Title
Vibrational Inelastic Electron Tunneling Spectroscopy of Surface Adsorbed Single Molecules at Sub-Kelvin Temperature

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Vibrational Inelastic Electron Tunneling Spectroscopy of Surface Adsorbed Single Molecules at Sub-Kelvin Temperature

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Physics

by

Chi-Lun Jiang

Dissertation Committee:
Professor Wilson Ho, Chair
Professor Ruqian Wu
Professor Ilya N. Krivorotov

2015
DEDICATION

To

my wife, Chia-Yu, who is truly my angel,

family and friends,

in recognition of their worth,

and

whoever left a trace in my life
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CURRICULUM VITAE

Chi-Lun Jiang

2003  B.S. in Physics
      National Chung Hsing University, Taichung, Taiwan

2004-07  Research Assistant, Surface and Nanoscience Lab
         Institute of Physics, Academia Sinica, Taipei, Taiwan

2007-14  Teaching Assistant, Physics Department,
         University of California, Irvine

2007-15  Research Assistant, Physics Department,
         University of California, Irvine

2015  M.S. in Physics,
      University of California, Irvine

2015  Ph.D. in Physics,
      University of California, Irvine

FIELD OF STUDY

Surface science, Scanning Tunneling Microscopy and Spectroscopy, Inelastic Tunneling Probe.

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ABSTRACT OF THE THESIS

Vibrational Inelastic Electron Tunneling Spectroscopy of Surface Adsorbed Single Molecules at Sub-Kelvin Temperature

By

Chi-Lun Jiang

Doctor of Philosophy in Physics

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Professor Wilson Ho, Chair

With a 600mk homebuilt UHV STM system, we studied molecular vibration at the solid surface with inelastic electron tunneling spectroscopy (IETS) of Acetylene single molecules adsorbed on Cu(100) surface and revealed five new vibrational modes that were previously inaccessible to STM-IETS at 8K temperature. The identification of vibrational IETS features with normalized conductance change ($\Delta\sigma/\sigma$) as low as 0.24% was demonstrated. Facilitated by the high energy resolution, we also revealed the anisotropic vibrational energy of carbon–monoxide (CO) molecule induced by substrate surface symmetry. The discrepancy in vibrational energy as small as 0.8meV can be resolved by STM-IETS. Our results also showed that the change in vibrational behavior of CO can be used to understand its environment. CO can be vertically transferred from substrate surface to STM tip and creates a scanning probe which has the characteristic vibrational signal of CO contained in the inelastic component of the tunneling current; i.e. the inelastic tunneling probe (itProbe). The itProbe senses the local potential energy landscape by imaging the spatial variations of CO hindered-translational mode and resolves the skeletal structure and bonding details of a surface adsorbed Cobalt-Phthalocyanine molecule (CoPc). The image
contrast of itProbe also reveals the interaction between one CoPc and the substrate surface as well as the interaction paths between neighboring CoPcs.
Chapter 1

Introduction

1.1 Background and Motivation

The invention of Scanning Tunneling Microscope (STM)[1] gives scientific community a powerful tool to understand the fundamental facts of surface phenomena with atomic scale resolution in real space. Tremendous efforts have been made to combine the atomic scale resolution of STM with additional analytical capabilities. For example, the local electronic properties of a sample can be extracted from the tunneling current signal.[2] Also contained in the tunneling current, the excitation process between the tunneling electron and the sample can be revealed by looking into the inelastic component of the tunneling current and has been proven to be useful at detecting vibrational,[3] rotational[4] and spin excitation[5][6] related to surface adsorbed molecules atoms since the first demonstration of STM inelastic tunneling spectroscopy (STM-IETS) in 1998.[7]

In this dissertation, we will focus on the discussion of the application of vibrational STM-IETS on surface adsorbed single molecule with 600mK temperature.

In 1968, Jaklevic and Lamb[8] first showed that the vibrational behavior of molecule can be observed by trapping molecules in the oxide layer between two metal electrodes. The energy of the tunneling electron can be adjusted by voltage bias across metal-oxide-metal device. With sufficient energy, the tunneling electrons can excite the molecules by losing energy and the
excitation opens up a new constant conduction channel. As a result, the electrical conductance of 
this metal-oxide-metal tunneling device will have nonlinear dependency with bias voltage, and 
bias thresholds for each conductance step corresponds to the vibrational mode energy of the 
embedded molecule in the oxide layer.

To detect vibrational signal in metal-oxide-metal tunneling device, \(10^9\) molecules are required. 
Almost right after the invention of STM in the early 80’s, people started to pursuit vibrational 
IETS with STM setup. However, it is not until 1998 that Ho group finally overcame the technical 
difficulties of maintaining a stable STM junction with an 8K STM system[9] and pushed 
vibrational IETS to single molecule level.[7]

In STM-IETS, a standard lock-in setup can be adopted from a metal-oxide-metal tunneling 
device. The electrical conductance can be monitored via the \(dI/dV\) signal extracted from the first 
harmonic output of the lock-in amplifier. The excitation of molecular vibration will open a 
constant conductance channel for electrons and result in a step-like feature in the first derivative 
of \(I-V\) curve. The onset bias voltage of the step is the vibrational energy. A 1% or smaller 
increase in conductance is typical for vibrational excitation. Therefore, to improve the 
sensitivity, \(d^2I/d^2V\) signal is used to make the feature clearer. A peak feature at the vibrational 
ergy can be found at the positive bias, and a dip feature can be found at the negative bias.

The width \(W\) of \(d^2I/d^2V\) feature is given by 
\[W^2 = W_I^2 + W_T^2 + W_M^2,\] 
[10] where \(W_I\) is intrinsic width, \(W_T\) is thermal broadening caused by finite temperature and \(W_M\) is modulation broadening 
classed by bias modulation for lock-in measurement. The typical intrinsic width for vibrational
mode is \sim 1\text{mV}. The thermal broadening \( W_T \) is estimated as 5.4 \( k_B T \) and the broadening caused by bias modulation is estimated \( W_M \) as 1.7 \( V_{\text{osc}} \) where \( V_{\text{osc}} \) is the RMS amplitude used by lock-in detection.

The physical meaning of the area under the \( dI^2/d^2V \) peaks is the change in electrical conductance \( \Delta \sigma \). For vibrational excitation, the normalized conduction change \( \Delta \sigma / \sigma \) represents the cross-section of electron-vibration coupling of certain vibrational mode in a given molecule/substrate system.

The normalized conduction change \( \Delta \sigma / \sigma \) can be described by a perturbative approach of electron- vibration coupling many-body Bardeen formulation for tunneling[11]-[13]. The leading order correction is consisted with two parts. One part is inelastic contribution, which describes how much energy the tunneling electrons lose to excite the adsorbed molecule. The other contribution is elastic, which describes the exchange of energy between a tunneling electron and an electron in the bulk. The elastic contribution will decrease the electrical conductance and the inelastic contribution will increase the conductance. The overall conductance change depends on the competition between these two parts and is closely related to specific vibrational mode and the bonding detail between the molecule and the substrate. Whether a mode on a molecule/substrate system is detectible or not is still an active research topic. Therefore, experimental data with high sensitivity would play a crucial role.
To maximize the sharpness of the vibrational feature, we should minimize the total width. The most direct way to reduce the total width is to lower the temperature. Nevertheless, lower temperature improves STM junction stabilities, which facilitate the tradeoff of using smaller modulation voltage with larger signal averaging. With a 600mk system, we have that the identification of vibrational mode as weak as 0.24% in normalized conductance change is possible compared to 1.5% at 8K.[14] as shown in chapter 3. Lower temperature also increases the energy resolution and enables us to study the environmental effect on molecular vibration with IETS spectroscopy. In chapter 4, we demonstrate that the molecular vibration can be modified by the surface symmetry[15][16] and the presence of STM tip. The CO vibration energy anisotropy due to 2×1 reconstructed Au(110) surface as close as 0.8meV can be resolved. In chapter 5, by transferring a single CO from the surface to the STM tip,[17] a scanning probe with vibrational feature of CO can be created, and we can use this vibrational feature to sense the environment in the tunneling junction. By scanning over a larger CoPc molecule with CO-tip and recording the Hindered-translational mode intensity of tip CO at the same time, we can resolve the skeleton structure of the CoPc molecule as well as the interaction path between two CoPcs and the interaction path between a CoPc and the substrate surface.[18]
Fig.1.1 I-V and Its Bias Derivative Curves of IETS

The energy of tunneling electrons can be adjusted by voltage bias across the tunneling junction. When the energy is higher than a certain vibrational modes of the molecule with vibrational frequency $\omega$, electrons can lose their energy to excite such vibrational modes. As a result, a constant conduction channel for electrons will be opened. The slope in I-V curve will change at the threshold voltage $\hbar \omega / e$ and $-\hbar \omega / e$. The change in conductance is usually very small. Therefore, 2$^\text{nd}$-derivative $d^2I/dV^2$ is helpful for identifying the weak feature in vibrational IETS.
1.2 Bibliography


Chapter 2
An Overview of the Instrument

2.1 mk-STM System Overview

Briefly, mK-STM is a very large UHV, helium and helium-3 cooled scanning tunneling microscope with a fairly complex design. The added complexity allows for measurements at extremely low temperatures (~ 600 mK, hence called mK-STM) in UHV while in the presence of a 9 T magnetic field in the normal direction of the sample. The system is mechanically and thermally stable enough to perform single molecule spectroscopy and single atom spin-excitation measurements.

The system is made of 4 interconnected UHV chambers: main chamber, preparation chamber, sample/tip loadlock chamber and main evaporator loadlock chamber. Each chamber can be isolated and vent individually. The sample/tip loadlock chamber allows quick turnaround time for tip/sample exchange into preparation chamber. The evaporator loadlock chamber is connected to the main chamber, which allows in situ dosing onto the sample in the STM scanner. Moreover, the evaporator can be swapped quickly without venting the main chamber, which minimizes the needs of completely warming up the cryostat.

The STM scanner is mostly compatible to other Ho group STM with similar Besocke type scanner. The major differences in electronics are 20 bits digital to analog convertor for bias and the control software modified accordingly to accommodate this feature.
2.2 An Update to mK-STM System

The mK-STM system was first designed and built by Dr. Xi Chen back to 2002, and the major construction of cryostat and vacuum system was established since then. The detail of the 1\textsuperscript{st} STM can be found in Dr. Xu Chen’s PhD. thesis published in 2004.[1] In 2007, Dr. Ungdon Ham gave the STM scanner a major re-design. The detail design of the 2\textsuperscript{nd} version scanner can be found in Dr. Ham’s PhD. thesis published in 2007.[2] The major difference between those two versions is the size of STM scanner. The 2\textsuperscript{nd} version scanner is smaller and the sample holder is compatible to other STM systems in Ho group. The additional clearance provided by the reduced diameter of the scanner assembly solves the major issue of the 1\textsuperscript{st} version scanner which easily got stuck due to the long mechanical path of thermal expansion and contraction. However, smaller size means lighter in mass. The lighter scanner increased the cut-off frequency of the spring-mass system, and eventually reduced the performance of vibrational isolation system. In 2009, Dr. Ham designed a 3\textsuperscript{rd} version of STM scanner that was essentially the same as the 2\textsuperscript{nd} version, but added with 2 major features of vibrational isolation. First, a massive copper damper was added to the bottom of the scanner. The copper damper was machined with oxygen free cooper. The additional mass was added in hopes of decreasing the cut-off frequency of the mass-spring system. We also vacuum annealed the damper to 400\degree C overnight to increase electrical conductivity in order to achieve better eddy current damping performance. The second feature is a permanent magnet array consisted of 128 symmetrically arranged Neodymium magnets to provide eddy current damping independent from the superconducting magnet.
2.2.1. Wax Anchor on Top of the Insert to Enforce Rigidity of the System

In mk-system, the STM scanner is attached directly on the He3-pot. The core of the sorption refrigerator including a 10L He4 Dewar is movable inside the center bore of the large He-4-I/II Dewar. This motion is done by a linear manipulator at the top of the system. To increase the rigidity of the system, 4 sets of wax anchors were installed to fix the insert. When we need to move the insert up and down for sample and tip transfer, the heater is turned on to melt the wax. This action disables the anchors and makes the insert free to move. When the insert is moved to the top position (where the STM tunneling junction is at the center of the superconducting magnet); the heater is turned off and the wax is set to solidify and fix the insert.

2.2.2. Additional Pneumatic Vibration Isolators, 2 Isolators for Each Corner, 8 In Total

The structure of the mK-system is constructed on an optical table and suspended by pneumatic vibration isolators at four corners. The original design was one isolator per corner. Due to the heavy weight of the whole system, the isolators had a hard time working properly. To make the things even worse, the imbalance of weight distribution among corners made the floating and de-flooding process very dangerous. To overcome this issue, new brackets were installed to allow us double the number of isolators: two at each corner, and the gas supply were connected in parallel at each group. Clamping mechanism was also installed at each corner of the optical table to minimize the need of de-flooding the system.
2.2.3. External Eddy Current Damper

Two sets of eddy current dampers were added to the sides of optical table to enhance the performance of vibrational isolation. Each damper set consists of 4 lifting magnets fixed on the ground, and a copper plate is secured firmly at the sides of the optical table, facing against the magnets.

The Mo base plate in 3rd version scanner has been changed slightly to accommodate additional bias connections for split-ramp sample holder. Each tungsten ball is connected separately and an update version of connection pin assignment map can be found in Fig. 2.4, Fig. 2.5 and Fig. 2.6.

2.2.4 Sample Heater Modification

Heating is one of the most important techniques for atomically flat crystal surface preparation. In order to reduce excessive outgassing from the sample holder, we add a sapphire washer to break the heat conduction path from crystal to the holder at high temperature. It would be ideal to focus the electron beam toward the center crystal to further reduce holder heating. Focus electron beam also has higher heating efficiency, allowing us to achieve same temperature with less filament current, which results in cooler filament and less outgassing.

To focus the heating electrons toward the center, the plate-style repeller is replaced by a cup-style repeller. In addition, the ion sputtering setup in mK-system needs to rotate the heater by 35 degree. This rotation will cause the sample to slide to one side of the heater. As a result, the
smaller electron beam could miss the crystal at the center of the holder. In order to solve this
problem, a 0-80 set screw made with Ta was added as an adjustable support to align the crystal
to the electron beam. A photo of the modified sample heater can found in Fig. 2.7 and the
schematics that illustrate the change of the repeller can be found in Fig 2.8.
A massive copper damper was added to the bottom of the scanner. The copper damper was machined with oxygen-free cooper. The additional mass was added in order to decrease the cut-off frequency of the mass-spring system. The damper was vacuum annealed to 400°C overnight to increase electrical conductivity for better eddy current damping performance. The second feature is a permanent magnet array made of 128 symmetrically arranged Neodymium magnets to provide eddy current damping independent from the superconducting magnet.
Identical to 2\textsuperscript{nd} version scanner

Copper damper

Permanent magnet array
Fig. 2.2 Wax Anchor Assembly.

Shown in picture, one of the wax anchors on top of the insert enforces the rigidity of the system. The assembly is made of a rod heater and a cup heater. The rod heater is fixed on the main Dewar, while the cup heater is attached to the insert, and these 2 heaters will move together with the STM scanner up and down by the linear translator. The space between the rod and cup is filled with wax. Melting the wax with the heater on can make the insert free to move.
Fig. 2.3 External Eddy Current Damper and Table Clamping Mechanism.

Shown in the top picture, the table side external eddy current damper, the optical table is floated pneumatically by 8 vibrational isolator, the table side eddy current damper can provide additional damping and increased stability of the system. Shown in the bottom picture, the clamping mechanism to minimized the need of de-floating the system.
Fig. 2.4 Connection Diagram for STM Base Plate and He3 Feedthrough Plate.
Feedthrough on He3 Pot, Front

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Fig. 2.5 Connection Diagram for Front-Left and Front-Right 10-Pin Connectors.
Front Left

LF 12
LE 14
LC HVZ
LG 13
LH 11
LA 5, 10, 15

Front Right

60 Ohms to GND
RJ 9
RD 1
RC 3
RG 8
RH 6
RI 7
RA 4
RB 2
Fig. 2.6 Connection Diagram for Back-Left and Back-Right 10-Pin Connectors.
Back Left

- Back LG He3 Heater
- Back LH He3 Heater
- 122 Ohms to GND
- 22 Ohms to GND

Back Right

- 60 Ohms to GND
- BRG STI-
- BRI STI+
- Bias1
- Bias2
- Back RD He3 I+
- Back RC He3 I-
- Back RA He3 V-
- Back RB He3 V+
Fig. 2.7 Modified Sample Heater with Cup-style Repeller and Alignment Adjusting Set Screw.
Cup-style repeller is jammed on one of the Ta studs by two Ta 0-80 nuts. It is electrically connected to one end of the filament inside.
Fig 2.8 Schematic of Sample Heater Inside the Mo Heater Main Body.

(a) Original plate-style repeller design, which can only compress electron beam from two sides.
(b) 0-80 Ta stud for filament support and electrical connection. To modify the existing heater, one of the studs needs to be made shorter to prevent contact with the repeller.
(c) Alumina enclosure.
(d) Sample holder; sit on the Mo main body (not shown).
(e) Modified cup-style repeller; Cup-style repeller is jammed on one of the Ta stud by two Ta 0-80 nuts. It is electrically connected to one end of the filament inside.
(f) Tungsten filament which is jammed on the 0-80 Ta stud with two Ta nuts on each end.
(g) 0-80 Ta nuts
2.3 Bibliography


Chapter 3

The Detection of Weak Vibrational Modes of Single Acetylene Molecules on Copper (100) Surface with Sub-Kelvin Temperature Vibrational Inelastic Electron Tunneling Spectroscopy

3.1 Abstract

Vibrational spectra for a single Acetylene (C₂H₂) molecule adsorbed on Cu(100) surface are revisited with inelastic electron tunneling spectroscopy (IETS) under sub-Kelvin temperature by scanning tunneling microscope (STM). Six vibrational modes (357.4meV, 117.7meV, 84.1meV, 58.5meV, 34.8meV, 22.1meV) can be observed in d²I/dV² signal below 400 meV. The 357meV mode (C-H in-plane asymmetric stretch) is consistent with previous STM-IETS results at 8K.[1] Five new modes are reported for the first time with STM-IETS. The identification of vibrational IETS features with normalized conductance change (Δσ/σ) as low as 0.24% is demonstrated in this chapter.

3.2 Introduction

Vibrational spectroscopy is one of the most important techniques for surface adsorbed molecules investigation. The extension of metal-oxide-metal style IETS[2] to tunneling junction of a STM allows direct acquisition of vibrational energy levels of active modes with sub-angstrom resolution on a single surface adsorbed molecule.[3] Combining with the capability of single molecule manipulation such as tip induced dissociation and formation of single chemical
binding,[4] the STM-IETS has served as the most direct source for chemical information in the emerging field of single molecular chemistry. Moreover, the excitation of vibrational modes also shows importance in understanding vibration-mediated motions and related reaction coordinate, which affects chemical reaction at single molecular level.[5][6] Recent progress on IETS also provides insights beneath the enhanced resolution and contrast of STM with functionalized-tip .[7]-[10]

Theoretical works based on perturbative approach of Tersoff-Hamann has established the detail process of change in conductance observed in STM junction due to electron-vibration coupling.[11] While good agreement was achieved with the experimental results[12] [13] there are still open questions regarding selection rules and mode excitation mechanisms. The goal for this work is to provide the community with more complete data in hope of a deeper understanding of STM-IETS. The leading contribution due to the effect of electron-vibration coupling can be separated into two parts, inelastic contribution and elastic contribution. The inelastic part, which describes an energy transfer between electron and adsorbed molecule, will increase the junction conductance. On the contrary, elastic part describes an energy exchange between the tunneling electron and electrons from the bulk; as a result, decreasing the conductance of the junction.[14] The competition among elastic and inelastic contribution will determine whether the conductance change is significant for detection experimentally. The sharpness of $d^2I/dV^2$ can be improved by reducing thermal broadening and modulation broadening.[15] Besides directly reduce in thermal broadening, lower temperature can also provide better mechanical stabilities of STM junction, in favor of greater signal to noise ratio to be achieved by signal averaging instead of using larger modulation amplitude. Here we present
new experimental STM-IETS results of Acetylene molecules on Copper (100) surface with higher sensitivity facilitated by a 600mK-temperature STM apparatus.

3.3 Experimental

The experiment was performed with a home-built ultrahigh vacuum STM with an adopted design as described in Ref [16]. The Cu(100) sample was repeatedly sputtered with 500eV Neon ion beam and annealed at 730K until a clean surface was conformed by STM topographic imaging with a chemically etched silver tip, followed by low coverage dosing of acetylene molecules of ~0.05 monolayer at temperature of 25K. The STM scanner and the sample were further cooled to 600mK for experiments with a single-shot He-3 sorption cooler. The STM topographic image of single acetylene on Cu(100) surface (Fig. 3.3B) was consistent with the previous studies done under 8K of temperature,[1] similar electronics with a homebuilt 20bits resolution (-5V to 5V) digital to analog convertor was used for applying sample bias. Sinusoidal modulation at 471 Hz with adequate root-mean-square amplitude no larger than 7mV was chosen and fed into a lock-in amplifier. dI/dV and d²I/dV² signals were acquired by calibrating first and second harmonic output from the lock-in amplifier respectively.

3.4 Results and Discussion

Six vibrational modes were identified with energy ranging from 0 to 400 meV by a single STM tip. A mode at 357.41mV with normalized ac-conductance change Δσ/σ=6.06% was found consistent with C-H asymmetric stretch at 8K.[1][17] In-addition, five vibrational modes with
energy level at 117.70 meV ($\Delta\sigma/\sigma = 0.42\%$), 84.07 meV ($\Delta\sigma/\sigma = 0.24\%$), 58.46 meV ($\Delta\sigma/\sigma = 1.18\%$), 34.80 meV ($\Delta\sigma/\sigma = 0.65\%$) and 22.12 meV ($\Delta\sigma/\sigma = 0.40\%$) were identified for the first time with STM-IETS due to finer energy resolution provided by 600 mK temperature. To further understand our STM-IETS result, density functional (DFT) calculation was performed by Dr. Yanning Zhang in Professor Ruqian Wu’s research group using the plane-wave-based VASP along with the projector augmented wave (PAW) method and 400 eV cut-off-energy was used for the plane wave basis. Generalized gradient approximation (GGA) was adopted to describe the exchange-correlation interaction among electrons. The vibrational frequencies of acetylene were determined by linear response method on a (7×7×1) Monkhorst-Pack k-point mesh grid Brillouin-zone. A list of comparison on previous studies regarding chemisorbed acetylene on Cu(100) surface can be found in Table 1.[5][18]-[20] A mode at 117.70 meV agreed with the symmetric in-plane C-H scissor ($\nu_5$) energy result obtained by DFT calculation and electron energy lost spectroscopy (EELS). Vibrational energies of 84.07 meV, 58.46 meV and 34.80 meV can be assigned to frustrated cartwheel ($\nu_7$), in-plane wagging ($\nu_8$) and in-plane rotation ($\nu_{10}$) mode respectively while the low energy mode at 22.12 meV fit into the range of rotation ($\nu_{10}$, 21 meV) and bend ($\nu_{11}$, 22 meV) mode for out-of-plane geometry. In comparison to the experimental result obtained from EELS, we found that asymmetric C-H stretch ($\nu_2$) and symmetric in-plane C-H scissor ($\nu_5$) were active to both STM and EELS techniques and the energy level matched to each other with very high accuracy. Except those lowest three vibrational modes ($\nu_{10}$, $\nu_{11}$, $\nu_{12}$) that are too close to the bulk phonon excitation to have a valid detections in EELS. We found two modes that are active to both EELS and STM-IETS ($\nu_2$, $\nu_5$), and seven modes act complementary in activity with EELS versus STM-IETS (IETS active: $\nu_7$, $\nu_8$; EELS active: $\nu_1$, $\nu_3$, $\nu_4$). Intensity of $d^2I/dV^2$ signals also vary with tip position (Fig. 3.3A).
The in-plane rotation (v10) and in-plane wagging (v8) modes intensity dropped significantly when STM tip was positioned on hydrogen site compared to the center of molecule, while no significant signal intensity change detected from other vibrational modes, suggesting that there was no center nodes on IETS spectral-imaging for those energies. As a result, the fact that symmetric in-plane C-H scissor mode (v5) and frustrated cartwheel mode (v7) are active to STEM-IETS suggests that further investigation and possible modification may be needed for the symmetric selection rule deduced from previous STM-IETS studies on acetylene isotope.[17]

3.5 Conclusion

In conclusion, STM-IETS measurement was performed on single C$_2$H$_2$ molecule on Cu(100) surface with base temperature of 600mK. We have shown that a detection sensitivity of 0.24% in tunneling junction conductance change is possible with STM-IETS, a six-fold improvement of sensitivity in comparison to the best result possible under 8K (1.5% in conductance change of C-O trenching mode).[12] Besides the well-known asymmetric C-H stretch mode, 5 additional modes were identified in the second harmonic signal in tunneling junction. A tentative mode assignment was made with the help of DFT calculation. In comparison to EELS result, asymmetric C-H stretch (v2) and symmetric in-plane C-H scissor (v5) were active to both techniques and results were matched to each other with high accuracy. STM-IETS and EELS fulfilled the rest of the vibrational spectrums in a complementary fashion outside the energy range of center phonon band (<40meV). At the lower energy range, a mode at 34.8meV can be assigned to In-plane rotation mode (v2) and a mode in 22.1 meV was found in the range of out-of-plane bend (v11, DFT result: 25meV) and out-of-plane rotation (v12, DFT result: 24meV).
The capability of detection of more vibrational modes enabled by 600mK STM could allow a deeper understanding of the IETS mechanism and greater analytical power of molecular identification by STM-IETS.
Table 3.1 Schematic Illustrating Different Vibrational Modes of Acetylene Molecule on Cu(100).

The motion in different vibrational modes are illustrated by green arrows (not to scale) and marked as ν1 to ν12, ordered by the mode energy obtained by DFT calculation in meV, which are shown in the second row. The third row shows STM-IETS results obtained with 600mK temperature with normalized conductance change shown in the parenthesis, and the EELS results adopted from Ref [5] in meV. The DFT calculation was performed by Dr. Yanning Zhang in Professor Ruqian Wu’s research group at UC Irvine.
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Fig. 3.1 STM-IETS of Single Acetylene on Cu(100).

-400mV to 400mV $d^2I/dV^2$ spectra of a single Acetylene on Cu(100), taken at the center of the molecule (Red) and on Cu(100) for background (Green). The background subtracted spectra (Blue) show multiple IETS features. Offset for clarity, the dash lines show the zero level. All spectra were taken with STM junction set point at 80mV/1nA; 7mVrms sample bias modulation at 471Hz. The bias step size is 2mV. Each spectrum was averaged over 40 bias scan passes and took about 80 minutes to complete.
**Fig. 3.2 STM-IETS of Single Acetylene on Cu(100), Fine Scan.**

(A) Background subtracted spectra taken from 6mV to 46mV and -6mV to 46mV. A feature at 34.8meV can be assigned to in-plane rotation mode ($\nu_{10}$, DFT result: 35meV), and the mode with energy around 22.1meV fits into the range of out-of-plane bend ($\nu_{11}$, DFT result: 25meV) and out-of-plane rotation ($\nu_{12}$, DFT result: 24meV). All spectra were taken with 3mVrms bias modulation at 471Hz, the step size was 400$\mu$V; STM junction set point was 8mV/1nA. Each spectrum shown was averaged over 40 bias scan passes and took about 40 minutes to complete.

(B) Background subtracted spectra taken from 40mV to 140mV and -40mV to -140mV. Features in IETS that can be assigned to symmetric in-plane C-H scissor ($\nu_{5}$, DFT result: 117meV), frustrated cartwheel ($\nu_{7}$, DFT result: 82meV) and in-plane wagging mode ($\nu_{8}$, DFT result: 57meV). All spectra were taken with 5mVrms bias modulation at 471Hz, the step size was 800$\mu$V; STM junction set point was 25mV/1nA. Each spectrum shown was averaged over 40 bias scan passes and took about 50 minutes to complete.
Fig. 3.3 Position Dependence of Peak intensity for ν10 and ν8

(A) The peak intensity of ν10 (86.9mV) and ν8 (35.4mV) show strong dependency on STM tip position. The spectra taken on the center of Acetylene molecule are shown in blue and the spectra taken on the Hydrogen site are shown in red. Spectra range from 6mV to 46mV was taken with 3mVrms bias modulation at 471Hz, bias step size 400μV and junction set point was 8mv/1nA. Each spectrum was averaged over 12 bias scan passes and took about 12 minutes to complete. Spectra rang from 48mV to 132mV was taken with 5mVrms bias modulation at 471Hz, bias step size 800μV and junction set point was 25mv/1nA. Each spectrum was averaged over 24 bias scan passes and took about 50 minutes to complete.

(B) STM topographic image of a single Acetylene molecule on Cu(100), taken with 38mV/1nA set point. Image size is 20Å×20Å.

(C) Top view schematic model shows the adsorption of Acetylene molecule on Cu(100) with same orientation as the STM image in (B).
3.6 Bibliography


Chapter 4

*Molecular Vibrations Modified by Surface Symmetry and The Presence of STM*

*Tip: Sub-Kelvin Temperature Vibrational Inelastic Electron Tunneling Spectroscopy of Carbon Monoxide on Au(110) and Cu(100)*

4.1 Abstract

Vibrational spectra of hindered translation (HT) and hindered rotation (HR) mode for isolated Carbon Monoxide (CO) molecules adsorbed on Au(110) and Cu(100) are investigated with inelastic electron tunneling spectroscopy (IETS) under sub-Kelvin temperature by a scanning tunneling microscope (STM). Anisotropic vibrational energy induced by surface symmetry can be resolved on Au(110). Two-fold vibrational energies of 3.9meV, 4.8meV for HT and 30.3meV, 32.4meV for HR on Au(110) 2×1 reconstructed surface can be found while single energy of 4.4meV for HT and 34.8meV for HR are measured on Cu(100) surface. Mode softening due to tunneling gap decreasing can be detected. Tip-induced dynamics of CO is also discussed.

4.2 Introduction

Vibrational spectra of chemisorbed molecules on surface reflect the local chemical environment that contains rich insight about the details of bonding and its fundamental properties. Facilitated by the localized nature of tunneling electrons, vibrational STM-IETS is proven to be powerful at depicting a complete understanding of surface chemistry at single bonding level.[1] In this
report, we study the effect on vibrational IETS based on the environment in the tunneling junction. Direct measurements of vibrational energy of an isolated CO molecule were used to investigate the effect of substrate symmetry on molecular vibration. A two-fold symmetric Au(110) $2\times1[2]$ surface was used in comparison to a four-fold symmetric Cu(100) surface. A doublet in HT and HR mode energy level can be resolved on Au two-fold surface and the vibrational modes in higher symmetrical Cu surface remains at single level. The effect of the STM tip on CO vibration is also investigated by decreasing the size of tunneling gap. Redshift in both HT and HR vibrational energy can be observed in tunneling region by approaching STM tips to the substrate. Furthermore, tip-induced spectra diffusion, CO hopping, CO desorption, and low energy vertical transfer of CO molecule to the tip can also be controlled.

4.3 Experimental

The experiment was performed with a home-built ultrahigh vacuum STM with an adopted design as described in.[3] Au(110) and Cu(100) were used in different runs of measurements. Both substrates were repeatedly sputtered with 500eV Neon ion beam and annealing (730K for Cu(100) and 660K for Au(110)) until a clean surface was confirmed by STM topographic imaging with a chemically etched silver tip, followed by low coverage dosing of CO molecules of ~0.05 monolayer at temperature of 25K. The STM scanner and the sample were further cooled to 600mK for experiments with a single-shot He-3 sorption cooler. 6K measurements can also be achieved without the activation of He-3.
4.4 Results and Discussion

The CO molecules was found be adsorbed on atop site of the Au(110)2×1 reconstructed atomic rows. C-O bond is vertical to the surface with Carbon atom attached to surface gold atom, (Fig. 4.1). Surface anisotropy between <110> (x-direction) and <001> (y-direction) result in different vibrational energies of CO. Previous studies of CO on Cu(110) with TOF-ESDIAD and HAS techniques both indicated a higher HT vibrational energy along x-direction,[4][5] and the results can be understood by the alignment of two-fold symmetric $2\pi^*$ orbitals for metal substrate causing a steeper potential in x compared to y.[4] Therefore, the vibrational energies of CO measurement by STM-IETS on Au(110) can be concluded as 4.8meV for HT-x, 3.9meV for HT-y and 32.4meV for HR-x, 30.3meV for HR-y.

On the other hand, CO molecules are chemisorbed on Cu(100) in a similar fashion with the Carbon atom attached to copper atop-site with a C-O bond vertical to the surface. Evidently, there isn’t any observable energy anisotropy in vibrational energy since the Cu(100) surface has higher symmetry. Our results show the vibrational energies for CO on Cu(100) are 4.4meV and 34.8meV for HT and HR respectively.

To study the effect on molecular vibration due to the presence of STM tip, we measured the vibrational energy with different tunneling gap dimension. With the approaching of STM tip, both HT and HR mode showed softening in vibrational mode. Similar non-linear dependency of HR vibrational energy on junction conductance had been obtain with CO/Cu(111) system down to point contact region at 5K.[6] In summary of our data, on Au(110), the CO HT mode energy
decrease by 45% and HR mode energy decrease by 1.9% when relative junction gap (Δz) decreased from 2.13Å (10mV/1nA) to 1.17Å (2.5mV/1nA), where the zero of Δz was set at STM junction set point of 1mV/1nA. Furthermore, the energy difference between X and Y direction in both HT and HR mode does not effected by the tip at this region. However, on the Au(110) surface, keep decreasing the junction gap will induce spectral diffusion[7][8] and the spectrum found switching between multiple line shapes in HT mode. The spectral diffusion shows tip-dependence, an example is shown in Fig. 4.4, illustrating that the STM-IETS spectra switches between 4 different types of line shape at Δz of 0.95Å. It suggest a possible explanation that there are 4 local minimums in potential contributed from the structures of STM tip due to angular dependence of chemical bonding force between the ad-atom on STM tip and surface adsorbed CO molecule.[9] On the other hand, CO on Cu(100) also shows mode softening, the vibrational energies in HT mode decrease by 35% and HR mode decrease by 1.2% when Δz decrease from 1.95Å(20mV/4nA) to 0Å(1.2mV/4nA). Notably, on both substrates, a clear discrimination of HT mode signal from zero bias conductance decrease(ZBCD) can be achieved under 600mK temperature. Evidently, the ZBCD feature was not subject to the influence of tip approaching nor to the existence of CO molecule in the junction.

For CO/Cu(100) system, no noticeable spectral diffusion can be observed before the CO molecule start hopping out of the tunneling junction when the STM junction set point closer than 1.2mV or higher on Cu(100) surface. On the other hand, instead of lateral hopping, a vertical transfer of CO molecule from Au(110) surface to STM tip will be induced when the junction set point is close than 1mV/1nA.
A Density Functional Calculation (DFT) was performed to provide more insight on CO/Au(110) system and shown on Fig. 4.7. The DFT calculation was performed by Dr. Yanning Zhang in Professor Ruqian Wu’s research group at UC Irvine. The DFT clearly show the mode softening due to the potential modified by the presence of the STM tip in both HR and HT mode. The results also suggest a higher HR-x energy compared to HR-y, while the energy order is reversed in HT mode compared to the previous TOF-ESDIAD and HAS results. The reversal of energy order in HT-x and HT-y is still inconclusive due to the technical challenge of applying DFT to low energy vibrational mode. Nevertheless, the DFT result agrees well with our experiments on the energy anisotropy and mode softening.

While mode softening of CO on Cu(111) had also been confirmed via first principle calculation,[6] an simplified yet intuitive picture can be rationalized by a recent study. In Ref[10], Emmrich et.al. use a frequency modulated qplus[11] AFM operated in lateral force mode to quantify the lateral manipulation force threshold of a surface adsorbed CO and concluded that the presence of STM tip will result in the lowering of CO diffusion barriers on surface. Based upon this result, one can imagine that the curvature of potential could also decrease due to the presence of tip, as a result, lowering the vibrational energy.

4.5 Conclusion

Molecular motion induced by tunneling electrons had been studied extensively by different experimental techniques and theoretical calculations.[12] CO molecule desorption can be induced on Cu(111) surface with high junction bias ~2.4V.[13] The explanation lays on the
excitation of CO-induced $2\pi^*$ resonance by energetic tunneling electrons.[14] In the case of low energy tunneling current, induced CO surface migration is relied on the excitation of C-O stretching mode which has energy level around 250meV.[15] While it is possible to use lower energy electrons to excite the C-O stretching mode by its inter-mode coupling to lower energy modes such as HR mode. However, our tip induced dynamics take place at energy below 1meV, which is too low for those mechanism mentioned above. Alternatively, the induced CO vertical transfer could be understood by “jump-to-contact” model.[16] When the tip getting closer to the CO, the CO starts to tilt away from its vertical orientation and which make carbon atom more accessible to the ad-atom on tip, and eventually, the bonding can be form between carbon atom and the tip atom, complete the vertical transfer of CO molecule (Fig. 4.8). Considering the case of tip induced hopping on Cu(100) surface, the lowering of the diffusion barrier was the dominate factor, the low diffusion barrier could not support the tilting of CO to complete the bonding between the carbon atom and tip ad-atom. Eventually, causing a tip induced hopping motion of CO instead of vertical transfer.

In conclusion, we have shown that STM-IETS can be used to investigate detail influences on CO vibrational behavior caused by its environment. The anisotropy surface structure results in energy splitting in HT as well as in HR mode. The approaching of STM tip will results in mode softening in HT and HR mode, in particular, HT mode is very sensitive to the presence of the tip. In addition, the ZBCD feature is very robust and not subjected to those change in the environment, therefore, it suggests that ZBCD has different physical origin other than vibrational nature. CO molecule can be induced by STM tip with very low electron energy (< 1meV). With high resolution vibrational IETS facilitate by sub-Kelvin temperature, we have demonstrated that
sensitivity of vibrational IETS could provide us insight about the potential energy landscape within the atomic scale tunneling junction.
Fig. 4.1 Schematics of Carbon Monoxide (CO) Molecule Vibrational Modes on Au(110)2×1 Surface and Cu(100) Surface.

CO adsorbs on atop sites vertically, with carbon atom (at the bottom) showed in black and oxygen atom showed in red.

The colored arrows indicate the exaggerated motion of carbon(black) atom and oxygen(red) atom for HT vibrational mode(AB, EF) and HR vibrational mode(CD, GH). On Au(110) surface, the vibrational motion along x-direction <001> (AC) and y-direction <110> (CD) experience different environmental effect due 2×1 reconstruction, while the environments on Cu(100) for two in-plane directions are identical.
Fig. 4.2 Δz Dependency of Hindered-Rotational Energy of CO on Au(110) Surface.

(A) $\frac{d^2I}{dV^2}$ spectra of single CO molecule on Au(110) 2×1 surface with different tunneling gap distance. The spectra were taken with a lock-in amplifier with voltage modulation of 500uV at 471Hz. The relative gap distance Δz was set to zero with STM junction at the set point of 1mV/1nA. The double peaks and dips feature can be identified around 30meV and 32meV, corresponding to the Hindered Rotational mode of CO.

(B) A clear mode softening can be observed when Δz decreased.
Fig. 4.3 Δz Dependency of Hindered-Translational Vibrational Energy of CO on Au(110) Surface.

(A) d²I/dV² spectra of single CO molecule on Au(110) 2×1 surface with different tunneling gap distance are shown. The spectra were taken with a lock-in amplifier with RMS voltage modulation of 300uV at 471Hz. The relative gap distance Δz was set to zero with STM junction at the set point of 1mV/1nA. The double peaks and dips feature can be identified around 2meV and 4meV, which correspond to the hindered translational mode of CO. The zero bias conductance decrease (ZBCD) feature shows no dependency on relative gap distance, suggesting that it is due to a different nature other than vibrational mode.

(B) A clear mode softening can be observed when Δz decreases.
Fig. 4.4 An Example of Spectra-Diffusion of CO HT Mode on Au(110) Surface.

The line-shapes switching between 4 different types at gap distance Δz of 0.95Å. The spectra were taken with RMS voltage modulation of 300uV at 471Hz. A possible explanation for the switching is that there are 4 local minimums in potential contributed from the structures of STM tip due to angular dependence of chemical bonding force between the ad-atom on STM tip and surface adsorbed CO molecule.[9]
Fig. 4.5 Δz Dependency of Hindered-Rotational Vibrational Energy of CO on Cu(100) Surface.

(A) \(\frac{d^2I}{dV^2}\) spectra of single CO molecule on Cu(100) surface with different tunneling gap distance. The spectra were taken with a lock-in amplifier with voltage modulation of 800uV at 471Hz. The relative gap distance Δz was set to zero with STM junction at the set point of 1.2mV/4nA. The peaks and dips feature can be identified around 34.5meV, which corresponds to the hindered rotational mode of CO. Different from the doublet feature on Au(110), the vibrational energy does not split due to the higher symmetry of Cu(100) surface.

(B) A clear mode softening can be observed when Δz decreases.
Fig. 4.6 Δz Dependency of Hindered-Translational Vibrational Energy of CO on Cu(100) Surface.

(A) $d^2I/dV^2$ spectra of single CO molecule on Cu(100) surface with different tunneling gap distance. The spectra were taken with a lock-in amplifier with voltage modulation of 500uV at 471Hz. The relative gap distance Δz was set to zero with STM junction at the set point of 1.2mV/4nA. The peaks and dips feature can be identified around 4meV, which corresponds to the hindered translation mode of CO. Unlike the doublet feature on Au(110), the vibrational energy does not split due to the higher symmetry of Cu(100) surface.

(B) A clear mode softening can be observed when Δz decreases.
Fig. 4.7 Density Functional Calculation (DFT) of CO/Au(110).

(A) Shows the calculation result of $\Delta z$ dependency of hindered-translational mode, HT-y(red) and HT-x(blue). The gap distance was measured from the center of oxygen atom to the center of the adatom on the STM tip.

(B) Calculation result of $\Delta z$ dependency of hindered-rotational mode HR-x(red) and HR-y(blue). The DFT clearly shows the mode softening due to the potential modified by the presence of the STM tip in both HR and HT mode. The results also suggest a higher HR-x energy compared to HR-y, while the energy order is reversed in HT mode compared to the previous TOF-ESDIAD and HAS results. The reverse in energy order in HT-x and HT-y is still inconclusive due to the technical challenge of applying DFT to low energy vibrational mode. Nevertheless, the DFT result agrees well with our experiments on the energy anisotropy and mode softening. The DFT calculation was performed by Dr. Yanning Zhang in Professor Ruqian Wu’s research group at UC. Irvine.
Fig. 4.8 Tip Induce Vertical Transfer of CO Molecule on Au(110) Surface.

(ACE), schematics that show the CO tilting and vertical transfer due to the decreasing of tunneling gap distance.

(BDF), STM constant current topography images of CO on Au(110) 2×1 surface, size 20 Å × 20 Å.

(A) 10mV/1nA (Δz =2.13Å on CO). The CO molecule was adsorbed on the atop site on the row.

(B) 3mV/1nA (Δz=1.33Å on CO). With closer set point, the CO image became asymmetric and the molecule tilted aside. Eventually, The CO molecule will jump to the tip with a scanning condition typically closer to 1mV/1nA (Δz=0Å on CO).

(C) 10mV/1nA scan with CO on tip at same area. An increase in resolution can be observed.
4.6 Bibliography


Chapter 5

Inelastic Tunneling Electrons as a Scanning Probe*

5.1 Abstract

STM-IETS has successfully achieved single-molecular level for vibrational[1]-[4] and rotational spectroscopy.[5] Combined with the manipulation capability of STM, STM-IETS facilitates tip-induced single molecular chemistry by discriminating and analyzing different compounds at the surface.[6][7] Additionally, previous research has shown that the vibrational signature of a molecule is sensitive to its environment, such as the presence of the tip,[8] the electronic coupling to the substrate,[9] and the arrangement of neighboring molecules.[10] Besides those features, STM-IETS can also be used to determinate the adsorption site of molecules.[11] Yet, thanks to high resolution spectroscopy at 600mK temperature, modifications of CO vibrational signature due to surface symmetry can be revealed and the information molecule and electro couplings can be extracted by IETS line shape. In this work, the versatility of IETS can be further extended to CO-functionalized tip and using the CO vibration to sense environment in the tunneling junction. We have demonstrated that by monitoring the hindered translation (HT) signature of CO on the tip while scanning over a Cobalt-Phthalocyanine molecule at the same time. The details of interior bonding structure, including covalent and coordination bonds of a surface-adsorbed CoPc molecule, can be revealed. The itProbe can also image bonding associated to hydrogen. On Ag(110) substrate, the interaction path between electron lone pair on imine nitrogen and adjacent C-H bonds can be imaged while
the interaction paths of C-H bonds to the surface gold atoms show clear contrast on 2 × 1 reconstructed Au(110) surface.[12] To our surprise, the interaction paths in both cases show bifurcation,[13][14] which suggests that the hydrogen can be shared by multiple centers. Evidently, the similar hydrogen sharing contrast can also be seen while imaging the inter-molecular interaction between a pair of CoPc molecule on Ag(110) surface. The position sensitive CO vibrational spectra also reveal the ordered energy shift by different groups within CoPC, which suggests an alternative route toward STM chemical discrimination on solid surfaces.[15]-[17]


### 5.2 Background

The energetic electron in STM can be used to excite vibrational state of a single molecule in the tunnel junction. By increasing the energy of tunneling electrons with junction bias higher than the excitation threshold for certain vibrational modes, the tunneling electrons can lose their energy to excite the molecular vibration. As a result, the vibration will induce a change to the electrical conductance in junction. In general, the vibrational effect on tunneling junction conductance can be described by a perturbative extension of Tersoff-Hamman theory.[18] The leading contribution due to the effect of electron-vibration coupling can be separated into two parts, inelastic contribution and elastic contribution. The inelastic part, which describes an energy transfer between electron and adsorbed molecule, will increase the junction conductance.
On the contrary, elastic part describes an energy exchange between the tunneling electron and electrons from the bulk; as a result, decreasing the conductance of the junction.\[19\] The competition among elastic and inelastic contribution will determine whether the conductance change is significant for detection or not. For example, the HT and HR mode of CO on metal surfaces are dominated by inelastic contribution,\[20\][21] which means a sharp increase in ac conductance can be detected, while molecular oxygen chemisorbed on Au(110) shows decrease in conductance because of the dominating contribution from elastic interaction.\[3\]

Practically, the detection of conductance change in tunneling junction can be realized by extracting ac conductance from the tunneling current with a lock-in amplifier.\[22\] In the inelastic dominating case, the excitation of a molecular vibration mode in the junction will create an additional constant conduction channel, which results in a step-like feature in the first harmonic signal\(\frac{dI}{dV}\) at the vibrational energy level of the molecule. More often, the peak-like second harmonic signal\(\frac{d^2I}{dV^2}\) can be used to extract weaker vibrational features and improve the contrast of IETS-imaging by STM. One of the most important factors of STM-IETS detection is the cryogenic environment of the apparatus. The width \(W\) of the peak in second harmonic signal can be described by \(W^2 = W_i^2 + W_T^2 + W_M^2\),\[23\] where \(W_i\) is the intrinsic width, \(W_T \sim 5.4k_bT\) is the thermal broadening and \(W_M \sim 1.7 V_{rms}\) is the broadening due to the lock-in modulation. Lowering the temperature not only directly reduces thermal broadening but also reduces the mechanical drift of the STM tunneling junction and provides better junction stability. Benefited from better stability, one can apply more signal average which allows us to use smaller modulation bias to preserve the sharpness of the signal.
5.3 Experimental and Results

In this work, we first focus on the preparation of a sample and the probe. Followed by typical annealing and ion sputtering techniques,[24] an atomically flat Ag(110) surface was prepared and checked by STM topographic image with a chemically etched Ag tip. The sample was dosed with small amount(<0.05L) of CO molecule by a variable leak valve, and co-adsorbed CoPc molecule with thermal evaporation at temperature of 25K. The sample and the STM scanner then were cooled further with a He-3 single-shot sorption pump refrigerator to 600mK. The CO on Ag(110) shows depression image contrast with a bare metal tip(Fig. 5.2-A), and can be conformed with STM-IETS. Typically 2.8 meV and 19meV feature can be identified, which corresponds to HT and HR mode CO vibration respectively(Fig. 5.1-B). We then needed to vertically transfer CO molecule from sample to the tip. Previous studies shows that a voltage pulse up to a few volts can excite such transfer with Tungsten tip.[6][15] In our case, we found that scanning with STM feedback set point ~ 1nA/1mV or closer on a CO molecule can also induce the vertical transfer, and this method seemed more suitable for Ag tip because soft silver tip is more likely to suffer from high voltage pulse damage. After picking up a CO on the tip, the contrast of topography image will change(Fig. 5.2-B). For a symmetric CO-tip, the image of CO shows a concentric feature with a center protrusion in a depression disc. Immediately, one can notice an increase in image resolution. In order to have a good result in experiment, a symmetrical CO-tip is necessary. From time to time, tip conditioning such as gently crashing the tip into substrate was needed. Besides the difference in image contrast and resolution produced
by CO-tip, IETS feature is the most unambiguous way to characterize a CO-tip. A typical IETS spectra od CO-tip on Ag(110) surface can be found at Fig. 5.1. Now, we have a scanning probe with a sharp CO vibrational feature in the inelastic channel, an inelastic tunneling probe, it-probe.

In principle, we can monitor any existing vibrational mode as long as it is active to STM-IETS (For this case, CO HT and HR mode). However, since the idea is to use CO vibration as a mean of sensing the environment in the junction, the low energy HT mode should be more sensitive. Furthermore, the noise in the current also decreases as the bias is lowered, which provides a better signal to noise ratio. Considering both factors, the HT vibrational mode of CO will be our choice.

It-probe can be used to take point spectroscopy as well as an imaging probe. For each measurement, we first have to decide which energy to take signal. Usually, point spectrosopies (fix point and ramp bias energy while recording $d^2I/dV^2$ signal intensity, Fig. 5.1, Fig. 5.3 & Fig. 5.4) can let us know which energy demonstrates better contrast. Once we pick an imaging energy, we can scan over the surface and record $d^2I/dV^2$ intensity at that specific energy to form an image.

Point spectroscopy of it-probe on different locations inside the CoPc molecule shows variation in peak energy, intensity and also in line shape. Notably, CO HT mode energy level over different parts of CoPc shows a trend as: six-member ring(3.2meV), five-member pyrrole ring(3.1meV),
inner six-member CoNC ring(3.0meV), Co atom(1.2meV), other sites on molecule(<2.5meV). (Fig. 5.3-B)

The $d^2I/dV^2$ image taken with 1.7mV energy (Fig. 5.5-A), shows the skeleton structure of CoPc molecule which is strikingly different from ordinary STM topography image.

We use 3 types of working mode in it-probe imaging: Constant Height(CZ), Constant Current(CI), and Semi-Constant Height(SCI).

The procedures for CZ mode are as followed: 1) Move the probe to the center of the molecule or other preferred point with set point 0.1V/0.1nA. 2) Turn off STM feedback. 3) Ramp sample bias to the energy of interest, typically 1.5mV~ 1.7 mV. 4) Move to the first pixel of the image. 5) Reduce the tunneling gap by about 1.7 Å. 6) Apply bias modulation and record $dI/dV$ and $d^2I/dV^2$ signals, and then record z and I without modulation. 7) Retract tip by 1.7 Å. 8) Move to next pixel. 9) Repeat 5-8 until finishing the images.

The procedures for CI mode are as followed: 1) Move the probe to the position of first pixel with set point 0.1V/0.1nA. 2) Ramp set point to 30mV/0.4nA for Au(110) and 30mV/1nA for Ag(110). 3) Turn off STM Feedback 4) Ramp sample bias to the energy of interest, typically 1.5mV~ 1.7 mV. 6) Apply bias modulation and record $dI/dV$ and $d^2I/dV^2$ signals, and then record z and I without modulation. 7) Recover the bias to 30mV. 8) Turn on Feedback, recover set point to 0.1V/0.1nA. 9) Move to next pixel and repeat from step1 until finishing the images.
The procedures for CI mode are as followed: 1) Move the probe to the position of first pixel with set point 0.1V/0.1nA. 2) Turn off STM feedback. 3) Ramp sample bias to the energy of interest, typically 1.5mV~ 1.7 mV. 4) Reduce the tunneling gap by about 1.7 Å. 5) Apply bias modulation, record dI/dV and d²I/dV² signals, and then record z and I without modulation. 6) Retract tip by 1.7 Å. and ramp bias back to 0.1V. 7) Turn on feedback and take another z measurement 8) Move to next pixel with feedback on 9) Repeat 2-9 until finish the imaging.

The bias modulation we used was 1.0meVrms at 471Hz. The idea behind these procedures is to get the probe close enough to have good signal and keep the probe intact at the same time. To keep the probe safe, we always move the tip with larger gap between pixels since we have found that moving with closed-in gap will destroy the probe easily. We also notice that CI mode gives better contrast resolving extra-molecular features (Fig. 5.5 and Fig. 5.8), since the feedback will normalize the gap conductance at each pixel, compensating the gap differences between the center of the CoPc and the region near the substrate. Nevertheless, CI mode takes longer time since we have to wait feedback to stabilize at each pixel. On the contrary, constant height mode (CZ) can work much faster. The spectra taken with CZ mode are also easier to interpret since the gap is kept constant instead and the trade-off is less sensitive to weaker signal.

In Fig. 5.2, we can see the CoPc molecule has 2 adsorption orientations, CoPc(×) and CoPc(+). The it-probe image contrast highlights different parts for CoPc(+) molecule on Ag(110). Fig. 5.5-A, taken in CZ mode, shows clearly the skeleton structure including the six-member ring, while CI mode emphasizes on the intra molecular interaction path between lone pair and the hydrogens on nearby six-member rings. On Au(110) 2×1 surface, the interaction path between the gold
substrate and the hydrogen can be seen (Fig. 5.5-E). Notably, both types of hydrogen interaction path show bifurcation.[13] Similar hydrogen related bifurcation path can be found in the region between the nearby CoPc molecules on Ag(110) (Fig. 5.8).

In summary, the change on CO vibrational behavior can provide insight on potential landscape at the surface. Point spectra show position dependent in the interior of a CoPc. The skeleton structure of a planner CoPc molecule can be resolved with $d^2I/dV^2$ imaging, and the contrast indeed is very close to “chemical bond” imaging. In addition, non-conventional intra and extra hydrogen bond paths have been suggested, yet, it is still an open question regarding to whether a hydrogen bond can been seen or not. [25][26]

5.4 Conclusion

The first successful technique to resolve chemical structure of surface molecule[27] was non-contact atomic force microscopy(nc-AFM). A frequency modulated q-plus[28] AFM system was used to resolve Pentacene molecule on NaCl/Cu(111) surface. Since then this method was broadly used in many works, such as working complementary to NMR structure determination ,[29] showing sensitivities on bond order,[30] and direct imaging of chemical product in a reaction[31]. More recently, hydrogen bond contrast in nc-AFM was also was reported.[32] Interestingly, the key to structure resolution for those AFM results was the functionalization of the tip with a CO molecule. On the other hand, the tunneling current based scanning tunneling hydrogen microscopy(STHM)[33] can also resolve molecular structure and intermolecular contrast on monolayer PTCDA molecules on Au(111) surface by trapping molecular hydrogen in
the junction.[34] Although hydrogen molecule is not visible to STM, it can modulate the tunneling current accordingly to the repulsive potential that correlated to the molecular structure. CO, Xe and CH$_4$ were also reported with similar effect in modulating tunneling current in STM. [35]

Indeed, functionalize a SPM probe with a small molecule had been proven crucial in modulating imaging signal (current or force gradient) in order to achieve “structural sensitive” imaging. Therefore, the fundamental understanding of the modulating mechanism shows great importance. Our vibrational approach to this question provides the insight for further development on this topic. An independent theoretical work by Hapala et al. based on our published data was reported.[36] The model was based on a semi-classical treatment of the tip CO interacting with a DFT-calculated surface potential of CoPc/Au(110). While the simulation agreed to our experimental results, they also pointed out that the importance of CO relaxation on sharpening the image. The role of CO relaxation was problematic for inter-molecular contrast because in a different work,[37] they have shown, by simply considering CO (H2) relaxation, at least in simulation, they can successfully re-created the intermolecular contrast in AFM and STHM system without the assumption of a bond path. An AFM experimental report of an almost impossible bond path contrast connecting two Nitrogen atom at nearby BPPA molecule further increase controversy in this topic.[38] Nonetheless, the topic of intermolecular interaction contrast would continue to draw attention to the community.
Fig. 5.1 Schematic Diagram and IETS Spectra by CO and CO-Tip.*

(A) Schematic diagram of a bare metal tip over a CO.

(B) Vibrational IETS spectra taken with a bare tip over Ag(110) surface (a), CO molecule (b). The background subtracted spectrum (c) is also shown. RMS sample bias modulation 600mV at 471Hz.

(C) Schematic diagram shows the CO-terminated tip on Ag surface.

(D) Vibrational IETS spectrum taken with a CO-tip over Ag(110) surface RMS sample bias modulation 600mV at 471Hz. The CO Vibrational feature can be seen everywhere on the surface.

* (B) and (D) are adopted from "Real-Space Imaging of Molecular Structure and Chemical Bonding by Single-Molecule Inelastic Tunneling Probe," C. Chiang, C. Xu, Z. Han, and W. Ho, Science 344, 885–888 (2014). Reprinted with permission from AAAS.
Fig. 5.2 STM Topography Taken with Bare Tip and CO-Tip at 600mK.*

(A) Constant current STM topography of CO co-adsorbed on Ag(110) surface. Two types of CoPc can be found, CoPc (×) and CoPc (+). Scan size 121 Å × 121 Å. Set point 100mV/0.1nA.

(B) Constant current STM topography image of the same area scanned by CO-tip. The CO indicated by arrow in (A) was vertically transferred onto the tip. A reverse in image contrast of surface CO can be found. The CO shows center protrusion with CO-tip instead of a round depression with bare tip image.

Fig. 5.3 Point Spectroscopy Revealing Variation of Hindered-Translational Feature of Tip-CO Over Different Parts of the CoPc(+) Molecule on Au(110).*

(A) Spatially resolved vibrational IETS spectra taken at locations indicate the schematic of the right lobe of CoPc(+) molecule. RMS sample bias modulation was 10.mV at 471Hz. STM junction gap was set with 100mV/0.1nA on center Co atom and then moved close to the surface by 1.7 Å after turning off the feedback. Note the different multiplication factors for four spectra. Number on the right side of each spectrum denotes the peaks position. The dashed line is drawn at sample bias V=1.7mV to show the variation in intensity that gives rise to the contrast in molecular imaging.

(B) Peak position of the hindered translation mode of tip-CO over locations of CoPc molecule indicated on the x-axis: Co (cobalt atom), NI (imine nitrogen), LP (lone pair on imine nitrogen), Co-N (cobalt-pyrrole nitrogen bond), C (carbon atom), C-C bond, C-N bond, NP (pyrrole nitrogen), BKG (Ag substrate), P (pyrrole ring) and CoNC (CoNCNCN ring). Insert shows a schematic diagram of CoPc.

Fig. 5.4 Point Spectra of Tip-CO Taken at 58 Different Points Over CoPc (+) Molecule.*

Vibrational IETS spectra taken with same condition as spectra in Fig. 5.3-(A). Labels for each spectrum corresponding to a location marked in the schematic diagram of CoPc are shown below the graph. The dashed line indicates sample bias \( V=1.5\text{mV} \).

Fig. 5.5 Skeletal Images of CoPc Obtained by Inelastic Tunneling Probe.*

(A) Constant-height image over CoPc(+) on Ag(110), 20.1 Å × 20.1 Å.

(B) Constant-current image of CoPc(+) on Ag(110), 20.1 Å × 20.1 Å.

(C) Constant-height image over CoPc(×) on Ag(110), 20.1 Å x 20.1 Å.

(D) Schematic showing the skeletal structure of CoPc(+) and the intramolecular hydrogen bonds highlighted in dashed ellipses in (B).

(E) Constant-current image over CoPc(+) on Au(110) 2×1 surface, 21.2 Å × 21.2 Å. A rectangular boundary is resolved and is attributed to the range of electronic influence of adsorbed CoPc. A similar boundary is less prominent on Ag(110) surface.

(F) Schematic diagram shows the skeletal structure of CoPc(+) on Au(110) 2×1 surface. The missing surface atom rows are aligned along the dark rows. The Co atom is over the missing row but is displaced to one side.

Fig. 5.6 Energy Dependent IETS Imaging.*

d²I/dV² images taken at different sample bias with CO-tip over two types of CoPc molecule: CoPc(+) in (A)-(F) and CoPc(×) in (G)-(L) on Ag(110) surface. All sized in 20.1 Å × 20.1 Å. The sample bias voltage for each images is marked in the panel. The intensity variation may result from the fact that the molecule is not commensurate with the substrate or the molecule is not flat.

Fig. 5.7 Complete Set of Images Taken With itProbe on Ag(110).*

(A)-(D) Constant-height images taken within a single sequence (A) $d^2I/dV^2$, (B) $dI/dV$, (C) $I$, (D) $Z$.

(E)-(H) Constant-current images taken within a single sequence (E) $d^2I/dV^2$, (F) $dI/dV$, (G) $I$, (H) $Z$. The variation in the current in (G) is due to the recording of the image after ramping down the bias voltage from 30mV to 1.7mV with feedback turned-off and the current is different for the two biases at the same junction gap $z$. Each image size is 20.2 Å × 20.2 Å.

Fig. 5.8 Images Showing Intermolecular Interaction Between a Pair of CoPc on Ag(110) Surface.*

(A) Constant current topographic image (60.6 Å × 60.6 Å) with set point 100mV/0.1nA.

(B) Constant-current itProbe image at 1.5mV (12.6 Å × 12.6 Å) over the white boxed area in (A).

(C) Constant-current itProbe image at 1.5mV (8.1 Å × 8.1 Å) over the white boxed area in (B).

(D) Schematic diagram of the image in (B). Dashed lines are the intermolecular interaction path involving hydrogen, and in yellow are the lone pairs of imine nitrogen. Four hydrogens are shared among four carbon atoms (asterisk) and one imine nitrogen (indicated by arrow).

5.5 Bibliography


Chapter 6

Conclusions and outlook

6.1 Vibrational IETS of Surface Adsorbed Single Molecules

In conclusion, we have demonstrated that with a 600mK apparatus, in Chapter 3, the detection of normalized conductance change as sensitive as 0.24% is possible. We have found 5 new modes on Acetylene/Cu(100) system that were previous inaccessible to STM-IETS at 8K. The additional vibrational modes provide the scientific community with a more complete experimental data and can help us tackle the open questions in vibrational IETS such as the selection rules and the nature of excitation mechanisms. Benefited by the 600mK low temperature again, we can distinguish the energy anisotropy between two different in-plane vibrational directions on Au(110) 2×1 reconstructed surface and the modes softening due to the present of the STM tip. We have found that the hindered-translational mode of surface adsorbed CO is particularly sensitive to its surroundings.

6.2 Vibrational IETS as a Scanning Probe

The high resolution and sensitivity of STM-IETS enable us to see the subtle variation of molecular vibration due to its environment at atomic scale. Transferring a CO vertically from surface to the STM tip allows us to create a scanning probe with characteristic vibration feature. Thus we can use STM IETS signal as a contrast to image another molecule on surface. The work reported in Chapter 5 serves as an example for that concept; the spatial variation of the CO HT
vibrational signal can reveal bonding details by sensing the local potential energy landscape[1]. Functionalizing a SPM probe with a small molecule is proven to be crucial in modulating imaging signal (current or force gradient) in order to achieve “structural sensitive” imaging which previously inaccessible to SPM with bare tip. The fundamental understanding of modulating mechanism is of great importance. Our vibrational IETS approach to this question provides the insight for further development on this topic. An independent theoretical work by Hapala et al. based on our published data was reported,[2][3] which put molecular vibration and AFM force detection on a common ground. This can lead to a more general understanding of probe-sample interaction for various types of scanning probe microscopy techniques including STM, SHTM and AFM.[4]-[7]

6.3 Spin-Flip IETS

One should not forget that the excitation process related to inelastic electron tunneling is not limited to molecular vibration. A famous alternative is spin-flip IETS in which the tunneling electrons can induce spin-flip excitation of a magnetic impurity on surface.[8] It is expected that a spin-flip version of itProbe can be useful in spin-spin interaction study with enhance resolution. The major technical challenge is expected to be the choice of magnetic molecule for functionalizing the STM tip since most of the known spin-flip results require separation layer between the magnetic molecule and conducting surface [8]-[12].
6.4 Bibliography


Appendix

Operation Procedures for mk-STM cryostat

A. 1 Procedure: Liquefying He3

A brief explanation of how He3 sorption cooler works is presented. Consider a simplified case: to reduce the boiling point of a liquid, we can use a pump to pump on the vapor. As simple as that, if we pump on liquid helium, we can make it cooler. At atmosphere pressure, He4 has its boiling point at 4.2K, and the lighter isotope He3 has its boiling point at 3.2K. We can buy liquid He4 in bulk and easily cool down the system to 4.2K. When we pump it on with a mechanical pump, the temperature in liquid He4 can go down to about 1K. If we pump on liquid He3, we can cool it down, in principle, to 300mK. However, He3 is very rare and expensive, so we need a more efficient way to pump it without loss. Moreover, because STM is very sensitive to vibration, the pump is preferred to be silent and vibration-free. In our system, charcoal is the pump. We activated the charcoal pump by cooling it with liquid He4 to 4.2K, and we deactivate the pump by heating it up to 40K.

When the system is at 4.2K, most of the He3 gas is absorbed in charcoal pump. To liquefy He3 gas, we heat up charcoal to 40K to “turn-off” He3 pumping, and we use mechanical pump to pump on liquid He4 in 1K-Pot. The He3 gas will be cooled by 1K-Pot and condense. The liquid He3 will drip down to He3-Pot. After we completely liquefy He3, we activate charcoal pump again by turning off the charcoal heater. The charcoal pump will start to pump on liquid He3 and bring the temperature of STM down to 600mK.
Each complete He3 liquefaction cycle is able to keep the system under 600mk for ~48 hours. To liquefy this much, however, the time spent liquefying may need to vary depending on whether you are beginning an experiment or not. If this is the first liquefy of an experiment, you may need to liquefy 2-3 hours. Otherwise 90 mins should suffice. You can liquefy the He3 before refilling He4 III (Insert) or after. We typically liquefy before refilling He4 III. In that case, you will need at least 1” to complete the liquefaction, which in practice means the He4 III (Insert) liquid level reading cannot be any lower than -3.5” to start with. Note that one can liquefy while the Superconducting Magnet is energized and one can also simultaneously energize or de-energize the magnet while liquefying. Finally, DO NOT attempt to liquefy downstairs unless you are prepared to deal with the possibility of the insert getting stuck.

A typical mk experiment run can last more than one month to collect enough data. Therefore being able to keep the sample and tip intact at the atomic level during and after the liquefaction is very important. In order to keep the tip and sample intact, three factors needed to be taken care of.

1) Retract the tip properly. First retract the tip normally with same z gain setting and go to “pre scan menu” in the program, uncheck “crash protection” option, and manually adjust the Z-offset to full retract (zero bit offset, with the Z offset adjustment bar all the way to the left). Remember to click on “send” after adjustment or else nothing will actually happen.
2) During the liquefying process, minimize the usage of 1K-needle valve. Always turn the needle valve gently and never pinch the valve completely closed.

3) Pay attention to the Dewar pressure during refilling of liquid helium, especially when refilling He-4-III. Over pressurization and excessive boiling of liquid helium during transfer can cause lots of vibrations and crash the tip, remember to switch the insert gas venting to the weak exhaust (lower pressure relief valve) setting during transfer. When the He-4-III pressure is too high (typical <850 Torr), depressurize the transport Dewar as needed to reduce the transfer speed.

A.2 Preparation for liquefaction:

1) Make sure there is no less than -3.5” in He4 III (Insert) before starting.

2) Go upstairs and carefully connect the bellows for the liquefying pump line (1K pumping). We pump on He4 in the 1K pot which is fed from the He4 III (Insert) 10L Dewar. You’ll need to make this bellows connection to allow for this pumping and you’ll need to disconnect after.

3) Go back downstairs and go to the pump room. Turn on the liquefaction mechanical oil pump. After turning it on, open the big ball valve to the pump line. Leave the door to the pump room open so that you can hear the pump and also as a reminder.

Starting the liquefaction:
4) Go to the front workstation (computer area) and turn the charcoal exhaust flow (Fig. A.19) all the way down to zero.

5) Go upstairs and close the 1K-pot isolation valve, the Charcoal cooling valve, and close the brass needle valve which feeds the 1K Pot so that it is only open to ¼ turn (marked with an X). Do not fully close the brass needle valve, since doing so will increase the chance of tip crashing.

6) If everything is ready, and the pump bellows has been connected, open the large ball valve and pump out the bellows. Then gently open the large right angle valve to begin pumping on the 1K Pot. You’ll hear a response in the mechanical pump and if your pre-amp is at Gain 10, you may see some flickering in the overload warning red light (this doesn’t mean your tip is actually crashing, but if you are too rough in opening/closing any of the valves mentioned above you can lose the tip).

7) Head downstairs and immediately activate the charcoal heater. To do this, press heater range, select the up arrows until 2.5 Watts appears, and then hit Enter. The electronics should already remember that the target temperature is 40 K, if not you may need to program this. If the controller is not responding, check the display panel to see if the controller is set to “remote” mode. Pressing the “local” button should bring the controller back to manual control.

8) Start the timer. Once the temperature in the charcoal reaches around 28-30 K you’ll see the He3 Pot temperature start to plummet; this is the temperature at which the charcoal starts to purge the He3 gas, where it then coalesces at the 1K Pot connection and drips down into the He3
Pot. The charcoal and He3 pot can be regarded as a connected chamber. The thermal conductivity between 1K Pot and He3 Pot is determined by the He3 gas pressure inside this chamber. Turning on the charcoal heater means switching off the pumping of the “charcoal pump.” This increases the pressure inside the chamber and therefore increases the thermal conductivity between 1K-Pot and He3-Pot.

9) Liquefy for 90 minutes or longer to achieve ~ 48 hours of He3 before running out.

10) Monitor the 1K Pot temperature, which should be ~ 1.5K or less. If it suddenly starts to rise, you may need to go upstairs and slightly open the brass needle valve. The more you open the brass needle valve, the faster you consume He4 III (Insert) helium however. You may see some small jumps in temperature while the charcoal is warming up to 40K, but once the charcoal is 40K it should remain steady. You need to be present and keep an eye on the 1K Pot temperature; do not leave mK-STM during this time. Also, periodically monitor the He4 III (Insert) liquid level to make sure you don’t accidentally drain it completely. The 1K-Pot temperature is decided by the competition between 4K “hot” helium and the cold helium pumped by the 1K-pot pumping line. The 1-K needle valve regulates how much “hot” helium can flow into the 1K-pot. Considering the extreme case, the lowest temperature can be achieved by completely close the 1K needle valve. However, since we need to keep pumping 1K-Pot, the helium inside will eventually dry out, causing the 1K-Pot temperature to shoot up. A balance between the hot helium supply and 1K-Pot temperature needs to be found (typically < 1/2 turn to start with and can be reduced to < 1/4 turn later).
11) As discussed in 8), the thermal conductivity between 1K-Pot and He3 Pot is correlated to the He3 gas pressure. When most of the He3 is liquefied by 1K-Pot the gas pressure will decrease, therefore the temperature response of He3 will become less correlated to the temperature of 1K-Pot. This is a sign of the completion of liquefying He3.

12) Check the Dewar pressure in He-4-III, it should be larger than 760 Torr (800 Torr). If the pressure is too low, closing the 1K-needle valve should bring back the pressure.

Finishing the liquefaction

13) After you are done liquefying, first turn off the heater (hit the Heater Off button).

14) Switch the tube connecting the input of the charcoal flow meter in the front workstation of mK-STM to the flow meter with the steel ball. Make sure this second flow meter knob is set to fully open.

15) Go upstairs and close the big ball valve to the mechanical pump and then the big right angle valve.

16) Make sure both of the valves in (15) are closed, (Check 12) then open the “green valve” to vent the bellows section with He gas. It is important to check the pressure in the He-4-III dewar, make sure it’s higher than 760 Torr before opening the green valve. If the pressure is lower than 760 Torr, we need to pressurize the Dewar with high purity helium gas before opening the green
valve. Watch the nearby pressure gauge to confirm it is vented before fully closing the green valve.

17) Open the charcoal cooling valve and listen for the metal ball to strike the top of the flow meter over at the workstation.

18) Open the 1K brass needle valve to 3 full turns open, marked by a line at the top of the valve.

19) Disconnect the pump bellows, being careful not to drop the KF components. Attach the KF blank to the bellows end and attach the plastic cap to the elbow on the pump line. Tape the pump bellows to the tube insulation post to prevent vibrations.

20) By this time the charcoal should be nearing 5K. Once the charcoal has cooled to 5K, plug the charcoal exhaust tube back into the charcoal exhaust flow meter and reset the flow value to around 2.5 – 3.

21) After ~30 minutes have passed, open the 1K Pot vent. The extra time spent keeping this exhaust closed is intended to help it warm up faster so that the overall system temperature stabilizes faster.

22) Go to the pump room and close the big ball valve to the pump line. Turn off the pump and vent the front of the pump using the vent valve. Make sure to close the vent valve tight after.
A.2.1 Charcoal Cooling Adjustment.

Once the charcoal is fully cooled to about 4.2K and He3-Pot temperature should be about 0.5K, we should adjust the charcoal cooling flow (see Fig. A.19) by the flowmeter at the front computer area. Close down and adjust the knob on the flow meter to modulate the pressure in He-4-III Dewar to about 800-810 Torr. The effect of charcoal cooling on He3-Pot temperature is not that obvious. However, He-4-III pressure will affect He-4-III consumption rate. Excessive charcoal cooling should be avoided.

A.3 Fully Warming Up and Venting mK-STM

There are two occasions that we need to fully warm up the system. 1. The main vacuum system need to be vented for maintenance or 2. The vacuum jackets of the Dewar(s) need to be re-pumped. When the vacuum inside the vacuum jacket go bad, the helium consumption rate will increase, pumping the vacuum jacket should bring the consumption rate back to normal. A typical liquid helium consumptions can be found in Tab. A.1.

Fully warming up the system from Helium temperature to room temperature will cause significant mechanical expansion. The idea behind most of the procedures is to reduce this mechanical stress. The complete process can take up to 3 weeks.

1) Take out STM tip from the tip socket. We have had bad experiences with silver tips getting stuck in the tip socket after fully warming up before. While the actual reason is still unclear, it is
safer to keep the socket empty since we are expecting the STM will be idle for a long period of time.

2) Move the insert completely up

3) Adjust the 4K shutter to half-closed position, this will relieve the tension in the cable and spring mechanism during the temperature change.

4) Open the needle valve between He-4-I and He-4-II and let the liquid Helium flow into He-4-I naturally. Since the liquid consumption rate is higher in He-4-I, doing so will speed up the warm up process. It will also help reducing the stress on the needle valve due to thermal expansion.

5) Turn off the helium level meter. Accidentally initiating the level measurement in an empty Dewar may cause damage to the level meter. Keep in mind that some of the helium level meters used in the lab will automatically make measurements every 24 hours by default, so it is important to completely de-power the electronics in order to prevent this.

6) Give the thermal shielding assembly a full rotation each day during the warm up process. This will prevent the shielding assembly from getting stuck due to mechanical expansion/contraction.

7) Fully open the 1K-Pot brass needle valve (3 turns, marked with a line at the top of the valve).

8) After the system is fully warmed up, start pumping the vacuum jackets.
A.4 Pumping the Vacuum Jackets of mk Dewar & Transfer Lines

There are 2 vacuum jackets on the system that need to be pumped out, Main Vacuum Can (MVC) and Insert Vacuum Can (IVC). The vacuum in MVC directly affects the thermal insulation of the large Dewar and therefore affects the liquid consumption rate of He-4-I. Vacuum in IVC is responsible for the thermal insulation between 1K-Pot and charcoal. The typical symptom of a bad IVC vacuum is the difficulty in maintaining a temperature difference between the 1K-Pot and charcoal during the He3 liquefy process. Both vacuum jackets should be pumped only when the system is at room temperature, so it is strongly recommended that one always pumps the vacuum jackets when the system is fully warm up regardless of whether problems have been observed since full warm-ups are infrequent events.

There are in total 4 transfer lines in the mk-STM system: the long Janis transfer line (the one connecting to the portable Dewar), He-4-I transfer line, insert transfer line and offset transfer line for insert, they all need to be pumped to maintain good insulation.

The long Janis transfer line and offset transfer line adapter for insert can be pumped while the system is cold since they can be separated from the system anytime, however, the He-4-I transfer line and insert transfer line are always inserted into the system dewars and can only be pumped after a full warm-up.

In short, there are in total 4 vacuum jackets need to be pumped when the system is at room temperature. The turbo pump and dry pump assembly should be set up at the 2nd floor properly
and connected to the pumping port with NW40 and CF2.75 fittings. An NW25 reducer will be needed at the vacuum jacket pump-out port and we should minimize the usage of NW25 in order to provide better pumping conductance. The total length of pumping line from the turbo pump to pump-out port should be less than 5 feet. With the cold cathode gauge installed right at the turbo inlet, the vacuum pressures should be: MVC, < $5 \times 10^{-7}$ Torr after 7 days, IVC, < $5 \times 10^{-7}$ Torr after 5 days, Transfer lines, < $1 \times 10^{-6}$ Torr after 2 days.

**A.5 Cooling Down mK-STM from the Fully Warmed Up State**

To cool down the system back to Helium temperature, we need to precool the system with liquid nitrogen. Before starting the precooling, we should check:

1) All vacuum jackets should be sealed.

2) The system is at room temperature, this is particularly important after main chamber baking. DO NOT start cooling while the system is still hot; wait until the system is fully cooled down to room temperature.

3) Same idea behind the procedures for fully warm up, we have to make sure the tip socket is empty, the insert is completely moved up and the 4K-shutter is half closed.

4) We should have at least 3 full 200L LN2 tanks and 3 full high purity Nitrogen gas cylinders.
5) Disconnect the system from the Helium recycle line, let all relief valves on the system be free to breath (switch each exhaust to the “weak” setting).

**A.6 Precooling He-4-I and He-4-II**

The one and most important idea to keep in mind is to prevent clogging of the system with ice (water, O2, N2 or otherwise), always think about avoiding impurity accumulation, purge out all the impurity before it turns into liquid and eventually solid. We should pay additional attention to the needle valve and capillary tubing between He-4-I and He-4-II since this is very easy to clog with ice. We should frequently check if this tubing is clear. The goal of precooling is to make the temperature on top flange of He-4-II reach 120K (CF4), it will take about 4 days to reach that temperature. We use a Teflon transfer tube for the initial LN2 transfer, keep in mind that the Teflon tube will contract quite a lot during cooling, causing the connector to slip out of the brass quick-disconnect assembly. We should use cable tides to tie up the coupling to prevent such slipping. Although we will precool the mk-insert after precooling I & II, it would be a good idea to purge He-4-III before actually put LN2 into the system to minimized the chance of contamination in He-4-III. The reason for this is that cooling He-4-I and He-4-II will inevitably lead to some cooling of He-4-III, which can trap water ice and other contaminates.

1) Connect the mechanical pump line to the pumping port to He-4-I and He-4-II. We have only one pump. However, the routing setup should allow us to pump them separately as well as pump them together.
2) Connect high purity Nitrogen gas to the pressurize port on He-4-I and He-4-II.

3) Isolate I & II by closing the needle valve.

4) Pump I & II until the pressure reading is < 20 Torr, stop pumping, refill I & II with Nitrogen gas, repeat at least 5 times.

5) Pump II, stop pumping, refill II through He-4-I by opening the needle valve. This is a good way to make sure the capillary tubing is clear, repeat this for at least 5 times.

6) Make sure the Dewar pressure is slightly higher than outside. Complete the purging procedure in next section and then come back to here.

7) Have the LN2 ready, connect and purge the black Teflon transfer tube by open the valve on the LN2 slightly until a stable flow of Nitrogen gas coming out, insert the black Teflon tube into the transfer line on He-4-I. DO NOT WAIT FOR ICING.

8) Adjust the needle valve between I&II and the relief valve on He-4-I, make sure the pressure in I is higher than II such that the Nitrogen gas will keep flowing into II through the capillary tubing.

9) DO NOT DIRECTLY PUMP ON LN2, IT WILL SOLIDIFY NITROGEN AND CLOG THE SYSTEM.
10) It will take about 30 hrs and 2 tanks of LN2 to have liquid accumulate in both He-4-I and He-4-II. He-4-II is accumulating liquid when the J-type thermal couple in He-4-II reads below 80K.

11) The goal of precooling is to make the temperature on top flange of He-4-II reach 120K (CF4), it will take about 4 days to reach that temperature. We may need to refill LN2 again to keep the system cooled at LN2 temperature.

12) Give the thermal shielding assembly full rotations from time to time during the cool down process; this will prevent the shielding assembly from getting stuck due to mechanical expansion/contraction.

A.7 Purging the He-4-III and Insert

The most important part of this purging is to clear out all the impurity in the charcoal cooling line and 1K-Pot.

1) Connect the mechanical pump to the 1K pumping line.

2) Connect the high purity gas cylinder to the insert pressurizing port.

3) Close the charcoal cooling valve.
4) Pump He-4-III through the 1K-Pot, refill N2 from He-4-III pressurizing port with by-pass valve opened.

5) Pump He-4-III through 1K-Pot, refill N2 from He-4-III pressurizing port with by-pass valve closed (make sure that the transfer line is clear).

6) Repeat 4-5 times.

7) Keep the insert pressure positive compared to the outside.

**A.8 Precooling the He-4-III and Insert**

Once there is liquid accumulated in He-4-I and He-4-II, we can start pre-cooling the insert. Note that we should complete the purging of Helium-4-III before introduce LN2 into He-4-I and II.

1) Repeat 4-5 in the purging procedures 3 times.

2) Pressurize He-4-III and open the charcoal cooling valve, make sure gases can blow out from it, then close the charcoal cooling line. And let the pressure inside positive.

3) Make sure the Teflon transfer tube is completely dry, use a new full tank of LN2 to start cooling the insert.
4) Open the outlet valve on the LN2 tanks and purge the Teflon transfer tube, insert it into the transfer line on He-4-III with the 1K-Pot needle valve open.

5) Regulate the insert pressure with the relief valve on the insert to let gas flush out of the 1K-Pot exhaust.

6) Open the charcoal cooling valve to flush the charcoal cooling line, make sure that the insert is under positive pressure before doing so.

7) The cooling of the charcoal and 1K-Pot is very sensitive to the status of 1-K needle valve and charcoal cooling valve. Adjust these accordingly. Do not let the temperature difference between them become too large. The charcoal cooling can be controlled with the charcoal cooling valve. The 1K-Pot cooling can be controlled by the insert pressure and 1K needle valve. Watch the chamber vacuum pressure carefully. It will have some response due to mechanical stress, keep the cooling between 1K and charcoal slow and balanced to reduce the stress. It will take up to 20 hours to make the charcoal and 1K-Pot stay at LN2 temperature, take your time.

A.9 Taking out LN2

Once the temperature of CF4 reaches below 120K (It takes about 4 days, we can always wait longer of course), we can start taking out LN2 and switch to LHe operation. At this point, we
should have at least 500L of LHe ready. It would be better to have 150L extra for planning the experiment.

1) Taking out LN2 in He-4-I:
   a) Close the needle valve between I & II.
   b) Pressurize He-4-I to ~ 850 Torr.
   c) Remove the plug on the He-4-I inlet transfer line. DO NOT USE THUMB TO PLUG IT, just insert the Teflon transfer tube quickly and let the LN2 come out by maintaining proper positive pressure in the He-4-I. You may choose a portable Dewar or just use a Styrofoam container to catch the LN2.
   d) When there is no more LN2 coming out of the transfer tube, disconnect the transfer tube and plug the He-4-I inlet properly.

2) Open the needle valve between I & II.

3) Pressurize He-4-II to push LN2 from II to I. Watching the pressure response in I & II, we can notice that when the capillary tubing is free of liquid, the pressure difference between I & II will become harder to maintain.

4) Close the needle valve between I & II.

5) Repeat from 1) to clear out all LN2 in He-4-I and He-4-II.
6) After there is no more LN2 can be push out of the Dewar, leave the needle valve between I & II open and wait for the last drop of liquid to evaporate. The sign of the liquid completely drying up would be a very sharp change in the slope of the rising temperature in CF6. Wait for this signal, it may take many hours. The safest way is just wait for at least 8 hours and let the CF6 warm up to ~100K and the He-4-II thermal couple should read 100K or more.

7) To take out the LN2 in He-4-III, close the 1K needle valve and pressurize He-4-III. It is important to close the 1K needle valve during this time to prevent addition LN2 from getting pushed into the 1K-Pot during pressurization.

8) Connect the transfer tube and push out LN2 in a similar manner as He-4-I/He-4-II. The signal that all of the LN2 has boiled off will be a sharp rise in the 1K-Pot and charcoal temperatures (also they should rise to at least 100K before you begin purging out the N2).

9) Open the 1K-pot needle valve 3 turns, pressurize He-4-III and let the gas flush out through Charcoal cooling line and 1K-pot exhaust. Do it several times, it would speed up the dry-out in 1K-Pot.

10) Wait, just wait for 1K and charcoal temperature to warm up to 100K or more.
A.10 Purge the System with Helium Gas

Before switch to liquid helium, we should purge all Dewar with helium gas, the procedure is very similar to the purging done before precooling with LN2. Noted that since the purging procedure need to use pump, we should wait for the complete dry-out of liquid nitrogen since pumping on nitrogen will cause it to solidify and clogging the system.

A.10.1 Purge He-4-III with Helium Gas

1) Connect high purity Helium gas to pressurizing port.

2) Leave 1K needle valve open, close the He-4-III normal relief exhaust, check weak relief is also closed.

3) Close charcoal cooling valve.

4) Close 1K exhaust valve.

5) Pump on He-4-III via 1K pumping port.

6) Stop pumping; refill He-4-III with helium gas.
7) With the He-4-III pressurized, open the charcoal cooling valve, let it flush.

8) Open the 1K exhaust valve, let it flush.

9) Open the He-4-III normal and weak relief, let them flush.

10) Close the by-pass valve and open the transfer line inlet valve; this will divert the helium gas flow into transfer line and make sure it is clear.

11) Open the by-pass valve.

12) Close charcoal cooling.

13) Close 1K exhaust valve.

14) Stop pressurizing flow and close the He-4-III weak relief.

A.10.2 Purge He-4-I & II with Helium Gas

Same as N2 purging, just replace the N2 gas with helium gas.

Really have to make sure the capillary tube between I&II are thoroughly purged!
A.11 Transferring Liquid Helium into He-4-I & II for the First Time after Precooling

Transferring LHe into the system after precooling is not that different from ordinary transferring. The differences are 1. We transfer with needle valve between I &II open and 2. WE GO SLOW.

1) Make sure we have 650L+ of LHe on hand.

2) Make all relief valves at low setting.

3) Check needle valve between I&II is open 5 turns.

4) Engage the transfer line properly and start the transfer. Use lower pressure for the portable Dewar to reduce the transfer speed. Fully insert the transfer line to block helium flow if needed.

5) Adjust the pressure in He-4-I by manipulating the relief valves configuration to have good helium flow keep flushing into He-4-II.

6) Check CF6 and RSM value to see if there is liquid accumulate.

7) If there is liquid already, turn-on level meter and measure the level.

8) Stop transferring when I&II are full.
A.12 Transferring Liquid Helium into He-4-III for the First Time after Precooling

Again, it is not that different, go slow, and making sure the 1K-Pot is properly flushed with helium at the beginning of the transfer.

1) The 1K needle valve should be open 3 full turns.

2) 1K exhaust valve should be opened.

3) Engage the transfer line and start transferring. Go slow.

4) Open charcoal cooling valve, He-4-III weak relief, check that gas flushing out of every exhausts.

5) Adjust the 1K and charcoal cooling; keep the cooling balanced between them.

6) When the He-4-III full, the rest of the insert will still take days to cool down, on can try to liquefy He3 to speed up that process.

A.13. Moving the mk-Insert Upstairs and Downstairs

Moving the Insert Upstairs/Downstairs is a somewhat risky operation and is best performed with at least one other person present. The dangers mainly have to do with the Insert getting stuck.
while moving (especially moving downstairs), which is thought to be due to temperature-induced stresses/strains changing the hanging angle of the Insert. In the last several years, some common practices have been established that so far seem to prevent the Insert from getting stuck. These will be described in the procedures below. In summary, the two most important rules are: 1) Do NOT attempt to move the Insert at all while the Superconducting Magnet is energized, and 2) Do NOT attempt to move the Insert downstairs while it is still cold (when He3 Pot is less than, say, 6K).

A.14. Procedure: Move the Insert Upstairs

Once the surface/system of study is ready for experiment, it is time to move the Insert into the Upstairs (high) position. Make sure the scanner is unclamped during this time (it should be)

Preparation for moving the Insert Up:

1) Step up from the surface ~5000 (do not fully step up).

2) Plug in the orange extension cord to the wax heater.

3) Turn on the motor electronics and the motor controller. One person should be positioned downstairs while the other should be upstairs.
4) The upstairs person needs to make sure the He4 III (Insert) recycling bellows is disconnected, the liquefying bellows is free (disconnected and not taped), and the Insert Stinger is free (not taped).

5) The upstairs person turns on the upstairs power supply for the heater. Don’t forget this step!

6) Moving the Insert Up. The downstairs person can then start the motor, moving in the UP direction. During this time the upstairs person needs to monitor the system as the Insert moves upward. Pay special attention to the Pre-Amplifier BNC cable, which can sometimes get caught as the Insert moves. Both persons need to look and listen for unusual sounds or signs of trouble. Use common sense!

7) Eventually the Insert will reach the melted wax and the heated rods will push through until the Insert reaches the preset stopping point. As soon as the Insert stops moving, the upstairs person should notify the downstairs person to stop the motor and turn off the motor controller and electronics.

8) Turn off the heater power supply upstairs and unplug the heater extension cord.

9) Secure the following items upstairs:
   a. Make sure the Insert Stinger is securely taped to the support post with foam padding.
   b. Connect the Liquefier Bellows in preparation for liquefying.
c. Connect the extension to the Insert recycling bellows.

d. Disconnect the two motor control cables. Make sure to loosen only the inner black knob on the Amphenol type connector. Store the cables on the protruding strut by the flow meters.

10) Close the 4K Shutter. Both persons then head downstairs and close the 4K Shutter:

a. One person will operate the feedthrough while the other person will hold the pulley taught with the wobble stick. To get into position, the feedthrough operator needs to retract the wooden platform, climb underneath the STM table (being careful not to bump into the feedthrough itself) then the wobble stick operator secures the wooden platform behind the feedthrough operator. The wobble stick operator then extends the wobble stick and places the closed jaws of the wobble stick into the pulley ring (left side).

b. Once the wobble stick operator is ready, the feedthrough operator then turns the 4K Shutter Feedthrough and the indicator should move upward. During this time the wobble stick operator should apply a gentle downward pressure to keep the cable tight.

c. The feedthrough operator closes the shutter to the indicated position (92-88 mm). During the last several turns, both operators may feel the cable start to loosen somewhat.

d. The wobble stick operator then fully retracts and secures the wobble stick. Finally, let the feedthrough operator out.

11) Isolate and spin down all three Big Turbo Pumps and two of the Small Turbo Pumps:

a. Isolate the front and back of the Main Chamber Big Turbo, the Prep Bottom Big Turbo and the Prep Side Big Turbo. The front should be a gate valve and the back should be right angle valves between the Big Turbos and the Small Turbos that back them.
b. Isolate the front and back of the Prep Bottom Small Turbo and the Prep Top/Load Lock Small Turbo. The Backing Valve for the Prep Bottom Small Turbo is a small diaphragm valve while the Backing Valve for the Prep Top Small Turbo is an In-Line Right Angle Valve.

c. Once all five Turbos have been fully isolated (check carefully), spin down the turbo pumps by pressing STOP on their respective controllers. DO NOT spin down the Main Chamber Small Turbo Pump which is located in the pump room, this is allowed to run at all times.

d. The Big Turbo Pumps spin down relatively quickly, but the Small Turbo Pumps take longer. Eventually, when all pumps are spun down fully (the Big Turbo controllers will indicate “Levitate” and the Small Turbos will have no bars on the speed indicators), turn OFF the controllers using the switches on the backside of each controller. The Big Turbos will “crash” as they stop levitating upon loss of power, this is normal.

12) Once all of the Turbos are spun down and turned off, then turn off the power switch on the Turbo Fan Surge Protector underneath the table where the Main Chamber is located.

13) Carefully unhook the bungee cable holding the lamp to the table and remove/unplug the lamp. Store it somewhere near the tools.

14) Top off He4 I, II and III as needed. Liquefy for at least 2 hours, float the table and finally energize the Superconducting Magnet.
A.15. Procedure: Move the Insert Downstairs and Ending Experiment

When an experiment is finished and you plan to move the Insert back to the Downstairs position, it is important to understand that the He3 Pot must have warmed up (all He3 boiled off). It is possible for the Insert to get stuck while moving down. One way to reduce this possibility is to wait at least 12 hours after the He3 Pot warms up (we typically wait overnight) before attempting to move down. There is a specific region during the downward motion where it typically gets stuck. In this region we usually stop the motor and move the Insert manually by turning the handle upstairs. The region is marked by red color (360-370 mm). See Fig. A.18 for details.

A.15.1 Preparing to Move Downstairs

1) As mentioned above, the He3 Pot must be allowed to fully warm up before attempting to move the Insert down. Wait overnight and do not be impatient with this.

2) While waiting for the He3 Pot to warm up, after de-energizing the Superconducting Magnet, you can clamp the table and start up all 5 Turbo Pumps. Once the Turbos are spun up, open the backing valves of the Small Turbos and then the front valves of the Small Turbos/backing valves of the Big Turbos. Do not open the front valves (gate valves) in front of the Big Turbos until they have been baked overnight.

3) Turn on the Turbo Fan Surge Protector to spin up the cooling fans for the Big Turbos.
4) Set up bake on the Big Turbos. If necessary, also set up bake on the Gas Handling System.

A.15.2 Opening the 4K Shutter

5) Before you can move the Insert down, you must open the 4K Shutter (or else you will crash into the Shutter on your way down). Unlike closing the 4K Shutter, one does not need to pull on the left pulley cable using the wobble stick. There is an electrical contact sensor however that will short once the 4K Shutter is fully open.
   a. Obtain a multi-meter with a sound indicator for low resistance and plug the 2-Prong Banana connector hanging near the main chamber into this multi-meter.
   b. Carefully withdraw the wooden platform for the Main Chamber and use the feedthrough to open the 4K Shutter until the multi-meter beeps, indicating a short.
   c. It’s time to move the mk insert downstairs.

NOTE: Make sure two people are available for this procedure whenever possible.

6) Before moving the Insert, make sure the following items are secure:
   a. The liquefying bellows is disconnected and free (also not taped to the support post).
   b. The insert stinger (offset adapter transfer line for He-4-III) is no longer taped to the support post.
   c. The He4 III (Insert) recycling bellows is disconnected and draped over the guard rail.
   d. Both of the motor cables are plugged in.
e. Use mirror to check and watch the scanner when the insert position is “higher” than 335 mm (Note that the “smaller” the reading in mm, the higher the insert position!!). You will need to remove the mirror to clear out the way for the insert before the red zone. See Fig. A.18

7) Plug in the extension cord to the wax heater power supply.

8) Turn on the motor electronics and ready the motor controller near the main chamber.

9) Obtain a multi-meter with sound indicator for electrical shorts and connect this multi-meter to the downstairs 2-prong banana connector. This is the check if the 4K shutter is fully opened.

10) One person should now head downstairs and one should head upstairs.

a. The downstairs person will operate the motor controller. They also need to use the wobble stick to grab the mirror in the main chamber in order to watch the Insert descending. Note that the shield must be opened (using the rotary feedthrough below the main chamber) and that, in order to move the mirror in and out of the shield opening, it must be turned sideways. Do not drop the mirror! The mirror should be removed around 335 mm.

b. The upstairs person will need to monitor the system upstairs while it moves in order to make sure nothing gets caught/trapped (especially gas tubes, bellows and the pre-amplifier BNC cable). The upstairs person will also need to communicate to the downstairs person when the Insert is approaching the “dangerous zone” (marked in red, 360 mm to 380 mm), so that the upstairs person can manually turn the motor through this region.
c. The He3 should already warm up to 8K or more by now, the person downstairs should use the mirror to watch the position of the scanner, usually, due to thermal expansion, the scanner tends to offset to the right, that is normal. If the offset is too large that you think it may touch the inner wall of Dewar, Pumping 1K-Pot (!!with proper procedure describe in the He3 liquefy section) for few seconds can cause the inset to move toward center, however, changing 1K-Pot temperature too much may increase the chance of insert getting stuck at red zone later.

11) Once both people are in place and everything is ready, the upstairs person needs to turn on the upstairs wax heater power supply and waits 5 minutes for the wax to melt.

12) With the wax melted, the downstairs person can then turn on the motor controller and set the movement to “Down” to begin movement.

13) The downstairs person should watch the mirror carefully. The mirror should be removed at the position around 335mm.

14) Proceed with downward movement. The downstairs person should be watching with the mirror for signs of trouble. It is typical for the insert to be bent to the right (not perfectly centered), but it should never touch the sides or get stuck.

15) Once the upstairs person sees the Insert level near 360 mm, they should immediately tell the downstairs person to stop the motor. At this point, you should already see the end of the scanner (of course, the mirror should already have been removed). With the motor stopped, the
upstairs person then turns the handle clockwise to move the Insert downward. The upstairs person should feel for a sudden resistance in the handle while the downstairs person should watch carefully with eye. People at downstairs should also be able to see symptoms of the insert getting stuck. If it gets stuck, the end of the insert will swing to the left. If it seems to get stuck, move the insert back up out of the danger zone and use the motor to move it back up. Wait another 6 hours or more. If after waiting the Insert gets stuck again, you will need to re-align the Insert. Hopefully this never occurs.

If you have successfully passed through the danger zone:

16) Once out of the danger zone (marked in red), turn on the motor again to continue moving down. Eventually, once the bottom of the Insert is visible from the shield opening (without the mirror), the downstairs person should stop the motor, retract the mirror from the shield and put it back in its storage place, retract the wobble stick and return it to the storage position, and finish the movement using the motor.

17) In principle one may stop first at the clamp position rather than proceeding all the way to the 4K Anchor position. Make sure you turn off all the STM electronics before clamping, turning each module off from above to below (excluding the DSP controller). After clamping the scanner, one can then move the Insert to the scanner position and remove the sample holder in order to place it on the room temperature storage station or the mobile cart.
18) The upstairs person can turn off the wax heater power supply and the downstairs person can unplug the corresponding extension cord.

**A.16 Repositioning Sample in the Scanner.**

Before activate the He3 for experiment, sample should be check with mK-insert is at downstairs position. When sample repositioning with wobble stick is needed at downstairs the steps below should be followed. The most important idea is to reduce the heating on the scanner. Close the shielding when you need more time to adjust the wobble stick.

1) Locate a tungsten tip. We should use tungsten tip to reposition sample holder since it is stronger and easier to handle.

2) Step up the sample holder. We should step up the sample holder to make proper gap between the crystal surface and the tip on the scanner.

3) Turn off the electronics. We should do this with any procedure that could disturb the electrical connection near the scanner to prevent short circuit on high voltage electronics.

4) Make sure the table is clamped. As usual, check that before we touch the chamber.

5) Move the insert up to clamping position.
6) Clamp the scanner.

7) Move the insert down again to proper position for sample manipulation. Find a position that is most comfortable to the operator.

8) Grab the tungsten tip with wobble stick.

9) Carefully use the tungsten tip to manipulate the sample holder. Use the center indentation or the edge of center hole on the sample holder. Do not poke hard on the back of the crystal.

10) Keep in mind, the wobble stick is “red hot” compare with the sample holder. we should minimize the contact between the tip and the sample holder.

11) When the reposition is done. Put tungsten tip back to where it was.

12) Move the mK-insert up to clamping position.

13) Un-clamp the scanner

14) Move mK-insert back down to 4K-anchored position

15) Turn on electronics and start tip approaching.
Table A.1 Useful Information about Each Liquid Helium Reservoir.

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Capacity (LHe L)</th>
<th>LakeShore Display Conversion</th>
<th>Typical Consumption Rate</th>
<th>Typical Refill Rate</th>
<th>Minimum Allowed Level</th>
<th>Maximum Allowed Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>He4 I</td>
<td>200</td>
<td>4.322 L / in</td>
<td>6.5-8.5 in/Day</td>
<td>4 Days</td>
<td>4.5 in</td>
<td>40 in</td>
</tr>
<tr>
<td>He4 II</td>
<td>50</td>
<td>1.608 L / in</td>
<td>2-2.5 in/Day</td>
<td>4-8 Days</td>
<td>6 in**</td>
<td>30 in</td>
</tr>
<tr>
<td>He4 III</td>
<td>10</td>
<td>~ 1 L / in</td>
<td>0.2 in/Hour Upstairs</td>
<td>36-40 Hrs Upstairs, 3-4 Days Downstairs</td>
<td>-3.5 in if liquefying -4.3 in Otherwise</td>
<td>6.5 in</td>
</tr>
<tr>
<td>Hc3 Pot</td>
<td>N/A</td>
<td>N/A</td>
<td>36-48 Hrs</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Fig. A.1 Top View Schematic of He-4-I and He-4-II.

(A) MVC evacuation port (see Fig.A.2)

(B) He-4-I cooling vent (see Fig.A.3).

(C) He-4-II pumping / pressurizing port (see Fig.A.4).

(D) He-4-I vent port/ pressurizing port (see Fig.A.5).

(E) He-4-I liquid helium filling port / where He-4-I transfer line always attached to (see Fig.A.6).

(F) He-4-II cooling vent (see Fig.A.7).

(G) Needle valve between He-4-I and He-4-II (see Fig.A.8).

(H) He-4-I vent port/ pumping port (see Fig.A.9).
Fig. A.2 MVC Pumping Port and Valves.

NW25 Angle valve and NW25 butterfly valve in series, connected to small turbo to pump on main vacuum can (MVC)
Valves to MVC evacuation port
Fig A.3 He-4-I Cooling Vent.

Cooling vent of He-4-I, showing weak and strong relief valve, the weak one is hidden inside the NW25-NW16 reducer and connected in series to the helium recycle line.
To helium recycle line

He-4-I weak relief valve 770 Torr

He-4-I strong relief valve 830 Torr
Picture showing He-4-II pumping and pressurizing port. NW25 angle valve for pumping He-4-II. Barb connector should be connected to high purity gas supply and use the pressurizing valve to control the pressure inside the He-4-II.
To high purity gas

Valve to He-4-II pressurizing port

Valve to He-4-II pumping port
Fig. A.5 He-4-I Vent and Recycle Line Assembly.

Picture of the exhaust port of He-4-I, the 800 Torr rated brass relief valve is hidden inside the NW40 aluminum cross manifold. A string is attached to the relief valve inside. Pull the string with the rotator will force open the relief valve.
D

Safety relief valve

He-4-1 big relief valve
800 Torr
(hidden inside)

To helium recycle line

Force relief rotator
Fig. A.6 He-4-I Pressurizing Assembly and Liquid Helium Inlet Port.

Picture at the bottom shows the pumping port for the vacuum jacket (VJ) of He-4-I transfer line (TL). Since the TL is always inserted into the Dewar, the vacuum jacket can only be pumped when the system is fully warm up.
Fig. A.7 He-4-II Cooling Vent.

Picture shows the front view of He-4-II cooling vent. This is the only gas vent for He-4-II. The weak relief valve is hidden inside the NW25-16 reducer and put in series to the helium recycle line.
Fig. A.8 Needle Valve Between He-4-I and He-4-II.

He-4-II does not have a direct liquid inlet port for refilling helium. The refilling of LHe in He-4-II is done by pushing LHe from He-4-I. This needle valve controls the liquid flow during liquid transfer of He-4-II.
Needle valve He-4-I/ He-4-II
When pumping of He-4-I is needed, connect pump to NW25 port and control the pumping with the angle valve.
Nw25 /To mechanical pump

Valve to He-4-I pumping port
Fig. A.10 Schematic of Ports on mK-Insert.

(I) IVC pumping port

(J) Seal for He3. DO NOT TOUCH IT! Open this seal will vent Helium-3 in the system

(R) Gas reservoir for Helium-3

(K) 1K needle valve

(L) Liquid inlet port for He-4-III. A sideway branch also work as gas vent.

(M) He-4-III transfer line

(N) Inlet of the He-4-III transfer line. An offset transfer line adapter will be attached to here (not shown)

(O) Valve to the pumping port of vacuum jacket of He-4-III transfer line.

(P) 1K-pumping port

(Q) Charcoal cooling vent
Fig. A.11 Picture of Ports on mK-Insert in Detail (#1).
Fig. A.12 Picture of Ports on mK-Insert in Detail (#2).
Fig. A.13 Picture of Ports on mK-Insert in Detail (#3).
Pumping port for vacuum jacket of He-4-III transfer line

Nw25 / To helium recycle line

Normal relief isolation valve

Weak relief isolation valve

branch port also works as gas vent
During normal operation, the pressure in He-4-III can be adjusted by the adjustable relief valve and flow meter. During liquid helium transfer, the normal relief should be isolated by closing the normal relief isolation valve, and the gas should be relief from weak relief valve by open the weak relief isolation valve.
Fig. A.15 Offset Adapter for He-4-III Transfer Line.
Fig. A.16 Insert Flow Manifold (#1).

(a) Inlet assembly of He-4-III inlet, connected to the insert flow manifold via a green Teflon tube.

(b) The “green valve”. This valve is normally closed, open shortly to vent 1K-pumping line after He3 liquefy.

(c) NW25 angle valve for 1K pumping.

(d) He-4-III pressurizing valve.

(e) Barb connector to high purity gas supply.
Fig. A.17 Insert Flow Manifold (#2).

(a) 1K exhaust flow meter and relief valve.

(b) Connection to charcoal cooling vent.

(c) Charcoal cooling vent gas outlet. Connected to charcoal flow meter at front panel downstairs (see Fig. A.19)

(d) Isolation valve for charcoal cooling vent.

(e) Connection to He-4-III branch gas vent. (L). used for pressurizing He-4-III.

(f) By-pass valve. closed this valve can direct the pressurizing flow to the inlet of He-4-III transfer line.

(g) He-4-III pressurizing valve.

(h) The “green valve”.

(i) Isolation valve to 1K vent (close when pump on 1K-Pot).
**Fig. A.18 Red Zone for Insert Moving Down.**

Picture of the ruler on linear translator which indicates insert position. The red zone (360mm-380mm) is where the insert has a high chance of getting stuck after the system warms up from 600mK to 8K. Do not move the insert with motor in the red zone. Instead, use hand crank and move it with care manually.

The 335mm is the suggested position to remove the mirror out of the way of the scanner when it is moving down.
Red Zone: Do not use motor to pass the red zone (360-380 mm).

Remove the mirror at this position (335 mm)
Fig. A.19 Charcoal Cooling Adjustment.

The charcoal cooling can be adjusted by the flow meter at the front computer area. We should use this to maintain pressure in He-4-III around 800-810 Torr.
To helium recycle line

Connected to charcoal cooling line ("c" in Fig.A.17)

Charcoal cooling adjustment knob. Adjust this knob to keep He-4-III pressure around 800-810 Torr during experiment.
Fig. A.20 mK-System Front View (#1).
Fig. A.21 mK-System Front View (#2).
Fig. A.22 mK-System Top Platform for Cryostat Operation.
Fig. A.23 mK-System Left View.
Fig. A.24 mK-System Right View
Fig. A. 25 Helium Re-Liquification System.