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Author Levy, Niv Binyamin

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Investigations into nanometer scale surface opto-electro-mechanical coupling

by

Niv B. Levy

A dissertation submitted in partial satisfaction of the

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in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Michael F. Crommie, Chair Professor Steven G. Louie Professor T. Don Tilley

Spring 2010

Investigations into nanometer scale surface opto-electro-mechanical coupling

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Abstract

Investigations into nanometer scale surface opto-electro-mechanical coupling

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Niv B. Levy

Doctor of Philosophy in Physics

University of California, Berkeley

Professor Michael F. Crommie, Chair

We have used scanning tunneling microscopy and spectroscopy to investigate electromechanical coupling in two different nanoscale systems coupled to a condensed matter environment - single molecules, where we observe light induced conformational changes (photoisomerization), and graphene, where we observe conformationally controlled pseudo gauge fields.

We have observed the effects of molecule-surface and molecule-molecule coupling in photoisomerization of TTB-Azobenzene molecules on the Au(111) surface. In addition, through measurement of the photoisomerization cross section of surface bound molecules and comparing the chirality of the initial and final products of the reaction, we have gained knowledge of the likely pathways. Our studies of graphene films catalytically grown on the Pt(111) surface have found strain-induced pseudo Landau levels, which are a unique consequence of how graphene's electronic structure interacts with the local environment. These studies have allowed us to gain insight into the quantitative and *qualitative* ways in which the environment affects electro-mechanical coupling of nanoscale structures.

Single molecule photoisomerization and strain-induced effects serve as complementary examples of electro-mechanical coupling, since in the former case the position of the molecule's constituent atoms is affected via electric fields, while in the latter the position of the constituent atoms modifies the electrical properties of the film. The combination of these two effects, e.g. by depositing photoswitching molecules on a gateable and strainable graphene membrane, may open the door to new applications and enable better control of matter at the nanoscale.

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List of Abbreviations

DFT	Density Functional Theory
dI/dV	Differential Conductance
DOS	Electronic Density of States
$E_{\rm F}$	Fermi Energy
\mathbf{FE}	Field Emission
LSP	Localized Surface Plasmon
FWHM	Full Width at Half Maximum
HOMO	Highest Occupied Molecular Orbital
IETS	Inelastic Tunneling Spectroscopy
LDOS	Local Density of States
OFHC	Oxygen Free High Conductivity
LUMO	Lowest Unoccupied Molecular Orbital
ML	Monolayer
RT	Room Temperature
LT	Low Temperature (around 77 K or lower)
LHe	Liquid Helium
LN_2	Liquid Nitrogen
STM	Scanning Tunneling Microscopy or
	Scanning Tunneling Microscope
STS	Scanning Tunneling Spectroscopy
AFM	Atomic Force Microscopy
UHV	Ultra High Vacuum
HB	Herringbone
TB	<i>tert</i> -butyl

DFT

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¹And for lending a general coolness to the lab.

²Special thanks go to Omicron for being fashionably tardy, forcing Sarah to find some other occupation.

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⁵Or at least not too much.

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Introduction

Control of opto-electro-mechanical coupling at the nanometer scale opens up new realms for manipulating material properties and creating unique devices. Achieving such control within the surface environment would be particularly useful by allowing us to build upon existing platforms and technology. Two possible methods of gaining this goal are (1) utilizing intrinsic opto-mechanical properties of single molecules, for example as displayed in azobenzene photoisomerization; and (2) developing graphene based devices, where the properties of the two dimensional membrane can be controlled through local deformation of the lattice.

Graphene is useful not only for its intrinsic electro - mechanical coupling, but also as a tunable substrate,¹ affecting the opto-mechanical properties of adsorbed molecules. Hence, combining these two paths in a single device would offer new opportunities, such as bi-stable optically controlled graphene devices, and form a closed cycle where gauge fields affect and are affected by mechanical properties.

To exploit these possibilities, and in particular use the mechanical control of the graphene membrane in combination with opto-mechanically controlled molecules, we must better understand the individual components and their interaction with their surroundings. To make progress towards this goal we have studied functionalized azobenzene molecules on the Au(111) surface, and in particular, the effects of coupling between a molecule and its surroundings on photoisomerization. In addition, we have started to explore graphene substrates and their electro-mechanical properties, studying graphene grown on Pt(111), where we observe large strain-induced effects.

The overall structure of this dissertation is as follows. Following a brief summary of environmental effects upon single molecules and graphene membranes and an introduction to scanning tunneling microscopy and spectroscopy, I shall delve into the main part of the work. Chapters 3 & 4 will introduce the TTB-Azobenzene- Au(111) system and describe the experiments performed, using a previously built instrument. These experiments included the study of environmental effects and the nature of the surface photoisomerization process. This section is based on our previously published co-authored research papers.^{2–5} The combined



Figure 1.1: Schematic diagrams of various possible surface related interactions. Molecules: (a) Molecule-substrate. (b) Direct molecule-molecule. (c) Substrate mediated moleculemolecule. Graphene: (d) Change in coupling to the substrate due to local delamination (e) Change in inter-atomic interactions due to corrugation and substrate induced strain.

STM and molecular light emission experiments we wish to perform will be described in the second part, consisting of chapter 5, where the physics of light emission from a tunnel junction will be explained, and chapter 6, where the new instrument we designed and built for these measurements will be described in detail. The third part, chapter 7, will discuss our measurements of graphene catalytically grown on the Pt(111) surface and our observation of strain-induced electronic effects.

1.1 Environmental effects

Coupling both single molecules and free standing graphene to a condensed matter environment should affect opto-electro-mechanical properties in these systems. Here I discuss briefly the potential issues that arise due to this coupling. These issues are addressed in greater detail by the research presented in this dissertation. In the case of single molecules, such coupling effects include molecule-substrate and molecule-molecule interactions. For graphene on a substrate, an analogous effect will stem from modulation of film-substrate coupling due to e.g. corrugation, and possible modulation of the inter-atomic coupling due to deformation. In both cases, it is not known, a priori, if the coupling to the substrate will introduce only slight quantitative changes or lead to a whole new *qualitatively* different behavior. Several possible effects are depicted in figure 1.1.

1.1.1 Molecular photoisomerization at the surface

The environmental effects of surface coupling on photoisomerization might potentially include:

Reduced excited state lifetime: Re-arrangement of a molecule's atoms requires that the

molecule remain in the excited state for a finite amount of time. For example, while azobenzene photoisomerization is a relatively fast process, on the order of a few picoseconds,⁶ the typical lifetime of an excited electronic state in a metal is of order tens of femtoseconds. This suggests that if the electronic states of the molecule are strongly hybridized with the metallic substrate, the transition will be quenched.

- **Changed excitation spectrum:** The effects of coupling might include a change in excitation spectrum, for example, due to charge transfer between the molecule and the substrate.⁷ Alternatively, a reduction in the confinement of the electrons to the molecule might introduce new excited states, drastically changing the system's spectrum.
- **Changes in optical absorption:** Due to the optical wavelength being much longer than the molecule's length scale, it is clear that absorption by the substrate, and subsequent transfer of the excitation to the molecule, might play a decisive role, so that the dominant optical transitions are a combination of molecular and substrate excitations rather than those of the isolated molecule.¹
- **Steric Hindrance:** The coupling of the molecules to the surface causes a reduction in their ability to move, as the atoms cannot freely move in three dimensions, but rather are confined to the surface. More specifically, a large energy cost is acquired for motion of parts of the molecule out of the surface. In addition, the close proximity to other molecules in molecular islands might aggravate these issues, since it will introduce new short range interactions which will make large changes in molecular configuration even more prohibitive.

1.1.2 Coupling of graphene to a metallic substrate

While coupling of graphene to an insulating substrate has several known effects including local doping variations^{8,9} and corrugation effects,^{8,10} we are currently more concerned with the substrate effects observed in graphene films on metallic substrates. These can range from a strong interaction of the film with the substrate, completely quenching the graphene electronic structure,^{11–13} to weak coupling cases, where the electronic structure of the film is similar to that of free standing graphene.^{14,15}

However, even when the graphene film is weakly coupled to the metallic substrate, in regions where the film is lying flat on the surface the substrate DOS might overwhelm that of the film. As a result, tunneling measurements might not be able to ascertain the contribution of the film to the total DOS in these regions. Moreover, electrostatic screening effects, due to image charge formation, might suppress any local electronic structure even for delaminated portions of the film, if the distance to the substrate is too small.

The unique coupling of strain to electronic properties in graphene¹⁶ opens up a new dimension of substrate-induced effects. In particular, these effects should be observable

¹A transparent substrate would mitigate these effects, but that precludes STM studies of the system, though it is an intriguing prospect for AFM studies.

for graphene films grown on metallic substrates at elevated temperatures, since the large mismatch in thermal expansion coefficients should create large strains when cooled down.

4

Scanning Tunneling Microscopy and Spectroscopy

The scanning tunneling microscope, invented in 1981 by Binnig and Rohrer,¹⁷ is currently the highest resolution tool for measuring electronic properties at the atomic scale.

I shall review the basic theory underlying scanning tunneling microscopy and spectroscopy, delaying analysis of light emission from the STM tunneling junction till after the basic azobenzene experiments have been described. I will not discuss other specialized subjects such as inelastic electron tunneling spectroscopy (IETS), spin-polarized tunneling or manipulation using an STM, since we did not employ these in the experiments performed for this dissertation. For a treatment of these subjects, and a more in-depth review of STM and STS, one of the excellent books on the subject can be consulted.^{18–20}

2.1 Practical STM operation and overview

The basic principle of operating an STM is to bring a conducting tip close enough to the sample so that a quantum mechanical tunneling current can flow between the two under a small applied bias. As a result, from a practical point of view, an STM can be broken down into

- 1. A sharp tip.
- 2. A mechanism for controlling the position of the tip close to the surface on an Å scale. This is achieved with piezoelectric transducers, having a typical maximum range of $\sim 1\mu m - 10\mu m$.
- 3. A controller consisting of current amplification and measurement, a feedback loop, piezo drivers and data recording.
- 4. A coarse approach mechanism, so that the tip can be brought near the sample, placing it within range of the piezoelectric transducers.



Figure 2.1: Typical STM operation. The sample is biased at V_{sample} , the current $(I_{tunneling})$ is collected from the tip, amplified and read by the controller. In topography mode the controller raster scans the tip across the surface and stabilizes the distance between the tip and the surface so that $I_{tunneling}$ is constant. The resulting height change forms the image.

The details of the coarse approach mechanism are, of course, not essential for the basic operation of the STM and will not be discussed in this chapter. However, in practice they are one of the more complex parts of constructing an STM, and more details of the coarse approach mechanism of our new instrument will be given in chapter 6.

2.2 Basic STM theory

Qualitatively, one can consider a one-dimensional model of tunneling through a square barrier to understand the current flowing between the tip and the sample and the basic distance dependence. However, a more satisfactory picture, due to Tersoff & Hamman²¹ is reviewed below. In the Tersoff & Hamman model (THM) the geometry close to the sample is defined by the tip radius R and distance d between the tip and the sample (figure 2.2)



Figure 2.2: Tersoff - Hamman model geometry

and the tip is assumed to have a simple s-wave state.¹ Under these assumptions, and at T = 0, the THM results in

$$I \propto \int_{0}^{eV_{sample}} \rho_s(E_F + \epsilon) \cdot \rho_t(E_F - eV_{sample} + \epsilon) \cdot T(\epsilon, V_{sample}, s) d\epsilon$$
(2.1)

where $\rho_s(\epsilon)$ and $\rho_t(\epsilon)$ are the sample and tip density of states (DOS), respectively. The tunneling matrix element $T(\epsilon, V_{sample}, s)$ can be estimated using the WKB approximation, assuming a trapezoidal potential barrier and discarding the contribution from electrons with non-zero parallel momentum as

$$T(\epsilon, V_{sample}, s) \approx \exp\left(-s \cdot \sqrt{\frac{4m_e}{\hbar^2}(\phi_t + \phi_s + eV_{sample} - 2\epsilon)}\right)$$

where s = R + d and $\phi_t \& \phi_s$ are the tip and sample work functions, respectively.

The most important characteristic of T, and hence I, is the strong exponential dependence on the distance s, which is the essential quality underlying the vertical and horizontal resolution of an STM.² For a typical work function of $\approx 5 eV$, the current behaves as

$$I \propto e^{-2\frac{\sqrt{2m_e}}{\hbar} \cdot s} \approx e^{-2.3 \overset{\circ}{A}^{-1} \cdot s}$$

A change in distance of 1\AA thus results in an order of magnitude change of the current. While the extreme vertical resolution is immediately obvious from the exponential factor in T, the lateral resolution can be understood to be due to the same factor, since it results in the current being dominated by protrusions that are only fractions of an \AA taller than their surrounding. In practice, this translates to single atoms that protrude from the tip, so that the current predominantly flows through a single atom for a well behaved tip, which gives

¹While this would seem to be somewhat unlikely for commonly employed tip materials such as Pt, W or Ir, in practice the tip conditioning proceeds until the images are satisfactory. Hence, the tip wave function is de-facto the assumed one, likely due to the tip apex being a substrate atom.

²As a consequence, the average work function of the tip and the sample can be measured by measuring I(z) at a fixed bias.

a lateral resolution on the order of the interatomic distances in the tip. In a case where more than one atom is at a similar distance to the sample, the image is a convolution of the (complex) tip shape and the sample's surface. The technical term for such a case is "bad tip".

An intuitive understanding of these equations can be gained by considering the case of a metallic tip which has $\rho_t(\epsilon) = C$, and a metallic substrate without any sharp spectroscopic features, shown in figure 2.3. Under a positive sample bias, electrons flow from occupied levels of the tip into unoccupied levels of the samples. Due to the exponential dependence of T on the energy, most of the current is due to electrons close to the Fermi level of the tip.³ The opposite situation occurs under a negative sample bias, where electrons flow from the sample to the tip, with most of the current due to electrons near the sample's Fermi energy. In the latter case, the tunneling current is sensitive to the details of the tip's electronic structure, which is undesirable, and tends to make acquiring information about the sample's occupied states somewhat more difficult. The quantitative picture is different at $T \neq 0$, since the occupation functions are no longer step functions but rather Fermi-Dirac distributions. As a result, there is current flow in both directions, regardless of the sign of the applied bias. However, the net current flow is still in the direction indicated, and the qualitative picture remains valid.



Figure 2.3: Tunneling current flow between sample and tip under negative (left) and positive (right) sample bias. The arrows indicate the direction in which electrons flow, with the magnitude of the arrow signifying the relative contribution of electrons at that energy. Adapted from Meier.²²

2.3 Topographic mode

The most common mode of STM operation is one in which a feedback loop is used to regulate the tunneling current under a constant applied bias (constant current mode), which is the

³This is a non-equilibrium situation, so the Fermi levels of the tip and the sample do not have to be equal, rather the applied bias is fixing them at a constant difference.

mode used for all of our work. In this mode, the tip height resulting from current regulation is recorded and forms the image. As is clear from the results of the THM theory, the tunneling current depends not only on the distance between the tip and the sample, but also on the integrated DOS of both.⁴ As a result, interpretation of the image as a true topographic representation of the sample's surface is somewhat naive. However, for metallic samples (and tips), this is a reasonable approximation. The situation is different of course for a semiconducting surface, where the strong variations in DOS between neighboring atoms suggest that the image contrast is mostly due to electronic structure effects, rather than a change in the actual locations of the atoms. Imaging of organic molecules is similar to the latter case, and extracting the geometry of a sample from the STM image requires matching it to a theoretical calculation of the DOS, and a simulated image.

While the THM theory's assumption of an atomically sharp s-wave tip would seem to be unrealistic, this turns out to be a minor issue. In practice, a wide variety of tip preparation methods have been employed over the years, from simply cutting wires, to electrochemical etching, or even mechanically ground tips.²³⁵ All of these rely on the simple fact that since the tunneling current is exponentially dependent on the distance, even a macroscopically blunt tip will almost always have a small number of protrusions that extend a few Å further than the rest, and hence will tend to dominate the current. However, typically tips that lack a macroscopically smooth shape will tend to be somewhat unstable, so that *in-situ* tip conditioning such as field emission is used to achieve a more stable apex. Tip conditioning is continued until a satisfactory tip is found, which depends on the desired experiment. For example, a tip suitable for imaging might have a very non-flat DOS, rendering it unsuitable for spectroscopy.⁶ In addition, in certain cases, such as measuring the light emitted from a tunneling junction, which we shall discuss in detail in chapter 5, the macroscopic shape of the tip *is* important, so that more care needs to be taken when creating the macroscopic tip. In practice, electrochemical etching is usually sufficient to achieve regular tips.

⁴There is also a dependence on the coupling matrix element, but for a constant bias voltage it is of no importance.

⁵Though that is one innovation of Binnig & Rohrer that did not catch on.

⁶Sharp tips often have a somewhat irregular shape, as can be seen e.g. in figure 7.6, where an adsorbate in the upper right corner clearly shows that the tip does not have a simple s-wave behavior.

2.4 Scanning tunneling spectroscopy (STS)

Differentiation of the tunneling current, equation 2.1, with respect to the applied bias yields

$$\frac{dI(V_{sample}, s)}{dV_{sample}} \propto \rho_s(E_F + eV_{sample}) \cdot \rho_t(E_F) \cdot T(eV_{sample}, V_{sample}, s) + \int_0^{eV_{sample}} \rho_s(E_F + \epsilon) \cdot \rho_t(E_F - eV_{sample} + \epsilon) \cdot \frac{d}{dV_{sample}} T(\epsilon, V_{sample}, s) d\epsilon + \int_0^{eV_{sample}} \rho_s(E_F + \epsilon) \cdot T(\epsilon, V_{sample}, s) \cdot \frac{d}{dV_{sample}} \rho_t(E_F - eV_{sample} + \epsilon) d\epsilon$$

$$(2.2)$$

Let us examine the second and third terms of this equation. The third term can usually be safely ignored, since one typically conditions the tip until the measured spectroscopy on a well characterized region of the sample matches that of a known reference, so as to ensure that $\rho_t(\epsilon)$ is indeed featureless. At a bias small compared to the work function (i.e. $V_{sample} \ll \phi_s, \phi_t$) $T(\epsilon, V_{sample}, s) \approx T(s)$, so that the second term can be dropped as well. Under these approximations the differential conductivity is

$$\sigma(V_{sample}, s) = \frac{dI(V_{sample}, s)}{dV_{sample}} \propto \rho_s(E_F + eV_{sample})$$
(2.3)

So that the differential conductivity is a *direct* measurement of the sample's LDOS at the tip position and at an energy of V_{sample} relative to E_F .

However, at larger biases the energy dependence of the tunneling matrix dominates, which lends an exponential background to the resulting differential conductivity, tending to mask variations of the sample's DOS. It is often useful to plot the logarithmic conductivity $\frac{d \log I}{d \log(V_{sample})}$ in order to remove this exponential dependence, though the result is problematic at low bias.¹⁸ Typically, one uses an empirical background subtraction in order to remove this and retain any small scale variations. While the resulting spectrum cannot be quantitatively compared to the LDOS in this case, the positions of any peaks or dips *do* match features in the sample's LDOS. A more rigorous treatment is described by Wahl *et al.*,²⁴ but rarely followed in practice.

Scanning tunneling spectroscopy is performed in practice by stabilizing the tip above the desired region, and then opening the feedback loop and sweeping the bias voltage. An obvious requirement is that vertical drift is low enough so that the distance between the tip and the sample does not change appreciably over the sweep time.⁷ Hence, the instrument's stability plays a crucial role in the quality of the acquired data, with the lower thermal expansion at low temperatures being a great benefit, as well the temperature stability inherent

⁷This can be checked in practice by sweeping the bias in both directions, and checking that the two measurements give the same result.

in a cryogenic environment. The measurement of the differential conductivity can be performed by directly differentiating the current. However, in practice this tends to be noisy. A better method is to modulate the sample bias, i.e. $V_{sample} = V_0 + V_{mod} \cdot \sin(\omega \cdot t)$, and detect the resulting change in current at the modulation frequency using a lock in amplifier. For an ideal lock-in, the resulting signal is a direct measurement of the differential conductivity.⁸ The measured signal is broadened by the modulation voltage, so that V_{mod} must be chosen smaller than the width of the features of interest. Typical modulation voltages are a few mV to a few tens of mV.

The treatment can be expanded for $T \neq 0$, of course, but the main result is a "washingout" of the spectroscopic features due to the Fermi-Dirac function. However, since all the features that we deal with in this dissertation are much broader than the thermal energy of, at most, $K_BT \approx 3meV$ for $T \approx 30K$, this is of little importance. The thermal induced broadening of a spectroscopic feature is

$$\Delta E = \sqrt{(\Delta E_{intrinsic})^2 + (\Delta E_{instrument})^2 + (3K_BT)^2 + (2.5eV_{mod})^2}$$

Where $\Delta E_{instrument}$ is the intrinsic instrumental noise, and $\Delta E_{intrinsic}$ is the feature's intrinsic width. As is clear, lower temperatures allow us to resolve finer spectroscopic features. However, the widths of the states that we measured in this dissertation were rarely less than 20meV, so that the thermal broadening on the order of 2meV for $T \approx 7.5K$ was relatively unimportant.

2.4.1 Spatial mapping of LDOS

Spatial measurement of LDOS can be performed by taking point spectroscopy over a large number of points and then taking a slice at the desired energy. However, in practice this is typically too slow, so that a different method is employed. A dI/dV map is performed by scanning over the sample in the typical constant-current mode, while adding a small modulation voltage to the bias, recording the topography and dI/dV signals simultaneously. While such "dI/dV maps" are slower than normal topography images, since the time per pixel must be longer than the lock-in time constant, they are still faster than collecting the same spatial resolution from individual point spectra. In essence, by taking multiple dI/dVmaps at different energies, rather than performing STS over a grid, one is trading energy and spatial resolution, and the preferred method depends on the relative importance of the two. The resulting image is subtly different from the "trivial" method of energy slicing an STS grid, since it was taken under a closed feedback loop. As a result, comparing two maps taken at different energies is non-trivial, since they were taken with different stabilization heights. Nevertheless, if the contrast in the topographic image is limited, so that the integrated DOS, and hence the height, are fairly constant, such a dI/dV map can be taken to be a faithful representation of the spatial distribution of a state at V_{sample} .

 $^{^{8}\}mathrm{A}$ very detailed discussion of the usage of lock-in techniques for measuring LDOS is given in R. Ya-machika's PhD dissertation. 25

The TTB-Azobenzene- Au(111) System

Azobenzene is a small (~ 9Å) organic molecule, which is known to photoisomerize, as an isolated molecule, from the Trans to the Cis form and vice-versa under UV and Blue light, respectively, as shown in figure 3.1.^{6,26} In recent years, azobenzene molecules and their derivatives have been used in a large variety of applications, such as "nano-scissors",²⁷ control of nerve cells,^{28,29} and transport of solution droplets.³⁰ However, these previous measurements were done in solution environments, while we would like to explore the same photoisomerization property in a condensed matter environment, with the molecules bound to a surface.



Figure 3.1: Azobenzene photoisomerization: The *Trans* isomer is converted to the *Cis* form under UV ($\sim 375nm$) light, and the reverse reaction is initiated by blue light ($\sim 440nm$).

As suggested by our initial discussion of the issues arising from having the molecules coupled to the substrate, we found it necessary to decouple the molecule from the substrate by employing four *tert*-butyl "legs", forming TTB-Azobenzene. This served to decouple the central, active, part of the molecule - the N=N bond region - from the surface and proved to be sufficient for observation of surface photoisomerization. These developments were discussed in detail in our previously co-authored paper² and will be briefly reviewed below. The instrument used for the measurements described in this part is a homemade UHV variable temperature STM cryogenically cooled by a liquid helium flow cryostat (ARS



Figure 3.2: Trans isomer of 3,3,5,5-Tetra-tert-butyl-azobenzene (TTB-Azobenzene).

LT3B Helitran^(R)). A detailed description of this instrument can be found in M. J. Comstock's PhD dissertation.³¹ All the measurements described were performed with the STM cooled to its base temperature, which at the time was $\approx 30K$. While this instrument provided sufficient performance for these experiments, it became a limiting factor for designing new experiments, due to its noise level (minimal tunneling current of $\approx 7pA$) and base temperature, leading us to design and build a new system, described later (chapter 6). 3,3,5,5-Tetra-*tert*-butyl-azobenzene molecules were synthesized via oxidative coupling reactions of 3,5-di-*tert*-butylaniline³² by F. Lauterwasser & D. Poulsen in the Fréchet group at UC Berkeley's Chemistry department. *Trans* isomers of the molecules were deposited via Knudsen cell evaporation onto clean Au(111) substrates held at 30 K. Samples were then annealed at room temperature for 10 min. STM images were acquired in the temperature range of 25-30 K using tunnel currents below 50 pA for stable imaging.

Following annealing, we observed monolayer high islands of Trans TTB-Azobenzene molecules on the surface. A detailed discussion of the detailed structure of both isomers of the TTB-Azobenzene molecules will be given in section 4.2. Our ability to re-image the same spot after retraction and re-approach allows us to image the same exact molecules and see which of them have changed. Irradiation with a near UV diode laser ($\lambda = 375 nm$, $I \approx 100 mW/cm^2$ for 1 hour) photoisometrizes about 5% of the molecules, as can be seen in figure 3.3. We verify that the transition is reversible by continuing to illuminate the sample and observing a fraction of the molecules which have been photoisomerized back to the Trans form (figure 3.4). In addition, the TTB-Azobenzene molecules can be isomerized using the tunneling current. We can switch photoisomerized *Cis* molecules back to the Trans form using the STM tip (figure 3.5a) or switch the Trans to the Cis form using the tip (figure 3.5b). This shows that the tip and light induced switching transition between the same initial and final states (or at least that these states are close enough that the tip excitation can switch the light created *Cis* out of their local energy minima), and serves as further proof that the process is a reversible one. Multiple tip induced cycles of the same molecules have been performed, without an apparent change in the molecule or probability of isomerization. Note that the molecules undergo both $Trans \rightarrow Cis$ and $Cis \rightarrow Trans$ isomerization under the same wavelength, albeit with different probabilities.



Figure 3.3: Photoisomerization of a TTB-Azobenzene molecule in a monolayer high island on the Au(111) surface.



Figure 3.4: Observation of a complete $Trans \rightarrow Cis \rightarrow Trans$ cycle of a specific molecule under UV light.



(a) Switching UV light created *Cis* isomers back to *Trans* form using the STM tip. The *Cis* isomers in the first image were created through UV irradiation and then subsequently switched back to the *Trans* form using STM bias pulses.



(b) *Trans* to *Cis* isomerization using the STM tip

Figure 3.5: Tip induced isomerization events.

3.1 Three different assemblies

Previous studies of the TTB-Azobenzene- Au(111) system have observed the molecules to be ordered in monolayer high islands. However, a careful examination of a large area shows that there actually are three different configurations - phases 1, 2, and 3 (figure 3.6), with each phase displaying very different photoswitching behavior. The analysis described henceforth is based upon our previously co-authored publication.⁴ All individual molecules appear the same before they are exposed to light, regardless of phase (they appear as a rectangular four-lobe structure, with each lobe indicating a *tert*-butyl (TB) "leg"). The three different island phases vary in their molecule-molecule ordering and in the orientation of molecules with respect to the underlying Au(111) herringbone (HB) surface reconstruction. Phase 1 islands are close-packed and have one molecule per unit cell that is oriented with its long axis tilted 87 ± 3 degrees with respect to the HB ridges (the HB ridge orientation, which is parallel to one of the three equivalent [112] crystal directions, is indicated by the black dashed line in figure 3.6). Phase 2 islands have a two-molecule unit cell with one molecule tilted 101 ± 4 degrees and the other 49 ± 4 degrees with respect to the HB ridges. Phase 3 islands are close-packed and have one molecule per unit cell tilted 40 ± 3 degrees with respect to the HB ridges. Phase 3 islands also display quasi-periodic stacking faults (white dashed line in figure 3.6c). Phase 2 and phase 3 islands occur with less frequency than phase 1 islands by about two orders of magnitude, which explains why they have not been previously reported.^{2,33} Figure 3.7 shows the different molecular orientations observed with respect to the surface.



Figure 3.6: Constant-current STM topographs of phase 1, 2, and 3 monolayer islands of *Trans* TTB-Azobenzene molecules on Au(111). Each white box surrounds a single molecule. All three images are oriented identically (HB ridges are parallel to dashed black line). Dashed white line in (C) shows phase 3 stacking faults.

3.1.1 Effects of light exposure

We examined how different surface orderings of identical molecules affect their photoswitching behavior by exposing all three TTB-azobenzene phases to UV light. Figure 3.8 shows



Figure 3.7: Ball-and-stick models of TTB-Azobenzene on the Au(111) surface showing the two main orientations of molecules relative to the Au surface for phases 1-3 (actual orientations vary by $\approx \pm 10^{\circ}$ as described in text).

topographic STM images of phase 1,2 and 3 islands, respectively, after equal exposures to UV light (approximately 100 hours, starting from an all-*Trans* initial state). The quantity and spatial distribution of *Cis* molecules are seen to be extremely different between the three phases. Phase 1 islands have a high concentration of *Cis* isomers ($\approx 40\%$) that appear to be randomly distributed spatially (Fig. 3.8a). Photoswitched molecules in phase 2 islands display an unexpected striped pattern (Fig. 3.8b). The "switching stripes" are oriented nearly perpendicular to the HB ridges and have a pitch that varies from 85Å to 115Å, depending on the island. All photoswitched molecules in these stripes are tilted 100 degrees with respect to the HB ridges (see figure 3.9). Within a stripe, the rate of photoisomerization is approximately the same as in a phase 1 island, but the rate plunges to nearly zero outside of the stripes. Photoisomerization in phase 3 islands (figure 3.8c) is highly quenched relative to phase 1 and 2 islands. The phase 3 switching rate is at least two orders of magnitude smaller than the phase 1 switching rate (phase 3 switched molecules appear to be randomly distributed spatially). For all three phases the overall photoswitching rate is independent of whether a molecule is above an *fcc* or *hcp* region of the reconstructed gold surface.

3.1.2 Molecule - surface interaction

Molecules in phases 1 and 3 have markedly different switching rates and different molecular orientations with respect to the gold substrate, but they share the same nearest neighbor molecule-molecule configuration. In addition, close examination of the active region ("stripe") of a phase 2 island shows that only those molecules that are oriented at 100 degrees to the HB ridges undergo photoisomerization. This dependence of the photoisomerization yield on molecular orientation correlates well with the behavior of phase 1 and phase 3 islands. The correlation between molecular orientation and photoswitching shared by all three island phases strongly suggests that intermolecule-based steric hindrance does not play a significant role in determining the photoswitching rates for these two phases, but that the switching rates are rather determined by orientation-dependent molecule-surface



Figure 3.8: Images after exposure to 100h of $\approx 90 mW/cm^2$ UV light.



Figure 3.9: Close-up image of a phase 2 island following UV exposure shows the photoisomerization orientation selectivity. The dashed white lines mark molecular rows having 100 degree orientation with respect to the local HB ridge orientation.

interactions. These likely induce variation in molecular excited state lifetimes and optical absorption, thus leading to the observed difference in photoswitching rates between phases 1 and 3. This effect can be considered a selection rule and will be named the 1^{st} photoisomerization selection rule.

3.1.3 Local study of electronic structure

While the molecular orientation dependence can be explained as a relatively straightforward case of molecule-substrate interaction, the main effect observed for phase 2 island - the *Cis* stripes - cannot. A possible cause of such an effect might be elucidated by studying the local electronic structure, as manifested in the local density of states (LDOS), to which end we employed scanning tunneling spectroscopy.

dI/dV spectra measured over the bare Au(111) surface between TTB-Azobenzene is-

lands showed a surface state band-edge at $\approx 0.5 eV$ below E_F , consistent with previous work (figure 3.10).³⁴⁻³⁶ dI/dV spectra measured over the TTB-Azobenzene islands, however, showed quite different behavior. Spectra measured for all three TTB-Azobenzene phases can be grouped into two position-dependent categories, designated as "bright" and "dark" (figure 3.10). Both types of spectra show a steep shoulder near $V_{sample} \approx -0.25V$ that is similar to the bare Au(111) surface state band-edge but is shifted up in energy by $\approx 0.2 eV$. The main difference between the bright and dark spectra is that the bright spectra have a steeper shoulder exhibiting more spectral weight than dark spectra (see difference spectrum in figure 3.10).

The spatial dependence of the two spectral types ("bright" and "dark") can be seen in constant current dI/dV maps acquired at $V_{sample} = -0.27V$ (the bias where they show greatest contrast) (figure 3.11). All island phases show a spatial modulation in LDOS that runs perpendicular to the HB ridges (the HB ridges are horizontal in figure 3.11). The pitch of this modulation exactly matches the HB reconstruction itself. For phase 1 and 3 islands, "bright" type spectra are observed in the brighter regions of the islands which lie above the hcp regions of the Au(111) surface, while "dark" type spectra are observed over the darker fcc regions. This perpendicular LDOS modulation is similar to HB-induced electronic modulation seen previously in the bare Au(111) surface state.³⁶ Phase 2 islands are different in that they have an additional spatial modulation running parallel to the HB ridges (figure 3.11b) that darkens previously bright hcp regions, and which causes "dark" type spectra to appear in the newly darkened regions. This behavior is compared to the behavior of phase 1 and phase 3 islands (both of which lack a parallel modulation) in the line scans shown in figure 3.12. The phase 2 parallel modulation has a pitch that varies from 85\AA to 115\AA between islands. No additional LDOS modulations at other biases were observed.

We find that the bright areas of the phase 2 parallel LDOS modulation occur at the same positions as the phase 2 photoswitching stripes. To confirm this connection between local electronic structure and photoswitching probability, we performed topographic and dI/dV imaging of a phase 2 island before and after exposure to UV light. Figure 3.13a shows a dI/dV map of an all-trans phase 2 island before light exposure, highlighting the typical phase 2 parallel modulations in LDOS. Figure 3.13b is an image of the same island after 100 hours of exposure to UV light. The positions of the switching stripes containing *Cis* isomers in figure 3.13b clearly match the bright regions of the parallel electronic LDOS modulations in figure 3.13a.

3.1.4 Molecule - molecule effects

We believe that as opposed to the molecular orientation effects, the self-patterned switching stripes observed in phase 2 are likely due to molecule-molecule interactions. Two questions naturally arise regarding this behavior: (i) What is the cause of the phase 2 parallel electronic LDOS modulation? and (ii) What is the mechanistic link between the phase 2 electronic LDOS modulation and the self-patterned molecular switching stripes? We do not believe



Figure 3.10: Two types of dI/dV spectra are observed for all TTB-Azobenzene islands ("bright region" type vs. "dark region" type) and are compared here to a dI/dV spectrum measured on bare Au(111) (TTB-Azobenzene spectra are spatial averages). Subtracted difference between bright region and dark region spectra is shown (bare Au(111) spectrum and difference spectrum are both shifted vertically for viewing clarity).



(a) Phase 1

(b) Phase 2

(c) Phase 3

Figure 3.11: dI/dV maps at $V_{sample} = -0.27V$ of phase 1, 2 and 3 islands (dashed lines mark the positions for line scans shown in 3.12). The "b" and "d" marks in 3.11b show typical positions for acquiring respective "bright" and "dark" point spectra.

that the phase 2 parallel LDOS modulation is related to island-induced size quantization of the underlying two-dimensional Au(111) Shockley surface state^{37,38} since it has neither the correct period nor the correct energy dependence. More specifically, we would expect to observe periodicities at multiple bias settings, corresponding to the ground and excited



Figure 3.12: dI/dV line scans in phases 1,2 and 3 at $V_{sample} = -0.27V$ show unmodulated phase 1 and phase 3 behavior compared to strongly modulated phase 2 behavior (phase 1 and 3 line scans are both shifted vertically for viewing clarity).

states of such a particle-in-a-box system, with the lowest state having a single peak in the center of the island (or rather a line for a 1D confinement effect). In addition, the pitch of the stripes does not have a strong dependence on the lateral extent of the island, which would also be expected for such a picture. A second possibility would be that the modulation is the result of a moire effect between the TTB-Azobenzene and the Au(111) lattices. However, the one dimensional nature of the effect and the incommensurability between the island and underlying surface argues against this possibility.

We believe that the phase 2 modulation arises from a strain modulation within phase 2 islands that influences the surface state local potential (thus resulting in the observed variations in dI/dV spectra). This could affect photoswitching through dependence of molecular steric hindrance on stresses arising from the induced strain.

Qualitatively, the strain modulation in a phase 2 island can be viewed in the limit of continuum elasticity theory. One can consider two points of view:

- 1. The combination of the monolayer island & the substrate is a bilayer system where the upper layer is at the infinitesimal thickness limit and is weakly coupled to the substrate.
- 2. A TTB-Azobenzene island can be considered a region of a single layer system where the surface energy is different.

The first point of view would suggest that the photoisomerization periodicity observed in phase 2 islands is due to buckling of the monolayer high island.³⁹ However, this would suggest that we should observe a change in the topography images, which we do not. The simplest explanation would be that the amplitude of the change is too small so that we do not resolve it. Moreover, it is important to remember that an STM image is *not* a true topography, but rather an image of the (integrated) electronic structure of the sample. As a result, a topographical change might be masked by an electronic structure change, so that the LDOS maps might be more sensitive, while the usual, integrated LDOS, images would fail to resolve a minute change. The second point of view leads one to consider an Asaro-Tiller-Grinfel'd stress driven surface diffusion instability.^{40–42} Such an instability would not have the same gross topological signature as a buckling instability, thereby perhaps making it a somewhat more likely scenario.

3.2 Conclusion

Our data reveals a strong dependence of TTB-Azobenzene surface photoswitching behavior on molecular assembly and orientation on Au(111). We can generalize this behavior into two empirical photoswitching "selection rules" for TTB-Azobenzene on Au(111):

- 1. The orientation of a molecule relative to the underlying crystallographic structure determines whether that molecule is switching-enabled or switching-quenched. Molecules oriented at 95 ± 10 degrees with respect to the HB ridges are switching-enabled (all phase 1 and half of phase 2 molecules), while those oriented at 45 ± 8 degrees are switching-quenched (all phase 3 and half of phase 2 molecules).
- 2. Regions of reduced electronic LDOS parallel to the HB ridges in phase 2 islands correlate with additional quenching.

We find that the first selection rule is due to molecule-substrate effects, while the second selection rule is due to molecule-molecule effects. This result has important implications for future photomechanical molecular device engineering at a surface, with the second selection rule suggesting new opportunities for nm-sized photomechanical molecular patterning.



(a) Before UV light



(b) After 100h of $\approx 90 mW/cm^2$ UV light

Figure 3.13: (a) dI/dV map taken at $V_{sample} = -0.27V$ for a phase 2 island containing only *Trans* TTB-Azobenzene molecules prior to UV exposure. Arrows identify bright regions of parallel LDOS modulation. (b) Constant current STM topograph of the same island after UV exposure. Arrows (same positions as in (a)) identify self-patterned phase 2 photoswitching stripes containing *Cis* isomers.
-4

Photoisomerization Dynamics

Following our study of the dependence of the photoisomerization rate on molecule-molecule and molecule-substrate interactions, we would like to understand the route by which the process occurs. We delved into this phase of the study using two tools:

- 1. Direct cross section measurement by counting the number of *Cis* isomers as a function of time.
- 2. Correlating the chirality of individual molecules before and after photoisomerization.

This chapter is based upon our previously published, co-authored publications.^{3,5}

4.1 Rate measurements

For a multi-particle process of order γ , the process's rate depends on the number of particles as N^{γ} , where N is the number (or number density) of the particles. This can be understood by noting that a γ^{th} order process would depend on the number of particles involved through $N_1 \times N_2 \cdots \times N_{\gamma}$, so that its overall dependence would be to N^{γ} . In the case of photoisomerization, there are two types of number densities involved - the photon flux and the molecules. Hence, there are two different orders involved - one indicating the number of photons involved - α and the second indicating the number of TTB-Azobenzene molecules involved - β . As a result, the overall rate is

$$\frac{dN}{dt} \propto I^{\alpha} N^{\beta}$$

Where I is the photon flux and N is the number density of the molecules.

To deduce whether the surface photoisomerization we study is a single or multi photon event, i.e. extract α , we need to study the rate vs. the photon flux. However, we could

not do that in any detail using our diode based light source, since we could not change the power.

We performed a short lived experiment using a pulsed, high intensity laser. This experiment employed the 3^{rd} harmonic of a Nd:YAG laser ("Big Sky Laser" model Ultra 355 HE) with $\lambda = 355nm$, a pulse length of 8nsec and pulse energy of 16mJ, at a 20Hz maximal repetition rate. Since the peak power proved to be too high with the beam left at its native diameter of $\approx 1mm$ (laser ablation of the gold layer was observed in initial testing), the beam was expanded to $\approx 15mm$ diameter, to yield a power density of $I = 16mJ \times 20Hz/(\pi \times (15/2)^2/sin(40^\circ)) \times 100 \approx 120 \frac{mW}{cm^2}$. A 3 minute long exposure to this power level yielded a *Cis* population of $\approx 2\%$, which would give (using a simple linear approximation and assuming a-priori a first order process) a cross section of $\sigma_{Nd:YAG} \approx 5.2 \times 10^{-22} cm^2$. As will be shown below, this matches the value we extract from our CW measurements at $\lambda = 375nm$ to within a factor of 3. As the ratio of peak power is of the order of $1/(\tau_{pulse} \times (repetition rate)) \sim 10^7$, this strongly supports the notion that the process is a single photon one. Ensemble averaged experiments performed by the Tegeder group (Freie Universität Berlin)⁴³ further support this conclusion.

We can deduce the number of TTB-Azobenzene molecules interacting during a photoisomerization event by fitting the number of observed *Cis* molecules vs. time at a fixed power (i.e. constant photon flux). Specifically, we shall attempt to model the overall fraction of *Cis* TTB-Azobenzene molecules on the surface using the following equation,¹ bearing in mind that there are two competing processes occurring - *Trans* to *Cis* and *Cis* to *Trans* photoisomerization.

$$\frac{dN_{Cis}}{dt} = \sigma_{Trans \to Cis} \times I \times N_{Trans}^{\beta} - \sigma_{Cis \to Trans} \times I \times N_{Cis}^{\beta}$$

For the case of a single molecule process, i.e. $\beta = 1$, the rate equation can be integrated analytically to yield the number of molecules in either isomer as a function of the integrated photon flux N:

$$N_{Cis} = N_{Cis}(\infty) \times (1 - e^{-N(\sigma_{t \to c} + \sigma_{c \to t})})$$

$$(4.1)$$

In particular, knowledge of the saturation concentration of each isomer directly yields the ratio between the forward and backward cross sections:

$$N_{Cis}(\infty) = \frac{\sigma_{t \to c}}{\sigma_{t \to c} + \sigma_{c \to t}}$$
(4.2)

The STM enables us to measure the fraction of *Cis* and *Trans* isomers by directly counting the number of molecules of each isomer in an island. In addition, since the STM used can return to the same spot following a macroscopic retraction, we are able to observe the same island before and after exposure to light. We were able to follow a particular island for four successive exposures. Following the fifth exposure we were unable to retain the same island and had to resort to averaging over a large number of islands. However, for

¹which assumes a process linear in photon flux.

extracting averaged cross sections this process is sufficient. Attempting to fit the observed *Cis* fraction as a function of total photon number shows a remarkably good fit to this simple case, suggesting that we indeed have a single molecule process, as seen in figure 4.1. The resulting cross sections for exposure to both UV and blue light ($\lambda = 444nm$) are shown in table 4.1. While the reduction in cross section by $\approx 10^3$ can be easily explained to be due to environmental coupling, the similarity of the cross sections upon exposure to blue and near UV light suggests that there is a qualitative difference between the surface photoisomerization and the process as it happens in an isolated molecule. As we saw in section 3.1, studies of the different surface ordered phases in the TTB-Azobenzene- Au(111) system support this notion. In particular, the dependence of the photoisomerization rate on molecule-substrate interaction suggests that while only a single molecule takes part in the process does not resemble in details the photoisomerization of an isolated molecule, despite the gross similarity.

	$\sigma_{Trans \to Cis} \ (cm^2)$	$\sigma_{Cis \to Trans} (cm^2)$
UV $(375nm)$	$2.3 \cdot 10^{-23}$	$2.3 \cdot 10^{-23}$
Blue (444nm)	$1.7 \cdot 10^{-23}$	$2.3 \cdot 10^{-23}$

Table 4.1: $Trans \rightarrow Cis \& Cis \rightarrow Trans$ cross sections under UV and blue light exposure.



Figure 4.1: Fraction of Cis isomers as a function of total photon exposure N.

4.2 A study in chirality

While measurement of the overall cross sections allows a glimpse into the photoisomerization process, the details of the process are not obvious. A partial lifting of the veil can be performed by analyzing *specific* molecules before and after they are switched. In this way we can utilize the basic STM mode, which inherently lacks temporal resolution, to gain insight into the *dynamics* of the process.

The phenomenon which forms the basis for this part of our studies involves the chirality of the adsorbed TTB-Azobenzene molecules. While TTB-Azobenzene molecules are a-chiral in free space, adsorption to a surface breaks the symmetry and creates left and right - handed enantiomers.² Since both the initial and final product of the photoisomerization reaction have a well defined chirality, it is possible to correlate the two. An image displaying a domain boundary between left and right-handed regions of a *Trans* TTB-Azobenzene island is shown in figure 4.2. As is clearly evident, the differences between the two enantiomers is small, with the average inclination of the parallelogram being $\sim 2^{\circ}$, as marked in figure 4.3. The angle shown in figure 4.3, which is the same to within experimental error for right and left-handed molecules, was averaged from 394 left-handed domain molecules and 125 right-handed domain molecules. In our previous studies we have been able to relate the



Right handed trans domain

Domain boundary

Left handed trans domain

Figure 4.2: STM topography image of a *Trans* TTB-Azobenzene island showing a domain boundary between left and right handed domains. The red and blue crosses mark the location of the lobes of a single right and left handed molecule, respectively. The dashed white line marks the domain boundary. *Trans* TTB-Azobenzene single-molecule structural models are superimposed on right-handed and left-handed configurations.

photoisomerization probability to the local molecular environment by studying the way in which different molecular orderings affect it. However, we are limited to studying molecules in phase 1 islands for the present study, since we cannot accurately determine the chirality of the *Trans* isomers in phase 2 islands.

Imaging an island following exposure to light shows a certain fraction of the molecules have been converted to the *Cis* isomer. However, we find that as opposed to earlier studies, we are able to distinguish between two meta-stable *Cis* forms. These are marked as *Cis* type I and type II, respectively, in figure 4.4. The ability to distinguish type I from type II *Cis* relies on exceptional imaging conditions, which explains why this feature has been overlooked previously. Both *Cis* types share a similar appearance: a bright (tall) lobe

²Enantiomers are defined as two non-superimposable chiral molecules which are mirror images of each other.



Figure 4.3: Schematic structure showing the average location of the lobes of a right handed *Trans* TTB-Azobenzene enantiomer. The angle between the line connecting the lobes and the axes is 2°. The left handed enantiomer shows the mirror image of the displayed structure.

surrounded by three dimmer (lower) lobes. However, the location of the bright lobe with respect to the dim lobes differs between the two types. For type I *Cis* isomers the bright lobe lies closer to the center line between the two far opposite dim lobes, whereas for type II *Cis* isomers the bright lobe lies further from this center line and closer to the diagonal point opposite the dim corner lobe, as shown in figure 4.5. Type I and type II *Cis* TTB-Azobenzene are both chiral, and their right-handed and left-handed enantiomers can be seen in the images of figure 4.5. Type I *Cis* occur approximately twice as frequently as type II *Cis*, which helps to explain the earlier ignorance of the existence of type II.

Examination of 338 *Cis* molecules shows that there is a strong correlation between the chirality of the *Trans* isomer and that of the resulting *Cis* isomer. We observe that left-handed *Trans* isomers produce right-handed type I or left-handed type II (with 9% of the molecules deviating from this selection rule). Similarly, right-handed *Trans* isomers produce either left-handed type I or right handed type II (with a 5% deviation).

To proceed and determine the constraints placed on the photoisomerization process by the observed selection rule, we need to know the structure of both the *Trans* and *Cis* isomers. Ab-initio DFT calculations, performed by D. Strubbe in the Louie group, were used to calculate the LDOS, derive the geometrical structure, and simulate STM topographies. The calculations were performed using the SIESTA package,⁴⁴ similar to earlier calculations of this system. The structures were simulated by relaxing isolated molecules and then composing two-dimensional grids following the experimentally determined lattice vectors of the TTB-Azobenzene islands. The comparison between the simulated and measured STM topographies is shown in figure 4.4. The simulated STM topographs of the *Trans* isomer show four lobes, arranged in a parallelogram with an angle of ~ 2° , matching the experimentally determined structure and confirming the existence of two *Trans* enantiomers on the surface. Calculations of the *Cis* isomers find two meta stable minima, shown in the lower panel of figure 4.4. These two *Cis* isomers correspond to the two types of *Cis* observed experimentally, allowing us to deduce the molecular structure. In both cases the phenyl





Figure 4.4: Upper panel: High-resolution STM image shows structure of two distinct types of photoswitched *Cis* TTB-Azobenzene isomers: a left-handed Type I *Cis* and a right-handed Type II *Cis*, contained within dashed white boxes. Lower panel: Ab initio DFT simulated STM image of the two *Cis* TTB-Azobenzene types surrounded by *Trans* TTB-Azobenzene molecules. Calculated structural models of *Trans* TTB-Azobenzene, type I *Cis* & type II *Cis* are shown.

ring lying on the surface has a CCNN dihedral bond angle of $\approx 30^{\circ}$. However, the two Cis isomers differ in the CCNN angle of the phenyl ring which is lifted off the surface. A type I Cis has a lifted phenyl ring CCNN angle of 50°, while a type II Cis has a -60° angle.



Figure 4.5: STM images showing different chiral states of single *Cis* TTB-Azobenzene molecules (within white boxes): (a) *Cis* type I, left-handed (within right-handed *Trans* domain), (b) *Cis* type I, right-handed (within left-handed *Trans* domain), (c) *Cis* type II, left-handed (within left-handed *Trans* domain), and (d) *Cis* type II, right-handed (within right-handed *Trans* domain). Location of single bright lobe is indicated by a green cross and the locations of three dim peripheral lobes are indicated by white crosses. Dotted lines are guides to the eye.

This difference in structure explains the different positions of the bright lobe observed in our STM images. While type I *Cis* have been previously observed by us and reported by other groups as well,³³ type II *Cis* were not distinguished previously, though their existence has been suggested based on theoretical calculations by Tiago *et al.*⁴⁵

4.2.1 Discussion

We can now try to use the correlation between the chiralities of the *Trans* and *Cis* isomers to extract information about the dynamical pathways underlying surface photoisomerization of TTB-Azobenzene on Au(111). While the overall photoswitching mechanism for isolated molecule is still under debate, $^{45-52}$ there are two commonly accepted pathways – pure rotation 45,46,48,51,52 and concerted inversion. 48,53

However, we can rule out both of these mechanisms for molecules constrained to a surface based on our observed selection rules:

- **Pure rotational motion:** In this case, $Trans \rightarrow Cis$ conversion happens by out-of-plane rotation of a phenyl ring as the CNNC angle is varied. This scenario leads to a type I Cis isomer of the same chirality as the initial Trans molecule, which clearly is excluded by our observations.
- **Concerted inversion:** This involves synchronous inversion of the phenyl ring as the two *NNC* bond angles are swept concurrently. As a result, the process acquires an *a-chiral* intermediate state in which the *CNNC* atoms are nearly co-linear. Such an intermediate state would be expected to produce equivalent number of left-handed and right-handed *Cis* isomers, while we observe a strong preference for a single handedness.

We suggest an alternative pathway for the surface bound $Trans \rightarrow Cis$ photoisomerization. Our suggested pathway, shown in figure 4.6 for a right-handed *Trans* molecule, is a variant of the inversion pathway.^{46,48,50,51} We propose that photoisomerization starts with the in-plane inversion of one phenyl ring and continues until steric hindrance between the moving phenyl ring and the stationary ring hinders the motion. At this point the process can proceed in two ways:

- 1. The mobile phenyl ring lifts out of the plane starting from the point away from contact, yielding a type II *Cis* configuration of the same chirality as the initial *Trans* isomer (lower left section of figure 4.6).
- 2. The stationary phenyl ring lifts out of plane starting from the point of contact, yielding a type I *Cis* configuration of the opposite chirality to the initial *Trans* isomer (lower right section of figure 4.6).

Since it is likely to be energetically more favorable for portions of the molecule to slide along the surface (as in inversion) rather than completely unbind and lift off of the surface (as in rotation), the proposed mechanism is energetically preferred over simple rotation and can be seen as a minimally lifting variant of inversion.

4.2.2 Conclusion

Our initial measurement of the reaction cross sections suggested that the photoisomerization is strongly hindered by the proximity to the Au(111) substrate, but could not determine whether the difference was qualitative or merely quantitative. However, correlating the chirality of the *Cis* isomer created via light exposure to that of the initial *Trans* isomers, we can exclude the reaction pathways commonly accepted for isolated molecules, suggesting that the process is *qualitatively* different. While our measurements are limited to the TTB-Azobenzene- Au(111) system, *qualitative* differences between the photoisomerization of isolated molecules and that of surface adsorbed molecules should be expected to be the rule rather than the exception.

To further explore the reaction pathways we would need a change in approach, which suggested analyzing an auxiliary channel - that of light emitted from the STM tunnel junction due to inelastic processes.



Figure 4.6: Proposed photoisomerization dynamical pathway for TTB-Azobenzene on Au(111). A photoexcited right-handed *Trans* TTB-Azobenzene molecule (top center, TB legs numbered) begins the isomerization process with an in-plane inversion of the left phenyl ring (middle center). With continuing inversion, steric repulsion due to contact between the phenyl rings forces either: left phenyl ring to twist out of plane, lifting TB #1 and producing right-handed type II *Cis* TTB-Azobenzene (bottom left), or right phenyl ring to twist out of plane, lifting TB #4 and producing left-handed type I *Cis* TTB-Azobenzene (bottom right).

Light Emission from the STM Tip-Substrate Junction

Light emission from the STM tunneling junction has been initially noticed as early as 1988 by Gimzewski *et al.*⁵⁴ As opposed to the purely elastic tunneling which we discussed in the basic STM and STS review, the light emitted can be understood to be due to an inelastic excitation of localized surface plasmons (LSP) by the tunneling current. The analysis can then be broken down to a (1) classical calculation of the relationship between the field in the vicinity of the tip-substrate junction and the field in a region far away from the junction, due to an electric dipole element localized at the junction, and (2) a quantum mechanical analysis of the spectral power density of the tunneling current in the junction. A schematic of the tip junction interface is shown in figure 5.1a. It is important to note that due to the exponential dependence of the tunneling current on the distance between the tip and the sample, a small *local* protrusion is likely responsible for all of the tunneling current, while the length scale for the local plasmon is much larger and can be approximated as $\sqrt{2R_{EM}d_{EM}}$ (figure 5.1b).

5.1 Vacuum barrier

For a vacuum barrier, the spectral power density of the exciting current is devoid of any structure and can be approximated by $\langle \delta I(\omega)^2 \rangle \approx 1 - \frac{\hbar\omega}{eV}$, where V is the bias across the tunnel junction.⁵⁵ As a result, the spectral power density of the overall light emission in this case is dominated by the electromagnetic coupling between the local excitation and the modes existing in the cavity. The electromagnetic spectral power density is due to excitation of localized interface modes (extending into the materials) in the cavity formed between the tip and the substrate. If the tip radius is large compared to the tip-substrate distance, as is typical, the effective cavity length is much larger than its height, $2r_{eff} \gg d_{EM}$, so that the modes can be viewed as interface plasmons in a planar geometry. While these cannot couple to free space radiation on perfectly smooth surfaces due to energy and momentum conservation, ⁵⁶ the finite extension of the tip allows coupling to photons via scattering at

the tip's edges. The allowed wave vectors are thus quantized, and hence the energies form a discrete set.⁵⁷ Note that this oversimplifies the role of the tip to "just" breaking the translational symmetry and allowing scattering. In a typical case, the tip's charge carriers actually contribute to the plasma oscillations. However, this does not change the qualitative picture, but rather the plasma resonances to be considered are due to a combination of tip and substrate charge carriers. If we just take a limiting case where the plasmon is a surface plasmon of the substrate, with the tip only setting the length scale, the allowed wave vectors are $q = N \frac{2\pi}{l_{eff}}$, and the resonances are at ⁵⁷

$$\omega(N) = \omega_P \sqrt{\frac{\tanh\left(N+1/2\right)\beta}{1+\tanh\left(N+1/2\right)\beta}}$$

where $\beta = \cosh^{-1}(1 + d/R_{eff})$ and ω_P is the substrate's plasmon frequency.

For our case where $d/R_{eff} \ll 1$, and for the lower modes, i.e. $N \approx 1$, this can be approximated as

$$\omega(N) \approx \omega_P \sqrt{N} (\frac{d}{2R_{eff}})^{1/4} = \omega_{SP} \sqrt{N} (\frac{2d}{R_{eff}})^{1/4}$$

The lowest mode is at $\omega_P(\frac{d}{2R_{eff}})^{1/4}$, and the higher modes approach the surface plasmon frequency $\omega_{SP} = \frac{\omega_P}{\sqrt{2}}$. Meguro *et al.*⁵⁸ showed that a Au tip tunneling into a Au(111) surface fits this model

Meguro *et al.*⁵⁸ showed that a Au tip tunneling into a Au(111) surface fits this model well, by calculating the energies as those of the interface plasmon's dispersion relation at the allowed wave vectors. It was later shown by Wu & Mills⁵⁹ and Buker & Kirczenow⁶⁰ that the two peaks observed for the case of a Ag tip & a Ag sample are just the optical and acoustic resonances of the two coupled surfaces.

Retardation effects can be neglected to leading approximation, since the effective cavity dimension, of order $\sqrt{2R_{eff}d} \approx 30 - 100 \text{\AA}$, is much smaller than the wavelength at optical frequencies.⁶¹ A later, more refined, calculation including retardation effects⁶² produced quantitative improvements, without a qualitative change to the underlying physical picture.

Reasonable values of the tip diameter ($R_{eff} \approx 300 \text{Å}$) and gap ($d \approx 10 \text{Å}$) suggest that the lowest peak would be located in the visible - near UV region of the spectrum, using $\omega_P \approx 4 eV$. However, near IR emission has been observed for relatively "fat" tips.⁶³ One should note, however, that the overall field enhancement depends on the tunneling current being near the maxima of the confined mode, i.e. near the center of the tip. For a very broad tip this would require a very regular shape, which is somewhat unlikely unless special measures (e.g. focused ion beam (FIB)) are taken during tip preparation. In addition, at this limit retardation effects are increasingly important and tend to reduce the effective field enhancement.⁶² Furthermore, surface scattering on the "walls" of the cavities will play an increasingly important role, effectively leading to higher losses and a lower cavity quality factor, which will reduce the enhancement as well.



rent vs. macroscopic scale. LSP excitation

Figure 5.1: Light emission via localized surface plasmon coupling.

5.2 Intramolecular light emission

In the case where there are structures in the tip-substrate junction which have typical energy scales of their own, e.g. molecular vibrations⁶⁴, charging states⁶⁵ or particle-in-a-box states,⁶⁶ the picture changes. If the coupling between the molecule and the substrate is sufficiently strong, the only effect would be a shifting of the resonance due to a change in the tip-substrate distance, essentially due to inserting a dielectric layer.⁶⁷ However, if the decoupling between the substrate and the adsorbate is sufficient, intra-molecular inelastic decay of the injected electron could lead to strong modulation of the resulting light emission, at energies matching these events. Theoretical predictions of the exact level shift and lifetime of molecules coupled to the substrate via an oxide (i.e. insulating) layer have been made for the case of Mg-Porphine on $Al_2O_3/NiAl(110)^{68}$ and Zn-etioporphyrin on $Al_2O_3/NiAl(110).^{60}$ However, these calculations do not seem to change the qualitative picture.

There are two common scenarios for the intramolecular decay which results in light emission, shown in figure 5.2. As the transition has to happen between two unoccupied levels, the most likely scenario is a $LUMO+n \rightarrow LUMO$ decay. However, in the event where the molecule is strongly decoupled from the substrate, the HOMO could be depopulated and $LUMO \rightarrow HOMO$ transitions can occur. This has been demonstrated for H_2TBPP molecules on Au(100)⁶⁹ and for C₆₀ molecules on NaCl/Au(111).⁷⁰ The influence of the tip could shift the molecular levels and split possible degeneracies, thereby complicating the picture. For example, in the specific case of Zn-etioporphyrin on $Al_2O_3/NiAl(110)$, Buker & Kirczenow⁶⁰ suggested that the transitions observed are between the HOMO and a LUMO level split due to tip effects.

5.2.1 Localized excitation of molecules by light

The same processes of LSP resonances which allow coupling of intramolecular radiative transitions happening in the STM junction to far field radiation can be used to excite the



Figure 5.2: Possible light emitting intramolecular processes.

molecules. In this case, light is focused onto the tunneling junction and the current is used as a local detector. The same considerations apply - while the excitation is localized to within a few nanometers to a few tens of nanometers, due to the spatial extent of the LSP,⁶⁸ the detection is highly local. One should note that other effects are important in this case, chief being local heating of the tip, causing thermal expansion, so that sufficient care must be taken to avoid spurious effects, through e.g. FM modulation of the exciting laser.^{71–74} In addition, if one wishes to directly excite vibrations through IR light, rather than use photon assisted tunneling between electronic levels,⁷⁵ other field enhancement effects become important - the local charge accumulation for a sharp object (aka "lightning rod effect") being first among them, scaling as λ/d .

5.2.2 Application to photomechanical molecules

We would like to study the excitations involved in optomechanical coupling at the single molecule levels for molecules on a surface. Analysis of the light emission from the molecule in the STM tunnel junction should serve well, as it allows for local excitation, so that the spatial dependence of the process and its energetics could be elucidated. While the excited species is the charged molecule rather than the neutral one, theoretical studies suggest that the process is somewhat similar, albeit with a reduced barrier.⁷⁶ Of the two options mentioned before for the transitions involved in light emission, the $LUMO + 1 \rightarrow LUMO$ is the more likely one for the case of azobenzene molecules, since the large gap would require tunneling biases close or exceeding the work function for $LUMO \rightarrow HOMO$ driven light emission, even if a quasi-symmetric barrier could be created (e.g. by using more than one layer of NaCl). In addition, for the isolated azobenzene molecule, the $n \rightarrow \pi^*$ is dipole forbidden, so that the fluorescence efficiency would be low. However, the symmetry selection rules tend to be somewhat relaxed due to the coupling to the surface, so this is most likely only a secondary consideration. Construction of a New Opto-STM Instrument

Our studies of the TTB-Azobenzene- Au(111) system, which utilized the older STM described in detail in M.J Comstock's dissertation,³¹ exposed some flaws and limitations of that instrument. Motivated by our desire to expand the range of parameters we can control and study, we decided to design and build a new STM capable of, among other things, optical coupling to the tunnel junction region.

The overall features of the new instrument are:

- A LHe bath cryostat with a 5 day hold time (manufactured by Cryovac GmbH) with $T_{base} \approx 7.5 K$.
- $I_{min} \approx 0.5 pA$.
- Efficient collection of light from the tip-substrate junction.
- A 3D coarse motion system.
- Tip exchange at LT.
- Multiple sample contacts.

An overview of the new system is shown in figure 6.1.

6.1 UHV system

The UHV system consists of two main chambers, a preparation chamber and an STM chamber. The two chambers are separated by a 6" VAT gate valve. The main pumping system consists of two Varian 500 L/sec Diode ion pumps, supported by Titanium sublimation pumps. Initial pumping and pumping during sample preparation are handled by a Varian V-551 Navigator turbo-molecular pump connected to the preparation chamber. The main turbo-molecular pump is backed by a multistage setup consisting of a Varian



Figure 6.1: Overview of the complete instrument. The STM chamber has been made transparent to enable a view of the STM and the heat shields. The optical table has been left transparent as well. Additional support "legs" used with the cryostat have been removed to improve clarity. Evaporation chambers and pumps are mounted onto the STM and preparation chambers for the left and right views, but are removed for the STM chamber in the dimetric view to enable a better view of the ports. Inset: a picture of the system's namesake⁷⁷ & mascot.

V-81M turbo-molecular pump, which is backed by a Triscroll SH-110 dry pump, so that the pumping system consists only of "dry" pumps. It is possible to vent and pump the preparation chamber without venting the STM chamber, but the reverse is not true. Samples are inserted into the preparation chamber through a load-lock which has a separate pumping system, consisting of a Varian V-81M turbo-molecular pump backed by a Varian Triscroll 300 dry pump. Drawings of both main chambers and a port list are contained in appendix A.7.

Bake-out is performed using the tried and true method of a large number of heating tapes individually controlled by variacs. Due to the low thermal conductance of the cryostat, it takes about two days to reach baking temperatures, so that total bake-out time is of the order of five days. An additional "complication" arising due to the cryostat is the need to admit a small amount of He gas to warm the system up to room temperature in a reasonable amount of time (e.g. prior to a vent). Typically, a few Torr of He are admitted once the STM temperature reaches $\sim 100K$.

Sample transfer between the load-lock, preparation and STM chambers is accomplished solely by magnetic transfer rods (Transfer engineering models DBLRM-36HD & DBLRM-24) employing Omicron transfer heads. The main transfer rod, used to transfer samples between the preparation chamber and the STM, uses a heavy duty version of the front bearing, since the older STM had frequent failures of a similar transfer rod due to the large torques during sample transfer into the STM. In addition, to limit sideways loads on this transfer rod, a heavy duty port aligner is used. Wobble sticks are used to operate the front and rear doors on the STM heat shields.

6.1.1 STM chamber

The STM chamber mainly serves to support the cryostat housing the STM. Notable points are:

- 1. Two evaporation ports, which have line of sight to the sample when the front doors are open.
- 2. Two light-access ports, which allow a complete reflective light path.
- 3. Rear view port in the plane of the sample, to enable tip exchange.
- 4. STM clamping is activated via a ball ended hex key since the clamping wobble stick is at $\sim 13^{\circ}$ to the screw.

6.1.2 Preparation chamber

The preparation chamber has a 4-axis (X, Y, Z, θ) main manipulator (Johnsen Ultravac Inc.). The vertical range is 12", allowing access to four separate focal points along the axis of the preparation chamber, which are used to restrict line-of-sight between e.g. evaporators and ion guns. A dual sample and tip preparation stage, shown in figure 6.2, is mounted onto the main manipulator. Both stages allow e-beam heating of the sample inserted, using filaments spot welded to a Kimball physics AEI glass filament base. However, the filaments are different: to allow the high power needed for sample preparation in the sample stage, a multi-coil configuration is used, while the tip stage is optimized for local heating of the end of a tip. Specifically, the e-beam filament of the sample stage is made of 5-6 turns of $0.004"\phi$ Tungsten wire, while the e-beam filament used for the tip preparation stage is an un-altered Kimball Physics ES-020, consisting of a V-shaped filament made from $0.005"\phi$ Tungsten - 3% Rhenium wire. Both filaments can be seen in the CAD drawing in figure 6.2.

6.2 Cryogenics

6.2.1 Cryostat

The cryogenics are based around a commercial bath type cryostat, manufactured by CryoVac GmbH & Co KG. A 13L LHe tank, surrounded by a 55L LN₂ tank is used to achieve a base temperature of $\approx 7.5K$ and a LHe hold time of ≈ 5 days.¹ The LHe level can be measured using a superconducting level meter, but there is no direct measurement of the LN₂ level.²

¹The hold time of the LN_2 tank is estimated to be on the order of 10 days - in practice it is filled together with the LHe tank.

 $^{^{2}}$ The LN₂ level can be checked by dipping a low thermal conductance rod, e.g. plexiglas, and observing subsequent condensation onto it.



Figure 6.2: CAD model of the tip and sample preparation stages mounted onto the main manipulator. A tip shuttle and sample are shown semi-inserted into the respective cassettes.

To ensure a long hold time, intermediate heat shields, coupled to the evaporating cryogens, are used for both the LHe ("20K shield") and the LN₂ ("200K shield") tanks. However, these do not extend below the cryostat base plate. While doing so will likely improve the hold time, it would make the system even more sensitive to misalignment than it currently is. A schematic, courtesy of CryoVac GmbH, is shown in figure 6.3. It is critically important to avoid any contact between the different parts of the cryostat, since that severely degrades the thermal insulation between them. Since the cryostat is not completely symmetric, the damping stage³ is employed to ensure that the LHe insert is properly hanging. It can be easily checked that such is the case, since it was found that if the two touch, the temperature measured on the cold plate rises by $\sim 0.3K$ after less than 30 seconds.⁴

6.2.2 STM thermal management

The temperature is measured on the cold plate ("4K plate") and on the STM itself using two Lakeshore DT-470-SD-12A Silicon Diodes, which specify an accuracy of $\Delta T \leq 0.5K$ below 100K. The diodes are connected as two-terminal devices to reduce the number of wires and heat load, which leads to an offset of ~ 0.3K at ~ 5K due to the finite resistance of the wires ($R_{circuit} \sim 200\Omega$).

Two radiation shields surround the STM. The first is coupled to the LHe tank, while the second is coupled to the LN_2 tank. The STM head is coupled to the rods forming the structure of the inner heat shield via two gold plated copper braids. Some notable points regarding the design are:

- 1. The heat shields are constructed as a cage with separate panels, so that the STM is securely supported (e.g. for repairs) even when all of the plates are removed.
- 2. Holes in the shield (e.g. wire feed-throughs) follow a meandering path, in order to reduce radiation leakage.
- 3. All parts are OFHC copper plated with gold, to ensure minimal emissivity and avoid tarnishing over time.
- 4. The shields are rather heavy $(m \sim 5kg)$, so that the system is very stable. However, the time needed for cool down is about a day due to this large mass.

There are two "extrinsic"⁵ sources of thermal load on the LHe cryostat. These are radiation impinging on the 4K shield, estimated at $Q_{rad} \sim 3mW$, and conduction along the electrical signal wires, estimated at $Q_{wire} \sim 25mW$.⁶ The specifications of the cryostat suggest that the "intrinsic" heat load, i.e. due to radiation and conduction inherent to the cryostat design, is of the same order.

³Described in section 6.3.

⁴Of course, the order of magnitude increase in LHe consumption might be a clue as well.

⁵i.e. due to the STM, rather than the cryostat itself.

⁶Use of Manganin wires would have cut this by an order of magnitude, but has detrimental noise issues.



Figure 6.3: Cryostat schematic.

Based on these facts, it is clear that optimizing the radiation heat load at the STM stage is essential for a low base temperature, but not for optimizing the hold time, since most of the "extrinsic" thermal load on the cryostat is due to the wires and not the STM itself. As a consequence, we can try to optimize the coupling between the STM head and the cryostat to achieve a minimal base temperature, with very little effect on the hold time. In an initial test, the only coupling between the STM head and the base plate was via the thin copper wires $(0.004" \phi)$ used for electrical connections to the STM.⁷ Under these conditions a base temperature of $\approx 12K$ was achieved. To lower the temperature, the STM was coupled to the base plate by connecting two gold plated copper braids between the STM head and one of the inner heat shield rods. The material for the braid wires is chosen to ensure maximal thermal conductivity, hence an OFHC copper core, and minimize radiation load on the wire itself, hence the gold plating. Since the braids degrade the vibration isolation between the STM and the LHe cryostat, it is important to try to optimize their size and construction. First, the braids are made from an as-thin-as-possible wire. In practice, $0.002^{\circ}\phi$ wire was used. Second, the STM temperature was calculated vs. the cross section of the braid (see appendix A.1), and the braids' cross section was chosen to be near the "knee" in the curve. The resulting base temperature is $T \approx 7.5 K$ at present.

6.2.3 Optical access requirements & cryogenics

Typically, low temperature operation suggests that optical access to the sample be eliminated, since it will allow room temperature (i.e. 300K) radiation to reach the sample. However, since one of the goals of our STM is to combine optical access with scanning probe measurements, we need to enable UV and visible radiation access, but block far IR radiation. The previous STM, used for the early TTB-Azobenzene studies, had plain holes in the heat shields. However, that instrument used an order of magnitude more cryogens, and its base temperature is limited to $\approx 12K$, even with the extremely strong coupling to the cryostat employed at present. A better solution is to employ relatively thick fused silica windows. As can be seen in figure 6.4, the minimal overlap between 300K, 77K and the optical transmission of fused silica suggests that such a window would block about 99% of the thermal background radiation. In practice, we used 0.25" thick windows (Lambda part no. SWI-1206U), for the entrance and exit windows of the inner and outer heat shields.⁸

6.3 Vibration isolation

The STM body is made of Ti alloy (Ti-6Al4V) to achieve a light structure with high rigidity, thereby increasing the resonant frequency.

⁷The suspension springs are a combination of stainless steel and BeCu and do not contribute significantly to the heat conduction between the cold plate and the STM head.

⁸i.e. allowing UV & visible light to enter the STM, reflect off the sample, and exit.



Figure 6.4: Thermal radiation spectral density overlaid on the transmission of common window materials at 4K. Adapted from F. Pobell "Matter and Methods at Low Temperatures".⁷⁸

Three stages are used to vibrationally isolate the STM:⁹

- 1. A custom optical table (TMC model 784) with a resonance frequency of $\sim 1Hz$.
- 2. Cryostat mounted damping stage which isolates the inner, LHe, insert from the outer LN_2 part, with a resonance frequency of ~ 5Hz.
- 3. Internal spring suspension with a resonance frequency of $\sim 3Hz$. To ensure that high frequency vibrations, traveling along the spring wires themselves, do not "short" the STM spring suspension, the springs are mounted onto Vespel[®] bushings. The springs are a combination of two home-made 0.01" ϕ BeCu and one commercial 302SS spring.¹⁰ While the a-symmetry is theoretically detrimental, it has not proven to be an issue in practice so far.

In addition, magnetic damping, using SmCo magnets, is currently employed on the internal spring stage and has been recently added to the LHe insert as well. A schematic view of the vibration isolation setup is shown in figure 6.5. The STM can be clamped to the heat shields to enable sample transfer using a $1/4-28 MoS_2$ plated SS304 set screw to push the STM against V-shaped slots mounted on the LHe shield.¹¹ The clamping screw is actuated

⁹The STM is housed in a sound proofed room. However, this was a legacy of an older project and is most likely not essential.

¹⁰We attempted to use the same BeCu spring used for the two front springs as the rear spring, but the spring wire proved too soft.

¹¹While clamping the STM also improves thermal coupling to the cryostat, in practice the braids provide a stronger coupling.



Figure 6.5: Schematic of vibration damping setup.

by the rear rotary wobble stick. 12-13 turns of the set screw are necessary to ensure that the STM is fully hanging.

6.4 Electronics

A commercial control system, made by Specs-Zurich GmbH (formerly known as Nanonis), is used to control the system. The sample is biased, and the current is collected via the tip wire and amplified using a Femto DLPCA-200 pre-amplifier.

All the connections from the room temperature feedthroughs down to the 4K stage are made using miniature stainless steel coaxial cables (Cooner wire inc. CW8022) to reduce the heat load on the cryostat while maintaining good electrical shielding. In total, there are 40 coaxial wires connected to the low temperature stage. Wire preparation and termination details are given in appendix A.3. The wires are heat sunk, and the coaxial shields are grounded, at the 4K stage.¹² The tip wire (used to collect the current) and one of the sample contacts are connected from the 4K stage to the STM using miniature gold plated copper coaxial wires (Cooner wire inc. CZ-1223-1f), while the rest of the signals are fed from the 4K stage to the STM using Formvar insulated 0.004" ϕ Copper wires. The room temperature resistance of a wire between the feedthrough and the STM is $\approx 150\Omega$, with wire capacitance being $\sim 0.1 - 0.2nF$. When the instrument is cooled down, wire resistance decreases to $\approx 110\Omega$.

Low pass RF filters (Mini-circuits BLP-1.9+ having $f_{cutoff} = 1.9MHz$) are used on all the coaxial feedthroughs to reduce noise.

6.5 STM

The STM design is based on a fixed sample and a tip which is mounted onto a 3D coarse motion walker. The walker is a combination of a traditional pan walker forming the Z axis and a planar walker forming the XY axes, with the Z-walker mounted onto the XY plate. Other notable features are the inclusion of a lens for efficient light collection, tip exchange and multiple sample contacts. A picture and annotated CAD drawings are shown in figure 6.6.

The main parts of the STM were machined out of a Titanium alloy - Ti-6Al4V. This alloy has a high mechanical rigidity and is much lighter than stainless steel, which increases the resonance frequencies of the structure. A drawback of this choice is the low thermal conductivity of Titanium and its alloys, on the order of stainless steel. A thin gold plating was deposited on all possible parts to lower the IR emissivity.¹³ An important consideration in building mechanical contraptions in UHV is avoiding contact between similar materials, since the combination of vacuum, the initial bake out, and a removal of the native oxide

 $^{^{12}}$ It would probably have been better to isolate the electrical ground from the chamber.

¹³Unsuccessful attempts were made at gold plating the pieces by a commercial manufacturer to increase overall thermal conductivity *and* give low emissivity.



Figure 6.6: Picture & CAD drawing of the STM head. One of the support posts was removed in the CAD drawing to enable a better view of the XY stacks.

layer due to "grinding" leads to welding of the parts to each other. The usage of a Ti alloy body easily solves this issue, since we can use standard 18-8 SS hardware in most places. Wire anchoring blocks are made mostly of macor[®]. The sample contacts are formed by four Molybdenum "fingers" housed in a Sapphire body, to avoid thermal strain between the two. The Z-walker body, which is mounted onto the sapphire XY-walker plate, is made out of Molybdenum for the same reason.

The STM was mostly machined in the physics department's machine shop, with the exception of the Sapphire parts, which were machined by Insaco Inc. and Precision Ferrites & Ceramics, Inc..

6.5.1 Scan tube

The scan tube is made of EBL#4 PZT material, with Nickel electrodes, and has dimensions of 0.25" $\phi_{od} \times 0.02$ " wall $\times 0.4$ ". The outer surface is split into four quadrants serving as the $\pm X \& \pm Y$ electrodes, while the complete inner surface forms the Z counter electrode. Scan range at $T \approx 7.5K$ is $\sim 1.2\mu m$ and the Z range is $\approx 400nm$, using a bias range of $\pm 400V$. While no part of the scan tube is used as a shield, the outer surface of the macor cup housing the tip exchange mechanism is gold plated and electrically connected to the shield of the coaxial tip wire to reduce cross talk between the scan tube signals and the tunneling current.¹⁴

¹⁴However, due to such cross talk the minimal approach current is limited to $\sim 50pA$ for a "hunt & seek" cycle of $\sim 3 - 4sec$.

6.5.2 Coarse motion

The Coarse motion employed in our STM is composed of a Z-walker based on S. H. Pan's design of a prism type "walker" ⁷⁹ and an XY walker. The XY walker is a planar shear stack based design which is a derivative of that used by the Heinrich (IBM Almaden Research Center) and Stroscio (CNST - NIST) groups. Both walkers use Molybdenum leaf springs to compensate for thermal expansion and are adjusted "on the bench", balancing step size and rigidity. Both the XY and Z walkers are driven in "stick-slip" mode. The current maximal step size at room temperature is ~ 200nm for all three axes. The low temperature step size has not been calibrated for the X & Y axes, while the maximal Z axis step size at $T \approx 7.5K$ is ~ 100nm. We expect the lateral step size to scale in a similar manner, so that the low temperature maximal step size for the Z axis at $T \approx 7.5K$ is ~ 5nm using a drive amplitude of $\approx 75V$, and the step size is roughly linear with driving amplitude between ~ 40% to 100% of the 350V maximal drive voltage.

Since we decided to make all the XY stacks similar, mounting them so that the wiring tabs are conveniently located requires that different stacks be activated using different polarities, as shown in figure 6.7. Hence, a two channel amplifier and signal source is necessary, since actuating an axis requires driving some of the stacks with the opposite bias to other stacks. Further details of the driving electronics are given in appendix A.2, while details of stack construction are given in appendix A.4. The relative polarity of the X and Y axis stacks is shown in figure 6.8. All of the Z-walker stacks share the same polarity, but since the driving electronics are multiplexed between the three axes, they are also driven by two channels. However, since we drive the walkers in "stick-slip" mode, the specific connection of a stack to a channel in the Z walker is of no importance. For convenience, we connected each pair of stacks next to a prism face to separate channels, as shown schematically in figure 6.9.¹⁵

6.5.3 Sample design

The sample is composed of an outer frame, a sapphire plate, and an inner Tungsten back plate, shown in figure 6.10. For samples requiring direct heating during preparation, the back plate is replaced with two small Molybdenum clips. The outer frame is made of either Titanium alloy (Ti-6Al4V) or 304SS.¹⁶ The former choice is preferred since the Omicron transfer heads we use are designed for the much lighter and smaller Omicron sample plates. As a result, the larger sample we use and the inverted orientation dictated by the STM design suggest that the sample's moment of inertia be made as small as possible. When assembled, the fork-like shape of the frame is under slight tension applied by the set screws.

¹⁵The assignment of a specific channel to the upper or lower shear stack is not necessarily consistent between prism faces.

¹⁶Whichever sample frame material is used, the screws that thread into it must be of the complementary material to avoid vacuum welding.



Figure 6.7: Schematic of the XY stacks and how their polarizations are oriented. The red arrows mark the directions the top layer of a stack (i.e. the layer in contact with the XY plate) will move under a positive bias.

The front end of the outer frame is open, allowing the frame to adjust to the thermal expansion changes of the front sapphire pieces and the central sapphire plate and thereby mitigating thermal expansion induced stresses.

The sapphire plate is used as a thermal switch, utilizing sapphire's high thermal conductivity at low temperatures to couple the sample to the STM and its low thermal conductivity at high temperature to allow heating of the sample itself without excessive outgassing due to sample holder heating.

To enable future experiments involving a combination of transport and STM, the sample employs multiple contacts. Four flexible Molybdenum "leaves" are clamped between two sapphire pieces and contact rigid Molybdenum "fingers".¹⁷

6.5.4 Tip exchange mechanism

The tip exchange mechanism which we use is a copy of the one designed and used by Prof. Wiesendanger's group at the University of Hamburg⁸⁰ and allows tip exchange with the STM kept cold. The mechanism and the tip shuttle (used to move the tip holder) are shown in figure 6.11. The tip is inserted into a Molybdenum tip holder and is kept stable solely by

¹⁷Even when performing standard STM it is advantageous to connect (at least) two of the contacts, since then it is easy to check whether the sample is properly inserted into the STM & preparation cassettes by measuring the resistance between these.



Figure 6.8: Wiring polarity for the X and Y shear stacks.



Figure 6.9: Wiring polarity for the Z shear stacks.

friction. The holder is inserted into a receptacle in the Z-walker prism, which is formed by a copper block (to which the tip wire is glued) and a specially bent 0.004" thick BeCu spring. The design is optimized towards high temperature processing of the tip, as is necessary for example for spin polarized STM. As is commonly the case, tip exchange requires removal of the sample from the STM, since the tip shuttle takes the place of the sample. For both tip insertion and extraction it is necessary to judge the exact height of the tip shuttle with respect to the tip holder, which can be done by viewing the STM through the rear door of the heat shields.

The tip shuttle is similar in design to the sample holder, utilizing an outer frame made of either SS304 or Ti-6Al4V, which of course has the same outer dimensions as the sample holder. Two sapphire pieces isolate the inner part both electrically and, at high temperatures, thermally. The inner part is made of Molybdenum and has two grooves that slide into matching slots on the tip holder and a $0.02^{\circ}\phi$ Molybdenum spring that retains the holder. Electrical connections to the tip for e-beam heating are made by a flat Molybdenum spring, touching the usual sample contacts.

To insert a tip, the shuttle is slid into the STM, and the coarse walker is used to guide the hanging tip into the receptacle. This is a (relatively) safe part of the process, since the coarse walkers cannot exert enough force to break the scan tube, so that attempting



Figure 6.10: Schematic of sample showing various parts. A standard "top-hat" sample is drawn. The frame and screws are marked with the two complementary material choices - Ti-6Al4V or SS304.

to walk vertically while the tip is not in the right position would not cause damage. Once the Z-walker has managed to walk to the point where the holder is pressed from below onto the grooves in the shuttle, one should walk back ~ 100 steps - enough to see the holder "relax" a bit, and then gradually, in several steps, pull the shuttle out of the STM. Each step should consist of pulling the transfer rod back by ~ 1mm, and then walking up and down, to ensure that there is no friction between the shuttle and the scan tube. Attempting to extract the shuttle while it's "dragging" the tip holder could break the scan tube.

Tip extraction, on the other hand, is dangerous from the get-go. The procedure starts with walking the STM to the exact vertical position so that the grooves on the tip shuttle can slide into the slots on the tip holder. One *must* be careful at this point - it is possible to break the scan tube if the shuttle is shoved at the wrong height. The shuttle is then *carefully* pushed into the STM, while observing the STM using the approach camera to ensure that the shuttle is "catching" the holder, rather than pushing it (and the STM). Once the shuttle is fully inserted, the STM Z-walker can be used to walk down, leaving the tip in the shuttle.



Figure 6.11: (a) Schematic of tip exchange mechanism. (b,c) Top and bottom view of the tip shuttle CAD model. (d) Top and front pictures of a tip shuttle using an older version of the frame.

6.6 Optical access & light collection

Optical access to the STM tunnel junction is provided via two symmetric 0.25" diameter holes in the XY walker plate, as shown in figure 6.12.¹⁸ These holes are set at an angle of 30° to the sample, which is optimal for light collection. We chose to leave one of these *as-is*, while the second has a small sapphire lens mounted as close as possible to the tip-sample junction for light collection.¹⁹ Optical fibers were considered as an alternative; however, the tip exchange mechanism requires a certain clear region around the tip of $\sim 2mm$. As a result, we would not be able to place an optical fibre, with its smaller diameter as compared to the lens, close enough to the junction to be efficient.

This setup fixes the location of the STM tip - sample junction relative to the collection optics. This solution has the advantage that the lens is aligned regardless of the position in the XY plane, so that we can collect light from different points on the sample, which is beneficial for studying devices. However, we cannot change the alignment *in-situ*, so that any shift, for example due to a bent tip, would reduce the efficiency. In addition, the height of the sample plane in the STM must be set precisely to achieve optimal collection efficiency. The sample plane must be $1.8 \pm 0.1mm$ below the sample frame plane, as defined in figure 6.13. For a standard 1mm thick sample and using the standard 0.03" thick back plates, this can be achieved by placing two #0 Molybdenum washers²⁰ between the sapphire plate and the Tungsten back plate.

The optimal efficiency of our light collection system, when using the trimmed 2^{nd} gen-

 $^{^{18}{\}rm The}$ image shown is of the current lens, while the CAD extract shows the custom lens that is yet to be installed.

¹⁹To eliminate thermal stresses, the lens is mounted in a semi-flexible Molybdenum holder that is semipress fit into the hole in the sapphire plate.

 $^{{}^{20}}t_{washer} = 0.4 - 0.42mm$ for the washers purchased from Thermoshield.



Figure 6.12: (a) Large cutout view showing the STM in the shields. (b) Close up showing the light collection lens. (c) Picture of the currently installed commercial lens.

eration chamfered lens (plano-convex f = 6.3mm, $\phi = 6.4mm$) is ~ 5%, while the current lens (plano-convex f = 10mm, $\phi = 5mm$) gives $\eta \approx 2\%$. For the current setup, the relative collection efficiency vs. offset from the focal point was calculated, based on the CAD model of the system, with the result being that for a slight defocusing, a lateral misalignment of up to ~ 0.3mm is tolerable. More details are given in section A.6.

Following collimation with the STM mounted lens, the light passes through the IR blocking windows and through a fused silica viewport. The light is then focused onto an optical fiber and coupled to a detector (Princeton instruments Spec-10:100BR LN_2 cooled CCD Detector) mounted onto a monochromator (Princeton instruments SP2358). As a second possibility, suitable e.g. for initial testing of a new system, we can direct the light into a photomultiplier tube (Hamamatsu H9305-03).

6.7 Testing

Initial testing of the new instrument consisted of measuring the topography and electronic structures of a few noble metals surfaces, which have been extensively characterized in the past.^{34–36,81–83} Here we show examples of atomic resolution on Cu(100) at room temperature (figure 6.14), Herringbone reconstruction and atomic resolution on Au(111) at $\approx 12K$ (figure 6.15), and atomic resolution on Pt(111) at $\approx 7.5K$ (figure 6.17). Furthermore, we tested the low current capability of the new instrument by imaging a sub-surface defect on Au(111) at I = 600 fA (figure 6.16).



Figure 6.13: Sample marked with the planes used to define the height of the sample plane for optimal light collection.



Figure 6.14: Room temperature topography of a Cu(100) surface. $I_{tunneling} = 18.2nA$, $V_{sample} = -20mV$.



Figure 6.15: Au(111) surface at $T \approx 12K$.(a) Herring-bone reconstruction $500\dot{A} \times 500\dot{A}$, $I_{tunneling} = 80pA$, $V_{sample} = -0.4V$. (b) Atomic resolution $63\dot{A} \times 63\dot{A}$, $I_{tunneling} = 1.4nA$, $V_{sample} = -0.46V$. (c) STS showing the Au(111) surface state band edge at -0.52V.



Figure 6.16: Low current images of the Au(111) at $T \approx 12K$. In both images a derivative of the topography is used to enhance contrast. $V_{sample} = 0.5V$. (a) $I_{tunneling} = 4pA$. (b) Close up on the region marked with a black square in (a), $I_{tunneling} = 600 fA$.



Figure 6.17: Pt(111) surface at $T \approx 7.5K$. (a) Multiple types of surface features are visible. $I_{tunneling} = 0.2nA, V_{sample} = -25mV(b)$ Smaller scale $25\mathring{A} \times 25\mathring{A}$ image showing atomic resolution and a single atomic scale defect, $I_{tunneling} = 0.5nA, V_{sample} = -40mV$.



Figure 6.18: Comparison of a low noise condition and a high noise one (strong $\sim 50Hz$ peak). $I_{tunneling} = 50pA \& V_{sample} = 0.55V$ for both.

6.7.1 Noise spectrum

The initial testing of the instrument showed promising results, with the main issue being a broad noise peak at $\sim 40 - 50Hz$, shown in figure 6.18. We believe this is the result of a cryostat mechanical vibration, due to our own observation of the noise being at its best midway between filling cryogens and discussion with another group using a similar cryostat who observe similar noise peaks. Due to the proximity between this noise peak and the electrical network's 60Hz cycle, there is a strong coupling between the two which somewhat complicates matters. We are currently revamping the magnetic damping setup of the STM and adding an additional magnetic damping stage for the LHe cryostat, shown in figure 6.5.

Mega-Gauss in Nanobubbles

The unique strain-induced effects predicted to exist in graphene suggest its use in the context of studying electro-mechanical coupling.^{84–89} In order to explore these effects, we have grown graphene on a Pt(111) substrate. The high strain created by the large thermal expansion mismatch between graphene and Pt would make this an ideal test case for observation of strain-induced effects.

Graphene on metal samples have been previously shown to display nanometer scale delaminated regions of the graphene film ("nanobubbles").^{90,91} We find that the high strain incorporated in the nanobubbles gives rise to pseudo gauge fields, which mimic the effect of a real magnetic field on the order of 300 - 400 Tesla. While these effects have been suggested theoretically, they have not been observed previously. These strain-induced effects serve as another example of strong coupling between mechanical and electronic properties of nanoscale materials, complementary to the opto-mechanical coupling we observed in TTB-Azobenzene islands. The high levels of strain observed open the door to studies of extremely high field regimes, beyond those currently available through conventional means, and could potentially be used as a complementary building block for mechanically controlled electronic devices, i.e. "strain-engineering".⁸⁴

In the future we are planning on using graphene on an insulator, where the electronic density can be easily tuned by an electrostatic potential ("gating").¹ The combination of gating, strain-induced effects and opto-mechanically active molecules may open the door to new device realms. Here I will provide an overview of graphene's electronic properties, including predicted strain-induced effects, and I will then discuss our own experimental findings in this area.

7.1 Graphene - an overview

Graphene, a single two dimensional sheet of sp^2 bonded Carbon atoms, has remarkable electronic structure and mechanical properties.

Many of graphene's unique properties arise from the Dirac-like behavior of charge carriers within the 2-D honeycomb lattice.^{16,92} While numerous observations of novel graphene phenomena have been made, including field effect carrier tuning,¹ extremely high mobility,¹ weak anti-localization,¹⁰ half-integer^{93,94} and fractional quantum Hall effects,^{95,96} and great mechanical strength,^{97,98} there remain many striking predictions which have yet to be demonstrated experimentally. One such prediction, which has no counterpart in 2D semiconductor materials, is that large, nearly uniform pseudo-magnetic fields can be generated in graphene by distorting the 2D honeycomb lattice, thus giving rise to a pseudo quantum Hall effect.⁹⁹

7.1.1 The graphene tight-binding model

Graphene has a honeycomb lattice with two atoms per unit cell, which we shall dub the A and B atoms, respectively. The primitive vectors, following Mañes¹⁰⁰ are

$$\vec{a}_1 = \sqrt{3}a\hat{x}$$
$$\vec{a}_2 = \frac{\sqrt{3}a}{2}\hat{x} + \frac{3a}{2}\hat{y}$$

Where $a = 1.42 \text{\AA}$ is the carbon - carbon bond length. The two atoms are located at

$$\vec{r_1} = \vec{a_1}/3 + \vec{a_2}/3$$

 $\vec{r_2} = 2 \cdot \vec{r_1}$

The Brillouin zone is formed by

$$\vec{G}_1 = \frac{2\pi}{\sqrt{3}a}\hat{x} - \frac{2\pi}{\sqrt{3}a}\hat{y}$$
$$\vec{G}_2 = \frac{4\pi}{3a}\hat{y}$$

A large number of graphene's properties can be understood through a rather simple tight binding Hamiltonian,¹⁰² with one p^Z orbital per atom. Specifically, it can be shown that the low energy excitations behave as chiral massless Dirac fermions, where the Fermi velocity acts as the equivalent of the speed of light.

The tight binding Hamiltonian, limited to nearest and next-nearest-neighbor interactions,¹ is given by¹⁶

$$\mathscr{H} = -t \sum_{\langle i,j \rangle,\sigma} (a^{\dagger}_{\sigma,i}b_{\sigma,j} + H.C.) - t' \sum_{\langle \langle i,j \rangle \rangle,\sigma} (a^{\dagger}_{\sigma,i}a_{\sigma,j} + b^{\dagger}_{\sigma,i}b_{\sigma,j} + H.C.)$$

¹The basic properties can be understood without including the next-nearest-neighbor interactions. However, the strain-induced scalar gauge field we shall discuss later is best understood by including these effects.



Figure 7.1: Graphene unit cell, Brillouin zone and primitive vectors. Adapted from Mañes¹⁰⁰ and Akola *et al.*¹⁰¹

Where $a_{\sigma,i}^{\dagger}$, $a_{\sigma,i}$ are the creation and annihilation operator for an electron on sub-lattice $A, \sigma = \uparrow, \downarrow$ defining the electron's spin. The $b_{\sigma,i}^{\dagger}$, $b_{\sigma,i}$ operators are the equivalent operators for the B sub-lattice. The t and t' parameters are the nearest neighbor (i.e $A \to B$) and the next-nearest-neighbor ($A \to A$) hopping energies, respectively. The nearest neighbor hopping parameter is known to be $t \approx 2.8 eV$, ¹⁶ while $t' \sim 0.1 eV$.¹⁰³

The energy bands are given by 102

$$E_{\pm}(k) = \pm \sqrt{3 + f(\vec{k})} - t'f(\vec{k})$$

where

$$f(\vec{k}) = 2\cos(\sqrt{3}k_ya) + 4\cos(\frac{\sqrt{3}}{2}k_ya)\cos(\frac{3}{2}k_xa)$$

Where the plus and minus signs apply to the upper (anti-bonding, π^*) and lower (bonding, π) bands, respectively. The electronic structure is hence a semi-metal, with the valence and conduction bands touching at six points in the Brillouin zone, as shown in figure 7.1c. However, there are only two inequivalent high symmetry points - K and K'. If we expand the overall solution around these points, defining $\vec{q} = \vec{k} - \vec{K}$, we get a linear dispersion

$$E_{\pm}(\vec{K}+\vec{q}) \cong \hbar v_F |\vec{q}|$$

where

$$v_F = \frac{3at}{2\hbar} \approx 10^6 m/sec$$

To leading order, the effect of the next-nearest-neighbor coupling is only to break the electron-hole symmetry and shift the energy of the Dirac points.
Under this approximation, one can show that the effective Hamiltonian is

$$\mathscr{H} = \hbar v_F \vec{\sigma} \cdot \vec{\hat{q}}$$

where $\vec{q} = \hat{q}_x + i\hat{q}_y$, $\hat{q}_{x,y} = -i\partial_{x,y}$, $\vec{\sigma} = \sigma_x + \sigma_y$ and σ_x , σ_y are the Pauli matrices. The wave functions are two component spinors, whose basis are electron wave functions localized on the A and B sub-lattices.² This is equivalent to the Hamiltonian obeyed by massless Dirac fermions, and hence electrons in graphene behave as such, with v_F playing the equivalent role to c, so that the coupling constant $\alpha_{graphene} = \frac{e^2}{\hbar v_F} \sim 1$, indicating that we are in the strong coupling regime. Further important consequences of the low energy band structure are the resistance to confinement due to potential barriers (aka "Klein tunneling")¹⁰⁴ and resistance to back scattering.¹⁰⁵

Behavior under an applied magnetic field

Under an applied magnetic field, a second length scale, in addition to the lattice constant a, is formed (in SI units)

$$l_B = \sqrt{\frac{\hbar}{eB}}$$

The Hamiltonian formed by applying minimal coupling $\vec{k} \to \vec{k} + \frac{e}{\hbar}\vec{A}$, and under a constant magnetic field applied perpendicular to the surface can be solved analytically.¹⁰⁶ The eigenstates are Landau levels, at energies of

$$E_N = sgn(n) \cdot \hbar\omega_c \sqrt{N} + E_{Dirac} \tag{7.1}$$

Where the magnetic energy scale³ is given by

$$\hbar\omega_c = \hbar\sqrt{2e\hbar v_F^2 B}$$

and E_{Dirac} is the energy of the Dirac point, which might be shifted due to e.g. doping.

In the case where both a magnetic field \vec{B} and an electric field \vec{E} exist, the energy of the existing Landau levels is shifted, and under extreme electric field they are completely quenched.^{107,108} The renormalized magnetic energy scale is given by

$$\Omega_c = \omega_c (1 - \frac{E^2}{v_F^2 B^2})^{3/4} \tag{7.2}$$

²This Hamiltonian is degenerate with respect to the real electronic spin \hat{S} , and hence \hat{S} does not appear in the Hamiltonian. Spin-orbit coupling is a very weak effect in graphene.

³The cyclotron energy differs by a $\sqrt{2}$ factor.

7.1.2 Lattice deformation as effective potentials

The effective Dirac Hamiltonian around the K and K' points, which is linear in $\vec{q} = \vec{K} - \vec{k}$, suggests that a local deformation potential could mimic the effect of a magnetically applied vector potential, since the minimal coupling recipe $\vec{k} \rightarrow \vec{k} + \frac{e}{\hbar}\vec{A}$ (SI units ⁴) is similar to such a Hamiltonian, where to leading order the terms are independent of \vec{q} .^{16,100,109–111} However, there are additional requirements that must be met before this unique relationship between strain and a pseudo vector potential is created.¹⁰⁰ In addition to the Dirac Hamiltonian, the system must be lattice based and lack the inversion symmetry, so that the symmetry of the vector potential and of the deformation Hamiltonian under spatial inversion will match. Even when these conditions are satisfied, the analogy can only be valid around specific \vec{k} points due to the overall different time reversal symmetries of the vector potential and phonons and is dependent on the symmetry properties of the group around these k-points.

We shall now give a short discussion of the way in which the strain in the graphene membrane can be represented as effective vector and scalar potentials. As a result of a change in the bond length due to elastic strain u_{ij} , where i, j = x, y (defining the \hat{x} axis to be along the zigzag direction), there is a resulting change in the $A \to B$ hopping amplitude. The hopping parameter is assumed to have an exponential dependence on the bond length rather than the more commonly assumed $1/l^2$ dependence.⁸⁹ The resulting change $t_{AB} \to t_{AB} + \delta t_{AB}$ can then be, to leading order, related to the strain by

$$u\sim\beta\frac{\delta t_{AB}}{t}$$

where

$$\beta = -\frac{d\log t_{AB}}{d\log a} \approx 2 - 3$$

The specific relationship between the effective potential and the underlying hopping parameters, and therefore elastic strain components, is fixed by symmetry considerations. Due to the symmetry group of the graphene lattice, the spatial and temporal transformation properties of the deformation Hamiltonian are identical to those of effective gauge fields \vec{A} and Φ .^{100,1125} The final result is that graphene under an applied effective strain behaves as if under a pseudo gauge potential given by, around the K point,⁶

$$ec{A_x} = rac{\hbareta}{ea}(u_{xx} - u_{yy})$$

 $ec{A_y} = -rac{2\hbareta}{ea}u_{xy}$

 $^{{}^{4}\}vec{k} \rightarrow \vec{k} + \frac{e}{\hbar c}\vec{A}$ in CGS units

⁵Note that the definitions of the primitive vectors are not consistent among these.

⁶The signs of the components of \vec{A} are reversed at the K' points.

In addition, a scalar potential of order

$$\Phi \approx V_0(u_{xx} + u_{yy})$$

where $V_0 \sim 3 - 4eV^{113}$ is experienced as well. As opposed to the pseudo vector potential which switches sign between the K and K' points, the pseudo scalar potential has the same sign. However, the effective scalar potential is screened by the charge carriers, so that for our case of a conducting substrate it is of lesser importance, though it might be important for bubbles of exceptionally high aspect ratio. An additional difference between the scalar and vector effective potentials is that the former is non zero even for the case of a uniform strain, while the latter vanishes.

In addition to the effective potentials resulting from the in-plane strain (i.e. change in bond lengths and the resulting changes in the $A \to B$ hopping parameters), there are additional effective potentials arising from the curvature of the deformed bubble, e.g. due to $\sigma\pi$ hybridization. However, due to the large corrugation and strain observed, these can be safely neglected, as they are expected to be orders-of-magnitude smaller.¹⁶

The gauge fields created by strain are predicted to have important consequences for the electronic structure and transport properties of graphene.^{84–86} In particular, pseudo Landau levels, similar to those created by real applied fields, are predicted to exist for strong enough strain fields,^{87,88} and for uniaxial strain above a threshold strain of $u \sim 20\%$, a gap opens.⁸⁹

Creation of large semi-constant B_s in specific geometries

It has been recently suggested^{99,114} that under appropriate strain constructions, a very large (10's of Telsa) nearly uniform pesudo magnetic B_s field could be created. The initial suggestion by Guinea et al.⁹⁹ produced a perfectly uniform B_s , but employed a complicated distribution of forces, which would be nearly impossible to create experimentally. The suggested shapes and forces are shown in figure 7.2, adapted from Guinea et al.⁹⁹ However, it was proposed in the same paper that stretching a hexagonal patch along the three equivalent (100) directions would produce a fairly uniform pesudo field near the center of the patch. One way to create this strain-field would be to grow nanobubbles of graphene on a surface displaying hexagonal symmetry, such as Pt(111). Here the forces would be along the three high symmetry directions, due to the symmetry of both the Pt(111) surface and the graphene layer. In addition, the large strain resulting from thermal expansion mismatch during post growth cool-down could create the necessary strain magnitude. Nanobubbles on Pt(111) could thus potentially form a good experimental realization of Guinea *et al.*'s uniform compression along the three symmetric directions. Hence we may expect a nearly uniform strain-induced pseudo magnetic field B_s to form in such nanobubbles, mimicking the effect of a "real" magnetic field applied perpendicular to the graphene membrane.⁹⁹ This would in turn cause Landau levels to form, obeying the same \sqrt{N} progression.



Figure 7.2: Highly Uniform B_s fields under selected strain and force distributions, from Guinea *et al.*⁹⁹

7.2 Growth of graphene nanobubbles on Pt(111)

Graphene films have been previously grown by catalytic decomposition of hydrocarbons on various catalytic substrtaes, such as Ru(0001), ^{11,90} Ir(111), ^{14,91} Pd(111), ¹² Pt(110), ¹¹⁵ Pt(100)¹³ and Pt(111). ^{116–118} The strength of the coupling between the graphene film and the underlying substrate has been studied by Preobrajenski *et al.* ¹¹⁹ and Gao *et al.* ¹²⁰ for various substrates, concluding that the weakest coupling exists for graphene films grown on Pt(111).

7.2.1 Sample preparation

Following Land *et al.*,^{116,117} we grew graphene films on the Pt(111) surface by decomposition of ethylene gas at elevated temperatures. Single crystal Pt(111) surfaces were prepared in ultra high vacuum (base pressure below $2 \cdot 10^{-10} torr$) by repeated cycles of Ar⁺ sputtering at 500V and annealing in $5 \cdot 10^{-7} Torr$ of O_2 at ~ 1200K for 30 min by e-beam heating followed by a brief flash in vacuum. After sufficient cycles to ensure a clean surface, ethylene gas (Matheson Tri-gas, research purity 99.999%) was leaked into the chamber at a partial pressure of $1 \cdot 10^{-7} Torr$ for 60 sec at room temperature, to give a saturation coverage of ethylene on the Pt(111) surface. High temperature annealing (~ 1200K) for 5 min of the ethylene/Pt(111) surface resulted in graphene patches with nanoscale bubbles (figure 7.3). All experiments were performed at $T \sim 7.5K$ using cut $Pt_{80}Ir_{20}$ (Goodfellow) tips.



Figure 7.3: STM image taken at 7.5 K of a Graphene monolayer patch on Pt(111) with four nanobubbles at the graphene-Pt border and one in the patch interior. Unreacted ethylene molecules and a small hexagonal graphene patch can be seen in the lower right $(I_{tunneling} = 50pA, V_{sample} = 350mV).$

7.2.2 Topography of graphene patches and bubbles on the Pt(111) surface

Figure 7.3 shows an STM topograph of the graphene/Pt(111) surface prepared in the manner described above. The image shows a flat graphene patch (surrounded by Pt) which encompasses five graphene nanobubbles. Graphene nanobubbles frequently appear near the edges of a graphene patch, but are also sometimes observed in the center of flat patches or near the boundaries between patches. These nanobubbles are likely related to previously investigated larger scale "wrinkle" structures observed by LEEM which form upon cooling as a result of the differing thermal expansion coefficients of graphene and the platinum surface.⁹¹ Individual nanobubbles often have a triangular shape (see figure 7.5), reflecting the lattice symmetry of the graphene and the underlying Pt surface, and are typically 4 nm - 10 nm across and 0.3 nm - 2.0 nm tall. Atomic resolution imaging of the nanobubbles confirms the honeycomb structure of graphene on the bubbles (see figure 7.5), though the lattice is distorted due to the large strain occurring in these structures.



Figure 7.4: Strain for a graphene film grown on Pt(111) at $T_{growth} = 1200K$ vs measurement temperature

Graphene - Pt thermal induced strain

To estimate the degree of strain likely "trapped" in a bubble, we should look at the differences in thermal expansion between Platinum and graphene. The strain resulting from the differences in thermal expansion between the substrate and the film can be calculated following

$$\frac{1}{1-\epsilon} = e^{\int_{T_1}^{T_0} dT'(\alpha_{graphene}(T') - \alpha_{Pt}(T'))}$$

where ϵ is the resulting (scalar) strain, T_0 is the growth temperature, T_1 is the measurement temperature, and $\alpha_{graphene}$, α_{Pt} are the thermal expansion coefficients of graphene (as calculated by Mounet & Marzari¹²¹) and Platinum,¹²² respectively. The resulting strain vs. measurement temperature, for $T_{grwoth} = 1200K$, is shown in figure 7.4. Since we do not observe the sample during cool down, we do not know at which temperature the bubbles form, so that the amount of strain "frozen" in the bubbles is somewhat uncertain. *In-situ* studies of graphene films grown on Ir(111), by N'Diaye *et al.*,⁹¹ show that wrinkles are formed at elevated temperatures, with a residual strain of $\epsilon_{Ir-grapheen} \approx 0.003$. While no such studies have been published on the graphene - Pt(111) system, this would suggest that the strain is somewhat reduced from maximum value of $max(\epsilon_{Pt-grapnene}) \approx 0.015$. As an order of magnitude estimate, we shall take $\epsilon_{Pt-grapnene} = 0.01$ from here on.

An atomically resolved image of an individual graphene nanobubble is shown in figure 7.5. The characteristic hexagonal lattice is clearly resolved, though it is distorted. In addition, the lattice seen in a typical flat region of the graphene film (figure 7.6) shows no visible distortion, and the Moire pattern observed due to the lattice matched growth suggests that the strain is minimal. As a result, it seems reasonable that the overall stress due to the difference in thermal expansion has been completely released by forming nanobubbles.

possible scenario for nanobubble creation is one in which a film with a weak adhesion to the surface (as corroborated by the ARPES measurements¹⁵) encounters a surface feature that impedes its motion during post-growth cool down. Since the overall strain-induced by the accumulated thermal expansion from a growth temperature of ~ 1200K to ~ 10K is ~ 1%, and the length of the bubble is typically about 1/10 of the length of the hosting patch, the concentrated strain is expected to be on the order of 10%. As we shall show later, this value agrees well with our estimate based on the energy scale of the spectroscopic features.

It should be possible, in essence, to extract the components of the strain tensor directly from the locations of the Carbon atoms measured using STM. However, due to a combination of the rich electronic structure and the inherent noise of our measurements, it was not possible to resolve the locations of individual atoms with sufficient accuracy to perform this analysis.



Figure 7.5: Topography of an individual nanobubble $(I_{tunneling} = 50pA, V_{sample} = 200mV)$.



Figure 7.6: Atomically resolved images of a flat graphene patch. The typical Moire pattern can be easily seen. The raised features at the edge of the patch may be nanobubble precursors. The image was processed using WSxM.¹²³ ($I_{tunneling} = 330pA$, $V_{sample} = 500mV$).

7.3 Estimate of the strain-induced pseudo-magnetic flux through a corrugated bubble

For the case of a bubble which is stressed purely due to the corrugation of the initially flat graphene membrane, there exists a simple estimate of the B_s value generated. However, this simple formula severely underestimates the B_s value when there exist extrinsic stresses, e.g. due to differing thermal expansion coefficients of the graphene membrane and the underlying substrate. Nevertheless, it does serve as a useful starting point.

For the case of a bubble of height h and length L, we can estimate the resulting in-plane strain by $\frac{h^2}{L^2}$ (see appendix B.1). The resulting pseudo potential is hence

$$|\vec{A}| \sim \frac{\beta}{a} \frac{h^2}{L^2} \frac{\Phi_0}{2\pi}$$

and the resulting pseudo magnetic flux is

$$\Phi \sim L |\vec{A}| \sim \frac{\beta}{a} \frac{h^2}{L} \frac{\Phi_0}{2\pi}$$

where $\Phi_o \approx 4 \cdot 10^{-15} Tesla \cdot m^2 (SI)^7$ is the quantum flux. The resulting pseudo magnetic field B_s is

$$B_s \sim \frac{\beta}{a} \frac{h^2}{L^3} \frac{\Phi_0}{2\pi}$$

For a typical bubble we observe h = 0.5nm, L = 5nm, which would give $B_s \sim \frac{3}{0.14nm} \frac{0.5nm^2}{5nm^3} \frac{4\cdot 10^{-15}}{2\pi} \approx 30 Tesla$. As we shall show below, this seems to be somewhat underestimating the size of the observed effective fields, suggesting that there is more strain than can be accounted for solely due to corrugation. For instance, assuming a strain of $\bar{u} \sim 0.1$ in a bubble of size $L \sim 5nm$, would result in a B_s field of $\approx \frac{\beta \bar{u}}{aL} \frac{\Phi_0}{2\pi} \sim 300 Tesla$. The magnetic length scale associated with a B_s field of $\sim 300 Tesla$ is $\sim 1.5nm$. As a result, for such a field, the degeneracy of each Landau level in a bubble of $\sim 5nm$ length is $\nu \sim 1 - 10$, which suggests that we are at the edge of applicability of the simple model, since a naive application of the theory requires that the B_s field be uniform on the magnetic length, i.e that $\nu \gg 1$.

7.4 Observation of Landau levels in LDOS

The extremely large B_s value expected in the highly strained graphene nanobubbles that we observe suggests that Landau levels with an energy scale between 0.1eV and 1eV should exist in the nanobubbles. To test this prediction, we studied the LDOS using STS measurements over different regions of the sample. The dI/dV spectra seen in figure 7.7 show the typical Pt(111) surface state over the clean Pt(111) region.⁸³ The tip was later calibrated in between

⁷In CGS units $\Phi_0 = \frac{hc}{e} \approx 4 \cdot 10^{-7} Gauss \cdot cm^2$



Figure 7.7: Representative STS of different regions on the sample. For viewing clarity, the flat graphene/Pt(111) spectrum is shifted upwards by $3 \cdot 10^{-11} \Omega^{-1}$, the nanobubble edge spectrum by $9 \cdot 10^{-11} \Omega^{-1}$, and the nanobubble center spectrum by $2.1 \cdot 10^{-10} \Omega^{-1}$.

measurements over the nanobubbles using the Pt(111) spectra. The spectra measured over the flat graphene region appear similar to the bare metal at low bias, with a larger slope at elevated bias, but no special features. Spectra taken near the edge of a nanobubble show a dip around E_F having FWHM of $127 \pm 9meV$, which has been associated with phonon assisted inelastic tunneling.¹²⁴ The appearance of the phonon mediated gap suggests that as opposed to the flat regions, where the typical graphene electronic structure is overshadowed by that of the Pt(111) surface, the nanobubble regions are decoupled from the substrate. These spectra are consistent with a Dirac point at 300mV, as observed by ARPES recently,¹⁵ but due to the Pt(111) surface state we are unable to unambiguously determine the Dirac point directly. As opposed to spectra taken over any other region, spectra taken over the central region of a nanobubble exhibit a series of peaks with spacing on the order of 0.5eV, which are unlike features previously seen on SiC^{105,125} and SiO₂^{124,126} and often overwhelm commonly observed features.

Figure 7.8 shows a series of point spectra taken along a line cut across a bubble. All the spectra shown display a strong peak series, which allows us to extract the spatial dependence of the B_s field, as well as the position of the Dirac point. Similar peak structure was observed on 10 different nanobubbles with 4 different STM tips, with some variation in peak spacing and amplitude presumably due to variations in strain-induced electronic structure arising from different nanobubble geometries. These peaks observed in the LDOS can be attributed to Landau levels originating from a strain-induced pseudo-magnetic field, similar to those observed for real magnetic field.^{127,128}

7.4.1 LDOS fitting

To extract the local value of the B_s field, the spectra were fitted using a series of Lorentzian peaks following the expected \sqrt{N} progression for Landau levels, as shown in equation 7.1.



Figure 7.8: dI/dV spectra $(T \sim 7.5K, V_{mod} = 20mV)$ taken along a line across a graphene nanobubble at points shown in the upper inset image. Red lines are data with quartic background subtracted, black dotted lines are Lorentzian peak fits (center of peaks indicated by dots, with blue dots indicating n=0). Vertical dash-dot lines follow the energy progression of each peak order. For viewing clarity, the spectra are vertically shifted by $6.25 \cdot 10^{-11} \Omega^{-1}$ from each other.



Figure 7.9: STS over a wide bias range showing both positive and negative Lorentzian peaks fitted to the spectra. The point indexes match those shown in figure 7.8.

The resulting effective magnetic field and Dirac point were extracted from the best fit to the data. Background subtraction was performed by using a simple fourth order polynomial. The resulting fit is shown in figure 7.8. For the first spectra shown the extracted B_s field is 350 ± 40 Tesla. While the peaks are observed over a wider bias range than seen here and follow the expected behavior, as seen in figure 7.9, the quality of the fit deteriorates, which could be due to deviations from the simple linear Dirac cone model at higher energies, such as trigonal wrapping and other non linear effects.^{16,129} Fitting was performed using the fityk package,¹³⁰ in combination with automated scripts generated by Matlab^(R) code.

To check the overall adherence of the peaks to the model, we performed a second stage fitting, where we took the peak positions for a given spectra from the best fit obtained during the model fitting performed in the first stage and used these as a starting point for a "free" fit. The resulting normalized peak positions $\frac{E_N - E_D}{\hbar\omega_c}$ were plotted against \sqrt{N} . As expected, the data taken from five different bubbles and with different tips collapse onto a straight line of unity slope, as seen in figure 7.10.

One trend which is noticeable when looking over the aggregated data is for odd numbered peaks to be more commonly seen than even numbered ones. One possible explanation is that the different parity of the odd numbered peaks matches the 3-fold symmetry better.



Figure 7.10: Normalized peak energies (taken from five different bubbles and with different tips) collapse onto a common line. The dotted line has unity slope, *without any adjustable parameters*.

7.5 Simulation

To calculate the pseudo field in the bubbles observed, the topography of a bubble was simulated by compressing a triangular graphene patch along the three (100) directions to an external strain of 10%. These calculations were performed by F. Guinea at Instituto de Ciencia de Materiales de Madrid (CSIC). A detailed comparison between the calculated and experimental spatial dependencies is presented below.

7.5.1 $z, B_s \& \Phi_s$ line cuts

Profiles of the B_s field and the location of E_{Dirac} across a strained nanobubble were extracted from the spectral peak spacing and positions at different positions along a line that traverses a nanobubble as shown in figure 7.11. The B_s profile is reasonably flat across the center of the nanobubble, indicating a relatively uniform pseudo-magnetic field of 300 - 400 Teslafor this particular geometry. The Dirac point energy, E_{dirac} , (which is coincident with the n = 0 Landau level) ranges from 0.2 eV to 0.3 eV across this region of the nanobubble. This variation in the Dirac point energy indicates scalar potential variations across the nanobubble, as expected for an elastic deformation that does not constitute a pure shear strain.^{16,131}

7.5.2 Pseudo field B_s

The spatial dependence of the calculated and measured pseudo field B_s is shown in figure 7.12.

The calculated B_s displays a reversal of the sign of the B_s field near the edges of the simulated bubble, with singularities near the corners. However, this is of little importance, since these regions are strongly coupled to the Pt(111) surface in reality, and hence the



Figure 7.11: (a) Experimental and (b) theoretical z, B_s and Φ_s Line cuts along a nanobubble. The topography of the experimental and simulated bubbles, with the position of the line cut marked, is shown in (c) and (d), respectively.

 B_s field cannot be measured. In addition, the corner singularities are likely artefacts of the sharp corners used in the calculation. In order to compare the calculated B_s field to the experimental results, figure 7.12b shows the field only in the central region where it is between 200 and 600 Tesla.

The data for the experimental part shown in figure 7.12a were interpolated from 20 points, chosen based on the quality of the fit - points which had a B_s relative error of above 15%, or a E_{Dirac} relative error of more than 30% were eliminated.⁸ Comparing the calculated spatial dependence to the experimental one, it is clear that there exist well defined extrema in the simulated results, which are absent from the experimental one, though it does show

⁸The results did not have a strong dependence on the exact quality cut off.

a qualitatively similar pattern. This can be partially attributed to the exact equilateral symmetry present in the simulated bubble, which of course is not matched experimentally, and hence partially "washes-out" the spatial variation.



Figure 7.12: Comparison of the spatial dependence of the pseudo magnetic field B_s between theory and experiment. The B_s field shown in (a) is interpolated from the points marked by white bubbles.

7.5.3 Scalar potential Φ_s

The pseudo scalar potential calculated for the simulated strain of a bubble under a 10% maximum strain is shown in figure 7.13b. We can compare these results to the location of the Dirac point that we extract from the fit, which would depend on the local doping and hence give a measure of the local scalar potential shift. As can be seen, as opposed to the B_s case, the theoretical plot is much smoother than the experimental one. One possible explanation is that since the scalar pseudo potential depends on the trace of the strain tensor, the strong changes in the relative size of the different components which create a stronger variation in the B_s field are averaged out. On the other hand, experimentally, the strain is less well behaved, so while this fails to create hot spots for the B_s field, it does create a stronger local isotropic compression and expansion, leading to larger changes of the scalar potential and local doping.

The pseudo electric fields observed experimentally are on the order of $E \sim \frac{0.3eV}{3nm} = 10^8 V/m$. Based on Lukose *et al.*¹⁰⁷ and Peres *et al.*¹⁰⁸ we would expect the effective magnetic energy scale to be renormalized according to equation 7.2. Taking $B_s \sim 400 Tesla$, we would expect an electric field of this magnitude to renormalize the effective magnetic energy by a factor of

$$\left(1 - \frac{(10^8)^2}{400^2(10^6)^2}\right)^{3/4} \sim 0.95$$

Hence, the change in effective magnetic field would be on the order of $1 - 0.95^2 \approx 10\%$. The dependence of the correction factor on E and B_s is shown in figure 7.14. It is clear that for



Figure 7.13: Comparison of the spatial dependence of the pseudo scalar potential Φ_s (theory) and the Dirac point E_D (experiment).

any B_s field above ~ 200 Tesla the correction factor is $\eta \leq 20\%$. However, for $E \sim 10^8 V/m$, the corrections become substantial below ~ 150 Tesla.



Figure 7.14: Correction to the effective magnetic energy scale due to lateral electric fields. The left panel shows the correction factor Ω_c/ω_c vs. B_s for a fixed electric field, while the left panel shows the dependence vs. E for a fixed B_s .

7.6 Discussion

7.6.1 Possible confinement effects in nanobubbles

Apart from strain-induced Landau levels, confinement of the Dirac electrons, i.e. particle-ina-box states, might be a possible source of LDOS modulation. It is possible to analytically solve Schrödinger's equation for electrons confined in an equilaterally shaped triangular bubble.^{132,133} The solution was later used for analyzing numerical calculations of electron states in a graphene flake^{101,134} and as the basis for exactly solving a triangular graphene patch.¹³⁵ Based upon this solution, we can take $k_{n,m} = \frac{4\pi}{3L}\sqrt{n^2 + m^2 - nm}$, where n,m are non zero integers, and L is the length of the triangle's *side*. As a result, we would expect peaks at energies $E_{n,m} = \hbar v_F k_{n,m} = \hbar v_F \frac{4\pi}{3L} \sqrt{n^2 + m^2 - nm}$. Ignoring degeneracies, the energies of the first few peaks would be at $\hbar v_F \frac{4\pi}{3L} \times [\sqrt{1}, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}, \sqrt{12}, \sqrt{13}, \sqrt{16}, \sqrt{19}]$. For L = 5nm, the resulting energy levels are 0.55, 0.95, 1.10, 1.46, 1.65, 1.91, 1.98, 2.20, 2.40 eV. One should note that the n=m states are not present for triangular patches with zig-zag sides.¹⁰¹ However, since the termination of the nanobubbles we observe is not as regular as the theoretical ones, and since the shape is not as regular, we might expect to see these states. It is also worth noting that while the energies of the confined graphene flake states close to E_F follow the simple pattern derived for confinement of free electrons, the spatial patterns of these states are very different. In particular, as opposed to the typical low energy confinement states which are low-k states (i.e. near the Γ point), these are states near the K or K' points, which are at the edge of the Brillouin zone. As a result, they contain high-k components, and rather than smoothly decaying at the cavity's bounds, they decay very abruptly, having significant weight close to the edge.^{101,134} An example of such a pattern, from Akola *et al.*,¹⁰¹ is shown in figure 7.15.



Figure 7.15: Akola *et al.*¹⁰¹: DOS of the lowest energy level above E_F common to zig-zag and armchair edged traingular patches, for an armchair edged patch. Large LDOS values can be seen close to the edges of the cavity.

We feel that the experimentally observed LDOS modulations are unlikely to be due to confinement effects for the following reasons:

- 1. Due to Klein tunneling¹⁶, Dirac particles are notoriously hard to confine. At the edge of the bubble we might expect some mixture of sp^3 and sp^2 bonding, which suggests that confinement might be possible at such a boundary. However, an analysis of a suspended graphene film under compression,⁸⁵ which has similar boundaries at the film-support interface, suggests that the transmission through such boundaries would be nearly unhindered, so that confinement would be ineffective.
- 2. The spatial dependence of the peaks does not follow a reasonable pattern for confined

states. For example, one would expect to see a strong modulation of the relative peak strengths as the tip position is changed, which we do not observe.

3. There would not be an N=0 state. Hence, our observation of symmetric peaks, with a peak at the "zero" point, would preclude this option. One such spectra is shown in figure 7.16. One could acquire a zero bias peak due to edge states. However, since the edge of our bubble gradually merges with the Pt(111) substrate, this seems somewhat unlikely, as the substrate would quench the edge states. In addition, while some mixture of $sp^2 - sp^3$ states would serve for scattering and hence confinement, the existence of edge states is more sensitive to the exact nature of the edge.



Figure 7.16: Background subtracted STS showing negative, positive and *zero* indexed peaks. The thin black lines show the contribution of each peak. The index of each point is written below the grey circles marking the peak positions.

4. The collapse of the aggregated data onto a single line following the \sqrt{N} pattern, as seen in figure 7.10, strongly supports the Landau level picture.

We feel that points 3 and 4 are the strongest, and together suggest that the peaks observed are due to Landau quantization rather than confinement effects. Furthermore, both the calculated confinement states in a graphene cavity, as well as the edge states necessary for a peak at the Dirac point, have a large spatial weight near the boundaries, and are sensitive to the exact nature of the boundaries. On the contrary, the Landau levels have a relatively uniform spatial distribution and are not sensitive to the nature of the boundaries. These observations suggest that Landau levels are a more likely explanation for the LDOS modulations *observed near a bubble's center*, compared to a combination of confined and edge states.

However, the possibility of confinement derived states cannot be completely eliminated a priori, and the two - Landau quantization and confinement - might coexist in certain situations. In particular, nanobubbles where we could not find a satisfactory fit to a simple Landau level picture might represent such an occurrence.

7.6.2 Are atomic defects present in the nanobubles?

The large strains present in the nanobubbles might cause the formation of atomic scale defects. Pentagon - heptagon (5-7) defects, and specifically Stone Wales defects, are considered a common pathway for formation of sp^2 structures.¹³⁶ Above a critical strain, on the order of 5%, the formation of defects is energetically favored. However, there still exists a finite barrier for defect formation, estimated at ~ 5eV, dropping to 2eV at a strain of 20%.^{137,138} The average strain energy per atom in a strained nanobubble can be estimated using simple continuum elasticity theory, through the in-plane shear modulus of graphene, $\mu \sim 10 eV/Å^2$,¹⁶.

For a nanobubble of length L, and size L^2 , the number of atoms is $N_{atoms} \sim 2 \cdot L^2 / A_{unit cell}$. Hence the strain energy per atom is

$$E_{atom} \sim \mu \bar{u_{ij}}^2 L^2 / N_{atoms} = \mu \bar{u_{ij}}^2 \cdot \frac{A_{unitcell}}{2}$$

For $\mu = 0.1$, with the graphene unit cell area $A_{unitcell} = \vec{a}_1 \times \vec{a}_2 = a^2 \frac{3\sqrt{3}}{2} \approx 5.1 \text{Å}^2$, we get $E_{atom} \sim 0.25 \ eV$, which is much smaller than the typical energy barrier for defect formation.^{137,138}

As a result, we can conclude that defect formation due to strain is an unlikely event on average. However, since the strain is non-uniform over a nanobubble, defect formation might be favorable in highly strained regions. In addition, while defect formation during uniform contraction of a graphene patch is deemed unlikely, a defect formed *during growth* might serve as the nucleus of a bubble, which would help explain nanobubbles seen in the center of a patch, as opposed to near the edges. In practice, it is clear that some of the bubbles are somewhat irregular near their crest, which might be due to defects.⁹ An example of such a case is shown in figure 7.17. The fact that we observe lower values of B_s on these bubbles ($B_s \sim 150 Tesla$ for the bubble shown in figure 7.17), which are also exceptionally tall, supports this hypothesis, as it suggests that some of the underlying strain was released through defect formation, allowing further buckling of the nanobbuble. However, we have not observed any charging effects due to varying tip height when performing STS, which would be expected for local defect induced states.

⁹However, the strong LDOS variations present make separating true topographic and electronic effect difficult, so that it is unclear whether these irregularities represent true topography.



Figure 7.17: Image of a bubble showing irregular structure along the crest. $V_{sample} = 0.35V$, $I_{tunneling} = 50pA$, $Z_{max} = 1.1nm$.

7.6.3 Corrections due to charging effects

The confinement of electrons when forming finite sized Landau levels causes an additional charging energy to be associated with such a level. The charging energy associated with a state of size l scales as $e^2/(\kappa l)$, where κ is the dielectric constant. The size of the n^{th} Landau level is $l_N \propto l_B/\sqrt{n}$, and hence the additional charging energy is $E_{charging} = e^2\sqrt{N}/(\kappa l_B)$. The total energy of the Landau level is thus

$$E_N \approx \omega_c \sqrt{N} + \frac{e^2 \sqrt{n}}{\kappa l_B} = \omega_c \sqrt{N} \cdot \left(1 + \frac{e^2}{\kappa v_F}\right)$$

This can be interpreted as an effective pseudo field

$$B_s^{eff} \approx B_s \times (1 + \frac{e^2}{\kappa v_F})$$

and effective magnetic length

$$l_B^{eff} \approx \frac{l}{1 + \frac{e^2}{\kappa v_F}}$$

In a graphene layer suspended at height h over a metal, electrostatic effects are suppressed by the formation of image charges for $h \ll l_B$. A scalar potential of strength V_0 induces a charge density n which is determined by V_0 and the potential arising from the image charge at distance h from the metal surface. This image charge is $n_{image} \approx -n$, and the induced potential is hence $V_{image} \approx 2h \cdot 2\pi e^2 n_{image}$. Using linear response theory, $n \approx \chi(\vec{\mathbf{k}})(V_0 + V_{image})$, where $\chi(\vec{\mathbf{k}}) = |\vec{\mathbf{k}}|/(2\pi v_F)$ is the susceptibility of Dirac electrons for $|\vec{\mathbf{k}}| \approx L^{-1} \ll k_F^{139}$. Finally, we obtain:

$$V \approx \frac{V_0}{1 + \frac{2e^2h}{v_FL}}$$

For a bubble of length $L \sim 5nm$, and height $h \sim 0.5nm$, and taking $e^2/v_F \approx 1$, the reduction of the bare scalar potential due to screening is about 10%, which lies within our overall uncertainty. As we mentioned previously, the absence of tip induced shifts in the energy of the observed states argues against strongly localized states.

7.7 Conclusion

We have observed strain-induced Landau levels due to pseudo-magnetic fields in excess of 300 Tesla in graphene nanobubbles. The exceptional flexibility and strength of graphene membranes coupled with the large strain-induced fields observed suggest that strain-engineering of nanoscale energy levels^{84,140} may be a feasible means of control over the electronic structure of graphene. The experimental demonstration of these enormous pseudo-magnetic fields also provides a new basis for the study of extremely high magnetic field regimes in a condensed matter environment.

Summary

In this dissertation we investigated the bi-directional coupling between mechanical properties and gauge fields in nanometer scale systems. Two separate instances of such behavior were explored:

- 1. Photoisomerization probability variations in a mono-layer high island of TTB-Azobenzene molecules: We examined the spatial variation in opto-mechanical coupling caused by strain in the islands, as well as variations caused by different couplings to the substrate. Preliminary studies of the dynamics allowed us to extract the photoisomerization cross section and exclude some possible reaction pathways.
- 2. Strain-induced states in graphene: We observed Landau level quantization in graphene nanobubbles grown on Pt(111) due to strain-induced pseudo gauge fields.

To continue our studies of opto-mechanical coupling, a new instrument was designed and constructed. The new instrument combines efficient optical access and the use of multiple contacts to the sample, enabling for example the use of gated graphene devices to control sample electron densities and affect molecule - substrate coupling. The efficient optical access will enable us to study the energetics via analysis of spatially resolved light emitted from the STM tunnel junction, as well as efficient excitation of molecules in the tunnel junction.

In the future, we would like to combine these two branches and investigate optical transitions between different states in graphene nanobubbles, and possible coupling to optical transitions of organic molecules deposited on strained graphene substrates. A further possibility would be controlling the strain of the graphene substrate by utilizing the optomechanical coupling in the organic molecules to form a complete cycle of light \rightarrow mechanical actuation \rightarrow electronic structure \rightarrow (pseudo) gauge fields.

A

Auxiliary Details of the New Instrument

A.1 STM to cryostat coupling

The coupling between the STM and the cryostat, which is controlled by the cross-sectional area of the two copper braids used to connect them, was calculated with the following assumptions and approximations:

- The STM is modeled as a spherical black body with emissivity $\epsilon_{STM} = 0.2$ and a radius of 50mm at temperature T.
- Sources of radiation load on the STM:
 - 1. The LHe coupled shield (T = 4.2K).
 - 2. The two windows (T=300K). We use a constant factor of 0.5 to approximate the amount of IR light that the windows absorb.
- No account is taken of 4.2K light escaping through the window; it's a very small correction.
- The thermal contact between the STM and the 4.2K reservoir is composed of the signal wires (4 mil bare copper and some copper coaxial wires) and a braid.
- The springs are included as additional "wires" but don't have much effect due to their relatively low thermal conductance.
- The thermal conductance of the copper wires is taken to be $1000 \frac{W}{m \cdot K}$, somewhere in between that of electrolytic pitch copper and OFHC copper. In practice, this probably reflects the thermal resistance in the wires' terminations, as well as the purity of the copper.
- LHe Shield area is estimated based on the CAD model: $S_{\text{LH}_e \text{ shield}} \approx 0.09 \, m^2$.

• The parameters were adjusted so that the equilibrium temperature in the absence of the braid would be close to the observed value of $T \sim 12K$. The simulation currently estimates $T_{nobraid} \approx 11K$, which is reasonably close.

As a result, we can calculate the equilibrium temperature of the STM vs. the cross sectional area of the braid, which we translate into the number of wires in the braid.¹



Figure A.1: T_{STM} vs. number of filaments in braid.

The "knee" of the curve is at $N_{strans} \approx 100 - 200$, so that would be a reasonable choice for the degree of thermal coupling beyond which we would start to see diminishing returns and potentially increase our vibrational noise due to coupling to the cryostat. Hence, we decided to use two braids of ≈ 60 filaments each. We are currently achieving $T \approx 7.5K$, which is reasonably close to this estimate, considering that there is also a 1K discrepancy for the predicted vs. measured temperature in the absence of a braid. In the future we might try to increase the cross sectional area to further lower the temperature.

A.2 Coarse motion driving electronics

The driving electronics employ a two channel high voltage amplifier having $V_{max} = 350V$ (Trek PZD 350-2) driven by a computer controlled NiDAQ 6715 card (National Instruments) which generates an arbitrary waveform. The output from the high voltage amplifier is then fed directly to the chosen stacks, using a multiplexing box controlled by digital signals from the same card producing the waveforms. The rise time for the amplifier under the load of the stacks is on the order of $20\mu sec$, which is rather slow. However, this has proved sufficient for our needs. Walking is initiated via a hardware trigger from the Nanonis electronics to

¹The braid is made of 2mil gold plated COA 101 copper wire - California Fine Wire Company.

the DAC card. The overall step size is controlled via the amplitude of the driving waveform and is linear to ~ 1/4 of the maximum voltage. The minimal signal amplitude which enables walking at low temperature is ~ 20% for the Z axis. "Hunt & peck" approach is typically performed with amplitudes of $40\% V_{max}$ at $T \approx 7.5K$. The minimal drive amplitude needed for the XY walker at low temperature has not been determined, but based on the bench top adjustment of the walker, it is expected to be similar to the Z axis value.



All stacks on the Z channel share the same polarity, so that the assignment of a stack to one of the two groups is not critical. However, due to the homogeneous XY stack construction, the X and Y channels require different polarity choices for the individual stacks, as shown in section 6.5.2. In particular, while the X channel uses a 3:3 set-up (i.e two groups of 3 stacks with opposite polarity), the Y channel uses a 2:4 set-up. The differentiation between the groups is accomplished by creating an adapter from each pair of outputs of the multiplexing box to one set of six stacks (i.e one axis) which selects the stack assignment.

Walker multiplexing box

The walker multiplexer box uses a small amount of discrete digital circuitry to demultiplex two input lines and connect two HV lines, fed by the PZD-350-2 high voltage amplifier, to the stacks. The inputs to the box are two TTL control lines, which encode the channel to be energized.² These lines are demultiplexed using 1/2 of a 74LS139 dual $1 \rightarrow 4$ demultiplexer. This approach ensures that it is impossible to energize two axes simultaneously. The TTL signal is then inverted and amplified using bipolar transistor switches. The switching is performed by miniature 2-pole dual throw 12V relays, each of which serves one axis. When not energized, the two channels of an axis are tied to a banana plug on the box, which should be directly tied to chamber ground.

 $^{^2 {\}rm The}$ association of an axis with a control word is hard coded in the MATLAB code.



Figure A.2: Schematic of the walker multiplexing box.



A.3 Miniature coax wire termination

The wires used between the room temperature feed-throughs at the top of the cryostat and anchoring blocks thermally sunk to the 4K cold plate are 38 ga. (inner conductor) coaxial wires, made from 316 stainless steel (Cooner wire inc. CW8022). It is known that they cannot be reliably soldered without using acidic flux that is impossible to clean from the braided wires, and we wished to avoid conductive epoxy, due to thermal stress. As a result, we chose to make crimping connections between the wires and the connectors at both ends.

Due to the extremely small diameter of the wire ($\phi \approx 3.5mil$) and the mismatch with the inner diameter of our chosen connector ($\phi = 32mil$, CeramTec 11288-02-X), an intermediate is needed. We use a 22 ga. 316SS tube ($\phi_{in} = 0.016$ " or 0.021", $\phi_{out} = 0.028$ "), for the

4K terminal, and a combination of a 22ga. tube and a 16ga. 304SS tube for the larger feedthrough pins (and connectors) on the RT terminal.

316SS tube annealing

The 316SS tubes must be annealed, since they cannot be crimped in the supplied semi-hard state. The tubes are annealed by passing direct current through them while under high vacuum in the test chamber.³

Cut $\sim 5cm$ long pieces and mount in this setup:



The following recipe is based on the one found in the "Heat Treater's Guide: Practices and Procedures for Irons and Steels"¹⁴¹

- 1. Anneal at $1040 1120^{\circ}$ C, as measured by a pyrometer. Typical power requirements are $\sim 12.5W$ at $\sim 5A$. Use enough time to get uniform temperature (a few minutes), then quench by simply turning off the power supply (radiative heat loss is efficient enough for these tubes to let them cool down in a few seconds).
- 2. Stress relieve at $230C 400^{\circ}$ C for a few hours. The temperature is too low to be measured directly with the IR pyrometer, so the power required for T=600K was estimated based on the Stefan Boltzmann law, suggesting $\approx 0.6W$.

Following annealing, pieces of $\sim 5mm$ length are cut using a rotary tool and a diamond coated grinding wheel. The cut tubes must be reopened since they are soft; use a piece of Tungsten wire.

LT terminating

1. Strip 25mm off the outer jacket with a mechanical stripper.

³Most likely the world's least efficient heat treatment set-up.



2. Spread the shield with a pair of tweezers and fold it back over the still jacketed part.

3. Put a $\sim 3mm$ piece of thin wall 15 ga. 304SS tube over the folded back jacket and *lightly* crimp it.



- 4. Strip 5mm of the insulation with a scalpel.
- 5. Slip on an annealed & cut piece of 22ga. tube.
- 6. Slip on a CeramTec 11288-02-X crimp connector.



- 7. Crimp the wire, tube and connector together with a pair of serrated pliers. Note:
 - The crimp connector and the insulated part should overlap to improve mechanical rigidity. The 22ga. tube cannot go over the insulated part.
 - Gently crimp the portion of the connector overlapping the insulation.
 - Crimp the exposed section *hard*.

RT terminating

- 1. Strip the outer jacket and shield for 10mm. The stripped parts can be cut off no need to fold them back, as there is no ground connection on the RT side.
- 2. Strip 5mm of the insulation with a scalpel.
- 3. Slip on an annealed & cut piece of 22ga. tube and crimp it hard.
- 4. Slip on a slightly pre crimped (left picture) 5mm long piece of 304SS 16ga. tube, and then crimp it onto the wire + small tube assembly.



- 5. Test the wire by measuring the resistance between a 32mil copper wire inserted in the LT side connector and an alligator clip on the RT side. Resistance should be $145 \pm 0.2\Omega$ for a $\approx 1.5m$ long wire. Re-crimp until the fluctuations are below 0.2Ω when wiggling the wire. The best wires are stable to within 0.1Ω when wiggling.
- 6. Slip on the larger (62mil) RT side connector (Ceramtec 2044-02-A) and crimp it using a standard 4-pronged crimper set to 0.057.



7. Re-test resistance.

A.4 Shear stack building

Overall, the stacks are assembled in a rather conventional manner, described below. However, the orientation of successive pieces for the XY stacks is critical. All stacks must be built using the following sequence:



Figure A.3: Orientation of shear piezos and contact tabs forming an XY stack. The tabs which are not marked as belonging to either X_{HV} or Y_{HV} are ground connections.

The Z stacks currently used were built using an older method, where 3 mil wires were used to make the interconnections between layers. However, that method is somewhat more sensitive, so in the event the Z stacks need to be replaced, the Z stacks should be built similar to the X axis of an XY stack (i.e. with the tabs points along the axis of polarization).

XY stack building details & steps:

• The stacks are built from four layers per axis of shear polarized EBL #4 PZT piezo-cermaic material with Ni electrodes.⁴

⁴In the past I have tested individual shear piezos using the interferometer. However, it is somewhat

- The size of an individual piece is $0.3" \times 0.3" \times 0.02"$.
- The pieces come from EBL Inc. with a black mark showing the polarization. This mark is removed using Acetone, and two small corners are filed off using a rotary tool and a diamond coated grinding wheel *in the fume hood*.



- The connections to the electrodes are made by incorporating 0.001" thick Molybdenum foil between the layers and allowing a piece about 1mm wide and 5mm long to stick out.
- Gluing:
 - H20E glue, cured in an Argon atmosphere at $\approx 120^{\circ}{\rm C}$ for a few hours, is used to make all connections.
 - A simple clamping jig is used to press the layers during curing.



 A small amount of glue is placed on each layer and the stack is built up in the opened clamping jig.

tedious, and I suspect that instances where pieces failed to show motion were due to poor contacts between the piezo electrodes and the testing apparatus.



- A small Aluminum piece ("cover plate") is placed on top of the layers to help even the clamping pressure. Note that these Aluminum pieces are not exactly symmetric, so they have an assigned orientation. The desired orientation can be found by rotating the piece until the set screw hits the prior indentation (the inner corner is also marked with a few scratches). The jig is then closed and the assembled stack clamped.
- The amount of pressure exerted by the clamping screw must be monitored carefully since the stacks are somewhat brittle.⁵
- The position of the screw in the current jigs is not directly above the center of the stack, so small shims made of Molybdenum foil are used to adjust the position.
- Care must be taken so that when pressing the stack it is not clamped unevenly
 in such a case the top and bottom plates will be noticeably non parallel.



- After the glue is cured, the stacks should be *carefully* filed with a diamond file, *in the fume hood*, to remove any residual glue from the sides.
- 0.003" ϕ Formvar insulated wires are glued to the Molybdenum foils using H20E glue.

⁵If you hear a crack while clamping a stack in the jig, it's too late.



• A 0.2" \times 0.2" \times 0.02" Alumina plate is glued on the top plate, using a simple jig with a spring.



The room temperature capacitance of each axis of a stack should be $\approx 5nF$, with the variations mostly due to filing the stack and layer misalignment.

Finished stacks are tested using a bench mounted Michelson - Morley interferometer. Expected movement is 3.5 - 4 fringes, using a red laser diode ($\lambda \approx 670nm$), over the bias range of $-400V \rightarrow +400V$. A low current source should be used - the ideal choice is a Keithley 2410 source meter.



As a final note, I miscalculated the actual thickness of the glue used when building the stacks, which forced me to "lift" the stacks when assembling the XY walker. This was achieved by placing a $0.25^{\circ} \times 0.25^{\circ} \times 0.016^{\circ}$ piece of Ti-6Al4V alloy between each XY stack and the body of the STM.

A.5 Tip wire, scan tube & prism assembly

The design of the STM dictates that the tip wire, and the wires connected to the scan tube, are not accessible once the assembly is complete. As a result, should one of these wires fail, the only solution is to utilize the sacrificial intermediate Macor piece and destroy the scan tube, Macor cup, and tip holder spring assembly, in order to salvage the prism.



Figure A.4: Scan tube and tip wire assembly.

All the connections are made with Epotek glues - either H20E or H77, depending on whether an electrically conductive or insulating joint is desired. The standard curing is under an Argon atmosphere at ~ 120°C. The steps for building the scan tube / tip assembly are

1. Glue scan tube to tube holder (aka "sacrificial connecting piece") with H77 - no special jig is needed, they fit well together. Use an 0-80 screw and nut to *lightly* clamp them together - preferably a material combination that would not weld during the curing cycle.

2. Glue $\pm x$, $\pm y$, z wires to scan tube - leave about 10cm long. Use 0.003" ϕ formvar coated copper. The tube/holder assembly is attached to an Al plate using an 0-80 screw, while the wires are stabilized by clamping underneath 2-56 screws on the same plate. The wires will be trimmed later, but the portion clamped might be used, so it's best to try and avoid breaking the insulation by over tightening.



3. Cut wires to length + ~ 20mm, strip last ~ 5mm, using a miniature butane torch, kim-wipes with methanol and potentially some fine "wet" sand paper and methanol. Thread the wires through the prism, using pieces of hypodermic tubing (~ 22 ga.) to guide the wires - it's impossible to do otherwise. Put some H77 on the Macor block before it goes into the sapphire cavity, as shown in pane (1). Carefully "Glide" the sapphire prism along the tubes, until the Macor connecting piece is seated against the sapphire. Carefully⁶ pull the tubes out. Hold everything together with a long 0-80 threaded rod and nuts.⁷



4. Glue the scan tube wires to the Molybdenum anchoring rods $(0.020^{\circ} \phi)$ with H20E.

 $^{^{6}}$ Yes, I would emphasize it more if I could - this step is sensitive, and it would be easy to break the bonding between the wires and the scan tube.

⁷I used a moly threaded rod, since I had one and no SS one, but I doubt it's important - though it should be a combination that is not likely to weld under curing temperatures.

The picture shows the wires prior to gluing to the anchoring rods. The rods should be glued to the prism with H77 - the two steps can be done in one curing cycle.



Set aside the prism and scan tube for a bit, and glue the tip wire to the tip holder Macor cup:

1. Strip the end of the tip coaxial wire (gold plated copper, Cooner Wire Inc. CZ-1223-1f), spread the shielding a bit, and trim the inner wire to a length matching the Macor cup / copper block. A special jig that uses a Teflon piece to press the shield against the Macor cup is used. Once the shield is glued to the Macor cup, it will not be possible to trim the inner wire again, so the length of the inner wire must allow it to be easily glued to the copper block in the next step. After the glue is cured and the wire and cup are removed from the jig, trim the connection as much as possible, and add some H20E to created a semi-uniform shield, since the braid is likely somewhat disordered. If the joint between the shield and the Macor cup is too thick, it will not fit later in the scan tube - there is only ~ 0.01 " of space between the outer surface of the Macor cup and the inner surface of the scan tube.



2. Glue the inner conductor: Tilt the Macor cup to get the wire to move off center. Slide the copper block in - the corner should be trimmed a bit with a knife to get it to slide

all the way in. First do a dry run, then smear some H20E on the inner part of the Macor cup and on the copper block and slide it in. You will have to play with the inner conductor till it sits against the copper and then dab some H20E on it. Note that it's hard to see into the Macor cup assembly. Check conductivity afterwards - (1) The connections between the coax's inner conductor and the copper block, and (2) Any shorts (up to 500V) between the inner and outer parts of the coaxial wire.



3. Bend tip clamping spring to shape and slide it into place. No glue is needed, but ensure that it is jammed fairly hard in - i.e. you should not be able to (easily) remove it afterwards with tweezers. Sadly, I cannot find a picture showing the shape of the bent tip spring before it was inserted into the Macor cup, but the shape can be made out from the view below. Note that if a new spring must be bent, there are a few spares of the precursors (wire-cut from 0.004" thick BeCu). After bending one into shape, it needs to be precipitation hardened at 320°C for 2 hours (in air).



4. Coat the tip holder cup assembly with gold in the hummer (Conductive epoxy - e.g. H20E - could be used instead, but the result is not as neat, and space is tight). Use $\sim 10 - 11mA$ at 60-80 mTorr Argon for 4.5 hours at 50% duty cycle. Shield the wire with some Aluminum foil. Use a small aluminum foil piece to shield the bottom $\sim 1.5mm$ of the Macor cup as well, so as not to short the scan tube later. If the gold
plating ends up too close to the end of the cup, it can be easily scraped off with a scalpel.⁸



Now we can connect the tip wire / cup assembly to the prism / scan tube assembly:

1. Glue the tip wire assembly to the prism / scan tube assembly with H77. A jig is used to clamp the assembly in place during curing. Use a minimal amount of H77 on the lip of the Macor cup.⁹



2. Anchor coax to prism with a bit of H77.

⁸The jig pictured was milled to allow gold plating close to the end of the tube, but it allows gold plating to reach too near the joint, so that some of the gold was scraped off.

⁹Note that the H77 epoxy is marginally conductive when un-cured, so that I observed a $\sim 100M\Omega$ short at 250V when the epoxy bridged the scan tube electrodes in an initial attempt. However, it is better to limit the amount of glue and not depend on the glue's level of insulation.



3. Glue 0.003" ϕ Formvar insulated copper wires to the anchoring block (can be done concurrently with previous step).



4. Assemble Z walker and glue wires to anchor block screwed into Z walker.



A.6 Effects of lens misalignment

The effects of having the source (i.e the tip-sample tunneling junction) misaligned with respect to the focal point of the light collection lens can be estimated using a series of

stops. Using the CAD model as the source for the dimensions of these stops, the relative collection efficiency calculated is seen in figure A.5, for a plano convex lens with f = 10mm and $\phi = 5mm$ (CVI Melles Griot PXS-5.0-7.7-S). The overall conclusion is that the lens should be under-focused by $\leq 0.5mm^{10}$, since in this case while we lose $\leq 10\%$, a lateral misalignment of $\sim 0.5mm$ is acceptable.



Figure A.5: Relative light collection efficiency for a source misplaced by x axially and y laterally relative to the focal point.

A.7 Chamber drawings

Below are the CAD drawings used by Nor-Cal to machine the chambers, including a list of ports. The only exceptions are the two light access ports and the rear view ports, since these are machined onto separate sub-assemblies. The details for these are

- 1. Light access ports : elevation angle is 30°, with a focal point 5mm below the sample plane (due to an error). The distance between the face of the viewport mounted onto the flange and the focal point is 314mm.
- 2. Rear view port : level, in the sample's plane.

In addition, the focal point for ports 6 and 7 on the STM chamber is 0.3" higher than indicated by the drawings due to an error by Nor-Cal.

¹⁰i.e. so that the source is too far.

Critical ?	×	×	z	z	z	z	z	z	z	Y - angle only	Y (most critical)	z	: >-	z	7	z	~	Z	V - andla only	Y - angle only
comments		integrated into bottom support plate (or support welded to it - whichever is easier)									ref port									
rotatable?	×	z	Z	z	>	z	z	>	z	z	~	>	. >	7	×	×	>	>	- >	- >-
azimuthal angle (degrees)	N/A	N/A	45	06	135	120	240	225	270	345	0	50	6	135	180	225	270	340	2 0	352
slevation angle degrees)	(06)	06	(30)	(45)	0	(45)	(45)	0	(45)	(28)	0	20	0	0	0	0	0	00	26	26
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focal point h (inches) h	N/A	A/N	0	9.975 0	2	7.2 0	7.2 0	2	9.975 0	8.5 0	11.5	5.52	7.87	2	8.3	2	7.87	5 53	10,00	12 0
focal point	N/A	N/A	ш	0	axis (3.5" above D)	ш	ш	axis (3.5" above D)	0	A	A	Ľ) I	۵	_	0	Т	Ċ	0 4	×
tube OD (inches)	N/A	NN	4" (std)	conical 60 deg	1.5 (Std)	conical 30 deg	conical 30 deg	1.5 (Std)	conical 60 deg	conical	4" (std)	conical 60	6" (std)	1.5 (Std)	6" (std)	1.5 (Std)	6" (std)	conical 60	1 5 (Std)	1.5 (Std)
size (CF inches)	12"	ō	6"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	4.5"	6"	2 75"		2.75"	8"	2.75"	.8	3 7E"	2.1.3 9.75"	2.75"
port name / use	cryostat	sa	aux window	side door window - left	aux	rear clamping viewport - left	rear clamping viewport - right	aux	side door window - right	window - sample transfer	connection to prep chamber	main door wobble stick - left	side light port - left	aux	rear port	aux	side light port - right	main door wobble	evenorator - left	evaporator - right
ort number	~	N	n	4	5	9	7	Ø	J	10	1	12	10	14	15	16	17	ä	0	20















ritical?			-	 - angle only 	-		-	 - angle only 	-	-	-	(most critical)	-		7			 - angle only 	-	-	-	-	-	-	-	-	7	-	-	7
comments	parallel to reference plane, leak check slot orientation perpendicular to azimuthal plane	parallel to reference plane, leak check slot orientation perpendicular to azimuthal plane		7	2	~		<i>-</i>	2	2		reference port		<i>-</i>	2	<i>_</i>	~	~		2	2	2	2			2	2			
rotatable?	~	~	N	0 Y	N	۰ ۲	Z	5 Y	5 Y	0 Y	7 Y	0 ×	5 Y	٨.0	2 N	۰ ۲	5 Y	Z O	5 Y	7 Y	3 Y	7 Y	3 Y	7 Y	3 Y	N O	٨ 0	٨ 0.	7 Y	3 Y
azimuthal angle (degrees)	A/N	A/N	e	6	13	18	26	31	22	31	33		4	6	13	18	22	27	31	2	9	11	15	20	33		6	18	23	30
elevation angle degrees)	(06)	6	0	0	0	0	0	0	15	25	25	0	0	0	0	0	0	0	0	30	0	0	30	30	30	0	0	0	0	0
neight (relative to eference plane) (12.75	(10.50)	7.50	7.50	7.50	7.50	7.50	7.50	terived	Jerived	lerived	0.00	0.00	0.00	0.00	0.00	0.00	(1.09)	0.00	terived	(3.50)	(3.50)	terived	Jerived	terived	(5.50)	(5.50)	(5.50)	(5.50)	(5.50)
distance to focal point (inches) r	N/A	N/A	80	80	œ	80	80	80	06	6	5	11.5	80	80	80	80	10	80	80	06	80	80	56	0	06	80	œ	œ	œ	80
focal point	NA	NA	A	A	A	A	A	A	A	A	A	-	B	в	۵	B	8	1.09" below B, on axis	в	в	o	U	B	B	в	٥	٥	٥	٥	٥
tube OD (inches)	4" (std)	6" (std)	6" (std)	4" (std)	2.5" (std)	6" (std)	4" (std)	1.75"	1.75"	1.75"	1.75"	4" (std)	1.75"	4" (std)	2.5" (std)	2.5" (std)	1.75"	6" (std)	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"	1.75"
iize (CF inches)		I.			1.5"	3"		2.75"	2.75"	2.75"	2.75"	10	2.75"		1.5"	1.5"	2.75"		2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"	2.75"
port name / use	top flange - xyz manipulator	bottom flange - to pump	window	RHEED e-gun	window 4	REED / AES	RHEED screen (ion gun	evaporator 2	evaporator 2	evaporator 2	connection to STM chamber	evaporator 2	AES / window 6	window (sample transfer) 4	main transfer rod	Loadlock 2	sample storage 8	H cracker	evaporator 2	IG / vent valve 2	leak valve	IG / aux	aux	aux					
port number	-	5	e	4	2	9	7	80	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30





Graphene Auxiliary Calculations

B.1 Simple bubble strain

A simple estimate for the strain in a bubble of height h and lateral extension (i.e diameter) L can be made, following the geometry in figure B.1. Using the simple geometric relationship $R = \frac{h}{2} + \frac{L^2}{8h}$ and the approximation $\theta/2 = \sin^{-1}\frac{L}{2} \approx \frac{4h}{L}$ we get for the length difference between the uncurved and the curved section

$$\delta = x - L = 2R(\theta/2) - L = 2R(\theta/2 - \sin^{-1}\theta/2) \approx 2R\frac{1}{6}\frac{\theta^3}{2} \approx (h + \frac{L^2}{4h})\frac{64}{6}\frac{h^3}{L} \approx \frac{8}{3}\frac{h^2}{L}$$

As a result, a good estimate for the magnitude of the strain is $\delta/L \sim 3\frac{h^2}{L^2}$



Figure B.1: Dimensions of a graphene membrane deformed along a constant curvature.

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