation must be stable at +1 V vs. Li/Li$^+$. Or alternatively, as most tabulated values are expressed in term of standard hydrogen evolution (SHE), the intercalant must be stable for at least a potential of -2 V vs. SHE. It is no surprise that other than alkali metals, there are very few report of direct intercalation into MoS$_2$.

This limit is not clear cut. We know, for example, that Magnesium, which have a redox potential of -2.35 V (vs. SHE), does not intercalate directly into MoS$_2$. In addition, concentration of cations in the solution, solution used, as well the countering anion may have a significant effect in the reactivity.

The search for organic based cation suitable for intercalation presented a challenge. During the initial phase of this research, the “charge transfer model” is not yet developed. Numerous types of organic cations such as crystal violet, methylene blue and methyl viologen was tested with only a few resulting in intercalation. Only by the development of the charge transfer model, a correlation of the intercalation reaction with an organic compound’s redox potential is now well understood. Table 5.2 is a summary of organic cations and whether an intercalation compound is likely to be formed.
<table>
<thead>
<tr>
<th>Group</th>
<th>Degradation potential (vs. SHE)</th>
<th>Intercalation formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary, Secondary, Tertiary ammonium</td>
<td>?</td>
<td>No</td>
</tr>
<tr>
<td>Quaternary alkyl ammonium</td>
<td>-3.15 to -3.23 V (lit)</td>
<td>Yes (observed)</td>
</tr>
<tr>
<td></td>
<td>-1.7 to -2 V (observed)</td>
<td>Stability depend on R</td>
</tr>
<tr>
<td>Imidazolium</td>
<td>-2.33 to -2.74 V (lit)</td>
<td>Not Tested Probable</td>
</tr>
<tr>
<td>Pyridinium</td>
<td>-1.36 to -1.44 V (lit)</td>
<td>Not Tested Unlikely</td>
</tr>
<tr>
<td>Viologen</td>
<td>-0.25 to -0.37 V (1st)</td>
<td>No (observed)</td>
</tr>
<tr>
<td></td>
<td>-0.67 to -0.80 V (2nd)</td>
<td></td>
</tr>
<tr>
<td>Crystal Violet</td>
<td>-0.357 to -0.456 V</td>
<td>No (observed)</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>?</td>
<td>No (observed)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low solubility</td>
</tr>
</tbody>
</table>

The product of the MoS\textsubscript{2} organic intercalants are found to have an expanded interlayer distance of 15.1 Å. This represent a 8.9 Å increase in the interlayer distance compared to the 6.2 Å interlayer distance of an unreacted MoS\textsubscript{2}. Our result shows that the crystal structure consist of a bilayer of quaternary ammonium compound laying parallel to the basal plane of the host structure. We also found that the intercalants containing short carbon chain is unstable at room temperature and can quickly evaporate from between the layers.

Different reaction condition can produce intercalated MoS\textsubscript{2} with even larger interlayer distance. Reaction in molten tetrabutylammonium bromide (4\textsubscript{3}N4Br) produce a product with an interlayer distance of 18.7 Å. It shows that control of the interlayer distance can be achieved by controlling the reaction process. We believe in this case that the lack of mobile solvent contributes to the larger interlayer distance observed.

Emergence in photoluminescence of intercalated MoS\textsubscript{2} shows that it behaves in a similar manner to a monolayer. Interestingly, it shows an optical band gap of 1.74 eV compared to 1.88 eV observed for pristine monolayer. In addition, Raman spectroscopy shows a significant decrease in the S-S bond strength after chemical reaction.

**Table 5.2. Summary of Organic compounds’ intercalation capability into MoS\textsubscript{2}**. Whenever possible, electrochemical degradation is presented with respect to SHE and the intercalation result. Degradation potential are taken from ref. 27-32.
Future Work

Further research can be done in the MoS$_2$-organic complex. First, the product stability should be greatly improved. Thermogravimetric analysis shows that (Figure 13) the product quickly degrade at 80°C. This can pose a significant problem when used as an electronic device. Second, intercalation of semiconducting organic compound may form an interesting hybrid structure with large tunable band energy. Several approaches to mitigate this problem include.

To improve its thermal stability larger organic molecule is needed. For example, an intercalation of very large molecular weight organic compounds to increase the thermal stability. We were unsuccessful in our attempt to intercalate very large polymer with 10,000 unit cells (PDADMAC), presumably due to the very low solubility of the polymer in acetonitrile and NMP. If an oligomer or shorter polymer chain can be inserted, surely the thermal stability can be greatly improved. It may also be possible to intercalate a self-polymerizing organic molecule or other cross-linkable double/triple bond such as triallyl amine based compounds.

Insertion of semiconducting organic polymer can produce an interesting and new semiconductor. For example, it is knows that pentacene can form a p-n junction with MoS$_2$. If the product is thermally stable, it may be a promising material for a thermoelectric device or an organic based solar cell.
References


CHAPTER 6. Monolayer phosphorene molecular superlattices

Black phosphorus (BP) was first synthesized by applying high pressure to red phosphorus and studied by P. W. Bridgman in 1914\textsuperscript{1}. However, its two-dimensional nature was not fully explored until 100 years later, when the thin BP transistor was fabricated, showing high current modulation up to five orders of magnitude and a respectable carrier mobility up to 1,000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} (ref. 2). The rediscovery of BP and phosphorene (monolayer BP) introduced the second important elemental two-dimensional layered material (2DLM) that balances carrier mobility and bandgap, in contrast with semi-metallic graphene and semiconducting transition metal dichalcogenides (TMDs), yet retaining all the merits of 2DLMs. This includes the ultimate limit for electronic scaling, versatile lateral and vertical integration, along with exceptional mechanical strength and elasticity for highly robust flexible electronics.

Combining high mobility, suitable direct bandgap, and highly anisotropic properties, phosphorene represents an attractive atomically thin semiconductor for next generation electronics and optoelectronics, including transistors\textsuperscript{2-4}, broadband photo-detectors\textsuperscript{5}, and diverse \textit{van der Waals} heterojunction devices\textsuperscript{6}. However, the difficulty in isolating and stabilizing monolayer phosphorene\textsuperscript{7-9} has limited most studies to date to multi-layer BP flakes rather than monolayer phosphorene. Demonstration of fundamental properties and devices from monolayer phosphorene has been severely limited by its intrinsic instability in ambient conditions. The much expected intrinsic properties including large direct bandgap or high mobility of monolayer phosphorene has been difficult to reach with traditional 2DLM processing and fabrication methods\textsuperscript{7,10,11}. 
Here we report electrochemical intercalation of BP with cetyltrimethylammonium bromide ((C\textsubscript{16}H\textsubscript{33})N(CH\textsubscript{3})\textsubscript{3}Br, abbreviated as CTAB) to form a monolayer phosphorene molecular superlattice (MPMS) with stable monolayer phosphorene characteristics. Using a home-built in situ electro-chemical-optical measurement (IS-ECOM) system, we conducted systematic investigations of the dynamic intercalation process and the evolution of its structure and properties. The evolution of electrochemical current and photoluminescence spectra during the MPMS formation suggests a stepwise reaction mechanism. Photoluminescence studies of the intercalation product shows a strong photoluminescence signal centered at 548 nm (2.26 eV), suggesting a monolayer with a strain-induced blue shift from the theoretically predicted band gap of ~2 eV (ref. 12). Atomic force microscopy (AFM) and X-ray diffraction (XRD) studies clearly demonstrate interlayer distance expansion from 5.23 Å in BP to 11.27 Å in MPMS, indicating the insertion of well-ordered molecular layers. Cross-sectional transmission electron microscopy (TEM) studies confirmed the highly ordered superlattice structure with alternative layers of monolayer phosphorene and self-assembled molecular (SAM) layers. Planar TEM studies reveal a significant expansion (by ~ 3\%) of the phosphorene in the armchair direction, which is further confirmed by Raman spectroscopic studies. Electrical transport studies based on MPMS field effect transistors (FETs) demonstrate the highest on/off ratio (>10\textsuperscript{7}) reported in BP to date, yet with a respectable mobility (328 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}). Sandwiched between molecular layers, the MPMS exhibits excellent stability in ambient conduction with >10 times longer lifetime than pristine BP devices with similar starting current. DFT calculations using the Vienna Ab-initio Simulation Package (VASP) with projector augmented wave (PAW) pseudopotentials gave the most probable atomic configuration of MPMS with the predicted interlayer distance, armchair strain, and widened bandgap matching well with experimental observations. Lastly, we show that a
lateral BP-MPMS heterojunction device can be created with diode characteristics. Our studies demonstrate the preparation of ambient-stable high-quality monolayer phosphorene for the first time. We expect that formation of MPMS could open up new opportunities in phosphorene electronics and photonics. To the best of our knowledge, this unique MPMS system is one and only platform that can demonstrate all key intrinsic properties of monolayer phosphorene to date, including the highest mobility of few-layer phosphorene, highest on/off ratio, largest optical bandgap and high stability.

**Electrochemical intercalation dynamics**

![Diagram of electrochemical intercalation](image)

**Figure 6.1. in situ electrochemical-optical measurement (IS-ECOM) platform to monitor electrochemical intercalation in real time.** a and b, schematics of the IS-ECOM platform for the BP intercalation process from BP (a) to MPMS (b). The IS-ECOM system can allow to simultaneously monitor electrochemical current, source-drain current, and photoluminescence/Raman spectra during the electrochemical intercalation process.

The intercalation of 2DLMs with selected molecules or ions can considerably modulate their electronic properties. Examples include phase transitions in MoS$_2$ or TaS$_2$ due to Li intercalation. However, the most typical intercalation of alkaline metals is usually unstable under ambient conditions. Here we report a systematic investigation of intercalation of BP with
organic molecules (CTAB) to produce stable intercalation compounds. We constructed a home-designed electrochemical-optical measurement platform for in situ monitoring the evolution of electronic and optical properties during the intercalation process (Fig. 1a, b). In a typical experiment, a standard back-gated BP FET was fabricated on a 300-nm-SiO$_2$/Si substrate (see methods for details) and immersed in a polydimethylsiloxane (PDMS) reservoir filled with supersaturated CTAB solution dissolved in N-Methyl-2-pyrrolidone (NMP) to facilitate the intercalation process after proper configuration of Pt counter electrode and Ag/AgCl reference electrode. This intercalation device can be placed under a Raman/photoluminescence microscope during the intercalation process. With this setup, the electrochemical current from the Pt counter electrode, the drain current from the metal drain electrode, and Raman/photoluminescence spectra can be simultaneously monitored while the BP is being intercalated.

The molecular intercalation process involves the insertion of CTAB into the BP interlayer gaps through edges during the electrochemical reaction. The electrochemical reaction consists of two half-reactions:

$$Br^- \rightarrow \frac{1}{2} Br_2 + e^- \quad (1)$$

and

$$BP + x(CH_3)_3NC_{16}H_{33}^+ + xe^- \rightarrow (BP)^x^+ [(CH_3)_3NC_{16}H_{33}]_x \quad (2)$$

The electrochemical current was monitored in situ from the Pt counter electrode (electrolyte gate) as the voltage was swept from 0 V up to ~ 3 V. Careful analysis of the electrochemical current curve ($I_{eg}$ in Fig. 2a) and its first derivative (Supplementary Fig. 1) shows apparent stepwise reactions, which may be attributed to the strong layer-number dependent bandgap and electronic properties of the BP (see Supplementary Note 1 and 2 for more detailed discussions).
The stepwise reaction can be partitioned into six regions based on minimum points of the first derivative of the electrochemical current (Supplementary Fig. 1):

- **0 - 1.0 V**: no obvious intercalation (due to over-potential for Br\(^-\) sub-reaction, see more details in Supplementary Note 1),
- **1.0 - 1.4 V**: major bulk intercalation occurring,
- **1.4-2.0 V**: few-layer (four to 10 layer, less than 5 nm thick) BP formation,
- **2.0-2.5 V**: trilayer BP formation,
- **2.5-3.0 V**: bilayer BP formation and
- **beyond 3.0 V**: monolayer phosphorene formation (Fig. 2a).

Fig. 2b shows the corresponding source-drain current of first scan (black) and last scan (red) in a multi-scan intercalation process, demonstrating relative small on/off ratio before intercalation and strong gate effects with ~ 10\(^5\) current modulation (limited by precise off-current measurement with the electrolyte gate) in the final fully intercalated materials.
Figure 6.2 Structural and property evolution from BP to MPMS during the dynamic electrochemical intercalation process. 

**a**, Electrochemical current as a function of the applied electrochemical potential from 0 V to ~ 3 V, showing stepwise reactions with 6 distinct regions during the BP intercalation with CTAB. Inset: false-color SEM image of MPMS transistors. Scale bar: 5 µm. 

**b**, Ionic gate transfer characteristics of the first scan (black, BP) and the last scan (red, MPMS) monitored simultaneously by applying the same electrochemical potential during MPMS formation at 0.01 V source-drain bias. 

**c**, Photoluminescence signals observed at 898 nm (1.38 eV), 710 nm (1.75 eV) and 548 nm (2.26 eV) during different stages of intercalation, roughly corresponding to band edge emission from trilayer, bilayer and monolayer phosphorene. 

**d**, The bandgap/electrochemical potential vs. layer number relationship showing a good correlation between electrochemical potential and the corresponding bandgap at bulk, bi, tri and monolayer
regions. e, Photoluminescence mapping centering at 550.0 nm with similar intensity demonstrating the relatively uniformity of the resulting MPMS. Inset: the corresponding SEM image of photoluminescence mapping sample; scale bar: 3 µm. f and g, AFM images of a BP flake (f) and the resulting MPMS (g) after CTAB intercalation, demonstrating the overall thickness increase by about 130 %. Scale bar: 300 nm. h, X-ray diffraction spectra of BP and MPMS verifying the interlayer distance expansion from 5.23 Å (16.93°) of BP (black) to 11.27 Å (7.84°) of MPMS (red).

An in situ monitor of the photoluminescence evolution in BP during the intercalation process reveals clearly the evolution from the absence of apparent photoluminescence in the visible-NIR regime in bulk BP (Supplementary Fig. 2) to prominent emission at ~898 nm (1.38 eV), then ~710 nm (1.75 eV) and eventually ~548 nm (2.26 eV) as the intercalation process progresses (Fig. 2c). These emission peaks correspond roughly to near band edge emission from trilayer, bilayer and monolayer phosphorene. Interestingly, the bandgap and the onset intercalation electrochemical potential exhibit a highly similar relationship with the layer number, suggesting a close correlation between electrochemical potential and the measured bandgap (Fig. 2d). To the best of our knowledge, the photoluminescence emission at 548 nm (2.26 eV) is the highest optical bandgap observed in phosphorene or thin BP based structures (values from 1.45-1.84 eV were observed previously), suggesting that we may have formed the true monolayer material. The observed optical bandgap of 2.26 eV is slightly higher than theoretical limit of ideal phosphorene (~ 2 eV) \(^\text{21}\), which may be attributed to the strain induced bandgap expansion and will be further discussed in TEM analysis section and explained by DFT calculations\(^\text{10,22}\). Photoluminescence map (at 550 nm) of MPMS flake show highly uniform contrast (Fig. 2e), indicating the relative structure uniformity of the resulting MPMS.
**Structural characterizations**

Compared with pristine BP (Fig. 2f), AFM studies show the thickness of the fully intercalated MPMS (Fig. 2g) is increased by about 130%. Importantly, X-ray diffraction (XRD) studies show clearly the minimum interlayer distance is expanded from 5.23 Å (16.93°) in BP to 11.27 Å (7.84°) in of MPMS with about 115% increase in the interlayer distance (Fig. 2h), which is consistent with AFM measurements. Second order peak of pristine BP at 2.62 Å (34.20°) as well as the high order peaks of MPMS at 5.65 Å (15.67°) and 3.76 Å (23.61°) further confirm the expansion of the interlayer distance. Besides the final MPMS structure, most intermediate structures before reaching complete intercalation show mixed phases with variable number of BP layers (Supplementary Fig. 3).

We have next conducted high resolution-transmission electron microscopy (HR-TEM) studies to further probe the MPMS structure, (Fig. 3). The cross sectional TEM images clearly show the distinct structure between layered BP (Fig. 3a) and MPMS superlattice (Fig. 3d) with strikingly different interlayer distance. Electron diffractions (ED) patterns (insets of Fig. 3a and 3d) clearly reveal the increased interlayer distance from 5.24 Å in BP to 11.21 Å in MPMS, which is further verified by direct measurement in the magnified cross sectional images (Fig. 3b and 3e). This directly observed expansion of interlayer distance is consistent with AFM thickness measurement and XRD analysis (Fig. 2f-h). The ~ 6 Å interlayer distance increase corresponds roughly to the end to end distance between the CTAB methyl-methyl substituent23. Planar TEM studies reveal ~ 3% lattice expansion from 2.17 Å of pristine BP (Fig. 3c) to 2.24 Å of MPMS (Fig. 3f) in the armchair direction (200) with negligible change in the zigzag direction (1.66 Å for (020) in both BP and MPMS). ED patterns of the corresponding samples further confirmed the lattice expansion in (200) (insets of Fig. 3c and 3f). This distinct ~3% expansion in the
armchair direction is also consistent with the observed photoluminescence blue shift in the monolayer due to strain induced bandgap expansion\textsuperscript{10}. Elemental analysis based energy dispersive X-ray (EDX) spectra gives an atomic ratio of P:N:Br ~33.2:1.2:1.0 (Supplementary Fig. 4), suggesting Br are also intercalated into the final superlattice structure. Although free Br\textsubscript{2} is produced and not intercalated into BP during the electrochemical intercalation process (see Equ. 1 & 2), the produced Br\textsubscript{2} during intercalation process may back-react with phosphorene\textsuperscript{-}CTA\textsuperscript{+} layers again after the release of electrochemical potential, in which process the Br\textsuperscript{-} ions are intercalated into the final MPMS structure to form phosphorene/CTAB superlattices (Supplementary note 1 for more details).
Figure 6.3 TEM characterization of structure evolution from BP to MPMS. a and d TEM cross section image comparison between BP (a) and MPMS (d) to show well-ordered intercalation of CTAB layer into BP monolayers. Scale bar: 3 nm; Insets are the corresponding electron diffraction to verify the increased interlayer distance. Scale bar: 2 1/nm. b and e are magnified high-resolution cross sectional TEM images to further demonstrating the insertion of CTAB layer between BP layers to form MPMS with the interlayer distance increasing from 5.24 Å in BP (b) to 11.21 Å in MPMS (e). Scale bar: 1 nm; c and f, Planar TEM images of BP c and MPMS f showing the lattice parameter expansion in armchair direction from 2.17 Å in pristine BP to 2.24 Å in MPMS and negligible change in zigzag direction (1.66 Å for both BP and MPMS). Scale bar: 2 nm; Insets: electron diffraction of the corresponding TEM images to
confirm the lattice parameter change in (200) and (020) and directions; Scale bar: 5 1/nm. g and h, three-dimensional (g) and cross sectional (h) atomic structure view of simulated structure of MPMS, verifying the 11.41 Å interlayer distance and 2.9 % expansion in armchair direction.

**DFT calculation of molecular structure and electronic structure**

To understand the formation MPMS and the molecular structure of the resulting MPMS, we conducted density functional theory (DFT) calculations using the Vienna ab-initio simulation package (VASP)\textsuperscript{24,25} with projector augmented wave (PAW) pseudopotentials\textsuperscript{26,27}. Based on average atomic ratio analysis from EDX analysis, the MPMS structure is modeled by a close-packing configuration, with 32 P atoms and 1 CTAB molecule in the supercell, as shown in Fig. 3g and 3h. The reciprocal space was sampled by Γ-centered Monkhorst-Pack scheme\textsuperscript{28} with 7x1x3 k-points. Both the cell parameters and the internal atomic coordinates are fully relaxed using Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional\textsuperscript{29}. Significantly, the relaxed structure gives an interlayer distance of 11.41 Å, matching well with the 11.27 Å value determined by XRD and cross sectional TEM. Furthermore, the relaxed structure also shows a 2.9 % expansion in the armchair direction compared with that of BP calculated using the same method and negligible lattice parameter change in the zigzag direction, consistent with our planar TEM observations (Supplementary Note 3 for more details). We attribute the strain to the repulsion between CTAB molecules, which leads to the expansion of BP lattice, similar to the strain observed in alkali-metal intercalated graphite\textsuperscript{30}.

The PBE calculations also show a bandgap expansion of 0.24 eV from monolayer phosphorene to MPMS, consistent with the increase of optical band gap. For accurate evaluation
of the electronic structure, we used B3PW91 functional as implemented in the CRYSTAL14 package\textsuperscript{31,32}, and all-electron 6-31G(d) basis sets of double-\(\zeta\) quality were used for H, C, N, O, P and Br. An extra-large grid, consisting of 75 radial points and 974 angular points, was used for accurate integration, and the reciprocal space was sampled by \(\Gamma\)-centered Monkhorst-Pack scheme with a 7\(\times\)1\(\times\)3 grid. As show in Figure 4a and 4b, MPMS have enlarged bandgap at 2.13 eV with 0.19 eV increment compared with monolayer phosphorene at 1.94 eV, which is in agreement with experimental observed bandgap of 2.26 eV in MPMS, compared with monolayer BP bandgap at around 2 eV\textsuperscript{20,21}. In addition, there are additional bands within the band gap of MPMS in Fig. 4b that are marked in gray dotted line, which are mainly composed of Br atomic p orbitals (ranging from 24\% to 56\%, larger than the averaged contribution of 8\%\text{"}~4\% from black phosphorus unit (P\textsubscript{4})), while the orange VBM-0 bands are with contributions from P dominating over from Br (less than 10\%). Our calculations of the frequency dependent dielectric matrix (at the PBE level) indicate that in the isolated monolayer BP, the VBM-1 (Fig. 4e) band and VBM-0 (Fig. 4d) have symmetrically equivalent charge density distributions, and thus they are very close to each other in energy, and they both contribute to the first absorption peak (Figure 4a), as they both have significant overlap with the CBM band state (Fig. 4c). However, for MPMS, only the VBM-1 (Fig. 4h) has largest overlap with CBM (Fig. 4f) and contributed significantly to the transition from VBM-1 to CBM. For VBM-0 (Fig. 4g) and CBM (Fig. 4f), due to small states overlap with each other, the transition between them is very limited. So the optical transition bandgap of MPMS was determined by the transition from VBM-1 (Fig. 4h, green band in Fig. 4b) to CBM (Fig. 4f, red band in Fig. 4b), which matched well with our experimental observation of enlarged bandgap in MPMS.
Figure 6.4. The calculated electronic band structure evolution from BP to MPMS. a and b, electronic structure of BP (a) and MPMS (b), demonstrating the enlarged bandgap from 1.94 eV in BP to 2.13 eV in MPMS as determined by the transition from first VBM-1 (green) and CBM (red). The newly introduced bands of MPMS marked as gray dotted lines are mainly from Br atomic p orbitals and the orange VBM-0 band mainly (~ 90%) from P, but almost didn't contribute to the optical transition due to its very small overlap with CBM. c, d and e, monolayer phosphorene charge density distribution of CBM (red in a), VBM-0 (orange in a) and VBM-1 (green in a), showing the transition bandgap determined by CBM and VMB-0/VMB-1 (energy very close); f, g and h, MPMS charge density distribution of CBM (red in b), VBM-0 (orange in b) and VBM-1 (green in b), showing the transition bandgap determined by VBM-1 and CBM due to large overlap of charge density.
Raman spectroscopic studies

We have also used Raman spectroscopic studies to probe the structural evolution from BP to MPMS. Raman studies show that all three characteristic BP Raman modes remain after intercalation, yet with considerable intensity wakening (by ~ 40 times) (Fig. 5a). A close analysis reveals considerable peak broadening and apparent peak position shifts. The $A_g^1$ mode is slightly red shifted from BP 360.93 cm$^{-1}$ to MPMS 359.77 cm$^{-1}$ (Fig. 5b), whereas $B_{2g}$ and $A_g^2$ modes are blue shift from 437.98 cm$^{-1}$ in BP to 438.21 cm$^{-1}$ in MPMS (Fig. 5c) and 465.45 cm$^{-1}$ in BP to 465.96 cm$^{-1}$ in MPMS (Fig. 5d), respectively. As depicted as atomic motions of three lattice vibrational modes in the insets of Fig. 5b-d, these peak shifts can be qualitatively understood as a consequence of ~3% armchair direction strain as observed in the TEM analysis and in the simulated structure. Basically, the armchair expansion originates from CTAB repulsion each other. Thus, the molecular orienting in zigzag direction exerts tiny external force along armchair direction to separate slightly two non-bonded but neighboring phosphorus atoms, which will contribute positively to projected components of $A_g^1$, but negative for projected motion of $A_g^2$. This leads to the red shift for $A_g^1$ and the blue shift for $A_g^2$. Though atomic motions associated with $B_g^2$ occur mostly along the zigzag direction, the armchair expansion will harden the zigzag direction atomic motions indirectly, resulting in a very small blue shift of $B_g^2$. Therefore, the energy spacing between $A_g^1$ and $B_g^2$ or between $A_g^1$ and $A_g^2$ modes increases under armchair stretching. Raman studies of MPMS also reveal a new peak around 1460.1 cm$^{-1}$ in MPMS (Supplementary Fig. 5), which corresponds to CH$_3$ antisym deformation or CH$_2$ scissors vibration, further confirming successful intercalated CTAB inside BP monolayers.
Figure 6.5. Raman characterization of BP and MPMS. a, Raman spectra to compare the relative peak intensity and FWHM evolution from pristine BP (black) to MPMS (red). The MPMS spectrum is multiplied by 20 times for easy comparison. b-d, A\(^{g}_{1}\), B\(^{g}_{2}\) and A\(^{g}_{2}\) mode comparison between pristine BP and MPMS to show red shift, blue shift and blue shift after MPMS formation, respectively. Insets: schematic illustration of atomic motion of each vibration modes.

**Electrical properties and stability analysis**

Due to its intrinsic instability, monolayer phosphorene has been difficult to access and its intrinsic properties are insufficiently explored to date. With the successful preparation of MPMS, we have further explored their electronic properties in depth. To reveal the electrical properties change before and after the intercalation process for same BP nanosheet, back gate BP and
MPMS transistors were studied. In general, the output characteristics (source drain current vs. source drain voltage: \(I_{sd}-V_{sd}\)) for both BP and MPMS show linear relationships (insets of Fig. 6a, b), suggesting the absence of an obvious contact barrier and an acceptable Ohmic contact. Back gate transfer characteristics of pristine BP show the typical p-type behavior with an on/off ratio <10 and mobility up to 721 cm\(^2\)V\(^{-1}\)s\(^{-1}\) (Fig. 6a). The MPMS device retains p-type properties with a respectable mobility of 328 cm\(^2\)V\(^{-1}\)s\(^{-1}\) (Fig. 6b), which outperformed the best few-layer BP devices and show comparable mobility but much higher on/off ratio than thin BP devices (see Supplementary Fig. 6 for a statistical analysis of the electrical properties of six MPMS devices and their comparison with few-layer and thin BP devices from other recent studies) and close to its theoretical limit (250 to 400 cm\(^2\)V\(^{-1}\)s\(^{-1}\))\(^{34-36}\). Significantly, the MPMS device can be completely switched off with a greatly increased current on/off ratio. For example, a current modulation up to \(10^7\) is achieved in MPMS structure at \(V_{sd}\) of 0.01 V (Fig. 6c), in contrast to an on/off ratio <10 for the same BP before intercalation. This on/off ratio of \(>10^7\) represents the highest on/off ratio ever achieved in phosphorene or thin BP nanodevices\(^{2,8}\).

To further understand the electrical properties of MPMS, we have also explored the transport properties of MPMS FETs at various temperatures from 1.9 K to 300 K (Fig. 6d,e). In general, the linear output characteristics are retained at low temperature down to 1.9 K, suggesting good Ohmic contact of the device. With the decreasing temperature, the on-current more than doubled from 1.74 \(\mu\)A at 300 K to 3.85\(\mu\)A at 1.9 K (Fig. 6d and inset). In addition, the field-effect mobility extracted from the transfer characteristics increased to 599 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 1.9 K, compared with initial mobility of 289 cm\(^2\)V\(^{-1}\)s\(^{-1}\) at 300 K. In the phonon limited temperature range (100–300 K), the mobility best fits the expression \(\mu \sim T^{-\gamma}\) with the exponent \(\gamma\) around 0.73 for
MPMS. A power law dependence with a positive exponent is indicative of a phonon scattering mechanism, which is consistent with other studies of thin BP that show band-like transport\textsuperscript{2,37}.

Importantly, with the sandwiching and encapsulation of monolayer phosphorene between molecular monolayers, the environmental stability of the material is greatly increased. For example, comparing a BP device and a MPMS device with similar on-current, the MPMS show no significant electrical degradation for as long as 300 hours exposure in ambient condition; this contrasts with the BP device that shows serious degradation after 20-30 hours exposure (Fig. 6f). We attribute this greatly improved stability of MPMS to the special superlattice structure, in which each phosphorene monolayer is sandwiched/encapsulated by the molecular layers, which considerably slows the oxygen and water diffusion believed to be the main cause of BP degradation.\textsuperscript{8,40,41} It is important note that electrical stability of MPMS compares favorably with those of BN-encapsulated/passivated or Al\textsubscript{2}O\textsubscript{3} passivated few-layer BP devices reported recently. Furthermore, the intercalation process of MPMS does not involve any complex fabrication steps and prevents the potential fabrication-induced performance degradation or unavoidable exposure to ambient atmosphere (Supplementary Table 1)\textsuperscript{8,37-39}.
Figure 6.6. Electrical properties evolution from BP to MPMS and stability comparison. a and b, back gate transfer characteristics of pristine BP and MPMS as the source-drain bias is stepped from 0.1 V (black curve) to 0.5 V (green curve) bias with 0.1 V step; insets: output characteristics of BP (a) and the corresponding MPMS (b) after CTAB intercalation, showing the absence of obvious contact barrier and acceptable Ohmic contact. c, comparison of typical transfer characteristics between BP (black) and MPMS (red) at a source drain bias of 0.01 V, demonstrating an on/off ratio $>10^7$ in MPMS vs. $<10$ in BP. d, output characteristics of MPMS at various temperature from 1.9 K (black) to 300 K (violet). Inset: on-current vs temperature of MPMS. e, transfer characteristics of MPMS at various temperature from 1.9 K (black) to 300 K (violet). Inset is the temperature dependence of mobility. f, Comparison of electrical stability between three MPMS (star marked) and three BP (triangle marked) devices with similar starting on-current, highlighting exceptional stability of MPMS without obvious electrical degradation for as long as 300 hours, which is more than 10-15 times longer lifetime than pristine BP.
Lateral BP-MPMS heterojunctions

Lateral integration of 2D materials by using either the same material with different dopants \textsuperscript{42,43} or two different materials with opposite doping type\textsuperscript{44,45} is an exciting topic for creating functional nanodevices. However, lateral integration of phosphorene based structure has not been sufficiently studied due to the difficulty in controllable and selective doping and the complexity in fabricating such devices. Inspired by superior electrical properties of MPMS, Fermi level mismatch between BP and MPMS as well as high controllability of intercalation process, we fabricated lateral BP-MPMS heterojunctions by partial interaction of a BP flake. Since the insertion of CTAB into BP occurs through the edges, partial intercalation can be achieved by selectively opening an intercalation window on a PMMA-covered BP and controlling the diffusion-limited intercalation time. The exposed edges underwent electrochemical reactions, forming a lateral junction between the intercalated MPMS and the passivated BP. Photoluminescence spectra mapping of a typical lateral BP-MPMS heterostructure show clear PL signal in the MPMS region and the absence of PL signal in the BP part (Fig. 7a). Similarly, corresponding Raman spectra mapping centering at 438 cm\textsuperscript{-1} showed considerably stronger signal in the BP region than that in the MPMS region (Fig. 7b). After standard electron beam lithography and metal deposition process to contact the BP region and MPMS region separately, we obtained a BP-MPMS heterojunction device (Fig. 7c and inset of 7f), which is schematically illustrated in the inset of Fig. 7d. Considering the large bandgap difference between monolayer phosphorene (MPMS) and BP, we expect a diode-like rectification from the band diagram (Fig. 7e) and indeed we observed it (Fig. 7f)\textsuperscript{46}. This demonstration of a unique lateral BP-MPMS heterojunction diode represents an essential step towards functional phosphorene electronics and optoelectronics.
Figure 6.7. Lateral BP-MPMS heterojunction. a, Photoluminescence (at 553 nm) mapping of a lateral BP-MPMS heterostructure to emphasize the MPMS part. Scale bar: 3 µm. The signal in the electrode area is due to a scattering induced background. b, The corresponding Raman spectral mapping centered at 438 cm$^{-1}$ to show the main BP region with stronger Raman signal. Scale bar: 3 µm. c, SEM image to show the lateral BP-MPMS heterojunction device. Scale bar: 3 µm. d, Schematic illustration of a lateral BP-MPMS heterojunction. e, Band diagram of the BP-MPMS heterojunction. f, The typical diode characteristics of a lateral BP-MPMS heterojunction; inset: optical microscope image of the corresponding BP-MPMS heterojunction. Scale bar: 3 µm.

Conclusion

With a unique two-dimensional geometry, a relatively high mobility, a suitable layer-number dependent direct bandgaps, phosphorene provides an alternative atomically thin semiconductor for a new generation of electronic and optoelectronic devices. The formation of MPMS structure with superior current modulation, intrinsic optical bandgap, outstanding stability, and the demonstration MPMS transistors with high mobility and record-high on/off
ratio and lateral BP-MPMS heterojunction diodes represents exciting advancements for phosphorene electronics both fundamentally and technically. This MPMS transistor and lateral BP-MPMS can be applied directly to functional phosphorene electronics devices, such as high performance radio frequency (RF) transistors or MPMS/MoS\textsubscript{2} vertical heterojunction transistors, further opening up exciting opportunities for creation of a wide variety of integrated devices, ranging from complementary logic devices, photovoltaics, photodetectors to light emitting devices. In addition to the intercalation dynamics study of BP, our \textit{in situ} electro-chemical-optical measurement (IS-ECOM) platform provides a general means to study diverse 2DLMs such as MoS\textsubscript{2} and graphene to produce a wide array of 2D superlattices with tunable electronics and optoelectronic properties, as already demonstrated in our preliminary studies. By varying the size and functional group of the molecules, it is also possible to further tune the intercalation parameters, leading to superlattices with variable interlayer distances, controllable doping and tunable electronic properties. Our study thus defines a general strategy to preparing 2D superlattices and opens up a new pathway to tailoring and taming the electronic properties of 2D materials for functional electronics and optoelectronics.

**Methods**

**BP FET fabrication.** BP was synthesized under a constant pressure of 10 kbar by heating red phosphorus (99.999 \%) to 1,000 °C and slowly cooling to 600 °C at a cooling rate of 100 °C per hour. Standard mechanical exfoliation method was employed to isolate thin BP on 300nm SiO\textsubscript{2}/Si substrate in N\textsubscript{2} filled glove-box. The thin BP transistors were fabricated using electron-beam lithography (EBL) followed by electron-beam deposition of 10/80 nm Cr/Au metal thin films.
**Structural characterizations.** SEM characterization was performed by FEI Nova Nano 230 at 15kV voltage. TEM cross section sample of BP was made through FIB cutting from thin BP. TEM cross section sample of MPMS was made though sonication of thick intercalated BP flakes to make MPMS nanoprism, then dipped the MPMS nanoprism onto TEM grid for imaging. Planar TEM sample was made by directly transferring mechanical exfoliated thin BP on TEM grid for the BP characterization; then using TEM grid with thin BP on top for intercalation process, then imaging the same intercalated sample. TEM characterization was performed by FEI Titan at 300kV accelerating voltage. XRD samples were prepared by transferring mechanical exfoliated thin BP to 300nm SiO$_2$/Si substrate with a 50/50 nm Ti/Au film on top. The whole metal covered substrate with thin BP was directly used for intercalation process, and then characterized by PANalytical X'Pert Pro power X-ray diffractometer with 45 kV voltage, 40 mA emission current and 1/4° beam slit. The micro-Raman and micro-PL studies were conducted using a Horiba Lab RAM HR Evolution confocal Raman system with Ar ion laser (488 nm and 633nm) excitation.
References


Supporting Information

1. Supplementary Figure 1. Stepwise reaction mechanism and its partition map

Supplementary Figure 1 | Stepwise reaction mechanism and its partition map. First derivative of electrochemical current in Fig. 2a. By analyzing original current curve and local minimum of first derivative, the stepwise reaction can be clearly identified, i.e. no major intercalation for 0-1.0 V (over-potential for Br\textsuperscript{-} sub-reaction), 1.0-1.4 V for few-layer structure formation, 1.4-2.0 V for few-layer BP formation, 2.0-2.5 V for trilayer BP formation, 2.5-3.0 V for bilayer BP formation and beyond 3.0 V for MPMS formation, which is also consistent with bandgap evolution from bulk, few, tri, bi and monolayer phosphorene.
2. Supplementary Figure 2. Photoluminescence spectrum of bulk black phosphorus

**Supplementary Figure 2 | Photoluminescence spectrum of bulk black phosphorus.**

Photoluminescence spectra of pristine thick BP sample taken from the bulk region in Fig. 2a, just showing the strong Raman peak, but no any observable PL peak at same range in Fig. 2c.
3. Supplementary Figure 3. XRD of mixed few-layer phosphorene molecular superstructure.

Supplementary Figure 3 | XRD of mixed few-layer phosphorene molecular superstructure. XRD peak with interlayer distance at 32.76 Å (five-layer phosphorene-molecular structure or mixed structure), 26.41 Å (four-layer phosphorene-molecular structure or mixed structure) and 16.34 Å (bilayer phosphorene-molecular structure), indicating the mixed structure during transition region. It's noted that peak with 5.23 Å is originated from non-intercalated BP. It is noted that small peak are high order peak of mixed structure.
4. Supplementary Figure 4. TEM EDX spectra of BP and MPMS

Supplementary Figure 4 | TEM EDX spectra of BP and MPMS. a and b showed the TEM EDX spectra at different range from same cross sectional TEM samples, showing the existence of Br and N after intercalation. Three average spectra gave atomic ratio of P : N : Br is 33.2 : 1.2 : 1.0.
5. Supplementary Figure 5. Raman peak of CH$_3$ antisym deformation or CH$_2$ scissors vibration from CTAB

Supplementary Figure 5 | Raman peak of CH$_3$ antisym deformation or CH$_2$ scissors vibration from CTAB. Raman peak around 1460.1 cm$^{-1}$ indicating the existing of CH$_3$ antisym deformation or CH$_2$ scissors vibration and successful intercalation of CTAB inside BP monolayers.
6. Supplementary Figure 6. Statistical analysis of six MPMS devices performance, compared with few-layer and thin BP devices of other recent studies.

Supplementary Figure 6 | Statistical analysis of six MPMS devices performance, compared with few-layer and thin BP devices of recent other studies. Six MPMS devices (red star) show average mobility of 270 cm$^2$V$^{-1}$s$^{-1}$ and averaged on/off ratio of 8.6*10$^6$. As comparison, we listed recent studies of few-layer (less than 5 nm, marked as blue triangle) and thin BP (5 nm to 15 nm, marked as black square). It's clear that MPMS devices outperformed the best few-layer BP devices as for the mobility and on/off ratio and show comparable mobility but much higher on/off ratio of thin BP devices. Data points indexed are adapted: data 1 from Ref. 1, data 2 from Ref. 2, data 3 from Ref. 3, data 4 from Ref. 4, data 5 from Ref. 5, data 6 from Ref. 3, data 7 from Ref. 6, data 8 from Ref. 7, data 9 from Ref. 3, data 10 from Ref. 8, data 11 from Ref. 9, data 12 from Ref. 10, data 13 from Ref. 11, data 14 from Ref. 12, data 15 from Ref. 13, data 16 from Ref. 9, data 17 from Ref. 14, data 18 from Ref. 9, data 19 from Ref. 15, data 20 from Ref. 16, data 21 from Ref. 17, data 22 from Ref. 18, data 23 from Ref. 19, data 24 from Ref. 20, data 25 from Ref. 21, data 26 from Ref. 22.
7. Supplementary Table 1. Device key characteristics compassion between MPMS and other recent studies

<table>
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<tr>
<th>Ref.: BP thickness, passivation approach,</th>
<th>bandgap (eV)</th>
<th>mobility (cm²/V/s)</th>
<th>on/off ratio</th>
<th>electrical stability (hour)</th>
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<tr>
<td><strong>This work (MPMS)</strong></td>
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<td>328</td>
<td>1.9E7</td>
<td>300+</td>
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<td><em>Ref. 14: 10 nm, aryl diazonium passivation</em></td>
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<td>1E6</td>
<td>83+</td>
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<td><em>Ref. 5: 5 nm, BN passivated in inert air</em></td>
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<td>118 (200K)</td>
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<td>48+</td>
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<td>n.a.</td>
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<td>n. a.</td>
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<td>1e3</td>
<td><strong>175</strong></td>
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Supplementary Table 1 | Device key characteristics compassion between MPMS and other recent works. Compared with key improvements of few-layer (less than 5 nm) phosphorene in past three years, this study represented a fundamental advance of few-layer and monolayer phosphorene intrinsic properties demonstration including highest optical bandgap, highest few-layer mobility, highest on/off ratio and extraordinary stability.
Supplementary Note 1. Intercalation chemistry of BP

The basic of this electrochemical reaction dictate that electrons are transferred from the HOMO level of the cathode/reducing agent towards the LUMO of the oxidizing agent on the anode. On the cathode, two bromide ions acts as the reducing agent each losing an electron to form $Br_2$, requiring around 1 V of electrochemical potential. On the anode side, electrons are pumped into the BP conduction band. The additional electron causes BP to be negatively charged. To stabilize the additional electron, $(CH_3)_3NC_{16}H_{33}^+$ molecules insert itself between the BP layers gap through edges acting as a counter ion.

The start of the major reaction observed at ~ 1 V can be explained by its HOMO/valence band and LUMO/conduction band difference around 0.35 eV and ~ 1 eV $Br$- sub-reaction electrochemical potential. The first insertion of $(CH_3)_3NC_{16}H_{33}^+$ does not require high applied potential due to the low (~0.35 eV) band gap of the bulk BP. As the intercalation continuing, the HOMO/LUMO gap of BP/substrate increases, hence causing it to become harder for the next reaction to occur. The intercalation decouples the neighboring BP layers and reduces the effective layer thickness, leading to blue shift of the photoluminescence peak wavelength, and a final peak was recorded at ~2.26 eV for MPMS, representing the highest observed optical gap.

During reaction, it's clear that $Br_2$ was formed at cathode with the emergence of the darker yellow $Br_2$ solution. However, after the electrochemical potential was withdrawn, due to high activity of $Br_2$, it will re-react with phosphorene$^{\text{CTA}^+}$ layers quickly to form final phosphorene/CTAB layered superlattice structure, which is consistent with the TEM EDX analysis and the DFT simulated structure.
Supplementary Note 2. Stepwise reaction mechanism

Due to strong layer-number dependent bandgap of black phosphorus, stepwise reaction mechanism is proposed mainly based on the characteristic stepwise electrochemical current curve\textsuperscript{25} and the corresponding photoluminescence spectra of bulk, few-layer, trilayer, bilayer and monolayer phosphorene as described in the main text. In addition, XRD spectra taken at different intercalation stage on a small Au/SiO\textsubscript{2}/Si substrate with couple of BP flakes or bulk sample was observed with peak around $\sim$16.34 Å, $\sim$ 26.41 Å due to bilayer or trilayer structure (Supplementary Fig. 3). The properties of CTA\textsuperscript{+} with one positive charge and relative large molecular size was expected to stepwisely intercalated based on modeling study.\textsuperscript{26}

In addition, for each region labeled with specific structure, like bilayer region, it means the majority of structure is bilayer, but it also included other structure, like trilayer, which can be explained from the bilayer PL spectra, where weak trilayer shoulder peak was observed as well. Even for the monolayer structure, from its XRD spectrum, tiny pristine BP peak can be observed as well. So for most intermediate structures, including few-layer, trilayer, bilayer, it's a mixed phase at some extent. Very careful scan times, scan step, scan duration and stop voltage should be adjusted to for relatively pure structure. Since monolayer structure is the final step, it's relatively easier to reach compared with those intermediate states.

The intercalation scan times, scan step, step duration and stop voltage have large effect on the final structure as well. Due to the diffusion limited intercalation progress, the structure may not form within one fast scan. To better control the intercalated process, the multi-scan method was employed in this study. In addition, too large scan step may lead to sample cracking at higher voltage. Too short step duration time are the reason for incomplete intercalation as limited by CTAB molecular supply or CTAB diffusion inside BP. Incorrect stop voltage will lead to
strongly mixed phase, especially in the intermediate states. Stop voltage above 3V for long time will result in sample cracking. Sometimes, multi-scan with different parameters may be employed to slowly tune the structure from mixed phase to relative pure phase by increasing the intercalation degree in small ratio. Those parameters setting are related to sample size, thickness, shape (sharp or rough edges) and expected structure. More systematic study with precise intermediate structure control may be isolated in future work.

**Supplementary Note 3. Simulated MPMS structure parameters and bandgap**

According to DFT calculations using the VASP with PAW pseudopotentials, lattice parameter in armchair direction changed from 4.62 Å of BP to 4.75 Å of MPMS with 2.9 % increment. For the zigzag direction, the change is negligible comparing 3.30 Å of BP with 3.28 Å of MPMS. For the bandgap of MPMS, we also calculate a bandgap of 1.14 eV with 0.24 eV increment by using PBE compared to 0.90 eV for monolayer phosphorene. It is noted that PBE underestimates band gaps but leads to bandgap increment of 0.24 eV of MPMS compared with monolayer phosphorene.

**References**


