STRUCTURE AND PROPERTIES OF MOLYBDENUM DISULFIDE-BASED INCLUSION MATERIALS

by

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B. Sc., Simon Fraser University, 2000

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

In the Department of Chemistry

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SIMON FRASER UNIVERSITY

Spring 2008

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ABSTRACT

The use of exfoliated MoS$_2$ layers as surfaces for adsorption have been examined. The properties of exfoliated and restacked MoS$_2$-malachite green (MG) inclusion compounds have been examined to provide insight into the MG-MoS$_2$ interactions that characterize these materials. The results of X-ray diffraction experiments indicate that MG included into the restacked structure adopts a flat orientation approximately parallel to the MoS$_2$ sheets. Second-harmonic generation (SHG) experiments conducted on the exfoliated and restacked materials provide information regarding the average orientation of the MG. Together with adsorption isotherm data, SHG results provide a model for the exfoliation, adsorption, and subsequent restacking of these MG-based inclusion materials and demonstrate the utility of nonlinear optical techniques as probes of these interesting layered structures.

The synthesis, structure and order of exfoliated and restacked MoS$_2$ - stearic acid inclusion materials are also reported. Highly ordered layered inclusion materials of MoS$_2$ and stearic acid are formed through exfoliation at the air/water interface followed by subsequent Langmuir-Blodgett deposition. The results of X-ray diffraction and molecular resolution AFM imaging experiments indicate that from this unique exfoliation process, the compound adopts a Y-type architecture with the stearic acid chains on a slight tilt with evidence of crystalline ordering within the amphiphile layers. The sum frequency generation vibrational
spectroscopy data of the monolayer films show distinct and characteristic features in its CH stretching region. Spectral analysis of the modes of alkyl chains of the adsorbate indicates a slight tilt of the terminal methyl groups. These methods were used to gain insight into the driving forces for adsorption and stabilization of inclusion structures.

Finally, the synthesis and structure of exfoliated and restacked MoS$_2$ – gold nanoparticle inclusion materials are reported. The results of TEM experiments indicate that gold nanospheres have been included in between MoS$_2$ layers to form a layered nano-inclusion composite. This new structure is characterized by an increase in conductivity of the material compared to exfoliated and restacked MoS$_2$ by more than one order of magnitude. These results represent a new method for the fabrication of three-dimensional architectures of nanoparticles and promise new material properties derived from their structure.

**Keywords:** molybdenum disulfide; inclusion materials; nonlinear optical spectroscopy; nanostructures

**Subject Term:** molybdenum compounds – inclusion materials
To my family,

Wiesława, Tadeusz and Mike Cetnarowski
ACKNOWLEDGEMENTS

Special thanks are given to my Senior Supervisor, Dr. Gary Leach for the encouragement, feedback and motivation that he has given to me. I would also like to thank my Supervisory Committee, Dr. Steven Holdcroft and Dr. Byron Gates, as well as my former Committee member, Dr. Ian Gay, for valuable discussions during my study.

I would like to express my gratitude to all my colleagues for who have helped me during my studies at SFU. It was my pleasure to learn from, work with and exchange ideas with Tom Johansson, Jusroop Mattu, Tianhong Xu, Dr. Tatyana Kiktyeva, Maeve Moriarty, Karen Chan, Dr. Claire McCague, Joseph Han, Brian Greenhalgh, Ante Mestrovic, Damien Waugh, Andrew Satrijo and Keith Abel. Special thanks to the numerous members of various laboratories in the Department of Chemistry for their support, especially Marianne Rodgers, Hidehiko Asanuma, Dr. Iain McKenzie, Monica Szczepina, Hanifa Jalali and Terry Gordon. I would like to thank Dr. Nancy Forde (Department of Physics) for the use of her centrifuge, Dr. Datong Yang for helpful discussions about MoS$_2$ and Dr. Li Yang for help with the transmission electron microscope.

I would like to thank Simon Fraser University and the Science Council of British Columbia for the generous financial support.

I would like to thank my family for their support.
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# GLOSSARY

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>cAFM</td>
<td>conductive AFM</td>
</tr>
<tr>
<td>CCD</td>
<td>charged coupled device</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(dimethylamino) pyridine</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>fcc</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>FR</td>
<td>Fermi resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
</tr>
<tr>
<td>HDS</td>
<td>hydrodesulfurization</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
<tr>
<td>MG</td>
<td>malachite green</td>
</tr>
<tr>
<td>OPG</td>
<td>optical parametric generator</td>
</tr>
</tbody>
</table>
PMT  photomultiplier tube
PSPD  position sensitive photodetector
SFG  sum frequency generation
SH  second harmonic
SHG  second harmonic generation
STM  scanning tunnelling microscopy
TEM  transmission electron microscopy
TGA  thermogravimetric analysis
TIR  total internal reflection
TOAB  tetraoctylammonium bromide
XRD  X-ray diffraction
CHAPTER 1: INTRODUCTION

Studies presented in this work are concerned with interactions governing adsorption properties of single layer molybdenum disulfide. Single layer MoS$_2$ is a single molecule thick structure that can be used in the generation of composite nano-sized structures through physical and chemical means. The ability to make use of potential physical properties of nanostructures relies heavily on the understanding of the processes and factors that control nanoscale structure synthesis. These factors are investigated in order to learn to control MoS$_2$-based nanostructure generation.

1.1 Molybdenum Disulfide

Molybdenum (IV) disulfide belongs to a family of the nearly forty different layered dichalcogenides, which display a variety of interesting properties primarily due to their crystal structure.[1] Their physical properties span the range of metal, semiconductor, insulator, and superconductor, depending on the nature of the metal and chalcogen atoms. An important feature of these materials is that they crystallize in a quasi two-dimensional layered structure, which imparts substantial anisotropy to many of their properties.

The primary uses of MoS$_2$ are as catalysts and as lubricants. As a catalyst, it has been used to remove sulfur and nitrogen from hydrocarbons.[2] In an effort to produce cleaner burning fuels and reduce the production of acidic
emissions and greenhouse gases into the Earth's atmosphere, the production of nitrogen and sulfur oxides is being limited. To minimize the emission of these gases, nitrogen and sulfur must be removed from fuel sources. The effects of climate change due to greenhouse gases are expected to be profound and thus North American and European governments have acted to enforce emission standards.[3] While these changes have improved air quality, the refining industry faces further pressure to decrease the level of sulfur in fuels. Sulfur is both naturally present in petroleum and introduced during the refining process.[4] These organic sulfur compounds are products of the degradation of sulfur containing biological components, present during the natural formation of the fossil fuel. MoS₂ is used as a hydrodesulfurization (HDS) catalyst in order to achieve this goal.

As a lubricant, MoS₂ finds a use primarily due to its unique structure. The forces holding the MoS₂ layers together are quite weak relative to the intralayer covalent forces.[5] The weak interlayer forces result in a low coefficient of friction in the lateral direction (μ < 0.1) causing a lubricating effect.[6] Coupled with the high melting point and low vapour pressure, the solid finds use as a lubricant in heavy machinery and for low-pressure applications. The structure maintains its lubricating effect up to 1200 K, which makes it a candidate for a lubricant in heavy machinery. As an aircraft engine lubricant, the material is mixed with oil lubricants. The lubricating effect persists even after complete loss of the oil because MoS₂ has a lower vapour pressure than oil and as such does not evaporate at low pressures.
A general application of the metal dichalcogenides is in energy storage devices. Due to the weak interlayer van der Waals interactions, MoS$_2$ can act as a host to a variety of electron donating atoms, such as lithium or sodium.$^7$ Insertion of electron donating atoms to covalently bonded networks has a much higher energy barrier due to the relative strength of the interaction. Intercalation of electron donating species can have a drastic effect on the electronic properties of the host material. Intercalations of alkali metals into the MoS$_2$ structure have yielded a transition from a semiconductor to a conductor.$^{8, 9}$ In other metal dichalcogenides, low temperature studies of intercalated materials have shown the onset of superconductivity below 3.5 K.$^{10, 11}$ Because of these properties, its availability and relatively low cost, MoS$_2$ has also found applications as a material for host-guest chemistry.

1.2 MoS$_2$ Single Layer Inclusion-Material

The transition metal dichalcogenides can act as hosts for a variety of electron donating species.$^{12}$ These intercalated species are generally of the alkali metal variety due to the high electron affinity of the host and the high Lewis basicity of the alkali metal.$^{7, 13}$ Molybdenum disulfide is one of the most stable and versatile members of this family of layered host materials.

The basic structural unit of MoS$_2$ consists of a layer of the transition metal atoms surrounded on either side by a layer of the chalcogens. In an MoS$_2$ layer, the sulphur atoms form a trigonal prismatic environment around the molybdenum centre as they do with most members of the Group 6 transition metals.$^{14}$ The 2H-MoS$_2$ (trigonal prismatic, 2 layers required for unit cell with hexagonal
geometry around the metal centre) layers are held together by van der Waals interactions\[15\] and are shown in Figure 1. Due to the van der Waals interactions, MoS\(_2\) can act as a host to a variety of electron donating atoms as mentioned above, such as Li, where the lithium intercalates in between the layers.

![Schematic representation of 2H-MoS\(_2\).](image)

**Figure 1:** Schematic representation of 2H-MoS\(_2\). The dark and light spheres represent Mo and S atoms, respectively. The layers are held together by van der Waals interactions represented here by the gap between the layers.

The intercalation of MoS\(_2\) with lithium is accomplished in hexane via a redox reaction resulting in the formation of the lithium intercalated MoS\(_2\) where the butyl lithium is the reducing agent and MoS\(_2\) is the oxidizing agent\[13\]

\[
nC_4H_9Li + MoS_{2(e)} \rightarrow Li_xMoS_{2(e)} + \frac{1}{2} nC_8H_{18}
\]  
with \(n\) being approximately 1.\[13, 16\] The hydrocarbon product is attributed to the irreversibility of the radical dimerization shown in equation (2) below. The
lithium-alkane bond is broken after the species is adsorbed by the MoS$_2$. The alkali metal is transferred in the lattice of MoS$_2$, at which point the radical rearranges to a more stable secondary position on the carbon chain. The metal donates an electron to the MoS$_2$ and exists as Li$^+$ in between the MoS$_2$ layers. The radical then dimerizes into an octane which then diffuses into hexane.

\[
\begin{align*}
\text{zigzag} & \quad \rightarrow \quad \text{octane} + \text{Li} \\
2 \quad & \quad \rightarrow \quad \text{octane}
\end{align*}
\]

(2)

Upon insertion of lithium into the MoS$_2$ lattice the lithium exhibits a slightly positive charge as determined by $^7$Li NMR studies$^{[14]}$ which results in a net negative charge of the MoS$_2$ layers.$^{[17]}$

The structure of 2H-MoS$_2$ distorts upon intercalation with Li such that the Mo atoms become coordinated in a distorted octahedral arrangement.$^{[18-20]}$ This MoS$_2$ (octahedral, $O_h$) structure has been investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy, X-ray diffraction (XRD) and electron diffraction.$^{[17, 21, 22]}$ The 2H and distorted octahedral structures are depicted in Figure 2. The electron of the lithium atom moves to the d-band of the Mo atom and the lithium migrates into the interlamellar spacing.$^{[14]}$ For small $n$ values ($n < 0.5$) from Equation (1), the MoS$_2$ can remain as the 2H structure.
rather than the distorted octahedral structure as determined by using Gibbs free energy calculations.\textsuperscript{[19, 23]} Once the onset of conversion from 2H to the distorted octahedral structure occurs, the entire crystallite is converted to the latter structure and no 2H structure remains.

![Figure 2: Schematic representation of 2H (A) and distorted octahedral (B) type structures. The dark and light spheres represent metal and chalcogen atoms, respectively.](image)

The electronic structure of Li\textsubscript{x}MoS\textsubscript{2} has been studied extensively in order to gain an understanding of the conductive properties of the lithium intercalated materials. In the 2H geometry, Mo\textsuperscript{4+} is a d\textsuperscript{2} system having the expected D\textsubscript{3h} (trigonal prismatic) d-block orbital energy diagram. The d-electrons of molybdenum occupy the lowest orbitals of d\textsubscript{z\textsuperscript{2}} which are separated from empty
valence band by the band gap of $\Delta_{e_g} = 1.2$ eV.\cite{24} Upon lithium intercalation and
donation of the lithium electron to the d-band of the metal due to its low electron
affinity, the system becomes a $d^3$ system and the geometry changes due to the
preferred lower energy that arises from the octahedral geometry. In octahedral
geometry, the three degenerate orbitals ($d_{z^2}, d_{xz}, d_{yz}$) are half-filled. The
decrease in energy that results from the geometry change is equal approximately
to $\Delta_{e_g}$ since all the electrons are now in the $t_{2g}$ energy level.
Figure 3: Schematic d-orbital diagram (top) representing the energy change between the 2H-MoS₂ (D₃h) and LiMoS₂ (O₄). The O₄ structure contains an extra electron due to the intercalation of lithium and donation of its electron. Represented is the energetically favoured crystal structure change. The analogous band diagram (bottom) is shown for the same compounds. The band gap energy becomes zero in the distorted O₄ form due to the change in the geometry around the metal.

The reason for the semiconductivity and the metallic behaviour of the 2H-MoS₂ and LiMoS₂ can be explained using the above energy diagram. In the former case, the band gap between the \( d_{z^2} \) and \( d_{x^2-y^2}, d_{xy} \) energy levels is large enough that the material exhibits semiconductive behaviour, i.e., the next electron would have to fill either of those two orbitals overcoming the band gap energy. In the latter case, the occupied orbitals are only half-filled, allowing for electrons to move in and out of these orbitals generating metallic behaviour. The presence of paramagnetic behaviour due to the unpaired electrons in the O₄
structure has been reported for lithium-intercalated transition metal dichalcogenides.\textsuperscript{[25]}

Reaction of the lithium-intercalated MoS\textsubscript{2} with species that contain acidic hydrogen results in H\textsubscript{2} formation in between the MoS\textsubscript{2} layers of the multilayer structure.\textsuperscript{[12]} Although water is the most common reagent for this generation of the gas, these redox reactions have been demonstrated using methanol, ethanol and isopropanol.\textsuperscript{[16]} Generation of H\textsubscript{2} is first achieved by hydration of Li\textsuperscript{+} cations which causes the negatively charged MoS\textsubscript{2} layers to reduce the acidic hydrogen rich species, in this case water, to H\textsubscript{2} and OH\textsuperscript{−}.\textsuperscript{[18]} As the amount of gas formed in between the layers increases, the pressure between the layers increases and the layers are subjected to a force which eventually separates the single layers from each other, overcoming the van der Waals interactions. As the reaction proceeds deeper into each crystallite, the layers become further separated. This process is referred to as exfoliation and produces single layers of MoS\textsubscript{2} suspended in basic solution.\textsuperscript{[26]} In this reaction, MoS\textsubscript{2} acts as an oxidizing agent and water acts as a reducing agent.

\[
\text{LiMoS}_{2(x)} + (1 - x)\text{H}_2\text{O} \rightarrow \text{MoS}_{2}^{(aq)} \rightarrow \text{Li}^{+}\text{(aq)} + (1 - x)\text{OH}^{-}\text{(aq)} + \frac{1 - x}{2}\text{H}_2(g)
\] (3)

MoS\textsubscript{2} remains in solution as a single layer material for several hours until it begins to collapse onto itself and restack.\textsuperscript{[27]} The restacking does occurs on a time scale of days because the partial negative charge of the MoS\textsubscript{2} single layers hinders spontaneous restacking.\textsuperscript{[28]} However, this restacking can be facilitated by centrifugation. In either case, the restacked structures are highly-ordered and
free of macroscopic defects. The structure of MoS$_2$ single layers has been studied by XAFS and it is reported that the chalcogen atoms are in a distorted octahedral environment around the metal centre.$^{[21]}$ The metals exhibit a slight puckering out of the metal plane.

If the restacking process is performed amidst the presence of a salt molecule, then the molecule will be incorporated into the restacked architecture of the material through adsorption, followed by restacking.$^{[12]}$ The first report of the inclusion of various species between the layers to yield a new family of inclusion materials has been used as a model to further include salt and organic molecules in the van der Waals gap. It has been shown that when these single layers are used as an hydrodesulfurization catalyst material in the presence of cobalt, the rates are increased by over an order of magnitude compared to the bulk catalyst.$^{[29]}$ The prospect of this catalytic property and other new chemical aspects of the single layer material have motivated the synthesis of numerous inclusion structures.

The inclusions of iron oxides, cobalt hydroxides and metal nitrates have been achieved through the above method. The incorporations have been attributed to ionic interactions due to the electronegativity of the MoS$_2$ layer and its ability to support positively charged species.$^{[12, 18, 26, 28, 30]}$ When adsorptions of silver and copper cations in between MoS$_2$ single layers have been made, it was suggested that the adsorption is favourable and remains stable due Coulombic interactions.$^{[31]}$ However, inclusion materials are not limited to
metallic materials or metal based salts. In fact, organometallic compounds have been successfully incorporated into MoS₂ as a guest material.

Ruthenium arene, ferrocene and cobaltocene – MoS₂ composite materials have been synthesized using not only the standard method, but also by using a phase dipping method. In the phase dipping method, one can use the phase separation and the spreading phenomena for transferring films of organic-containing single layers of MoS₂ onto various substrates by dipping the substrates into the phase-separated, horizontal water-immiscible liquid interface. The resulting MoS₂ films are highly oriented with the basal surfaces of MoS₂ parallel to the substrate. Generally, liquid molecules are trapped between the layers of MoS₂; molecules of volatile materials eventually desorb. MoS₂ films devoid of foreign materials can be obtained by baking in an inert atmosphere. A volatile solvent that is immiscible with water that contains a solute of interest can be used to obtain a film of MoS₂ with most likely a monolayer of that material included between the layers – that is all available host sites were taken up by the guest molecules. Alternatively, one can simply pour off the liquids and dry the sample to make a powder. While it has been argued that the reason for the adsorption of ruthenium arene complexes in a particular geometry is due to a physical interaction, suggestions have been made that inorganic molecules must be electron donors in order to adsorb whereas organic molecules adsorb through a physical means.

Adsorptions of numerous aliphatic and aromatic organic molecules have also been reported. Many inclusions have been performed using the phase-
dipping method or by vigorously stirring the guest molecule in the presence of the host molecule.\textsuperscript{[27, 33-39]} While the phase dipping technique utilizes the amphiphilic nature of the guest, others have utilized this nature of the guest molecules by incorporating in the host structure using the Langmuir-Blodgett (LB) technique to achieve the desired structure.\textsuperscript{[36, 37]} The material generation was attributed to, once again, a favourable physical interaction between the guest and the host.

Following the inclusion of organic molecules, polymers were included yielding a new class of composite materials. Polyaniline, polystyrene, polypyrrole are just a few of a large number of polymers included using the technique of vigorously mixing two phases containing the guest and host molecules\textsuperscript{[40-43]} or by the phase dipping method.\textsuperscript{[27]} Inclusions of excess amounts of the guest species result in near-monolayer coverage as determined by X-ray diffraction and combustion analysis,\textsuperscript{[32, 33, 35]} which suggests a strong driving force for adsorption.

Various guest molecules have been included leading to numerous studies of the guest-host chemistry employed. The materials produced have yielded new structural and physical including magnetic, thermal and optical properties.\textsuperscript{[30, 31, 44]} These materials have led to further study of HDS\textsuperscript{[18]} and have motivated a significant number of studies of other guest-host chemistries.
1.3 MoS$_2$ Restacking

It has been suggested that the restacking process can be hastened by introducing guest molecules with a net positive charge to take advantage of the ionic interactions.$^{[17]}$ This suggestion agrees with the numerous reports that the MoS$_2$ layers contain a net negative charge upon exfoliation. Upon aging, metallic 1T-MoS$_2$ (distorted octahedral, 1 layer required for unit cell with trigonal geometry around the metal centre) reverts to the more stable semiconductive 2H phase.$^{[19]}$ However, the transformation from $O_h$ to $D_{3h}$ is very slow and takes months to complete at room temperature.

While the final result of the process that starts with single layer MoS$_2$ and ends in the restacked included material is well-known and documented,$^{[12, 27, 30, 32, 34, 35, 40]}$ the process itself has not been the subject of much study.

A study on protonated and non-protonated phenanthroline provides insight into the ionic mechanism for inclusion compound formation from single layer
It was shown that only protonated phenanthroline initiates fast inclusion material precipitation. Thus it was considered that mainly protonated species are included in the interlayer space of MoS$_2$, which can require a shift of the protonation equilibrium of phenanthroline, i.e., conversion of neutral molecules into the mono acidic form. While this illustrates the favourability of MoS$_2$ to adsorb ionic species compared to neutral ones, as mentioned earlier non-ionic species form heterostructures with MoS$_2$ as well.

The nature and dynamics of the restacking process are not entirely well understood. It is uncertain whether adsorption of guest molecules occurs on either side of an MoS$_2$ single sheet, followed by restacking or whether the processes happen simultaneously. It is generally believed that full monolayer coverage is indeed the end result as mentioned earlier.

### 1.4 Environment of Adsorbed Molecules

While the salt and metal hydroxide adsorption and restacking process can be treated as the inclusion of spherical atoms, the inclusion of organic or organometallic molecules is slightly more complex due to their size and symmetry. Generally, the geometry of inclusion is determined from X-ray diffraction, which yields the distance between the restacked MoS$_2$ layers. Knowing the distance, the orientation of the adsorbed organic or organometallic species can be postulated. In certain cases, other techniques have provided insight into the environment of guest species. Using a combination of X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS), it was determined that guest ruthenium arene species form a dimer in between the...
MOS₂ single layers. Fourier-transform infrared spectroscopy (FTIR) has been used to deduce amphiphile guest molecule orientation. The FTIR analysis required several assumptions the most important of which was that all the hydrocarbon chains have the same orientation in the LB films. An electron energy loss spectroscopy (EELS) study has been undertaken in order to obtain evidence of the different orientations of included phenanthroline. The phenanthroline $1s \rightarrow \pi^*$ transition was probed as a function of the angle between the MoS₂ layer c-axis and the incident electron beam. While probing of the phenanthroline species parallel to the MoS₂ layers was successful, difficulty was found in modeling the orientation dependence of the transition intensity arising from species that were not parallel to the MoS₂ single layers. Determining quantitatively the effective orientation of the organic molecules with respect to the MoS₂ sheets was found to be challenging.

1.5 Guest-Host Interactions

The inclusion of many different neutral molecules has been performed at the interface of two immiscible phases, but it has been shown that these inclusions are independent of the method. When the host restacks the end result is a physical inclusion via van der Waals interactions. In order to gain information as to whether there is a difference between the traditional inclusion and the phase dipping method, an electron donor, decylamine, was used as an inclusion molecule. It was found that the end result was independent of the method. The main reason for adsorption is that there is a van der Waals interaction. Suggestions were made that the organic molecules adsorb due to
physical interactions and inorganic molecules due to electron donating interactions.\textsuperscript{[33]}

1.6 1T-MoS\textsubscript{2} Stability

While the 2H form of MoS\textsubscript{2} is thermally stable, the 1T form will revert to the 2H form either at high temperatures, after a long period of time or under applied pressure under room temperature. Differential scanning calorimetry (DSC) studies have shown that the octahedrally coordinated layers transform to the more stable D\textsubscript{3h} form at approximately 96 °C.\textsuperscript{[41, 45, 46]} The conversion temperature for the 1T-MoS\textsubscript{2} to 2H-MoS\textsubscript{2} varies depending on the guest molecule involved and the associated interlayer spacing.\textsuperscript{[41]} This phenomenon implies that the guest atom or molecule plays a large role in stabilization of the metastable 1T-MoS\textsubscript{2}, as can be expected from the d-electron energy diagram of molybdenum (Figure 3).

The level of stabilization varies on the guest material as determined by the temperatures obtained at which expulsion occurs. Generally, metal and metal organic guest molecules form oxides in air.\textsuperscript{[18, 31, 32]} It was observed the formation of ruthenium oxide from an initial inclusion of ruthenium arene upon heating at 500 °C in air. They attributed further decomposition of the guest molecule past 700 °C to the production of ruthenium metal.

They later argued that copper counter-ions attached to the layers by partial covalent bonds stabilize this structure, which resulted in a higher 1T-MoS\textsubscript{2} to 2H-MoS\textsubscript{2} transition temperature than the expected one by over 100 °C.\textsuperscript{[31]}

A
decrease in conductivity of a LB film of alternating layers of MoS$_2$ and stearyl ammonium halide by less than an order of magnitude over four months was probably due to a gradual structural transformation from the metastable 1T-MoS$_2$ to 2H-MoS$_2$ structure indicating the room temperature instability of the 1T-MoS$_2$ structure.$^{[37]}$ Although the conductive mechanism was not dependant on the LB deposited organic species, the decrease in the conductivity of the composite LB films with time was due to this transformation.

1.7 Interface Spectroscopies

Due to the single molecular layer nature of MoS$_2$ and its nature as an adsorption host, surface characterization techniques can be employed to further advance understanding of the guest-host interactions, adsorbate orientation, and ordering. Surface characterization tools are essential for better understanding of surface phenomena because in many cases traditional methods do not have the sensitivity required to probe the properties of adsorbates.

Certain traditional techniques are limited in probing interfacial phenomena. Secondary ion mass spectrometry is used to analyze the composition of solid surfaces and thin films by sputtering the probed surface with a focused ion beam and collecting and analyzing ejected secondary ions. Although the elemental, isotopic, or molecular composition of the surface can be measured with high sensitivity, this technique is destructive.$^{[47]}$ Electron spectroscopies such as Auger electron spectroscopy (AES) and high-resolution EELS are surface techniques that can be used to identify surface composition and chemical bonds. Auger electron spectroscopy is limited in application by heating of the sample.
due to a constant flux of the electron beam. This temperature change may interfere with very sensitive samples. Scanning tunnelling microscopy (STM) is a powerful technique for viewing surfaces at the atomic level, but since it is based on the concept of quantum tunnelling, it is limited to probing only metallic or semiconducting surfaces. Atomic force microscopy is limited to durable samples and is subject to thermal drift obstacles. All of the above mentioned techniques possess some barrier in probing interfaces.

Conventional optical techniques, such as infrared vibrational spectroscopy and Raman spectroscopy, are non-destructive and do not require high vacuum, but they do not have the surface sensitivity characteristics of the electron spectroscopies. If the interfacial species of interest are present in the adjacent bulk media, the resultant spectroscopic signal will likely be dominated by the contribution of molecules residing in the bulk. Often the electronic and the vibrational structure of interfacial molecules is perturbed significantly due to the asymmetry of the interfacial forces. Substantial energy shifts of surface species may result. Even then, it may be difficult to distinguish the bulk and the interface spectral features because of spectral broadening due to surface inhomogeneity or other broadening mechanisms such as local defects.

Optical second harmonic generation (SHG) is intrinsically surface-specific as it is forbidden in centrosymmetric bulk media, but necessarily allowed at a surface or an interface, which lacks inversion symmetry. First applied by Shen to monitor the oxidation/reduction reactions of silver on a silver electrode in an electrolyte solution, surface enhanced SHG demonstrated sensitivity in
detection of small fractions of molecular monolayers on the metal surface. Second harmonic generation has been successfully employed since then to characterize other systems and has been proven to be a particularly effective and versatile probe for surface studies. A comprehensive review written by Shen gives detailed theoretical treatment of the optical surface SHG and provides historical perspective on the technique development and extensive discussion of its applications in various fields.\textsuperscript{[50]} Second harmonic generation has been extended greatly beyond the original metal surface application to a wide range of interfacial environments, including electrochemical systems,\textsuperscript{[51]} liquid/liquid and liquid/air interfaces\textsuperscript{[52-54]} and molecular adsorbates on solid surfaces.\textsuperscript{[53, 55]}

The main advantages of optical SHG as a surface probe over the conventional surface characterization techniques can be summarized as follows. The experimental setup is relatively simple and the technique is applicable to any interface between centrosymmetric bulk phases that is accessible by light. As the signal of interest is coherent and monochromatic directional radiation, it can be easily separated from the incident radiation, background fluorescence or contaminating light from other sources. The technique has demonstrated excellent spatial, spectral and temporal resolution for \textit{in-situ}, non-destructive probing of interfacial species in a variety of interfacial environments with sub-monolayer sensitivity.

In SHG, light at frequency $\omega$ interacts with a nonlinear medium that has a nonzero second order susceptibility, $\chi^{(2)}$,\textsuperscript{[56, 57]} to generate radiation at twice the frequency, $2\omega$. When the light at the fundamental or doubled frequency is in
resonance with electronic transitions of the adsorbates, the SHG signal exhibits resonant enhancement. The intensity of the second harmonic (SH) signal is proportional to the square of the second order macroscopic susceptibility, $\chi^{(2)}$, which in turn is proportional to the number of the adsorbate molecules giving rise to the signal, their microscopic nonlinear hyperpolarizabilities, and their average molecular orientation. Each nonzero susceptibility component of the second order susceptibility tensor can be probed at a particular combination of the input and the output radiation polarization. Once obtained the components of $\chi^{(2)}$ can be related to the molecular nonlinear polarizability to extract the molecular orientation distribution function and in-plane surface symmetry properties of the adsorbed molecules.

The SHG process can be considered as a special case of the more general phenomenon of sum frequency generation (SFG) which is also forbidden in centrosymmetric media. In SFG, light at two different frequencies, $\omega_1$ and $\omega_2$, interacting with a nonlinear medium generates radiation at the sum frequency, $\omega_1 + \omega_2$. Sum frequency generation-based techniques have been applied to the same interfacial systems and exhibit the same advantages over the traditional surface characterization techniques. When SFG is implemented in an infrared-visible configuration, the infrared light being in resonance with a vibrational transition, resonant enhancement of the resultant signal at the sum frequency allows for vibrational spectroscopy. This enhancement formed the foundation for one of the most powerful techniques in the characterization of adsorbate molecules, SFG-based vibrational spectroscopy with surface specificity and
submonolayer sensitivity. Developed initially by Shen and coworkers and employed to study C-H stretch vibrations of molecular monolayers at air/solid and air/liquid interfaces,\cite{58, 59} it has been extended to different spectral regions and interfaces by others.\cite{51, 60, 61}

Taking advantage of very short infrared pulses, the excitation of the vibrational modes over a particular spectral region within the pulse bandwidth can be obtained without tuning the infrared frequency.\cite{62, 63} This short pulse method offers an advantage over the conventional SFG techniques, which use a longer infrared pulse width thereby limiting them to the specific vibration of interest. In conventional techniques, probing of a specific vibration is followed by tuning of the infrared radiation to explore the next vibration of interest, which may only be a few wavenumbers away energetically. The tuning of the infrared (IR) frequency in order to probe nearby vibrations introduces undesired variables to spectra acquisition such as intensity variations.

Taking advantage of the single layer nature of MoS$_2$, SHG and SFG may be used if the single layers are placed at the interface between two media. In probing the interface with no signal contribution from the adjacent media, an advantage to conventional experimental techniques in MoS$_2$ guest-host characterization is gained, overcoming obstacles that others have encountered.

1.8 Nanoparticle-Based Architectures

The science of design, fabrication and application of phenomena of nanostructures and nanomaterials can be summarized as nanoscience. Interest
in nanoscience stems from the fact that while micrometer and larger sized structures exhibit properties the same as those of the bulk form, nanometer sized structures exhibit properties that may be distinctly different from the bulk material.\[64\] A transition from molecular to bulk behaviour takes place in this size regime. The ability to synthesize nanomaterials and nanostructures is of the highest importance in nanoscience in order to explore novel physical properties and phenomena and realize potential applications of nanostructures. Nanostructure synthesis is a key component in rapid advances in areas such as information storage and nanoelectronics,\[64-69\] which utilize physical properties of nanostructures.

Nanostructures embody a wide variety of materials having at least one dimension on the nanometer scale including nanorods, nanowires, thin films, bulk materials made of nanoscale building blocks or nanostructures.\[70\] Technologies employed for nanostructure generation are numerous. Some of the important ones include electroplating, anisotropic growth, molecular beam epitaxy and self-assembly.\[64\]

Nanostructure generation can be grouped into two sub-categories, namely, the “top-down” and “bottom-up” approaches. Microfabrication of larger structures into smaller ones is an example of the “top-down” approach. Crystal growth is a typical “bottom-up” approach, which utilize growth of specific species following assembly into desired structures. The “top-down” method begins with large homogeneous objects and removes material needed to create smaller scale structures. The “bottom-up” approach involves putting together smaller
components such as individual atoms or molecules to form larger and more complex systems.

Of the approaches mentioned, the more popular approach to create nanoparticles is, however, the "bottom-up" approach. This approach utilizes particle nucleation and growth, which, in essence, is a mimic of biological systems by exploiting the order-inducing factors that are inherent to the system. In recent years, nanoscience has developed to such an extent that it has become possible to fabricate, characterize and tailor the functional properties of nanoparticles for specific applications. For example, the magnetic properties of each oxidation state of iron in iron oxide nanoparticles can be utilized to position the particle to a specific area aiding with magnetic resonance imaging for medical diagnosis.\(^{[71]}\) To apply nanoparticles in various potential devices and architectures, it is very important to control the size and shape and to maintain the thermal and chemical stability of the nanoparticles. As the size of nanoparticles decreases, the surface effects become more significant due to the increase in the volume fraction of surface atoms within the whole particle.

The combination of methods and structure types can lead to creation of nanocomposite materials, which are multiphase materials where one, or more of the phases have at least one dimension of 100 nm or less. The properties of composite structures can display improvements over those of the individual component phases. Furthermore, unusual and often enhanced properties can be realized. The most important technological applications of nanocomposites are semiconductor heterostructures due to the tunability of their electronic and
photonic properties$^{[64]}$ and metallic superlattices due to their magnetic properties arising from coupling between ferromagnetic phases in specific geometries.$^{[72]}$

During the synthesis of colloids, surfactants are essential to disperse and stabilize nanoparticles in the solvent. For this purpose, molecules (capping agents) are physisorbed or chemisorbed on the surface of colloids. Various surfactants have been used to stabilize a large variety of metal nanospheres. This capping agent chemistry has become a vast sub-field of nanoscience because of its implications to nanostructure synthesis and the interactions that arise between neighbouring nanoparticles.$^{[73]}$ Ordered arrays of metal nanoparticles exhibit properties that can be controlled via particle size and interparticle distance.$^{[74]}$ To achieve control, the use of organic-shell capped metal clusters is of great advantage. Capping agents around the particles play a crucial role in the self-assembly, which is mainly driven by the interacting forces of the shell molecules.$^{[75]}$ Many important features of metal nanoparticles, such as their chemical reactivity and/or optical properties, depend on the nature of the ligand and the ligand-metal bond. Capping agents span a broad range of aliphatic and aromatic molecules with functional groups ranging from thiols, acids, amines to polymers. The molecules are utilized for the specific properties that they imprint on the nanoparticle such as solubility, synthesis and incorporation properties.$^{[76-82]}$

Despite steady progress toward these applications in recent years, an understanding of nanoparticle surface chemistry must be obtained before nanoparticles can become essential building blocks for advanced optical and
electronic devices. This goal is important because surface bound molecules will likely be used to make interparticle contacts. Moreover, surface-bound ligands are known to effect particle optical and electronic properties\cite{73, 74} emphasizing the importance of effects of surface chemistry on these properties.

A major motivation for research in this field remains the challenge to understand and control how ordered or complex structures form spontaneously by self-assembly. For the purpose of controlling formation in order to prepare structures with a pre-determined geometry, it is important to build a broad experimental database, from which a better fundamental understanding of self-organization processes and eventually a predictive insight can be developed. While the range of synthetic methods commonly available has yielded much progress in nanoparticle chemistry, assembling them into three-dimensional architectures remains a significant challenge. Three-dimensional architectures generated have been shown to be dependant on the size and charge of the building blocks\cite{83, 84} and thus introduce limitations in advancement and development of these materials.

1.9 Project Overview

The present work investigates the adsorption of molecules on single layer MoS$_2$ through which the restacking process, along with adsorbate molecule organization due to guest-host interactions, could be investigated. One can consider gaining an understanding of the building of simple blocks in nanostructure assembly a first step to a broader picture of nanostructure generation. Upon gaining insight into the processes that are associated with the
favourable interactions that generate materials with adsorbate molecules included in MoS$_2$, these interactions are applied towards synthesis of a new type of three-dimensional MoS$_2$-nanoparticle composite materials.

This thesis is organized as follows. The second chapter outlines the theoretical basis of the nonlinear optical experiments performed. Chapter 3 provides the details of the sample preparation and schemes of the experimental procedures as well as a brief outline of analytical methods employed during the course of the investigation. Chapter 4 discusses the use of exfoliated MoS$_2$ layers as surfaces for adsorption. The properties of exfoliated and restacked MoS$_2$-malachite green (MG, 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline) inclusion compounds are examined to provide insight into the interactions between MG and MoS$_2$. Through the use of UV spectroscopy and XRD, an adsorption isotherm of the model molecule (MG) on MoS$_2$ is obtained. Orientation-specific information on this molecule is obtained using SHG. A model for the exfoliation, adsorption, and subsequent restacking of these MG-based inclusion materials is provided and the utility of nonlinear optical techniques as probes of these interesting layered structures is demonstrated. Chapter 5 describes the types of surface interactions that occur between the guest and host. Described is a novel exfoliation technique at the air/water interface followed by subsequent LB deposition. The results of XRD and molecular resolution AFM experiments are presented. The sum frequency generation vibrational spectroscopy data obtained from a monolayer film is used to observe characteristic features in its CH stretching regions. The above
techniques are used in a complementary fashion to investigate host film ordering. In chapter 6, the results of synthesis and structure of new exfoliated and restacked MoS$_2$ – iron oxide and gold nanoparticle inclusion materials are reported. By altering capping agents on nanoparticles, nanostructure architecture is investigated using TEM and XRD. Conductivity of the material is obtained using the four-point probe method. Taken together, the methods presented here provide a new approach for the controlled fabrication of nanostructured architectures.

Two appendices follow the conclusions. Appendix 1 discusses the details of the Fresnel coefficients required for fitting procedures employed in the analysis of the polarized SHG studies. Appendix 2 outlines the Euler transformations required in relating the molecular and laboratory reference frames used in the molecular orientation analysis.

The goal of the thesis is to investigate the use of MoS$_2$ layers as surfaces of adsorption. The interactions of adsorbate molecules have been investigated. Based on the information gained from these studies, a new type of three-dimensional nanostructure composite from gold nanospheres and MoS$_2$ has been generated.
CHAPTER 2: NONLINEAR OPTICAL PHENOMENA

Second harmonic generation has been proven to be a particularly effective and versatile probe for surface studies and has been extended to a wide range of interfacial environments. The technique has demonstrated excellent spatial, spectral and temporal resolution of *in-situ*, non-destructive probing of interfacial species in a variety of environments with sub-monolayer sensitivity. It is because of these characteristics that this technique will be employed as a major analysis tool in order to gain insight into the MoS$_2$ single layer systems.

Nonlinear optics is a branch of optics that results from the interaction of light with materials in which the polarization response is nonlinear with respect to the electric field of light. This nonlinear response can produce photons of frequencies that are different from the initial fundamental wave and as a result can give rise to many interesting phenomena. If the intensity of light is high enough, such as that associated with laser light, the phenomena include the generation of the higher harmonic frequencies. The polarization, $P$, of the nonlinear material can be expressed as the power series\textsuperscript{[57, 85]}

\begin{equation}
P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + ... 
\end{equation}

where $\chi^{(n)}$ is the $n$th order susceptibility of the material and $E$ is the electric field strength. For $n = 1$, $\chi^{(n)}$ is the linear dielectric susceptibility of the material and for $n > 1$ $\chi^{(n)}$ is the higher order susceptibility of the material (second, third,
etc...). In a nonlinear medium, an infinite number of waves of nonlinear polarization, \( P_{\text{nonlinear}} \), are produced

\[
\vec{P}_{\text{nonlinear}}(\omega) = \chi^{(n)} : \vec{E}_1 \vec{E}_2 \vec{E}_3 \ldots \vec{E}_n
\]  

(5)

at frequencies \( \omega = \sum_{m=1}^{n} \omega_m \), where the \( \chi^{(n)} \) is a rank \( (n + 1) \) tensor. The magnitude of a subsequent susceptibility component is typically 3 to 5 orders of magnitude less than the previous one,\(^{[57]}\) and thus investigating the higher order nonlinear optical phenomena requires light of very high peak intensity. The nonlinear processes can be induced by the high electric fields associated with high power laser radiation and become the basis for novel spectroscopic techniques such as multi-photon absorbance spectroscopy, SHG and SFG.

In media which posses inversion symmetry, the even-order susceptibility components reduce to zero making this technique extremely powerful in investigating geometries where such inversion symmetry will necessarily be broken.\(^{[59]}\) Because the magnitude of the susceptibility components decreases as the order of the optical process increases, the lowest order process capable of probing interfacial phenomena is the second order polarizability. The higher even-order polarizability processes can be utilized here as well, but they require electric fields that are 4 to 6 orders of magnitude higher than those required for the second order process.\(^{[86]}\) Boundaries between two centrosymmetric bulk media lack inversion symmetry and thus even-ordered nonlinear optical phenomena arising from that interface will yield selective information about that interface with no contribution from the adjacent bulk media. Investigating
geometries where the inversion symmetry is broken can provide insight into many interfacial phenomena that are important in science. This geometry makes the second order nonlinear optical phenomena an exciting tool when investigating processes where interfaces are of utmost importance.\cite{51, 59, 60, 87}

Figure 5: Schematic representation of generation of a SH photon on an interface where centrosymmetry is broken.

2.1 Second Harmonic Generation

When light of frequency $\omega$ impinges on a medium, it will induce overtone dipole oscillations in each molecule in the medium at frequencies $\omega, 2\omega, 3\omega$, etc. because each molecule acts as an anharmonic oscillator. The focus turns now on the second order optical phenomenon at frequency $2\omega$ since it is the lowest order nonlinear optical phenomenon that will arise from the interface between two centrosymmetric media. The induced dipole moment per unit volume or polarizability is proportional to the square of the field strength $E(\omega)$ (at frequency $\omega$).\cite{59}

$$\vec{P}^{(2)}(2\omega) = \chi^{(2)}(\omega) \vec{E}(\omega) \vec{E}(\omega)$$  \hspace{1cm} (6)
where the constant of proportionality is the nonlinear susceptibility $\chi^{(2)}$ and is characteristic of the medium involved in light generation. This equation is the second term of equation (4). In a centrosymmetric medium, light of field strength $E(\omega)$ and $-E(\omega)$ must induce dipoles $P^{(2)}(2\omega)$ and $-P^{(2)}(2\omega)$, respectively. This expression only holds true with equation (6) if $\chi^{(2)} = 0$ and thus second order radiation will not occur in a centrosymmetric medium. At the interface where the symmetry is broken, the second order susceptibility component is not reduced to zero and hence radiation at $2\omega$ will be generated. As a result, SHG from the interface between isotropic bulk phases is surface-specific.

In this description, one ignores local field effect, that is, the contributions from neighbouring induced dipoles, the effects of optical magnetic fields and the refractive index of the monolayer. It is assumed that the dipole induced is only the result of the applied electric field.\(^{[88]}\) The second order susceptibility can be written as a sum of the interface susceptibility without the adsorbate molecules, $\chi_0^{(2)}$, and the susceptibility of the molecular layer deposited at the interface\(^{[56]}\), $\chi_{\text{mol}}^{(2)}$

$$\chi_i^{(2)}(2\omega) = \chi_0^{(2)}(2\omega) + \chi_{\text{mol}}^{(2)}(2\omega)$$  \hspace{1cm} (7)

Both contributions to the surface second order susceptibility must generally be considered unless the contribution from $\chi_{\text{mol}}^{(2)}$ is much larger than that from $\chi_0^{(2)}$ due to the probe molecules being highly polarizable.
The SH intensity, $I_{2\omega}$, that results when a light beam of frequency, $\omega$, and intensity, $I$, is given by\[^{69,88}\]

$$I_{2\omega} \propto \frac{32\pi^3\omega^2}{c^3}\sec^2\theta_{2\omega}\left|\vec{E}_{2\omega}\chi_s^{(2)} : \vec{E_{2\omega}}\right|^2 I_{\omega}^2$$

$$I_{2\omega} \propto \left|\chi^{(2)}_{\text{eff}}\right|^2 I_{\omega}^2 \quad (8)$$

where $\vec{E}_{\omega}$, $\vec{E}_{2\omega}$ are vectors that indicate the direction of the polarization of light at frequencies $\omega$, $2\omega$, respectively and $c$ is the speed of light in vacuum. The angle $\theta_{2\omega}$ is the angle of the resulting beam with respect to the surface normal and $\chi_s^{(2)}$ is the second order susceptibility tensor of the surface containing 27 components.

If the surface molecules have a random orientation with respect to rotation about the surface normal, then the expression of $\chi_s^{(2)}$ can be reduced considering the symmetry of the film. By applying the intrinsic permutation symmetry, $\chi_{ijk}^{(2)} = \chi_{ikj}^{(2)}$, to equation (6), $P_i^{(2)}(2\omega) = \chi_{ijk}^{(2)} E_j(\omega)E_k(\omega)$, $\chi_s^{(2)}$ can be reduced to 18 independent elements

$$\chi_s^{(2)} = \begin{bmatrix}
\chi_{xxx} & \chi_{xxy} & \chi_{xzx} & \chi_{xzy} & \chi_{xzz} & \chi_{xzy}
\chi_{yxx} & \chi_{yxy} & \chi_{yxx} & \chi_{yy} & \chi_{yx} & \chi_{yzy} \\
\chi_{zxx} & \chi_{zxy} & \chi_{zxx} & \chi_{zz} & \chi_{zzy} & \chi_{zzy}
\end{bmatrix} \quad (9)$$

due to the rotation symmetry. Considering now the reflection through the surface plane, $yz$, one arrives at $\chi_{xxx} = \chi_{xxy} = \chi_{xzx} = \chi_{xzy} = 0$. Considering the reflection in the $xz$ plane, the only nonzero element remaining is $\chi_{zxz}^{(2)}$. Similarly after
considering $P_y^{(2)}$ and $P_z^{(2)}$ the only nonzero independent elements remaining are $\chi_{xxx}^{(2)}$, $\chi_{xxx}^{(2)}$ and $\chi_{zzz}^{(2)}$. Thus, these components form a complete set of linearly independent elements. The values of these three components can be extracted from equation (8) and by measuring the polarization-selected signal as a function of the polarization angle of the incident light. The intensity of the SH signal can be simplified in terms of only the independent elements and can be expressed as a function of the polarization angle.\cite{89} $\psi$, 

$$I_\psi(2\omega) \propto \left| \frac{c_1 \chi_{xxx} \cos 2\psi \sin 2\psi}{\left[ (c_2 \chi_{xxx} + c_3 \chi_{zzz} + c_4 \chi_{zzz}) \cos 2\gamma + c_5 \chi_{zzz} \sin^2 2\gamma \right] \cos \psi} \right|^2 I^2(\omega) \tag{10}$$

where $\psi = 0^\circ$ and $\psi = 90^\circ$ correspond to p and s-polarizations of the SH light, respectively. If the incident radiation is polarized by a half wave plate, then these p and s components of the incident light can be expressed as

$$E_p(\omega) = E_0(\omega) \cos 2\gamma \quad E_s(\omega) = E_0(\omega) \sin 2\gamma \tag{11}$$

where $2\gamma$ is the polarization angle controlled by the half wave plate.

The constants, $c_i$, in equation (10) describe the magnitudes of the electric fields in the surface monolayer and are proportional to the Fresnel factors describing transmission and reflection at each interface encountered, as well as the appropriate dielectric constants for the materials used. The calculation of these constants has been outlined for the total internal reflection geometry that is used\cite{89} and is described in more detail in Appendix 1. The values of the three
components, $\chi_{zzz}$, $\chi_{zxx}$ and $\chi_{xzx}$ can be obtained from the polarization selected SH signal as a function of the polarization angle of the incident light.

Since the sum frequency signal comes from the interface species, each of which gives rise to a signal, the susceptibility tensor may be written as an average of the individual molecular polarizability contributions, $\beta^{(2)}$.

\[ \chi^{(2)}_{ijk} = N_s \sum \langle l_i l_j k \rangle \beta^{(2)}_{i' j' k'} \]  \hspace{1cm} (12)

where $N_s$ is the number of molecules that are giving rise to the signal and the brackets represent the averaged adsorbate orientation obtained from the Euler rotation matrix, $l$, from the molecular frame, $i' j' k'$, to the laboratory frame, $ijk$. The transformation of coordinates from the molecular frame to the laboratory frame is briefly discussed in Appendix 2. Upon obtaining the elements of the susceptibility tensor, $\chi$, the molecular nonlinear hyperpolarizabilities can be calculated. The coordinates of the molecular frame and the laboratory frame are defined in Figure 6. The Euler angles, $\delta, \theta, \varphi$, define the orientation of the molecule (chosen to be MG in the experiments to follow) with respect to the prism plane. The molecular orientation of MG has been reduced to be a function of only $\theta$ on the basis that the molecule is quite small and is symmetric about the molecular $z'$ axis.
2.2 Sum Frequency Generation

Second harmonic generation represents a special case \( (\omega_1 = \omega_2) \) of the more general sum frequency generation process that occurs when two photons of frequencies \( \omega_1 \) and \( \omega_2 \) overlap in space and time on an interface as shown in Figure 7. When one of the incoming frequencies is at the same energy as one of the vibrational frequencies of the interfacial species being investigated, then the sum frequency light generated will be resonantly enhanced. To take advantage
of this phenomenon one of the incoming beams is tuned to the vibrational frequency of the spectral region being investigated. Due to the enhancement, the sum frequency signal will carry vibrational information from the interface.\textsuperscript{[58]}

![Diagram of sum frequency generation](image)

**Figure 7**: Schematic representation of generation of a sum frequency ($\omega_3 = \omega_1 + \omega_2$) photon on an interface where centrosymmetry is broken.

An alternative approach to tuning one of the fundamental beams to the vibrational frequency under investigation is to use a broadband pulse in order to capture a larger portion of the vibrational spectrum in the sum frequency signal and not just one vibrational peak. This broad pulse removes the task of tuning that incoming pulse to every frequency of interest for every vibrational peak being investigated.
Figure 8: Schematic representation of Sum Frequency Generation energies where $\omega_1$ is the infrared broadband pulse that overlaps the vibrational region of interest and $\omega_2$ is the visible pulse which gives rise to the entire spectrum mapped out by $\omega_3$.

The SFG process is a three-wave mixing process that is governed by the non-linear polarization

$$\bar{P}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi^{(2)}: E(\omega_1)E(\omega_2)$$

(13)

where $\chi^{(2)}$ consists of a resonant and a nonresonant, $\chi_{NR}$, component.

$$\chi^{(2)} = \frac{A}{\omega_{IR} - \omega_\nu - i\Gamma} + \chi_{NR}$$

(14)

Here $\chi^{(2)}$ is related to the SFG amplitude, $A$ is proportional to the IR transition moment and the Raman transition moment, when the incoming IR pulse, $\omega_{IR}$, is near the vibrational resonance, $\omega_\nu$. $\Gamma$ is the Lorentzian half width of the vibrational mode and $\chi_{NR}$ represents the nonresonant contribution to $\chi^{(2)}$, i.e.,
signal arising from the substrate. The nonresonant contribution from materials that are not very polarizable is generally quite small (1% of the resonant-based intensity in the experiments to follow). Because $A$ is a function of the IR transition moment and the Raman transition moment, a vibrational mode must be both IR and Raman active in order to be SFG active.

The surface SFG technique can be considered analogous to linear vibrational spectroscopy, which is based on the linear polarizability. Instead, it provides vibrational information that is surface specific. In addition, buried interfaces between two centrosymmetric media can be investigated with no contribution to the sum frequency signal from the adjacent media.

The single layer structure of MoS$_2$ will allow for the deposition of single layers on the interface between two bulk media. In this geometry, the surface spectroscopic techniques may provide insight to the geometry and dynamics of adsorbate molecules on MoS$_2$. 
CHAPTER 3: EXPERIMENTAL

3.1 Preparation of MoS$_2$ and Probe Molecules

Exfoliated samples of molybdenum disulfide (Aesar) were obtained by lithium intercalation following conventional literature protocols. Typically, 1 mL of 2.5 M n-butyl lithium (Aldrich) in hexane was reacted with 0.1 g of the disulfide in a 50 mL container under an argon atmosphere inside a glove box. This ratio of reactants generated an excess of Li relative to $n=1$ as per equation (1). The mixture was filled to 50 mL with hexane and allowed to sit for 24 h before proceeding. In hexane, the mixture was stable for months provided it was sealed from moisture. When the sample was to be used further, the hexane was removed, and 50 mL of water was added which caused spontaneous exfoliation of the Li$_x$MoS$_2$ to occur. Formation of the restacked material was induced following washing of the aqueous suspension with water three times and centrifugation at 3000 rpm for 10 min.

3.1.1 Gold Nanoparticle Synthesis

Gold nanoparticles were prepared using two different methods. The first method was first described by Slot and Geuze$^{[78]}$ and is capable of controlling the size of the nanoparticles produced. The production of a gold nanoparticle solution required preparation of two solutions, A and B. Solution A is an Au$^{3+}$ solution containing 1 mL of 1% HAuCl$_4$ in 79 mL distilled water. The 1% HAuCl$_4$ solution was made by dissolving a stoichiometric amount of the gold salt (Aldrich).
in distilled water. Solution B is a reducing mixture containing 4 mL of 1% trisodium citrate (BioShop), 0 to 5 mL of 1% tannic acid\[^{[78]}\] (Aldrich), 25 mM K\(_2\)CO\(_3\) (BDH) (same volume as 1% tannic acid) and distilled water for a total volume of 20 mL. All percentages were calculated by mass. Solutions A and B were brought to 60 °C on a hot plate and combined while stirring. The nanoparticles were formed instantly as evidenced by a sudden colour change. The amount of tannic acid added has a profound effect on the size of the nanoparticles produced. Au\(^{3+}\) is being reduced by sodium citrate. The detailed chemistry of this is complex and beyond the scope of the thesis. By varying the amount of tannic acid in the synthesis, the particle diameter can be controlled from 3 to 18 nm. The resulting particles are citrate capped in an aqueous solution with a gold content of 57.6 \(\mu\)g/mL.

The second method employed for preparing gold nanoparticles is the Brust two-phase method.\[^{[82]}\] An aqueous solution of HAuCl\(_4\) (500 mg in 40 mL) was mixed with a solution of tetraoctylammonium bromide (TOAB, Fluka) in toluene (3.06 g in 100 mL). The two-phase mixture was vigorously stirred until all of the HAuCl\(_4\) had transferred into the organic phase to give a deep orange solution. A fresh aqueous solution of NaBH\(_4\) (EMD, 525 mg in 30 mL) was added slowly while stirring. The organic phase almost immediately turned ruby red. After 12 h of stirring, the organic layer was extracted and washed with Millipore water (three times) and then dried over anhydrous sodium sulfate. The solution was then diluted to 250 mL. The result was a solution of TOAB-stabilized gold metal nanoparticles (TOAB-Au).
The gold nanoparticles were transferred to water following the method proposed by Gittins and Caruso.[81] An aqueous solution of 4-(dimethylamino)pyridine (DMAP; Fluka) (3.05 g in 250 mL) was added to a solution of TOAB-Au nanoparticles in toluene. Phase transfer of the particles occurred spontaneously, and the ruby red aqueous solution of DMAP-stabilized Au nanoparticles (DMAP-Au) with a gold content of 1 mg/mL[90] was isolated.

3.1.2 Fe₃O₄ Nanoparticle Synthesis

Iron oxide (Fe₃O₄) nanoparticles were prepared using literature protocols.[77] The metal–oleate complex was prepared by reacting metal chlorides and sodium oleate. In order to synthesize the iron–oleate complex, 1.08 g of FeCl₃·6H₂O, (4.0 mmol, Aldrich, 98%) and 3.65 g of sodium oleate (12.0 mmol, TCI, 95%) was dissolved in a mixed solvent composed of 4.0 mL ethanol, 6.0 mL distilled water and 14.0 mL hexane. The resulting solution was heated to 70 °C and kept at that temperature for four hours. When the reaction was completed, the upper organic layer containing the iron-oleate complex was washed three times with 5 mL distilled water in a separatory funnel. After washing, hexane was removed by evaporation, isolating an iron–oleate complex as a waxy solid.

The monodisperse iron oxide nanocrystals were made from 3.6 g (4.0 mmol) of the iron-oleate complex and 0.57 g of oleic acid (2.0 mmol, Aldrich, 90%) dissolved in 20.0 g of 1-octadecene (Aldrich, 90%) at room temperature. The reaction mixture was heated to 320 °C with a constant heating rate of 3.3 °C/min, and then refluxed at that temperature for 30 min. When the reaction
temperature reached 320 °C, a series of minor explosions occurred and the initial transparent solution became turbid and brownish black. The resulting solution containing the nanocrystals was then cooled to room temperature, and 50.0 mL of ethanol was added to the solution to precipitate the nanocrystals. The nanocrystals were separated from the solution by centrifugation.

3.2 Sample Preparation

Samples were prepared using a variety of techniques that depended on the method used for characterization and will be discussed in detail later. Washing of restacked MoS$_2$ samples with water involved centrifuging using a centrifuge (MSE, Mistral 1000) at a frequency of 60 Hz for 10 minutes three times. The drop cast technique, spin coat technique as well as the well known LB$^{[91]}$ techniques were employed. Drop cast films were prepared by withdrawing a solution of the material of interest and dropping it on substrate used for a particular characterization and drying it for several hours. Spin coating is a deposition technique used to prepare films from volatile solvents. The solvent evaporates during substrate spinning, leaving the probe molecules on the substrate. Samples were prepared by dropping the suspension onto the substrate from an aqueous solvent and spinning at 50 Hz until the solvent evaporated. The spinner consisted of a small motor, which spun the substrate holder. The motor current was adjusted to obtain the spin speed, which was measured with a strobe light. The current was maintained for the duration of the procedure.
3.2.1 Langmuir-Blodgett Technique

The LB technique is used to deposit monolayers of amphiphilic molecules from a liquid/air interface onto solid substrates. Single MoS$_2$ monolayers with stearic acid were prepared by the LB method with the use of a LB trough (Nima Technology Ltd., model 61M300). Water was used as a conventional subphase for the Langmuir film formation.$^{[92, 93]}$ Generally, 10$\mu$L of 1mM chloroform solution of the amphiphile of interest was spread from a syringe onto the surface of distilled and deionized water (Millipore, Milli-Q, with resistivity of 18.2 M$\Omega$/cm). A high water quality was essential in the process of the LB monolayer or multilayer preparation and its subsequent transfer onto a glass substrate. Depositions were made on fused silica prisms, CaF$_2$ prisms or silica microscope slides. The pH of the subphase as well as the presence of ions and contaminants have been shown to affect film quality.$^{[91]}$ The monolayer of amphiphilic molecules was compressed at a rate of 4 mm/min while monitoring the surface pressure to form a monolayer. Fused silica prisms and glass slides were cleaned with a “piranha bath” (sulfuric acid – hydrogen peroxide 4/1 mixture) followed by rinsing with copious amounts of distilled water in order to activate hydroxyl groups of silica thereby increasing its hydrophilicity. Caution needs to be exercised in doing this due to the strong oxidizing nature of the bath. Transfer pressures varied from 15 to 35 mN/m depending on the experiment being performed.
Applying various methods of film deposition will yield different types of films. The head-to-head and tail-to-tail association of amphiphiles results in the so-called Y-type architecture, which is the result of a deposit of the film on to the substrate on each stroke. Instances in which the floating monolayer is then transferred to the substrate as it is being inserted into the subphase result in head-to-tail (X-type) films. Similarly, instances in which the floating monolayer is only transferred to the substrate as it is being removed from the subphase result in Z-type films. Alternate layer depositions can be used to make a complex variety of multilayer films as well.

Figure 9: Schematic representation of transferring the LB monolayer of amphiphilic molecules onto a solid substrate.
3.3 Analytical Methods

3.3.1 Atomic Force Microscopy

The atomic force microscope (AFM) is a high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer. In AFM, a sharp tip is used to probe the surface of a sample. The tip is less than 100 Å in diameter and a few μm long and is located at the end of a cantilever which is a few hundred μm long. Forces between the sample and silicon nitride tip cause the cantilever to deflect along a direction path. The deflection is

Figure 10: LB film types: (A) Y-type (B) Z-type (C) X-type (D) alternate layer.
measured by a detector and thus a topographical image of the surface can be produced. Contact mode AFM makes use of the van der Waals interaction between atoms and thus the tip is typically a few angstroms from the sample surface. Since contact mode makes use of the repulsive interaction between atoms, the van der Waals force counters any attempt to bring the probe close to the samples surface.\cite{94} The cantilever position is detected with a laser and a position sensitive photodetector (PSPD) as shown in Figure 11. The PSPD drives a feedback loop adjusting the tip height such that the cantilever is no longer being deflected. The image is generated based on the signal that keeps the cantilever height constant.

![Figure 11: Schematic representation of the detection of the beam bouncing off the cantilever.](image)

Atomic force microscopy studies were carried out using a TM Microscopes Explorer scanning probe microscope system consisting of the microscope itself
operated through a personal computer outfitted with SPMLab 5.01 software. Atomic force microscopy measurements were taken to assess the overall quality of the films. An advantage of AFM is that it provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatment that would irreversibly change or damage the sample and the samples can be probed at atmospheric pressure. Two-dimensional Fourier transform software was used to generate crystal lattice repeat-unit images and calculate atomic spacing.

3.3.2 X-ray Diffraction

X-ray Diffraction is a non-destructive technique which is used to gain information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. X-ray photons are diffracted upon the interaction with electrons generating interference patterns. Constructive interference resulting in reflection of waves from layers of atoms leads to the Bragg equation,[95]

\[ n \lambda = 2d \sin \theta \]  

(15)

where \( \lambda \) is the wavelength of the X-ray, \( d \) is the interlayer separation, \( n \) is the number of waves and \( \theta \) is the angle of diffraction. Diffraction efficiency increases as the atomic number value of the atom increases because of the increased electron density of the heavier nuclei.
The crystallite sizes of the diffracting medium can be estimated from their powder X-ray diffraction patterns by using a simplified version of the Scherrer formula.\cite{Scherrer1917}

\[ D = \frac{51.6\lambda}{\beta \cos \theta} \]  

(16)

where \( D \) is the average crystallite size in Ångstroms, \( \lambda \) the wavelength of the radiation Ångstroms, \( \beta \) the peak full width at half-maximum (FWHM) in 2\( \theta \) degrees and \( \theta \) is the position of the peak in degrees.

Material structure and quality were inferred by XRD studies. Low-angle X-ray diffraction experiments were carried out using both a RAPID (Rigaku) X-ray diffractometer with a copper target (\( \lambda_{\text{Ka}} = 1.542 \ \text{Å} \)) and an image plate detector and a D8 Discover (Bruker) \( \theta-2\theta \) X-ray diffractometer with a copper target (\( \lambda_{\text{Ka}} = 1.542 \ \text{Å} \)). The angles scanned ranged from zero to \( 40^\circ \) depending on the sample. X-ray diffraction patterns were obtained using a 300 μm collimator inserted into the path of the incident X-rays. Exposure times were varied and were dependent on the sample being probed and the geometry of the experiment, i.e., low angle diffraction, etc. Long acquisition times were required when expected peaks resulted from films comprised of low mass atoms since the primary mechanism for interaction of X-ray photons with matter is through the electron density of the matter.
3.3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a method used on samples to determine changes in mass with respect to change in temperature in air. Information available from these experiments includes degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials and decomposition of materials. The analyzer usually consists of a high-precision balance with a pan loaded with the sample. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. Analysis is carried out by raising the temperature linearly and plotting weight against temperature. Because mass loss changes can be very subtle, a derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Thermogravimetric analysis obtained at scan rates of 2 °C/min were performed with a TGA50 Shimadzu thermogravimetric analyzer.

3.3.4 Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Transmission electron microscopy (TEM) is a technique in which a beam of electrons is transmitted through a sample thus forming an image on a collection screen. The technique is sensitive to the volume and density of the material being investigated as sufficiently thick or dense samples will not allow for the transmission of electrons. An FEI Technai G2 Microscope equipped with energy dispersive X-ray spectroscopy (EDX) was used for TEM and EDX measurements.
To stimulate a measurable EDX response from a specimen, an electron beam is used to excite core electrons of an atom, prompting their ejection and resulting in the formation of electron holes. An electron from an outer, higher-energy shell then fills the hole and, in doing so, attains a lower energy state and dissipates the excess energy in the form of an X-ray photon. The energy of the photon is characteristic to that of the atom to which it is attributed. Thus, spectral lines that are fingerprint patterns of atoms can be obtained.

Transmission electron microscopy electrons were accelerated through a potential of 200 keV. Samples were prepared by dipping a carbon coated Cu grid in the suspension containing the material to be investigated. Samples were dried for four hours before measurements were to be taken in order to minimize the amount of water introduced into the TEM vacuum.

3.3.5 The Four-Point Probe Method

The co-linear four-point probe technique is a common method for measuring conductivity. This method circumvents the need to know the contact resistance at each metal probe/surface contact as well as the spreading resistance of the current, which occurs when the current flows from the metal probe into the sample being probed. In this method, two probes pass a current through the sample and the other two probes are used to measure the voltage. Generally, the four probes are in a linear arrangement as shown in Figure 12. While the two outside probes which carry the current are subject to the resistance issues mentioned above, the inner probes are not. The inside probes measure the voltage with a very high resistance voltmeter, which draws very little
current. The resistivity, defined as the inverse of the conductivity, \( \rho = \frac{1}{\sigma} \), of a material measured using the four-point probe method is given by \(^{[96]}\)

\[
\rho = \frac{2\pi s V F}{l}
\]  

(17)

where \( s \) is the probe spacing, \( V \) is the measured potential between the two voltage probes, \( l \) is the current carried by the two outside probes and \( F \) is a correction factor that depends on the sample geometry.

**Figure 12:** Schematic representation of the four-point probe. The four vertical lines represent the four probes. The two outer probes pass the current through the sample while the two inner probes measure the voltage with a voltmeter of very high internal resistance. The probes are equidistant from each other with a distance of \( s \). The dark cylinder is the sample of thickness, \( t \), diameter, \( h \). The probes are a distance, \( d \), away from the nearest edge of the sample.

The correction factor is the product of three independent correction factors \(^{[96]}\)
\[ F = \frac{\ln(2)F_1F_2F_3}{\pi} \]  

(18)

where \( F_1 \) corrects for sample thickness, \( F_2 \) corrects for lateral sample dimensions, and \( F_3 \) corrects for placement of probes relative to the sample edge.

For a conducting sample of thickness, \( t \leq \frac{s}{2} \), the correction factor, \( F_1 \), is\(^{97}\)

\[ F_1 = \frac{t}{2s \ln 2} \]  

(19)

For circular samples of diameter, \( d \), the correction factor \( F_2 \) is given by\(^{98}\)

\[ F_2 = \frac{\pi}{\ln 2 + \ln \left( \frac{d}{s} \right) + 3} - \ln \left( \frac{d}{s} - 3 \right) \]  

(20)

The value of \( F_3 \) arrives at the asymptotic value of unity as the distance from the probes to the sample boundary, \( h \), becomes large, \( \frac{h}{s} \geq 2 \).\(^{99}\) The correction factors, \( F_i \), above are for samples deposited on non-conducting substrates. Measurements were performed using a probe (Model 280, Four Dimensions, Inc. Probe R\(\mu\)25) with \( s = 1.0 \) mm. Thickness measurements were performed using a surface profilometer (Alpha Step IQ).

3.4 General Description of the Laser System

Non-linear optical measurements were performed under total internal reflection conditions utilizing the regeneratively amplified output of a mode-locked
Titanium:Sapphire oscillator either directly or after being passed through an optical parametric generator (OPG) depending on whether a SFG or SHG experiment was being performed. Figure 13 shows a schematic representation of the system used.

**Figure 13:** Schematic representation of the laser system used for nonlinear optical experiments.

A 6W of output light at 532 nm from a CW laser (Coherent, Verdi) was used to pump a mode-locked Ti:Sapphire oscillator (Spectra Physics, Tsunami 3960) which produced a pulsed train at 82 MHz, with a wavelength tuneable from 750 to 850 nm and pulse duration of 65 fs. A portion of this pulse was sent to a Ti:Sapphire chirped pulse regenerative amplifier (Positive Light, Spitfire) for
amplification. The amplifier was pumped by a pulsed intracavity frequency-doubled, Q-switched Nd:YLF laser (Positive Light, Merlin), which operated at a repetition rate of 1 kHz. The amplifier produced pulsed radiation with the pulse duration of 100 fs, pulse energy of 1 mJ, and wavelength tuneable from 750 to 850 nm.

Only a small portion (~10 mW) of the output was used in the nonlinear optical studies in order to avoid any damage of the samples by the high power radiation. The power of the beam was optimized for a particular experiment by monitoring the nonlinear optical response of the sample. Care was taken to avoid photon-induced damage to the samples.

3.4.1 Second Harmonic Generation Setup

Second Harmonic Generation experiments were performed by analyzing the polarization dependence of the interface SH response. The amplified Ti:Sapphire laser light was used to conduct SHG experiments. To ensure polarization purity of the incident beam, it was passed through a Glan-Taylor polarizer (CVI Laser). The polarization of the incident radiation was varied by passing the beam through a quartz zero-order, half-wave plate (CVI Laser). An interference filter was placed before the sample in order to remove any SH light that may have been generated at previous interfaces on the mirrors or in the half wave plate along the beam path. The layout of the setup is shown in Figure 14.

Conducting these types of experiments in total internal reflection (TIR) geometry rather than in a conventional external reflection geometry allowed one
to gain a factor of several orders of magnitude in the SH signal generated.[54, 61]
Before light is internally reflected it propagates along the surface some distance
which increases the effective interaction length of the light with the molecules
being probed.

Optical quality right angle fused silica prisms (CVI Laser) were used as
substrates for the samples being investigated. The probe molecules were
deposited on the hypotenuse side of the prism using one of the techniques
discussed earlier.
The light was directed onto the small face of the prism at near normal incidence angle, controlled by a rotation stage (Melles Griot) with 0.1° resolution to attain the condition of TIR on the prism hypotenuse. The SH light generated at the prism hypotenuse exited the prism at approximately a right angle with respect to the incident beam, and was spatially separated from the fundamental light due to the difference in the refractive index for the two wavelengths. The fundamental and the SH light were spatially filtered and the SH light was passed through an additional interference filter to avoid any possible contamination of the
signal at the fundamental wavelength. The SH light was passed through a Glan-Taylor polarizer for analyzing different polarization components and focused with a short focal length (5 cm) lens on the entrance slit of a 0.25 m monochromator (CVI Laser, Digikron 240). The light, spatially filtered in the monochromator was detected with a photomultiplier tube (PMT; Hamamatsu, T212) whose analogue signal was processed with a boxcar integrator (Stanford Research Systems, SR 240, time gate width ~10 nm, signals averaged over 3000 laser shots), amplified with a 300 MHz preamplifier (Stanford Research Systems, SR 245) and processed with a personal computer. A relative error associated with the alignment procedure of 2% was estimated by realigning the same sample several times.

3.4.2 Sum Frequency Generation Vibrational Spectroscopy Setup

The OPG allows for the generation of an ultrafast (~100 fs) broadband infrared beam. It has been demonstrated previously that the broad IR pulses are advantageous in that all vibrational modes within the spectral bandwidth of the pulse are excited without tuning the infrared frequency. The two beams, IR and 800 nm (Figure 15, also see section 2.2) propagate through the small face of a CaF₂ prism under TIR conditions. The temporal overlap of the pulses is accomplished by a computer-controlled optical delay line at the hypotenuse surface of the prism containing the sample and generate the sum frequency light. The SFG signal is filtered spatially from the fundamental frequencies due to the difference in the refractive index of the prism at different wavelengths. The broadband SFG signals generated from the surface are
dispersed in a spectrograph (Oriel 260i) and collected with an electron-multiplying charge coupled device (CCD) camera (Andor). The resulting signals are sent to and processed with a personal computer.

**Figure 15**: Schematic representation of the SFG IR spectroscopy setup.
CHAPTER 4: EXFOLIATION, ADSORPTION AND RESTACKING DYNAMICS

The ability of MoS$_2$ to encapsulate a large range of diverse species has stimulated much interest in the structure of the exfoliated and restacked material.$^{[17, 18, 21, 100, 101]}$ While the potential environmental and economic benefits to such new technologies can be readily appreciated, the specific host-guest interactions required for effective encapsulation are not well understood. Presented here are the results of experiments on the exfoliation and restacking of MoS$_2$ in the presence of water and the cationic dye MG in order to extend the current level of understanding of its adsorption and encapsulation abilities. Investigated in the current chapter, is the adsorption interactions of MG to single layers of exfoliated MoS$_2$ and the properties of the resultant restacked inclusion materials. Sections of this chapter are reproduced with permission from G. Cetnarowski and G. W. Leach, *Langmuir* 2006, 22, 8995 Copyright 2006 American Chemical Society.$^{[102]}$

4.1 Environment of Adsorbed Water

To assess the general characteristics of the exfoliated and restacked MoS$_2$ materials as a function of solvents varying in acidity, TEM images of their drop-cast films were obtained. Figure 16 shows typical TEM micrographs of the exfoliated and restacked material as a function of various solvent conditions. The extent of restacking is shown to vary as a function of the acidity of the
solvent. The image of MoS$_2$ exfoliated using water shows clearly the presence of overlapping thin sheet structures attributable to the layered restacked material. Note that there appears to be little or no orientational order between individual sheets. Distinct from the highly ordered nature of its parent crystalline form, this lack of ordering of MoS$_2$ sheets is known to be characteristic of the restacked material. The image of MoS$_2$ exfoliated using methanol also shows the presence of overlapping thin sheet structures attributable to the layered restacked material but to a lesser extent. There are areas in this micrograph where a number of sheets reside on top of each other indicating material that was never exfoliated into single layers. The image of MoS$_2$ exfoliated using octanol shows no presence of overlapping thin sheet structures. There are large regions of bulk MoS$_2$. Thus, the dependence of the level of exfoliation on the acidity of the available hydrogen, which needs to be removed from the solvent in order to form H$_2$, is as expected. When there is no available hydrogen to form H$_2$, i.e., the acidity of the solvent is low, the monolayer material will not be formed.
Figure 16: TEM micrographs of exfoliated and restacked MoS$_2$. The images show the results of exfoliation process performed in water, methanol and octanol.

Figure 17 shows an AFM image from an exfoliated and restacked MoS$_2$ film. The image shows the presence of the restacked sheets that appear as squares of typical dimension (250 nm by 250 nm). Also evident from the image is that the restacked material has an overall average morphology consistent with the basal planes of the layers lying parallel with the substrate. These images are typical of films comprised of the “bare” exfoliated material and are consistent with structures determined by XRD where planar stacking of MoS$_2$ sheets was observed.$^{[27,34]}$
Figure 17: AFM image of exfoliated and restacked MoS$_2$ indicating the approximate 250 nm by 250 nm dimensions of the restacked crystallites deposited on a glass microscope slide.

It should be noted that the XRD pattern from exfoliated and restacked MoS$_2$ immediately following restacking shows an intense diffraction feature at $2\theta \approx 7.5^\circ$ that disappears with time. This peak corresponds to a layer separation of $d \approx 11.8$ Å which reflects a 5.6 Å expansion due to the inclusion of water. This peak reflects the incorporation and subsequent loss of H$_2$O initially adsorbed between the layers. Over time, this included water is eventually lost as the material dries.

The restacking mechanism was further investigated via the MoS$_2$ interlayer separation as a function of time as the material restacks as shown in Figure 18. Samples were drop cast from suspensions of the exfoliated material by a pipette onto a microscope glass slide and allowed to dry at room temperature. The diffraction pattern of crystalline MoS$_2$ shows a prominent diffraction peak (002) at $14.5^\circ$, corresponding to an interlayer separation of 6.1 Å.
Å, consistent with known observations. This feature is narrow and characteristic of a highly ordered crystalline structure. In contrast, the diffraction patterns of the exfoliated and restacked materials all display diffraction features that are substantially broadened relative to that of crystalline MoS$_2$. The crystallite size of pristine MoS$_2$ used was calculated to be 160 Å using equation (16). The crystallite size upon the inclusion of water is 80 Å as determined by equation (16). This reduction of the crystallite size is characteristic of exfoliated and restacked MoS$_2$ as shown in XRD here and elsewhere.
Figure 18: X-ray diffraction patterns obtained for exfoliated MoS$_2$ as a function of time and crystalline MoS$_2$. Denoted in the legend is the time elapsed after exfoliation.

The prominent trend in the diffraction pattern is the disappearance of the peak at $\sim 2\theta = 7.5^\circ$, which is attributed to layer separation resulting from water encapsulation in MoS$_2$. As time passes, the decrease in the intensity of this peak and the increase of the (002) peak intensity at $\sim 2\theta = 14^\circ$ is observed which is characteristic of the restacked material. The presence of water was corroborated by TGA (Section 4.2). The decrease of the peak at $\sim 2\theta = 7.5^\circ$ is the result of a decrease in the separation of MoS$_2$ of 5.7 Å due to the loss of water from the
layers over time. As the water is removed from the layers, the layer separation changes and the materials structure approaches that of restacked MoS$_2$. The expulsion of the water molecules over time suggests that the water inclusion structure is not thermodynamically stable.

An examination of the water molecules in the adlayer via SFG methods was undertaken in order to observe the presence of water adsorbate molecules further. This apparatus has been previously used to monitor the spectroscopy and coherent vibrational dynamics in an amphiphilic monolayer. For the studies presented here, the spectral resolution was typically 8 cm$^{-1}$. In this analysis, all spectra have been normalized for infrared intensity differences to the nonresonant SFG signal from a thin film of MG. The SFG experiments were performed on films deposited onto CaF$_2$ substrates. Samples were prepared by the spin coat technique from suspensions of the exfoliated material.

Figure 19 shows the SFG spectra in the OH region. The spectrum exhibits a sharp peak at ~3701 cm$^{-1}$, which is associated with the free asymmetric OH (non hydrogen-bonded) stretch. The stretch is the result of water present in the MoS$_2$ structure after exfoliation. This peak indicates that there exist enough non H-bonded hydrogen atoms to yield a significant SFG signal. That is, there are a substantial number of non H-bonded H$_2$O molecules in the guest lattice indicating that H-bonding may not be a predominant interaction of H$_2$O/MoS$_2$ materials. The symmetric stretch is not allowed due to the requirement of a dipole change in a vibration for an SFG signal. Attempts to observe a bonded OH stretch at 3100 - 3400 cm$^{-1}$ proved unsuccessful. There
were no signs of a free OH stretch for the material that was given a longer time lapse to restack after deposition.

In order to investigate interaction associated with the restacking of the exfoliated MoS$_2$, studies turned to investigation of inclusions of molecules yielding materials that result in a persistent, time-independent guest-host structure and hence allow rigorous probing of the sample.

![SFG spectrum of the free asymmetric OH stretch of water in restacked MoS$_2$.](image)

**Figure 19:** SFG spectrum of the free asymmetric OH stretch of water in restacked MoS$_2$.

A molecular modeling technique was employed using a HyperChem Lite (MM+ energy minimization routine) software package (version 2.0) to provide a connection between our results observed from the XRD studies and those from
SHG studies. Molecular mechanics calculations provide a measure of the water molecular dimensions and, combined with the information from the SHG measurements, provide an expected MoS$_2$ layer separation. While it is recognized that this modeling may over-simplify the environment of water, it nevertheless provides insight into the material. Showed in Figure 20 is a possible arrangement of water molecules included in the MoS$_2$ structure. The MoS$_2$ layer separation and structure was fixed while the water molecules were allowed to arrive at an energy minimum.

![Figure 20: Schematic representation of water molecules between MoS$_2$ layers. Hydrogen is represented in green, oxygen in red, molybdenum in black and sulphur in yellow.](image)

The separation of the MoS$_2$ layers in the water-included structure coupled with the SFG data suggests that there exists a bilayer of water, which does not posses a well-established hydrogen-bonded network, unlike ice. Since there is no well-established network it is expected that this water is not very well
stabilized at room temperature and as a result evaporates over time such as is the case here.

4.2 Adsorption Isotherms of Malachite Green MoS$_2$ Inclusion Materials

Malachite green has been the subject of considerable interest and investigation over the past two decades, in part, because of its use as a saturable absorber used to generate ultrashort laser pulses. More recently, the excited-state dynamics of MG adsorbed on silica have been investigated by picosecond time-resolved surface SHG. Malachite green has been previously employed as a probe molecule to investigate the orientation, aggregation, and interaction of species at the solid/air interface$^{[106]}$ and is thus an excellent molecule to use as a probe for single-layer adsorption studies.

The MG-based inclusion materials were obtained following addition of stoichiometric amounts of solid MG (Aldrich, 99%) to the freshly exfoliated and water-washed MoS$_2$. Care was taken to ensure that the added MG was completely soluble in the water-based suspension. This step was followed by extensive additional washing to ensure both a constant final pH$^{[21, 103]}$ of the aqueous suspension. This was achieved through removal of excess of LiOH produced in exfoliation so that any MG detected in the subsequently restacked material that was adsorbed and associated with the exfoliated MoS$_2$ layers prior to restacking.
To obtain the adsorption isotherm data, the MG-based inclusion materials were prepared by addition of stoichiometric amounts of solid MG (Aldrich, 99%) to the freshly exfoliated material followed by a pH adjustment to 5.5 using hydrochloric acid. A constant final pH of the aqueous suspension was necessary to facilitate the removal of excess of LiOH produced in exfoliation and to provide control of the (pH-dependent) electronic structure of MG that is adsorbed onto the exfoliated sheets.

Since MG is an acid-base indicator, the pH of the solution in which it is dissolved will change its structure and thereby electronic properties. For the purposes of these experiments, its low pH structure, shown in Figure 21, is detrimental to the absorption maximum in that it overlaps with the 400 nm beam of the SHG signal. Shown below are the structures of MG in acidic and basic conditions.
Addition of MG to the suspension of exfoliated MoS$_2$ resulted in its adsorption to the highly active surface layers. Adsorption was evident by the disappearance of the characteristic green color of MG over the course of minutes. Figure 22 shows the TGA of the exfoliated and restacked MoS$_2$ as well as the MG/MoS$_2$ inclusion material at a molar ratio of 1/10. The TGA of the restacked MoS$_2$ shows a relatively rapid mass loss from room temperature to approximately 100 °C, after which the rate of mass loss decreases until the onset of MoS$_2$ decomposition at ~650 °C. The initial decrease is attributed to the loss of water adsorbed between the MoS$_2$ layers. This loss of water is expected and has been previously observed in MoS$_2$ inclusion materials.$^{[17, 32]}$ The TGA of the MG/MoS$_2$ inclusion material, on the other hand, shows a relatively slow and steady mass loss from room temperature to approximately 300 °C. Between 300
°C and 400 °C the loss is rapid. Above 400 °C, the rate of loss decreases significantly until the onset of MoS$_2$ decomposition is reached. The rapid mass loss between 300 °C and 400 °C is attributed to the loss of MG from the inclusion material. The observed mass loss shown for the MG/MoS$_2$ inclusion material at a molar ratio of 1/10 is consistent with a stoichiometry of 9.6 ± 1.0 calculated from the TGA based on a 20 % mass loss.

![Figure 22: TGA of exfoliated and restacked MoS$_2$ and the MG/MoS$_2$ inclusion material at a molar ratio of 1/10.](image)

To characterize the adsorption process, a measurement of the adsorption isotherm was undertaken. Obtaining reliable and reproducible concentrations of
suspended exfoliated material following the previously described preparation protocols proved to be difficult. As a result, the degree of MG adsorption was inferred from the knowledge of the concentration of MG added to suspension and the concentration of “free” MG remaining in solution as measured via absorbance, following filtration of the exfoliated MoS$_2$. Note that this measurement precludes washing of the suspension and subsequent removal of unadsorbed MG. In addition, such a measurement is complicated by the fact that under the conditions employed for exfoliation, the resulting suspensions are very basic due to the presence of excess LiOH produced in the exfoliation procedure. Also, the degree of adsorption is expected to be highly pH-dependent and dictated by the net charge residing on the exfoliated MoS$_2$ sheets.$^{[103]}$ In addition, MG is often used as an indicator due to the sensitivity of its electronic structure to pH.$^{[107]}$ In basic environments, MG is colourless and has a dramatically different absorption profile than under neutral or acidic conditions as is shown in Figure 23 due to the change in its structure as mentioned earlier. The transition pH range for this change is between 11.9 and 14. Not controlling the pH would result in the inability to monitor the amount of MG in the materials being probed using the particular SFG experimental setup employed here.
Figure 23: UV/Vis absorption spectra of $1.0 \times 10^{-5}$ MG in neutral (black) and basic (grey, multiplied by a factor of 5) conditions.

Thus, it was necessary to normalize all suspensions and mixtures to a common pH value, chosen to be ~5.5. The MG loadings obtained by TGA were in good correspondence with the amount of adsorbed MG determined via optical absorption measurements. The concentrations were generated from the well-known MG extinction coefficient of $148900 \text{ M}^{-1}\text{cm}^{-1}$ at 617 nm. The amount of MG adsorbed on MoS$_2$ was determined by quantifying the absorbance spectrum of the solution after filtering off the restacked solid.
The resulting adsorption isotherm is displayed in Figure 24. The figure shows that at low MG concentrations the isotherm shows a linear increase with MG loading. No detectable (unadsorbed) MG remains in solution, implying that all MG added to the suspension is adsorbed, and that the adsorption/desorption equilibrium characterizing the suspension is heavily shifted toward adsorption. This behavior persists until a MG/MoS₂ molar ratio of approximately 0.12 is reached. At this concentration of added MG, one observes the onset of free
(unadsorbed) MG remaining in solution, and a corresponding plateau in the isotherm. On the basis of this behaviour, the appearance of the plateau is attributed as an indication of monolayer adsorption. The MG/MoS$_2$ molar ratio of 0.12 is consistent with this idea, given the molecular dimensions of MG in comparison to the dimensions of the MoS$_2$ unit cell as shown in Figure 25.

![Figure 25: Comparison of the dimensions of MoS$_2$ and MG.](image)

Figure 26 shows the results of XRD studies on crystalline MoS$_2$ and its exfoliated inclusion materials. Displayed are the XRD patterns from crystalline
MoS$_2$, exfoliated and restacked MoS$_2$ in the absence of MG, and the diffraction patterns of the inclusion materials in which the MG/MoS$_2$ molar ratios were varied over the range from 1/60 to 1/1. The XRD patterns are displayed on an expanded scale to highlight the differences in the diffraction patterns. The diffraction pattern of crystalline MoS$_2$ shows a prominent (002) diffraction peak as mentioned earlier. This feature is narrow and characteristic of a highly-ordered crystalline structure. In contrast, the diffraction patterns of the exfoliated and restacked materials all display diffraction features that are substantially broadened relative to those of crystalline MoS$_2$. This broadening is likely due to a less well-developed long-range order due to defects in restacking following the exfoliation process, as well as the finite, nanometer scale size characterizing the restacked materials. The diffraction signals from the exfoliated and restacked MoS$_2$ with no MG present show a prominent peak at $2\theta = 14.4^\circ$, corresponding to an interlayer MoS$_2$ spacing of 6.15 Å. While this interlayer spacing is similar to that of crystalline MoS$_2$, it is clearly distinct and reflects an interlayer separation consistent with the restacked structure.\textsuperscript{[17, 21, 109]}
Figure 26: XRD patterns obtained for crystalline MoS$_2$ prior to exfoliation, exfoliated and restacked MoS$_2$, and MoS$_2$-MG based inclusion compounds of differing MG/MoS$_2$ molar ratios.

Adsorption of MG to the exfoliated layers results in diffraction patterns that depend on the molar ratio of MoS$_2$ to MG. At relatively low MG concentrations, (1/60 molar ratio of MG/MoS$_2$) the diffraction intensity of the peak associated with MoS$_2$-alone decreases. The diffraction pattern also shows the appearance of a new peak at lower angles ($2\theta = 8.1^\circ$), corresponding to a larger interlayer separation (~10.5 Å). Increase in the molar ratio of MG results in the disappearance of the feature at 14.4°, with a concomitant increase in the intensity of the (001) peak at lower angles as well as the onset of a broad (002) peak at $2\theta = 16.2^\circ$. These changes are attributed to the restacking of MoS$_2$ sheets that have adsorbed MG from solution. The larger layer spacing is a
reflection of the incorporation of MG into the layered structure. Note that with the increase in MG concentration, the lower angle diffraction peak grows in intensity and shifts slightly to smaller angle, indicating a small increase in layer spacing with increased MG adsorption. For MG/MoS$_2$ molar ratios in excess of 1/10, the XRD patterns also begin to show the appearance of a broad, higher order, (002) diffraction peak characteristic of the MG/MoS$_2$ inclusion material. This peak appears at 2θ angles of $\sim 16^\circ$ and indicates the onset of longer range order in the direction normal to the MoS$_2$ planes.

### 4.3 Orientation of Malachite Green

To determine the molecular orientation of MG, the second order molecular hyperpolarizability tensor has to be considered in order to determine which of its three linearly independent components are dominant. These components depend on the electronic structure and the selection rules of the electronic transitions.\[^{[88]}\] The optical properties of MG are determined by the dominant components of the molecular hyperpolarizability tensor. Knowledge of the complex hyperpolarizability tensor of an isolated molecule is essential for determination of molecular orientation parameter in the adsorbed layers. The calculation of the hyperpolarizability, $\beta$, is complicated, however, for most aromatic molecules it is often assumed that the $\pi$-electronic structure is the main contributor to $\beta$ in the UV/visible spectral region.\[^{[56, 110]}\]

The electronic structures of MG and other triphenylmethane molecules have been studied and are well known.\[^{[111, 112]}\] There are two orthogonally
polarized electronic transitions in MG in the visible spectral region. The $S_1 \leftarrow S_0$ transition is from the ground to the first excited state and appears at $\approx 610$ nm and is polarized in the $x'$ direction as per the coordinate system defined in Figure 6. The $S_2 \leftarrow S_0$ transition is from the ground state to the second excited state and is polarized in the $z'$ direction of the molecule. This transition is observed in the absorption spectrum at $\approx 410$ nm. Since there is more than one low-lying, optically accessible electronic excited state, contribution from both $\beta_{z'x'x'}$ and $\beta_{x'x'z'}$ hyperpolarizability components must be considered. However, since the $S_2 \leftarrow S_0$ transition overlaps with the SH wavelength produced, it offers a resonant enhancement on the order of 300 times of the signal intensity.\cite{85} This enhancement indicates that $\beta_{z'x'x'}$, expected to be approximately proportional the square root of the SH intensity, is approximately 15-20 times larger than $\beta_{x'x'z'}$ when an 800 nm fundamental light pulse is used. On this basis, any contribution from $\beta_{x'x'z'}$ when considering the SH signal has been ignored. This assumption significantly simplifies the analysis of the SHG experiments described here.
The linear and nonlinear Fresnel coefficients are summarized below for the exhibited conditions using the method described in Appendix 1 with the values of $\lambda = 800$ nm, $\theta = 44^\circ$ inside the prism, $n_\omega = 1.45332$ and $n_{2\omega} = 1.47012$.

\begin{align*}
    f_x &= -0.03983 + 9.25903i \cdot 10^{-3} \\
    f_y &= 5.51132 \cdot 10^{-3} - 0.01968i \\
    f_z &= 0.14334 - 0.04014i \\
    F_x &= -0.93183 - 0.06043i \\
    F_y &= 0.01311 - 0.0935i \\
    F_z &= -0.64202 - 0.01927i
\end{align*}

(21)

The second order susceptibility components are related to the molecular hyperpolarizability components according to equation (12) where the reference frames are defined in Figure 6 and further explained in Appendix 2. Because MG is symmetric with respect to the molecular $z'$ axis, an orientation analysis can be performed.\[^{53}\] Using the dominant $\beta_{z'x'x'}$ component and averaging over $\delta$, the
orientation angle $\theta$, the molecular tilt angle with respect to the surface normal, can be determined using the values of the susceptibility components.\[86\]

$$\cos^2 \theta = \frac{2 \chi_{zz} - \chi_{zzz}}{2 \chi_{zz} + \chi_{zzz}} \quad (22)$$

Second harmonic generation measurements on films of MoS$_2$ containing no MG showed modest signal levels, readily distinguishable from the SHG signals due to the fused silica/air interface alone. Adsorption of MG onto the exfoliated layers resulted in additional changes in the nature of the SHG response. These changes fell into one of two categories depending on the MG loading. At high MG surface coverage, that is for MoS$_2$/MG molar ratios <12/1, the signals due to the MoS$_2$-MG inclusion material were readily distinguished from those of the MoS$_2$-covered surfaces due to their distinct polarization behavior. This observation was consistent with previous observations of the polarization behavior of MG adsorbed at the fused silica/air interface conducted in the laboratory.\[106\] At MoS$_2$/MG molar ratios >12/1, the polarization dependence of the MoS$_2$-MG inclusion material was indistinguishable from the polarization dependence of MoS$_2$-covered surfaces. However, when the magnitude of their SH responses are compared, the second-harmonic intensities from the MoS$_2$-MG inclusion materials were consistently significantly smaller than the signals arising from the equivalent MoS$_2$ surfaces with no MG adsorbed. This observation is consistent with a MG-based SH response, but one that is characterized by a phase opposite to that due to the MoS$_2$ alone. Under these circumstances, the radiating second-harmonic electric field from the MoS$_2$
interferes destructively with that from the MG yielding a reduction in the overall SH response.

To quantify the signal contributions from MG, it was thus necessary to remove the non-negligible “background” signal contributions arising from a surface with an equivalent MoS$_2$ coverage. For each data set, the intensity of the polarized SH response from the MoS$_2$-covered surface was subtracted from the MG-MoS$_2$-covered surface using the expression $I_{MG} = \sqrt{I_{MoS_2+MG} - I_{MoS_2}}^2$. This procedure avoids including cross terms of the form $\chi^{(2)}_{MoS_2} \chi^{(2)}_{MG}$ in the subtraction process that arise from $I_{MoS_2+MG} \propto |\chi^{(2)}_{MoS_2} + \chi^{(2)}_{MG}|^2$. This background subtraction procedure was carried out for each data set prior to analysis of the SH polarization curves and extraction of the nonlinear susceptibility components due to MG.

Figure 28 shows the data and calculated fits to the data for the s- and p-polarized SH response used to obtain the film nonlinear susceptibility for MoS$_2$/MG molar ratios of 30/1, 5/1, and with no MG present. The experimentally determined values of the SH intensity are displayed as individual points, and the solid lines are fits to these data according to equation (10). The functional dependence of the s-polarized, ($\psi = 90^\circ$) SH response (open circles) on the input polarization angle is 4-fold periodic and a signature of the assumed isotropic distribution of molecules in the surface plane. Since the s-polarized SH intensity is proportional to the susceptibility component, $\chi_{121}$, the intensity maxima observed for incident polarization angles of $45^\circ$, $135^\circ$, $225^\circ$, and $315^\circ$ have been
used to determine the value of this tensor component via nonlinear least-squares fitting. Also shown in Figure 28 is the incident polarization angle dependence of the p-polarized ($\psi = 0^\circ$) SH response (filled circles). The p-polarized SH response is then used to obtain a value of the linear combination of susceptibility components $\chi_{xxz}$, $\chi_{xxx}$, and $\chi_{zzz}$. For this determination, the value of $\chi_{xxz}$ is fixed at the value obtained from analysis of the s-polarized SH response. The values of $\chi_{zzz}$ and $\chi_{xxx}$ are then determined by a best fit of the data to equation (10) with the use of the nonlinear least-squares fitting algorithm.
Figure 28: Polarized SH intensity vs. input polarization angle (p-polarization, filled circles; s-polarization, open circles) obtained for (a) MoS$_2$-covered substrate, (b) MoS$_2$/MG molar ratio of 30/1, and (c) MoS$_2$/MG molar ratio of 5/1. The solid lines are nonlinear least-squares fits to the data as per equation (10).
Analysis of the susceptibility components at different surface coverage can be used to obtain the averaged orientation of the MG in these inclusion materials at various MG loadings. The susceptibility components and corresponding averaged orientation angles calculated via equation (22) are presented in Table 1. Note that the calculated orientation angles assume that the MoS$_2$ layers orient themselves parallel to the surface of the fused silica substrate, consistent with earlier AFM observations. The results of Figure 28 and Table 1 indicate that there appear to be two regimes of behavior for the surface SHG measurements. At low MG loadings (MoS$_2$/MG molar ratios > ~12/1), the SHG measurements provide large averaged orientation angles, in the neighborhood of ~70 – 75°, indicating that the molecules lie flat, with their planes almost parallel with the MoS$_2$ layers. At high MG concentrations, (MoS$_2$/MG molar ratios < ~5/1), the SHG analysis provides orientation angles of approximately 20 – 25°, consistent with a more upright orientation. At intermediate MG coverage, the averaged orientation angles lie between these two ranges.
Table 1: Nonlinear susceptibility components and MG averaged tilt angle of exfoliated and restacked MoS$_2$-MG inclusion compounds for different MG loadings.

<table>
<thead>
<tr>
<th>MoS$_2$/MG</th>
<th>$\chi_{zzz}$</th>
<th>$\chi_{xxx}$</th>
<th>$\chi_{zzz}$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>$-5.82 \times 10^{-8}$</td>
<td>$4.78 \times 10^{-8}$</td>
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<tr>
<td>45</td>
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<td>69.3</td>
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<tr>
<td>30</td>
<td>$-1.44 \times 10^{-7}$</td>
<td>$7.47 \times 10^{-8}$</td>
<td>$1.79 \times 10^{-7}$</td>
<td>72.5</td>
</tr>
<tr>
<td>20</td>
<td>$-1.27 \times 10^{-7}$</td>
<td>$9.73 \times 10^{-8}$</td>
<td>$1.56 \times 10^{-7}$</td>
<td>70.6</td>
</tr>
<tr>
<td>15</td>
<td>$-1.85 \times 10^{-7}$</td>
<td>$1.08 \times 10^{-7}$</td>
<td>$2.31 \times 10^{-7}$</td>
<td>79.4</td>
</tr>
<tr>
<td>12</td>
<td>$-5.14 \times 10^{-8}$</td>
<td>$6.35 \times 10^{-8}$</td>
<td>$7.79 \times 10^{-8}$</td>
<td>60.7</td>
</tr>
<tr>
<td>10</td>
<td>$-9.65 \times 10^{-8}$</td>
<td>$1.38 \times 10^{-7}$</td>
<td>$9.81 \times 10^{-8}$</td>
<td>46.4</td>
</tr>
<tr>
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<td>$7.23 \times 10^{-8}$</td>
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<td>$1.38 \times 10^{-7}$</td>
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<td>$4.63 \times 10^{-7}$</td>
<td>$1.47 \times 10^{-7}$</td>
<td>31.6</td>
</tr>
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</table>

Molecular modeling techniques have been employed to provide a connection between results observed from the XRD studies and those from SHG studies. This correspondence is displayed in Figure 29. Geometric calculations provide a measure of the MG molecular dimensions and, combined with the tilt angle information from the SHG measurements, provide an expected MoS$_2$ layer separation. This separation, obtained indirectly from the SHG data, is compared to the layer separation obtained directly from XRD measurements.
Figure 29: Layer separation vs. MoS$_2$/MG molar ratio extracted directly from the XRD data (squares) and indirectly from the SHG analysis and molecular modelling (triangles). Error bars reflect a 10% uncertainty in the magnitude of the susceptibility components. The primary source of this uncertainty results from subtraction of background MoS$_2$ signals and represents the uncertainty in obtaining MoS$_2$-MG signals and MoS$_2$ background signals representing equivalent quantities of MoS$_2$.

4.4 Restacking Model

A measure of the volume occupied by MG within the MoS$_2$-MG inclusion material can be extracted from the XRD data. The XRD data of Figure 26 shows that the layer separation of the MoS$_2$ in the absence of MG is $\sim$6.2 Å ($2\theta =$ 14.4°). The layer separation of the MG-based inclusion material is $\sim$11.5 Å ($2\theta =$ 8.1°). This result implies a host interlayer expansion of 5.3 Å upon inclusion of the MG. Malachite green, a triphenylmethane-based indicator, has dimensions in its plane in excess of this value. The only way that the MoS$_2$ can accommodate the MG with such an interlayer expansion is with the MG molecular plane at a large tilt angle with respect to the layer normal, or roughly parallel to the MoS$_2$. 
layers. This situation is depicted in Figure 30. Second harmonic generation measurements at low MG loadings support this idea and predict an interlayer separation of approximately 11.5 Å based on the separation that results from the determined orientation of MG.

In this procedure, the geometry of MG was first optimized using HyperChem Lite (MM+ energy minimization routine) software package (version 2.0). The optimized geometry averaged orientation angles extracted from SHG data were used in conjunction with MG geometry to determine the MoS$_2$ layer separation based on geometric considerations. The interlayer separation is obtained by taking the projection of the MG in-plane dimensions according to the tilt angles obtained through SHG analysis. This atom-to-atom length is increased by 1 Å in order to account for the van der Waals dimension of the molecule and added to the interlayer separation of 6.2 Å characteristic of the exfoliated and restacked material in the absence of MG. This was performed for each MG/MoS$_2$ molar ratio. For averaged orientation of MG that was upright the corresponding predicted layer separation is accordingly larger.

Figure 29 shows that there is good agreement between the layer separations obtained directly from the XRD measurements and indirectly from the SHG analysis at low MG loadings. This agreement seems to persist until a MoS$_2$/MG molar ratio of ~15/1 is reached, at which point, further decreases in the molar ratio yield substantially smaller MG tilt angles and predict correspondingly larger layer separations.
The departure from agreement between the XRD- and SHG- based layer separations can be understood by examination of the adsorption isotherm shown in Figure 24. As described previously, the isotherm shows the appearance of a plateau consistent with the onset of monolayer adsorption at MG/ MoS$_2$ values of approximately 0.12 (MoS$_2$/MG molar ratios of approximately 8/1) and consistent with a strong driving force for MG adsorption. According to the XRD and molecular modeling studies, the subsequent restacking of the exfoliated MoS$_2$ host material (now presumably decorated with a monolayer of MG on both sides of its plane) results in a layered structure incorporating one monolayer of MG between its sheets, and it does so in such a way that the guest molecule adopts an orientation with its molecular plane roughly parallel with the MoS$_2$ layers, as shown in Figure 30. This step must involve the expulsion of excess MG from the layered structure during the restacking process. It is possible that expelled MG
resides at the polar edge sites of the MoS$_2$ planes or otherwise decorates polar adsorption sites on the exterior of the restacked crystallites. In so doing, the MG adopts an averaged orientation consistent with its adsorption in unrestricted, polar environments,[106] i.e., with a more upright orientation characterized by interaction of its polar dimethylamino substituents with a polar interface. The resulting SHG data at high MG loadings would then be expected to reflect both signal contributions from MG in flat orientations between the MoS$_2$ sheets and contributions from expelled MG residing outside of the layered structure. The SHG results are consistent with this behaviour. At low MG loadings, the SHG results indicate MG orientations consistent with a flat geometry and residence within the layered structure. As the MG concentration is increased, (MoS$_2$/MG molar ratios <15/1), the SHG data show a consistent drop in the averaged orientation angles of the MG, consistent with an increasing signal contribution from expelled MG that adopts a more upright orientation outside of the restrictions of the layered structure.

It is interesting to note that the onset of upright MG orientations as detected in the SHG results occurs at MoS$_2$/MG molar ratios of ~15/1 or roughly half of the concentration required to achieve monolayer coverage (MG/ MoS$_2$ ~0.12 or MoS$_2$/MG molar ratios of ~8/1) as extracted from the adsorption isotherm data. This observation is consistent with a picture in which individual MoS$_2$ layers adsorb MG on both sides of the exfoliated molecular layers, and upon restacking, expel roughly half of the material from the resulting interlayer region. While this model may reflect a mere coincidence in observed MG
concentration behavior, it nevertheless provides a connection between the well-known ability of the exfoliated MoS\textsubscript{2} sheets to adsorb strongly a range of potential adsorbates from solution and the observation of single-molecule thick guests included between the host MoS\textsubscript{2} layers. The procedure is admittedly limited in accuracy based on the quality of the model and the assumptions made in its application. Nevertheless, the results provide qualitative understanding and mechanism of the restacking dynamics.

The properties of exfoliated and restacked MoS\textsubscript{2}-MG inclusion compounds have been examined to provide insight into the MG-MoS\textsubscript{2} interactions that characterize these materials. The results of XRD experiments indicate that MG included into the restacked structure adopts a flat orientation approximately parallel to the MoS\textsubscript{2} sheets. Second harmonic generation experiments conducted on the exfoliated and restacked materials provide information regarding the averaged orientation of the MG. At low MG coverage, the results corroborate the XRD findings, and yield large averaged orientation angles consistent with a flat orientation of MG between the MoS\textsubscript{2} layers. However, as the MG coverage is increased, the SHG results indicate averaged MG orientations that are much more upright, consistent with the expulsion of excess MG from the layers to the outside of the restacked crystallite. Together with XRD and adsorption isotherm data, the SHG results provide a model for the exfoliation, adsorption, and subsequent restacking of these MG-based inclusion materials.
These results help to elucidate the interactions responsible for the formation of MoS$_2$-based inclusion compounds. This is believed to be the first report of using nonlinear optical probes to study layered structures and thus demonstrated is the utility of nonlinear optical techniques as probes thereof. The understanding of the restacking mechanism is a key stepping stone in gaining control over the ability to generate ordered structures using guest adsorbate molecules.
CHAPTER 5: GUEST-GUEST AND GUEST-HOST INTERACTIONS IN MOLYBDENUM DISULFIDE-BASED INCLUSION MATERIALS

The layered structure of the metal dichalcogenides opens windows for new properties because of its ability to be a versatile inclusion host for guest species. These include magnetic, superconductive, optical and electrical properties. While the potential for new types of materials is vast, the ability to control material characteristics will depend on understanding specific guest host interactions.

Chapter 4 reported on the restacking mechanism of MoS₂ systems in order to extend the current level of understanding of their adsorption and encapsulation abilities and examined the mechanism of the restacking process. Investigations now turn to the types of interactions occur during adsorption between guest and host in order to optimize the packing of the host molecule. Presented here are the studies of interactions between MoS₂ single layers and stearic acid. Described is a novel fabrication method of depositing amphiphilic adsorbate molecules into the MoS₂ host material, and the resulting host-guest and guest-guest interactions that characterize these materials.

5.1 Y-Type Bilayer Separation of MoS₂ Sheets

Approximately 2 mg of suspended Li intercalated MoS₂ in hexane was added to a chloroform solution containing the amphiphile (~1.00 mg/mL).
Exfoliation of the MoS$_2$ in the presence of the stearic acid occurred when the above-mentioned mixture was spread on a pure water subphase contained within a polytetrafluoroethylene LB trough. The exfoliation thus occurred in the presence of the guest amphiphile at the air/water interface. After chloroform evaporation, the Langmuir monolayer and multilayer LB films were obtained by compression followed by deposition onto hydrophilic substrates at a dipping rate of 4 mm/min. Multilayer films were fabricated by deposition onto clean microscope slides prepared by immersion in a piranha bath for 15 min followed by extensive washing with water.

Langmuir-Blodgett multilayer MoS$_2$ stearic acid films were obtained by compression to a surface pressure of 20 mN/m while cadmium stearate films were obtained by compression to a surface pressure of 30 mN/mm. Cadmium stearate was prepared by depositing stearic acid on the surface of a subphase in the presence of a cadmium salt in the subphase of the LB trough. Figure 32 shows the results of XRD studies on exfoliated MoS$_2$ with stearic acid included into the MoS$_2$ structure by this unique fabrication method as well as amphiphilic salts. The diffraction pattern of MoS$_2$ and stearic acid shows a prominent (001) peak at $2\theta = 2.31^\circ$ corresponding to an interlayer separation of $\sim 38$ Å. This feature is narrow and characteristic of a highly ordered crystalline structure and is supported by the appearance of higher order peaks at $2\theta = 4.60^\circ$, $6.86^\circ$. The pattern of this multilayer MoS$_2$ structure is then compared to a pattern of MoS$_2$ - based inclusion materials fabricated from cadmium stearate. The narrow (00$l$) peaks at $\sim 1.94^\circ$, $3.83^\circ$, $5.69^\circ$, $7.54^\circ$, $9.47^\circ$ are separated by $\sim 1.94^\circ$ and
correspond to a separation of 44.8 Å, corresponding to the head-to-tail length of two amphiphilic molecules. This distance is consistent with the bilayer spacing expected for a Y-type film consisting of a head-to-head, tail-to-tail architecture in which each alkyl chain is fully extended in an all-trans configuration. While the MoS\(_2\)/stearic acid pattern also shows a pattern consistent with a Y-type film, the separation is slightly smaller. This difference indicates that the architecture is that in which each alkyl chain is extended but on a small angle from the MoS\(_2\) sheet normal in an all-trans configuration as in Figure 32 or that the amphiphile chain slightly tilted. In addition, the alkyl chain or the cadmium salt does have the cation associated with the hydrophilic end which adds to the layer separation (radius = 160 pm). Furthermore, the deposition pressure may have an effect on the bilayer separation. The cadmium stearate films were deposited at a higher pressure yielding a phase that is more “solid” compared to that of the stearic acid film. The “solid” phase of the film yields a more upright configuration of the amphiphilic molecules. Attempts to deposit a film at 30 mN/m for stearic acid – MoS\(_2\) failed due to Langmuir film collapse.

Visual inspection of contact angles of the LB transfer supports a Y-type architecture – on the upstroke a contact angle < 90° was observed while on the downstroke a contact angle > 90° was observed. This report is in contrast to other recent MoS\(_2\)-amphiphile LB work which shows a Z-type structure\(^\text{[36, 37]}\). It should be pointed out that the structure preparation method employed here is the vertical dipping technique rather than the horizontal one\(^\text{[36, 37]}\) and thus one prone to producing Y-type structures from amphiphilic monolayers. In the horizontal
dipping technique, a substrate is lowered into a subphase consisting of the amphiphile of interest. The substrate face is parallel with the subphase when it comes in contact such that when the transfer occurs the amphiphilic layer is transferred onto the face of the substrate all at once.

Figure 31: XRD patterns obtained for MoS$_2$ with cadmium stearate (top) and MoS$_2$ with stearic acid (bottom) adsorbed in between the single layers. The peak near 3° is a reflection that results from the measurement geometry.
In Figure 32, the proposed structure consistent with stearic acid is shown schematically to have associated itself to MoS$_2$ using the hydrophilic end. This orientation is expected of the amphiphile, based upon the XRD observation and the hydrophilic nature of the MoS$_2$ single sheets.$^{[27]}$ The hydrophilic groups interact with the surface of the MoS$_2$ sheets whereas the hydrophobic tails attach themselves to the tails of the next adlayer. The known ability of MoS$_2$ to support charged species$^{[26]}$ and the ability to achieve a high surface pressure when preparing the film supports this film structure. Adoption of the opposite orientation by the amphiphile would make LB films difficult to produce because of the hydrophobicity of both sides of a MoS$_2$-stearic acid domain.

![Schematic representation of the arrangement of stearic acid within the MoS$_2$-stearic acid layered structure.](image)

**Figure 32**: Schematic representation of the arrangement of stearic acid within the MoS$_2$-stearic acid layered structure.
5.2 Sum Frequency Measurements

In order to characterize further the inclusion interaction of the guest amphiphiles with the MoS$_2$ structure, a series of SFG studies were undertaken. The technique has been previously employed to study amphiphilic monolayer structure and film orientation.$^{113}$ Monolayer films of stearic acid-MoS$_2$ for SFG study were prepared on the hypotenuse of a CaF$_2$ right-angle prism held in a mount designed in-house for this purpose. For these studies, the substrate was held in the water subphase of an LB trough until the monolayer was prepared and deposition occurred upon substrate removal through the monolayer. The sample was prepared by adding suspended Li intercalated MoS$_2$ in hexane to a chloroform solution containing the amphiphile. Exfoliation of the MoS$_2$ in the presence of the stearic acid occurred when the mixture was spread on the pure water subphase contained within the LB trough. The exfoliation thus occurred in the presence of the guest amphiphile at the air/water interface. After chloroform evaporation, the Langmuir monolayer film was obtained by compression followed by deposition onto hydrophilic substrates at a dipping rate of 4 mm/min.
Sum frequency generation spectra in the CH region were obtained using the tunable, broadband, 100 fs mid-IR light produced by difference frequency generation of the signal and idler beams from a custom-built OPG. This apparatus was previously used to monitor the spectroscopy and coherent vibrational dynamics in an amphiphilic monolayer.\textsuperscript{62} For the studies presented here, the spectral resolution was typically 8 cm\textsuperscript{-1}. Sum frequency generation spectra were collected in four polarization combinations. Polarization control in the infrared was achieved with a multiwavelength CaF\textsubscript{2} wave plate (Alphalas). Polarization control at 800 nm was accomplished with the zero-order half-wave
plate. The SFG signal was polarization-selected with a quartz Glan-Thompson polarizer (CVI). All spectra have been normalized for infrared intensity differences to the nonresonant SFG signal from a thin film of MG.

In order to characterize the ordering of adsorbate molecules further, an examination of the average orientation of the amphiphiles in the monolayer via SFG methods was undertaken. Figure 34 shows the SFG spectra in the CH region obtained under three different polarization conditions for monolayer film of stearic acid adsorbed on MoS$_2$. Four polarization combinations were collected, but for the sake of clarity, only the SSP, PPP and SPS polarization combinations are displayed since the SPS and PSS polarization combinations are very similar and have very low signal to noise intensity. Polarization combinations refer to the sum frequency signal, 800 nm, and infrared polarizations, respectively.
The vibrational mode assignments in this spectral region are well-known.\cite{114,115} The vibrational modes at 2880, 2965, and 2940 cm\textsuperscript{-1} are attributed to the methyl group and have been assigned as the symmetric stretch ($r^+$), the asymmetric stretch ($r^-$) and Fermi resonance (FR) between the symmetric stretch and two quanta of the bending mode, respectively. The modes at 2850 cm\textsuperscript{-1} and 2920 cm\textsuperscript{-1} have been assigned to the symmetric ($d^+$) and asymmetric ($d^-$) stretches of the CH\textsubscript{2} groups, respectively. The mode appearing at 2910 cm\textsuperscript{-1} has been assigned as a methylene symmetric stretch Fermi resonance.
A brief description of how one derives molecular orientation information from the SFG spectra is given here. The nonlinear susceptibility component is given by

\[
\chi^{(2)}_{\text{eff}} = \left[ \tilde{e}(\omega) K(\omega) \right] [\hat{\chi}^{(2)} : \left[ \tilde{e}(\omega_1) L(\omega_1) \right] \tilde{e}(\omega_2) L(\omega_2)]
\]

(23)

where \( \tilde{e} \) is the unit polarization vector, \( L \) is the linear Fresnel factor describing the incident electric fields at the interface, and \( K \) is a combination of linear and nonlinear Fresnel factors describing the outgoing SFG field. \( L \) and \( K \) are both geometry-dependent and dependent on how one models the refractive index of the film. The macroscopic \( \chi^{(2)} \) is related to the microscopic molecular hyperpolarizability according to equation (12). If \( \beta \) is known, then by
measuring $\chi^{(2)}_{ijk}$, one can deduce the average orientation of the vibrational mode in question. The values for the Fresnel coefficients were calculated for the exhibited conditions and using the method described in Appendix 1 with the values of $\lambda = 800$ nm, $\lambda_{IR} = 3.250$ μm, $\theta_i = 45^\circ$ inside the prism, $n_{\omega} = 1.45332$, $n_{IR} = 1.414448$ and $n_{\omega_{20}} = 1.432638$. The values of $L_{ijk} = K_i L_j L_k$ for a CaF$_2$ substrate are summarized below

\begin{align*}
L_{zzz} &= (- 5.9658 - 8.359309i) \cdot 10^8 \\
L_{yyz} &= (1.677 - 4.313i) \cdot 10^8 \\
L_{yzy} &= (2.8477 + 4.313i) \cdot 10^8 \\
L_{zyy} &= (- 2.8067 - 4.3745i) \cdot 10^8
\end{align*}
\quad (24)

The orientation of the terminal CH$_3$ group can be determined by analyzing its symmetric stretch mode as well as its asymmetric stretch mode. The CH$_3$ group possesses C$_{3v}$ symmetry and has three nonzero independent elements in its hyperpolarizability tensor, $\beta_{zzz}$, $\beta_{xxz} = \beta_{yyz}$ (associated with the $r^+$ mode), and $\beta_{zzx}$ (associated with the $r^-$ mode). Assuming an isotropic sample in the plane of the CaF$_2$ surface, averaging over Euler angles, one obtains

\begin{equation}
\chi_{yyz} = \chi_{xxz} = \frac{1}{2} N \beta_{zzz} \left[ (\cos \theta)(1 + R) - (\cos^3 \theta)(1 - R) \right]
\quad (25)
\end{equation}
where \( \theta \) denotes the angle between the methyl symmetry axis and the surface normal, which is oriented along the \( z \) axis yields\(^{117, 118} \) and \( R = \frac{\beta_{zzz}}{\beta_{zzz}} \). Similar expressions hold for the \( \text{CH}_3 \) asymmetric stretch mode

\[
\chi_{zzz} = -2 \chi_{yzz} = N \beta_{zzz} \left[ \cos \theta - \langle \cos^3 \theta \rangle \right]
\]

\[
\chi_{yzy} = \chi_{yzy} = \chi_{yzy} = \chi_{zxx} = \frac{1}{2} N \beta_{zzz} \langle \cos^3 \theta \rangle
\]

The presence of the Fermi resonance band perturbs the intensity of the \( r^+ \) mode. To evaluate the unperturbed intensity, the following expression has been used

\[
A_{\text{r}^+, \text{unperturbed}} = \sqrt{A_{r^+}^2 + A_{\text{FR}}^2}
\]

The spectra were fit according to the above equations using a fitting routine personalized for performing simultaneous nonlinear least-squares regressions. All peaks were fit to Lorentzian line shapes. Observation of a relatively weak nonresonant background signal originating from the \( \text{CaF}_2 \) substrate warranted the introduction of a complex nonresonant background to each spectrum. While this contribution was generally approximately 1-3% of the resonant signal intensities, inclusion of this contribution into the fitting procedure resulted in substantial improvements in the fits of the \( \text{CH}_3 \) asymmetric stretch region.

It is clear from Figure 34 that the fitting procedure is able to reproduce the experimentally observed spectra with good accuracy. The parameters used for
the fits displayed in Figure 34 are presented in Table 2. The solid lines represent the best fits to the data.

**Table 2:** Parameters resulting from the simultaneous fitting of the SSP, PPP, SPS, and PSS SFG spectra of the stearic acid monolayer on MoS$_2$.

<table>
<thead>
<tr>
<th>$A_{ssp}$</th>
<th>$A_{ppp}$</th>
<th>$A_{sp}$</th>
<th>$A_{ps}$</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>372.1 ± 13.8</td>
<td>591.3 ± 21.9</td>
<td>89.7 ± 3.3</td>
<td>-35.8 ± 1.3</td>
<td>2851</td>
<td>12.12</td>
<td>CH$_2$ d$^+$</td>
</tr>
<tr>
<td>953.4 ± 35.3</td>
<td>926.4 ± 34.3</td>
<td>-132.8 ± 4.9</td>
<td>26.9 ± 1.0</td>
<td>2877</td>
<td>6.48</td>
<td>CH$_3$ r$^*$</td>
</tr>
<tr>
<td>732.1 ± 27.1</td>
<td>1445 ± 53</td>
<td>321.3 ± 11.9</td>
<td>367 ± 14</td>
<td>2910</td>
<td>20.12</td>
<td>CH$_2$ d$^+$</td>
</tr>
<tr>
<td>886.7 ± 32.8</td>
<td>785.3 ± 29.1</td>
<td>12.7 ± 0.5</td>
<td>-77.5 ± 2.9</td>
<td>2938</td>
<td>8.32</td>
<td>CH$_3$ FR</td>
</tr>
<tr>
<td>-176.2 ± 6.5</td>
<td>1092 ± 40</td>
<td>-115.2 ± 4.3</td>
<td>241.0 ± 8.9</td>
<td>2964</td>
<td>6.44</td>
<td>CH$_3$ r$^*$</td>
</tr>
</tbody>
</table>

**Table 3:** Nonresonant contribution resulting from the simultaneous fitting of the SSP, PPP, SPS, and PSS SFG spectra of the stearic acid monolayer on MoS$_2$.

<table>
<thead>
<tr>
<th>Polarization combination</th>
<th>$\chi_{nr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP</td>
<td>18.3</td>
</tr>
<tr>
<td>PPP</td>
<td>50.6</td>
</tr>
<tr>
<td>SPS</td>
<td>6.47</td>
</tr>
<tr>
<td>PSS</td>
<td>.555</td>
</tr>
</tbody>
</table>

The spectra in the CH region are characteristic of well-ordered, fully extended all-trans alkyl chains. Little intensity is observed in the methylene modes, consistent with a locally centrosymmetric environment in which intensity from individual CH$_2$ groups of the alkyl chain is compensated for by adjacent groups.

Various methods have been used to extract orientation information from SFG spectra.$^{[117-124]}$ Two different approaches to determine orientation
information are employed here. The first method relies on the ratio of symmetric stretch intensities in the SSP and PPP polarization combinations. The second method uses the ratio of intensities observed for the asymmetric and symmetric stretches in the PPP combination to determine the orientation. These methods have been described in detail[119-122] along with other methods that make use of SPS and/or PSS spectra. The signal to noise ratio in the SPS and PSS spectra is low (Figure 34) and thus only the methods that make use of PPP and SSP spectra were employed.

The first method relies on the ratio of symmetric stretch intensities in the SSP and PPP polarization combinations.[119] While this SSP/PPP ratio is easily measurable, this method is subject to the extreme sensitivity of the Fresnel factor associated with the PPP polarization combination on the assumed refractive index of the film, n'. With an appropriate choice of n', the orientation can thus be deduced. Assumptions of n' = 1.2 have lead to determination of adsorbate monolayer orientation which have been corroborated with other spectroscopic methods independent of the value of n'.[119, 120] It was argued that the use of n' = 1.18 is appropriate for an amphiphilic monolayer of molecules[118] and hence this value was assumed to be that of the SFG signal generating system here.

While refractive index is a bulk parameter, refractive properties of interfaces are well-known to be modified by one layer of molecules. The n' values can be determined by spectroscopic ellipsometry.
Secondly, the ratio of intensities observed for the symmetric and asymmetric stretches can be used to determine the orientation if the ratio of \( \frac{\beta_{zzz}}{\beta_{zzx}} \) is known.\(^{[122]}\) However, the value of this ratio is also not well-known; literature reports give values ranging from 1 to 16.\(^{[118, 121, 122]}\) This method is also restricted to the PPP polarization combination since it is the only polarization combination with significant intensity in both the symmetric and the asymmetric modes.

While the parameters \( R, n', \) and \( \beta_{zzx} \) used in these methods are subject to considerable uncertainty, one way of minimizing the uncertainty is to fit the methyl intensities simultaneously for both polarization combinations and try to find a single parameter set that yields a consistent set of orientation angles. Through the use of the values \( n' = 1.18, \ R = 2.4, \) and \( \beta_{zzx} = 4\beta_{zzz}, \)\(^{[116, 120]}\) the orientation angle was calculated using these methods (method I: ratio of \( r^+ \) peak in the SSP/PPP spectra; method II: ratio of \( \frac{r^-}{r^+} \) in the PPP spectrum). Table 4 shows the results of using both methods to determine orientation information for the film of stearic acid adsorbed on MoS\(_2\). The table shows that both methods give results in reasonable agreement with each other and indicates consistency in the methyl group orientation angle determination.
Table 4: Orientation angles of the methyl group calculated using both methods discussed in the text.

<table>
<thead>
<tr>
<th>Method</th>
<th>Methyl group angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I: ( r^+ \rightarrow (\text{SSP/PPP}) )</td>
<td>43.2 ± 2.6</td>
</tr>
<tr>
<td>II: ( \text{PPP} \rightarrow \left( \frac{r^-}{r^+} \right) )</td>
<td>52.3 ± 2.4</td>
</tr>
</tbody>
</table>

Of the two methods employed for architecture analysis, more weight is given to method I. The reason is that the spectral fitting of the \( r^- \) mode in the PPP polarization combination is subject to several assumptions, which cannot be verified due to the restricted resolution of the apparatus. Nevertheless, the two methods provide orientations that are in reasonable agreement with each other.

The averaged methyl group orientation angle obtained is 48°, corresponding to a tilt angle of the alkyl chain of \( \sim 13 \pm 4° \) with respect to the surface normal assuming a rigid chain. The appearance of intensity in methylene modes can be attributed either to the number of gauche defects within the film or to the possibility of other sources of uncompensated CH\(_2\) oscillator strength within the alkyl chain such as localized chain bending or extended chain curvature.
Figure 36: Geometric representation of the orientation of a stearic acid molecule adsorbed on the MoS$_2$ interface. $\theta = 48^\circ$ is the orientation of the methyl group with respect to the surface normal and $\rho = 13^\circ$ is the tilt angle of the alkyl chain with respect to the surface normal.

The fully extended all-trans alkyl chain picture is consistent with the XRD results discussed earlier. There is evidence of highly ordered, fully extended chains with the possibility of slight curvature from the nominal CH$_2$ activity and
XRD. From analysis of the CH₃ peaks, the conclusion can be made that the acid chains are slightly tilted and highly ordered.

The uncertainty associated with the molecular hyperpolarizability of the individual vibrational modes was calculated from the signal to noise ratio of the spectra. In comparing the SFG result to the XRD result, it should be noted that the SFG result can only be obtained for a single monolayer of stearic acid adsorption since a bilayer Y-type structure would result in cancellation of the signals from the oscillators because their orientation would be opposite to each other.

5.3 Crystalline Packing of Adsorbates - Single Layer Deposition

Atomic force microscopy measurements were taken to assess the extent of organization of the adsorbed molecules as well as the quality of the exfoliated MoS₂. Substrates for AFM studies were freshly cleaved atomically smooth mica for the LB-based architecture and microscope glass slides for crystalline and restacked MoS₂. X-ray diffraction shows proof of long range ordering with respect to layer separation, but does not address the ordering of the individual stearic acid molecules within a monolayer. To address the nature of the adsorption, efforts turned to AFM studies to investigate the ordering in each monolayer of stearic acid on MoS₂. Figure 37 is an AFM image of bulk crystalline MoS₂ with hexagonal packing with a spacing of \( a = 3.05 \pm 0.16 \) Å which is in agreement with previous reports using XRD and XAFS.[21] While AFM images of the bulk crystalline material were readily achievable, obtaining images of the exfoliated restacked material proved to be more challenging. The exfoliated
MoS$_2$ suspension was dropped onto the sticky side of Scotch tape and allowed to dry. After drying, the sample was sandwiched between two pieces of sticky tape by pressing onto the sample with another piece of tape and then pulling off the latter piece of tape to expose a fresh surface of the exfoliated restacked sample. Initial attempts to expose a fresh surface of MoS$_2$ proved unsuccessful due to the preference of the sample to one type of adhesive over another. Shown in Figure 38 is an AFM image of freshly cleaved exfoliated restacked MoS$_2$. Because of the difficulty of obtaining this pattern, the quality is not as high as those obtained from crystalline MoS$_2$. However, hexagonal packing distance of the sulphur atoms of the restacked material $a = 3.84 \pm 0.54$ Å. This lattice constant is slightly higher when compared to other reports ($a = 3.22$ Å).\cite{21} The much larger standard deviation is an indication of the quality of the image and the difficulty of obtaining such an image as well as the quality of a repeat unit.

There exists a possibility that it may be difficult to image MoS$_2$ that is freshly restacked and cleaved after exfoliation with water. In this case, it is likely that what is being imaged is a layer of water on the MoS$_2$ surface. Previously, in Chapter 4, it was shown that the time scale for water expulsion from the MoS$_2$ structure is on the order of days. This sample was imaged as soon as it had dried and thus water may be present in the structure. The interference of water with imaging MoS$_2$ may help to explain the lower quality of the image compared to that of crystalline MoS$_2$. Thermal drift has been observed to skew real space images and distort the reciprocal space lattice vectors. A method based on averaging the space lattice vectors by scanning in several opposite directions
could not be applied here because the image was very sensitive to the scan direction. This difficulty was yet another obstacle that was encountered enroute to obtaining a high quality scan with this sample.

Figure 37: AFM image of freshly cleaved crystalline MoS$_2$. The inset is a Fourier transform of the image showing average spacing of $a = 3.05 \pm 0.16$ Å.
Figure 38: AFM image of exfoliated restacked MoS$_2$. The inset is a Fourier transform of the image showing average spacing of $a = 3.84 \pm 0.54$ Å.

After looking at the exfoliated restacked material, studies turned to the adsorbed stearic acid thereon. Shown in Figure 39 is a molecular resolution AFM image of stearic acid adsorbed on exfoliated restacked MoS$_2$. The sample was prepared by adding suspended Li intercalated MoS$_2$ in hexane to a chloroform solution containing the amphiphile. Exfoliation of the MoS$_2$ in the presence of the stearic acid occurred when the mixture was spread on the pure water subphase contained within the LB trough. The exfoliation thus occurred in the presence of the guest amphiphile at the air/water interface. After chloroform evaporation, the Langmuir-Blodgett monolayer film was obtained by compression followed by deposition onto hydrophilic substrates at a dipping rate of 4 mm/min.
The image shows the pseudo regular spacing that characterizes the formation of crystalline hexagonal packing of the stearic acid molecules with a spacing of $a = 5.35 \pm 0.70$ Å. Previous work in the laboratory has allowed for the imaging of long chain amphiphiles deposited onto freshly cleaved mica using the LB technique. The current experiments show that this lattice constant is consistent with those measurements. To ensure the region being imaged had stearic acid on MoS$_2$, initial large-scale images were obtained on which MoS$_2$ platelets were evident. All subsequent scans of this sample were taken on a region that was covered by an MoS$_2$ sheet. Thus, an image of the single layer crystallization of stearic acid on single layer MoS$_2$ was produced which demonstrated the ability to control the ordering on the MoS$_2$ sheets. In Figure 32, the acid molecules are drawn with a slight tilt in accordance from X-ray data presented in section 5.1 and are in a hexagonal arrangement.
The properties of adsorption of amphiphilic molecules on MoS$_2$ single sheets have been studied in order to study the types of interactions that occur between the host and guest materials. The results of XRD experiments indicate that through careful exfoliation of MoS$_2$ in the presence of stearic acid on the interface of water followed by vertical deposition of the film, stearic acid can be included in a Y-type fashion in an upright position in between MoS$_2$ monolayers. MoS$_2$ favours interaction with the hydrophilic end group of the amphiphile. Through AFM, it was shown that a single layer of stearic acid adopts a crystalline pseudo-hexagonal packing on the surface of MoS$_2$. By using SFG spectroscopy, spectral features characteristic of well-ordered, fully extended all-trans alkyl chains in an upright conformation were observed. The high degree of order in
the film is supported by SFG results and thus demonstrates the ability to control the deposition of adsorbate molecules on the surface of MoS$_2$ single layers for the purpose of generating new types of composite nanostructures.
CHAPTER 6: INCLUSION OF NANOPARTICLES IN
RESTACKED MOLYBDENUM DISULFIDE

Nanoparticle science has been intensively pursued not only because of
the fundamental new physics and chemistry that nanoparticles display, but also
for the many potential applications of nanoparticle-based materials and
processes. Nanoparticle fabrication methods fall into two primary categories
commonly referred to as the “top-down” and “bottom-up” approaches. In the
“top-down” approach, the tools typically employed in the lithographic deposition
of materials for the semiconductor industry are used to create nanometer scale
features into larger patterned architectures. In the “bottom-up” approach,
synthetic chemical methods are used to build up nanoscale particles and crystals
from atomic and molecular components, with many of these growth mechanisms
taking place in the solution phase. While the synthetic chemistry to fabricate
these structures is becoming well developed, it remains a significant challenge to
be able to assemble these nanoparticles into three-dimensional architectures.
The ability to join quantum scale components into complex assemblies creates
many opportunities for scientific discovery. These assemblies include possibility
of three-dimensional assemblies, and the potential for inexpensive mass
fabrication.

The layered structure of the metal dichalcogenides offers a unique
opportunity in this regard if one can utilize the ability of the material to be a
versatile inclusion host for nanoparticles. Coupling of properties of metal
dichalcogenides with properties of nanoparticles can yield new types of
materials. The ability to control material assemblies will depend on various
properties of the nanoparticles. It remains a major challenge to understand how
ordered or complex structures form spontaneously by self-assembly and how
such processes can be controlled to prepare structures with a pre-determined
geometry. In order to obtain nanostructured architectures, one must understand
how to control the generation of stable building blocks, their shapes and sizes, as
well as their chemical versatility. An understanding of these parameters allows
one to control the chemistry of nanoparticle assemblies for three-dimensional
architectures of diverse functionality.

The studies described in Chapter 4 and 5 provide insight into the nature of
guest-host and guest-guest interaction in MoS$_2$-based inclusion materials.
Described here are attempts to fabricate three-dimensional layered architectures
of nanoparticles through control of nanoparticle capping agent - MoS$_2$
interactions.

6.1 Iron Oxide Nanoparticles

The first efforts to generate MoS$_2$-nanoparticle structures utilized
syntheses of Fe$_3$O$_4$ nanoparticles. These nanoparticles were chosen because
they are magnetic, relatively inexpensive to synthesize, easy to characterize and
may yield potentially interesting magnetic properties. Following the synthesis
procedure described in Chapter 3, the iron oxide nanoparticles were contained in
oleic acid. The nanoparticles are oleate capped with the acidic group associated
with the metal surface and the hydrophobic ends forming an outer surface of the nanoparticles. The TEM images in Figure 40 show both the monodispersity and the shape of the nanoparticles which are approximately 15.6 ± 3.4 nm in diameter. The monodispersity was an important feature when attempting to generate uniform MoS$_2$ nanoparticle structures because structures generated from non-uniform nanoparticles would be difficult to characterize and the ability to control size and uniformity is important when attempting to generate macro-scale properties from the assembly of nanoparticle constituents. Figure 40 also indicates that these nanoparticles are crystalline. The crystallinity is inferred by the darkness of the images of certain particles, which result from various orientations of the nanoparticle crystal lattice with respect to the TEM electron beam. Figure 41 represents schematically the relative size of the Fe$_3$O$_4$ nanosphere and the capping molecule, oleic acid.
Figure 40: TEM micrographs of Fe₃O₄ nanoparticles deposited on a carbon-coated copper grid.
Figure 41: A representation of the relative size of the Fe$_3$O$_4$ nanosphere and the capping molecule, oleic acid.

The first attempt to include the iron oxide nanoparticles was through exfoliation of MoS$_2$ in the presence of water followed by extremely vigorous mixing with the nanoparticle solution to induce nanoparticle adsorption. The resultant structures obtained by centrifuging and drying the solid, were analyzed by XRD to determine the level of inclusion. From the sample diffraction pattern shown in Figure 42, a peak at $2\theta = 7.7^\circ$ is observed which can be attributed to an interlayer spacing consistent with the inclusion of water. However, no peak at low angles due to a spacing resulting from nanoparticle inclusion was observed. Transmission electron microscopy images also showed no indication of adsorption of iron oxide nanoparticles onto the single sheet planes.
Figure 42: XRD pattern of attempted MoS$_2$/Fe$_3$O$_4$ structures.

This result was attributed to the nature of the capping agent used in the Fe$_3$O$_4$ synthesis. The outer surface of the nanoparticle is terminated with a hydrophobic methyl group. Due to the charged and electron-accepting nature of the MoS$_2$ sheet, it would be unfavourable to adsorb via this termination group to the MoS$_2$ sheets. Films obtained by dipping a wet glass substrate through the phase-separated MoS$_2$ suspension and a nonpolar liquid in which the guest molecule of interest was dissolved, have been shown as the only method thus far to include nonionic molecules into MoS$_2$. However, attempts employing this method proved unsuccessful as well. It should be noted that a large variety of nonpolar solvent soluble molecules adsorbed through this method possessed an electron system which was capable of interacting with the MoS$_2$ plane.\textsuperscript{[27, 33, 35]} It has also been noted that lone pairs play an important role in interaction of
adsorbate molecules with conducting surfaces.[127, 128] In the case of the oleate-capped nanoparticles, neither of these situations apply.

An attempt to exchange the oleic acid capping agent with 4-(dimethylamino) benzoic acid (Aldrich, 98%) was made in order to modify the outer hydrophobic layer of the nanosphere. The molecule was chosen due to its functional groups. It was proposed that one end of the molecule possessing the acid group would exchange with the oleic acid leaving the nanoparticle capped to avoid aggregating, while the other end of the molecule containing the dimethylamino functional group would associate favourably with MoS$_2$ as shown previously. Capping agent exchange reactions have been performed before using phase boundary partitioning and physisorption methods.[81]

The iron oxide nanoparticle solution in oleic acid was added to an aqueous solution of 4-(dimethylamino) benzoic acid which was sparingly soluble in water. The aqueous solution was heated to 50 °C to dissolve as much of the acid as possible. Vigorous stirring for several hours resulted in no colour change of the aqueous layer. A small amount of the aqueous solution was dropped onto a microscope slide and allowed to dry prior to taking an XRD pattern. No evidence of iron oxide was observed in the diffraction pattern which led us to conclude that the iron oxide nanoparticles were not transferred to the aqueous phase from the organic phase.

A possible reason for the inability to transfer from the organic to aqueous phase likely lies in the stability of the oleate chains when they are adjacent to each other. Studies of stabilizing forces between the capping molecules indicate
an increase in stability with longer chain lengths.\cite{129,130} Additionally, it has been reported that capping molecules of less than five carbon atoms produce nanoparticles that tend to degrade over several weeks, whereas colloids with longer chains can be kept under ambient conditions for months without showing any sign of degradation.\cite{131} This stability makes it difficult to break apart the oleate chain system through physical means. In order to overcome this obstacle, several routes are suggested.

The first is to use a micelle-type route to associate molecules with the outer oleate perimeter such that an adlayer of a new molecule will be formed on the nanoparticle, specifically one that will contain two sites of interest. The first site is a site that will readily associate itself with the oleate alkyl end physically such that the oleate is no longer on the perimeter of the nanoparticle as described pictorially in Figure 43. The second site would be a group that has been show to adsorb to MoS$_2$ such as a dimethylamino group.
aqueous medium

Figure 43: Schematic representation of the desired interaction and structure of the capping layers of the iron oleate nanosphere. The dark grey boxes indicate the end groups are of most importance in the molecule rather than the chain.

The second route is to alter the iron oxide nanoparticle synthesis such that the capping agent does not form a stable network. This network may be achieved with the use of a shorter carbon chain alkyl analog, i.e., an eight carbon chain. Producing a less stable network of alkyl chains would present the
possibility of generating a capping agent exchange such that the alkyl chain of the prior agent would be substituted with a new agent which possesses properties that are of use in nanoparticle inclusion chemistry. The capping agent would be soluble in water and terminated with a group that has been shown to adsorb to MoS$_2$ favourably.

A route utilizing oleic acid derivatives enables altering of the nanoparticle after its synthesis. Instead of oleic acid, a derivative with a double bond at the hydrophobic end may used, such as (9Z)-octadec-9,17-dienoic acid. After the synthesis of the nanoparticle, the double bond may be replaced with some electron donor group such as an acid or amine, which would then potentially form a favourable interaction with the MoS$_2$ single layers.

Several steps could be taken to achieve conversion of an –ene end group into an amino group.$^{[132]}$ The first step is to convert to alkyl bromide in an anti-Markovnikov manner with peroxide and HBr to generate primary alkyl halide.$^{[133]}$ The second step is to react with benzyl amine to generate the protected N-benzyl compound.$^{[134]}$ Protection of amines prevents polymerization. Although the amines are bound to the nanoparticle, it is possible that primary amines will polymerize. The last step is to deprotect the benzyl group using H$_2$/Pd.$^{[134]}$ The final product would be 18-amino-(9Z)-octadec-9,17-dienoic acid and would contain an end group which might form a favourable interaction with the MoS$_2$ single layer.
6.2 Citrate-Capped Gold Nanoparticles

Having looked at structure considerations in generating MoS$_2$-Fe$_3$O$_4$ nanomaterials, studies turned to nanoparticles for which the established synthesis had yielded nanoparticles in aqueous media. The citrate-capped gold nanoparticles were generated following the synthesis procedure described earlier.[78] The TEM images in Figure 44 show the size and quality of the nanoparticles, which are approximately $7.2 \pm 1.5$ nm in diameter. The crystallinity here is evident by the fringe patterns of the nanospheres, which result from diffraction of electrons from the crystal lattice as well by the diffraction pattern shown which is characteristic of a gold metal structure.[135] The crystallite size of the nanosphere was calculated to be 50 Å from the Au (111) peak using equation (16) which is reasonably close to the observed value.
Figure 44: TEM images of citrate-capped gold nanoparticles on a carbon-coated copper grid.
Figure 45: XRD pattern of gold nanoparticles on a silicon wafer. The peaks at $2\theta = 38^\circ, 45^\circ, 66^\circ, 78^\circ$ are assigned to Au (111), (100), (110), (311). The remaining peak results from the silicon substrate.\[138\]

The gold nanoparticles were first included into MoS$_2$ using standard techniques such as those described earlier for MG. MoS$_2$ was exfoliated in the presence of the gold nanoparticle solution followed by washing and centrifuging. Adsorption was evident following addition of the gold nanoparticles by the disappearance of the characteristic dark red color of the nanoparticle solution over the course of minutes. The resulting structures were analyzed by XRD to determine the level of inclusion, however, no peak at low angles due to a spacing resulting from nanoparticle inclusion was observed.
The MoS$_2$-Au nanoparticle sample was prepared for TEM studies by dipping a Cu grid in the suspension of interest followed by drying the sample for 24 hours. From the resulting image shown in Figure 46, it can be observed that successful adsorption of the gold nanoparticles on the MoS$_2$ single sheets was achieved. The micrograph shows that the gold nanoparticle coverage is not complete, in fact, it is clear that there is a substantial amount of MoS$_2$ area that is not covered by the nanoparticles. This low coverage is attributed to the ratio of gold to MoS$_2$ in the reaction mixture. The concentration of gold in the solution was 57.6 $\mu$g/mL. Thus, one can alter the coverage of the MoS$_2$ single sheets by synthesizing smaller nanospheres since the concentration of gold remains constant. The nanospheres that were synthesized here were towards the smaller size limit of the range of sizes allowed by varying the synthesis stoichiometry. By creating smaller particles, one creates more of them (assuming the concentration of gold remains constant) and potentially allows for more complete Au-nanoparticle coverage between the MoS$_2$ sheets.
In addition to an incomplete coverage, an observation that can be made from the micrograph is that the nanoparticles tend to cluster together on the MoS$_2$ surface. The gold nanoparticles show preference of adsorption on MoS$_2$ on the plane and not the single sheet edge. In order to show that those were indeed gold nanoparticles that were being probed, an EDX spectrum of one of the gold nanoparticles adsorbed on the MoS$_2$ single sheet was obtained. From the resulting spectrum, which is shown in Figure 47, peaks that are assigned to gold atoms are observed.
Figure 47: EDX spectrum of a region of Figure 46, that contains a gold nanoparticle adsorbed on a MoS$_2$ single layer. The carbon and copper peaks are due to the carbon-coated copper grid that the sample was deposited on.

The TEM shown above was the result of the maximum Au/MoS$_2$ ratio that was generated while still introducing enough MoS$_2$ into the mixture such that the samples could be analyzed. Earlier attempts at these materials yielded such low coverages of gold nanospheres that it was difficult to see one nanosphere on a given TEM micrograph.

6.3 Dimethylaminopyridine-Capped Gold Nanoparticle Experiments

6.3.1 Nanoparticle Characterization

Being limited by the concentration of gold nanoparticles that were produced, studies turned to routes that increased the effective concentrations of gold nanoparticles while utilizing the chemical properties of the capping agents in
order to interact strongly with MoS$_2$. With this approach, it was expected that the effective nanoparticle coverage of MoS$_2$ would be increased substantially. Following the nanoparticle synthesis\cite{62} and phase transfer\cite{81} as described earlier, the DMAP stabilized gold nanoparticles were prepared in an aqueous solution. The concentration of gold in this solution was 1 mg/mL and hence approximately twenty times greater than that of the citrate capped gold nanoparticles.

The DMAP-Au nanoparticles in water exhibited a characteristic surface plasmon absorption band at $\lambda_{\text{max}} = 517$ nm.\cite{81,90}

![UV/Vis absorption spectrum of dispersions of DMAP-Au nanoparticles in water.](image)

**Figure 48:** UV/Vis absorption spectrum of dispersions of DMAP-Au nanoparticles in water.
It has been shown that the synthesized nanoparticles are DMAP capped where the orientation of DMAP with respect to gold is as shown in Figure 49.[90] The DMAP is bound to the nanosphere via the endocyclic nitrogen as determined by electrochemistry and surface plasmon resonance studies. This orientation of the capping agent was envisioned to be crucial in order to achieve maximum interaction with MoS$_2$ because it has already been shown that the dimethylamino group adsorbs well to MoS$_2$.[102]

![Figure 49: Schematic representation of the orientation of DMAP capping a gold nanoparticle.](image)

The TEM micrograph in Figure 50 shows the size, quality, and crystallinity of the nanoparticles, which are 5.0 ± 1.2 nm in diameter. Contrasts can be made between the ordering of the iron oxide (Figure 40) and gold nanoparticle in the TEM images (Figure 44 and Figure 50). While the citrate-capped gold nanoparticles are randomly scattered and subject to some small degree of aggregation, the DMAP-capped gold and iron oxide nanoparticles form two-dimensional arrays and in the latter case the ordering is quite dense.
Individual nanoparticles can undergo aggregation or self-assembly processes which may represent an important aspect when attempting to generate nanoparticle-based architectures. The main driving factor for the self-assembly mechanism has its origin in the interaction force between the capping agents\textsuperscript{137} and so a brief discussion of capping agents is presented here.

Interaction forces between capping agents play a prominent role in the crystallization process and can outweigh the van der Waals forces between the metal nanocores by two orders of magnitude.\textsuperscript{75} It has been speculated that shorter capping molecule chains only interact weakly with the shells of other nanoparticles, thus exhibiting only a small tendency to crystallize into denser islands, whereas shells comprised of longer capping molecules, give rise to a much stronger interaction force between the shells, which leads to a strong crystallization force.\textsuperscript{129} In the case of two long chain amphiphilic molecules interacting, interlocking bundles are formed between adjacent molecules. In this example of interlocking of molecules used as capping agents, the distance between nanoparticles will be determined by the length of the capping molecule.\textsuperscript{137} Thus, the use of specific capping chains determines the order of the two-dimensional monolayer. While DMAP is not a long hydrocarbon chain, interactions between molecules may lead to ordering via van der Waals interactions.
Figure 50: TEM micrograph of DMAP-stabilized gold nanoparticles on a carbon-coated copper grid.

6.3.2 Nanoparticle – Molybdenum Disulfide Inclusion Materials

Molybdenum disulfide was exfoliated in the presence of the gold nanoparticle solution followed by the washing and centrifuging process. Typically, 6 mg of MoS$_2$ was exfoliated in 50 mL of the nanoparticle solution. Adsorption was evident following addition of the gold nanoparticles by the disappearance of the characteristic dark red color of the nanoparticle solution over the course of minutes. The resulting structures were analyzed by XRD to determine the level of nanoparticle inclusion. From the sample diffraction pattern shown in Figure 51, the presence of a broad peak at $2\theta = 1.6^\circ$, which corresponds to a MoS2 layer separation of 5.5 nm, is displayed. The peaks at $2\theta$
137

= 7.2°, 14.4° are assigned to exfoliated restacked MoS$_2$ (001) and (002). The broad peak at $2\theta = 38^\circ$ results from Au (111).

From this observation, it is suggested that a restacked material where there exists partial adsorption of gold nanospheres in between the MoS$_2$ single sheets is obtained. The layer separation associated with the peak at $2\theta = 1.6^\circ$ is consistent with the diameter of an average Au nanosphere. The broadness of the peak indicates that the separation of the single sheets varies substantially. This observation is attributed to the non-uniform inclusion of nanoparticles. It can be seen that the broad peak tails into the $2\theta = 7.2^\circ$ peak which is attributed to the inclusion of water. It is suspected that this observation is due to signals arising from all separations of MoS$_2$ sheets from the maximum distance of a gold nanosphere to the minimum distance of a water molecule residing in between the MoS$_2$ sheets. The crystallite size of the gold nanospheres in the inclusion material was reaffirmed to be 50 Å using equation (16) using the Au (111) peak which is in good agreement with the TEM measurements. Determination of the crystallite size of the nanoarchitecture was not possible because of the nature of the origin of the signal giving rise to the low angle peak which will be discussed later.
A nanostructure where sandwiched between MoS₂ sheets are regions of gold nanoparticles and regions of vacancies resulting in varying MoS₂ separation yielding intensity between $2\theta = 1.6^\circ$ and $2\theta = 7.3^\circ$ is proposed and is schematically represented in Figure 52. Intensity below $2\theta = 1.6^\circ$ is attributed to MoS₂ layer separation arising from nanosphere clusters and nanospheres of diameter greater than the average nanosphere diameter. Intensity above $2\theta = 1.6^\circ$ is attributed to MoS₂ layer separation arising from nanoparticles vacancies and separation arising from separation due to nanoparticles of diameter smaller than the average nanoparticle diameter. Judging by the intensity of the $2\theta = 7.3^\circ$ peak, one can conclude that a significant amount of MoS₂ remains without
included nanoparticles. This type of structure introduces inaccuracies when trying to determine an accurate crystallite size of the nanoparticle-MoS$_2$ material using the Scherrer formula because it is expected that the broadness of the peak arises from a broad range of interlayer separations and not from the crystallite size.

Figure 52: Schematic representation of the proposed structure (left) giving rise to the peak at $2\theta = 1.6^\circ$ (left) in Figure 51. The structure is compared to a uniform architecture resulting from a complete nanosphere coverage (right).

TEM studies were performed on this material to corroborate the XRD results. From the resulting image shown in Figure 53, it can be observed that adsorption of the gold nanoparticles on the MoS$_2$ single sheets was achieved. Although the micrograph shows that the gold nanoparticle coverage is not complete, it is much more complete than that obtained by using the previous citrate-capped gold nanoparticles. This observation is attributed to the increase
in ratio of gold to MoS$_2$ in the reaction mixture and to the favourable choice of DMAP as a capping agent.

Figure 53: TEM micrograph of MoS$_2$/Au nanospheres.

Several points of interest can be made about the TEM micrograph above. The Au nanoparticle coverage of MoS$_2$ has been increased substantially. In fact, there exist regions where the nanoparticles are exhibiting close packing on the MoS$_2$ surface. Nanoparticles are adsorbed on all regions of an MoS$_2$ sheet, moreover, there are regions where the gold nanoparticles have formed clusters and aggregates on the MoS$_2$ single sheets. In certain regions, it is observed that the aggregates are quite thick from the intensity in the micrograph, which
indicates that it is possible that the gold nanoparticles form a three-dimensional structure, which is consistent with intensity in the XRD pattern in the \( \theta < 1.6^\circ \) region. From the FWHM of the peak at \( 2\theta = 1.6^\circ \), a broad range of interlayer separations is evident. The separation distances resulting from intensity at lower \( 2\theta \) values of the peak maximum suggest that giving rise to these intensities are either multinanoparticle structures or anomalously large nanoparticles, both of which were seen in the preceding micrograph.

The nature of the orientations of the MoS\(_2\) planes with respect to the TEM electron beam makes it difficult to gain insight into the multilamellar nature of the restacked material. For very thick regions, i.e., those containing multiple MoS\(_2\) layers containing many Au nanospheres, the presence of heavy nuclei makes it impossible for the electrons to pass through to the image plate detector and thus no electron intensity is observed. This high density is evident in the upper region of the micrograph in Figure 53. In order to overcome these high intensity difficulties, the cross sectional TEM method is proposed.

### 6.4 Gold Nanoparticle Monolayer Coverage

In order to determine how much Au added to MoS\(_2\) would yield monolayer coverage, the packing of atoms and nanospheres has to be considered. The micrograph in Figure 53 was produced from a Au to MoS\(_2\) mass ratio of approximately 6.25 (5.11 mole ratio) (which did not produce monolayer coverage. Based on the unit cell size of MoS\(_2\) and a hexagonally close packed (hcp) array of Au nanospheres, in which the atoms \( r_{\text{Au, van der Waals}} = 166 \text{ pm} \) are face centred
cubic (fcc), [135, 138] the mass ratio that would yield a maximum coverage can be calculated. The MoS₂ exhibits a distorted hexagonal structure as shown in Figure 54 with well known dimensions. [21] For a maximum adsorption of the gold nanospheres on the MoS₂ sheet, the gold spheres would have to pack in a hcp fashion. Knowing the crystalline gold structure, a mass ratio of 21 gold to MoS₂ (17.2 mol ratio) is expected to result in a full coverage of gold nanospheres. This ratio is proportional to the radius of the gold nanospheres which has been reported to be in the range of 0.5 - 3.1 nm [81, 82, 90, 139] using the synthesis route employed here, it is calculated to be 2.5 nm based on the TEM images and capping agent size effects. Since this radius has a large range of values, the mass ratio required for monolayer coverage will as well.
Figure 54: Schematic representation of comparison of unit cell size of MoS$_2$ and Au nanospheres in an hcp arrangement. The left portion represents an MoS$_2$ single layer in which the large circles are sulphur (light is above the plane of the page and dark is below the plane of the page) and the small circles represent molybdenum atoms. The unit cell dimensions are $a = 3.22$ Å, $b = 5.68$ Å. Note that is the dark sulphur circles that give rise to the hexagonal, ordered images in Figure 38. This is then compared in size to the unit cell of gold nanospheres on the right side of the figure in an hcp arrangement with the rhombus representing the unit cell of size $2r = 5$ nm where $r$ is the radius of a gold nanosphere.

Another assumption that is made in these calculations is that trapped in between two layers of MoS$_2$ is exactly one layer of nanospheres with no imperfections in the direction normal to the plane of the MoS$_2$ nanosheet. As can be observed in the TEM micrograph in Figure 53 there exist regions where the gold nanospheres seem to be clustered locally to form three-dimensional gold aggregates. Generation of these local aggregates will increase the ratio of Au/MoS$_2$ needed for full monolayer coverage. It is quite difficult to determine this value quantitatively because aggregate formation is random and causes very low intensity in the micrograph and thus becomes difficult to count the nanospheres from the TEM image. Aggregate formation may be minimized with an appropriate choice of capping agent.
In order to increase the nanoparticle coverage, the amount of solution containing the gold nanoparticles was increased threefold compared to the synthetic route described in Section 6.3, while keeping the amount of MoS₂ constant. This stoichiometry yielded a mass ratio of gold to MoS₂ of 19/1. Adsorption was evident following addition of the gold nanoparticles by the disappearance of the characteristic dark red color. This time, however, the solution took overnight to become clear. The resulting structures were analyzed by XRD to determine the level of nanoparticle inclusion. The peaks at 2θ = 1.1°, 2.1° are assigned to the MoS₂-nanoparticle material structure. The peak at 2θ = 7.3°, which is assigned to MoS₂, is much less intense compared to the previous pattern. The broad peak at 2θ = 38° results from Au (111).

From the sample diffraction pattern shown in Figure 55, the presence of a peak at 2θ = 1.1°, which corresponds to a MoS₂ layer separation of 8.0 nm, was observed. The layer separation associated with the peak at 2θ = 1.1° is slightly larger than the diameter of an average Au nanosphere. In sandwiching the nanospheres, it is expected that the MoS₂ layer separation would be reflective of the largest nanospheres as well as aggregates that are included in the structure. From the TEM micrograph in Figure 50 it can be seen that instances where nanospheres are larger than the average size and even as large as the layer separation corresponding to the peak at 2θ = 1.1° exist. The peak at 2θ = 7.3°, which is attributed to the inclusion of water, is still present although much reduced in intensity indicating that the inclusion of nanospheres in MoS₂ is much more complete. The crystallite size of the nanospheres was calculated to be 50
A, which corresponds well to the diameter of the nanospheres as measured from the TEM micrographs.

Figure 55: Diffraction pattern of MoS$_2$/Au nanospheres resulting from a Au/MoS$_2$ mass ratio of 19. The inset is an amplification represents an amplification of the signal by a factor of 40.

The diffraction patterns (Figure 51 and Figure 55) resulting from materials from the two different gold to MoS$_2$ ratios were compared after a three hour collection time. By increasing the amount of gold nanospheres in the inclusion mixture, the intensity of the primary diffraction peak at $2\theta = 1.1^\circ$ has significantly increased with respect to the intensity of the peak at $2\theta = 7.3^\circ$. The narrowing of the feature and the increased intensity are signs of increased architectural ordering. The peak at $2\theta = 7.3^\circ$ has decreased as is expected from a higher gold nanoparticle coverage. The presence of the nanoparticles gives rise to the Au
(111) peak in both cases. That the peak at \(2\theta = 7.3^\circ\) has not disappeared as the ratio of Au to MoS\(_2\) is increased indicates that there exist regions where MoS\(_2\) has Au vacancies. This observation is expected since the ratio of Au to MoS\(_2\) is still not as high as was needed for full coverage from the previous calculation. Nevertheless, much insight is provided here into how crucial the role of stoichiometry plays in the ability to control nanostructure architectures.

The MoS\(_2\)-Au material, prepared by the drop cast technique on a microscope slide, exhibited a very broad surface plasmon absorption band at \(\lambda_{\text{max}} = 632\) nm. The presence of the surface plasmon band indicates that the gold nanoparticles are present in the structure generated. The broadening is characteristic of the inhomogeneous nanosphere environment compared to the nanosphere suspended in water.\(^{[140]}\) The redshifting and broadening of the surface plasmon band has been shown to be characteristic of interactions between gold nanoparticles and are expected when nanoparticles are brought close together due to plasmon coupling effects.\(^{[140]}\) In the nanostructures generated in this work it is expected that the nanoparticles are very close to each other as well as to the MoS\(_2\) layer, which may explain the shifting of the plasmon band. The low intensity of the peak may be due to the strong absorption of MoS\(_2\). The existence of the band is significant for two main reasons. First, it supplements the TEM observation of the presence of nanoparticles in the nanostructure. Secondly, it indicates that a macroscopic property of the nanoparticles is retained and is introduced into the nanostructured material.
Because the MoS$_2$ layers have a large surface area per mass ratio, it is quite challenging to produce nanoparticle solutions that will yield a monolayer coverage. By using as little MoS$_2$ as possible one can increase the Au/MoS$_2$ ratio. Nevertheless, the amount of MoS$_2$ used had to be sufficient such that appropriate characterization could be performed.

### 6.5 Hybrid Structure Conductivity Measurements

After having used this approach to generate a new type of nanostructured architecture, observations of their macroscopic properties were made. Conductivity measurements were made using a four-point probe apparatus. The
samples of exfoliated and restacked MoS$_2$ were compared to exfoliated restacked MoS$_2$ with DMAP-capped Au nanoparticles adsorbed. Samples were prepared by the drop cast technique on a glass microscope slide from a Au/MoS$_2$ suspension of mass ratio 19.

The results of the contrast of the two samples are summarized in Table 5. The uncertainty in the sample thickness value, $t$, reflects the range of thicknesses obtained by taking four measurements. Six readings were taken of each film from various film locations, all of which were far away from the sample edges. The uncertainty of the conductivity reflects the range of values of the conductivity that were obtained for each sample. While the values obtained for the exfoliated restacked MoS$_2$ sample covered a narrow range of conductivities, the values obtained form the restacked MoS$_2$ with gold nanoparticles included varied in value over an order of magnitude. This result is attributed to the film structure of the composite film. Knowing that the measurement is path dependent, it is suspected that paths that electrons travel between different sets of arbitrary probe points on the film are quite different from each other resulting in different resistances between the points, this point is reflected in the range of values obtained and hence the uncertainty.
Table 5: Conductivity comparison of restacked MoS$_2$ with gold nanoparticles included and exfoliated restacked MoS$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MoS$_2$/Au</th>
<th>Restacked MoS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>3.75±0.49 μm</td>
<td>2.30±0.24 μm</td>
</tr>
<tr>
<td>$F_1$</td>
<td>$(2.71±0.36)\times10^{-3}$</td>
<td>$(2.35±0.35)\times10^{-3}$</td>
</tr>
<tr>
<td>$F_2$</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>$F_3$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma$ (S/cm)</td>
<td>20.3 ± 6.5</td>
<td>1.80 ± 0.15</td>
</tr>
</tbody>
</table>

The thickness measurements themselves were subject to a large standard deviation which is a result of the varying thickness of the samples at various locations. The effects of $F_2$, the correction term that relates the effects on conductivity due to the relationship between sample size and inter probe distance, were largely negligible because the samples are quite large compared to the inter probe distance. The effects of $F_3$, the correction term that relates the effect on conductivity due to the distance from sample edge compared to inter probe distance, were calculated for probe placements far away from linear boundaries. This sample did not have straight line boundaries; however this value was set to unity because the probes were not placed near the sample edges when taking the measurements. It should be mentioned that the correction factors assume uniform samples of uniform conductivity and that the surface on which the probes rest is flat. Due to the nature of the deposition of
the sample and the thickness data taken with the profiler, there is some ambiguity as to whether this is indeed the case.

The conductivity obtained for the MoS$_2$ powder after the intercalation-exfoliation treatment is an order of magnitude higher than that observed in the literature.$^{[37]}$ 1T-MoS$_2$ is a conductor as discussed in Chapter 1. An enhancement in the lateral conductivity has been reported by increasing layer separation with the use of aliphatic organic guest molecules such as aminooctadecane, however these measurements were conducted using the two-point probe method and as such are subject to the inaccuracies described earlier related to the contact resistance. The conductivity was shown to decrease with increasing interlayer distance. The conductivity was independent of the type of organic molecule so it was argued that the conductivity in that case did not occur through the guest molecule but rather through electronic coupling via the adjacent layers. It is shown here what is believed to be the first instance of high conductivity resulting from MoS$_2$ with a “large” interlayer separation. In this case, the guest material is very conductive and thus is expected to be of significant importance with respect to the conductivity enhancement. An enhancement of the conductivity of $11.2 \pm 3.7$ was observed compared to the restacked unintercalated MoS$_2$.

It is also generally recognized that conductivity in nanoparticle systems is determined, in part, by the capping agent. Studies performed on the conductivity of metal nanoclusters showed that the conductivity decreases as a function of the capping agent chain length.$^{[130]}$ It was shown that intervening chains are potent
barriers to electron transfers between Au cores. The conductivity falls off by approximately two orders of magnitude per each four-carbon increment in an alkyl chain (5.0 Å). Dimethylaminopyridine is not an alkyl chain and contains a delocalized \( \pi \)-system which is expected produce a cluster conductivity that is larger than which arises from alkane capped clusters. However, the effective resistance of DMAP chains remains unknown.

Materials with a higher ratio of Au/MoS\(_2\) than that produced by the above-described routine require the use of a substantial amount of the gold nanoparticle solution and a very minute amount of the MoS\(_2\) suspension. The synthesis of these structures will be vital in determining further conductivity properties of a composite structure such as that mentioned above. In order to get around the "random walk" phenomenon of the four-point probe measurement due to lack of long range ordering in the material, conductive AFM (cAFM) measurements are proposed. In cAFM, a potential is put across the sample and the conductivity of the sample is probed as a function of the cantilever location. This method may allow for the gaining of further insight into the conductivity of the film.

In summary, the adsorption dynamics of nanoparticles on MoS\(_2\) have been investigated to generate a new type of nanostructure. The results of XRD experiments indicate that nanoparticles are included into the restacked structure. Structures generated from aqueous nanoparticle solutions were dependent on the nanoparticle to host material ratio. Using nanoparticles with capping agents containing groups that are known to adsorb strongly to MoS\(_2\) has been shown to be advantageous. These new structures lead to an increased conductivity of the
materials compared to the unincluded materials. Thus, from applying what was learned in the previous chapters, a method for constructing three-dimensional architectures of nanoparticles has been developed. These materials have macroscopic physical properties that are retained from the nanoscale building blocks.
CHAPTER 7: CONCLUSIONS AND FUTURE PROJECTS

The structure of several MoS$_2$ inclusion materials were studied through means of several surface and spectroscopic techniques. The studies were aimed at understanding the MoS$_2$ single layer restacking mechanism, gaining insight into the interactions that define these materials and thereby generating ordered structures and using this knowledge to synthesize novel nanomaterials.

The properties of exfoliated and restacked MoS$_2$-MG inclusion compounds have been examined to provide insight into the MoS$_2$-MG interactions that characterize these materials. The orientation of MG included into the restacked structure was obtained. Second harmonic generation experiments conducted on the exfoliated and restacked materials provided information regarding the averaged orientation of the MG. Second harmonic generation results in conjunction with XRD findings showed how the averaged orientation angles change as a function of the amount of MG that is adsorbed. The expulsion of excess MG from the layers to the outside of the restacked crystallite appears to accompany the restacking process.

Together with XRD and adsorption isotherm data and this first use of SHG to study layered structures, results provided a model for the exfoliation, adsorption, and subsequent restacking of these MG-based inclusion materials. According to the XRD and molecular modeling studies, the subsequent
restacking of the exfoliated MoS₂ host material resulted in a layered structure incorporating one monolayer of MG between its sheets.

The properties of adsorption of amphiphilic molecules on MoS₂ single sheets have been studied in order to study the types of interactions that occur between the host and guest materials and between guest molecules adsorbed on host materials. The exfoliation of MoS₂ in the presence of stearic acid on the interface of water has not been reported before in the literature. By performing a vertical deposition of the film, stearic acid can be included in a Y-type fashion in an upright position between MoS₂ monolayers. Through AFM, it was shown that a single layer of stearic acid adopts a highly crystalline hexagonal packing on the surface of MoS₂. By using SFG spectroscopy, spectral features characteristic of well-ordered, fully extended all-trans alkyl chains in an upright conformation were shown, consistent with this observation.¹⁴¹

Second harmonic generation and SFG were used due to the two-dimensional property of the material being probed allowing it to be placed at the interface between two media. These results demonstrate the utility of nonlinear optical techniques as a complimentary tool in probing of these interesting layered structures which took advantage of the single layer nature of MoS₂.

The adsorption dynamics of nanoparticles on MoS₂ were investigated to generate a new type of nanostructure by utilizing and applying what was learned about interactions of MG and stearic acid with the host MoS₂. Iron oxide inclusions proved to be challenging yet provided insight into the important role that the capping ligand plays in nanostructure generation and synthesis. Using
XRD, the level of nanoparticle incorporation into the restacked structure was determined. The coverage of the single layers of MoS$_2$ was found to vary proportionally as a function of the nanoparticle to MoS$_2$ ratio. Using nanoparticles with capping agents containing groups yielding a favourable interaction with single layer MoS$_2$, was shown to be advantageous in generating large nanosphere coverages. The conductivity of these new structures increased compared to the exfoliated restacked materials alone by more than one order of magnitude.

It has been shown how crucial a role capping molecules play in nanostructure generation. Their importance ranges from nanostructure stabilization to nanostructure interactions. Since ordered arrays of metal nanoparticles exhibit properties that can be controlled via particle size and interparticle distance, the use of organic-shell capped metal clusters is of great advantage. Many important features of metal nanoparticles such as their chemical reactivity and optical properties depend on the nature of the ligand and the ligand-metal bond. The capping molecules are utilized for the specific properties that they imprint on the nanoparticle solubility, synthesis, incorporation properties and affinity for capping different metals.

With this in mind, several avenues can be taken in order to control synthesis of MoS$_2$/nanoparticle structures. In terms of iron oxide nanospheres, the use of a micelle-type method may be employed to associate molecules with the outer oleate perimeter such that an adlayer of a new molecule will be formed on the nanoparticle. Altering of iron oxide nanoparticle synthesis such that the
capping agent does not form a stable network would allow for exchange with more desirable capping agents. Another approach is to use oleic acid derivatives that enable modification to be performed to alter the nanoparticle capping layer after its synthesis. These derivatives would possess a functional end group to allow reactions to be performed.

The role of the capping agent was shown to be crucial. Control of particle growth and spacing and assembly has been well documented. Nanoparticle size has a profound effect on the optical and mechanical properties of nanostructures and is a gateway to the ability to tailor structures with specific characteristics. While iron oxide and gold nanospheres were utilized because their chemistry had been well documented, other metals nanospheres may be adsorbed continuing to yield a new generation of MoS$_2$/metal nanosphere composite materials. The use of superparamagnetic nanoparticles in the MoS$_2$ framework may lead to new structures exhibiting interesting magnetic properties with potential memory applications. Desired electronic properties may be attained with the use of other metals as the guest material. Improvement over current catalysts and lubricants may also be realized by varying the material composition thereby by providing control over material porosity. The use of other metal chalcogens may prove useful in the generation of materials with a broad range of new physical properties.

The many variables in nanostructure generation make nanoscience an exciting field that is still in its youth. The possibilities for novel structures are limitless and generate much speculation as to the advances of nanoscience that
may arise. An important goal for future research efforts remains to design and prepare three-dimensional objects of precisely controlled geometry, including multicomponent systems which do not only contain one type of nano-sized building block, but rather several different types of structurally cooperating components, i.e., combinations of different kinds of nanoparticles. This approach may lead to the development of new materials and structures with functional properties superior to those of conventional materials. The results presented in this thesis can be seen as a further step towards closing the narrowing gap between structures prepared by microfabrication and chemically designed structures.
APPENDICES

Appendix 1: Fresnel Coefficients

Described in this appendix is the method of obtaining the values of $c_i$ in equation (10). These values are a function of the Fresnel linear and nonlinear prefactors that depend on experiment geometry and are required in order to determine the second order susceptibility components in equation (10). The details of the formulation can be found in work performed by Felderhof et al. and only brief summary is given here.

The prism cross-section shown in Figure 57 will be the basis for the discussion. The sample is located on the prism hypotenuse, AB, and this is where the SH signal is generated. The wavevector of the beam being considered is $\vec{k}_0 = \frac{\omega}{c}$.

If we let $(0, p_0, q_0)$ be the components of $k_0$ in the $(x, y, z)$ coordinate system and $(0, p'_0, q'_0)$ be the components of $k_0$ in the $(x', y', z')$ coordinate system then

$$p_0^2 + q_0^2 = p_0'^2 + q_0'^2 = k_0^2$$  \hspace{1cm} (30)

Similarly for $k_1$

$$p_1^2 + q_1^2 = p_1'^2 + q_1'^2 = \varepsilon \omega k_0^2 = k_1^2$$  \hspace{1cm} (31)
Figure 57: The coordinate system used for calculation of the Fresnel coefficients and wavevectors of the fundamental \((k_0, k_1, k_2)\) and SH \((k_3, k_4)\) signal.

where \(\varepsilon_n = n_e^2\) is the dielectric constant of the silica prism. Similar relationships can be made for \(k_n\) \((n = 2, 3, 4)\) and as a result the final wavevector, \(k_4\), can be calculated from the initial wavevector, \(k_0\).

We define s-polarized light as polarized perpendicularly to the plane of incidence with the component oscillating in \(x\) direction and p-polarized as light polarized in the plane of incidence with components in \(y\) and \(z\) directions. The Fresnel equations that describe the transmission coefficients for s- and p-polarized light are used for relationships between the electric field components on both sides of an interface.\textsuperscript{[142]}
The subscripts \( i \) and \( t \) refer to the incident and transmitted light, respectively, and \( n \) is the refractive index of the medium in question. But since the angle of incidence, \( i \), can be expressed as a function of wavevector components in the \( x' y' z' \) frame,

\[
\sin \theta_i = \frac{q_0'}{k_0}, \quad \cos \theta_i = \frac{q_i'}{k_0}
\]

then the Fresnel equations can be expressed as a function of the components of the \( x' y' z' \) frame

\[
t_{0i}^{\prime} = \frac{2q_0'}{k_0} = \frac{2n_0q_0'}{q_i' + \epsilon_i q_0'}
\]

Similarly,

\[
t_{0i}^{\prime} = \frac{2q_0'}{q_0' + q_i'}
\]

here the \( 01 \) denotes the interface, \( AC \), of the prism air interface. We now summarize the other four Fresnel expressions in the remaining coordinate systems and through the remaining interfaces.
Based on our definition of s- and p-polarization we can express the electric field components of the radiation in terms of $E_x, E_y, E_z$ in the $x'y'z'$ frame.

$$E_x = E_s$$

$$E_y = E_p \cos \theta_i = E_p \frac{q_0'}{|k_0|}$$

$$E_z = -E_p \sin \theta_i = -E_p \frac{p_0'}{|k_0|}$$

or more generally

$$\bar{E}_0(\bar{r}, \omega) = \left( E_s^0, E_p^0 \frac{q_0'}{|k_0|}, -E_p^0 \frac{p_0'}{|k_0|} \right) e^{i(p_0'y'+q_0'z')}$$  \hspace{1cm} (39)

Analogously the expression for $\bar{E}_1$ in the $x'y'z'$ frame can be obtained

$$\bar{E}_1(\bar{r}, \omega) = \left( E_s^0 t_{01}', E_p^0 \frac{q_0'}{|k_0|} t_{01}', -E_p^0 \frac{p_0'}{|k_0|} t_{01}' \right) e^{i(p_0'y'+q_0'z')}$$  \hspace{1cm} (40)

In similar fashion the field $\bar{E}_2$ can be obtained in each coordinate frame and specifically in the $xyz$ frame

$$\bar{E}_2(\bar{r}, \omega) = \left( f_x E_p^0, f_y E_s^0, f_z E_p^0 \right) e^{i(p_2'z'q_2')}$$  \hspace{1cm} (41)

where we introduce the Fresnel pre-factors.
The field $\vec{E}_2$ described in equation (41) excites a nonlinear SH response in the film deposited on face, $AB$, of the prism. The components of this surface polarization can be described as

\begin{equation}
\vec{P}_{\text{surface}}^{(2\omega)} = \chi_{\alpha\beta\gamma} \vec{E}_{2\beta}(\omega) \vec{E}_\gamma(\omega)
\end{equation}

where $\chi_{\alpha\beta\gamma}$ is the nonlinear surface susceptibility and $E_{2\beta}$ are the fields described in equation (41). The generation of the SH response coupled with total internal reflection geometry will cause a propagation of a wave inside the prism at frequency $2\omega$. Upon exiting the prism the SH field $E_4(2\omega)$ can be described as

\begin{equation}
E_4(2\omega) = \left( \vec{E}_s^{(2\omega)}, \vec{E}_p^{(2\omega)}, \vec{E}_s^{(2\omega)}, \vec{E}_p^{(2\omega)} \right) e^{i(p_x y - q_y z)}
\end{equation}

where $\vec{E}_s^{(2\omega)}$ and $\vec{E}_p^{(2\omega)}$ are the components parallel and perpendicular to the incidence of the plane and are given by

\begin{align}
\vec{E}_p^{(2\omega)} &= \frac{1}{\sqrt{\varepsilon(2\omega) q_4^{(2\omega)}}} q_3^{(2\omega)} \vec{E}_p(2\omega), \\
\vec{E}_s^{(2\omega)} &= t_0^{(2\omega)} \vec{E}_s(2\omega)
\end{align}

and
$$\begin{align*}
\vec{E}_p(2\omega) &= 8\pi |k| \left( F_x \vec{P}_{\text{surface}} + F_z \vec{P}_{\text{surface}} \right), \\
\vec{E}_s(2\omega) &= 8\pi |k| \left( F_y \vec{P}_{\text{surface}} \right)
\end{align*}$$

$\vec{P}_{\text{surface}}$ is the surface polarization given in terms of the incident field. Here we introduce the nonlinear Fresnel factors

$$\begin{align*}
F_x &= \frac{2}{\omega c} \frac{1}{q_2 + q_3}, \\
F_y &= \sqrt{\varepsilon_{2\omega}} \frac{q_2}{\varepsilon_{2\omega} q_3 + q_3}, \\
F_z &= \sqrt{\varepsilon_{2\omega}} \frac{p_3}{\varepsilon_{2\omega} q_3 + q_2}
\end{align*}$$

which are the analogues to the linear Fresnel factors.

If the incident beam is polarized as outlined in by equation (11), then the ratio of intensities of the outgoing SH beam to the intensity of the incoming fundamental beam for s- and p-polarizations is

$$\begin{align*}
R_s &= \left( t_{10}'' \right)^2 a_{ssp} \sin^2 2\gamma \\
R_p &= \frac{1}{\varepsilon_{2\omega} q_4''} \left( q_3'' \right)^2 \left( a_{ppp} \cos^2 2\gamma + a_{psp} \sin^2 2\gamma \right)^2
\end{align*}$$

where the coefficients are given by

$$\begin{align*}
 a_{ppp} &= 8\pi |k| \left[ 2 F_x f_x f_z \chi_{xxx} + F_z \left( f_z^2 \chi_{xx} + f_x^2 \chi_{zz} \right) \right] \\
 a_{psp} &= 8\pi |k| F_y f_z^2 \chi_{xx} \\
 a_{ssp} &= 16\pi |k| F_y f_z \chi_{xxx}
\end{align*}$$

Thus if we combine equation (11) and (48) we arrive at equation (10) where all the constants, $c_j$, are related to the linear and nonlinear Fresnel
coefficients outlined above and $\psi = 0^\circ$ and $\psi = 90^\circ$ correspond to p and s-polarizations of the SH light, respectively.
Appendix 2: Euler Transformations

Described in this appendix is the transformation from the molecular coordinates to the laboratory coordinates as described in equation (12). The molecular and surface reference frames are shown in Figure 6. The direction cosines required to evaluate the molecular distribution function can be obtained through the Euler transformation from the molecular, $x'y'z'$, coordinate frame to the laboratory, $xyz$, coordinate frame. This transformation can be described by three successive counter clockwise rotations. First, a rotation by $\delta$ about the molecular $z'$ axis to yield the $x''y''z''$ coordinate frame where

$$
\begin{bmatrix}
x'' \\
y'' \\
z''
\end{bmatrix} =
\begin{bmatrix}
\cos \delta & \sin \delta & 0 \\
-\sin \delta & \cos \delta & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x' \\
y' \\
z'
\end{bmatrix}
$$

(50)

Second a rotation about the new $y''$ axis through an angle $\theta$ to give the coordinate frame $x'''y'''z'''$ where

$$
\begin{bmatrix}
x''' \\
y''' \\
z'''
\end{bmatrix} =
\begin{bmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{bmatrix}
\begin{bmatrix}
x'' \\
y'' \\
z''
\end{bmatrix}
$$

(51)

And finally a rotation by $\phi$ about the new $z'''$ axis to result in the laboratory $xyz$ frame where
\[
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix} =
\begin{bmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
x'''' \\
y'''' \\
z'''' \\
\end{bmatrix}
\] (52)

Substituting the above equations into each other, one can obtain an expression of the laboratory frame in terms of the molecular frame.

\[
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix} =
\begin{bmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta \\
\end{bmatrix}
\begin{bmatrix}
x' \\
y' \\
z' \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix} =
\begin{bmatrix}
\cos \phi \cos \theta \cos \delta - \sin \phi \sin \delta & \cos \phi \cos \theta \sin \delta + \sin \phi \cos \delta & -\cos \phi \cos \theta \\
-\sin \phi \cos \theta \cos \delta - \cos \phi \sin \delta & -\sin \phi \cos \theta \sin \delta + \cos \phi \cos \delta & \sin \phi \sin \theta \\
\sin \theta \cos \delta & \sin \theta \sin \delta & \cos \theta \\
\end{bmatrix}
\begin{bmatrix}
x' \\
y' \\
z' \\
\end{bmatrix}
\] (53)

The elements of the transformation matrix in equation (53) represent direction cosines denoted as \( l_{ii}' \) in equation (12). For example, \( l_{xx}' = \cos \phi \cos \theta \cos \delta - \sin \theta \sin \delta \) and \( x = l_{xx}'x' + l_{xy}'y' + l_{xz}'z' \). For an isotropic distribution about the \( xy \) plane, the integration over all angles, \( \phi \), yields the following relationships, which allow one to simplify the orientation distribution function of the two remaining parameters \( \delta \) and \( \theta \).
\[
\sin \phi \cos \phi = \langle \sin 2\phi \rangle = 0 \\
\cos^2 \phi - \sin^2 \phi = \langle \cos 2\phi \rangle = 0 \\
\sin^2 2\phi = \frac{1}{2} \\
\cos^2 2\phi = \frac{1}{2} 
\]

(54)

We can now show, for example, a relationship between the second order susceptibility component, \( \chi_{zzz} \), and the dominant molecular hyperpolarizability component, \( \beta_{z'x'x'} \), that arises from using equations (12) and (53).

\[
\chi_{zzz} = \langle l_z l_z l_{z'} \rangle \beta_{z'x'x'} \\
\chi_{zzz} = \langle \cos \theta \sin^2 \theta \cos^2 \delta \rangle \beta_{z'x'x'} 
\]

(55)

Thus, all three independent nonzero \( \chi \) components can be expressed in terms of the dominant \( \beta_{z'x'x'} \) hyperpolarizability. Expressions describing the adsorbate molecule orientation, such as can be seen in equation (22), can be derived by solving for the appropriate variables and combining the expressions.
REFERENCE LIST


