DEVELOPMENT OF THE TWO-PHOTON PHOTOEMISSION TECHNIQUE
FOR THE STUDY OF INTERFACES BETWEEN
METAL SUBSTRATES AND THIN CONJUGATED POLYMER FILMS

by

JESSICA MARGARET AMENT

B.Sc., McGill University, 1997

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

January 2001

© Jessica Margaret Ament, 2001
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver, Canada

Date February 28, 2001
Abstract

This thesis examines the novel application of two-photon photoemission to the investigation of interfacial electronic structure between a metal substrate and a thin conjugated polymer film. Experimental considerations of the technique are discussed in detail. Theoretical aspects of employing the technique to study metal/conjugated polymer interfaces are compared to those of other, existing methodologies. Preliminary results from two-photon photoemission studies of poly(3-hexylthiophene) films on Au(111) substrates illustrate the ability of the technique to directly probe unoccupied interfacial states involved in electron transfer. The lowest unoccupied molecular orbital (LUMO) of poly(3-hexylthiophene) is found to lie 2.0eV above the Fermi level of the gold substrate, corresponding to a 0.8eV downward shift of the polymer energy levels upon interface formation. Results also illustrate the high sensitivity of the two-photon photoemission technique for studying these systems. A nearly 5000-fold increase in signal intensity from the polymer compared to the bare metal is attributed to the existence of long-lived excited states in the conjugated polymer.
# Table of Contents

Abstract \hspace{10pt} ii
Table of Contents \hspace{10pt} iii
List of Tables \hspace{10pt} v
List of Figures \hspace{10pt} vi
Acknowledgments \hspace{10pt} ix

## Chapter 1 - Introduction

1.1 General \hspace{10pt} 1
1.2 Background Theory and Literature Review \hspace{10pt} 3
  1.2a Spectroscopy of Electronic States at Metal Surfaces \hspace{10pt} 3
  1.2b 2PPE Studies of Image States at Metal Surfaces \hspace{10pt} 8
  1.2c 2PPE Studies of Metal/Adsorbate Systems \hspace{10pt} 10
  1.2d Conjugated Polymers and Metal/Polymer Interfaces \hspace{10pt} 14
1.3 Research Objective \hspace{10pt} 30

## Chapter 2 - Experimental

2.1 Ultrahigh Vacuum System \hspace{10pt} 32
  2.1a General \hspace{10pt} 32
  2.1b UHV Chamber \hspace{10pt} 34
  2.1c UHV Pumps \hspace{10pt} 35
2.2 Major System Components \hspace{10pt} 38
  2.2a Concentric Hemispherical Analyzer \hspace{10pt} 38
  2.2b Magnetic Shielding \hspace{10pt} 44
  2.2c Auger Electron Spectrometer \hspace{10pt} 47
  2.2d Sputter Ion Gun \hspace{10pt} 48
2.3 Samples \hspace{10pt} 48
  2.3a Sample Preparation \hspace{10pt} 48
List of Tables

<table>
<thead>
<tr>
<th></th>
<th>Calculation of mean free paths for carbon and gold Auger electrons</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>Summary of data for 2PPE spectra of bare gold and P3HT/Au samples</td>
<td>80</td>
</tr>
</tbody>
</table>
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Schematic of the valence electronic structure of a metal.</td>
<td>4</td>
</tr>
<tr>
<td>1-2</td>
<td>Schematic energy diagrams for (a) photoemission (b) inverse photoemission and (c) two-photon photoemission.</td>
<td>7</td>
</tr>
<tr>
<td>1-3</td>
<td>The polymer structure showing four monomer units of (a) polythiophene and (b) a general poly(3-alkylthiophene).</td>
<td>16</td>
</tr>
<tr>
<td>1-4</td>
<td>Three possible regioisomers of a thiophene dimer showing (a) head-tail (b) head-head and (c) tail-tail linkages.</td>
<td>17</td>
</tr>
<tr>
<td>1-5</td>
<td>Effect of sterically induced chain twisting on conjugated polymer band gaps [35].</td>
<td>18</td>
</tr>
<tr>
<td>1-6</td>
<td>Schematic representation of the self-localized energy levels in conjugated polymers showing (a) the band gap of a neutral polymer (b) an electron polaron state and (c) an electron bipolaron state.</td>
<td>21</td>
</tr>
<tr>
<td>1-7</td>
<td>Schematic diagram of the cathode/polymer interface under forward-bias conditions.</td>
<td>22</td>
</tr>
<tr>
<td>1-8</td>
<td>Vacuum level shift (Δ) due to the creation of a dipole at the metal/organic interface.</td>
<td>25</td>
</tr>
<tr>
<td>1-9</td>
<td>Principle of the UPS technique for studying energy level alignment at metal/organic interfaces.</td>
<td>28</td>
</tr>
<tr>
<td>2-1</td>
<td>Schematic and photographic representation of the VG100AX concentric hemispherical energy analyzer [56].</td>
<td>40</td>
</tr>
</tbody>
</table>
2-2  Views of the custom magnetic shield, used to prevent stray magnetic fields from affecting photoelectron trajectories between the sample and the detector.

2-3  ESCA-style sample stub and sample mounting system.

2-4  Non-magnetic sample holder for two-photon photoemission experiments.

2-5  Sample heating dock.

3-1  AFM image and line profile for a flame-annealed bare Au(111) surface.

3-2  Auger electron spectra for a bare Au(111) surface in an (a) uncleaned (b) partially cleaned and (c) clean state.

3-3  Auger electron spectrum for a P3HT/Au(111) sample.

3-4  AFM image and line profile for a P3HT/Au(111) sample.

3-5  Au(4f) XPS spectrum for a P3HT/Au sample.

3-6  AFM image and line profile for a P3HT/Au(111) sample, taken after recording XPS spectra, illustrating the presence of holes in the polymer film.

3-7  Two-photon photoemission kinetic energy distribution for an Au(111) substrate cleaned by sputtering and verified by AES.

3-8  Two-photon photoemission kinetic energy distribution for an Au(111) substrate cleaned by flame annealing.
| 3-9 | Two-photon photoemission kinetic energy distribution for a P3HT/Au(111) sample. | 81 |
| 3-10 | Two-photon photoemission kinetic energy distributions for an Au(111) substrate cleaned by flame annealing (red line) and a P3HT/Au(111) sample (blue line). | 82 |
| 3-11 | Energy level diagrams for Au(111) and poly(3-hexylthiophene) (a) before and (b) after interface formation. | 83 |
| 3-12 | Schematic energy level diagram of a conjugated polymer/metal interface, illustrating a decrease in ionization potential due to upward bending of the polymer bands. | 86 |
Acknowledgements

I would like to sincerely thank my supervisor, Dr. J. Todd Stuckless, for his academic guidance over the course of my degree. I am also grateful to Youngku Sohn for his considerable help with the sample preparation and characterization work included in this thesis, to Richard Murdey for his assistance in the lab and for reading and commenting on the manuscript, and to the technicians in the departmental shops for their work producing and maintaining the research equipment. Financial support from NSERC, CFI, Dr. Stuckless, and the Department of Chemistry is gratefully acknowledged.

I would also like to express my appreciation the many people who contributed in a more personal way to the writing of this thesis. Thank you to Kaoru Kumabe for being consistently wonderful, to my parents for their love, and to my friends, especially Kira Anthony, for support and laughter. I am also extremely grateful to Nick Fameli for his encouragement, to Ian Cavers and Lee Gass for believing in me, to Deborah Schwartz for sanity, and to Bruce Lennox for inspiration.
CHAPTER 1

INTRODUCTION

1.1 General

In recent years, there has been a growing interest in the electronic properties of conjugated polymers [1]. Potential applications include sensors, batteries, and integrated circuits. In particular, polymers used as semiconducting materials are promising for applications such as light-emitting diodes and other electroluminescent devices.

Polymer-based organic light-emitting diodes (OLEDs) are constructed by sandwiching a thin conjugated polymer film between two electrodes, where the anode is typically indium-tin-oxide (ITO) and the cathode is a low-work function metal. Upon applying a bias voltage to the device, electrons and holes are injected from the electrodes to the organic layer. These charges travel through the polymer film and light is emitted when two opposite charges meet and undergo radiative recombination. The wavelength of emitted light depends on the energy levels of the polymer used. Advantages of polymer-based OLEDs over competing technologies include low cost, ease of processing, and the colour versatility made possible by using and fine-tuning a variety of polymer structures. At present, the principal shortcomings of these devices are low quantum efficiencies and relatively short lifetimes.
It has been recognized by several authors that the efficiency and lifetime of an OLED ultimately rely upon the understanding and control of charge injection at the electrode/polymer interfaces of these devices [2]. Quantum efficiency is defined by the ratio of photons emitted to the number charges injected. It is often the case that initial hole injection exceeds initial electron injection, resulting in reduced efficiency. Thus, achieving balanced charge injection at OLED interfaces is highly desirable. Also, high energetic barriers to charge injection require large applied voltages to achieve a given injection current, producing excessive power dissipation. This can result in device degradation and reduced lifetimes. In order to avoid these outcomes, a thorough knowledge of the electronic structure of these interfaces is essential.

This thesis focuses on the energetics of electron transfer at the interface between a metal and a thin conjugated polymer film, as studied by two-photon photoemission (2PPE). The introductory chapter begins with a description of electronic states at metal surfaces and some of the spectroscopic techniques used to investigate these states: This is accompanied by a review of the literature pertaining to 2PPE studies of bare and adsorbate-covered metal surfaces. Next, an overview of theoretical aspects of conjugated polymers is presented, together with a discussion of their interfaces with metal substrates. The chapter ends with a synopsis of the goals of the research described within this thesis.

The second chapter describes the instrumentation and other hardware and software needed to carry out the two-photon photoemission experiments. This includes a discussion of several specialized methods and techniques that were developed in our laboratory.
The third chapter comprises a presentation of our sample characterization and two-photon photoemission results for clean Au(111) and P3HT/Au(111). This is followed by a discussion of the significance of the 2PPE technique for studying metal/semiconducting organic interfaces and of how this method complements various techniques already in use. The final chapter contains summarizing remarks and some suggestions for continued research.

1.2 Background Theory and Literature Review

a) Spectroscopy of Electronic States at Metal Surfaces

Photoelectron spectroscopy (PES) is a well-established technique for studying the electronic structure of solids. Due to the relatively short mean free path of electrons with less than a few keV of energy, PES is a surface sensitive technique.

The valence electronic structure of a metal (figure 1-1) can be described as a band of energy states, where the highest occupied state at zero degrees Kelvin is known as the Fermi level, \( E_F \). In order for an electron at the Fermi level to escape from the solid, it must gain sufficient energy to overcome the difference in potential between the interior and the exterior of the solid. The vacuum level of a surface, \( E_{\text{vac}} \), corresponds to the energy of an electron at rest outside the surface, where it is still affected by any fields generated by the surface but does not itself lead to polarization of the solid [3]. The work function, \( \Phi = E_{\text{vac}} - E_F \), is the minimum energy required at zero degrees Kelvin to remove an electron from inside the solid and across a surface. Different surface structures are associated with different work functions because atomic geometry
Figure 1-1: Schematic of the valence electronic structure of a metal. $E_{\text{vac}}$ is the vacuum level, $E_F$ is the Fermi level, and $\Phi$ is the work function of the surface.
govern the size of the surface dipole. A surface dipole results when electron wavefunctions exhibit non-zero amplitudes in the first few Ångstroms above a surface. The resulting excess of negative charge just outside the surface is balanced by a migration of positive charges from the bulk. The presence of adsorbates may also affect the magnitude of a surface's work function via the surface dipole, especially if considerable charge transfer takes place upon adsorption [4].

Based on the photoelectric effect, UPS (ultraviolet photoelectron spectroscopy) utilizes ultraviolet photons of a defined wavelength to excite valence electrons. If the photon energy exceeds the work function of the metal, then electrons can be emitted from the surface. This process is depicted in figure 1-2a. If the kinetic energy of these electrons is measured and it is assumed that no inelastic scattering has occurred, then the energy of an electron's initial state, \( E_{\text{initial}} \), with respect to the Fermi level, can be determined:

\[
E_F - E_{\text{initial}} = hv - \Phi - E_{\text{kin}}
\]  

(1.1)

where \( hv \) = energy of the incident photons  
\( \Phi \) = work function of the metal surface  
\( E_{\text{kin}} \) = kinetic energy of emitted electrons, at the surface

This approach is suitable for studying occupied states below the Fermi level. To first approximation, a UPS kinetic energy spectrum is an idealized representation of the density of initial states.

With UPS, the energy levels between \( E_F \) and \( E_{\text{vac}} \) are wholly inaccessible. Fortunately, there are a variety of techniques used to investigate these unoccupied electronic states [5]. One widely used approach is inverse photoemission [6-8]. Shown schematically in figure 1-2b, inverse photoemission (IPE) can be described as the time reversal of UPS.
Here, low energy electrons are incident on a surface and decay into unoccupied states above $E_F$, accompanied by the emission of a photon of measurable energy. The energy distribution of emitted photons mirrors the density of unoccupied states.

A significant drawback of IPE is the surface damage associated with an incident electron beam. In addition, the energy resolution of IPE is limited to about 0.5eV by the thermal energy distribution of the incident electron beam. A high-resolution alternative to IPE for studying electronic states between $E_F$ and $E_{vac}$ is two-photon photoemission [9], illustrated in figure 1-2c.

Two-photon photoemission (2PPE) is a second-order process. One photon populates an unoccupied state above the Fermi level, and a second photon excites the electron from its intermediate state to a final state above $E_{vac}$. As with first-order UPS, the kinetic energies of the photoemitted electrons are measured and analyzed. In the case of 2PPE, the energy distribution provides information about the energy of both the initial and intermediate states, $E_{initial}$ and $E_{int}$ with respect to $E_F$:

\[
E_F - E_{initial} = 2h\nu - E_{kin} - \Phi \\
E_F - E_{int} = h\nu - E_{kin} - \Phi \\
\Phi = 2h\nu - E_{kin}^{max}
\]

where equation 1.4 is simply equation 1.2 with $E_{initial} = E_F$. It is possible to establish whether a particular peak in a 2PPE kinetic energy spectrum is due to an initial state below $E_F$ or an intermediate state between $E_F$ and $E_{vac}$ by assessing the peak's dependence on photon energy. The kinetic energy of initial state peak will shift as $(2h\nu)$ while an intermediate state peak will shift as $h\nu$. 


Figure 1-2: Schematic energy diagrams for (a) photoemission or UPS (b) inverse photoemission and (c) two-photon photoemission.
There are some important aspects of 2PPE to consider. First of all, the photon energy used must be less than the work function of the metal surface in order to avoid first-order UPS, which would completely obscure the 2PPE signal. Furthermore, the photon energy must be greater than $E_{\text{int}} - E_F$ in order to successfully populate the intermediate state. Finally, signal strength depends on the lifetime of the intermediate state, its absorption cross-section, and the incident photon flux.

b) Two-Photon Photoemission Studies of Image States at Metal Surfaces

One type of electronic state at a metal surface is an image state. Image states exist because electrons can be bound to a surface by Coulombic attraction to their image charge. The presence of an electron at a given distance from a metal surface produces an electric field perpendicular to the surface and a series of bound hydrogenic states along the gradient of this potential. The series converges towards $E_{\text{vac}}$, as calculated by Echenique and Pendry [10]:

$$E(n) = E_{\text{vac}} - \frac{0.85eV}{n^2} \quad n = 1,2,3... \quad (1.5)$$

An electron in one of these states has an energy less than $E_{\text{vac}}$ and yet will not be able to penetrate the surface if there is an absence of momentum-allowed states in the metal. Under such conditions, the electron is trapped just outside the surface in an image state. Because they exist outside the solid, where electron-electron and electron-phonon interactions are quite weak compared to those in the bulk or surface states, image states are expected to have relatively long lifetimes.
Image states at metal surfaces have been studied extensively with 2PPE. Steinmann and coworkers performed the pioneering work in this field. Early studies illustrated two-photon photoemission from Ag(111), Cu(111), and Ni(111) using image states as intermediates [11,12]. These studies also established the dominant 2PPE process to be resonant excitation, as opposed to excitation followed by relaxation into an intermediate state.

Later work by both Steinmann and Fauster determined intrinsic linewidths for the first two members of the series [13]. Linewidth data is desirable because it is related to the lifetime of the image state by the uncertainty principle (\(\Gamma \times \tau = \hbar\), where \(\Gamma\) is the linewidth and \(\tau\) if the lifetime of the state). This work was continued to include lifetime data for the image states on a variety of metal surfaces, including Ag(100), Ni(100), and Cu(111) [14,15]. Using this method, lifetimes of \(n=1\) image states were found to be on the order of 10 fs. However, while a standard 2PPE experiment provides excellent resolution for the measurement of image state binding energies, the relative resolution when probing the lifetime of these states is quite limited.

The femtosecond-duration pulses of the Ti:sapphire laser allow lifetimes to be determined much more precisely in the time domain. With this tool, lifetime information is obtained directly, by varying the time delay between two ultrashort laser pulses. Time-resolved two-photon photoemission (TR-2PPE) has been used to investigate the lifetimes of image states at clean and adsorbate-covered metal surfaces. Wolf and coworkers have extensively studied the lifetimes of electrons in the image states of clean, Xe-covered, and CeF₆-covered Cu(111) surfaces [16,17]. They have demonstrated that image state lifetimes increase by a factor of 2 to 4 due to monolayer
coverage with Xe. This is attributed to decreased coupling of the image state with bulk states, resulting from the work function reduction associated with gas adsorption. On the other hand, molecularly adsorbed CeF$_6$ was found to significantly decrease the lifetime of Cu(111) image states. This effect is due to the presence of a CeF$_6$-induced energy level to which the image state electron efficiently decays. The work of Fauster et al. has focused on the n=1,2,3 image states of Cu(100) and Ag(100) and the influence of adsorbed CO thereon [18,19]. Lifetimes of 40±6, 120±15, and 300±20 fs for Cu(100) and 55±5, 160±10, 360±15 fs for Ag(100) were reported. Other investigations involving TR-2PPE have directly probed hot electron dynamics at the surfaces and interfaces of metals and semiconductors [20].

c) Two-Photon Photoemission Studies of Metal/Adsorbate Systems

Very recently, several research groups have used two-photon photoemission to study electronic states of adsorbates or self-assembled monolayers (SAMs) on metal surfaces. These investigations are presented here to illustrate the advantages of 2PPE and the nature of the information it can convey about this type of system.

One driving force for these studies is the desire to identify adsorbate-induced electronic states in order to better characterize the chemisorption process. Knowledge of these states also contributes to an understanding of such processes as photodesorption of molecular adsorbates, believed to occur through a photoexcited state [21], and surface photochemical reactions.
Two-photon photoemission is also an excellent technique for investigating heterogeneous electron transfer, a process that is poorly understood yet ubiquitous in a wide range of disciplines. While the ultrashort lifetimes expected for states exposed to the strong coupling between an adsorbed molecule and a solid surface do make 2PPE experiments difficult to perform, this regime is inaccessible to most other techniques. For interfaces where the different electronic states are well characterized, 2PPE can be used to establish which of these states are involved in the electron transfer mechanism.

Self-assembled monolayers of conjugated oligomers or molecules on metal surfaces have a promising future in the microelectronics industry. As such, electron transport in model SAM systems has been studied by a number of groups [22]. Of all the techniques used, only 2PPE can directly probe interfacial states, thereby providing insight into the interaction between conjugated molecules and the metal substrate. Furthermore, 2PPE allows both occupied and unoccupied states in these systems to be investigated.

The earliest 2PPE study of a metal/adsorbate system comes from work by Steinmann et al, concerning atomic oxygen on Cu(111) [23]. Using 2PPE, these researchers were able to detect both an occupied and an unoccupied oxygen-derived state on Cu(111) with high energy resolution. These states appeared as two new peaks in the kinetic energy distribution; they were differentiated based on their response to changing the incident photon energy.

Munakata and coworkers have studied the electronic states of NO/Cu(111) by 2PPE [24,25]. Theirs were the first 2PPE studies of transient molecular negative ion states in adsorbed molecules. The negative ion state of adsorbed NO, populated by
photoexcitation from an occupied NO-induced state, was found to lie 1.26±0.07 eV above EF. By using polarized laser light, these researchers were able to examine the spatial orientation of the adsorbed NO molecules.

Wolf and Ertl performed 2PPE of unoccupied electronic states associated with CO/Cu(111), including time-resolved studies [26,27]. Their work focused on determining the specific molecular orbital contributions to chemisorption in this system. Prior theoretical and experimental results had suggested a variety of possible MO interactions leading to the formation of the CO-Cu bond. Wolf and Ertl’s results using polarized laser light indicated the existence of a single unoccupied adsorbate-induced state with π-symmetry. This shows that CO-Cu bonding is predominantly derived from the interaction of the CO 2π* orbitals with occupied metal orbitals having the correct symmetry. Furthermore, the 2π* level of CO was found to lie 3.35±0.1 eV above EF.

Time domain experiments were carried out for the CO/Cu(111) system in order to probe the electron dynamics of states involved in photoinduced surface reactions and other phenomena. The lifetime of the CO 2π* state was found to be <20 fs, thereby requiring femtosecond pulses in order to obtain adequate electron emission at a given laser fluence. This lifetime is consistent with relaxation by fast tunnelling from the adsorbate state to unoccupied states of the metal through a barrier of atomic scale dimensions.

Zhu and coworkers have studied the interfacial states in C₆F₆/Cu(111) [28,29]. Their 2PPE results illustrate that C₆F₆ adsorption reduces the work function of the Cu(111) substrate, but not by as much as does C₆H₆. This observation is consistent with the
lower electron-donating character of \( \text{C}_{6}\text{F}_{6} \) compared to that of \( \text{C}_{6}\text{H}_{6} \). Additionally, their results show that although its intensity is greatly decreased, the \( \text{Cu}(111) \) surface state persists even with \( \text{C}_{6}\text{F}_{6} \) coverages over one monolayer. In tandem with previous findings that surface states are quenched by a chemisorbed layer [27] but endure in the presence of a physisorbed layer [16], this suggests that the interaction between \( \text{C}_{6}\text{F}_{6} \) and the copper surface is quite weak.

For \( \text{C}_{6}\text{F}_{6} \) coverages above one monolayer, a new peak appears in the 2PPE spectrum which, based on its position in the spectrum and its photon energy dependence, corresponds to an unoccupied state at 2.9eV above \( E_F \). Through consideration of the electronic states of gas-phase or condensed-phase \( \text{C}_{6}\text{F}_{6}^- \), this unoccupied interfacial state is established as being the \( \sigma^* \) LUMO of \( \text{C}_{6}\text{F}_{6}^- \). Compared to the gas phase, this \( \sigma^* \) negative ion state is stabilized by 1.1eV due to the attractive potential between \( \text{C}_{6}\text{F}_{6}^- \) and the surface.

Zhu and coworkers also studied interfacial states for thiolate self-assembled monolayers on metal substrates [29,30]. Their primary systems of study involved SAMs of thiophenolate (\( \text{C}_{6}\text{H}_{5}\text{S}^- \)) on \( \text{Cu}(111) \) because of the simplicity of this thiolate and the extensive characterization of \( \text{Cu}(111) \) by previous 2PPE work. Zhu et al found that \( \text{C}_{6}\text{H}_{5}\text{S}^- \) coverage leads to the disappearance of the copper surface state and a striking increase in secondary electron emission. These results are attributed to the effect of chemisorption and a surface work function reduction from 4.90eV to 3.70eV. Additionally, two new SAM-induced peaks are observed, one of which has a kinetic energy that scales linearly with photon energy and one of which maintains a constant position when photon energy is changed. Thus, these two peaks are assigned as an
intermediate unoccupied state 0.4eV below $E_{vac}$ and a final unoccupied state 2.7eV above $E_{vac}$. Nearly identical results were recorded for two alkanethiolate SAM systems, indicating that the observed interfacial structure is derived wholly from the C–S–Cu unit as opposed to the conjugated ring. This finding suggests that these SAM systems may not be good model systems for conjugated polymer-based OLEDs. Our 2PPE experiments focus, for the first time, on the interface between metals and actual conjugated polymers, thereby more closely representing real devices.

d) Conjugated Polymers and Metal/Polymer Interfaces

The discovery of high electrical conductivity in doped polyacetylene in 1977 [31] initiated the very active field of conjugated polymer research. The subsequent discovery of electroluminescence in the undoped form of poly(p-phenylenevinylene) (PPV) [32] caused a shift in interest from the conducting to the semiconducting properties of these polymers. Progress in conjugated polymer electroluminescence for use in a variety of photonic devices remains the focus of an ever-increasing volume of research [33,34].

Among the most widely studied of conjugated polymers are the polythiophenes [35], based on the thiophene monomer and pictured in figure 1-3a. These polymers are characterized by particularly high chemical stability, a versatility derived from facile structural modification, and controllable electrochemical behaviour. Although polythiophene (PT) itself is insoluble and therefore lacks processability, substitution with an n≥2 alkyl group at the 3C position (see figure 1-3b) renders the polymer soluble in a wide variety of solvents. Poly(3-alkylthiophenes) (P3ATs) generated by the earliest synthetic routes are termed irregular or regiorandom due to the fact that they contain
2,2' (head-head) and 5,5' (tail-tail) linkages in addition to 2,5' (head-tail) linkages (see figure 1-4). The steric effects associated with head-head linkages lead to a twisting of the thiophene rings and a resultant loss of conjugation and wider band gaps (see figure 1-5). As such, synthetic approaches were devised to produce regioregular P3ATs characterized exclusively by head-tail linkages [36]. These syntheses involve the regiospecific coupling of asymmetric organometallic monomer intermediates. The resulting polymer chains are able to achieve a planar geometry that supports high conjugation. Regioregular P3ATs are candidates for applications ranging from chemical sensors to optoelectronics devices. The study of their properties, particularly as regards their interface with metals, is a highly active field of research. The P3HT used in the work described in this thesis have at least 98.5% head-to-tail regiospecific conformation.

The development of polymer-based electronic devices such as OLEDs has advanced concurrently with an attempt to understand the fundamental physics of conjugated polymers [37,38]. A defining feature of organic semiconducting materials is the strong coupling between their electronic structure, geometric structure, and chemical bonding. A solid knowledge of the underlying principles governing polymer and device behaviour will foster improvements in performance.

Conjugated polymers possess a backbone of sp² hybridized carbon atoms, with the remaining pₑ atomic orbital on each carbon undergoing π-overlap with pₑ orbitals on adjacent carbon atoms. Such an arrangement of atomic orbitals produces a molecular electronic band structure characterized by electron delocalization along the length of the polymer. The delocalized π-electron system imparts several important properties to the conjugated polymer.
Figure 1-3: The polymer structure of (a) polythiophene and (b) a general poly(3-alkylthiophene) showing four monomer units. If R = (CH₂)₅CH₃ then (b) is poly(3-hexylthiophene).
Figure 1-4: Three possible regioisomers of a thiophene dimer showing (a) head-tail (b) head-head and (c) tail-tail linkages.
Figure 1-5: Effect of sterically induced chain twisting on conjugated polymer band gaps [35].
Firstly, the electronic band gap is rendered relatively small, resulting in semiconductor properties and allowing for low energy excitations. The band gap of a typical conjugated chain of monomers is dependent on conjugation length, with a polymer representing the $n \to \infty$ limit [39]. Theoretically, oligomers of acetylene will have progressively narrower band gaps as chain length increases, with polyacetylene being expected to possess a single half-filled band and metallic properties. However, electron-phonon coupling described by the Peierls distortion leads to relaxation manifested as alternating bond lengths along the conjugated chain. This doubling of the unit cell produces a gap in the band structure of the polymer. Due to the nature of $\pi$-overlap, these transitions are on the order of 1–3eV, corresponding to the energy of visible light. By comparison, a $\sigma$-bonded, non-conjugated polymer such as polyethylene is an insulator due to a band gap of about 8eV.

Furthermore, conjugated polymers are easily oxidized or reduced, a process that is usually carried out via charge transfer with chemical dopants. And finally, the delocalized $\pi$-electron system allows the charge carriers in conjugated polymers to travel along the polymer chain with higher mobilities than in a non-conjugated polymer.

Once electrons or holes have been injected across the electrode/polymer interface, they must travel through the polymer layer in order to encounter a partner with which to undergo recombination. Because of the strong coupling between electronic and geometric structure, and the quasi-one-dimensional nature of the conducting polymer, charge carriers are self-localized [38]. In other words, the presence of a charged species produces local changes in polymer geometry, which in turn generates local changes in
electronic structure including the creation of new energy levels within the band gap. Therefore, rather than being free electrons or holes, charge carriers in conducting polymers are described as quasiparticles, entities defined by the coupling between a charge and a lattice deformation. The mathematical description of quasiparticles in conducting polymers was first presented by Brazovskiï [40] and later refined by Kim and Lee [41].

The exact nature of quasiparticles is dependent on the symmetry of the ground state of the conjugated polymer. For degenerate ground state conjugated polymers, such as polyacetylene, charge carriers exist as solitons. For the majority of conjugated polymers, including the polythiophenes, charge carriers exist as polarons. An electron polaron can be described as an unpaired electron in association with a local lattice relaxation or as a self-localized energy level within the forbidden band gap, as shown in figure 1-6a. In many cases, it is energetically favourable for two polarons to pair up and form a doubly-charged, spinless bipolaron, shown in figure 1-6b. When an electron polaron and a hole polaron encounter one another and interact, a polaron exciton is formed. This is the polymer excited state which may undergo radiative decay, thus producing electroluminescence.

As mentioned previously, the injection of electrons from the metal cathode to the polymer film of an OLED has a major influence on overall device performance. This interface under forward-bias conditions is depicted in figure 1-7. Ideally, the Fermi level of the metal and the $\pi^*$ conduction band of the polymer are closely matched, but in practice this correspondence is not realized and there is usually a substantial energy barrier to electron injection.
Figure 1-6: Schematic representation of the self-localized states in conjugated polymers showing (a) the band gap of a neutral polymer (b) an electron polaron and (c) an electron bipolaron state.
Figure 1-7: Schematic diagram of the cathode/polymer interface under forward-bias conditions. $B_e$ is the barrier height to electron injection from the Fermi level of the metal to the LUMO of the polymer.
One description of electron injection is Parker's model [42] wherein device efficiency and I-V characteristics are injection-controlled. Following from a series of experiments involving OLEDs based on MEH-PPV, Parker proposed that electrons enter the polymer by tunnelling through the triangular energy barrier created at the metal/polymer interface when a bias voltage is applied. This behaviour can be described by the Fowler-Nordheim theory [43], which states that the tunnelling current through a barrier under an applied bias voltage is given by:

\[ I \propto F^2 \exp\left(\frac{-\kappa}{F}\right) \]  \hspace{1cm} (1.6)

where

- \( I \) is current
- \( F \) is electric field strength
- \( \kappa \) is a parameter dependent on barrier shape

Assuming rigid bands at the interface and a triangular barrier, \( \kappa \) is given by:

\[ \kappa = \frac{8\pi\varphi^{3/2}\sqrt{2m^*}}{3qh} \]  \hspace{1cm} (1.7)

where

- \( \varphi \) is the barrier height
- \( m^* \) is the effective mass of the electron

Research by the groups of Hümmelgen and Heeger has confirmed the fundamental validity of Parker's model based on Fowler-Nordheim tunnelling [44]. However, device performance is found to deviate from the Fowler-Nordheim description in the form of strong temperature dependence at low fields. As such, provision for injection by thermionic emission, especially at higher temperatures and lower barrier heights, is included. This contribution can be quantified by assuming a temperature dependent distribution of electrons in the metal [45].
Parker's analysis of charge injection is based exclusively on the individual electronic structures of the two materials [42]. This model assumes that no electron redistribution takes place at the polymer/metal contact and that the traditional view of a common vacuum level applies. Parker justifies these assumptions by citing the low carrier concentration of MEH-PPV. However, recent reviews of the ongoing investigation of metal/polymer interfaces emphasize that interactions do occur during the formation of these interfaces, including charge transfer and chemical reaction [46,47]. Even in the absence of chemical interactions, physical effects may include modification of the metal's surface dipole and/or polarization of electron density in the polymer [3]. Each of these factors can lead to a change in potential across the interface and the creation of an interface dipole, with a resultant shift in energy levels of the polymer relative to those of the metal (see figure 1-8). Therefore, the implicit assumption of a common vacuum level limits Parker's model in its ability to correctly predict injection barrier heights at interfaces.

At most metal/organic interfaces, the dipole is directed towards the metal, caused by electron redistribution directed towards the metal, and leading to a lowering of the polymer electronic levels [3,48]. However, there are exceptions to this general trend. Firstly, conjugated molecules with relatively large electron affinities are strong acceptors and will act as the recipient of charge transfer from most metals, causing an upward shift of their energy levels with respect to the metal [3]. This also occurs for several metal/conjugated polymer interfaces. In general, the direction of observed shifts can be explained by considering the relative position of the Fermi level in each material before interface formation. For example, if the Fermi level of the metal lies below that of the organic layer, then interface formation will likely result in electron transfer to the
Figure 1-8: Vacuum level shift (Δ) due to the creation of a dipole at the metal/organic interface. $B_e$ and $B_h$ represent the barriers to electron and hole injection.
metal. Thus, the organic side of the interface is left with a positive charge and its electronic energy levels are lowered.

Another possible consequence of interaction at metal/organic interfaces is band bending. This phenomenon results from the presence of a concentration gradient of charged carriers normal to the interface, which creates an electric potential gradient within the semiconductor film. This causes the energy of electronic states to depend on their position through the material. Therefore, the extent of band bending depends on the thickness of the organic film and on the density of free carriers in the material.

For metal-quinolate films 1–64Å thick deposited onto Ag foil, Kafafi and coworkers illustrate that observed deviations from vacuum level alignment cannot be satisfactorily explained by band bending because of the large carrier densities that would be required [49]. Similarly, Seki et al describe the occurrence of band bending resulting from the potential formed due to Fermi level-equalizing charge flow, but emphasize that this phenomenon requires a thick organic layer to provide sufficient charge carriers [3]. They conclude that for nanometer thick molecular organic films the length scales of band bending are such that interfacial charge injection is not significantly affected.

A different situation may arise, however, when the organic layer is a semiconducting polymer or sufficiently large oligomer. In this case the availability of mobile charges, originating extrinsically, may be adequate to produce significant band bending within 10nm of the interface [3]. Further research on this topic is required in order to establish the correct description of conjugated polymer energy levels in the charge injection region. Distinguishing between interface dipole effects and band bending effects is
important because of the implications for injection barriers. The interface dipole model allows the use of a triangular tunnelling description of carrier injection, as long as initial energy level alignment is taken into account. Band bending on these short length scales requires the modification of the triangular tunnelling barrier to include the effect of the curvature of the electronic bands.

Knowledge of the magnitude and direction of the vacuum level shift and the extent of interfacial band bending, allows the $E_F$-LUMO barrier height to be calculated. In performing such measurements, the interface of a polymer film deposited on a metal substrate should be differentiated from the metal-on-polymer interface. For example, in their studies of the interface between calcium and 5PV (a polyphenylenevinylene oligomer), Gao et al contrast Ca/5PV and 5PV/Ca systems by citing metal diffusion into the organic layer during Ca deposition [50]. Because of the difficulty of depositing a polymer layer on a metal substrate in situ, most investigations of organic-on-metal interfaces have involved conjugated molecules or oligomers.

The most widely employed technique for measuring vacuum level shifts at these interfaces is UPS, described on page 5. For the clean metal, the high energy cutoff in the recorded kinetic energy spectrum corresponds to emission from $E_F$ and the low energy onset is defined by the vacuum level. When the metal is coated with an organic film, scattering of electrons originating in the metal typically causes photoemission from the polymer to dominate. In this case, the highest energy photoelectrons correspond to emission from the HOMO and the low energy onset indicates the new vacuum level. Thus a comparison of the UPS spectrum for the clean metal with that for the
Figure 1-9: Principle of the UPS technique for studying energy level alignment at metal/organic interfaces. $E_{v,F}$ is the energy difference between the valence band (HOMO) of the polymer and the Fermi level of the metal.
polymer/metal system allows the interface dipole shift and the relative positions of the HOMO and $E_F$ of the metal to be determined (see figure 1-9).

Although UPS has successfully explained the injection characteristics of a variety of interfaces, its approach to determining electron injection barriers is indirect in that it assumes equivalent shifting for all electronic levels in the polymer. We propose that some interfacial chemical reactions may affect electronic bands in the polymer to varying degrees, potentially resulting in a change in the band gap. This will happen if interface formation affects, for example, the conjugation length of a polymer. Therefore, it is not necessarily correct to apply the measured shift of the vacuum level to all polymer energy levels. Furthermore, using the UPS technique relies on knowledge of the absorption band gap in order to extrapolate the position of the LUMO from the measured position of the HOMO. For conjugated polymers, the polaron band gap is more accurate for determining injection barriers. However, polaron energy levels can only be determined by direct charge injection. There are a few techniques that can probe unoccupied states and therefore measure the injection barrier height in a more direct fashion. These include STM-related methods, near-edge x-ray absorption fine structure (NEXAFS), and 2PPE. Results from these techniques can be used to verify and complement UPS results.

Before the work reported in this thesis, 2PPE had not yet been used to investigate the interfacial electronic structure of a conjugated polymer film on a metal surface. 2PPE involves excitation into unoccupied states of the polymer, the same states involved in actual device operation. In addition to being able to probe the energy of these states, the emission intensities of 2PPE signals provide information regarding transition cross-
sections and electron transmission factors which affect the efficiency of transfer across the interface.

Furthermore, the 2PPE technique may be especially suited to studying systems involving conjugated polymers because of its relatively high sensitivity to excitation from these overlayers. This sensitivity can be explained in terms of the ratio of 2PPE excitation from the overlayer compared to the metal being much greater than the same ratio for 1PPE excitation. While the ratio in both cases will depend on the number of available states in each material, the intensity of 2PPE also depends on the lifetimes of intermediate states. When states in conjugated polymers are long-lived compared to states in the metal, 2PPE from these overlayers will be enhanced.

1.3 Research Objective

The impetus for this research stems from the established importance of understanding the process of electron transfer at metal/polymer interfaces. Although great strides have been taken towards the commercial success of polymer-based OLEDs, progress has been hindered by a deficiency of knowledge regarding the exact nature of their interfacial structure. Previous research has focused on determining the valence electronic structure of conjugated polymers through photoelectron spectroscopy and quantum chemical modelling [51]. In some cases, this work has been extended to include the effect of depositing metal atoms on the polymer surface [46,47]. Other research groups have used several different techniques to investigate electron transfer and electronic states at the interface of metal substrates and various overlayers,
including diatomic molecules [24-27], self-assembled monolayers [30], conjugated molecules [52,53], oligomers [48], and polymers [54]. This work, however, is the first application of two-photon photoemission to the investigation of interfacial electronic structure of a conjugated polymer film on a metal surface.

All the original work reported in this thesis was performed by Jessica Ament, with help from Dr. J. Todd Stuckless, including the design and construction of the vacuum chamber, magnetic shield, sample holders, and other peripheral equipment, the writing of the necessary computer programs, and the collection and analysis of AES and 2PPE data. The notable exception is the sample preparation and characterization (AFM and XPS) work carried out by Youngku Sohn.
CHAPTER 2

EXPERIMENTAL

2.1 Ultrahigh Vacuum System

a) General

All experiments were performed in an ultrahigh vacuum (UHV) chamber, with a base pressure less than 1x10^-9 torr. There are two principal reasons why UHV conditions are required for surface science experiments. Firstly, it permits the use of low energy electron beams without undue interference from scattering by residual gas molecules. From the kinetic theory of gases, a particle's mean free path, the average distance that it travels between collisions with gas molecules, is given by:

\[
\lambda = \frac{kT}{\sqrt{2\pi P\delta^2}}
\]  

(2.1)

where

- \( \lambda \) = mean free path (m)
- \( k \) = Boltzmann's constant (1.38 x 10^{-23} J/K)
- \( T \) = temperature (K)
- \( P \) = pressure (N/m^2)
- \( \delta \) = molecular diameter (m)

Given a typical electron-source to electron-detector separation of 30 cm, a system temperature of 298 K, and using the molecular diameter of N\(_2\) (3.78x10^{-8} cm), pressures better than 0.02 Pa or 1.5x10^{-4} torr are desired.
A factor that more stringently requires vacuum conditions is the need to avoid contamination of the sample under investigation. Such contamination can strongly influence the outcome of a surface science experiment. The pressure of residual gas in the vacuum system must be such that the time required for contaminant build-up is substantially greater than the time required to conduct an experiment. The relationship between pressure and the incident flux of particles on a surface can be calculated by:

\[
F = \frac{P}{(2\pi mkT)^{1/2}}
\]

where

- \( F \) = incident flux (molecules/m^2/s)
- \( P \) = pressure (N/m^2)
- \( m \) = molecular mass (kg)
- \( k \) = Boltzmann's constant (1.38 \times 10^{-23} \text{ J/K})
- \( T \) = temperature (K)

The amount of time required for a clean surface to be covered with a monolayer of adsorbate can be estimated using this equation, assuming that all incident molecules stick to the surface (sticking coefficient = 1) and that a typical monolayer (ML) of residual gas has a density of \( 10^{19} \text{ molecules/m}^2 \). At a pressure of \( 1 \times 10^{-9} \text{ torr} \) (\( 1.33 \times 10^{-7} \text{ Pa} \)) and using the molecular mass of \( \text{N}_2 \), it will take about 40 minutes for an entire monolayer of contaminant gas molecules to build up.

It should be noted, however, that the assumption of a sticking coefficient equal to one does not apply to every substrate/gas combination. In some cases sticking can be nearly negligible, thereby vastly increasing the time necessary for contaminant build-up. Due to their inherent inertness, our Au(111) samples are expected to support little sticking. Therefore, we anticipate that our base pressure is sufficiently low to prevent the
accumulation of even a fraction of a monolayer within the time required to perform our experiments. This conclusion is supported by our experimental findings.

b) UHV Chamber

The UHV system (see Appendix One) was designed and constructed specifically to undertake the work described within this thesis. It consists of a preparation chamber and a photoemission chamber. A 6" gate valve separates these two regions of the system so that the preparation chamber can be vented while the photoemission chamber is maintained under vacuum conditions.

The larger preparation chamber features a cylindrical mirror electron analyzer (CMA) with an on-axis electron gun for Auger spectroscopy, a sputter ion gun and leak valve, a diffusion pump (with a liquid nitrogen trap) which can be isolated from the chamber by an 8" gate valve, an ion gauge, various sample positioning tools, a sample heating dock, the sample signal feedthrough, and several viewports. A metal sealed vent valve connects the chamber to a stainless steel gas manifold with gas inlet valves, a thermocouple pressure gauge, an ion gauge, a mechanical roughing pump, and a zeolite sorption pump.

The smaller photoemission chamber includes a concentric hemispherical analyzer (CHA) for the detection of photoemitted electrons, a water-cooled titanium sublimation pump, a metal shield, a fused-silica (Suprasil-1) UV-grade laser entry window whose transmission range extends to 200nm, and a laser exit window.
The chamber itself is made from stainless steel, a desirable vacuum material because of its low permeability to gas, high resistance to corrosion, and ease of outgassing by heating. The various components of the UHV system are mated through ConFlat metal/metal seals. Each of these UHV seals consists of a flat copper gasket captured between the knife-edges of two adjoining stainless steel flanges.

Throughout the preparatory and experimental procedures, an ionization gauge (KJL G8140-DI with KJL IG-4400 or VG IGP3 controller) was used to monitor chamber pressure. This Bayard-Alpert gauge measures pressure by using electron impact to ionize a fraction of the residual gas molecules. The resulting positive ions are collected and the magnitude of the consequent electrical current is proportional to pressure.

c) UHV Pumps

UHV pressures are achieved and maintained through the use of a series of vacuum pumps. Starting from atmospheric conditions, the chamber was roughed out with a two-stage rotary vane pump (Alcatel 2010). This oil-sealed mechanical pump has a base pressure of $2 \times 10^{-3}$ torr, but low conductance through the vent valve and gas manifold typically prevented the attainment of pressures less than $1 \times 10^{-2}$ torr.

After initial chamber roughing a sorption pump was used, also operating through the vent valve and gas manifold. The main advantage of this type of pump is its non-contaminating nature. Furthermore, its zeolite material has a particularly high affinity for water vapour, a major contributor to the residual gas presence in our chamber.
Once pressures of $1 \times 10^{-3}$ torr were obtained, the vent valve was closed and the 8" gate valve to the diffusion pump was opened. Pressures less than $1 \times 10^{-6}$ torr were easily reached within minutes. Our diffusion pump (Varian VHS-4) utilizes Santovac-5 as pumping fluid, is backed by a two-stage rotary vane pump (Edwards RV12), and is augmented by a liquid nitrogen cryotrap to intercept backstreaming oil and to enhance pumping speed for condensables. The decision to use a diffusion pump as opposed to another major pumping method was based on a number of factors. Although diffusion pumps often have higher ultimate pressures than other UHV pumps and can leave residual hydrocarbons, the vacuum quality is sufficient for our experiments. Important advantages of diffusion pumps include high pumping speed and a comparatively wide pressure range, two factors that provide the freedom to vent the chamber for purposes of sample entry without significant time constraints. Diffusion pumps are also relatively non-selective, except that heavier molecules are pumped more efficiently than less massive species. They have a considerably lower initial cost than turbomolecular pumps, ion pumps, or cryopumps. Finally, while ion pumps in particular are often used, and can provide clean, oil-free vacuum conditions, the magnetic fields involved in their operation preclude their presence in the vicinity of our low energy electron experiments.

In order to reach pressures $\leq 1 \times 10^{-8}$ torr, it is necessary to perform a system bakeout. This heating process removes adsorbed impurities from the chamber's internal walls at an accelerated rate, leading to reduced outgassing and much improved pressures after the bakeout is complete. It is important to ensure that there is uniform baking over the entire vacuum system in order to be certain that a low ultimate pressure will be achieved. With this in mind, a bakeout system was designed specifically for the chamber described within this thesis. Heating was provided by five finned strip heaters.
(Omega OTF) and several lengths of heating tape or cord (Thermolyne). During the bakeout, a tent of aluminized fiberglass (Burnaby Insulation Supplies) insulated the chamber, and temperatures were monitored using several Chromel/Alumel thermocouples. Wattage output by the various heaters was adjusted through the use of variacs in order to achieve even heating throughout the system. Temperatures of 130°C were typically used for the course of a 36-hour bakeout. The cold trap was left at room temperature for the majority of the bakeout; however, for the last 8 hours it was kept filled with liquid nitrogen. Subsequent to the bakeout the trap was kept continuously full, requiring that it be topped up at least every 10 hours. Periodically, the trap itself was subjected to a bakeout procedure. This involved heating the trap to 130°C with a silicone band heater (Omega SRFG) for 24 hours while the 8” gate valve was closed. The trap was then filled with liquid nitrogen and after 30 minutes to several hours the gate valve was reopened.

After the bakeout, a titanium sublimation pump (TSP) was used to further reduce chamber pressure. The TSP is highly effective for the pumping of active gases, including H₂, N₂, and CO. As such, it complements the diffusion pump, which is somewhat lacking in the removal of residual hydrogen. In operation, the TSP filament was degassed for several minutes and then a layer of Ti was deposited. Water cooling of the gettering surface was employed to minimize outgassing during deposition.
2.2 Major System Components

a) Concentric Hemispherical Analyzer

In order to obtain a kinetic energy spectrum for photoemitted electrons during the 2PPE experiments, some method of differentiating the electrons based on their energy is required. Three established approaches are time-of-flight, retarding field analyzers, and deflection analyzers. For the work performed in our laboratory, the latter was chosen after consideration of the advantages and disadvantages of each method, as described here.

The time-of-flight (TOF) technique involves the measurement of electron flight time over a known distance. Therefore, in order to achieve high resolution it is restricted to use with very low energy electrons and requires a long electron path length. This renders the technique highly susceptible to the effect of stray fields. TOF detection has been used successfully in several 2PPE studies, including those of Zhu [28-30] and Wolf [16,17]. The main advantage of TOF is its simultaneous detection of all emitted electrons, called multiplexing, as opposed to detecting electrons in one energy window at a time. This makes TOF a highly sensitive detection technique despite the decrease in collection efficiency for the small collection angles associated with long electron flight paths. Our signals, however, are large enough that multiplexing is not a necessary feature.

The retarding field analyzer, used in 2PPE experiments by Naaman and coworkers [55], measures kinetic energy by determining the magnitude of potential required to stop the
transmission of particles through a grid or aperture. Although simple and highly sensitive, these analyzers suffer from poor signal-to-noise and resolution because of their high background throughput.

Deflection analyzers are generally considered to be the best choice for high-resolution spectroscopy and have been used extensively in 2PPE studies [9,24,25]. In this case, electron energies are determined by passing the electron beam to be analyzed through a region of controlled electric field, where the degree of deflection of individual electrons is dependent upon their energy. For our purposes, a concentric hemispherical analyzer, (see figure 2-1) was used (VG Microtech VG100AX). The spherical electrostatic field is created by two concentric hemispheres, the inner being held at a positive voltage and the outer at a negative voltage. Both voltages are measured with respect to the retarding potential \(-R\) at the entrance slit. Higher energy electrons will strike the outer hemisphere, while lower energy electrons are more easily deflected and will strike the inner hemisphere. Thus the CHA acts as a sensitive band-pass filter, allowing the transmission of only those electrons with a particular kinetic energy. Over the course of an experiment, this chosen energy can be systematically changed in order to obtain a full kinetic energy view.

For a potential difference \(V\) across the hemispheres, only electrons with kinetic energy equal to \(H\cdot V\) can pass through the analyzer, where \(H\) is an instrumental constant determined by the radii of the concentric hemispheres. Thus, \(H\cdot V\) is referred to as the pass energy of the analyzer.
Figure 2-1: Schematic and photographic representation of the VG100AX concentric hemispherical energy analyzer [54].
The kinetic energy of an emitted electron at the sample is given by:

\[ E_{\text{kin}} = 2\hbar \nu - \Phi_{\text{sam}} - E_b \]  

(2.3)

where \( \hbar \nu \) is the photon energy, \( \Phi_{\text{sam}} \) is the work function of the sample, and \( E_b \) is the electron’s initial binding energy relative to the Fermi level. Between the sample and the analyzer, the electron is accelerated by the retarding potential \((-R)\) on the entrance slit of the spectrometer and by the contact potential between the sample and the analyzer due to their different work functions \( (\Phi_{\text{sam}} - \Phi_{\text{CHA}}) \). An additional accelerating bias voltage \( (A) \) may be applied to the sample to help ensure that the very low energy photoemitted electrons can reach the analyzer without large angle deflection by stray fields. The pass energy, or the final kinetic energy, of the electron is the initial kinetic energy of equation 2.3 plus these three accelerating terms. Therefore, the binding energy of the electron is given by:

\[-E_b = H\nu - 2\hbar \nu + \Phi_{\text{CHA}} - A + R\]  

(2.4)

and the electron energy can be scanned by ramping the hemisphere voltages and/or the retarding potential.

The CHA can be operated in either of two modes, namely constant analyzer energy (CAE) and constant retard ratio (CRR). CAE mode involves holding the pass energy constant and ramping only the retarding potential on the entrance slit. Since analyzer resolution is proportional to pass energy [57], this mode offers constant energy resolution over all kinetic energies. CRR mode, on the other hand, entails scanning kinetic energy by ramping both \( R \) and \( H\nu \) in such a way that \( \frac{R+H\nu}{H\nu} \) maintains a
constant value ≥ 1, called the retarding ratio. In this case, pass energy increases as kinetic energy increases, and so analyzer resolution is better at lower energies.

For the VG100AX operating in CAE mode, the manufacturer's setting for the pass energy is 7.5eV. This relatively low value provides good resolution, but we find that throughput is sacrificed. This is probably because some fraction of the low energy electrons is deflected off axis by stray electric and magnetic fields within the spectrometer. For example, electric fields may develop due to charging of contaminating particulate matter. For the low energies and narrow energy range of our experiments and an accelerating bias of 24V, CRR=1 mode produces the most desirable results. In this case the pass energy of the CHA is on the order of 25eV. At higher retarding ratios, throughput is again significantly limited by low pass energy values.

In cases where enhanced angular resolution is desired, a minimum accelerating bias would be used, thus requiring improved shielding of the region between the sample and the spectrometer. For smaller accelerating voltages, the pass energies associated with CRR=1 mode would be exceeded by that of CAE mode, and the latter would become the preferred choice.

The reason why the CMA, also a deflection analyzer, was not used for the 2PPE experiments bears mentioning. The configuration of a CMA is such that only electrons entering the analyzer at an angle of 42.3° from the surface normal will follow an appropriate trajectory. However, the very low energies of electrons produced in a 2PPE experiment require the use of an accelerating bias voltage. This steers electrons
towards normal emission trajectories, necessitating collection of electrons travelling in
this direction, as occurs for the CHA.

After passing through the CHA, electrons are detected by a channel electron multiplier,
or channeltron (Galileo 7010). The inner surface of this spiral-shaped glass tube is
covered with a doped SiO₂ coating that has excellent secondary electron emissive
properties. Additionally, a voltage is applied along the length of the channeltron tube so
that secondary electrons are accelerated towards the end, meanwhile producing their
own secondary electrons. This combination of conditions produces an avalanche effect,
where a single electron input can emerge as a 10-20 ns pulse of more than 10⁶ electrons,
which can easily be detected.

There are two possible modes of channeltron operation. In analog mode, the
channeltron voltage is set low enough that the output current is always proportional to
the flux of input electrons. Pulse counting mode involves increasing the gain to the
point where the channeltron is operating under saturation conditions. Under these
circumstances an input electron produces a large, fixed amplitude output pulse 10–20ns
long, during which time the channeltron cannot respond to new input electrons. This
mode is used when, on average, much less than one electron is expected in any given 10-
20 ns time window.

In our experiments, the time period over which electrons of a given pass energy arrive is
about equal to the 20ns duration of the laser pulse. Consequently, if more than one
electron of a given pass energy arrives after a single laser pulse and a high channeltron
gain is being used, then the maximum channeltron output current will be exceeded.
Therefore, analog mode is our desired choice for operation. The exception occurs at the high energy edge of the kinetic energy spectrum, where very little photoemission takes place. In this case, much less than 1 electron is expected for each energy channel so that pulse counting mode can be used without danger of channeltron pile-up.

b) Magnetic Shielding

The photoelectrons involved in our experiments are very low in energy, and are therefore very susceptible to deflection by magnetic fields. Sources of magnetic interference include the Earth’s field and scientific equipment such as ion pumps, magnetically-coupled sample transporters, motors, and current-carrying cables. A charged particle moving through a magnetic field, \( B \), is subjected to a force predicted by the Lorentz force law:

\[
F = qv \times B
\]  

where \( v \) is the velocity of the particle and \( q \) is its charge. As such, it is extremely important that the region of space between the sample and the detector be well shielded from stray magnetic fields. This is accomplished by using a magnetic shield constructed of \( \mu \)-metal, a nickel/iron alloy that is highly permeable to magnetic fields. This shield provides a highly favourable path for magnetic field lines, thereby guiding the magnetic flux around the critical area.

The most efficient magnetic shield shape is a spherical shell. A more practical choice is a cylindrical tube, where the ratio of length to diameter is 4:1. Any required access holes should be kept as small as possible and should be equipped with cylindrical
extensions that are at least one hole diameter in length. Finally, the shield should be hydrogen annealed to ensure maximum permeability.

Our custom magnetic shield (Magnetic Shield Corporation) is pictured in figure 2-2. It was suspended in the UHV chamber by attachment to the inner face of a flange. The shield has a diameter of 2.0" and is 8.0" in length. It contains entry ports for the laser beam and the sample as well as exit ports for the reflected laser beam and for the photoemitted electrons. The entry and exit ports for the laser beam are oriented such that the beam is incident on the sample an angle of 75° to the surface normal. The shield is fabricated from 0.050" CO-NETIC® AA alloy and is coated with a water-based colloidal graphite called Aquadag (Acheson Colloids Company). This coating greatly reduces the emission of secondary electrons that could interfere with data collection. It also prevents the development of variations in work function and chargeable oxide patches on the surface of shield, both of which could deflect low energy electrons.

In order to apply the Aquadag to the μ-metal surface, a dip-coating method was used. Approximately 750mL of Aquadag was placed in a 4L glass beaker. This concentrate was stirred in order to break up the gel structure, and 2.5L of deionized water was very slowly added with continuous stirring. Before coating, the magnetic shield was carefully cleaned and degreased and was preheated to 60°C in a laboratory oven in order to hasten drying and reduce drip lines. After dipping, the freshly coated shield was dried at 60°C for 5 minutes and cured at 200°C for at least 60 minutes. This dipping and curing procedure was then repeated.
Figure 2-2: Views of the custom magnetic shield, used to prevent stray magnetic fields from affecting photoelectron trajectories between the sample and detector.
c) Auger Electron Spectrometer

Auger electron spectroscopy (AES) is a sensitive technique used to determine the elemental composition of a surface. The Auger process begins with the removal of a core electron due to an incident photon or high-energy electron. The excited ion can then relax to a lower energy state through a two-electron process; an electron from a higher-lying energy level fills the core shell vacancy and an Auger electron is simultaneously emitted from the surface. The energy of this Auger electron is characteristic of its parent atom, thus allowing for the determination of elemental composition. The competing relaxation mechanism of x-ray fluorescence, which involves the emission of an x-ray photon rather than an Auger electron, is more probable for atoms with high atomic numbers. The surface sensitivity of AES arises from the relatively short mean free path of electrons with less than a few keV of energy. Only those electrons that originate within an escape depth of a few Ångstroms of the surface will exit the sample before energy loss events occur. Moreover, because the electrons of the incident beam are high in energy compared to the Auger electrons, the latter are created uniformly over their escape depth.

Our AES instrumentation includes a cylindrical mirror analyzer (Omicron CMA 100) with integral linear retraction and a high intensity on-axis electron gun (EKI 50). The operating principle for a CMA is very similar to that of the CHA. Here, the deflecting electric field is created by two coaxial cylinders. The voltage across these two cylinders is ramped in order to systematically allow the passage of electrons of different kinetic energies. Transmitted electrons are detected by a channeltron in analog mode. In the
present work, AES was used primarily to verify the cleanliness of the gold substrate surface.

d) Sputter Ion Gun

Ion bombardment is a common method used for cleaning solid surfaces within UHV. Such cleaning is done using an ion gun (Physical Electronics 04-161) to produce a beam of inert gas ions. When these ions are incident on a solid surface, they will sputter-etch and remove the top few atomic layers, including any surface impurities.

Energetic ions are created by accelerating electrons from a hot filament into a region containing an inert gas, such as argon. The ions are subsequently focused by a lens system to produce a beam at the grounded target surface. The size of the incident beam can be adjusted through the variation of a potential applied to a focusing electrode. Because of the destructive nature of ion bombardment, it is often necessary to heat the target during and after the sputtering process to anneal out any damage.

2.3 Samples

a) Sample Preparation

The Au samples used were purchased from Molecular Imaging Corporation, where they are prepared by metal evaporation onto freshly cleaved mica substrates. The gold film is ~150nm thick and very smooth, with large atomically flat (111) terraces. The 1.0 x
1.1 cm substrates were stored under N₂ until immediately before their use. They were cut in half with laboratory scissors prior to use.

The conjugated polymer used to make thin films on the Au(111) substrate was regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) [58]. A known mass of solid P3HT (Aldrich) was dissolved in chloroform; undissolved residues were filtered and weighed. The concentration of the resulting solution was 0.2mg/mL. The Au(111) substrate was carefully flame annealed with a butane microtorch for 1 min before being dipped in the P3HT solution for 2 sec. The dipping procedure was repeated 3 times.

b) Sample Holders

In order to mount the samples in a simple and reliable way, an ESCA-style stub was used (see figure 2-3). The stub was fabricated from OFHC (oxygen free high conductivity) copper and was coated with Aquadag in order to ensure a uniform work function and reduce opportunities for charging. Due to spatial restraints, a low-profile method was needed for the mounting of a sample onto the stub. As such, two Aquadag-coated, semi-circular pieces of beryllium-copper along with two miniature OFHC Cu screws were used to press the sample against the face of the stub. This mounting system also provided the necessary electrical contact between the sample face and the stub.

In order to perform the 2PPE experiments, a specialized sample holder was designed. The assembly was constructed entirely of non-magnetic materials, so as to avoid altering the path of the low energy photoelectrons, and it allowed for the entry of the
Figure 2-3: ESCA-style sample stub and sample mounting system.
sample through the narrow opening in the magnetic shield. The successful design is depicted in figure 2-4. The main body is made of OFHC copper, with two circular beryllium-copper collars and a leaf spring being connected to the Cu rod using molybdenum threaded rod and nuts. A sapphire ball bearing completes the spring-loaded stub holder. The entire assembly is coated with Aquadag and is attached to, but insulated from, the stainless steel transfer arm using alumina rods, molybdenum wirenuts, and tungsten compression springs. This insulation is necessary because the entire sample holder is used when applying the sample bias and when measuring total yield charge. It is the presence of these exposed insulators that requires the collars mentioned above to shield the sample region from the effects of possible charging.

When preparing samples for surface science experiments, in situ sample heating is often desirable in order to remove impurities from the sample surface. Heating is also required for vacuum annealing, providing a flatter, more homogeneous surface. As such, a heating dock was designed which could hold the ECSA-style sample stub and simultaneously conduct heat to the sample (see figure 2-5). This heating dock comprises a solid OFHC Cu cylinder with a socket for the sample stub, a stainless steel leaf spring and ball bearing assembly to hold the stub in place, a UHV button heater (Heat Wave 1136) for resistive heating, and a solid Macor base to provide sturdiness and electrical insulation. The heating dock is also equipped with vacuum feedthroughs for a thermocouple and for electrical power supply to the button heater. The thermocouple, used to measure the temperature of the sample during a heating cycle, is attached to the face of the OFHC Cu cylinder near where the sample stub is held. Previous experiments in our laboratory have shown that the temperature difference between the
Figure 2-4: Non-magnetic sample holder for two-photon photoemission experiments.
Figure 2-5: Sample heating dock.
sample face and the location of the thermocouple junction is not significant in the temperature range used for heating [59].

A thermocouple consists of two wires that are joined at a junction at the location where temperature is to be measured. In general, any metal wire will develop an electrical potential gradient due to a temperature gradient along its length, in order to maintain a uniform thermodynamic potential. Our two thermocouple wires, Chromel and Alumel, develop significantly different potential gradients for a given temperature gradient; the resulting difference in voltage at their open ends can be used to determine the temperature at the junction end of the thermocouple.

c) Sample Motion

Because of the necessarily remote location of the magnetically shielded 2PPE chamber compared to the rest of the sample cleaning and analysis tools, it is important to have some method of moving the sample between various positions within the UHV chamber. In order to transfer the sample stub between the 2PPE sample holder and the heating dock, a wobble stick (VG ZWS225) equipped with a handling fork was used. The fork easily grabs the collar of the ESCA-style stub in order to insert it in, or remove it from, each socket. A spring clip on the fork keeps the stub tightly in place.

The 2PPE sample holder is located at the end of a magnetically-coupled transporter (MDC MTM-24). This transporter provides a linear travel of up to 60cm, allowing the sample to be moved from the preparation chamber to the required position of 39mm from the CHA snout within the photoemission chamber. It also provides the option of
full 360° sample rotation around the axis of linear travel, useful for specifying sample orientation.

The heating dock sample holder is used when performing Ar ion sputtering or AES. In both of these instances, well-defined sample positioning is necessary. This is achieved by mounting the heating dock on a modular UHV manipulator (Fisons OMNIAX 100, Fisons RD2, Fisons SH2). The xy module and the z module allow ±25mm and ±50mm of linear motion in their respective directions, while the RD2 component provides full 360° axial rotation and the SH2 component provides ±108° of azimuthal rotation.

2.4 Optical System

a) Excimer Laser

The photon source used to perform the photoemission experiments is a XeCl excimer laser (Lambda Physik COMPex 102). This laser produces 308nm (4.0eV) radiation with a pulse duration of 20ns, pulse frequencies of 1–20Hz, and pulse energies of up to 200mJ. The excimer laser takes its name from the term 'excited dimer', used to refer to a diatomic molecule that is bound when in an excited electronic state but dissociates upon relaxation to the ground state. Most commonly, excimers are inert gas halides such as ArF, KrF, or XeCl. In the presence of an electrical discharge, inert gas ions and halide ions will form and undergo chemical reaction:

\[
\begin{align*}
\text{Xe} + e^- & \rightarrow \text{Xe}^+ + 2e^- \\
\text{Cl}_2 + e^- & \rightarrow \text{Cl}^- + \text{Cl} \\
\text{Xe}^+ + \text{Cl}^- + \text{He} & \rightarrow \text{XeCl}^+ + \text{He}
\end{align*}
\]
Where the helium acts as a buffer. From its short-lived excited state, the XeCl molecule returns to its ground state configuration by producing ultraviolet radiation at a distinct wavelength (308nm). Because ground state molecules immediately dissociate, they are unavailable to reabsorb any radiation. This built-in population inversion is a special feature of excimer lasers.

b) Optical Train and Peripherals

Between the laser and the sample, the photon beam encounters a variety of optical steering and conditioning devices. In order to aim the laser beam directly at the sample surface, three UV-reflective mirrors, supported within cubes, are positioned near the laser output. The latter two cubes are mounted on precision translation stages (Oriel 16121) with micrometer control to permit sensitive and reproducible positioning. One mirror is also mounted on a 360° rotation stage (Newport RSP-2) that allows for significant lateral motion of the laser beam. Furthermore, each mirror can be tilted within its cube for additional beam steering. The laser beam also passes through two iris diaphragm apertures (Newport ID-1.0) to reduce the diameter of the beam to 1.5mm.

The output of the excimer laser is unpolarized, meaning that the electric field of the light waves have no preferred orientation. In many cases, light with its electric field oriented parallel to a surface's plane of incidence (p-polarized light) will interact differently with that surface than will light with its electric field oriented perpendicular to the surface's plane of incidence (s-polarized light). Therefore, the production of polarized light is experimentally desirable. A birefringent material, such as calcite, is
optically anisotropic; it exhibits a different index of refraction for each of the two electric field orientations of light travelling perpendicular to the crystal's optical axis. As such, the two components of an incoming beam will travel along different paths within the birefringent material. A Glan-Taylor polarizer (Halbo Optics PH10-M) exploits this phenomenon in order to separate unpolarized light into two plane-polarized components. The polarizer consists of two calcite prisms cut at a defined angle and separated by an air gap. At the calcite/air interface, one component undergoes total internal reflection while the other propagates in its original direction. By rotating the polarizer it is possible to select a particular polarization orientation with respect to the plane of incidence of the sample.

Finally, the laser light encounters a UV-grade synthetic fused silica lens (Melles Griot 01 LQP 029), which serves to focus the laser beam onto the sample surface. The lens is mounted on a carrier/rail assembly (Oriel 11621/Oriel 11492) that allows its distance from the sample to be easily adjusted. Because of extremely high laser power densities near the focal region, the lens is never situated exactly at its focal length of 30cm from the sample.

In order to measure the energy of the steered and attenuated laser beam, a Joulemeter (Molectron J25) was employed. This detector functions by converting optical energy into heat, which is then translated into a measurable current by a pyroelectric element. This current is passed through a capacitative circuit to produce a voltage with a peak value proportional to the original energy input. The calibrated response of the meter is 8.35 V/J.
2.5 Interfacing

In order to convert the output of the electron spectrometers into meaningful data, the signal must be passed through several interfaces including signal-conditioning electronics, a data acquisition card capable of A/D conversion, and specialized software programs.

a) Electronics

The output of the 2PPE experiment is a set of electron pulses, whereas the output of the Auger experiment is a continuous current. The 2PPE signal is passed through a charge-sensitive preamplifier (Oxford TC174) where the charge is translated into a voltage ($10^{12}$ V/C), and a lock-in amplifier (EG&G 5209) which functions as a line filter (60 and 120 Hz) and secondary signal amplifier. When performing Auger spectroscopy, the CMA output is passed through a current preamplifier to a lock-in amplifier that performs not only line filtering and secondary signal amplification, but also phase-sensitive detection. The pass energy of the CMA is modulated by a signal from the lock-in; only the component of the input current that matches the phase and frequency of this modulation is amplified. This increases signal-to-noise ratios.

b) Computer Interface

The voltage signal from the lock-in amplifier travels to a data acquisition card (Computerboards PCI-DAS1602/16) in order to allow communication with computer software. The card also converts commands from the software into signals that control the pass energy of the CMA or CHA.
LabVIEW software (©National Instruments) was used to create programs for data acquisition and instrument control. LabVIEW is an icon-based programming system that generates programs called virtual instruments (VI{s}). Each VI consists of a user interface and the source code, which may include instructions for calling other VI{s}, then referred to as subVI{s}. For the purposes of the present research, three primary LabVIEW programs were written and used. A detailed description of these, including a description of the subVI{s} within each, is presented in Appendix Two.

Briefly, the program used to acquire 2PPE spectra begins by converting user-input values for CHA pass energies into voltages to ramp the potential of the hemispheres. For each step of the ramp, the program writes a voltage to the A/D card, which is in turn sent to the CHA control unit. While sitting at a particular CHA pass energy, a pre-determined number of laser pulses is incident upon the sample. Each pulse triggers the program to record an array of signal data over a time period of about 5ms. This array is averaged with the data generated by previous laser pulses at the same CHA pass energy and a baseline-subtracted signal intensity is calculated for that energy. As the CHA pass energy is ramped, as many times as is required, the program records a running average signal intensity for each step of the ramp. This data is presented as a kinetic energy spectrum.

An alternative program acquires 2PPE data by event counting. After each laser shot, the magnitude of the baseline-subtracted signal is compared to a user-input threshold value; only the presence or absence of a supra-threshold signal is documented. In this way, a digitized version of the kinetic energy spectrum, less susceptible to the effects of
noise, is recorded. This approach is used when less than one electron per laser pulse is expected for each energy window and the channeltron is set at high gain.

The program used to acquire AES spectra starts by calculating and setting CMA voltages based on user-input CMA pass energy values. At each step within the ramp the CMA output signal is recorded as an array of values taken over a 1000ms period. These values are averaged to give a signal magnitude for that particular CMA pass energy. As the pass energy is ramped, as many times as desired, the program records a running average of signal magnitude for each step of the ramp.

2.6 Experimental Procedure

A new Au(111) substrate is mounted on the sample stub and placed in the chamber. After satisfactory UHV conditions are achieved, the various filaments within the chamber are degassed. The ion gun filament is degassed at a beam voltage of 0.5kV and an emission current of 30mA for 15 minutes. The electron gun is degassed at a filament current of 2.5A for 15 minutes.

The sample is heated to 750K for 90 min to remove any weakly adsorbed surface impurities. The surface is further cleaned by ion bombardment using an Argon pressure of 1x10^-6 torr, a beam voltage of 1kV, and an emission current of 15mA for 15 min at a temperature of 500K. After the sputtering procedure, the sample is held at this temperature for a further 30 min.
In order to confirm the cleanliness of the Au(111) surface, an Auger spectrum is obtained. The beam energy is set at 4keV and the filament current is set at 2.2A, resulting in a beam current of about 0.2\(\mu\)A and a sample current of about +0.3\(\mu\)A, as measured by an electrometer (Keithley 602). Optimum sample position for Auger analysis is established by monitoring sample current as the electron beam is scanned over the sample surface. When the beam reaches the edge of the sample, sample current changes abruptly. The position of the sample when one of these sudden changes occurred was noted, so that the beam could be made to be incident near the centre of the sample. Auger spectra are typically recorded by using the CMA to measure the electron electron emission signal as a function of electron energy, from 50-1000eV with a resolution of 5eV. Each energy window is sampled for 1000ms and the entire scan is repeated 5-10 times.

Once a clean Au(111) surface is achieved, laser 2PPE experiments are performed. The sample is transferred in situ from the heating dock to the non-magnetic sample holder and is moved into position by the magnetic transfer arm. Several steps are taken in order to ensure that the laser strikes the sample in the optimum position. First of all, a visible diode laser beam is used to correctly position the beam-steering mirrors, and the iris diaphragm apertures are used to refine this beam path. The focusing lens should be in place while making these adjustments. The excimer laser is then made to pass through the established apertures by adjusting the rotation of the second beam-steering cube and the tilt of the mirror in the third beam-steering cube. Finally, the accuracy of the resulting excimer beam position on the sample is assessed visually, by measuring the total photoelectron yield of the irradiated sample, and by viewing the quality of the reflected laser beam on a fluorescent sheet. The 2PPE spectra are obtained by recording
the CHA photoelectron signal as a function of electron kinetic energy. Typical scans spanned 8eV with a resolution of 100meV. Each energy window was sampled for 2000ms, and up to 20 scans were performed and averaged to produce a final spectrum.

In practice, the cleaning procedure precedes the laser photoemission, which is followed by Auger spectroscopy. This sequence ensures that any damage caused by the incident electron beam does not affect the 2PPE results.

In order to perform 2PPE on the P3HT/Au samples in these initial studies, a new gold substrate was flame annealed with a butane microtorch, coated with a polymer film using the dip-coating procedure previously described, and placed in the chamber. It should be noted that the polymer solution may introduce contaminant residue at the interface and that no Auger analysis was performed to verify that the substrate is atomically clean. Kinetic energy spectra were obtained immediately after re-establishing UHV pressures. The development of a sample introduction system wherein the sample is maintained in an inert atmosphere during the ex situ dip-coating procedure is currently underway.
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Sample Characterization

a) Clean Au(111)

The substrates used in this work were 150nm films of Au(111) evaporated onto freshly cleaved mica. We used atomic force microscopy (AFM) to image the Au(111) surface [58]. A representative 3D image and line profile of a sample surface after our flame-annealing process are presented as figure 3-1. The 1µm x 1µm scan reveals that the surface possesses atomically flat regions at least 300nm across, consistent with the manufacturer's specifications. STM results in the literature report monoatomic steps of ~2.4Å for a clean, well-annealed Au(111) surface [60]. Our AFM line profile reveals height variations across the surface occurring as ~2.8Å and ~6Å steps, corresponding approximately to monatomic and diatomic steps respectively. The areas labelled A through D in figure 3-1a are atomically flat regions separated by these atomic-scale steps. It should be noted that the Au(111) surface is known to undergo a herringbone reconstruction; however, the AFM technique does not provide the lateral atomic resolution necessary to observe this phenomenon.

Auger electron spectroscopy (AES) was used to verify the cleanliness of the Au(111) samples. We found that carbon was the principal contaminant, perhaps due to
Figure 3-1: AFM image and line profile for a flame-annealed bare Au(111) surface [58].
backstreaming of diffusion pump fluid (polyphenyl ether). Representative AES spectra for a sample prior to and after a typical cleaning process are shown in figure 3-2. A spectrum for a partially cleaned sample is also included. Within the 50–500eV scan range, the gold signal is expected to include a large peak at 74eV, with smaller peaks at 99, 154, 164, 243, and 259eV [61]. The recorded spectrum is seen to be consistent with these reference values. Carbon appears as a single peak at 275eV.

The quantitative determination of carbon present on the Au(111) surface was based on the well-known work of Seah and Dench [62]. This approach compares observed Auger intensities to standard reference intensities and considers the mean free path of electrons through each layer of a sample in order to determine the composition of the outermost layer of a given sample.

The mean free path \( \lambda \) of an electron is dependent on its energy and on the nature of the material through which it is travelling. Through compilation and analysis of mean free path measurements, Seah and Dench derived a general formula for predicting \( \lambda \):

\[
\lambda_m = \frac{A_m}{E^2} + B_m \sqrt{E} 
\]

where \( E \) is the energy of the electron (eV), \( A \) and \( B \) are constants that depend on the material being considered, and the subscript \( m \) indicates that \( \lambda \) is expressed in terms of monolayers of the material. In cases where the overlayer atomic structure is not known, the number of monolayers is calculated from thickness assuming a monolayer
Figure 3-2: Auger electron spectra for a bare Au(111) surface in an (a) uncleaned (b) partially cleaned and (c) clean state.
where \( a \) is in nm, \( A_w \) is the atomic weight of the material in g/mol, and \( \rho \) is its bulk density in g/cm\(^3\).

For a substrate with partial coverage of monolayer thickness, and assuming that backscattering of electrons by the adsorbate layer is approximately equal to backscattering by the substrate layers, the Auger signals observed for the adsorbate and the substrate can be expressed as:

\[
I^{\text{ads}} = X I^{\text{ads}}_{\text{bulk}} \left[ 1 - \exp \left( \frac{-\sec \theta}{\lambda^{\text{ads},\text{ads}}} \right) \right]
\]

\[
I^{\text{sub}} = I^{\text{sub}}_{\text{bulk}} \left[ 1 - X + X \exp \left( \frac{-\sec \theta}{\lambda^{\text{sub},\text{ads}}} \right) \right]
\]

where \( X \) is the fractional coverage, \( \theta \) is the emission angle to the surface normal, and \( \lambda_{x,y} \) refers to the mean free path, measured in monolayers, of Auger electrons originating in \( x \) and travelling through the matrix of \( y \). By taking a ratio of these two equations, instrumental factors contributing to the Auger signal cancel out, thereby eliminating the need for absolute calibration and allowing the use of tabulated sensitivity factors for the magnitude of bulk signals.

In the present work, we wish to quantify the coverage of carbon on gold in order to verify the cleanliness of our surfaces. The major characteristic Auger peaks for these
elements are located at $275\text{eV}$ and $74\text{eV}$ respectively. Equation 3.1 was used to calculate mean free paths for electrons of these energies travelling through carbon or gold. $A_m$ and $B_m$ values were taken from reference [62]. Results are listed in Table 3-1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_m$</td>
<td>538</td>
<td>688</td>
</tr>
<tr>
<td>$B_m$</td>
<td>0.210</td>
<td>0.209</td>
</tr>
<tr>
<td>$\lambda_m (74\text{eV})$</td>
<td>1.91</td>
<td>1.92</td>
</tr>
<tr>
<td>$\lambda_m (275\text{eV})$</td>
<td>3.49</td>
<td>3.48</td>
</tr>
</tbody>
</table>

**Table 3-1: Calculation of mean free paths for carbon and gold Auger electrons.**

The Auger spectra were analyzed by measuring the peak-to-peak height of the Au signal at $74\text{eV}$ and the negative excursion of the C signal at $275\text{eV}$ and then solving for fractional coverage, $X$, in a ratio of equation 3.4 to equation 3.3. The angle $\theta$ is determined by the entrance angle of the CMA (42.3°). Reference signals for bulk gold and carbon (2.163 and 0.5453 respectively) were taken from sensitivity factors for these two elements. Values for our 4keV beam were calculated by averaging the tabulated values for 3keV and 5keV beams [61]. Furthermore, the sensitivity factor for carbon was multiplied by 0.77 in order to account for the fact that only the negative excursion of the signal, as opposed to the peak-to-peak height, was measured. This was due to the difficulty of resolving the positive excursion from the nearby minor gold peak at $259\text{eV}$.

Using this approach, the unsputtered sample was determined to possess greater than monolayer carbon coverage, and the partially cleaned sample in figure 3-2b possesses 77% of a monolayer. For the sample shown in figure 3-2c, which we take as a clean surface, the carbon signal at $275\text{eV}$ cannot be distinguished from the noise level. We estimate that the limiting sensitivity of our measurement of carbon coverage is about
5% of a monolayer, governed by excursions in the spectral baseline. Further evidence for the cleanliness of this surface comes from the fact that we measure its work function to be 5.30±0.07eV, as described in Section 3.2a. This value is in agreement with the literature value of 5.31eV for clean Au(111) [63].

**b) P3HT/Au(111)**

The morphology of an organic thin film on a metal substrate is expected to have a direct effect on measured photoemission signals. For example, the thickness and structure of the film will influence electron scattering and transmission. The thickness of an overlayer also has important consequences for the extent of band bending in the interfacial region, as discussed in Section 1.2d.

Our attempt to quantify P3HT film thickness by AES is illustrated in figure 3-3. Neither a gold peak nor a sulphur peak (153eV) is observed; a wide carbon peak at 275eV dominates the spectrum. Subsequent to the AES experiment, a small, circular, black region was observed on the sample surface. These results confirm our expectation that the incident electron beam severely damages the polymer surface, thereby precluding its analysis by this technique. Successful Auger analysis of ultra-thin polymer films typically requires cryogenic cooling techniques to avoid damage by the electron beam [64]. The mean free path of 74eV electrons in our organic film is <1nm [62], so the absence of a gold peak in the Auger spectrum may indicate that the polymer film is at least 2.5nm thick.
Figure 3-3: Auger electron spectrum for a P3HT/Au(111) sample.
Kaneto and coworkers have studied the morphology of thin films of various poly(3-alkylthiophenes) on Au(111) by scanning tunnelling microscopy (STM) [65]. Their results demonstrate that regioregular P3ATs have a rod-like structure and that the strong interaction between thiols and Au that leads to self-assembly does not occur between the sulphur atoms of the polymer and the Au surface. Individual regioregular polymers with an average molecular weight ($M_w$) on the order of 29,000 were seen to be about 20nm long and 3nm wide. Our polymers have an average molecular weight of 87,000.

We used AFM to further investigate the nature of the P3HT films on our flame-annealed gold substrates [58]. A typical image and its associated line profile are presented in figure 3-4. These results show that the average height variation over a 2μm region of the film surface is about 4nm. This is consistent with Kaneto's measurement of a 3nm width for individual polymer rods [65]. However, AFM can only probe surface topography; it provides no information about possible underlying layers. As such, AFM cannot be used to determine the overall thickness of the P3HT film, except where a sharp film edge can be imaged.

Polymer thickness below the region of surface roughness was investigated with x-ray photoelectron spectroscopy (XPS) [58]. Using this technique, the thickness of an overlayer can be based on the measured attenuation of the substrate XPS signal:

$$\frac{I}{I_o} = \exp\left(-\frac{d}{\lambda}\right)$$

(3.5)
where $I$ is the attenuated signal intensity and $I_0$ is the measured signal intensity for a bare surface, both taken for normal emission, $d$ is the thickness of the attenuating layer, and $\lambda$ is the mean free path of electrons through the layer.

In cases where film thickness varies across the surface region probed by the x-ray beam, XPS and AFM results can be used together to determine film thickness. Equation 3.5 can be rewritten as:

$$I = \frac{\sum_{i=1}^{n} \exp(-\frac{d_0 + d_i}{\lambda})}{I_0}$$

where $d_0$ is the thickness of a uniform underlayer and $d_i$ is the measured height of a subinterval of the AFM line profile. The thickness of the underlayer is determined by fitting the calculated $I$ to the measured $I$, using $d_0$ as an adjustable parameter.

The Au(4f) spectrum is shown in figure 3-5. The area under the Au(4f$_{7/2}$) and Au(4f$_{5/2}$) peaks was determined using Peak Fit v4.0. The value for mean free path was again based on the work of Seah and Dench [62]. For a disordered organic overlayer a meaningful value for monolayer thickness cannot be determined, thus mean free path is defined as:

$$\lambda_d(mg/m^2) = \frac{49}{E^2} + 0.11\sqrt{E}$$

$$\lambda_d(nm) = \frac{\lambda_d}{\rho}$$

where $E$ is the energy of the electrons being considered and $\rho$ is the density in g/cm$^3$ of the layer through which the electrons are travelling. In the present case $\rho = 1.11g/cm^3$.
Figure 3-4: AFM image and line profile for a P3HT/Au(111) sample [58].
Figure 3-5: Au(4f) XPS spectrum for P3HT/Au sample [58].
and $E = 1402.6\text{eV}$, from the difference between the energy of the Al $K\alpha$ x-ray source (1486.6eV) and the binding energy of the Au(4f) electrons. Using the combined XPS/AFM approach of equation 3.6, the total average thickness of the P3HT film was calculated to be about 6nm.

AFM images of the P3HT/Au samples after performing XPS reveal the presence of circular holes with raised edges in the polymer film (see figure 3-6). This observation has consequences for the accuracy of the XPS determination of film thickness. The holes could be due to sample heating caused by the unmonochromatized x-ray source, leading to thermally-induced dewetting of the gold surface [67]. Another potential explanation is film damage due to electron emission from the gold substrate. Based on the assumption that the deepest craters extend to the bare gold surface, we conclude that the actual thickness of the polymer layer is about 15nm. The 6nm thickness determined by the XPS analysis can be explained by considering that significant emission occurs from the regions of bare gold created during x-ray irradiation, thereby leading to the prediction of a thinner film than actually exists.
Figure 3-6: AFM image and line profile for a P3HT/Au(111) sample, taken after recording XPS spectra, illustrating the presence of craters in the polymer film [58].
3.2 Photoemission Results and Interpretation

a) Clean Au(111)

These two-photon photoemission experiments were performed with incident laser energies of 200mJ and beam areas of about 3mm². The samples were found to exhibit quadratic power law behaviour with respect to total photoelectron yield, a result that is consistent with a two photon process [9]. Figure 3-7 shows a 2PPE kinetic energy spectrum taken for an Au(111) surface cleaned by sputtering and verified by AES. Figure 3-8 shows a spectrum for a surface cleaned by flame annealing with a butane microtorch and degassed at 750K for 90 minutes, but whose cleanliness was not verified by Auger analysis. The two spectra exhibit similar peak shapes and peak widths. As explained in Section 1-2a, the width of a 2PPE spectrum is equal to twice the photon energy minus the work function of the sample. In both spectra the kinetic energy distribution spans 2.7eV. This corresponds to a work function of 5.3eV, which is equal to the literature value of 5.31eV for the work function of clean Au(111) [63]. It can reasonably be assumed that the two surfaces in figures 3-7 and 3-8 are similar, despite their different preparation procedures.

b) P3HT/Au(111)

These two-photon photoemission experiments were performed with significantly lower incident laser energies, yet total yields comparable to those for the bare Au(111) samples were observed. Preliminary investigations into the total yield behaviour of these samples suggest a power law exponent less than two. This is in agreement with results reported for two-photon photoemission of bulk conjugated polymers [68].
Figure 3-7: Two-photon photoemission kinetic energy distribution for an Au(111) substrate cleaned by sputtering and verified by AES.
Figure 3-8: Two-photon photoemission kinetic energy distribution for an Au(111) substrate cleaned by flame annealing.
less than quadratic intensity dependence of total photoelectron yield can be explained by a second-order decay mechanism of intermediate states on the nanosecond time scale of the laser pulses. Figure 3-9 shows the 2PPE kinetic energy distribution recorded for an Au(111) substrate cleaned by flame annealing and coated with a P3HT film about 15nm thick. The apparent width of this spectrum is 2.0eV, which would correspond to a work function of 6.0eV. Figure 3-10 shows the spectra in figures 3-8 and 3-9 overlaid for purposes of comparison. In both cases, the incident laser light was p-polarized. Table 3-2 provides additional comparisons between these two spectra.

<table>
<thead>
<tr>
<th></th>
<th>bare gold</th>
<th>P3HT/Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>incident laser energy</td>
<td>200mJ</td>
<td>5.5mJ</td>
</tr>
<tr>
<td>peak area (total yield)</td>
<td>0.907</td>
<td>3.107</td>
</tr>
<tr>
<td>signal normalized to 5.5mJ according to $I^2$</td>
<td>2.2x10^{-4}</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3-2: Summary of data for 2PPE spectra of bare gold and P3HT/Au samples.

At first inspection it would appear that the P3HT film has the effect of increasing the work function of the Au(111) surface, as indicated by the 0.7eV reduction in width. However, two arguments can be made against this conclusion. First of all, it is highly probable for a work function increase to be accompanied by an overall decrease in photoemission intensity, whereas the results clearly illustrate much higher signal intensity for the P3HT/Au sample than for the bare gold. Secondly, we believe that the presence of P3HT should decrease the work function of the Au(111) surface. Noting the relative position of the Fermi levels in these two materials (figure 3-11a), it can be reasonably expected that Au/P3HT interface formation will be accompanied by electron transfer from the polymer to the metal. The resulting interface dipole would cause a work function reduction for the metal.
Figure 3-9: Two-photon photoemission kinetic energy distribution for a P3HT/Au(111) sample.
Figure 3-10: Two-photon photoemission kinetic energy distribution for an Au(111) substrate cleaned by flame annealing (red line) and a P3HT/Au(111) sample (blue line).
Figure 3-11: Energy level diagrams for Au(111) and poly(3-hexylthiophene) (a) before and (b) after interface formation [63,69].
Our results can be explained by referring to the energy level diagrams for Au(111) and P3HT in figure 3-11. We suggest that the observed onset of photoemission corresponds to excitation using the LUMO of P3HT as an intermediate state. Electrons with lower kinetic energies would involve transient intermediate states within the band gap of the polymer. In the 2PPE spectrum, the lowest energy electrons observed correspond to initial states lying 2.0eV below the Fermi level. Combined with the knowledge that our 2PPE photons have 4.0eV of energy, this places the LUMO of P3HT 2.0eV above the Fermi level. Thus, interface formation involved a 0.8eV downward shift of the polymer energy level (figure 3-11b). These preliminary results illustrate the potential of the two-photon photoemission technique to directly probe the position of unoccupied states at metal/conjugated polymer interfaces.
3.3 Discussion

A recent study by Onoda et al involved the determination of energy level alignment at various conducting polymer/metal interfaces, including P3HT on Au [69]. One-photon photoemission thresholds were measured in order to determine the ionization potential (Ip) of each polymer, spin-coated in thicknesses ranging from 1–22nm onto a metal substrate. For the polymer/metal combinations where the work function of the metal is exceeded by the Ip of the bulk polymer, a decrease in Ip within 5nm of the interface was observed and attributed to upward bending of the polymer bands, induced by charge transfer from the metal to the polymer (see figure 3-12). For P3HT/Au interfaces, where Φ>Ip, the corresponding increase in Ip near the interface was not observed. Consequently, Onoda et al conclude that no charge transfer takes place between these two materials and no shift or bending of the polymer energy levels occurs. This result conflicts with our findings that the P3HT levels shift downwards by 0.8eV. We can offer two arguments against Onoda's conclusions. First of all, Onoda et al neglect the possibility of deviation from vacuum level alignment caused by effects other than band bending. As discussed previously, the formation of an interface dipole can cause a shift in the polymer energy levels without charge transfer. This process would not necessarily change the Ip of the polymer, and therefore would not be observable by Onoda's technique. Nevertheless, this dipole is extremely important when considering interfacial electronic structure. Alternatively, it is possible that Onoda's technique is generally unable to observe downward-directed band bending. Its use in such a situation requires that the region of the polymer valence band located above the Fermi level of the metal be completely depleted of valence electrons. This is not likely to be
Figure 3-12: Schematic energy level diagram of a conjugated polymer/metal interface, illustrating a decrease in ionization potential (Ip) due to upward bending of the polymer bands.
the case, so downward-directed band bending would not be accompanied by an increase in the photoionization threshold of the polymer film.

A number of research groups have used the UPS approach described on page 27 to measure interfacial energy level shifts. Sawatsky and coworkers investigated energy level alignment at the interfaces of 5-10nm films of PPV and MEH-PPV oligomers deposited onto Ag and Au substrates [48]. In all cases, the energy levels of the oligomer were found to shift downwards due to the formation of an interface dipole. The magnitude of this shift ranged from 0.4eV to 1.2eV, on the same order as our own measurement of a 0.8eV shift for a similar system. Interestingly, the magnitude of the shift in each case was such that the barrier to hole injection was nearly constant (1.4eV) and independent of the metal's work function or the polymer's ionization potential. Our much lower barrier to hole injection (0.2eV) can be explained by the p-type properties of P3HT [69]. This places the Fermi level of the polymer near the top of the valence band instead of near the middle of the band gap, as occurs for the oligomers in Sawatsky's study.

Khan and coworkers used UPS to determine vacuum level shifts for the interfaces between a variety of metals and 5–10Å films of organic molecular semiconductors (PCTDA, Alqa, CBP, and α-NPD) [52]. Their results indicate that the magnitude of the shift is interface dependent and in general is correlated with the difference between the work function of the metal and the ionization energy of the thin organic film. Seki et al described similar results for interfaces of various conjugated organic molecules with Mg, Al, Ag, and Au [53]. Vacuum level shifts associated with each molecule were found to be proportional to the work function of the metal substrate. Furthermore, the measured
magnitudes of the shift successfully account for the observed charge-injecting nature of each interface, thereby substantiating the validity of this technique.

The results of these two studies [52,53] can be used to calculate the expected vacuum level shift for P3HT/Au. If the measured shift for each semiconductor/Au sample is plotted against the ionization energy of the organic film, an approximately linear relationship is observed. Extrapolating to the 4.7eV ionization energy of P3HT predicts a vacuum level shift of 1.4–1.6eV, much larger than our observed value of 0.8eV. Once again, this can be explained by the p-type nature of the conjugated polymer compared to conjugated molecules.

The UPS technique was also used by Gao et al to study interfacial electronic structure for the 5PV/Ca system [50]. The evolution of the spectrum was monitored as the oligomer was gradually deposited, finally producing a 10nm film. This approach allowed the researchers to ascribe changes in energy level alignment to polymer band bending in the region 10nm from the interface. An abrupt downward energy level shift of 0.15eV was observed and accounted for by the formation of an interface dipole, but band bending due to charge transfer results in a 0.5eV upward shift. This is the first indication in the literature that band bending may be an important factor in the determination of injection barrier magnitudes at interfaces between metals and conjugated oligomers or polymers.

A limitation of the UPS technique for studying systems involving very thin organic films is that photoemission from the metal substrate may dominate, thereby making the HOMO of the organic overlayer difficult to detect [3]. On the other hand, the high
sensitivity of 2PPE to emission from long-lived polymer states allows this technique to be used with extremely thin films without worry of interference by photoemission directly from the metal. Our results illustrate a nearly 5000-fold increase in signal intensity from the polymer compared to the bare metal. As such, the 2PPE technique could be used to measure band bending near the interface by measuring the position of the LUMO as a function of polymer film thickness.

Furthermore, researchers using UPS must rely on the established optical band gap of the bulk polymer in order to determine the position of the LUMO. However, this band gap may be altered during interface formation. In the case of conjugated polymers, the optical band gap may not be an appropriate value to use, due to the existence of polaron states. In comparison, the 2PPE technique directly measures the position of the LUMO at the interface.

The behaviour of two polythiophene-based systems, poly(3-octylthiophene) (P3OT) and α-sexithiophene (α6T), upon metallization with aluminum has been investigated by Salaneck and coworkers [70]. For Al coverages of 1-5Å, XPS was used to analyze charge transfer between the metal and the polymer, and UPS was used to probe the valence band structure of the polymer, which relates to its degree of conjugation. This work complements a theoretical investigation of the PT/Al interface performed by Brédas et al [71]. In both approaches, Al was found to form strong covalent bonds with the α-carbon atoms of the thiophene rings, resulting in charge transfer to both sulphur atoms and carbon atoms in the polymer. This interaction is found to strongly affect the electronic properties of the organic systems by disrupting the conjugation along the chain. This illustrates a case where interface formation may be accompanied by a
change in the band gap of the polymer, so that extrapolation of the LUMO position from the measured HOMO position may not produce accurate results.

Selmani et al have studied interface formation between 100nm P3HT films and various transition metals [72,73]. By monitoring peak shifts and the appearance of new features in the S(2p), C(1s), and metal 2p XPS spectra during polymer metallization, the type and extent of chemical interaction at the interface was established. For coverages of 0.5–40Å it was found that Cu reacts strongly and exclusively with the sulphur atoms of P3HT, forming a sulphide-like complex. Similar but less pronounced results were found for Ag, while Au showed no evidence of reaction with P3HT. In a subsequent study, Cr, V, and Ti were shown to react with the sulphur atoms of P3HT during the initial stages of interface formation. Continued metallization to give coverages >3Å results in additional reaction with the β-carbon atoms of the polymer. In all cases where reaction occurred, XPS evidence was indicative of charge transfer from the metal to the thiophene ring.

These and other XPS studies provide clear evidence of chemical interaction during metal/polymer interface formations, but are not able to probe the valence electronic effects of such interaction. The 2PPE technique could be used in tandem with these investigations to supply this important information.

Two other techniques that directly probe unoccupied states are near edge x-ray absorption fine structure (NEXAFS) and scanning tunnelling spectroscopy. NEXAFS involves x-ray excitation of a core electron into unoccupied states. A subsequent Auger process produces a measurable emission current. The variable magnitude of this
photocurrent as the x-ray energy is changed is indicative of the density of unoccupied states. A NEXAFS study by Gao and coworkers explored interface creation when Ca or Al is deposited onto a PPV derivative [74]. Their results indicate that Ca/PPV interface formation is accompanied by the creation of new unoccupied states, whereas the deposition of Al has no such effect. This difference is attributed to the occurrence of charge transfer from Ca but not from Al. However, as a method of measuring the magnitude of the EF-LUMO barrier, NEXAFS is perhaps only semi-quantitative due to possible changes in the position of core levels with respect to EF and the strong effect of the core hole on the outgoing electron [3].

Alvarado and coworkers have used a unique STM technique to examine interfacial electronic states in a metal/polymer system. Their approach involves maintaining a constant tunnelling current while monitoring tip height as a function of tip bias relative to EF of the metal. This allows the density of states to be directly probed. Alvarado et al used this technique to determine the energies required to inject electrons or holes into 2–12nm conjugated polymer films from the Fermi level of an Au(111) substrate [54]. It was found that for poly(9,9'-dioctylfluorene) (PFO), the minimum energy required for hole injection was $-1.50\pm0.05\text{eV}$ and the threshold for electron injection was $1.70\pm0.05\text{eV}$. For poly(1,12)AOPV-co-PPV, they equal $-1.30\pm0.10\text{eV}$ and $1.35\pm0.05\text{eV}$. In both cases, values are consistent with a downward shift of the polymer energy levels relative to the metal. It would be interesting to apply 2PPE to these systems, both to provide results for comparison and to investigate the relative merits of these two techniques.
CHAPTER 4

CONCLUSION

4.1 Concluding Remarks

In this thesis, the use of two-photon photoemission to probe electronic structure at metal/conjugated polymer interfaces is investigated. The preliminary use of this technique to characterize the interface between poly(3-hexylthiophene) and Au(111) is described. Our results suggest that 2PPE can be used to determine the energy of unoccupied electronic states involved in electron transfer at these interfaces. For the P3HT/Au system, the position of the LUMO was measured to be 2.0eV above the Fermi level of the gold substrate, corresponding to a 0.8eV downward shift of the polymer energy levels upon interface formation. This shift may be due to band bending and/or the effects of an interfacial dipole. We also observe considerable photoemission from the Au/P3HT sample, which we attribute to the high sensitivity of 2PPE to states with long lifetimes. Accordingly, this technique is shown to be particularly good for the study of systems involving conjugated polymers, due to the nature of the excited states within these materials.

4.2 Future Research

The preliminary results presented in this thesis could be expanded in several ways. The experiments described here should be repeated. Additionally, the use of different
photon energies in 2PPE experiments would allow the nature and energy of the observed unoccupied state to be confirmed. Specifically, if the position of the peak varies as hν, this would confirm that it is in fact due to photoemission from an intermediate state. It would also be very interesting to more closely investigate the low energy end of the 2PPE spectrum for P3HT/Au in order to look for band gap states or to observe the real low-energy photoemission onset. In this way, work function reduction due to the polymer film could be directly measured.

In addition to continued development of the currently used dip-coating method, new avenues of sample preparation could potentially be explored. These may include self-assembly or in situ deposition of organic films. Along with improved sample characterization techniques, particularly with regards to the measurement of film thickness, this would allow for 2PPE investigations of the thickness dependence of polymer energy level positions. In this way, interface dipole and band bending contributions to energy level alignment in conjugated polymer systems could be determined.

As a technique newly applied to the study of metal/conjugated polymer interfaces, possibilities for the novel use of 2PPE in this field are numerous. It would be of great interest to employ this method of investigating electron injection barriers to a variety of such interfaces. Studies of metal/polymer combinations most often used in OLEDs, such as MEH-PPV, would be especially instructive.
REFERENCES


[58] I wish to gratefully acknowledge Youngku Sohn for his considerable help with the sample preparation and characterization work included in this thesis.


A magnetic transfer arm
B manipulator
C CHA
D photoemission chamber
E CMA
F sorption pump
G diffusion pump
H sputter ion gun
J gas manifold
APPENDIX TWO

Program One

c:\Labview\User.lib\Jessica's Vis\Programs\July99\HprogJl12(CHAscanfinal).vi

Function:
Acquires a two-photon photoemission spectrum (kinetic energy distribution) by collecting and analyzing analog data during scan(s) of CHA pass energies.

Input:
Maximum, minimum, and step size for CHA pass energy; shots per voltage (pass energy) within scan; signal collection specifications including total number of samples collected, sampling rate, full-scale voltage range of the A/D card, and a corresponding voltage multiplier value.

Output:
Average kinetic energy distribution for one or more scans of CHA pass energy.

Structure:
This program consists of three loops. The innermost loop is responsible for the individual single laser that occurring while sitting at a given CHA pass energy. The number of loop iterations is defined by 'shots per voltage within scan'. The output of this loop is an average, baseline-subtracted value for photoemission intensity at a particular voltage. The intermediate loop controls a scan over a single ramping of CHA energies, collecting intensity values at each voltage point. Its output is a complete kinetic energy distribution for a single scan. The outermost loop is responsible for averaging successive scans to produce the final distribution. Its number of iterations is controlled by an on/off switch.
Details:
CHA pass energies (maximum, minimum, and step size, in eV) inputted by the user are converted into A/D card voltages by CHAtocard. Conversion constants are determined experimentally by calibration curve. Given these values, math calculates the number of voltage points within the scan (equal to the number of iterations of the intermediate loop). Meanwhile, xaxistime calculates the timescale of the measured pulses (ms) using inputted values for total number of samples collected and the sample collection rate. Ramp calculates the card voltage (binary) for the current point within a scan and send this value to AOut (ComputerBoards) which writes this value to the A/D card. Cardvolts also calculates the current card voltage (decimal) and send this to CHAeV, which then calculates the current CHA pass energy. Shotloop collects signal vs. time data for each laser pulse. It includes ApretrFg (ComputerBoards), which is triggered by the laser sync out and collects a specified number of analog samples for each channel, returning array(s) of binary data. To volts converts these binary values into volts, accounting for the user-defined range setting of the card. SelChan (ComputerBoards) separates the data collected at individual channels and RunAvg (1D) creates a running average signal vs. time array. Peakht extracts two blocks of data from the array, corresponding to the user-defined baseline and the user-defined peak. The height of a single or average pulse is determined by averaging each block and calculating the difference between them to produce the output of the innermost loop. These values are paired with their corresponding CMA pass energies to produce the output array of the intermediate loop. In the outermost loop, AVG (2D) creates a running average array of this signal vs. CHA voltage data. When the program is stopped by the user, this array is written to a text file.

Program Two

Function:
Acquires a two-photon photoemission spectrum (kinetic energy distribution) by event counting during scan(s) of CHA pass energies.
Input:
As for Program One, plus a threshold value. This value is determined visually with each use of the program, as it depends on experimental factors.

Output:
A digitized version of an average kinetic energy distribution for one or more scans of CHA pass energy.

Structure:
As for Program One.

Details:
As for Program One, except that the output of shotloop (an average peak height) is compared to the threshold value; if the peak height equals or exceeds threshold then the value 1 is returned, otherwise the value 0 is returned. For a given voltage step within a ramp, these returned values are summed, and this sum represents the recorded signal.

Program Three

Function:
Acquires an Auger electron spectrum by collecting and analyzing data during scan(s) of CMA pass energies.

Input:
Maximum, minimum, and step size for CMA pass energy; signal collection specifications including total number of samples collected, sampling rate, full-scale voltage range of the A/D card, and a corresponding voltage multiplier value; index and array length values to specify which values within the signal vs. time array should be included in the calculation of average signal value.
Output:
Average Auger electron spectrum for one or more scans of CMA pass energy.

Structure:
This program consists of two loops. The first (inner) loop involves the creation of a signal vs. CMA pass energy array. The number of iterations of this loop is defined by the CMA pass energy parameters (max/min values and step size) inputted by the user. The second loop, controlled by an on/off switch, records a running average of the arrays received from the first loop.

Details:
CMA pass energies (maximum, minimum, and step size, in eV) inputted by the user are converted into A/D card voltages by CMAtocard. Conversion constants are determined experimentally by calibration curve. Given these values, math calculates the number of voltage points within the scan (equal to the number of iterations of the inner loop). Ramp calculates the card voltage (binary) for the current point within a scan and send this value to AOut (ComputerBoards) which writes this value to the A/D card. CMAeV, calculates the current CHA pass energy. Augerloop collects signal vs. time data over a specified time period and averages a defined subset of these values to generate an average signal value for each voltage step. It includes AInScFg (ComputerBoards), which collects a specified number of analog samples, returning an array of binary data. to volts converts these binary values into volts, and accounts for the user-defined range setting of the card. A user-specified subset of these collected values are averaged to produce the output of Augerloop. This average value is paired with its corresponding CMA pass energy to produce the output array of the inner loop. In the outermost loop, AVG (2D) creates a running average array of this signal vs. CMA voltage data. When the program is stopped by the user, this array is written to a text file.