Coupling spatially and spectrally resolved optical measurements with a scanning probe system

by

Tanya Roussy

B.A.Sc., The University of British Columbia, 2014

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Applied Science

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Engineering Physics)

The University of British Columbia

(Vancouver)

August 2016

© Tanya Roussy, 2016
Abstract

Developing a bottom-up understanding of the physics behind charge transfer processes on the nanometer scale will enable the focused design and synthesis of new materials which will revolutionize everything from solar cells to wearable electronics.

Pushing our understanding of these processes to the nanometer scale is critical for next generation device development for two primary reasons. Firstly, modern electronic devices are fabricated ever smaller; to date IBM Research has already produced working chips using with gate widths only 14 atoms (7 nm) wide [1]. Secondly, for many devices which rely on charge transfer the important action is at the interface between materials; it is here that the energy level offset and other parameters can make or break a device. For modern organic devices, the interfacial region is in essence a nanometer-wide region: energy levels can differ by hundreds of meV only a few molecules away from an interface [2].

This thesis presents the design and execution of experiments which couple optical measurements with a scanning probe system. The marriage of optical and scanning probe systems enables simultaneous exploration of two complementary dimensions (optical and electronic) of the physics of the system under study, enabling the probing of parameters affecting charge transfer between single molecules. The custom-built system was used to explore optical and electronic properties of two prototypical organic molecules forming an acceptor-donor pair: 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and copper (II) phthalocyanine. This proof-of-concept will allow future users to explore a wide variety of systems which may offer clues to how charge transfer processes occur at the nanometer scale.

In the first part of this work I describe the motivation for our experiment as well as the experimental design and set-up. In the second part I detail how we used the enhanced optical-electrical scanning probe to observe real-space energy levels, luminescence (or lack thereof), and attempted optical excitations between two single organic molecules. Analysis of scanning tunnelling spectroscopy data coupled with laser excitation as well as the results from experiments which in principle can measure sub-molecularly resolved luminescence show that the new optical system works as expected.
Preface

The data analyzed in this thesis is the result of a significant collaborative effort between myself, my supervisor Dr. Sarah Burke, and my colleagues Katherine Cochrane and BingKai Yuan. Many others played a supporting role, and all were invaluable in the creation of this thesis.

My contributions and the contributions of my collaborators to the present work are as follows:

- The day-to-day maintenance of the Omicron STM/AFM was carried out by myself, Katherine Cochrane, and BingKai Yuan.
- The sample preparation was carried out by myself and Katherine Cochrane.
- The Matlab code written to analyze the data was written by myself, Katherine Cochrane, Agustin Schiffrin, and Gary Tom.
- The optical spectrometer and lasers used in this thesis were specified and purchased by Dr. Burke.
- The specialized electronics were all built and designed by David Tonkin and Benny Ng at the Chemistry electronics shop in consultation with myself.
- Debugging of all electronics and code used for optical measurements was performed/written by myself.
- Arthur Mills provided invaluable feedback, help, and ideas during the development of the optical spectrometer alignment process.
- The concept and basic structure for the MATE scripts, for extending the raster time during optical spectroscopy grids and for performing KPFM grids (in the future), was offered by Jürgen Köble and implemented and modified by myself.
- The specialized mechanical components were designed by myself and fabricated by myself or the machinists in AMPEL and Chemistry: Harish Gautam, Pritesh Padhiar, and Des Lovrity.
• The knudsen-cell evaporator used to deposit NaCl was built and debugged by myself (with
detailed design done by myself), with the original design concept coming from the Crommie

• The LabView code written for optical spectroscopy was written by myself with some help
from Robert Delaney.

• The data analyzed and images presented were primarily collected by myself, with major con-
tributions coming from Katherine Cochrane and BingKai Yuan.

• The 3D models of the Omicron were drawn by myself based on drawings from Omicron
Scienta.

• The data analysis presented in this thesis was performed by myself.

• Dr. Burke is responsible for the overall experimental plan, and provided invaluable guidance,
help, and advice throughout the process.

• Repairs on the Omicron STM/AFM were executed by Dr. Burke, Katherine Cochrane, BingKai
Yuan and myself.

• The Omicron service engineers, in particular Alex Skripnik, Jürgen Köble, and Eike Schrenk
answered dozens of questions and provided valuable support in the development of the exper-

• The tips used for STS measurements were prepared by Katherine Cochrane. The tips used for
AFM measurements were prepared by BingKai Yuan. The tips used for luminescence mea-
surements were prepared by myself, based on a method developed by Floren Rubio, Nandini
Mukherjee, Dr. Burke, Niv Levy, and Dr. Crommie.
Table of Contents

Abstract ....................................................................................................................... ii
Preface ....................................................................................................................... iii
Table of Contents ....................................................................................................... v
List of Tables ............................................................................................................. viii
List of Figures ........................................................................................................... ix
Glossary ....................................................................................................................... xx
Acknowledgments ..................................................................................................... xxii

1 Introduction ............................................................................................................. 1
  1.1 Motivation ........................................................................................................... 1
  1.2 Scanning probe techniques and the power of real-space, atomically-resolved mea-
      surements ........................................................................................................... 4
  1.3 Molecular acceptor-donor pair: towards an understanding of charge transfer in an
      organic electronic device .................................................................................. 6

2 Experimental techniques ......................................................................................... 7
  2.1 Scanning tunnelling microscopy ........................................................................ 7
      2.1.1 The tunnelling current ............................................................................... 9
      2.1.2 Scanning tunnelling spectroscopy ............................................................... 13
  2.2 Atomic force microscopy .................................................................................... 21
      2.2.1 Frequency modulation atomic force microscopy ....................................... 21
      2.2.2 The forces acting on the tip ....................................................................... 23
      2.2.3 Kelvin probe force microscopy ................................................................... 25
  2.3 Scanning tunnelling microscope induced luminescence ...................................... 26
2.4 Optical excitation .................................................. 29

3 Experimental setup .................................................... 30
  3.1 Scanning probe system ............................................. 30
    3.1.1 Ultra-low vibration facility .................................. 30
    3.1.2 Omicron UHV STM/AFM .................................... 31
    3.1.3 Optical access in the scanning probe system .............. 32
  3.2 System under study: copper (II) phthalocyanine and 3,4,9,10-perylene tetracarboxylic dianhydride on NaCl on metal surfaces .................................................. 35
    3.2.1 Substrates: Ag(111) and Au(100) with bi- and tri-layer NaCl ........................................... 35
    3.2.2 Sample preparation ........................................... 37
    3.2.3 Tip preparation .............................................. 40
  3.3 External optical system ........................................... 41
    3.3.1 Mechanical components ...................................... 41
    3.3.2 Electrical components ....................................... 43
    3.3.3 Photomultiplier setup and alignment ....................... 50
    3.3.4 Spectrometer setup .......................................... 51
    3.3.5 Laser setup .................................................. 54

4 Optical excitation of an acceptor-donor pair ......................... 55
  4.1 Characterization of spurious signals: the influence of the tip/substrate and thermal expansion of the tip-sample junction ............................................. 57
    4.1.1 The effect of the tip and specific location on the substrate ........................................... 58
    4.1.2 Thermal expansion of the tip-sample junction ..................... 61
  4.2 Optical excitation of the system with a Ag(111) substrate ..................... 64
  4.3 Discussion ....................................................... 70
    4.3.1 Vibrational excitation leading to possible tunnelling current changes ......................... 72
    4.3.2 STS of CuPc-PTCDA on NaCl(2ML)/Au(100) .................. 76

5 Scanning tunnelling luminescence measurements .......................... 83
  5.1 Luminescence measurements on bare Ag(111) ........................ 83
  5.2 Luminescence measurements of CuPc-PTCDA on NaCl/Ag(111) ........ 90
  5.3 Point optical spectra collected on NaCl/Ag(111) ................... 93
  5.4 Discussion and suggestions ....................................... 94
    5.4.1 The signal seen on NaCl ..................................... 94
    5.4.2 The molecular luminescence, or lack thereof .................. 95
    5.4.3 Suggestions for future experiments and improvement of the current experimental set-up ............ 98
6 Conclusions and future directions .......................... 100
  6.1 Kelvin probe force microscopy ............................. 100
  6.2 Optical spectroscopy on NaCl/Ag(111) .................... 101
  6.3 Large area photomultiplier tube luminescence measurements for finding luminescent molecules .......................... 101
  6.4 Scanning tunnelling luminescence on supported molecules ...................... 102

Bibliography .......................................................... 103

A Supporting materials: knudsen cell evaporator for epitaxial growth of NaCl: design and assembly .......................... 112
  A.1 Parts .............................................................. 113
    A.1.1 Evaporator body ............................................ 113
    A.1.2 Shutter ..................................................... 115
  A.2 Construction .................................................... 117
    A.2.1 Base ......................................................... 117
    A.2.2 Quartz cell ............................................... 118
    A.2.3 Heater wire ............................................... 120
    A.2.4 Thermocouple ............................................. 120
    A.2.5 Radiation shield ......................................... 120
    A.2.6 Shutter .................................................... 122
  A.3 Assembly ......................................................... 124

B Supporting materials: laser power study STS spectra averaged over smaller portions of the molecule .......................... 126
  B.1 Masking ......................................................... 126
  B.2 STS results for masking over only part of the molecules: laser excitation study ... 130
  B.3 STS results for masking over only part of the molecules: CuPc-PTCDA on NaCl/Au(100) .................................................. 136
List of Tables

Table 4.1  $z(t)$ results for 488 nm laser. Note that the first fit for 10 mW appears to be poor, though it was within a 95% confidence interval. In addition, the initial $\tau$ should be 0, but it is likely that we are seeing the piezo drift. This means that the piezo drift and the laser-induced thermal expansion are both present in the measurements taken. Even with the piezo drift, we can see that the longest time one needs to wait before reaching steady state is 6 minutes. For the 488 nm laser, we can conclude that $\geq$6 minutes is a safe time to wait after turning it on or off to any power to be confident that the tip and sample have reached thermal equilibrium, assuming piezo drift is at an acceptable value.
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Cartoon depicting the formation of an exciton</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Energy level schematic for an exciton in the charge transfer state at an acceptor-donor interface. $E_{opt}$ is the energy of the exciton, $E_{gap}$ is the bandgap energy of a free electron-hole pair in the bulk, and $E_b$ is the difference between the two: the exciton binding energy.</td>
<td>3</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Spatial and energetic evolution of the local density of states for a single CuPc molecule (left) which is adjacent to a single PTCDA molecule (right) as imaged via scanning tunnelling spectroscopy. Yellow indicates the presence of states.</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>STM constant current image ($11\text{nm}^2$, $I=5\text{pA}$, $V_b=-0.5\text{V}$, $T=4.3\text{K}$) of CuPc and PTCDA clusters on NaCl(2ML)/Ag(111). The CuPc images here as a ‘cross’. The edge of the NaCl island is clearly visible with right-angled lines.</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>A model system: organic photovoltaics reduced to a molecular acceptor-donor pair. Copper (II) Pthalocyanine (CuPc) and 3,4,9,10-Perylene Tetracarboxylic Dianhydride (PTCDA) on NaCl/Ag(111) and NaCl/Au(100).</td>
<td>6</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Schematic for basic Scanning Tunnelling Microscope (STM) operation</td>
<td>7</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>STM image of two different configurations of Copper (II) Pthalocyanine (CuPc) and 3,4,9,10-Perylene Tetracarboxylic Dianhydride (PTCDA) on NaCl(2ML)/Ag(111) ($5\times5\text{nm}^2$, $I=5\text{pA}$, $V_b=-0.5\text{V}$, $T=4.3\text{K}$). The CuPc is imaged as a ‘cross’ here. Note the PTCDA images differently depending on its location with respect to the CuPc.</td>
<td>8</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>STM image of CuPc and PTCDA clusters on NaCl(2ML)/Ag(111) taken with a PTCDA functionalized tip ($15\times15\text{nm}^2$, $I=5\text{pA}$, $V_b=0.5\text{V}$)</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Schematic of the energy levels for a metal tip (left) and a semiconducting sample (right). The filled states are in darker colours, while the unfilled states are lighter. The fermi levels are offset by eV. An electron at a given energy in the tip can tunnel into an empty band in the sample if it is available, but it cannot tunnel when there are no states to tunnel into.</td>
<td>14</td>
</tr>
</tbody>
</table>
Figure 2.5  Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated CuPc molecule stabilized at the corner of a trilayer step. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 17

Figure 2.6  Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated CuPc molecule stabilized at the corner of a trilayer step. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 18

Figure 2.7  Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated PTCDA molecule. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 19

Figure 2.8  Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated PTCDA molecule. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 20

Figure 2.9  Schematic of the AFM. The electronics are left out for simplicity. A piezo drive controls the position of the probe tip, as before. A tip is placed on an oscillating cantilever, and tip-sample interaction forces change the resonant frequency of the cantilever. The frequency shift is taken as the imaging signal. 21

Figure 2.10 Energy levels of the sample and tip in three cases: 1) tip and sample separated by gap with no electrical contact, 2) tip and sample are in electrical contact, and 3) an external DC bias is applied to cancel the CPD and the tip-sample electrical force. $E_{\text{vac}}$ is the vacuum energy and $E_F$ are the fermi levels. Adapted from [3]. 26

Figure 2.11  Schematic indicating the basic process in scanning tunnelling microscope induced luminescence. 27
Figure 3.1 Photographs of our system. a. The Omicron STM/AFM in its ‘pod’, without the optical components. The cryostat stands tall. b. Front view of the UHV system. The LT chamber is on the left and the prep chamber is on the right. c. The scanner head showing the optical access without the lens tube installed (indicated with white circle and red arrow) and the fins for eddy current damping. d. The scanner head with no tip or sample as seen from the sample access side. e. The system as seen in a) but with the optical table installed (indicated with the red arrow). Detailed location of the optical table and components with respect to the Omicron LT chamber can be found in the 3D model. See Section 3.3 for more information about the placement and assembly of the optical table.

Figure 3.2 Photo of the scanner head indicating the optical paths available. The right path is the one used for optical collection and excitation: our lens was placed on the right at a distance of approximately 18mm from the tip-sample junction. The left path is used in conjunction with a camera to visualize tip and sample transfer as well as coarse tip approaches. The central path is the one used by the experimenter when transferring samples (or tip carriers) into and out of the head.

Figure 3.3 Standard viewport transmission curve (kodial design). The 3dB points are at \( \sim 310\text{nm} - \sim 2800\text{nm} \). Image courtesy of [4].

Figure 3.4 In-vacuum viewport transmission (KG5). The 3dB points are at \( \sim 350\text{nm} - \sim 620\text{nm} \). Image courtesy of [4].

Figure 3.5 STM images of the Ag(111) surface. a) Clean Ag(111) surface. b) Clean Ag(111) surface showing the surface state scattering off of impurities and step edges.

Figure 3.6 STS spectra showing the Ag(111) surface state.

Figure 3.7 STM images of Au(100). a) Clean Au(100) surface with screw dislocation. b) NaCl islands on Au(100).

Figure 3.8 Images of the sample holder.

Figure 3.9 STM images of NaCl on NaCl/Ag(111). a) Ag(111) surface with bi-, tri-, and quadlayer NaCl. b) Atomic resolution on NaCl/Ag(111) showing the expected square lattice and a Moiré pattern due to the lattice constant mismatch between Ag(111) and NaCl.

Figure 3.10 STM images of Au(100). a) Clean Au(100) surface. b) Atomic resolution of NaCl on Au(100).

Figure 3.11 STM images of CuPc and PTCDA on Ag(111). a) NaCl island and bare Ag surface with deposited molecules, before 2 minute room temperature anneal. b) CuPc and PTCDA clusters formed on NaCl/Ag(111) after a 2 minute room temperature anneal.
Figure 3.12  STM images of CuPc and PTCDA on NaCl/Au(100). Both images indicate clearly the positioning of PTCDA with respect to the underlying Au(100) substrate: the PTCDA adsords normal to or parallel to the Au(100) reconstruction. Image b) also indicates the positioning of CuPc with respect to the underlying Au(100) substrate. a) CuPc and PTCDA near the edge of a NaCl island. b) CuPc and PTCDA near the edge of a NaCl island. Submolecular resolution is visible. Image taken with a PTCDA functionalized tip.  

Figure 3.13  STM image of CuPc and PTCDA on NaCl/Au(100). NaCl lattice is visible, indicating the positioning of both CuPc and PTCDA with respect to the underlying NaCl layer. Image taken with a PTCDA functionalized tip.  

Figure 3.14  Solidworks model of the Omicron.  

Figure 3.15  Various views of the optical set-up, used in this case for the spectrometer, as designed in Solidworks. The beam path is highlighted in red.  

Figure 3.16  Photo of the STM/AFM with optical components installed.  

Figure 3.17  Photos of the optics integrated with the Omicron STM/AFM. a. Birds-eye view of the optical table and flange optics, b. Close-up view of the beam path going into the spectrometer. c. View of the supports for the optical table, which used only the holes already present in the table and can handle considerable weight and impact.  

Figure 3.18  Image of the Ag(111) sample, looking in from the camera side (where illumination is coming in from the optics flange). Left, original image. Center, image with sample outlined with a red oval. Also outlined in red is the tip and the tip’s reflection. Right, yellow indicates the image of the optics viewport as seen reflected in the sample (with no optical components mounted on the flange). Yellow demarcates the portion of the sample to which we have optical access. The result is that only the back half of the sample offers optical access.  

Figure 3.19  PMT photon counting circuit block diagram.  

Figure 3.20  Schematic for the timing signals cabling and the isolator box.  

Figure 3.21  Aligning the PMT. Images show the Ag(111) sample as seen with the camera.  

Figure 3.22  Solidworks model of the dark box. The frame is built with aluminum t-slot extrusion and the panels are made from corrugated plastic. The panels are caulked into the frame to prevent light leaks. Note the panels are actually black, but are purple in the model to ease visualization.  

Figure 3.23  Schematic indicating the connections and cabling for the optical spectrometer set-up.  

Figure 3.24  Image of the tip-sample junction as seen after the lens before the spectrometer slit.
Figure 4.1 STM constant current image (5x4nm², $I=3$ pA, $V_b=-2$ V) of the ‘XO’ configuration of CuPc and PTCDA on NaCl(2ML)/Ag(111). CuPc images as a ‘flower’ here. ....................................................... 55

Figure 4.2 STM constant current image (5x5nm², $I=10$ pA, $V_b=0.5$ V) of the ‘XO’ configuration of CuPc and PTCDA on NaCl(2ML)/Au(100). CuPc images as a ‘cross’ here, which is why it is called the ‘XO’ configuration. Note this would be different from a +O configuration, where the CuPc would be rotated 45° with respect to the PTCDA. Submolecular resolution is visible. Image taken with a PTCDA functionalized tip. ....................................................... 56

Figure 4.3 STS spectra averaged over the entire molecule (either CuPc or PTCDA) in the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different specific molecules. The location and shapes of the peaks change with different tips and locations on the substrate. ......................... 57

Figure 4.4 STS spectra averaged over the entire CuPc molecule in the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different molecules. Spectra shown correspond to the ‘0 mW’ data point for each data set shown in section 4.2 58

Figure 4.5 STS spectra averaged over the entire PTCDA molecule in the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different molecules. Spectra shown correspond to the ‘0 mW’ data point for each data set shown in section 4.2 59

Figure 4.6 STS spectra averaged over the NaCl surrounding the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different molecules. Spectra shown correspond to the ‘0 mW’ data point for each data set shown in section 4.2 60

Figure 4.7 Schematic indicating how the laser power was ramped up and down over time to collect the $z(t)$ data with the 488 nm laser. Note with the 687 nm laser the basic scheme remains the same, but the maximum power is 30 mW. ........... 61

Figure 4.8 Data and fit for $z(t)$ as measured with the initial 5 mW of radiation from the 488 nm laser. ....................................................... 62

Figure 4.9 STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the whole molecule. Data taken on NaCl(2mL)/Ag(111). ................................. 64

Figure 4.10 Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 685 nm laser. Spectra are averaged over the entire molecule. ....................................................... 65
Figure 4.11  Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 640 nm laser. Spectra are averaged over the entire molecule. ......................................................... 67

Figure 4.12  Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 561 nm laser. Spectra are averaged over the entire molecule. ......................................................... 67

Figure 4.13  Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 519 nm laser. Spectra are averaged over the entire molecule. ......................................................... 68

Figure 4.14  Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 488 nm laser. Spectra are averaged over the entire molecule. ......................................................... 68

Figure 4.15  Spatial and energetic distribution of the LDOS, imaged via slicing the STS grid at selected energies. The spatial distribution showed little variation in each data set. Yellow indicates the presence of a tunnelling resonance. Slices shown are from the 561 nm 0 mW grid (taken on NaCl(2mL)/Ag(111)). ......................... 69

Figure 4.16  Topography of the same XO showing both the lower (left) and upper (right) PTCDA configurations, which we call ‘A’ and ‘B’. Comparing the two images above, the PTCDA jumps ≃0.362 nm downwards, which is close to the spacing between adjacent Cl⁻ top sites in the NaCl (0.353 nm) as measured from Figure 3.9b. Images taken on NaCl(2ML)/Ag(111). ......................... 72

Figure 4.17  Constant height NC-AFM images using a PTCDA-functionalized tip of the XO configuration on NaCl(2ML)/Ag(111). The oxygen end of the PTCDA which is adjacent to the CuPC is closer to one isoindoline subunit of the CuPc than the other. Image size 3.2x3.2nm²; oscillation amplitude A = 15 mV. Note the image in a is the Laplace transform of the gaussian smoothed raw data. Image taken on NaCl(2ML)/Ag(111). ......................... 73

Figure 4.18  Exciting a vibrational mode in PTCDA on NaCl(2ML)/Ag(111) at 2V, showing reversible and controllable jumping between two XO configurations. Jumping occurs during scan 2 (down) and scan 5 (up). ......................... 74

Figure 4.19  STM-IETS spectra for PTDCDA in the XO configuration on NaCl(2mL)/Ag(111), with no illumination. Note the resonance at 2.12 V. ......................... 74

Figure 4.20  Topography for all of the STS grids taken during the laser excitation study, showing how the PTCDA jumped (and the CuPc rotated) multiple times during most grids. Note that there was no correlation with the change in the 2.2 V peak height and the number of jumps observed in the images above. ......................... 75

Figure 4.21  dI/dV spectra for the XO configuration on NaCl(2ML)/Au(100) ......................... 77
Figure 4.22  dI/dV spectra for the XO configuration on NaCl(2ML)/Ag(111)  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
Figure 5.1  STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm², I=300 nA, V_b=-10 V. Note there are some tip changes which, while visible in the topography, are quite pronounced in the PMT image. 85

Figure 5.2  STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm², I=5 nA, V_b=-3 V. Note the tip is slightly double in this image. The quenching of the luminescence at the end of the screw dislocation is interesting. 86

Figure 5.3  STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm², I=500 pA, V_b=-3 V. 86

Figure 5.4  STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm², I=250 pA, V_b=-3 V. 87

Figure 5.5  STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm², I=100 pA, V_b=+3 V. 87

Figure 5.6  Point optical spectra on bare Ag(111) (I=200 pA, V_b=+3 V, 100 µm slit, and CCD exposure time = 100 s). 88

Figure 5.7  Bottom left, Integrated optical spectroscopy grid. Counts integrated from 450 - 730 nm. Top left, Example spectra collected at first pixel in grid. Right, Associated STM image for optical grid (30x30 nm², I=50 pA, V_b=0.03 V). Optical grid taken at I=50 nA, V_b=3.25 V, with 50 ms CCD exposure time. The grid was aborted early so a scan taken at the same resolution before the grid was started is the one shown. The area delineated in red in the STM scan corresponds to the section plotted as the integrated optical grid. 88

Figure 5.8  STML image (left) and STM image (right) of adjacent isolated CuPc and PTCDA on NaCl(2ML)/Ag(111) (9x6 nm², I=100 pA, V_b=-3 V). The luminescence is quenched on both molecules, the bare NaCl/Ag substrate shows more emission than the molecules. 90

Figure 5.9  STML image (left) and STM image (right) of adjacent CuPc and PTCDA on NaCl(2ML)/Ag(111) (4.5x6 nm², I=100 pA, V_b=-3 V). The luminescence is quenched, the bare NaCl/Ag substrate shows more emission than the molecules. 91

Figure 5.10  Point optical spectra on CuPc and PTCDA in XO configuration (I=200 pA, V_b=-3 V, 250 µm slit, and CCD exposure time = 200 s). Note the measurement over the CuPc molecule shows the emission seen on bare NaCl but attenuated (see Section 5.3 for a discussion of the NaCl emission). The measurement over PTCDA shows no emission, even though both bare Ag and NaCl showed emission prior to this measurement. This is roughly consistent with what was observed in the PMT images; namely the luminescence is strongly quenched over the molecules compared to the bare NaCl or Ag. 92
Figure 5.11  Point optical spectra on CuPc and PTCDA in XO configuration ($I=200$ pA, $V_b=+3$ V, 250$\mu$m slit, and CCD exposure time = 200 s). Note the luminescence is totally quenched over both molecules. Both bare Ag and NaCl were showing emission immediately prior to this measurement.  

Figure 5.12  Point optical spectra of bare NaCl taken at 550 nm center wavelength showing a bimodal peak ($I=200$ pA, $V_b=+3$ V, 100$\mu$m slit, and CCD exposure time = 200 s).  

Figure 5.13  Point optical spectra of bare NaCl taken at 650 nm center wavelength showing multiple strong peaks ($I=200$ pA, $V_b=-3$ V, 250$\mu$m slit, and CCD exposure time = 200 s).  

Figure 5.14  Point optical spectra of bare NaCl taken at 650 nm center wavelength showing multiple strong peaks ($I=200$ pA, $V_b=+3$ V, 250$\mu$m slit, and CCD exposure time = 200 s).  

Figure 5.15  Schematic indicating the basic STML mechanism as described by Buker and Kirczenow. Adapted from [5].  

Figure 5.16  STM constant-current image of a PTCDA island grown on Ag(111) with CuPc around the edges and on top (40x40 $nm^2$, $I=5$ nA, $V_b=0.35$ V).  

Figure A.1  Evaporator without heat shield or shutter  

Figure A.2  Sophomoric diagram of major evaporator components  

Figure A.3  Drawing for one of the Macor disks. Dimensions are in millimetres. Solidworks files are on our internal Wiki.  

Figure A.4  Drawing of the reducer flange with machined holes dimensioned.  

Figure A.5  Rendering of the base flange with standoffs supporting the macor disks and crucible. On the left, the flange has been rendered transparent to help visualize the locations of the machined holes and other features. On the right, the macor disks have been rendered transparent to help visualize the standoffs mating with each other.  

Figure A.6  The copper heat shield  

Figure A.7  Solidworks drawing of the heat shield. All units are in mm.  

Figure A.8  The shutter assembly  

Figure A.9  Rendering of the knudsen cell assembly in stages. In the center the heat shield and flange are made transparent, and on the right the heat shield is removed exposing the macor/crucible/standoff assembly.  

Figure B.1  STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the oxygen end of the PTCDA molecule.
Figure B.2 STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the center of the CuPc molecule.

Figure B.3 STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the perimeter of the CuPc molecule.

Figure B.4 Comparison of dI/dV spectra for the XO configuration under illumination from the 685 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.5 Comparison of dI/dV spectra for the XO configuration under illumination from the 685 nm laser. Spectra are averaged over the center of the CuPc and the oxygen end of the PTCDA.

Figure B.6 Comparison of dI/dV spectra for the XO configuration under illumination from the 640 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.7 Comparison of dI/dV spectra for the XO configuration under illumination from the 640 nm laser. Spectra are averaged over the center of the CuPc and the oxygen end of the PTCDA.

Figure B.8 Comparison of dI/dV spectra for the XO configuration under illumination from the 561 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.9 Comparison of dI/dV spectra for the XO configuration under illumination from the 561 nm laser. Spectra are averaged over the center of the CuPc and the oxygen end of the PTCDA.

Figure B.10 Comparison of dI/dV spectra for the XO configuration under illumination from the 519 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.11 Comparison of dI/dV spectra for the XO configuration under illumination from the 519 nm laser. Spectra are averaged over the center of the CuPc and the oxygen end of the PTCDA.

Figure B.12 Comparison of dI/dV spectra for the XO configuration under illumination from the 488 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.
Figure B.13 Comparison of dI/dV spectra for the XO configuration under illumination from the 488 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.

Figure B.14 Comparison of dI/dV spectra for the XO configuration on NaCl(2ML)/Au(100). Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.15 Comparison of dI/dV spectra for the XO configuration on NaCl(2ML)/Au(100). Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
Glossary

AFM  Atomic Force Microscope
AMPEL  Advanced Materials and Process Engineering Laboratory
CPD  contact potential difference
CRTC  central real time controller
CT  Charge Transfer
CU  control unit
CuPc  Copper (II) Pthalocyanine
DOS  density of states
KPFM  Kelvin Probe Force Microscopy
LCPD  local contact potential difference
LDOS  local density of states
LSP  localized surface plasmon
LT  low temperature
MO  molecular orbital
OMBE  Organic Molecular Beam Epitaxy
PMT  photomultiplier tube
PTCDA  3,4,9,10-Perylene Tetracarboxylic Dianhydride
STM  Scanning Tunnelling Microscope
STM-IETS  scanning tunnelling microscope inelastic tunnelling spectroscopy

STML  Scanning Tunnelling Luminescence

STS  Scanning Tunnelling Spectroscopy

UHV  ultra-high vacuum
Acknowledgments

Thank you to my supervisor Dr. Sarah Burke, for teaching me so much and giving me this opportunity.

Thank you to Dr. Doug Bonn for being an awesome un-official co-supervisor.

Thank you to our post-docs, Agustin Schiffrin and BingKai Yuan, for everything I have learned from you.

Thank you to my lab partner, Katherine Cochrane, for being a great person to do science with and for always having my back.

Thanks to everyone in the LAIR, for your friendship, ideas, and laughs.

Thank you to Arthur Mills, you were a fantastic sounding board for all my post-Masters worries, and I don’t think I could have succeeded with the optical spectrometer experiment if it weren’t for your help. And thank you to Dr. David Jones, for setting me up so well for the next phase of my education!

I am extremely grateful for all the support I had from my family, Rob’s family, and Rob.

Thank you to all of my friends who always stuck around for BBQ’s, roadtrips, and epic breakfasts even though I would disappear for months at a time with a strange work schedule.

This thesis is dedicated to Stephanie Groethe and Kory Campbell. You are missed. Your bright souls bring light to my heart. “Like Honey, hard to get off!”
Chapter 1

Introduction

1.1 Motivation

As the planet heats up [6], so does the search for better, cheaper and more robust solar power technology. Building solar panels from organic semiconductor materials would solve a number of problems inherent to inorganic (often silicon-based) semiconductor devices: organic materials are low-cost, flexible, compatible with high-throughput processing techniques, and have significantly lower embedded energy than their inorganic counterparts. However, organic materials will not be adopted until their cost/kW (which involves conversion efficiency, lifetime, and manufacturing cost) is less than that of inorganic devices. For now, organic devices perform quite poorly when compared to crystalline semiconductor devices: at the time of this writing, a multi-junction InGaP/GaAs/InGaAs cell has an independently confirmed efficiency of 37.9%, while the best organic thin film devices have confirmed efficiencies of about 11% [7]. A critical difference between inorganic semiconductors and organic semiconductors lies in the differing photoconversion mechanisms: a photon absorbed in an inorganic semiconductor generally produces free carriers (electron and hole which move freely through the material), while a photon absorbed in an organic material generally results in the formation of an exciton: an electron-hole pair which remain bound together by the Coulomb attraction.

For organic semiconductor-based devices to have any energy production value, the excitons must be dissociated into free carriers. Dissociation can occur in the presence of high electric fields, at defect sites, or at the interface between two materials which have mismatched energy levels [8]. C. W. Tang famously demonstrated a two-layer organic photovoltaic cell in 1986 with the basic structure of positive electrode - donor - acceptor - negative electrode [9]. In Tang’s cell, the donor - acceptor organic interface consisted of a 500 Å thick perylene tetracarboxylic derivative layer evaporated
onto a 300 Å thick copper phthalocyanine (CuPc) layer. The interface region in this cell was “crucial” in determining its photovoltaic properties. This is because the interface is responsible for generating free charges: dissociation at the interface consists of charge transfer between donor and acceptor materials [9], [10]. In general, interfacial processes dominate charge generation in excitonic solar cells, and it is these interfacial processes which we seek to understand in this thesis.

The absorption of a photon in organic semiconductors generally results in an exciton rather than free charges for two reasons. First, the electron’s wave function is (relatively) spatially localized over its ‘parent’ molecule; thus the excited electron ends up localized in the potential well of its conjugate hole. Second, the attractive potential well caused by the hole tends to be less well-localized than the electron’s excited-state wavefunction due to low dielectric constants of the material (so charges are poorly screened) [11], [10]. The result is generally a localized Frenkel exciton, mobile but electrically neutral, to first order unaffected by electric fields, with an energy corresponding to the optical bandgap $E_{\text{opt}}$ of the parent molecule.

If the exciton can diffuse to then dissociate at the boundary, why are organic photovoltaic cells so much less efficient than inorganic? There are a number of reasons. One is that an exciton produced in the ‘bulk’ can only diffuse so far. Another is that excitons which reach the boundary do not always result in free carriers: there are a number of criteria which must be met first. The energy

\[ E_{\text{opt}} \]

\[ E_{\text{gap}} \]

\[ E_f \]

\[ e^- \]

\[ h^+ \]

**Figure 1.1:** Cartoon depicting the formation of an exciton

\[ E_{\text{opt}} \]

\[ E_{\text{gap}} \]

\[ E_f \]

\[ e^- \]

\[ h^+ \]

\[ \text{Note that even though dissociation can occur at defect sites, we do not focus on this process because dissociation at a defect generally results in one trapped carrier and one free carrier and is less viable for energy production} [11]. \]

\[ \text{[1]} \]

\[ \text{[2]} \]
Energy level schematic for an exciton in the charge transfer state at an acceptor-donor interface. $E_{\text{opt}}$ is the energy of the exciton, $E_{\text{gap}}$ is the bandgap energy of a free electron-hole pair in the bulk, and $E_b$ is the difference between the two: the exciton binding energy.

Figure 1.2: Energy level schematic for an exciton in the charge transfer state at an acceptor-donor interface. $E_{\text{opt}}$ is the energy of the exciton, $E_{\text{gap}}$ is the bandgap energy of a free electron-hole pair in the bulk, and $E_b$ is the difference between the two: the exciton binding energy.

of an exciton, $E_{\text{opt}}$, is less than the bandgap energy of a free electron-hole pair ($E_{\text{gap}}$) in the bulk, and we call the difference between the two the exciton binding energy: $E_b$. It follows that at the interface the band offset must be greater than the exciton binding energy (see figure 1.2). Note the binding energy is usually much greater than $k_B T$ (where $k_B$ is the Boltzmann constant and $T$ is the temperature) for organic materials, so the exciton cannot thermally dissociate.

Once the exciton reaches the donor-acceptor heterojunction it is called a Charge Transfer (CT) state. The CT state consists of a Coulombically bound electron and hole residing on opposite sides of the junction, in either neighbouring or adjacent molecules [12]. The energy of the CT state is generally around 0.5 eV, which exceeds the thermal energy (at ambient conditions) of 0.026 eV [13] [14], thus begging the question: how do the electron and hole manage to get away from each other and become truly free charges (and more importantly, a photocurrent)?

The method by which a CT state overcomes its binding energy to realize true charge separation remains elusive and the subject of some debate. Local molecular ordering/crystallinity (which increases both carrier mobility and wavefunction delocalization) has been shown to have an effect on charge separation at hetero-interfaces [12] [13] [15] with charge delocalization in particular playing a key role [14] [16] as it lowers the Coulombic barrier. The intricate details of the spatial properties...
of the delocalized excited state wavefunction have been shown to play an important role [17], while others have argued that charge diffusion within an energetically disordered medium increases the entropy of the system, and thus underpins charge separation [18]. Local polarization can induce significant energy level shifts at the interface, either inhibiting or encouraging charge transfer states to form in the first place [2]. Vibrational coherence has been shown to play a role [14] [19] [20], and some propose that strong and coherent vibronic coupling between the nuclear and electronic degrees of freedom is what promotes the delocalization necessary to reduce the Coulomb barrier to below the thermal energy [20].

The importance of the local characteristics of the heterojunction drives the desire to take a local view of the system. Scanning probe techniques, with their ability to provide a sub-nanometer view of the electronic and optical properties of a system, are not only powerful but in this case are necessary for expanding our understanding of organic photovoltaic systems.

1.2 Scanning probe techniques and the power of real-space, atomically-resolved measurements

In 1981 Gerd Binnig and Heinrich Rohrer introduced a revolutionary new imaging technology to the world: the Scanning Tunnelling Microscope (STM) [21]. Five years later, Binnig, Quate and Gerber extended the concept to create the Atomic Force Microscope (AFM) [22]. Both the STM and the AFM have become indispensable tools for the materials scientist, the condensed matter physicist, the physical chemist, the biologist, and many more. The STM and the AFM both provide real space information about the structure and electronic states of a surface (or an adsorbate on a surface), from the confinement of surface state electrons [23] to the resolution of the chemical structure of a single molecule [24].

The STM can be used to map out, with sub-nanometer resolution, an approximation to the local density of states (LDOS) via Scanning Tunnelling Spectroscopy (STS). These real-space images of the energy landscape of a surface and its adsorbates are critical for optimizing the heterointerfaces in organic photocells: one can see with exquisite precision how subtle changes in molecular configura-
Figure 1.4: STM constant current image (11nm², I=5pA, Vb=-0.5V, T=4.3K) of CuPc and PTCDA clusters on NaCl(2ML)/Ag(111). The CuPc images here as a ‘cross’. The edge of the NaCl island is clearly visible with right-angled lines.

...tions and conformations not only affect the spatial characteristics of the molecular orbitals, but also how changes affect the relative energy levels between individual molecules. When imaging with AFM, one can determine exactly how two molecules on a surface are positioned both with respect to the substrate and to each other with atomic precision. Kelvin Probe Force Microscopy (KPFM), another type of scanning probe microscopy, can be used to map out parameters related to the charge distribution (the local contact potential difference) in the system under study, a critical piece of information when trying to determine how conformation and configuration affects charge transfer [25].

In addition to the direct measurements offered by scanning probe devices, one can simultaneously obtain complementary information by introducing optical measurements. The tip and concomitant tunnelling current act as a very local source of hot electrons; which, when tunneling inelastically through the sample into the substrate, emit photons which can be detected, counted, and spectrally resolved. This Scanning Tunnelling Luminescence (STML), as it is often called, can be used to elucidate the vibrational energy levels of a single molecule [26] or to gain insight into coherent dipole-dipole coupling in real space [27]. This technique is particularly important since a number of studies have pointed to the pivotal role vibronic quantum coherence may play in enabling or preventing charge separation in both biological and synthesized inorganic light harvesting systems [28], [16], [19], [14], [29]. In addition, STML can be used to visualize excitonic coupling spanning several molecules [27], which is crucial for charge transfer [30]. Finally, one can probe the sample...
in an excited state by coupling illumination into the tip-sample junction and imaging the charge distribution via KPFM [25].

1.3 Molecular acceptor-donor pair: towards an understanding of charge transfer in an organic electronic device

In this thesis, we look exclusively at a model acceptor-donor molecular system: small clusters of Copper (II) Pthalocyanine (CuPc) and 3,4,9,10-Perylene Tetracarboxylic Dianhydride (PTCDA) adsorbed on NaCl on metal (Ag(111) and Au(100)) substrates. Using these prototypical and often-studied molecules (and harkening back to Tang’s seminal paper) we have explored in depth one particular configuration, composed of a single acceptor and donor molecule adjacent to each other\(^2\), in which we have developed a molecular scale picture of the electronic states and performed proof-of-concept experiments coupling light into and out of the tunnelling junction. From here we can begin to piece together how the spatial configuration of individual molecules, with respect to both the substrate and other molecules, affects exciton creation and dissociation.

\(^2\)Using small clusters like this allows us to eliminate the complications introduced by the exciton diffusion length [31], and with a configuration this small we can to first order ignore the exciton motion itself [32] as well as have some hope that the system can be treated in an ab-initio theoretical framework.
Chapter 2

Experimental techniques

In this chapter, we review the basic theories behind the experimental techniques used in this thesis.

2.1 Scanning tunnelling microscopy

The STM employs quantum tunnelling and precision mechanical control of a conducting tip to map out, in real space, the electronic properties of a material. The core of the general apparatus consists of a conducting tip held very close (5-15 Å) to a conducting sample. At this distance, the electron wavefunctions of the tip and sample can overlap significantly, such that electrons can
Figure 2.2: STM image of two different configurations of CuPc and PTCDA on NaCl(2ML)/Ag(111) (5x5nm\(^2\), \(I=5\)pA, \(V_b=-0.5V, T=4.3K\)). The CuPc is imaged as a ‘cross’ here. Note the PTCDA images differently depending on its location with respect to the CuPc.

A bias is applied between the tip and the sample so that a single direction of electron tunnelling is favoured, giving a measurable net current. The current is amplified and transduced into a voltage. The tip height and position are controlled by a piezodrive, which can precisely position the tip in space with sub-nanometer resolution. If the tip height is held constant (known as constant-height operation), then the current is plotted as a function of \(x\) and \(y\). Generally, it is preferable to use a feedback loop to keep the tunnelling current constant by adjusting the tip height (known as constant current operation), and in this case the tip height as a function of \((x,y)\) is plotted. The tip height is measured against a calibration where a certain voltage corresponds to a given height. The result is a sub-nanometer resolved contour plot of the equal current tunnelling surface (see Figure 2.2) [33].

In addition to constant-current (or constant-height) imaging, one can obtain an approximation to the LDOS via STS, which is explained in more detail in section 2.1.2. In an STS measurement, the tip is held at a constant location in \((x, y, z)\) and the voltage is swept. The resulting current is recorded as a function of voltage. Doing this at each \((x, y)\) location (pixel) in an image results in a 3 dimensional image in \((x, y, E)\) which can then be processed numerically to obtain an approximation to the local density of states.

The STM apparatus used in this thesis is held inside an ultra-high vacuum (UHV) chamber to prevent the introduction of impurities which could confound the measurement, and is kept at low temperatures (4.3 K) both to cool the molecules such that they will adsorb securely and won’t move on the surface, and to improve energy resolution when taking STS measurements. In addition, because mechanical noise is very undesirable (see sec 2.1.1) the entire apparatus is kept in a carefully-designed ultra-low vibration facility.

Unfortunately, finding an accurate analytical relation between the measured quantity (the tunnelling
current) and the relevant physics of the sample (say, the LDOS) is not entirely straightforward. It follows that the interpretation of the images one obtains with the STM requires some careful consideration of the apparatus, the physics involved, and the system under study.

2.1.1 The tunnelling current

The tunnelling current is often given to be approximately proportional to the integrated LDOS. This loose equivalence, first described by Tersoff and Hamann, is derived from Bardeen’s transfer Hamiltonian approach to tunnelling with additional approximations added in [33], [34], [35], [36]. Analytically, this model only holds for the simplest (free-electron-type) metal surfaces, and once one is imaging with atomic resolution or even just at ‘large’ biases (roughly $\geq |2| V$) this model no longer holds (because the approximations made to obtain it are violated). In practice, this model is actually remarkably useful with more complex systems (like semiconducting surfaces or single molecules), despite its limitations.

For anything but the simplest metal surfaces imaged at low bias, a more careful exploration of the theory is warranted. One should be forewarned that there is still considerable debate about a number of issues with STM (and AFM) imaging, and that there remains much work to be done before we have a truly complete theoretical framework for the apparatus. Nevertheless, considerable work has been done to advance our understanding of the physics at play, and it pays handsomely to consider what we do know before continuing on to discuss our results.
The systems explored in this thesis consist of a double-barrier tunnelling junction with a ‘semiconducting’ sample (the molecules) sandwiched between the barriers. The theoretical work we will review in this section was been done with the presumption of a single barrier tunnelling junction with a free-electron metal sample and tip. More complex models are beyond the scope of this thesis.

The most commonly used tunnelling theory is Bardeen’s transfer-Hamiltonian approach which was reformulated for the STM by Tersoff and Hamann [34], [35], [36]. It has been pointed out that it is not possible to deduce Bardeen’s theory “firmly from first principles”, and that Bardeen’s model is not sufficient to treat many body effects properly [37].

The most rigorous and complete description of tunnelling theory comes from Feuchtwang and Caroli et. al [37], [38], [39], [40], [41], [42]. In addition to being the most rigorous, these theories can handle electron-electron and electron-phonon interactions if desired. Feuchtwang and Caroli’s formalism is used in principle by theorists who model STM measurements, however there is to date no known way to utilize their formalism to invert experimental data to get a desired quantity like the LDOS. Because of this, the transfer-Hamiltonian approach of Bardeen/Tersoff and Hamann remains the ‘industry standard’ (for experimentalists).

Because our analysis is based on the transfer-Hamiltonian approach, including our newly-developed normalization schemes (see sec 2.1.2), it is this model which we briefly review in this section. Note that this approach disregards electron-electron interactions, so it cannot reasonably be used for single-electron charging effects which we had hoped to encounter in this thesis. Schulz et al. have recently explored many-body effects inside single molecules via scanning tunnelling spectroscopy, and their theoretical approach points to a reasonable path forward for experimentalists examining such systems [43].

I would urge the interested experimentalist to explore Feuchtwang’s and Caroli et. al.’s models, however, as I think that a careful consideration of their expressions for the tunnelling current will lead to a better intuitive understanding of any STM results the experimentalist may encounter, and will give them some ideas for a path forward when they encounter more complex systems.

The transfer-Hamiltonian approach to tunnelling

This section is a brief summary of Bardeen’s tunnelling theory, with some help from Gottlieb and Wesoloski [44], C-T Chen’s dissertation [45], and Feuchtwang [38]. Feuchtwang in particular provides a very nice overview of Bardeen’s theory in ref. [38] if the interested reader is finding the original somewhat opaque. Bardeen used first-order time-dependent perturbation theory, a ‘trans-

1Apparently, both theories are adaptations of a transport theory due to Keldysh, written in Russian, titled ‘Ionization in the field of a strong electromagnetic wave’ and published in 1964.
fer Hamiltonian’, a ‘separable’ system, and Fermi’s golden rule to derive an expression for the tunnelling current.

To begin, we take the full Hamiltonian for the entire system (tip + sample) to be separable into three parts, namely: $H = H_{tip} + H_{sam} + H_t$ where $H_t$ is a weak perturbation which couples the two subsystems (the tip and sample, which are nearly independent).

The Hamiltonians for the tip and the sample are of the usual form

$$H_{tip} = \sum_l \varepsilon_l c_l^\dagger c_l$$  \hspace{1cm} (2.1)

$$H_{sam} = \sum_s \varepsilon_s c_s^\dagger c_s$$  \hspace{1cm} (2.2)

Where $c_l^\dagger, c_l$ are the creation and annihilation operators for the one particle states which characterize the (unperturbed) tip and sample Hamiltonians (where $\{c_l, c_l^\dagger\} = 0$), and $\varepsilon_l$ is the single particle eigen-energy.

Let $\psi$ be a many-body state of the whole system. Let $\psi_t$ and $\psi_s$ differ in the transfer of the electron from the tip to the sample, and let $\psi_t$ be a solution to the time-independent Schrödinger equation with Hamiltonian $2.1$ but not Hamiltonian $2.2$ and vice-versa. This follows from the assumption that the wavefunction for the quasi-particle $n$ drops to zero on the opposite side of the barrier.

The transfer Hamiltonian which couples the two states has the form:

$$H = \sum_{s,t} T_{s,t} \{c_t^\dagger c_t + c_s^\dagger c_s\}$$  \hspace{1cm} (2.3)

where $T_{s,t}$ is the tunnelling matrix element. This is the probability amplitude to transfer an electron from, say, the tip to the sample. Fermi’s golden rule states that the probability to transition per unit time from an initial state $|i>$ to a final state $|f>$ is given by $P = \frac{2\pi}{\hbar} |<f|H'|i>|^2 \rho(f)$, where $\rho(f)$ is the ‘density of final states’. Assuming that the transition rate for an electron to move from the tip to the sample is given by this rule, and taking both $H_t$ and $H_{sam}$ as perturbations to the ‘tip state’ $\psi_t$
(since $\psi_t$ is not a good solution to $H_{sam}$) we find

$$P = \frac{2\pi}{\hbar} |\langle \psi_s | H_{sam} + H_t | \psi_t \rangle |^2 \rho_s(E) \quad (2.4a)$$

$$= \frac{2\pi}{\hbar} |\langle \psi_s | H - H_{tip} | \psi_t \rangle |^2 \rho_s(E) \quad (2.4b)$$

$$= \frac{2\pi}{\hbar} |\langle \psi_s | H - W_t | \psi_t \rangle |^2 \rho_s(E) \quad (2.4c)$$

where $W_t$ is the energy of the many-body wavefunction $\psi_t$ (obtained after $H_{tip}$ operates on $|\psi_t\rangle$). We recognize that $t \cdot P$ (where $t$ is time) would be our $T$ from eq[2.3]. Also, $P$ as written above is the rate at which electrons in the tip would tunnel into the sample if all the sample states were vacant and all the tip states were full (and the tip DOS is flat) and all of the vacant states were energetically aligned with the full states. To correct for the reality of the situation, we invoke Pauli’s exclusion principle and multiply by the correct fractions of occupied tip states and unoccupied sample states, which are described by the Fermi-Dirac distribution $F_{\mu,T}$. We also account for the fact that a bias is applied when expressing the Fermi-Dirac functions, since the Fermi level of the tip is higher than that of the sample (for a positively biased sample). We reference $E$ to the Fermi level of the sample. Finally, we multiply by the electron charge $e$ and a factor of two (to account for spin) and sum over all energies to get the current:

$$I = \frac{4\pi e}{\hbar} \sum_n \{F_{\mu,T}(E_n - eV)(1 - F_{\mu_s,T}(E_n)) - (1 - F_{\mu,T}(E_n - eV))F_{\mu_s,T}(E_n)\} |\langle \psi_s | H - W_t | \psi_t \rangle |^2 \rho_s(E) \quad (2.5)$$

Note that $F_{\mu,T}$ is the Fermi-Dirac distribution $F_{\mu,T}(E) = \frac{1}{1 + e^{(E - \mu)/k_BT}}$, $\mu_t$ and $\mu_s$ are the chemical potentials of the tip and sample, respectively, $T$ is the temperature, and $k_B$ is Boltzmann’s constant. Multiplying out the Fermi-Dirac distributions, we note that the two ‘cross terms’ cancel:

$$I = \frac{4\pi e}{\hbar} \sum_n \{F_{\mu,T}(E_n - eV) - F_{\mu_s,T}(E_n)\} |\langle \psi_s | H - W_t | \psi_t \rangle |^2 \rho_s(E) \quad (2.6)$$

The sum can be approximated by an integral where instead of $P = |\langle \psi_s | H - W_t | \psi_t \rangle |^2$ we use $T(E)$. $T(E)$ is the average value of $P$ over all sample states whose energy is near to $E$.

$$I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} T(E)f_{1,2}(E,V)\rho_s(E)dE \quad (2.7)$$
Here, \( f_{1,2} = F_{\mu,T}(E_n - eV) - F_{\mu,S}(E_n) \).

There are three things to note here. One, the above expression is only valid for single particle wavefunctions. For the more general interacting system with many-body effects, we should write the tunnelling current in terms of the spectral functions of the two electrodes [46]. Details of this formalism are beyond the scope of this thesis. Two, the actual tunnelling current measured will have its features broadened by roughly \( 3.5k_B T \) (in our case, \( \approx 1.3 \text{ mV} \)). Three, we have assumed a flat (constant) density of states (DOS) for the tip, which is not always true but is a reasonable approximation\(^2\). One should also note that all of this assumes that the tip-sample distance is constant during the measurement. If the tip-sample distance changes, the current magnitude changes exponentially, resulting in a drastically altered measurement of the signal (the tunnelling current). The mechanical stability of the tip-sample junction is thus paramount, and considerable effort is put into minimizing mechanical vibrations of the tip-sample junction. This will be discussed further in Chapter 3.

There are some important limitations to this theory. Some of these limits were pointed out in section [2.1.1] and there are others which we will not discuss here. However, the expression derived from the transfer Hamiltonian approach is still valid within a certain regime and is very useful, both conceptually and as a tool for data manipulation.

Feuchtwang studied the issues with Bardeen’s approach in detail and investigated the validity of the transfer Hamiltonian formalism [38]. Happily, through a more rigorous analysis, he found that an ‘obvious generalization’ (writing the current in terms of the spectral functions of the tip and sample) of Bardeen’s expression for the tunnelling current agreed with his, and found that one can interpret “Bardeen’s matrix element of the transfer Hamiltonian as a pseudopotential representing the boundary conditions at the interface”. Thus, the simple expression we have for the tunnelling current (eq. 2.7) is relevant to our studies\(^3\) and provides an important jumping-off point for analyzing our STS results.

### 2.1.2 Scanning tunnelling spectroscopy

While we have a reasonable expression for the tunnelling current, it’s not terribly useful to the physicist. What we really want is either a real space map of the LDOS at some energy \( E \) or the LDOS as a function of \( E \) at some location. Though we can’t measure the LDOS directly, we can obtain an approximation to it via scanning tunnelling spectroscopy.

\(^2\) The user can alter the tip DOS through pulsing or ‘nano spot-welding’ and can check that it is reasonably flat by taking spectra on a surface with a known DOS

\(^3\) Except, of course, when electron-electron interactions are a concern; then the full many-body spectral function must be considered.
Figure 2.4: Schematic of the energy levels for a metal tip (left) and a semiconducting sample (right). The filled states are in darker colours, while the unfilled states are lighter. The fermi levels are offset by eV. An electron at a given energy in the tip can tunnel into an empty band in the sample if it is available, but it cannot tunnel when there are no states to tunnel into.

An STS measurement proceeds as follows: the tip is moved to a specific location in (x,y) and the feedback loop is turned off (the z height is now constant). The voltage is varied through a specified range at a specified rate, and the current is recorded as a function of voltage at a specified number of points. This can be done at a single point (point spectroscopy) or it can be done at every pixel in an image to create a 3D ‘grid’ of I(V) in (x,y).

As the bias is swept the tip electrons ‘see’ more states that they can tunnel into. For a sample with features in the density of states (like a semiconductor or a molecule), this means a new tunnelling channel will open up each time the bias becomes large enough for the filled states in the tip to access an empty band in the sample. When the bias is negative, it is the electrons in the sample which tunnel into the tip, with a new channel opening up each time the bias becomes large enough for a new filled band to see the empty states in the tip. In the I(V) curve, one observes a ‘kink’ each time a new tunnelling channel opens up. Taking the derivative makes it easier to visualize the local electronic structure of the sample.

In practice it isn’t quite so simple as taking the derivative and equating that to the local band structure (the LDOS), as detailed above. However, STS point spectra or 3D grids do allow us to extract an approximation to the LDOS. The procedure for this extraction is detailed below.
Obtaining approximations to the local density of states from scanning tunnelling spectroscopy

In this section we mostly follow Koslowski et al. [47]. We then test their method on our data and find that their correction term is not needed, but their general derivation remains useful.

We begin with eq. 2.7, and add one small modification:

\[ I = \frac{4\pi e}{h} \int_{-\infty}^{\infty} T(E,V) f_{1,2}(E,V) \rho_s(E)dE \]  

(2.8)

In this case, T(E,V) has been modified to include a voltage dependence. As before, we are taking the energy with respect to the Fermi level of the sample. In some cases, the DOS in eq 2.8 above should be weighted to reflect potential selectivity of tunnelling in k space.

Applying the one-dimensional WKB approximation plus a trapezoidal approximation, we have a bias-dependent transmission coefficient

\[ T(E, V) = e^{-z\sqrt{\Phi + V/2 - E}} \]  

(2.9)

where \(\Phi\) is the effective barrier height, \(V\) is the applied voltage, and \(E\) is the energy. If we take the derivative of the tunnelling current with respect to \(V\) we obtain

\[ \frac{\partial I}{\partial V} \approx \rho_s(V) T(E = V) - \int_{-\infty}^{\infty} \rho_s(E) T(E,V) f_{1,2}(E,V) \frac{z}{4\sqrt{\Phi + V/2 - E}} dE \]  

(2.10)

Where the equivalence is approximate rather than exact since we approximate \(\frac{\partial f_{1,2}}{\partial V} \approx \delta(E - V)\). It is common to neglect the second term here, and assume that \(T(E, V)\) is featureless, giving \(\frac{\partial I}{\partial V} \approx \rho_s(V)\). However, Koslowski et al. claim that the second term is comparable to the first and should not be neglected.

We then apply the generalized mean value theorem for integrals (setting the mean value to \(\frac{z}{4\sqrt{\Phi}}\)) and find

\[ \frac{\partial I}{\partial V} \approx \rho_s(V) T(E = V) - \frac{z}{4\sqrt{\Phi}} I(V) \]  

(2.11)

We solve for the LDOS to obtain

---

\(^{4}\)At least for the tunnelling conditions explored in this thesis.
\[
\rho_s(V) \approx \frac{1}{T(E = V)} \left( \frac{\partial I}{\partial V} + \frac{z}{4\sqrt{\Phi}} I(V) \right)
\]  \hspace{1cm} (2.12)

If one has both an I(z) grid and an I(V) grid, one can extract all the parameters needed to solve this equation (using \( z \) as given by the topography). In our case, we only have a few I(z) grids. To proceed, we use an averaged \( \Phi \) for each molecule from the I(z) grids we do have and implement eq 2.11 numerically (with the averaged values of \( \Phi \) and \( T \)) to obtain our LDOS. For STS grids obtained on isolated PTCDA and isolated CuPc molecules we implemented the Koslowski scheme for obtaining \( \rho \) and compared it to the results obtained by taking simply \( \frac{\partial I}{\partial V} \). We found that there was no effect on the location of the peaks. The only effect seen with the Koslowski implementation was one of vertical scaling. Figures 2.5, 2.6, 2.7, and 2.8 show the results. Given the nature of these results (in terms of introducing the Koslowski correction term vs not) for the data explored in this thesis\(^5\), the analysis of STS data was done by taking \( \rho \propto \frac{\partial I}{\partial V} \). Note that in Equation 2.12 there is a factor of \( \frac{1}{T(E = V)} \) out front. Even if we neglect the second term, the \( \frac{\partial I}{\partial V} \) term should take this into account. Commonly, \( \frac{1}{T(E = V)} \frac{\partial I}{\partial V} \) is approximated by \( \frac{\partial I}{\partial V} / I \). Because our data shows both negative differential resistance and noise near 0, dividing by \( I \) introduces infinities where \( I \) crosses 0. This in turn can be solved by instead dividing by \( I^T \), where \( T \) is some constant, but in this thesis we will use simply use \( \rho \propto \frac{\partial I}{\partial V} \).

\(^5\)In addition, because the majority of the STS grids collected don’t have an accompanying I(z) grid, our implementation of this scheme would have been less than ideal in any case.
Figure 2.5: Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated CuPc molecule stabilized at the corner of a trilayer step. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$.
Figure 2.6: Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated CuPc molecule stabilized at the corner of a trilayer step. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 
Figure 2.7: Comparing the Koslowski normalization scheme to plain $\frac{\partial I}{\partial V}$ for an isolated PTCDA molecule. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 
Figure 2.8: Comparing the Koslowski normalization scheme to taking only $\frac{\partial I}{\partial V}$ for an isolated PTCDA molecule. Plots shown are the average over the individual spectra taken inside the area delineated in red as shown in the topography image. The peaks for the Koslowski method are in the exact same location as those obtained by taking only $\frac{\partial I}{\partial V}$. 
2.2 Atomic force microscopy

Figure 2.9: Schematic of the AFM. The electronics are left out for simplicity. A piezo drive controls the position of the probe tip, as before. A tip is placed on an oscillating cantilever, and tip-sample interaction forces change the resonant frequency of the cantilever. The frequency shift is taken as the imaging signal.

Early in the development of the STM it was realized that relatively strong forces act between the probe tip and the sample [48]. This observation led Binning, Quate, and Gerber to develop a microscope based on the detection of these forces: the AFM. The modern AFM detects forces as small as $10^{-18}$ N between the probe tip and the sample via frequency shifts in an oscillating cantilever [22], [49]. The cantilever has a small, STM-like tip attached to it which acts as the probe\(^6\). The resulting real-space map of the force (or some function of the force) between the tip and sample reveals a surprising amount of physics, such as the chemical structure of a single molecule, the bond order of individual bonds, or the charge state of a single atom [24], [50], [51]. In this thesis, our AFM uses a self-detecting sensor, the qPlus quartz tuning fork, and operates in non-contact frequency modulation mode.

2.2.1 Frequency modulation atomic force microscopy

In non-contact frequency modulation mode, pioneered by Albrecht et al, a constant-amplitude oscillator’s resonant frequency will shift as the tip is exposed to different forces while it scans across the surface [49].

\(^6\)In our system, we use an STM-like tip. In other systems, one can have a microfabricated cantilever with an integrated tip at the end.
In this mode, a cantilever is excited by a mechanical actuator to oscillate on resonance \( (f_0) \). It is kept oscillating on resonance at a specific amplitude through controlled positive feedback. The sensor detects its own deflection (through piezoelectricity\(^7\)), and this signal is phase-shifted and amplitude-controlled then sent back to the actuator\(^5\). Any change in the force gradient \( \partial F / \partial z \) causes a change in the oscillator frequency by \( \Delta f \). A phase-locked loop determines the oscillation frequency \( f = f_0 + \Delta f \), and the frequency shift \( \Delta f \) is the imaging signal.

Let us consider the relation between the imaging signal and the force acting on the AFM tip. If we consider the cantilever to be a 1D harmonic oscillator, then the free oscillation frequency \( f_0 \) is given as

\[
\frac{1}{2\pi} \sqrt{\frac{k}{m^*}}
\]  

(2.13)

where \( m^* \) is the effective mass of the cantilever and \( k \) is the spring constant. A force acting on the tip changes the effective spring constant by some value \( \delta k \), so we find a new resonant frequency

\[
f = \frac{1}{2\pi} \sqrt{\frac{k + \delta k}{m^*}}
\]  

(2.14)

if \( \delta k = \partial^2 V / \partial z^2 = -\partial F / \partial z \) is constant over the whole range of the oscillating cantilever. If it is also true that \( \delta k \) is small compared to \( k \) (the small-amplitude approximation\(^8\)), we can expand the square root in a Taylor series and obtain

\[
\Delta f = f_0 \frac{\delta k}{2k}
\]  

(2.15)

This looks nice, but what if the force is not constant over the oscillation amplitude range? There are a few options for calculating \( \Delta f \) in this case. The most common path forward is to use first order perturbation theory and the Hamilton-Jacobi approach\(^5\). This leads to a rather complex expression, which is simplified via integration by parts. The result is rather intuitive\(^4\):

\[
\Delta f = f_0 \frac{\delta k(z)}{2k}
\]  

(2.16)

where

---

\(^7\)The deflection of the quartz cantilever produces charge at the electrodes on the surfaces of the two prongs. This can be detected electrically to give the deflection signal.

\(^8\)The qPlus sensors we use are generally safely in the small amplitude regime.
\[ <\delta k(z)> = \frac{1}{A^2 \pi/2} \int_{-A}^{A} \delta k(z - q') \sqrt{A^2 - q'^2} dq' \]  

(2.17)

where \(A\) is the amplitude and \(q\) is the deflection of the cantilever. Note that eq [2.16] is almost the same as eq [2.15] except that \(\delta k\) is replaced by a weighted average \(<\delta k>\).

### 2.2.2 The forces acting on the tip

As always, the (negative) gradient of a potential gives a conservative force. Since there is a potential \(V\) between the tip and the sample in an AFM, we can take the \(z\) component of the gradient to find the \(z\) component of the force between the sample and the tip: \(F_z = -\partial V/\partial z\). This is then related to a tip-sample spring constant \(k = \partial F/\partial z\). The force which the AFM measures is a sum of contributions from a number of sources. In UHV, we can reasonably limit our consideration to 3 contributions: the Van der Waals force, the electrostatic force, and the chemical force [48], [54].

The Van der Waals force is caused by fluctuations in the electric dipole moment of an atom interacting with an induced dipole moment in another atom. For a spherical tip of radius \(R\) at a distance \(z\) from the surface we can express this force as [55]:

\[ F_{vdw} = -\frac{Hr}{6\varepsilon^2} \]  

(2.18)

Where \(H\) is the material-dependent Hamaker constant, \(r\) is the tip radius, and \(z\) is the distance between the tip and the surface. Note that the Van der Waals force goes like \(z^{-6}\) for two atoms separated by a distance \(z\), while the expression above is for two macroscopic bodies; in this case, the tip and sample with the tip modelled as a sphere [48], [54]. For a pyramidal and conical tip model, a \(1/z\) force law is found [53]. The Van der Waals force is always attractive, and is often quite large.

The electrostatic force is self-explanatory. When one has a conductive tip and conductive sample, the system can be regarded as a capacitor with a distance-dependent capacitance \(C(z)\). In this case, the electrostatic force is given by

\[ F_{es} = \frac{1}{2} \frac{\partial C}{\partial z} \left( U_{DC} - \frac{\Delta\phi}{e} - \frac{\Delta pol}{e} \right)^2 \]  

(2.19)

\(^9\)In the small amplitude limit.

\(^{10}\)One should also consider magnetic forces but these are not relevant to the systems and tips under study in this thesis.

\(^{11}\)The force is calculated with the Hamaker approach by making some assumptions about the geometry and integrating over the respective volumes. It is also assumed that the forces are additive and nonretarded.
Where $U_{DC}$ is the applied bias, $\Delta \phi$ is the difference in the tip and sample work functions, and in a polarizable medium (which is relevant for our analysis, since PTCDA and CuPc are polarizable) we have a term describing the charge induced dipole barrier $\Delta_{pol}$ [56], [57], [58]

$$\Delta_{pol} = -\sum \frac{\alpha q_i^2}{8\pi\varepsilon_0 r_{ij}^4}$$

(2.20)

where $\alpha$ is the polarizability of the sample, $q_i$ are the charges in the tip at distances $r_{ij}$ from the $j$th induced dipole in the sample.

Note that (classically, at least\(^\text{[12]}\)) $\frac{\partial C}{\partial z}$ is always negative (and the other factor is squared), so the electrostatic interaction is always attractive. The term $\frac{\partial C}{\partial z}$ depends on the tip geometry, so it cannot be calculated exactly in every case. If we model the tip as a sphere of radius $R$ on a truncated cone, then

$$\frac{1}{2} \frac{\partial C}{\partial z} = -\pi \varepsilon_0 \frac{R}{z}$$

(2.21)

assuming that $z << R$, there is zero contact potential, and the tip is electrically grounded [59]. Note that this expression diverges at 0 thus it cannot be a correct model at close tip-sample distances. Kurokawa and Sakai wrote an excellent review of both the theoretical and experimental work done (up to 1997) on the capacitance of the STM junction in ref [60], and presented their own results exploring the STM junction capacitance in the non-tunnelling regime in ref [61]. In ref [61], they point out that the calculated capacitance of the ‘truncated cone + half sphere tip’ (eq. 2.21) reasonably reproduces their observed C-z characteristics and its dependence on tip geometry, indicating that this model is a reasonable assumption to make and to use in our calculations.\(^\text{[14]}\) In addition, Kurokawa and Sakai point out that even though the capacitance increases with decreased gap distance, the sensitivity $\frac{\partial C}{\partial z}$ decreases with decreased gap distance, so the capacitance does not diverge as $z \to 0$.

The so-called chemical force is generally considered to be a short-range force, and can have both attractive and repulsive regimes. The Lennard-Jones potential is often used to describe the force [63] between a neutral pair of molecules (or atoms) at ‘close’ distances, where ‘close’ means the...
electron wavefunctions in the tip and sample overlap. This is almost by definition the regime of STM/AFM measurements. The Lennard-Jones potential is given as

\[ V_{LJ} = E_m \left[ \left( \frac{z_m}{z} \right)^{12} - 2 \left( \frac{z_m}{z} \right)^6 \right] \]  

(2.22)

Where \( E_m \) is the potential minimum and \( z_m \) is the equilibrium distance. Taking the negative gradient in the \( z \) direction gives us the force

\[ F_{LJ} = 12 \frac{E_m}{z_m} \left[ \left( \frac{z_m}{z} \right)^{13} - \left( \frac{z_m}{z} \right)^7 \right] \]  

(2.23)

Alternatively, one can use the Morse potential to describe the close range forces. Both the Lennard-Jones and the Morse potentials lack anisotropy, so a more complete description of chemical bonding forces is often given by the Stillinger-Webber potential \cite{48}. Discussion of the specific potentials used to explain atomic features in AFM images is beyond the scope of this thesis.

### 2.2.3 Kelvin probe force microscopy

Kelvin probe force microscopy (KPFM), pioneered by Nonnenmacher et al \cite{64}, uses the AFM to measure the local contact potential difference (LCPD) between the sample and the tip. The contact potential difference (CPD) is most easily described with two metals, as in fig 2.10, which is adapted from \cite{3}. When two different metals are electrically connected\footnote{For example, through an external circuit.} but there remains a vacuum barrier between them, the Fermi levels align and electrons flow to the material with the higher work function. The result is a voltage drop \( V' = \Delta \Phi / e \) across the barrier, a positive charge on the material with the smaller work function, a negative charge on the material with the larger work function, and an electrostatic force between the sample and the tip. The CPD can be compensated by applying a DC voltage across the barrier which nullifies the tip-sample electrical force.

The DC voltage required to nullify the force gives the CPD between the tip and the sample. Because the tip is so small at its apex, and because the piezodrive offers precise control over the tip position, with KPFM we call it the local contact potential difference (LCPD). The LCPD can be imaged quantitatively with \(~ 50\) nanometer resolution\footnote{In the FM-KPFM mode.}, offering detailed information about the electronic state of a surface \cite{57}. In practice, instead of applying a DC voltage to nullify the tip-sample force, we determine \( V' \) directly from \( \Delta f(V) \) spectroscopy. Re-examining eq 2.19, we note that the \( \Delta f(V) \) spectrum is parabolic and peaks at \( \frac{\Delta \phi}{e} - \frac{\Delta \text{pol}}{e} \). If there is no polarizability term, then the LCPD is
Figure 2.10: Energy levels of the sample and tip in three cases: 1) tip and sample separated by
gap with no electrical contact, 2) tip and sample are in electrical contact, and 3) an external
DC bias is applied to cancel the CPD and the tip-sample electrical force. $E_{\text{vac}}$ is the vacuum
energy and $E_F$ are the fermi levels. Adapted from [3].

given as the maximum of the $\Delta f(V)$ spectra. With a polarization term, however, the fit is slightly
more complicated - one must first obtain an estimate for the polarizability term before fitting the
parabola to find the estimated LCPD.

Perhaps most importantly, KPFM can be sensitive to the charge state of a surface, making it the
perfect tool to image real-space charge transfer between two molecules. Adding a single electron
to an atom can increase the force on the AFM tip by a few piconewtons. With the addition or
removal of an electron, the LCPD will be shifted either up or down depending on the sign of the
charge. Given that sub-molecular contrast in charge distribution has been observed [51], it should
in principle be possible to image a change in charge state over a single molecule when the molecule
is ‘given’ a charge by an optically excited donor$^{17}$.

2.3 Scanning tunnelling microscope induced luminescence

Scanning tunnelling microscope induced luminescence (STML) measurements merge the sub-nanometer
resolution of the STM with photon collection from the tunnelling junction to produce atomically-
resolved optical images of the sample.

In 1976 J. Lambe and S. L. McCarthy discovered a new way to generate light [65]. Working at
Ford Motor company at the time, the two scientists were exploring metal-insulator-metal tunneling
junctions with very thin oxide layers ($\simeq$ 30 Å). If a voltage was applied to the junction they
noticed visible light emanated from the entire junction. They interpreted the effect as one of inelastic
tunnelling exciting optically coupled surface plasmon modes.

$^{17}$Or, conversely, when an optically excited donor loses a charge.
With the invention of the STM, it was quickly noticed that a similar tunnelling barrier was present, only in this case with a very sharp counter-electrode, so luminescence should in principle be possible to observe. It is indeed.

In STML, the tip acts as a very localized source of hot electrons. When those electrons tunnel inelastically into the sample, they excite a localized surface plasmon (LSP) which can decay radiatively [66]. Collecting the photons emitted from the tunnelling junction gives the user clues about the optical properties of the system under study. Photon information can be collected at each pixel in a topographic image, giving the user optoelectronic information with sub-nanometer resolution.

The photons collected can be either counted to give an intensity map or spectrally resolved to give a 3D spectral grid \((x, y, h\nu)\). Obtaining photon maps like this is quite difficult due to the low quantum efficiency of photons produced by tunnelling electrons: \(\sim 10^{-5} \text{ to } 10^{-3} \text{ photons per electron} \) [67], [68], [66]. With typical tunnelling currents in our system on the order of \(100^{-12} \text{ A} \) (at best), and assuming \(10^{-5} \text{ photons/electron} \), one could expect

\[
100^{-12} \frac{C}{s} \cdot 6.242 \cdot 10^{18} \frac{e}{C} \cdot \frac{10^{-5} \text{ photon}}{e} \approx 600 \text{ photons/s}
\]
but due to geometrical considerations (we only collect a small solid angle of the total light emitted, which is assumed to be a point source) and the transmission efficiency of the windows, mirrors, and lenses in the beam path, we can only expect to collect about 5% of the photons emitted. This leaves us with **only $\sim 30$ photons per second!** If we can instead assume a quantum efficiency of $10^{-3}$ photons per electron, we can expect 3000 photons per second. All of this makes obtaining data with a reasonable signal to noise ratio difficult. The photon count can be increased by increasing the tunnelling current, which is undesirable with our samples\footnote{Stable imaging of molecules adsorbed on NaCl is usually constrained to the 2 pA, 0.5-3 V regime. Increasing the tunnel current to even 50 pA tends to result in disturbed molecules which move on the substrate, or the tip picking up molecules and crashing/becoming unstable.}, or, when taking spectrally-resolved data or using a photon-counting-type photomultiplier tube (PMT), increasing the collection time at each pixel. Of course, background noise (in this case stray photons) becomes a serious concern with long integration times - so care must be taken to ensure that ambient conditions are very dark.

The tip plays a critical role in the generation of luminescence from the tunnelling junction. The tip-sample junction forms a plasmonic nano-cavity, and resonance in this cavity can enhance the radiative decay rate by *three to five orders of magnitude* \cite{69}. Given the low efficiency per tunnelling electron and the low currents needed to image molecules on a thin insulating layer, achieving this kind of resonant enhancement is critical for successful imaging. Chen *et al* argue that that the plasmonic nanocavity enhances the radiative decay through plasmon enhanced vacuum fluctuations, not through a stimulated emission process \cite{69}. Because the LSP depends on the detailed geometry of the tip-sample junction, tip changes can have drastic effects on the light emission - for better and for worse \cite{66}. In addition, the dielectric properties of the tip will affect the radiative decay - tips which are fabricated from a lossy material in the wavelength range of interest will quench the photon emission. It has been shown that silver (Ag) and gold (Au) tips achieve an order or magnitude better emission than tungsten (W) tips in the relevant wavelength regimes for systems so far studied \cite{70}, \cite{71}. This is because both Ag and Au have a small imaginary component of their dielectric constant in the visible \cite{72}, \cite{73}.

There remains considerable debate surrounding the exact physical mechanism behind luminescence from supported molecules in the STM junction \cite{69}, \cite{74}, \cite{75}. Possible models which could explain our results are discussed in Chapter 5.

In our experiment, a lens was installed at the focal distance away from the tip-sample junction. This lens collimates some subset of the total emitted luminescence, and sends the beam out of the vacuum (through the windows in the heat shield and the chamber) and onto a tip-tilt mirror. The beam is then either a) directed into a second lens and focused on the slit of a spectrometer, or b) directed onto the active area of a PMT. The signal from either the PMT or the spectrometer was then collected simultaneously with topography data from the STM. See Section 3.3 for more details
of the experimental set-up.

2.4 Optical excitation

In addition to collecting light from the junction it is possible to couple light into the junction. We have done so in this thesis using simple solid-state diode lasers and a tip-tilt mirror mounted on the chamber flange to direct the laser. The lens inside the vacuum focuses the light onto a small spot, ≃ 20µm, which is much larger than the tunnel junction but serves as a reasonable concentration of the signal. Our goal is to see if molecular acceptor-donor pairs can be excited optically to induce charge transfer between the molecules. The results will be determined with KPFM while STS will also be recorded to look for additional signatures of excitation and charge transfer.
Chapter 3

Experimental setup

In this chapter, we review the experimental set-up in detail.

3.1 Scanning probe system

All of the measurements in this thesis were performed with a commercial low-temperature UHV STM/AFM. The Omicron STM/AFM has a base temperature around 4.3K\(^1\) a base pressure below \(5 \cdot 10^{-11}\) mbar, and optical access to the tunnelling junction. The system is housed in an ultra-low vibration facility and sits on a 36 ton concrete block which ‘floats’ on pneumatic isolators.

3.1.1 Ultra-low vibration facility

Our UHV STM/AFM system is located in an ultra-low vibration facility in the basement of the Advanced Materials and Process Engineering Laboratory (AMPEL) building (the ‘main’ building). Each instrument in our facility is housed in its own ‘pod’, a building-within-a-building designed to protect our instruments from external mechanical vibrations. Each pod contains a large concrete block (often called an ‘inertia block’) which ‘floats’ on pneumatic isolators which themselves rest on an isolated foundation\(^2\). The Omicron’s pod, which we call ‘omegapod’, houses the Omicron STM/AFM. The system sits directly on the inertia block - a second set of pneumatic isolators sits under the Omicron’s table, but a small study performed by looking at the noise in the tunnelling junction showed that using only the isolators under the inertia block and the internal damping stage provided the best vibration isolation. Each pod is surrounded by a double-walled enclosure. The

\(^{1}\)All of our measurements were taken at 4K, but the system will image at 77K and at room temperature as well. In addition, a heating stage in the STM head allows for sample heating above the base temperature while the cryostat is cold.

\(^{2}\)The foundation of each pod is connected to the surrounding building only indirectly through the earth.
inner walls are either reinforced concrete or concrete block anchored to the foundation of the pod and the outer walls are concrete block anchored to the main building’s foundation. Acoustically absorptive material is placed in between the walls to further damp any vibrations transmitted between them. Access to the pods is through a double set of acoustic doors, and suspended aluminum decks act as the floor where there is no block. The pods communicate electrically with the surrounding building via small feedthroughs in the walls which cables are led through. After all the cabling is fed through to the main building, the remaining space in the feedthroughs are plugged with foam. B. MacLeod describes the facility in detail as well as studies of its vibration isolation capabilities in his thesis [76]. Our instrument control unit is housed in the main building. This unit in turn communicates with a computer in the control room, where users control the microscope remotely. Inside the microscope, additional vibration isolation is achieved by a) suspending the whole STM/AFM stage from 3 springs, and b) an eddy current damping stage.

3.1.2 Omicron UHV STM/AFM

The UHV system, shown in fig. 3.1, consists of two main chambers separated by a gate valve: the prep chamber and the low temperature (LT) chamber. Almost all sample preparation (sputtering, annealing, and NaCl deposition) is done in the prep chamber. This keeps the LT chamber very clean and the base pressure very low ($\approx 10^{-11}$ mbar). The molecules in this thesis were deposited onto the substrate at 4K, so this deposition is done in the LT chamber from an Organic Molecular Beam Epitaxy (OMBE) cell (Kentax UHV equipment). The LT chamber houses the bath cryostat and the scanner head, and this is where measurements are taken. In fig. 3.1 a) the prep chamber is on the left side of the photo and the LT chamber stands tall on the right side. The height is due to the cryostat. The cryostat is a liquid helium bath cryostat with a liquid nitrogen shield. The scanner head is thermally connected to the cryostat through thermal braids, and is generally at $\approx 4.3$ K during measurements.

The system is baked after any venting to 150 C for at least 60 hours to ensure a low base pressure. Both the prep and the LT chambers are pumped with individual ion getter pumps and titanium sublimation pumps. The prep is additionally pumped with a turbo-molecular pump (backed by a dry scroll pump) during sputtering and annealing. The sputtering is done with Argon leaked into the chamber which is ionized then accelerated with an LK Technologies sputter gun. The samples are annealed with an e-beam heating stage with built-in temperature PID control. NaCl is thermally evaporated onto our metal substrates using a home-built Knudsen cell (built by the author, see appendix A) mounted on the prep chamber.

Samples and tips are exchanged through a high vacuum load lock, which is pumped by the same

---

3 Omegapod has 3 reinforced concrete inner walls and one concrete block inner wall due to construction constraints.
Figures 3.1: Photographs of our system. a. The Omicron STM/AFM in its ‘pod’, without the optical components. The cryostat stands tall. b. Front view of the UHV system. The LT chamber is on the left and the prep chamber is on the right. c. The scanner head showing the optical access without the lens tube installed (indicated with white circle and red arrow) and the fins for eddy current damping. d. The scanner head with no tip or sample as seen from the sample access side. e. The system as seen in a) but with the optical table installed (indicated with the red arrow). Detailed location of the optical table and components with respect to the Omicron LT chamber can be found in the 3D model. See Section 3.3 for more information about the placement and assembly of the optical table.

turbo-molecular pump and scroll pump as the prep chamber. Samples are brought through the prep chamber via a magnetically coupled transfer arm, and placed into a carousel in the LT which can hold up to six samples or tips. Coarse motion is achieved through a stick slip drive. Tips are approached to the sample automatically using a piezodrive and a feedback loop, and samples are placed into the scanner head in the LT chamber via a wobblestick. The tip is moved with respect to the sample (for scanning and small movements) via a piezotube. At 5 K the piezosensitivity in $x$ and $y$ is 3.6 nm/V, and in $z$ is 1.2 nm/V.

3.1.3 Optical access in the scanning probe system

The Omicron STM/AFM offers optical access to the tip-sample junction. Figure 3.2 shows the main optical paths to the junction as seen when looking in on the wobblestick side. In this view, the left side is used to mount a camera with zoom lens for coarse tip approaches and sample transfers. The right side contains the lens and is the path we use for optical excitation and collection.
Figure 3.2: Photo of the scanner head indicating the optical paths available. The right path is the one used for optical collection and excitation: our lens was placed on the right at a distance of approximately 18mm from the tip-sample junction. The left path is used in conjunction with a camera to visualize tip and sample transfer as well as coarse tip approaches. The central path is the one used by the experimenter when transferring samples (or tip carriers) into and out of the head.

A planoconvex 10mm diameter sapphire lens (Melles-Griot PXS-10.0-15.4-S) is situated about 18 mm from the tip-sample junction in the STM scanner head. This lens has a back focal distance of 18.4 mm, a focal length of 20 mm, a radius of curvature of 15.4 mm, an edge thickness of 2 mm, and an f# of 2.0. This allows collection of roughly 5% of the half solid angle above the sample surface, where luminescence will be emitted assuming a point source. It should be noted that the 25° angle is close to the angle of maximum emission from the tip-sample junction, which is situated roughly 30° with respect to the surface [77], [78]. For luminescence, collection losses are due to the geometry just explained as well as the windows in the heat shields, the vacuum chamber, and any optical component encountered along the beam’s path.

The wavelength range accessible to us is currently limited primarily by the windows (viewports) in the heat shields, and secondarily through the viewports in the LT chamber. Photons originating from the tunnel junction pass through two heat shield viewports and one standard viewport before they reach air (where they are then bounced of a silver mirror and pass through other optical components). The in-vacuum viewports (see fig [3.4]) limit our experiments to the wavelength range\(^4\sim350-620\) nm. This is one of the biggest constraints on our system for luminescence experiments.

\(^4\)There is a considerable design tradeoff here: limiting the wavelength range accessible via these windows limits the sample stage’s exposure to radiation, which causes heating. Replacing the current windows with ones allowing access to a broader wavelength range would reduce our liquid helium hold time (which is currently only about 56 hours) and could increase the base temperature of the sample stage (which is currently about 4.3 K).
**Figure 3.3:** Standard viewport transmission curve (kodial design). The 3dB points are at $\sim 310\text{nm} - \sim 2800\text{nm}$. Image courtesy of [4].

**Figure 3.4:** In-vacuum viewport transmission (KG5). The 3dB points are at $\sim 350\text{nm} - \sim 620\text{nm}$. Image courtesy of [4].
3.2 System under study: copper (II) phthalocyanine and 3,4,9,10-perylene tetracarboxylic dianhydride on NaCl on metal surfaces

The system under study in this thesis consists of small clusters of CuPc and PTCDA adsorbed onto NaCl (bi-, tri-, and quad-layer) on either Ag(111) or Au(100).

3.2.1 Substrates: Ag(111) and Au(100) with bi- and tri-layer NaCl

Two substrates are used in this thesis. The first, Ag(111) was chosen for its optical properties - the plasmon resonance should be ~600nm and thus accessible through our heat shield viewports. The second, Au(100) was chosen because it has a larger work function than Ag(111), altering the energy level alignment between the molecules and the underlying substrate.

The Ag(111) sample is a chemo-mechanically polished single crystal (MaTeck). Ag(111) has a hexagonal lattice with a lattice constant of 2.88 Å [79]. Ag(111) also has a Shockley-type surface state at ~-67mV which forms a two-dimensional electron gas at the surface which can be imaged with STM (see Figures 3.6 and 3.5b) [80].

The Au(100) sample is a chemo-mechanically polished single crystal (MaTeck). Au(100) has a 1x5 surface reconstruction of hexagonal geometry on top of the bulk square geometry. The result is a
Figure 3.6: STS spectra showing the Ag(111) surface state buckling of the surface and a characteristic ‘wavy’ appearance (see Figure 3.7) [81].

Figure 3.7: STM images of Au(100). a) Clean Au(100) surface with screw dislocation. b) NaCl islands on Au(100).

Both samples were clamped to Omicron’s sample plates with a molybdenum foil piece. Through holes were drilled in the sample plates, and the foil piece as well as a ‘locator’ piece were cut with a waterjet cutter. The locator piece centers the sample in the correct location on the plate. Details for this sample holder including materials, screw sizes, and Solidworks files are available on the internal LAIR group wiki, under ‘AgHolder’.

36
3.2.2 Sample preparation

The Ag(111) surface and Au(100) surface were cleaned via repeated cycles of $Ar^+$ sputtering and subsequent annealing. Ag(111) was annealed at 770K, and Au(100) was annealed at 700 K.

NaCl powder (TraceSELECT 99.999%, Fluka), was evaporated at $\sim$800 K onto the Ag(111) sample held at 370 K and the Au(100) sample held at 350K resulting in (001) bilayer, trilayer, and quadlayer islands covering $\sim$50% of the surface (see Figures 3.9 and 3.10b).

![Figure 3.8: Images of the sample holder.](image)

**Figure 3.8:** Images of the sample holder.

**Figure 3.9:** STM images of NaCl on NaCl/Ag(111).  
(a) 100x100nm$^2$, $I=20\text{pA}$, $V_b=0.3\text{V}$  
(b) 2x2nm$^2$, $I=100\text{pA}$, $V_b=1\text{V}$
To create the clusters we studied, PTCDA was deposited before CuPc. Both molecules were outgassed in UHV for several hours before deposition. Degas temperatures were ramped up from well below evaporation temperature while watching the pressure in the chamber. Once the pressure dropped, the temperature would be increased until it reached about 50 K less than the evaporation temperature. After the initial degas, one or two ‘fake’ depositions were executed to ensure the molecules were sufficiently clean prior to their actual deposition.

PTCDA (98%, Alfa Aesar) was thermally deposited at 598.15 K onto the NaCl/Ag(111) or NaCl/Au(100) surface held at ∼4.3 K.

CuPc (99.95%, Sigma-Aldrich) was the subsequently thermally deposited at 678.15 K onto NaCl/Ag(111) or NaCl/Au(100) surface held at ∼4.3 K.

Clusters were formed via subsequent ‘high’ temperature annealing of the sample for 2 minutes. This was achieved by removing the sample from the STM/AFM stage and holding it in the wobblestick inside the UHV chamber for two minutes, then re-inserting the sample into the STM/AFM stage. The exact temperature which the sample reaches in this process is unknown.

![STM images of Au(100). a) Clean Au(100) surface. b) Atomic resolution of NaCl on Au(100).](image)

**Figure 3.10:** STM images of Au(100). a) Clean Au(100) surface. b) Atomic resolution of NaCl on Au(100).

---

5To perform a fake deposition, just do everything the same as for a real deposition but don’t open the heat shields.
Figure 3.11: STM images of CuPc and PTCDA on Ag(111).  
(a) NaCl island and bare Ag surface with deposited molecules, before 2 minute room temperature anneal.  
(b) CuPc and PTCDA clusters formed on NaCl/Ag(111) after a 2 minute room temperature anneal.

Figure 3.12: STM images of CuPc and PTCDA on NaCl/Au(100). Both images indicate clearly the positioning of PTCDA with respect to the underlying Au(100) substrate: the PTCDA adsords normal to or parallel to the Au(100) reconstruction. Image b) also indicates the positioning of CuPc with respect to the underlying Au(100) substrate.  
a) CuPc and PTCDA near the edge of a NaCl island.  
b) CuPc and PTCDA near the edge of a NaCl island. Submolecular resolution is visible. Image taken with a PTCDA functionalized tip.
Figure 3.13: STM image of CuPc and PTCDA on NaCl/Au(100). NaCl lattice is visible, indicating the positioning of both CuPc and PTCDA with respect to the underlying NaCl layer. Image taken with a PTCDA functionalized tip.

3.2.3 Tip preparation

In this thesis, we used cut Ag-terminated Platinum-Iridium (Pt/Ir) tips, electrochemically etched silver (Ag) tips and qPlus sensors with electrochemically etched tungsten (W) tips.

The Pt/Ir (Goodfellow, 0.38mm dia) tip preparation is straightforward: the tip is cut and clamped in Omicron’s custom tip holders. Pt/Ir tips were used for STS measurements on the molecular clusters on Ag(111). Pt/Ir tips were prepared by K. Cochrane.

The Ag tips were etched in 40-50% w/w reagent grade citric acid (Fisher Scientific) under an applied 39V AC bias (from a variac) with a cylindrical mesh electrode (counter electrode) surrounding the tip. The negative terminal was attached to the tip and the ground terminal to the counter electrode. The Ag wire (Alfa Aesar, 0.404mm dia, annealed, 99.9%) is covered in teflon tubing except for a 1-2mm length which is immersed in the solution and centered in the counter electrode. The portion of the wire which is not covered by teflon tubing is where the etching occurs. We always used the ‘dropped’ tip from the etching procedure (because etching terminates as soon as it drops), rather than the top half which remains connected to the electrical circuit and continues to etch, dulling it. Tips were imaged under an optical microscope before cleaning and clamping in the tip holder to ensure they were straight and of the correct shape macroscopically. After etching, tips were cleaned in de-ionized water and methanol. Ag tips were used for luminescence collection data. Ag tips were prepared by the author.
The AFM sensors were etched tungsten (Goodfellow, 0.025mm dia, 99.95%) glued to quartz Qplus sensors. AFM sensors were prepared by B. K. Yuan, and instructions below are as described by B. K. Yuan. AFM sensors were used for all KPFM experiments and AFM imaging. The Qplus preparation followed these general steps:

1. Glue one prong of the tuning fork to the substrate on the tip holder with electrically insulating epoxy.
2. Brush electrically insulating epoxy to the end area of the free prong of the tuning fork.
3. Glue tungsten wire to the electrically insulating epoxy with conductive epoxy.
4. Glue a thin gold wire between the tip and the electrode for the tunnelling current.
5. Brush conductive epoxy between the electrode of the tuning fork for collecting the oscillation signal and the corresponding electrode on the tip holder.
6. Etch the tip with KOH (Fisher Scientific, ∼1 mol/L) solution using the meniscus method and a 5V DC bias with the ring electrode negative with respect to the tip.

### 3.3 External optical system

The STM/AFM system was integrated with an external optical system. This integration required mechanical design, electrical design, and coding in Matlab, MATE, and LabView.

#### 3.3.1 Mechanical components

Two primary mechanical components were designed and fabricated: supports to hold the breadboard securely on the Omicron table and the ‘flange optics’ assembly to enable secure attachment of optical components directly to the flange. In addition, a number of mounts and other small parts were made to enable optimal mating of various components.

An accurate model of the LT chamber and the Omicron table was constructed in Solidworks to ensure the correct mating of all mechanical parts. All solid models can be found on the internal LAIR group wiki under ‘Omicron3Dmodel’. A ‘flange optics’ system was designed and fabricated which allows the user to attach a tip-tilt angled mirror as well as other desired components to the flange used for optical access. Aluminum supports were designed to hold the breadboard and other optical components. The breadboard supports were designed to use only the threaded holes already present in the table to prevent any damage which may have occurred when drilling holes in the table, and to allow the table to float freely on its isolators if desired. Because the breadboard
Figure 3.14: Solidworks model of the Omicron.

Figure 3.15: Various views of the optical set-up, used in this case for the spectrometer, as designed in Solidworks. The beam path is highlighted in red.

and spectrometer are themselves quite heavy, and there is a non-negligible chance that the entire assembly will be ‘bumped’ forcefully by the users of the pod in some sort of manner (and because the spectrometer itself is quite valuable and would not survive a fall from the table), the supports were designed with a safety factor of $\sim5$ and are secure enough to withstand considerable abuse.
The breadboard is securely bolted to the supports which are securely bolted to the table, making for a rigid assembly which should maintain the alignment of optics even if the table is disturbed (though temperature changes etc may lead to misalignment for particularly precise set-ups). Recently, the alignment of the beam into the spectrometer was preserved through a cryogen filling cycle, proving the whole assembly is sufficiently rigid to preserve alignment through considerable disturbances.

Figure 3.16: Photo of the STM/AFM with optical components installed

The beam from the sample/tip can be steered into its target via the tip-tilt mirror on the flange, and if present a second tip-tilt mirror and/or a lens mounted onto an $xyz$ stage. The flange is slightly misaligned with respect to the sample, so there is only optical access to the back half of the crystals we used (see fig 3.18). Use of a smaller sample ($<$10mm) will further reduce the area one has optical access to.

The photomultiplier tube was mounted to an off-the-shelf 3-axis translation stage (though only 2 axes are needed) via a simple mounting plate. The lasers were mounted onto the same stage via another simple mounting plate. The spectrometer was placed directly onto the breadboard and two mirrors as well as a lens steered and focused the signal onto the slit.

### 3.3.2 Electrical components

To take simultaneous optical and STM/AFM images, specialized electronic components were built. The specialized electronics are only needed for optical imaging with the photomultiplier tube (PMT) and the spectrometer. No specialized electronics were built for laser radiation. Future experiments could include modulation of the laser power, which may require further electronic design.

---

6Initially, I was concerned that the noise of the shutter opening and closing (which is loud enough to be audible) would disturb the tip. Luckily this is not the case, as far as I can tell, so the spectrometer can be bolted to the breadboard if needed.
Figure 3.17: Photos of the optics integrated with the Omicron STM/AFM. a. Birds-eye view of the optical table and flange optics, b. Close-up view of the beam path going into the spectrometer. c. View of the supports for the optical table, which used only the holes already present in the table and can handle considerable weight and impact.

The PMT used in this thesis (Hamamatsu H9305-04) was powered and amplified by a home-built amplifier/power circuit, loaned to us from another group. There is no known documentation for this circuit, but operation proved relatively self-explanatory. Section 3.3.2 details a more optimal PMT selection and counting circuit which will improve signal quality.
Figure 3.18: Image of the Ag(111) sample, looking in from the camera side (where illumination is coming in from the optics flange). **Left**, original image. **Center**, image with sample outlined with a red oval. Also outlined in red is the tip and the tip’s reflection. **Right**, yellow indicates the image of the optics viewport as seen reflected in the sample (with no optical components mounted on the flange). Yellow demarcates the portion of the sample to which we have optical access. The result is that only the back half of the sample offers optical access.

**Over-voltage protection box**

The PMT’s amplified analog output signal was sent directly to the auxiliary input of the Omicron control unit (CU) via a coaxial cable. Communications with Omicron service engineers revealed that the auxiliary inputs of the CU do not have any over-voltage protection, and a maximum input voltage of ∼+/-10V, so a simple over-voltage protection box was built by Chemistry electronics. This box contains one TVS diode (Littelfuse, SA8.5CA) which is connected across the signal input and ground of the BNC connector. The diode is bi-directional and can clamp the voltage to +/- 10.4 V. The box has a single BNC connector at the output, and from there a short coax can take the signal into the CU.

**Photon counting circuit**

Inside the CU, the PMT signal is digitized via a 16 bit ADC and then can be plotted by the Matrix software at each (x, y) pixel as the STM scans across the surface to create an image of the emission. The PMT used in this thesis produced an analog signal, so one could not drastically improve the signal quality by scanning slower and collecting more photons - scanning slower will simply result in a better average measurement of the light level over the pixel scan time and a slightly cleaner image. In addition, relatively high currents (≥200pA) were needed to see a signal. PMT imaging signal quality can be significantly improved by using a photon counting head instead (recommended choice: Hamamatsu H7828-01 or H10682-01). With a photon counting head, signal amplitude (and thus, signal to noise ratio) can be improved by scanning slowly and collecting more photons at each pixel. This will enable PMT imaging with sensitive samples which can only withstand very low cur-
rents (≈ 1 pA). In addition, because an absolute count can be obtained, quantitative measurements of luminescence can be effectively obtained, which will enable comparisons to theory and point to a better understanding of the physics at play in the STM-induced luminescence process.

All of the necessary details for a photon counting circuit optimized for input to the Matrix CU’s auxiliary input have been discussed with the Chemistry electronics shop, and the circuit can be built as soon as the part number of the photon counting head is confirmed. Figure 3.19 shows the block diagram for the proposed circuit.

**Figure 3.19:** PMT photon counting circuit block diagram

This circuit is ideal for input to the Matrix CU for a number of reasons:

1. The output is analog, which is required for input to the auxiliary channel on the CU (ironically, it will be re-converted back to digital by the CU’s ADC). Off-the-shelf counting circuits from Hamamatsu output a digital count, which will need to be converted to analog before input to the CU, and indexing the count to the pixel scan clock will be difficult with an off-the-shelf option (see next point).

---

7 The count given is the most accurate measure of the number of photons collected given the geometric and material losses.

8 A spectrometer also gives quantitative count numbers, but the PMT simplifies matters by offering a known transmission function which does not depend on changing variables like centre wavelength, etc, and the beam passes though fewer optical components on the way to the PMT than it does on its way to the spectrometer.

9 In addition, the up-front cost to build this circuit is the same as an off-the-shelf option from Hamamatsu which would require post-purchase modifications to work, so the total cost is less.
2. The count is automatically indexed to the pixel scan clock. Every time the tip moves to a new pixel, there is a timing signal (TTL pulse) sent from the CU which will trigger the conversion of the current count to an analog voltage and the beginning of a new count. This will ensure we get the photon count which corresponds to each pixel. This is a very clean way of getting an integrated photon map while imaging.

3. The DAC in the circuit has the same resolution as the ADC in the CU, resulting in maximum resolution in photon counts possible (16 bits).

4. The cabling for routing the timing signal from the CU as well as an isolation box to protect the CU from electronic noise coming from the PMT have already been built and installed.

5. The whole circuit will be ‘plug and play’ so that the user simply needs to connect the PMT to the circuit and the output of the circuit (coax) to the input of the CU\(^{10}\).

6. The circuit will be very well shielded (especially compared to off-the-shelf versions), and will be connected directly to the isolation box (to receive the TTL signal) described in section 3.3.2.

7. The circuit will include an interlock tied to the dark enclosure, protecting the PMT head from accidents where the lights are turned on in the pod during measurement, etc.

8. The circuit will plug into wall power.

The details of the signal flow for the auxiliary inputs can be found in the Matrix Technical Reference manual [82].

**Timing signals**

Both spectrometer imaging as well as photon-count imaging require synchronization with the Matrix CU. This synchronization is achieved primarily through the use of timing signals (TTL pulses) originating from the CU’s central real time controller (CRTC) board. These TTL signals trigger some event in either spectrometer or photon-counting mode. In photon counting mode, TTL pulses trigger the beginning and end of photon acquisition and subsequent conversion of the count to an analog voltage. In spectrometer mode, a TTL pulse sent at the beginning of each pixel triggers the acquisition of a spectrum. The timing signals from the CU are brought to the spectrometer/PMT set-up via the ‘timing signals cable’. This is a DD50\(^{11}\) connector which has the correct pins wired

\(^{10}\)Technically, to the input of the over-voltage protection box.

\(^{11}\)It is common to refer to all connectors of this type as ‘DB’ but the correct generic name is ‘D-sub’ (for D-subminiature). The naming convention for this type of connector uses D as the prefix for the whole series, followed by A, B, C, D, or E denoting the ‘shell size’ (the ‘container’, if you will), and then a numeral indicating the number of
to coaxial lines to carry the desired signals to the isolator box (described in section 3.3.2). The connector is very well shielded, and the pins which are carried on each line are clearly labelled. Currently, the timing signals cable connects to pins 13, 29, and 30:

- Pin 13 is the acquisition clock. This triggers every time at least one channel is acquiring data. This is the signal used for the optical spectroscopy experiments in this thesis.

- Pin 29 is the line trigger. It triggers at the end of each line in a scan. This should be useful for optical spectroscopy collection, to save time writing data to file (currently the bottleneck in terms of time spent per pixel) - the data should be stored in a buffer and only written to file when it sees this trigger.

- Pin 30 is the pixel scan clock. This triggers every time the tip moves, not just when scanning (ie a digital pulse is seen at each pixel while scanning, but also when the scanner walks back to the corner of the scan area after pressing 'stop'). This pin should be used for photon counting.

\[ \text{pins. In our case, the connector is actually a DD50 connector, not a DB50 connector [83].} \]
In the timing signals cable, all pins are referenced to one of the ‘analog ground’ pins in the connector. Other TTL signals are accessible via the CRTC board. Preliminary testing can be done with the breakout board purchased from Winford Engineering, and further lines can be added to the timing signals cable by Chemistry electronics. All TTL pulses are currently 1.25 µs long. The TTL pulse width can be modified if you connect to a web-server on the CRTC board: type 10.0.42.2 for the address in your preferred Web-Browser (on the Omicron computer). Then find the proper trigger and set the time in µs.

Isolation box

Noise isolation is critical with STM and AFM imaging. Connecting anything directly to the CRTC board on the Matrix CU will add 60Hz electronic noise if care is not taken to isolate the CRTC (and CU) from whatever is connected on the other side. Since the timing signals extracted from the CRTC connect to both a noisy digital i/o device, which is powered by a noisy desktop computer (see section 3.3.2) and (in the future) a photon counting circuit, an isolation box was built to protect the CU from unwanted electronic noise. The box was built and designed by Chemistry electronics with consultation from the author. The box is designed to allow the user to extract a timing signal and to connect that signal to any other electronic device without introducing noise from that device to the CU.

The box is placed very close to the CU (in the back of the CU desk, beside the CRTC board) to minimize noise picked up on the coaxial cables running from the CRTC to the box. The box is wall-powered through a 5V adaptor, plugged into ‘dirty’ (beige plug inlet) power.

The box is also ‘plug and play’, the user simply needs to connect their timing signal on the input and output via coax. There are currently 3 ports, so pins 13, 29, and 30 can be used simultaneously to control both spectrometer and PMT imaging modes.

The schematic and board layout for the isolator box can be found on the LAIR internal wiki, under ‘IsolationBox’.

NI USB digital i/o device

To interface the TTL pulses with LabView, a simple digital i/o device was purchased from National Instruments: NI USB 6501. This is by a wide margin the most affordable digital i/o device offered which suits our needs (The NIUSB 6501 costs $150 compared to most DAQ’s which cost roughly a few thousand dollars). The device has 24 digital input and output lines as well as a 32 bit counter. Preliminary testing to verify if the device was ‘seeing’ the TTL pulses from the CU was done with
the ‘Counter - Count Edges’ example VI in LabView.

The NI USB 6501 counter requires a minimum pulse width of 100ns (minimum high = minimum low = 100ns). It runs at USB 2.0 full speed (12Mb/s).

The timing signals from the CRTC (and isolation box) are sent to this device for integration with LabView, which uses them to trigger acquisition of spectra (and in the future writing the data to file) via the optical spectrometer. The screw terminal wiring should be 16 to 28 AWG copper conductor. The screw terminal inputs are single-ended.

### 3.3.3 Photomultiplier setup and alignment

The PMT used in this thesis is a Hamamatsu model H9305-04, which was loaned to us from another group. For PMT measurements, the PMT was bolted to an $xyz$ stage via a small mounting plate. The stage was positioned at the edge of the breadboard nearest to the angled mirror mounted on the ‘optics flange’, and roughly aligned via $xy$ motion. To align the tip-sample junction with the PMT, the image of the PMT as seen in the sample is used. First, the user approaches almost all the way to the sample, using a light shining in from the camera side. Second, the user shines a second light onto the face of the PMT. An image of the PMT will now appear in the sample. The user can then drive the tip so that the tip-sample junction is centered on the image of the active area of the PMT. Note all of this should be done with the PMT **OFF**. Exposing the PMT light levels this high will ruin it.

![Image](image1.png)

(a) Tip and tip reflection visible in Ag(111) sample, with no light shining on the PMT.

![Image](image2.png)

(b) Tip, tip reflection, and PMT image visible in sample (light shining directly on PMT).

**Figure 3.21:** Aligning the PMT. Images show the Ag(111) sample as seen with the camera.

For the PMT used in this thesis, the offset of the power supply/amplifier should be set to about -9.5V so that the PMT signal with no light (dark state) hovers around -9.5V. This will give the user the
entire +/-10 V range of the auxiliary input for any light value above the dark state.

The room must be carefully darkened before using the PMT, otherwise the real signal will be indistinguishable from the background (and the PMT could be ruined). The control rack is darkened via a curtain (blackout fabric from ThorLabs) drawn across the front. Any little blinking lights or other light sources in the room are similarly darkened. A dark enclosure was built to protect the PMT and to improve the signal integrity (and to provide additional safety when using the laser sources). If the photon counting PMT is set-up, the dark box will be connected to an interlock which will power off the PMT head whenever the door of the enclosure is opened.

**Figure 3.22:** Solidworks model of the dark box. The frame is built with aluminum t-slot extrusion and the panels are made from corrugated plastic. The panels are caulked into the frame to prevent light leaks. Note the panels are actually black, but are purple in the model to ease visualization.

### 3.3.4 Spectrometer setup

The optical spectrometer is set up to take both point spectra and optical spectroscopy grids.

To align the spectrometer, the user should follow these steps:

1. If this is the first time the spectrometer has been used in a while, or if the spectrometer has been moved at all, perform both an intensity and a wavelength calibration using *IntelliCal* and the included calibration lamps.

2. To begin, use the same alignment procedure as the PMT: approach the tip very close to the sample using only a light shining in from the camera side. For the spectrometer set-up, the tip needs to be very close to tunnelling ($\leq 100$ steps away from tunnelling). Then, shine a light on the slit and try to line the tip sample junction up with the image of the slit.

3. Install a lens mounted on the $xyz$ stage as shown in figure 3.17b.
4. You no longer need the camera. Move it out of the way and shine the light from the camera side into the middle of the viewport.

5. Use a white card to look at the image coming out of the STM after the lens which is directly in front of the slit. You should see the tip and its reflection, as in figure 3.24.

6. If you do not see the tip and its reflection centered in the circle of light, you need to move the tip. The directions to move on the remote box are exactly backwards from the direction you want to see it go on the card (ie if you want the image of the tip to move left (-x), push right (+x). Similarly, if you want the image to move down (-y) push up (+y)).

7. Once the image of the tip and its reflection are centered in the light spot, align the light spot to the spectrometer slit. Start with the slit open quite wide, and try to make the light spot disappear as you move the \textit{xyz} stage.

8. Once you feel like the coarse alignment is satisfactory, move to the control room and complete the approach (turn off all lights in the room, and darken the room as you would for PMT imaging). Leave the tip tunnelling over a large clean terrace at very high current (100nA). Take a single spectrum to get a reference value (initially, you may want to set the CCD exposure time to 20s).

9. Press ‘backwards’ on the remote control box, so that the tip is no longer tunnelling. Don’t go into the pod with the tip tunnelling! This can ruin a very good luminescence tip.

10. Go into the pod and adjust the alignment by moving the \textit{xyz} stage. Begin by moving the stage...
in the direction which goes across the slit (let’s call this $x$). Each division on the micrometer is $10\mu m$, so pick an appropriate step size. For example for a $250\mu m$ wide slit, $50\mu m$ steps are reasonable. Iterate by moving the stage one step, exiting the pod, re-approaching, and taking a spectrum. You should see the signal decrease as you move one direction, then increase and decrease again as you move the opposite direction.

11. Once you have found the maximum in the $x$ direction, position the micrometer there and take another reference spectra. Now iterate by moving the $xyz$ stage in the $y$ or $z$ direction.

12. Again, once you have found the maximum in one direction repeat for the last direction.

13. It is important to align the beam in all 3 directions, since the CCD has some variability in where it is most efficient, so even the vertical direction can make a huge difference.

14. If the beam is well-aligned, you should be able to close the slit further with no major signal losses. If you have a large loss, re-do the alignment procedure with this slit width.

15. Once the alignment is complete, you can begin measuring. With all components securely bolted to the breadboard, after a cryogen filling cycle you should be able to skip steps 1 and 2 and only have to do a small fine alignment.

Figure 3.24: Image of the tip-sample junction as seen after the lens before the spectrometer slit.

To collect an optical spectroscopy grid, one needs to use the LabView program. The LabView program interfaces with both LightField, the spectrometer’s control software, and the Matrix, via TTL pulses. The current incarnation of the program for optical spectrometer imaging takes the TTL signal from the CRTC at the beginning of each new pixel to trigger the acquisition of an optical spectrum. The data is saved in a flat file which is unflattened in Matlab.
3.3.5 Laser setup

The lasers used in this thesis are Coherent OBIS LX and LS series lasers. They are solid state continuous wave lasers with simple plug-and-play packaging. The laser set-up is the same as that for the PMT: the laser itself is mounted via a mounting plate onto an \( xyz \) stage. Preliminary alignment can be done by shining the laser through a target hanging from cage rod on the flange optics. The user first approaches the tip to the sample using only a light shining in from the camera side, then a light is shone directly on to the face of the laser so that an image of the face appears in the sample. The tip is then moved such that the tip-sample junction is aligned with the aperture of the laser. If the aperture is not visible in the sample, adjust the tip-tilt mirror mounted on the flange until you can see it.

The lasers are controlled remotely via the ‘Coherent Connection’ software. The laser is connected to the computer via an ethernet cable and USB extender. The laser power is kept inside the pod.

For safety, the black box should be placed over the optical table to minimize stray beams in the room.
Chapter 4

Optical excitation of an acceptor-donor pair

Figure 4.1: STM constant current image (5x4nm$^2$, $I_0=3$ pA, $V_b=-2$ V) of the ‘XO’ configuration of CuPc and PTCDA on NaCl(2ML)/Ag(111). CuPc images as a ‘flower’ here.

In this chapter, we explore STS results obtained in conjunction with optical excitation of the system. In particular, we explore a single adjacent CuPc-PTCDA configuration which I refer to as the ‘XO’ geometry (see Figure 4.2). The long-term experimental plan is to take KPFM data to determine the charge state of adjacent acceptor-donor molecules, and to see if charge is transferred upon optical excitation. STS data will be taken concomitantly, so that one can explore how the STS spectrum is affected by having a molecule in an excited state.

Unfortunately, all of the data explored in this chapter were taken with a misaligned laser. The tip-sample junction was aligned with a secondary reflection of the laser beam, not the primary beam. It
Figure 4.2: STM constant current image (5x5nm$^2$, $I=10$ pA, $V_b=0.5$ V) of the ‘XO’ configuration of CuPc and PTCDA on NaCl(2ML)/Au(100). CuPc images as a ‘cross’ here, which is why it is called the ‘XO’ configuration. Note this would be different from a +O configuration, where the CuPc would be rotated 45° with respect to the PTCDA. Submolecular resolution is visible. Image taken with a PTCDA functionalized tip.

was not noticed that this was an issue until the spectrometer was being set up months later, as the spectrometer required very careful inspection of the optical path. Plans were in place to perform optical excitation with KPFM data collection on the system (with a correctly aligned laser), but several issues with the Omicron have deferred data collection. See Section 3.3 and Figure 3.18 for details regarding the alignment issue. As such all of the data in this chapter should be taken as inconclusive. The studies performed (drift($t$) as well as STS with laser illumination) should be repeated with a properly aligned laser as described in Section 3.3.5 if the future experimenter desires conclusive data with this system. In all cases, a thorough drift($t$) study will need to be completed for any study of a system under illumination, since the thermal expansion coefficients will depend on the specific tip and sample being used. Because a secondary reflection was used instead of the primary beam in this study optical power was still incident on the sample but it was significantly reduced. In any case, what was attempted here provides a useful template for further studies. Discussion of the results follows in section 4.3.
Figure 4.3: STS spectra averaged over the entire molecule (either CuPc or PTCDA) in the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different specific molecules. The location and shapes of the peaks change with different tips and locations on the substrate.

4.1 Characterization of spurious signals: the influence of the tip/substrate and thermal expansion of the tip-sample junction

A steady tip-sample distance is critical for quality STM and STS measurements. Because laser radiation causes both the tip and sample to thermally expand, it is important to understand the transient effects observed when one turns the laser on or off. Once the transient effects of turning the laser on or off are understood, one knows how long they must wait before taking a measurement to ensure they are measuring a system which is (nominally) in the steady state. In addition, the specific tip, molecules, and substrate do affect the measurement, so each set of data must be taken with the same tip at the same location (see Figure 4.3) to be comparable. There is considerable variation present when taking data with different tips at different locations on the substrate.
4.1.1 The effect of the tip and specific location on the substrate

Different tips and specific locations on the substrate introduced various artifacts into the data which became very relevant in this study. Because it is not known what one should see in STS when the molecule under study is in an excited state, features like ‘side humps’ and small wiggles could be a real signal. The tip, substrate, and other factors can introduce very subtle wiggles and so on which are not related to the state of the molecule, but resemble something interesting. For any meaningful comparison, then, one needs to collect each set of data with the same tip, on the same set of molecules, at the same location on the substrate. Refer to Figure 4.3 and note that both the February 23 PTCDA and the Feb 15 CuPc appear to have bimodal peaks around 1 V. These ‘ghost peaks’ are red herrings, and appear in all the data collected with that given tip at that given location. This kind of variation is present in any two sets of data taken with different tips in different locations, and this kind of variation should be kept in mind for the experimenter looking for small signals. To control for this, STS grids were collected in sets with the same tip on the same 2 molecules in the same location. Each set consisted of a grid taken at 0, 5, and 15 mW of laser power. Generally, this

\footnote{Despite the best effort of the experimenters to obtain a flat DOS, some very subtle tip-related effects persisted and affected some of the measurements. It is also possible that ‘invisible’ defects were present in the substrate which affected the measurements.}
Figure 4.5: STS spectra averaged over the entire PTCDA molecule in the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different molecules. Spectra shown correspond to the ‘0 mW’ data point for each data set shown in section 4.2.

would use up the majority of the hold time of the cryostat so that the next set would necessarily be taken with a different tip on a different two molecules, etc.
Figure 4.6: STS spectra averaged over the NaCl surrounding the XO configuration on NaCl(2mL)/Ag(111) taken with different tips on different molecules. Spectra shown correspond to the ‘0 mW’ data point for each data set shown in section 4.2.
4.1.2 Thermal expansion of the tip-sample junction

Measurements of the drift in $z$ as well as in $(x,y)$ were taken with both 488 nm and 687 nm radiation. A time constant in $z$ was extracted from the $z(t)$ data, and an estimate for the $(x,y)$ drift was obtained from tracking the position of a specific molecule in successive images (the position of the scan box was set at (0,0) and was not moved, and the successive images show a molecule drifting across the screen). This drift analysis only gives a lower bound on the laser-induced drift due to the laser misalignment.

For the $(x,y)$ drift measurements, the drift without any radiation was taken prior to the drift with radiation. The difference between the two is reported as the drift due to the laser. For the 488 nm laser at 20 mW, the drift in $x$ was found to be $\approx 5.3$ pm/min, and the drift in $y$ was found to be $\approx 2.2$ pm/min. For the 687 nm laser at 20 mW, the drift in $x$ was found to be $\approx 6.7$ pm/min, and the drift in $y$ was found to be $\approx 5.3$ pm/min.

For $z(t)$ measurements, the laser power was ramped up in 5 mW increments from 0 to 20 mW for 488 nm laser and from 0 to 30 mW for 687 nm laser then back down to 0 mW at 5 minute intervals (see Figure 4.7). For the ramp, the power was turned on for 5 minutes then off for 5 minutes before the next increment. At each power, a $z(t)$ trace was taken. The tip was positioned over NaCl/Ag(111) at (0,0).

![Figure 4.7: Schematic indicating how the laser power was ramped up and down over time to collect the $z(t)$ data with the 488 nm laser. Note with the 687 nm laser the basic scheme remains the same, but the maximum power is 30 mW.](image)

A two-term exponential model with 95% confidence bounds was fit to the data:

$$y = ae^{bx} + ce^{dx}$$

(4.1)

Two terms were used to deal with the offset: since $z(t)$ wasn’t centred at 0 (or since the functions
don’t decay to 0) the exponential function we want to fit to should have the following form

\[ y = ae^{bx} + C \]  

(4.2)

Given that the exponential is decaying ‘up’ or ‘down’ (the sign is changing on \( a \)), and there were 38 traces to fit, putting all the data in a for loop with no need for initial guesses was the easiest way to proceed. As such, the Matlab function ‘exp2’ was used for the fit since one of the terms essentially acts as the constant - one of the decay constants was always very small (on the order of \( 10^{-6} \)) such that \( e^{dx} \approx 1 \), and the associated amplitude is a good fit for the offset given the start and end points of the data. For example, for the 488 nm laser initially turned on to 5 mW the fit values were \( a = -1.057 \cdot 10^{-1}, b = -0.0211, c = -5.540 \cdot 10^{-8}, d = -5.915 \cdot 10^{-7} \), giving a time constant of \( \tau = 47.448 \) s, an offset of \( C = 55.404 \) nm, and a ‘time to steady state’ of 237.24 seconds or 3.954 minutes. The data and the fit can be seen in Figure 4.8. With an exponential fit, the time constant \( \tau \) is the time for the function to reach \( 1/e \) of its initial value (for a decay), and \( 5* \tau \) is the approximate time before the function reaches steady state.

A similar procedure was followed with the 687 nm laser. Since the results aren’t really valid, we won’t explore them in detail. With the ramp going up to 30 mW and back down, the largest \( \tau \) was
### Table 4.1:

<table>
<thead>
<tr>
<th>laser power [mW]</th>
<th>$\tau$ (seconds)</th>
<th>$5\tau$ (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.588</td>
<td>2.632</td>
</tr>
<tr>
<td>5</td>
<td>47.448</td>
<td>3.954</td>
</tr>
<tr>
<td>0</td>
<td>62.128</td>
<td>5.177</td>
</tr>
<tr>
<td>10</td>
<td>26.797</td>
<td>2.233</td>
</tr>
<tr>
<td>0</td>
<td>57.363</td>
<td>4.780</td>
</tr>
<tr>
<td>15</td>
<td>71.234</td>
<td>5.936</td>
</tr>
<tr>
<td>0</td>
<td>55.429</td>
<td>4.619</td>
</tr>
<tr>
<td>20</td>
<td>57.083</td>
<td>4.757</td>
</tr>
<tr>
<td>0</td>
<td>65.549</td>
<td>5.462</td>
</tr>
<tr>
<td>15</td>
<td>64.668</td>
<td>5.389</td>
</tr>
<tr>
<td>0</td>
<td>55.912</td>
<td>4.659</td>
</tr>
<tr>
<td>10</td>
<td>56.374</td>
<td>4.698</td>
</tr>
<tr>
<td>0</td>
<td>56.707</td>
<td>4.726</td>
</tr>
<tr>
<td>5</td>
<td>55.224</td>
<td>4.602</td>
</tr>
<tr>
<td>0</td>
<td>47.210</td>
<td>3.934</td>
</tr>
</tbody>
</table>

$z(t)$ results for 488 nm laser. Note that the first fit for 10 mW appears to be poor, though it was within a 95% confidence interval. In addition, the initial $\tau$ should be 0, but it is likely that we are seeing the piezo drift. This means that the piezo drift and the laser-induced thermal expansion are both present in the measurements taken. Even with the piezo drift, we can see that the longest time one needs to wait before reaching steady state is 6 minutes. For the 488 nm laser, we can conclude that $\geq 6$ minutes is a safe time to wait after turning it on or off to any power to be confident that the tip and sample have reached thermal equilibrium, assuming piezo drift is at an acceptable value.

178.77 seconds, giving a wait time of at least 15 minutes.
4.2 Optical excitation of the system with a Ag(111) substrate

The XO configuration’s response to (misaligned) laser illumination was studied in depth via the collection of STS grids on the system under varying power levels (0, 5, and 15 mW) and wavelengths of radiation (488 nm, 519 nm, 561 nm, 640 nm, and 685 nm). Each set of data consists of three STS grids taken on the exact same two molecules (in the XO configuration, on NaCl(2 ML)/Ag(111)) with the same tip, with one laser illuminating them at 0, 5, and 15 mW (note with the 488 nm laser, the 5 mW data point is replaced with one at 10 mW). The spectroscopy grids were analyzed by averaging the individual spectra over either the entire molecule or some portion of the molecule, and comparing the results for different levels of illumination.

Figure 4.9: STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the whole molecule. Data taken on NaCl(2mL)/Ag(111).

The spectra shown on the following pages are averaged over the whole molecule. Because it is possible that averaging over the whole molecule could average out an interesting signal which was found only on part of the molecule, averaging was also done over only the perimeter of the CuPc molecule, the center of the CuPc molecule, and the oxygen end of the PTCDA molecule. No significant differences are found for these sets of spectra compared to those obtained by averaging over an entire molecule, so they are not included in the main body of the text. See Appendix B for
these results.

Figure 4.9 shows the topography and STS slice where the average was taken for the whole molecule (the area which was averaged is delineated in red, called a ‘mask’) for the entire 561 nm data set. Figure B.1 shows the topography and STS slice where the average is taken over just the oxygen ends of the PTCDA. Figures B.2 and B.3 show the topography and STS slice where the average is taken over just the center or the perimeter of the CuPc.

The masking for averaging was done by comparing, at a given energy, the value of $\frac{\partial I}{\partial V}$ at each pixel to some threshold value. The energy chosen for this comparison was selected as one offering high contrast between the desired area and the remainder of the grid as seen in a STS slice. Matlab code was written by K. Cochrane which goes through each pixel in a STS slice at a user defined energy and assigns a ‘1’ if the $\frac{\partial I}{\partial V}$ value is above the user defined threshold, or a ‘0’ if the $\frac{\partial I}{\partial V}$ is below the user-defined threshold\(^2\). This 2D matrix of 1’s and 0’s then multiplies each slice in the full STS grid so that only the pixels which meet the threshold criteria are kept. The $\frac{\partial I}{\partial V}$ data at each pixel in the new, ‘masked’ grid is then averaged to obtain the plots shown.

**Figure 4.10:** Comparison of $dI/dV$ spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 685 nm laser. Spectra are averaged over the entire molecule.

Recall that the peaks in a $\frac{\partial I}{\partial V}(E)$ plot are related to the tunneling resonances of the molecule. In general, the peaks below Fermi (0 V) are associated with the occupied molecular states and the peaks

\(^2\)Note there is actually an upper and lower bound defined by the user, but in practice one generally only uses the lower bound.
above Fermi are associated with the unoccupied molecular states. So, for Figure 4.11 considering only the blue solid line for the CuPc molecule as measured with 0 mW of laser power, one finds the highest occupied tunnelling resonance (or molecular orbital (MO)) at -2.01 V, the lowest unoccupied tunnelling resonance at +1 V, and the second lowest unoccupied tunnelling resonance at ≥ 2.5 V.

It is probable that PTCDA is negatively charged on NaCl(2mL)/Ag(111) [2], [84]. The result is a partial occupation of the lowest unoccupied MO. When probing this state with STS, one sees a splitting of the state above and below Fermi. This is because the state is half occupied: you can see it below Fermi because you can extract an electron from it; conversely you can also see it above Fermi since you can inject an electron into it. The split states are separated by the Hubbard energy. Thus, with PTCDA on NaCl(2ML)/Ag(111), instead of the straightforward highest occupied MO and lowest unoccupied MO, we see the split LUMO as well as the usual highest occupied MO and then the second lowest unoccupied MO (which for PTCDA is expected to be nearly degenerate with the next highest MO [85]). In addition, one cannot be confident that the Hubbard states are not overlapped with the other states, so state identification is tentative. In any case, the peaks remain visible and shifts in energy are detectable, even though the peaks are not easily identifiable.

A discussion of the results, including what we may have expected to see, follows in Section 4.3.

In addition to plotting the averaged spectra, one can plot ‘slices’ of the 3D STS grid, showing the spatial distribution of $\frac{\partial I}{\partial V}$ as the energy is varied. A slice is obtained by plotting the value of $\frac{\partial I(E)}{\partial V}$ at each pixel for a given energy $E$. Note that the relative intensity is the primary concern in an STS slice. In Figure 4.15 yellow indicates the presence of a tunnelling resonance. The spatial distribution of $\frac{\partial I}{\partial V}$ was not observed to change with illumination. Figure 4.15 is representative of all of the laser excitation data collected.

---

3I conjecture that a similar effect may be observed with an optically excited molecule, but in that case two states would be split across Fermi: the half occupied ‘HOMO’ and the half occupied ‘LUMO’.

4Aside from PTCDA jumps, that is. See Section 4.3.1 for a discussion on that.
Figure 4.11: Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 640 nm laser. Spectra are averaged over the entire molecule.

Figure 4.12: Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 561 nm laser. Spectra are averaged over the entire molecule.
Figure 4.13: Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 519 nm laser. Spectra are averaged over the entire molecule.

Figure 4.14: Comparison of dI/dV spectra for the XO configuration on NaCl(2mL)/Ag(111) under illumination from the 488 nm laser. Spectra are averaged over the entire molecule.
Figure 4.15: Spatial and energetic distribution of the LDOS, imaged via slicing the STS grid at selected energies. The spatial distribution showed little variation in each data set. Yellow indicates the presence of a tunnelling resonance. Slices shown are from the 561 nm 0 mW grid (taken on NaCl(2mL)/Ag(111)).
4.3 Discussion

We note that no ‘obvious’ signal is present when comparing spectra for illumination vs no illumina-
tion. For example, none of the peaks shift in energy when the sample was illuminated by the
misaligned laser. No new peaks appear in illuminated vs un-illuminated samples. The peak heights
change, but not in a fashion which is correlated with the laser power. This could be due to the
misalignment, or it could also be due to other factors. However, there is one notable feature in each
data set: the amplitude of the 2.4 V peak in the PTCDA spectra changes considerably, for all lasers
used:

- For the 685 nm laser, and spectra averaged over the entire molecule, the 5 mW peak is the
  largest, followed by the 15 mW then 0 mW peaks (see Figure 4.10). For spectra averaged
  only over the oxygen end, the 5 mW peak remains the tallest, with the 0 mW and 15 mW
  peaks approximately the same height (see Figure B.4).

- For the 640 nm laser, and spectra averaged over the entire molecule, the 0 mW peak and 15
  mW peaks are the largest, followed by the 5 mW peak (see Figure 4.11). For spectra averaged
  only over the oxygen end, the peaks are all approximately the same height (see Figure B.6).

- For the 561 nm laser, and spectra averaged over the entire molecule, the 0 mW and 5 mW
  peaks is the largest, followed by the 15 mW peak (see Figure 4.12). For spectra averaged only
  over the oxygen end, the 0 mW peak remains the tallest, then the 5 mW peak is the second
  larges, and the 15 mW peak the smallest (see Figure B.8).

- For the 519 nm laser, and spectra averaged over the entire molecule, the 0 mW peak is the
  largest, followed by the 5 mW then the 15 mW peaks (see Figure 4.13). For spectra averaged
  only over the oxygen end, the peaks are all roughly the same height (see Figure B.10).

- For the 488 nm laser, and spectra averaged over the entire molecule, the 0 mW and 15 mW
  peaks are the largest, followed by the 10 mW peak (see Figure 4.14). For spectra averaged
  only over the oxygen end, we find the same thing (see Figure B.12).

There are two main things to note from the list above. First, the height change does not correlate
consistently with the laser power. Second, the height changes are different if you average over the
whole molecule versus if you average over only part of the molecule.

What could this indicate? First we should consider that, if laser excitation is happening at all, it is
unlikely to be happening with all of the lasers used. Therefore, some sets of data should show a
signal and some sets show none if the signal is related to laser excitation. It is possible that more
than one laser could excite a given molecule, since the lasers are separated in energy by \( \sim 130-150 \)
meV. In particular, we would expect something close to the 640 nm laser to excite CuPc, and either
the 488nm laser or a shorter wavelength laser\(^5\) to excite PTCDA [86], [87], [88]. Considering that the 2.4 V peak height varies in all data sets, this may indicate that the peak height is not correlated to a signal seen in STS from successful laser excitation.

However, Yeyati and Flores calculated the tunnelling current for a small molecule such as CO or NO in the tunnel gap excited by radiation, and they found that one can expect an increase in tunnelling current of about 1-3% when molecular vibration is excited by radiation [89]. They performed this calculation with a laser intensity of 2 kW/cm\(^2\). In our system, the laser intensity is unknown due to the misalignment. If the laser were properly aligned, for 5mW of power and a spot size of roughly 20µm, we would have an intensity of 2.5 W/cm\(^2\), three orders of magnitude less than Yeyati and Flores considered. In addition, as noted previously, none of the sets of data considered here shows the largest peak being 15 mW (except in the case where both 15 mW and 0 mW peaks are the largest, which clearly contradicts the premise).

Grafström points out that the increased tunnelling resistance found in most adsorbate layers will be accompanied by a decrease in Yeyati and Flores’ expected signal, which will eventually become undetectable [90]. This could be the case here, but that still leaves the variation in peak height unexplained. Grafström et al. investigated the possibility that an additional tunnelling channel could open up in an excited adsorbate (they investigated co-adsorbed layers of PTCDA and octylcyanobiphenyl liquid crystals on highly ordered pyrolytic graphite) [91]. They did not perform STS, but did find that a small increase in tunnelling current (100 fA at a laser intensity of 3.5 kW/cm\(^2\)) was present when the PTCDA islands were irradiated\(^6\). They did not propose a specific origin for their signal, and only could only tentatively claim it was not due to thermal expansion.

Smith and Owens also observed a laser-induced resonance effect when tunnelling into a monolayer of the \(J\)-aggregating dye 1,1′-diethyl-2,2′-cyanine bromide on a silver substrate [92]. They proposed that the signal originated from the nonradiative decay of the excited molecular state into the substrate, causing local heating and thermal expansion, which in turn caused a change in the tunnel gap width and an increase in tunnelling current. Im et al. performed a similar experiment to that of Smith and Owens, but this time with a flattened tip, and found transient currents were induced when they irradiated a thin molecular film\(^7\) deposited onto a gold substrate with pulsed light [93]. They proposed that the transient currents were due to photoassisted charge injection.

In general, all of these explanations are contradicted by our results, because for each set we should see an increase in the laser-induced tunnelling current with increasing laser power. In our case, that would mean that the (2.4 V) peak height for 15 mW radiation should be the largest in amplitude

\(^{5}\)The shortest wavelength laser we were able to use in this experiment was 488 nm.

\(^{6}\)In this experiment, they used an Ar\(^+\) laser and a tunable dye laser of unspecified wavelength.

\(^{7}\)In this experiment they explored a number of films: high molecular weight hydrocarbons, polymethylmethacrylate, octadecanethiol, and anthracene.
(and 0mW the smallest). This is not what is observed.

The experiments of Grafström et al., Im et al., and Smith and Owens, as well as the theory from Yeyati et al., point to a different study for this same system, however: one can simply hold the tip in place and measure the tunneling current with the laser off then measure it again at least 7 (or 15) minutes after turning the laser on (when thermal expansion effects should have reached steady-state) [94]. If the current with the laser on is larger than it is with the laser off, then this should indicate that an additional tunnelling channel has opened up due to the adsorbate being excited by the radiation.

4.3.1 Vibrational excitation leading to possible tunnelling current changes

There is one more possibility, which Yeyati and Flores as well as Smith and Owens point to: the role of excited vibrational modes affecting the magnitude of the tunnelling current. During the laser power study, it was noticed that the PTCDA in the XO configuration was very jumpy. It was often impossible to get a full grid where the PTCDA didn’t jump; see Figure 4.20.

After the laser power study was completed, it was noticed that the PTCDA was specifically jumping between an ‘upper’ and a ‘lower’ configuration with respect to the CuPc; see Figure 4.16. Since ‘upper’ and ‘lower’ depends on which way you are looking at the XO configuration, we named the two configurations A and B. Note that the CuPc also rotates slightly depending on if the PTCDA is in the A or B position. Hopping of single molecules caused by inelastic tunnelling-induced vibrational excitations has been observed before with STM, for example in the work of Komeda et al. [95].

![Figure 4.16: Topography of the same XO showing both the lower (left) and upper (right) PTCDA configurations, which we call ‘A’ and ‘B’. Comparing the two images above, the PTCDA jumps ≃0.362 nm downwards, which is close to the spacing between adjacent Cl⁻ top sites in the NaCl (0.353 nm) as measured from Figure 3.9b. Images taken on NaCl(2ML)/Ag(111).](image-url)

72
Comparing the two images in Figure 4.16, and using the CuPc molecule in the bottom left corner as
a reference to adjust for piezo drift, the PTCDA jumps \( \approx 0.362 \text{ nm} \) downwards, which is close to the
spacing between adjacent Cl\(^-\) top sites in the NaCl (0.353 nm as measured from Figure 3.9b). The
positioning of the PTCDA with respect to the CuPc was demonstrated clearly with AFM imaging;
see Figure 4.17. The PTCDA is not symmetric with respect to the centre of the CuPc, as one may
have expected when examining only STM images. The PTCDA jumping distance combined with
the AFM-resolved positioning of the PTCDA with respect to the CuPc center likely indicates that
the PTCDA is jumping between adjacent Cl\(^-\) top sites, and, since the PTCDA is not symmetric with
respect to the centre of the CuPc, that the CuPc is not centred on a Cl\(^-\) top site.

![Image](image-url)

(a) Laplace transform of original image  
(b) Raw data

**Figure 4.17:** Constant height NC-AFM images using a PTCDA-functionalized tip of the XO
configuration on NaCl(2ML)/Ag(111). The oxygen end of the PTCDA which is adjacent
to the CuPC is closer to one isoindoline subunit of the CuPc than the other. Image size
3.2x3.2nm\(^2\); oscillation amplitude \( A = 15 \text{ mV} \). Note the image in a is the Laplace transform
of the gaussian smoothed raw data. Image taken on NaCl(2ML)/Ag(111).

Finally, controlled jumping of the PTCDA between the A and B configurations was demonstrated
when tunnelling into the centre of the molecule at +2V; see Figure 4.18. This switching was
achieved by taking an ‘STS’ point spectra, from +2V to +2V, for 200 points with a raster time
of 30 ms. This switching was also possible with a PTCDA-terminated tip.

Stipe et al. pioneered single molecule vibrational spectroscopy, which they coined scanning tunnelling
microscope inelastic tunnelling spectroscopy (STM-IETS), and showed that vibrational excitation could result in a change in tunnelling current due to the change in the molecule’s location
with respect to the tip [96], [97]. STM-IETS \( \frac{dI}{dV} \) spectra for PTCDA in the XO configuration
shows an STM-IETS resonance at 2.12V, see Figure 4.19.
Figure 4.18: Exciting a vibrational mode in PTCDA on NaCl(2ML)/Ag(111) at 2V, showing reversible and controllable jumping between two XO configurations. Jumping occurs during scan 2 (down) and scan 5 (up).

Figure 4.19: STM-IETS spectra for PTDCDA in the XO configuration on NaCl(2mL)/Ag(111), with no illumination. Note the resonance at 2.12 V.

It is possible that inelastic tunnelling into a vibrational mode at 2 eV excites the PTCDA sufficiently to cause it to jump. This vibrational excitation could also cause a change in tunnelling current, as suggested by Yeyati and Flores (except in our case the mode is excited by tunnelling, and not absorption of a photon) and demonstrated by Stipe et al.. However, Stipe et al. found a different, and very simple, mechanism for the change in tunnelling current: when the molecule rotates after excitation, the position of the tip changes with respect to the molecule, leading to a different tun-
nelling current. In their experiment, they excited an acetylene molecule adsorbed onto Cu(100) into a rotational state via inelastic tunnelling. They found that the current was high when the tip was over the plane of the molecule, then low when the molecule rotates and the tip is no longer over the plane of the molecule.

**Figure 4.20:** Topography for all of the STS grids taken during the laser excitation study, showing how the PTCDA jumped (and the CuPc rotated) multiple times during most grids. Note that there was no correlation with the change in the 2.2 V peak height and the number of jumps observed in the images above.

Because all of the STS grids so far discussed in this chapter scan the voltage through +2eV, hundreds
of times per grid, it is likely that the PTCDA jumped between the A and B configuration many times in each grid. If the final topography image does not show any jumps, there still may have been jumps in each line of STS and it was just lucky that the PTCDA jumped back to its starting configuration before the imaging along that line occurred. The variation in peak height, then, can be thought of as the result of averaging over the vibrational excitations in each grid; some grids had more vibrational excitations (and therefore a larger amplitude 2.4 V peak) and some grids had less vibrational excitations (and therefore a smaller amplitude 2.4 V peak). Note there is no correlation between the observed peak height differences for a set of data and the number of jumps observed in the topography for the grids in that set.

Another point of interest is that difference in amplitude of the 2.4 V peak in the PTCDA STS spectra is different when spectra are averaged over just the oxygen end of the PTCDA versus the whole molecule. In general, one sees less variation in the peak height when averaging only over the oxygen end of the PTCDA. This may indicate that the induced vibrational mode has some non-uniform spatial dependence over the molecule, or that the coupling of tunnelling electrons to the jumping of the molecule is orbital-specific [97].

In our case, it is unlikely that the vibrational mode was excited by the lasers, but that cannot be completely ruled out. Since the mode can be excited by tunnelling into PTCDA at 2V, we may also be able to excite the mode with a laser of ≃620 nm. Of course, we don’t have a laser at exactly 620 nm but, if the vibrational band is wide enough, then the 640 nm laser (only 62.5 meV different in energy from 2eV) could excite it. However, the data so far don’t indicate any special amount of variability in the 2.4 V peak in the 640 nm set of data versus the other sets, so it would appear unlikely that laser excitation of PTCDA was achieved.

### 4.3.2 STS of CuPc-PTCDA on NaCl(2ML)/Au(100)

Because the STS data taken so far imply that laser excitation was not successful with this system, the plan for future studies involves laser illumination and STS/KPFM exploration of the same molecular system on a different substrate: Au(100). Au(100) has a larger work function than Ag(111), and importantly the work function should be larger than PTCDA’s electron affinity, so PTCDA on NaCl(2ML)/Au(100) should not be charged. STS of the same molecular system in the same ‘XO’ configuration on NaCl(2ML)/Au(100) was briefly explored and the results are intriguing. Interestingly, some of the tunnelling resonances in the PTCDA molecule appear to be barely shifted when comparing measurements on NaCl(2ML)/Au(100) vs Ag(111): the lowest resonance above Fermi level [97].

---

8Since PTCDA is likely charged on one substrate, but neutral on the other, it is hard to say which states correspond to which, so we can’t draw any firm conclusions about how much any specific state has shifted; but we can talk about the tunnelling resonances.
shifts down from 0.98 eV (as measured on Ag(111)) to 0.90 eV (as measured on Au(100)). The total shift is only 0.08 eV. See Figures 4.21 and 4.22.

Figure 4.21: dI/dV spectra for the XO configuration on NaCl(2ML)/Au(100)

Figure 4.22: dI/dV spectra for the XO configuration on NaCl(2ML)/Ag(111)
Note that because PTCDA is charged on NaCl(2ML)/Ag(111), in STS the LUMO appears split into states above and below Fermi \([2][84]\), while on NaCl(2ML)/Au(100) this is likely not the case.

Meanwhile, the highest occupied tunnelling resonance disappears for PTCDA on Au(100) - at least up to -2.5 V\(^9\). For CuPc, the lowest tunnelling resonance above Fermi is significantly shifted when measured on Ag(111) vs Au(100): the lowest peak energy shifts up from 1.03 eV (as measured on Ag(111)) to 1.86 eV (as measured on Au(100)); which is a shift of 0.83 eV. A similar shift up in energy happens for the highest tunnelling resonance below Fermi, resulting in an almost unchanged gap but very different individual energy levels. In general, the spectra for CuPc looks similar on both substrates, just shifted. See Figures 4.23, 4.21, and 4.22.

**Figure 4.23:** Comparison of the gap as measured via STS of PTCDA and CuPc in the XO configuration on NaCl(2ML)/Au(100) vs NaCl(2ML)/Ag(111). Note the gap indicated for PTCDA on Au is an estimate, since no tunnelling resonances were observed below Fermi for the XO configuration (which was only explored to -2.5V) but was observed at \(\simeq -3V\) for isolated PTCDA.

The shifts of specific resonances are interesting as these change the level alignment. The gaps as measured by STS also change. The gap as measured on Ag(111) vs Au(100) for PTCDA changes by \(\simeq 2.3\) eV, while the gap for CuPc only changes by \(\simeq 0.07\) eV. This is likely due to the charge state of PTCDA on the two different substrates: as noted earlier, it is likely that PTCDA is charged on Ag(111), but it may not be on Au(100).

It is important to note that a change in substrate will shift all of the energy levels as measured with respect to Fermi for both molecules. This is because our 0 V is referenced to the Fermi level of the substrate. When a molecule is adsorbed onto a substrate, assuming it is strongly coupled to the

---

\(^9\)Note that the first tunnelling resonance below Fermi for PTCDA on Au is not visible in Figure 4.21, it was not measured for the XO configuration. It was measured for isolated PTCDA molecules on NaCl/Au(100), and was found to be at -3 V.
substrate, then one still measures the ionization potential and electron affinity with respect to the vacuum level, but this time the vacuum level is defined with respect to the substrate, as defined by the work function.

![Figure 4.24](image_url)

**Figure 4.24:** Schematic indicating the energy level alignment for a molecule in the STM barrier without an applied bias, assuming the molecule is more coupled to the substrate than the tip.

Because of the change in the substrate work function, we can get an estimate for how the energy levels of the molecule as measured via STS (i.e., with respect to Fermi of the substrate) will change when measured on one substrate vs another (see Figure 4.24). Ag(111) has a work function of \( \sim 4.46 \) eV\(^{10}\)\(^{[98]} \). If we let the electron affinity of neutral PTCDA be \( X \) (and we assume the vacuum level of the molecule is aligned with that of the substrate) then on Ag(111) we should see the LUMO at \( 4.46 - X \) eV. On the other hand, Au(100) has a work function of \( \sim 5.22 \) eV, so we should see the LUMO of neutral PTCDA at \( 5.22 - X \) \(^{[99]} \). All of this means that for neutral molecules we should see all of the energy levels shift ‘rigidly’ by a value close to the difference between the two substrate’s work functions when we measure them on one substrate vs another. Of course, for PTCDA this is confused by the fact that it is charged on Ag(111). However, for CuPc we do see a fairly rigid shift of all energy levels of about \( \sim 0.84-0.91 \) eV, which is close to the difference in the two substrates’ work functions (0.76 eV).

One should note that even for a molecule adsorbed onto a bare metal substrate, the vacuum level for the molecule isn’t exactly aligned with the vacuum level of the substrate - there is some energy drop due to a dipole barrier \(^{[100]} \). In our case, for a molecule adsorbed onto (2ML) NaCl, the work function of the substrate is changed due to the surface dipole from the adsorption of NaCl. In any case, the difference between the energy shift we observe and the difference in work functions can likely be made up by the work function change due to the NaCl, polarization of the surroundings,\(^{[99]} \).

\(^{10}\)In this paper, they show that the work function approached a steady value as the sample was cleaned more and more thoroughly (by Ar\(^+\) bombardment). It was quite nice, clean physics ;)

79
Figure 4.25: Cartoon indicating how the energy levels as measured with STS shift or change under various conditions. A, energy levels for a neutral molecule vs a charged molecule. When the molecule is charged, the LUMO splits across Fermi. B, energy levels for a substrate with a larger work function vs those for a smaller work function. Energy levels shift up when measured on a substrate with a larger work function. C, energy levels for a molecule in unperturbed surroundings vs polarized surroundings. When the surroundings are polarized, the ionization potential is reduced (so the HOMO moves closer to Fermi) while the electron affinity is increased (so the LUMO moves closer to Fermi).

In any case, the probable different charge state of the PTCDA, as well as the different energy level alignments in general for both molecules with respect to the substrate, results in energy levels which are shifted considerably compared to those on NaCl(2ML)/Ag(111). Figures 4.21, B.14, and B.15.

Incidentally, I calculated the ‘stark shift’ expected from the neighbouring charged PTCDA and found that the field of the charge alone caused a shift of 8.7 meV, while the field of a dipole (due to the image charge in the substrate) caused a shift of 0.5 meV, both of which are relatively small - especially when one considers that the molecule is in a much larger electric field due to the applied bias.
indicate the energy levels for the same (XO) configuration, as measured by STS on NaCl/Au(100).

With this change in energy level alignment, molecules adsorbed on NaCl/Au(100) offer a much likelier pathway for optical excitation and charge transfer. See Figure 4.26.

**Figure 4.26:** Schematic indicating the energy level alignment and possible optical excitation pathways for molecules adsorbed on NaCl/Ag(111) vs NaCl/Au(100). The relative energies are not exact. On Ag(111) we could see an excitation from the HOMO of the CuPc to the LUMO of the CuPc (process 1). In this case, there is no driving force for charge transfer to PTCDA since the energy levels are almost aligned (and the LUMO of PTCDA is half occupied). We could also see an excitation from the lower Hubbard state on PTCDA to the LUMO+1/LUMO+2 (process 2). In this case, there would be a large energy drop into CuPc’s LUMO, but PTCDA’s LUMO is also at this energy so it is possible that the electron would just relax to there instead of being transferred across molecules. There are other possibilities as well. On Au(100), we could see an excitation from CuPc’s HOMO to LUMO, then transfer to PTCDA’s LUMO (process 3). This energy level alignment appears to be quite favourable for charge transfer between the two molecules.

As before, spectra were also averaged over only part of the molecule in case any interesting features emerged which were averaged out otherwise. No major features of interest were noted. Those results are in Appendix B.
Figure 4.27: STS slices of the XO configuration on NaCl/Au(100) indicating the spatial and energetic distribution of the LDOS. There is only one visible state below Fermi in the experimental energy range, on the CuPc molecule.
Chapter 5

Scanning tunnelling luminescence measurements

In this chapter, we explore the scanning tunnelling luminescence (STML) measurements obtained with the optical system coupled to the STM/AFM. Measurements were taken on bare Ag(111) as well as clusters of CuPc and PTCDA on NaCl(2ML)/Ag(111). In the first part of this chapter, we discuss the proof of principle experiment, where luminescence is collected from the tunnelling junction with both the photomultiplier tube (PMT) and the optical spectrometer on bare Ag(111). In the second part of this chapter, we discuss the luminescence measurements taken on the CuPc-PTCDA-NaCl/Ag(111) system. Finally, we discuss our results and make some suggestions for future modifications to the experimental setup as well as suggest some experiments to try next with the current setup.

5.1 Luminescence measurements on bare Ag(111)

The photomultiplier setup and the optical spectrometer setup described in Section 3.3 were used to collect luminescence from the tunnelling junction on bare Ag(111) with a Ag tip. The PMT provides a wavelength-integrated measurement, so images created with this setup show lighter pixels corresponding to more photons collected and darker pixels corresponding to less photons collected. The spectrometer provides wavelength-resolved measurements, and 3D grids can be taken and integrated over a wavelength range to give an image in (x,y) of the luminescence similar to the one obtained with a PMT. It is important to recall that our measurement can only access emitted photons with wavelengths between $\approx$350-650 nm due to the radiation blocking coating on the in-vacuum viewports. It is also important to note that a background subtraction was performed for the optical
spectrometer, which sometimes results in negative counts in a given spectrum.

The initial proof of principle experiment was to collect luminescence from bare Ag(111) with the PMT, since imaging on bare Ag allows for very high tunnelling currents to be used (which should correspond to larger photon counts) and because we knew what we should see if successful: an image resembling the topography but with the luminescence quenched at the step edges [78], [102],[103], [104], [105]. The quenched luminescence at the step was interpreted by Berndt et. al [102]. They noted that the tunnelling current density is typically peaked along the surface normal, but at a step the tunnelling current vector ceases to be peaked in this direction. When the tunnelling current vector is no longer normal to the surface, it also ceases to be parallel to the dipole moment of the tip-induced plasmon mode, which gives rise to photon emission. Note that the tip-induced plasmon mode is presumed to stay approximately unchanged at a step due to its relatively large lateral extent (Aizpurua et al. later quantified the lateral extent of the plasmon more precisely [104]).

The vector mismatch between the tunnelling current filament and the plasmon mode dipole moment reduces the inelastic tunnelling matrix element. If one takes a simple model where the current is roughly perpendicular to the surface and that the orientation of the plasmon dipole is constant, then the inelastic tunnelling probability is proportional to \( \cos^2(\alpha) \), where \( \alpha \) is the angle between the surface normal and the tip’s central (long) axis.

The general method to get started with a luminescence data collection run was to bring 3 different Ag tips into vacuum, since the success rate for luminescence tips can be low. Each tip was tested by first ‘cleaning’ it on clean Ag(111) via dozens (likely hundreds) of high voltage pulses (+/- 10V), being careful to avoid crashing as this can ruin the tip. Once the tip was clean and imaged stably at high (nA) currents, the tip-sample junction was aligned with the PMT active area and the room was prepared for luminescence detection (all sources of light were removed or blocked). The initial test to see if the tip luminesced was to approach completely\(^1\), then take one step back and reapproach, watching the voltage in the Auxiliary channel as a function of time. One could approach and retract at multiple currents and voltages, as well as tunnel while changing the voltage and current, to get a sense of how responsive the luminescence signal is to changes in tunnelling parameters and to determine which voltage provides the most luminescence. In the end, for my first batch of tips, one tip barely luminesced while the other two did. Of the two tips which did luminesce, one showed a larger voltage jump when moving from not approached to approached at the same voltage and current, so this tip was taken as the ‘most luminescent.’ The other two tips were brought out of vacuum and the experiment was begun.

Because it is known that a scan over bare Ag(111) step edges should result in a photon map with

\(^1\)When doing this initial testing, as well as the alignment to the optical spectrometer, care should be taken to position the tip at (0,0) and above a large clean terrace of Ag so that surface defects, drift, or other spurious signals do not affect the luminescence. This way you can reasonably compare each spectra / data point you take.
quenched luminescence at the steps, a suitable clean area of Ag with a few steps was found for PMT imaging. The PMT image is formed by the time-averaged Aux(t) channel at each pixel. Scanning more slowly improves the noise (via averaging) but does not increase the signal amplitude, thus improvements in the signal to noise ratio are limited to reducing the noise. The scans shown in Figures 5.1-5.5 show the results for gradually decreasing current.

It is interesting to note that the step edge in Figure 5.1 displays increased luminescence rather than decreased luminescence. Note that this image was taken at very high currents compared to any other PMT image in this section and compared to most images in the literature. In addition, Figure 5.1 was the only image taken with $V_b=-10$ V. The difference in luminescence at the step edge is likely because at these parameters we are in the field emission regime. Different processes are likely to be at play here.

It is also interesting to note that while defects appear prominently in both the PMT and STM images in Figure 5.1, they appear prominently in the PMT image and less prominently in the STM image in Figure 5.2. A similar phenomenon (luminescence images betraying defects and impurities which are invisible or faint in the STM images) was noted in [78]. Note that a 20 ms $t_{\text{raster}}$ (time spent at each pixel) was used for Figures 5.1-5.2.

Obtaining images at lower tunnelling currents required slower scanning to reduce the noise. A 50 ms $t_{\text{raster}}$ was used for Figures 5.3-5.5.

A slight improvement in signal quality (in this case, amplitude) was achieved when switching from
Figure 5.2: STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm$^2$, $I=5$ nA, $V_b=-3$ V. Note the tip is slightly double in this image. The quenching of the luminescence at the end of the screw dislocation is interesting.

Figure 5.3: STML image (left) and STM image (right) of clean Ag(111) steps. 30x30 nm$^2$, $I=500$ pA, $V_b=-3$ V.

negative to positive bias. This can be easily checked when initially testing the tip, by toggling the bias while watching Aux(t).

Once we knew that PMT imaging could work, we performed wavelength-resolved measurements with the optical spectrometer. Preparation of the set-up and alignment followed the procedure outlined in Section 3.3.4. Again, we knew what was expected, namely the photon emission corresponding to the plasmon resonance of the tip-sample junction, which should be a peak centered
somewhere in the neighborhood of 600 nm [77]. We collected point spectra of the surface as well as an optical grid, see Figures 5.6 and 5.7. Note that for point spectra on bare Ag(111), the location and amplitude of the peak would change considerably depending on the state of the tip. The peak could be centered anywhere between 500-600 nm, and the amplitude would vary between 30 counts and 200 counts (for +3 V, 200 pA tunnelling).

Unfortunately, as one can see in Figure 5.7 the optical spectroscopy grid did not work out as expected. The image formed from plotting the integrated spectra at each pixel shows that the grid
Figure 5.6: Point optical spectra on bare Ag(111) ($I=200$ pA, $V_b=+3$ V, 100µm slit, and CCD exposure time = 100 s).

Figure 5.7: Bottom left, Integrated optical spectroscopy grid. Counts integrated from 450 - 730 nm. Top left, Example spectra collected at first pixel in grid. Right, Associated STM image for optical grid (30x30 nm$^2$, $I=50$ pA, $V_b=0.03$ V). Optical grid taken at $I=50$ nA, $V_b=3.25$ V, with 50 ms CCD exposure time. The grid was aborted early so a scan taken at the same resolution before the grid was started is the one shown. The area delineated in red in the STM scan corresponds to the section plotted as the integrated optical grid.
started out correctly, but that the steps seem to drift across the screen as the up scan continues. The problem was that saving the data to file took a little bit too long at some pixels: the time spent at each pixel was set to 3 seconds, with only 0.5 seconds of that time CCD exposure time; the remainder of the time was allocated to saving the data and running the code. The readout for the CCD should only take 50 ms, and the code running should only add a few hundred more milliseconds. Observing the grid while it was running revealed that saving the data (writing it to file) was the most time-consuming aspect of each pixel. As the grid continued, every once in a while the data would still be saving when the next TTL pulse was sent. This resulted in that TTL pulse being missed and that pixel not getting a spectrum. Since this happened randomly throughout the grid, there was no way to unflatten it properly to create an image.

This problem can be solved immediately by further extending the \( t_{\text{raster}} \) for scanning - the MATE script which extends the \( t_{\text{raster}} \) can simply be edited to have a sleep time of 4 seconds instead of 3 seconds (replace `sleep(3000)` with `sleep(4000)`). Of course, this is an undesirable solution since this will mean that optical grids take even longer than they already do - adding a second per pixel in an 150x150 pixel grid adds an additional 6.25 hours to the grid running time. The better solution is to buffer the data and only write it to file at the end of each line, when the tip is walking back to the start of the line. This usually takes several seconds when scanning slowly, and can be adjusted by adjusting the ‘move time’ in the Matrix. The TTL pulse (line scan clock) which triggers at the end of the line is already extracted from the CRTC and is on the timing signals cable, all one has to do is adjust the LabView code to change the saving to occur after it sees the line scan clock. This will have the additional benefit of either drastically reducing the time required to take a grid (since one will only need about 1 second per pixel) or allowing one to take grids with longer CCD exposure times, improving the signal quality.

Note that when running optical spectra grids, one should keep the actual \( t_{\text{raster}} \) short and adjust the MATE script to get desired time spent at each pixel. Adjust the move time as desired to ensure that the tip walks at a reasonable speed back to the start of the line scan. If the \( t_{\text{raster}} \) is set to be long (like 500ms), then the move time will default to being long as well- even if you ‘decouple’ them and specify it should be short (there seems to be a hard-coded setting in the Matrix where the move time can only be half the \( t_{\text{raster}} \)). Having the tip walk back to the start of each line very slowly will make your grid take at least 1.5 x as long.
5.2 Luminescence measurements of CuPc-PTCDA on NaCl/Ag(111)

Luminescence was also collected from the CuPc-PTCDA system on NaCl/Ag(111)\(^2\). Unfortunately, the molecules did not luminesce in our experimentally accessible wavelength range. Figures 5.8 and 5.9 show the results for PMT imaging of both isolated CuPc and PTCDA as well as the XO configuration of CuPc and PTCDA. Note both images were taken at negative bias, but the result should be the same at positive bias since the luminescence mechanism is roughly symmetric with respect to Fermi \([5], [74]\)\(^3\). Note the molecules in Figures 5.8 and 5.9 appear somewhat skewed, this is due to the long scan time \(t_{\text{raster}}=50\) ms combined with piezo drift.

![Figure 5.8: STML image (left) and STM image (right) of adjacent isolated CuPc and PTCDA on NaCl(2ML)/Ag(111) (9x6 nm\(^2\), \(I=100\) pA, \(V_b=-3\) V). The luminescence is quenched on both molecules, the bare NaCl/Ag substrate shows more emission than the molecules.](image)

We also collected point optical spectra on CuPc/PTCDA clusters to see if perhaps some luminescence could be extracted with a little luck (even though we knew that would be unlikely due to the PMT imaging results). All of the optical spectra discussed in this chapter were taken with the 300g/mm grating (500nm blaze) with varying centre wavelength. Note that I did not perform an intensity calibration before collecting this data, but I did perform a wavelength calibration. Not performing an intensity calibration was a mistake! See Section 5.3 for more details of how this may have affected the measurement. The lack of intensity calibration may mean that two of the same measurement at different center wavelengths could look different. Luckily, most measurements were taken with both a 650 nm center wavelength and a 550 nm center wavelength, so there is no chance that any variability in the intensity between the two measurements could have ‘hidden’ the luminescence signal.

\(^2\)Spectra were collected on both bilayer and trilayer NaCl.

\(^3\)Changing bias either changes the states one would see transitions between (for a LUMO-LUMO+1 type transition) or changes the direction of a LUMO-HOMO transition. For PTCDA the energy gaps between HOMO and HOMO-1 are almost the same as between LUMO and LUMO+1, and for both molecules the energy gap between HOMO-LUMO remains constant no matter which direction the transition between them goes. In addition, no luminescence was observed at positive bias when taking point spectra.
To collect luminescence from the molecules, we tried collecting spectra at both positive and negative bias, at both 550 nm and 650 nm center wavelengths, on both bilayer and trilayer NaCl, and even with the molecule attached to the tip (both tunnelling over Ag and NaCl). In all cases, the molecules did not appear to luminesce.

For example:

1. At -3V, for an XO on a bilayer, the PTCDA shows no emission at all and the CuPc shows modified NaCl emission (see Section 5.3 for a discussion of the NaCl emission). See Figure 5.10 for an example of the type of ‘spectra’ we observed. Measurements were taken at both 550 nm and 650 nm center wavelength.

2. At +3V, for an XO on a bilayer, neither molecule showed any emission. See Figure 5.11 for an example of the type of ‘spectra’ we observed. Note the PTCDA was jumpy and no spectra on the PTCDA were obtained where the PTCDA did not jump. The CuPc did not jump in the spectra shown. Measurements were taken at both 550 nm and 650 nm center wavelength.

3. At +3V, for isolated molecules as well as XO on trilayer, no emission was evident. Measurements were taken at 550 nm center wavelength.

4. At +3V, we picked up both CuPc and PTCDA (separately) and tried to see if there was emission when the molecule was attached to the tip. There was not. Interestingly, picking up molecules slowly killed any emission from that tip, even when tunnelling over Ag at larger currents. Measurements were taken at 550 nm center wavelength.

---

4 Even though we were not tunnelling into the known vibrational resonance at ~2.1 V, there may have been another vibrational resonance at 3 V.
Figure 5.10: Point optical spectra on CuPc and PTCDA in XO configuration ($I=200 \text{ pA}, V_b=-3 \text{ V}, 250\mu\text{m slit, and CCD exposure time = 200 s}$). Note the measurement over the CuPc molecule shows the emission seen on bare NaCl but attenuated (see Section 5.3 for a discussion of the NaCl emission). The measurement over PTCDA shows no emission, even though both bare Ag and NaCl showed emission prior to this measurement. This is roughly consistent with what was observed in the PMT images; namely the luminescence is strongly quenched over the molecules compared to the bare NaCl or Ag.

Figure 5.11: Point optical spectra on CuPc and PTCDA in XO configuration ($I=200 \text{ pA}, V_b=+3 \text{ V}, 250\mu\text{m slit, and CCD exposure time = 200 s}$). Note the luminescence is totally quenched over both molecules. Both bare Ag and NaCl were showing emission immediately prior to this measurement.
5.3 Point optical spectra collected on NaCl/Ag(111)

While we did not see any emission on the molecules, we did see an interesting signal on the bare NaCl. For weeks I thought the source of the signal was a molecule on the tip, which is why we tried picking up molecules and collecting luminescence. However, the result of that experiment showed that the signals shown in Figures 5.13, 5.14, and 5.10 is not due to a molecule on the tip - it is a genuine signal from the bare NaCl. My oversight in not performing an intensity calibration really delayed me figuring out that this was a real signal - the signal is almost unremarkable when measured at a center wavelength of 550 nm, but is notable when measured at a center wavelength of 650 nm. I would advise the reader to be careful and always perform a full wavelength and intensity calibration at all relevant center wavelengths if the spectrometer has been moved or has been left unused for some time. Note that the signal is real and not simply due to the lack of intensity calibration. If it were due only to the lack of intensity calibration, the same spurious signal would have been visible on bare Ag. Bare Ag always showed the same single peak (moving, but a single peak, consistent for a given tip) at both 550 and 650 nm center wavelength. Even at 550 nm center wavelength, the spectra on NaCl is not what would be expected for a ‘regular’ surface plasmon: it has two to three side peaks which indicate something more is going on (see Figure 5.12). When spectra were collected at a center wavelength of 650 nm, the uniqueness of the signal becomes evident: see Figures 5.13 and 5.14.

Figure 5.12: Point optical spectra of bare NaCl taken at 550 nm center wavelength showing a bimodal peak ($I=200$ pA, $V_b=+3$ V, $100\mu m$ slit, and CCD exposure time = 200 s).

The spectrum shown in 5.13 and 5.14 are taken with different quality tips. One can see that the emission in Figure 5.14 is stronger and cleaner than that in Figure 5.13. In either case, as well as in Figure 5.10, where the spectra was collected over CuPc revealed only the quenched NaCl emission, one can see a signal which is clearly different from that of bare Ag(111).
Figure 5.13: Point optical spectra of bare NaCl taken at 650 nm center wavelength showing multiple strong peaks ($I=200$ pA, $V_b=-3$ V, 250$\mu$m slit, and CCD exposure time = 200 s).

Figure 5.14: Point optical spectra of bare NaCl taken at 650 nm center wavelength showing multiple strong peaks ($I=200$ pA, $V_b=+3$ V, 250$\mu$m slit, and CCD exposure time = 200 s).

The potential source of this signal is discussed in Section 5.4.

5.4 Discussion and suggestions

5.4.1 The signal seen on NaCl

When NaCl is adsorbed on Ag(111), the Ag(111) surface state band remains, forming a two-dimensional interface state which is confined to the insulator/metal interface. Note that the interface state is shifted up in energy from the Ag(111) surface state. This interface state is unpopulated, so
one can inject a charge into it [106], [80]. Inelastic tunnelling into this interface state can excite
a surface plasmon, which we can detect if it is coupled to the nanocavity and in our detectable
wavelength range.

In general, a surface plasmon would not have multiple strong peaks. The simplest explanation is
that the NaCl confines the electrons to a quantum well, and the spectrum shown corresponds to
radiative transitions between energy levels in this quantum well [107].

It is possible that the source of this signal is a surface plasmon polariton, whose dispersion relation
is altered by the presence of the Na$^+$ and Cl$^-$ ions on the surface, creating a periodic boundary
condition in the 2D space. Further complexity can be introduced by considering the phonon modes
of the NaCl and how those modes would in turn alter the surface plasmon polariton’s dispersion
relation. One may also want to consider the relative placement of the Ag atoms to the Na$^+$ and
Cl$^-$ ions at the interface, as the Moire effect may manifest here in the surface state modulation. The
electronic structure of crystalline and thin film NaCl has been explored both theoretically and exper-
imentally, for example in [108], [109], [106], [110], [111]. Hövel et al. studied the modification of
the Ag(111) surface state with STM after the adsorption of Xe, and found that a modified standing
wave pattern emerges in $\frac{\partial I}{\partial V}$ maps in both the Ag(111) and the Xe islands [80]. Repp et al. studied
NaCl/Cu(111) and showed that the interface state band shows strong standing wave patterns which
obey Snell’s law at the NaCl island step edges [111].

Note the two strong signals shown in Images 5.13 and 5.14 were both taken about 4nm away from
the NaCl step edge. It is possible that the interface state band in our case has a dispersion relation
with more than one term, which would lead to peaks in the observed luminescence spectra. This
can be determined by following Repp et al.’s method carefully, and taking a more complex fit to the
$k$ vector data.

There are more possibilities which could explain this signal. Unfortunately, an in-depth exploration
of this signal is outside the scope of this thesis due to time constraints. In any case, this signal and its
implications warrant further investigation once confirmed by measuring with an intensity calibrated
spectrometer.

5.4.2 The molecular luminescence, or lack thereof

Detectable molecular luminescence in a tunnel junction is a complex interplay of a number of fac-
tors, and there remains some debate about the specifics. Buker and Kirczenow along with Chen et
al. are responsible for some of the most in-depth theory surrounding the phenomenon of molecular
luminescence in a STM junction [112], [74] [113]. Buker and Kirczenow took a semi-classical ap-
proach to the problem, and Chen et al. built on their results to introduce a full quantum theory of
molecular electroluminescence in STM junctions. In addition, Hoffmann et al. showed that the specific geometry of the tip can have a significant affect on the emission spectrum, both in the shape of the emission peak and the location in energy of the peak [103]. Aizpurua et al. showed that increasing the tip-sample distance results in an overall blue shift of the emission, while the spectral shape remains unaffected. They also note that the overall aperture (sharpness) of the tip is responsible for the rough position of the emission peak [104].

Figure 5.15: Schematic indicating the basic STML mechanism as described by Buker and Kirczenow. Adapted from [5].

Because the Ag(111) resonance was often seen to be between 500-600 nm, the tip-sample distance effect could play a role in pushing the resonance out of our experimentally accessible window. For example, the Ag resonance was often measured at 200 pA over bare Ag. The tip was then moved over a molecule on (2 or 3 ML) NaCl, at the same current. The tip would then be farther from the underlying substrate, blueshifting the Ag resonance, possibly right out of the range we can detect. The best mitigation for this is to widen the bandwidth of the in-vacuum windows. But this alone does not answer why the CuPc and PTCDA did not luminesce even within our allowable wavelength range. To consider other reasons, we turn to Buker and Kirczenow along with Chen et al..

The basic model is that the detectable luminescence is the product of resonant enhancement from radiatively-coupled surface plasmons excited from inelastic tunnelling into the underlying substrate and photons due to radiative decay between the LUMO - HOMO of the molecule (or the LUMO+1 - LUMO, etc). Cavity QED indicates that coupling the molecular photons with the plasmon enhances emission by several orders of magnitude. For this to occur, the LUMO-HOMO gap must be inside the energy window defined between the tip and substrate Fermi levels for a radiative transition to be possible, see Figure 5.15. In addition, optical transitions between the higher energy orbital and the
lower energy orbital must not be forbidden. A key aspect of Buker and Kirczenow’s theory is that the energy levels of the molecules are not pinned to their values at zero bias; they shift as a bias is applied. To calculate this shift, Buker and Kirczenow assumed that the total charge of the molecule stays constant as a bias is applied, which necessitates a shifting of the energy levels. As the HOMO shifts upward towards and past Fermi, it becomes partially or wholly unoccupied, which is what allows a transition into that orbital.[6]

Buker and Kirczenow predicted that the photon emission rate is very sensitive to coupling asymmetries between the molecule and tip and the molecule and underlying substrate. This is predicted to lead to significant quenching of the luminescence if there is asymmetric coupling between the substrate and molecule vs the molecule and tip. Consider for example that the molecule is more strongly coupled to the substrate than the tip. In this case, the electrons incoming from the tip have a relatively low probability for entering the molecule and a high probability for exiting into the substrate. In this case, there will be a relatively large number of surface plasmons excited but relatively few photons to couple to. One needs a balance of electrons entering into the substrate, exciting plasmons, and entering into the molecule, decaying radiatively from the LUMO to the HOMO, to get the kind resonant enhancement which is necessary for successful luminescence detection.

The asymmetrical coupling may not be the culprit for our lack of luminescence since we explored both bilayers and trilayers of NaCl, but the exact coupling strengths remain unknown so we can’t say for sure either way. Conversely, our ‘low’ tunnelling current of 200 pA could amount to molecules which are more coupled to the substrate than the tip.[7] What seems more likely is that the radiative transition from LUMO - HOMO or LUMO+1 - HOMO was not well-matched to the plasmon resonance. If this is the case, then there will be no resonant enhancement effect, and the luminescence which is produced is at such a low level that it is undetectable.

We have one clue from the PMT images: the substrate emission was not seen when tunnelling into the molecules. This implies that the asymmetric coupling may not be the problem: If that were the case we would likely see the substrate emission, and not a ‘darkness’ where the molecules lie. This is because the electron has a high probability of entering directly into the substrate and exciting a plasmon which would resonate with the nanocavity, as shown on bare Ag(111) and bare NaCl(2ML)/Ag(111). Also, if the molecular HOMO-LUMO gap did not lie in the Fermi window we would also likely see the substrate, again for the same reason. This leaves us with the plasmon resonance being mismatched to the radiative decay in the molecules, leading to little or no resonant enhancement of the fluorescence and an essentially undetectable signal. Rough calculations,

---

6The luminescence found by Qiu et al. was most likely a LUMO+1 - LUMO transition, but Buker and Kirczenow’s discussion is centered around LUMO-HOMO transitions.

7In fact, the negative charge of PTCDA on bilayer NaCl indicates that there is definitely considerable coupling between PTCDA and the underlying substrate.
taking the CuPc transport energy levels as equivalent to the optical energy levels\textsuperscript{8} and considering the LUMO-HOMO gap as well as the LUMO+1-HOMO gap, we find that the luminescence from CuPc would be either $\simeq 250$nm or $\simeq 400$nm. Neither of these values is close to the 500-600nm resonances we saw on Ag\textsuperscript{9}. In addition, the NaCl signal may be playing a role - if the NaCl is strongly modulating the Ag plasmon mode in some way where it can’t couple to radiation emitted from the molecules, we would similarly see a lack of detectable luminescence.

A final option for explaining the observed lack of luminescence from the molecules is that the molecules actually are luminescing, and the Ag plasmon is resonating with that luminescence, but outside of our experimentally accessible window. Note that STM-induced luminescence has been observed from thin films of CuPc on Au(111) \cite{114}. The resonance was around 700 nm. The combination of thin films and a different substrate would have drastically shifted the energy levels compared to small clusters on NaCl/Ag(111). In any case, adjusting all the relative energy levels via a change in substrate and or molecules will likely solve the problem, and widening the optically accessible range will make future attempts more likely to succeed.

5.4.3 Suggestions for future experiments and improvement of the current experimental set-up

For future studies, a change in substrate and/or molecules is warranted. Luminescence has been demonstrated on Au(111) with a plasmon resonance at 500-600nm, which is just inside our accessible range. Expanding the experimentally accessible wavelength range by replacing the in-vacuum windows with ones allowing a broader band of radiation through will open up the selection of potential molecules and substrates but will decrease the cryogen hold time, presenting a tradeoff to the user. The tradeoff can be mitigated by using smaller windows, or by using the same diameter windows with shutters which can be closed when the system is not being used for optical measurements.

Another option is to use molecules as spacers instead of NaCl: Dong \textit{et al.} demonstrated success with this model using porphyrin molecules on Au(100) (note their resonances were in the range of 600 - 700 nm) \cite{5}. When using molecules as spacers, it is easy to explore how the STML changes with increasing thickness, and once the desired thickness of one molecule (say, PTCDA) is found then one can deposit the second molecule (say, CuPc) right on top. Another advantage of this method is that this will more closely resemble the interface of a real thin-film organic electronic device. Note that instead of plasmon-mediated emission, this approach will result in molecular

\textsuperscript{8}The optical gap is likely smaller than the transport gap, which may push the luminescent photons into the range of the plasmon resonance, so this can’t be concluded for sure.

\textsuperscript{9}As others have found, the peak of the Ag resonance shifts considerably with tip changes.
fluorescence from hot electron injection excitation, which involves radiative decay associated with HOMO-LUMO transitions and Frank Condon transitions from the excited state to the ground state [5], [113].

**Figure 5.16:** STM constant-current image of a PTCDA island grown on Ag(111) with CuPc around the edges and on top (40x40 nm$^2$, $I=5$ nA, $V_b=0.35$ V).

An approach to this type of molecular layering was achieved in December of 2015, when we grew large PTCDA islands on Ag(111) then added in CuPc; see Figure 5.16.

Iterating through growing ever thicker layers of PTCDA and testing the luminescence will be relatively easy since the sample won’t need to be cleaned between depositions: the new layers can be added right on top. Once the PTCDA spacer is optimized, a single deposition of CuPc results in isolated molecules sprinkled on top of the PTCDA islands.
Chapter 6

Conclusions and future directions

In this thesis, we have demonstrated the successful coupling of optical measurements with a scanning probe system. New experimental capabilities now include illumination of the tunnel junction and local detection of the potential excitation by STS and KPFM, tunnelling luminescence detection by PMT (offering an integrated signal), and tunnelling luminescence detection by optical spectrometer (offering a wavelength-resolved signal). The luminescence collected can be imaged at each $(x,y)$ pixel to create either a 2D luminescence map (directly from the PMT signal or from an integrated spectrometer signal) or a 3D $(x,y,h\nu)$ optical grid. In principle, additional modes involving illumination and tip enhancement of fluorescence or Raman spectroscopy are also possible with the apparatus.

The system under study (CuPc and PTCDA clusters on NaCl/Ag(111)) provided no clear signal in STS measurements for illuminated vs not illuminated molecules. This could be due to poor optical alignment and/or energy level alignment both of which can be addressed; immediate plans involve STS and KPFM measurements on illuminated CuPc-PTCDA clusters on NaCl/Au(100). Tunnelling luminescence measurements on molecules showed quenching of the modified plasmon resonance seen over bare NaCl. Understanding this result, as well as the modified plasmon resonance observed over bare NaCl, will require further investigation.

A number of options for future directions are offered below.

6.1 Kelvin probe force microscopy

The immediate plan moving forward is to perform KPFM, which can measure local charge distributions, on small clusters of CuPc and PTCDA on NaCl/Au(100), both with and without optical
excitation. If this experiment works, we will have achieved real-space imaging of charge transfer between single molecules. If this occurs, then further exploration of the specific system may be warranted. In particular, measurements of the luminescence spectra to correlate vibronic levels with charge transfer would be a logical next step. Because Au(100) may have a redshifted plasmon resonance compared to Ag(111), we may have to replace the in-vacuum viewports with windows which allow a wider band of radiation to pass through. In addition, a tip etching procedure for Au will have to be optimized, but there are some options in the literature which will provide a good starting point (for example [115], [71]). Other studies which do not require changes to the system could include detailed studies of excited state wavefunctions, via simple high-resolution STM imaging, or IETS mapping using \( \frac{d^2I}{dV^2} \).

6.2 Optical spectroscopy on NaCl/Ag(111)

The signal seen on NaCl/Ag(111) is intriguing, and it is regrettable that it could not be explored further in this thesis due to time constraints. A thorough literature review would be the first step. Then, if the theory warrants further measurements, obtaining several 3D \((x, y, h\nu)\) grids of some NaCl islands on Ag(111)\(^1\) as well as some high-resolution point spectroscopy would be very useful for untangling the origin of the signal observed.

6.3 Large area photomultiplier tube luminescence measurements for finding luminescent molecules

As suggested in Section 3.3.2, implementing the photon counting scheme as detailed will enable the collection of high-quality large area scans which can discern if only a few clusters of molecules are luminescing. This will allow the experimenter to ‘zoom in’ on those clusters of interest quickly, saving considerable time hunting for clusters which luminesce amongst a forest of those who don’t. In addition, the implementation of photon counting will offer (more direct) quantitative measurements\(^2\) of the emission for a given system, allowing for direct comparison to theories which are working towards a better understanding of the origin of STM-induced luminescence.

\(^1\) Of course, any further measurements should be performed with a properly intensity and wavelength calibrated spectrometer.

\(^2\) The measurements performed with a PMT are more directly quantitative than those performed with a CCD, since the CCD and optical spectrometer introduces additional modifications to the photon count.
6.4 Scanning tunnelling luminescence on supported molecules

Obtaining sub-molecularly resolved STML grids is now possible. Finding a combination of substrate and molecules which will work given both the experimental constraints and the factors discussed in Section 5.4.2 will require some careful planning as well as some luck. It is possible that several substrate/molecule combinations will need to be tried before one finds success. As discussed in Section 5.4.3, one can also take the approach of using molecules both as spacers and emitters, which may work for the current substrate and molecules already in the system, and would be the quickest option to try next in terms of set-up and debugging time.
Bibliography


polarization-induced energy level shifts at boundaries of organic semiconductor 
nanostructures. Nat Commun, 6, oct 2015. → pages ii, 4, 66, 78


and S. Mashiko. Vibrationally Resolved Fluorescence from Organic Molecules near Metal 
Surfaces in a Scanning Tunneling Microscope. Physical Review Letters, 92(8):086801,
2004. → pages xvii, 90, 96, 98, 99


2015):1–9, 2015. → pages 1

[8] Sean E. Shaheen, David S. Ginley, and Ghassan E. Jabbour. Organic-Based Photovoltaics: 

1986. → pages 1


→ pages 2


109


Appendix A

Supporting materials: knudsen cell evaporator for epitaxial growth of NaCl: design and assembly

![Figure A.1: Evaporator without heat shield or shutter](image)

This appendix describes the fabrication and assembly of the home-built Knudsen cell which was used in this thesis to deposit NaCl onto substrates. This Knudsen cell is designed to be able to deposit a multitude of molecules at a variety of operating temperatures and currents: from 80-600°C and 0.7-4.0 A. A photograph of the evaporator without the heat shield and shutter is shown above. The evaporant is placed inside a quartz crucible, in the middle of the assembly. The quartz cell is
Figure A.2: Sophomoric diagram of major evaporator components

wrapped with a tungsten wire which acts as the heater coil, and a thermocouple wire is attached to a button on the glass. The temperature of the cell is controlled manually by passing current through the heater coil with a power supply while monitoring the temperature read by the thermocouple. The assembly is supported by two stainless steel rods, screwed into the reducer flange, and two macor ceramic disks, held by wire to the rods. The current design can be improved further with some minor modifications which are discussed in the body of this document.

A.1 Parts

A.1.1 Evaporator body

1. Zero Length Reducer Flange, 1 1/3” to 2 3/4’
   MDC PN: 150001
Qty: 1

2. Mini Thermocouple and two pin copper feedthrough
   Insulator Seal (MDC) PN: 9392007 - 50 mil copper rods or
   Insulator Seal (MDC) PN: 9392015 - 100 mil copper rods
   The 50 mil feedthrough is preferred

3. Quartz Tube
   Chemglass, Inc. PN: CGQ-0800-05
   6mm - outer diameter
   4mm - inner diameter
   We obtain our quartz crucibles from the Chemistry glass shop.

4. Tungsten wire
   0.01 in (10mil). Purchase about 10 ft in to have on hand
   Qty: 1 ft

5. 316 stainless steel set screw shaft collars
   McMaster-Carr PN 9943K11 - for 50 mil rods
   McMaster-Carr PN 9943K13 - for 100 mil rods
   These will be used to clamp the W wire to the copper feedthroughs, and the TC wire to its
   feedthroughs. You should purchase 10, as they get lost easily. Make sure you purchase 316
   SS to reduce outgassing when assembly is hot.
   Qty: 4

6. Thermocouple wire
   Chromel:
   i. 10mil
   ii. Omega PN: SPCH-010-50ft
   Alumel
   i. 10mil
   ii. Omega PN: SPAL-010-50ft
   Qty: 6in each

7. 316 stainless steel threaded rod
6-32 threading
The rods will make up the support structure for the evaporator.
Qty: Two, 4in each

**Suggestion:** Better structural support would be provided by standoffs which hold the macor in place. The suggested design for the standoffs is explained in the construction and assembly sections. Materials required would be 316-SS non-threaded rod, approximately 5mm diameter for the machinist to use for constructing the standoffs.

8. Copper foil - (Oxygen Free) e.g. Alfa Aesar - Stock no: 13380, Lot no: D22N38
   5 mil thick (not important)
   This will be the thermal radiation shield for the evaporator. It allows for higher achievable temperatures at lower currents.
   Qty: 6x6 in², but you need a large piece to secure properly for waterjetting.

9. Macor Disks
   We had these machined to our specifications from a macor rod we purchased. The solidworks files are available on our internal wiki. Figure 3 below illustrates the general shape. The two disks used are the same save for the centre hole: in one disk the hole is large enough for the crucible to pass through, in the other it is not.
   Macor: McMaster-Carr: part no: 8489K81
   Macor rod - diameter: 7/8”, 3” length rod
   Qty: one of each style of disk. Of course, get more than 2 of each machined in case any are broken during assembly.

A.1.2 Shutter

1. Rotary motion feedthrough
   MDC Part Number: 67000
   Mini flange mountable
   Qty: 1
Figure A.3: Drawing for one of the Macor disks. Dimensions are in millimetres. Solidworks files are on our internal Wiki.

2. Double edge 2 3/4 flange with mini side port
   MDC Part Number: 140013-2001
   This is a specialty item that MDC made for us. $200
   Qty: 1

3. Stainless steel threaded rod
   m2 thread
   Qty: 4-6 in
   Be careful to keep the rod as straight as possible, this will facilitate the assembly. The small diameter rod will bend easily.

4. Molybdenum sheet
   5 mil thick (not important)
   This sheet will be made into the actual shutter. It will be attached to the SS rod.
Qty: 2 in², but you need a larger piece to secure for waterjetting

5. Nuts
   m2 thread
   Used to hold shutter on rod
   Qty: 2

6. Lock Washers
   for m2 thread
   Used to hold shutter on rod
   Qty: 2

7. Set Screws
   4-40 thread
   Used to hold rod in place on the feedthrough
   Qty: 1

8. Hex screws m3 thread
   Socket cap hex screws are used to screw down the heat shield tabs. Note these need to be vented.
   Qty: 2

All quantities given are the actual number used in the assembly. More than the minimum should be purchased and cleaned in case something is dropped or lost. All steel items should be 316 SS, and any copper should be OFC.

A.2 Construction

A.2.1 Base

The evaporator base consists of a 2 3/4 to mini reducer flange with four blind tapped holes machined on the 2 3/4 side. The holes should be drilled as indicated in Figure 4. Unless you are comfortable machining stainless steel flanges, this job is left best to the machine shop - especially tapping of the holes and minding the knife edge on the flange. Two of these holes (m3) are used
Figure A.4: Drawing of the reducer flange with machined holes dimensioned.

for mounting the copper heat shield. The stainless steel support rods (or, in an improved version, the standoffs) are screwed into the other two holes (m2.5). The mini port side is used to attach the filament/thermocouple feedthrough.

1. Machine the 2 3/4 to mini reducer flange as indicated in Figure 4.

2. Cut the 6-32 SS threaded rod to the desired length to make the two support rods. Note it needs to be vented on the end which screws into the flange.

   Alternatively, have the machinist fabricate the SS standoffs for supporting the structure. Relevant Solidworks files for the standoffs are on the wiki. Note the standoff screws need to be vented.

3. Clean all pieces thoroughly to ensure they are UHV compatible.

A.2.2 Quartz cell

The Chemistry department has a glass working shop which can make nearly any specialized piece of glass. Write up your desired dimensions appropriately and send them to the shop for fabrication. We added 'buttons' to the side of the crucible to wrap the thermocouple (TC) around. Wrapping the TC around a button on the side of the crucible rather than the base of the crucible serves two purposes. First, it allows for an improved placement of the TC - it can be placed near to the (top) surface of the matter in the crucible, which is ostensibly where the matter will be evaporating from. Second, it reduces the overall length over which the TC is shorted, improving the reading's accuracy. Any short along the length of a TC acts as a new junction, and it is the 'last' short on the line.
Figure A.5: Rendering of the base flange with standoffs supporting the macor disks and crucible. On the left, the flange has been rendered transparent to help visualize the locations of the machined holes and other features. On the right, the macor disks have been rendered transparent to help visualize the standoffs mating with each other.

whose temperature you will read. Preventing shorts along the length or at least keeping them very close to the location where you would like to read the temperature is optimal. Also, shorts from wrapping have poor electrical contact and may be unreliable or changeable - which is why using the actual (welded) junction is optimal.

Each button used for a TC must have two accompanying buttons, above and below, to act as insulators from the filament wire. If you have only a single exposed button with your TC wrapped around it, the filament wire can scootch down the crucible and short onto the TC wire. Obviously, this is bad.

Don’t forget to clean the crucible so that it is UHV compatible.
A.2.3 Heater wire

1. Cut 1 foot of 10 mil tungsten wire.

2. Wrap the middle of the wire around a screwdriver with a diameter that is slightly smaller than the diameter of the quartz cell. For 0.24 inch diameter cell use a 0.15 in screwdriver. Wrap the heater wire very tightly, this will ensure the heater wire is tightly wrapped around the cell.

3. Make about 10 turns

4. Ensure there is at least 2 in of wire left over on either side. You will use this to make contact with the copper feedthroughs.

5. Make sure it is cleaned to be UHV compatible.

A.2.4 Thermocouple

1. Spot weld the chromel wire to the alumel wire on one of the ends. Sometimes spot welding can be difficult with very fine wires, so I used a hydrogen torch to melt the ends together. This made a beautiful junction which was covered in an oxide. I removed the oxide with the help of an optical microscope and a razor blade.

2. Before proceeding any further, take the time to test the thermocouple gives you appropriate readings.

3. Clean the thermocouple to be UHV compatible.

A.2.5 Radiation shield

The radiation shield is made out of a thin copper sheet, rolled into a tube as shown in Figure 6. The shield reflects back the thermal radiation emitted by the hot tungsten filament allowing for more concentrated heating. The shield also minimizes radiative heating of nearby chamber walls. The shield is secured to the flange via two tabs at the base which screw into the flange. The copper sheet was cut with the waterjet, and a separate lid was also made to reduce the aperture width (allowing for a smaller shutter). The relevant solidworks files for reproducing this heat shield are on the wiki.

1. Use the solidworks files from the wiki to cut the shield and lid pieces using the waterjet. If you do not know how to use the waterjet, the shield can be cut by hand or you can get someone to help you with the waterjet.
2. Roll up the copper shield along the long side to make a cylinder. Slide the 5 tabs along the one side through the holes on the other side. Bend the tabs backwards to keep the cylinder snugly closed.

3. Bend the tabs on the bottom outwards, carefully as they can snap easily.

4. Bend the tabs on the lid piece downwards and slide into the slots at the top of the cylinder from the outside (see fig. 5), then flatten on the inside of the cylinder to keep them snug.
A.2.6 Shutter

1. Contact the machine shop to perform the following step. They must be reminded to be careful of the knife edge on the part - it is helpful to them if you bring a gasket for them to use to cover the knife edge. On the inner shaft of the rotary motion feedthrough, drill a 4-40 tap hole about 1.5mm away from the edge of the shaft. This will be the hole for the set screw. Perpendicular to this hole, as close to the end of the shaft as possible, drill an m2 tap hole through the rod. Tap both holes appropriately.

2. Cut the shutter rod to the desired length (4-6 in, depending on geometry of the crucible assembly).

Figure A.7: Solidworks drawing of the heat shield. All units are in mm.
3. Cut the shutter from the molybdenum sheet into the desired shape. You can cut the shutter on the waterjet, relevant solidworks files are on the LairWiki. Otherwise, you can use some scissors and a punch to create the hole where the rod feeds through.

4. Clean all parts to make them UHV compatible (including the set screws, lock washers and nuts).

5. Attach the threaded rod to the rotary feedthrough (by threading it in!) using the set screw to hold it in place.

6. Attach the shutter to the shutter rod by sandwiching it between m2 nuts and lock washers:
   nut → lock washer → shutter → lock washer → nut
   Be sure to tighten the whole assembly well so that it does not loosen with thermal cycling.
Figure A.9: Rendering of the knudsen cell assembly in stages. In the center the heat shield and flange are made transparent, and on the right the heat shield is removed exposing the macor/crucible/standoff assembly.

A.3 Assembly

1. Clean all parts to make UHV compatible

2. Screw the 316-SS support rods / standoffs tightly into the base.

3. Attach the feedthrough with filament and thermocouple leads to the base.

4. Use a small alumel wire ’bridge’ across the SS support rods to support a macor disk about 1/2” from the base. You should choose the macor piece with the smaller central hole- this one is meant to support the base of the crucible. You will need to thread the power feedthroughs and the thermocouple feedthroughs through the holes in the disk. Alternatively, use the standoff set-up as shown in figures 5 and 9 to secure the lower (one with smaller central hole) macor disk in place.

5. Wrap the thermocouple wire tightly around a button on the crucible.

6. Feed the crucible through the heater wire you constructed earlier. Fix the ends of the heater wire to the copper feedthroughs using the sleeves and set screws. Position everything such
that the base of the crucible rests in the lower macor disk’s central hole.

7. Slide the second macor disk in place, near the top 1/3 of the crucible. This one should have the centre hole large enough to fit the crucible through. It will be held in place by either the SS rods or the standoffs. See the photo at the beginning of this document.

8. You can fill the crucible at this point.

9. Cut off any excess power or TC wire to avoid shorts. Check for shorts at the feedthroughs using a multimeter.

10. Slide the heat shield over the whole assembly. Bolt it to the base using the 2 tabs and m3 socket head screws. Bolt the heat shield tightly to the base to ensure it is well secured.

11. Check for shorts again at the feedthroughs using a multimeter.

12. Place a gasket appropriately and slide the shutter assembly over the knudsen cell assembly.

13. Place another gasket appropriately and slide the cover flange over the whole assembly.

14. Check to make sure the shutter works as desired, and write down the ‘open’ and ‘closed’ positions.
Appendix B

Supporting materials: laser power study
STS spectra averaged over smaller portions of the molecule

This appendix shows the STS results obtained when averaging the spectra over smaller subsets of the molecule. This was done to verify that potentially small and important differences which may have been present in only one part of the molecule (such as the copper center of the CuPc) weren’t getting averaged out when averaging over the whole molecule. The smaller portions of the molecule averaged over in this section are: the center of the CuPc molecule, the perimeter of the CuPc molecule, and the oxygen end\(^{1}\) of the PTCDA molecule. The results indicate that there are no major differences when compared to averaging over the entire molecule; except, for the case of the laser excitation study, that the amplitude change of the PTCDA 2 V resonance is less pronounced when averaging only over the oxygen end. See Section 4.3.1 for a discussion of the amplitude difference and its possible relation to vibrational excitation.

B.1 Masking

This section shows where the masks were taken on each molecule for averaging the STS spectra over smaller parts of the molecules.

\(^{1}\)The PTCDA molecule has two oxygen ends, in this section we are referring to the end which is farthest from the CuPc molecule.
Figure B.1: STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the oxygen end of the PTCDA molecule.
Figure B.2: STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the center of the CuPc molecule.
Figure B.3: STM and STS images showing the bounded area over which individual STS spectra were averaged for each plot. The image shown is from the 561 nm data set, and shows the areas taken to obtain an average over the perimeter of the CuPc molecule.
B.2 STS results for masking over only part of the molecules: laser excitation study

This section shows the averaged STS spectra obtained from averaging over smaller portions of each molecule. No relationship of the STS spectra shown here to the applied laser power is apparent.
Figure B.4: Comparison of dI/dV spectra for the XO configuration under illumination from the 685 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.5: Comparison of dI/dV spectra for the XO configuration under illumination from the 685 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
Figure B.6: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 640 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.7: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 640 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
**Figure B.8:** Comparison of dI/dV spectra for the XO configuration under illumination from the 561 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

**Figure B.9:** Comparison of dI/dV spectra for the XO configuration under illumination from the 561 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
Figure B.10: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 519 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.11: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 519 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
Figure B.12: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 488 nm laser. Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.13: Comparison of $dI/dV$ spectra for the XO configuration under illumination from the 488 nm laser. Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.
B.3 STS results for masking over only part of the molecules:
CuPc-PTCDA on NaCl/Au(100)

Figure B.14: Comparison of $dI/dV$ spectra for the XO configuration on NaCl(2ML)/Au(100). Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.

Figure B.14: Comparison of $dI/dV$ spectra for the XO configuration on NaCl(2ML)/Au(100). Spectra are averaged over the perimeter of the CuPc and the oxygen end of the PTCDA.
Figure B.15: Comparison of dI/dV spectra for the XO configuration on NaCl(2ML)/Au(100). Spectra are averaged over the centre of the CuPc and the oxygen end of the PTCDA.