

Scanning Tunneling Microscopy and Single Molecule Conductance

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Pre-Lab Reading Assignment

Read Section 18.12 (pg. 627-628) and Section 24.10 (pg. 938-940) in Levine

Introduction

Self-assembled monolayers (SAMs) are ubiquitous to the field of nanotechnology. These systems are composed of a head group that attaches strongly to a gold surface, and an alkyl chain that may or may not contain other functional groups. The alkyl tail groups can range from 1 to over 30 CH₂ units in length. SAMs based on alkanethiols are very well ordered on the molecular scale, and their ease of preparation and robustness lend them to both research and application. Molecular conductance through these chains is of particular interest in the field of nanoscale molecular electronics. Better understanding and quantification of electron transfer within these molecular frameworks will enable more unique and novel applications in the future. Scanning tunneling microscopy (STM) is ideally suited for these types of measurements because it is based on electron tunneling which is very sensitive to small changes in distance between the STM tip and surface and can measure very small surface features including atoms and adsorbed molecules. STM has the capability to both spatially select and make direct electronic measurements of molecules supported on a surface. An example of STM images of a SAM are shown below.

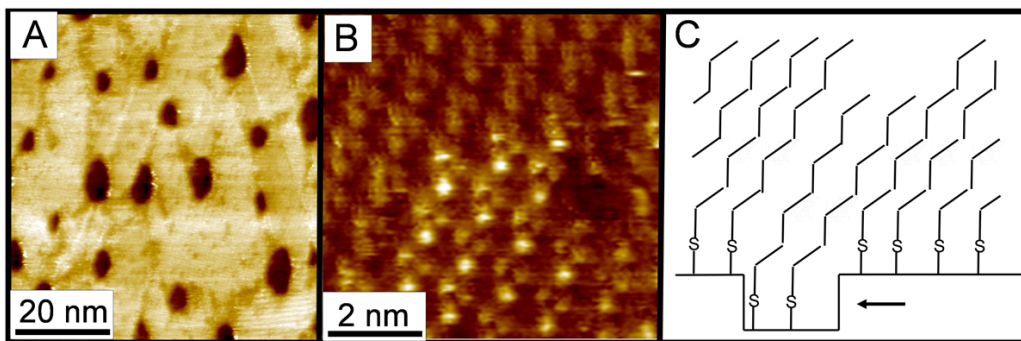


Figure 1A. STM image of a self-assembled monolayer of C₈ thiol which contains an alkyl chain with 8 carbon units and a sulfur head group. The dark ovals in this image are areas where one atomic layer of gold atoms is missing, so-called “etch pits”. **Figure 1B.** In this image it is possible to see the tops of individual C₈ thiol molecules. **Figure 1C.** Schematic showing the ordering of a self-assembled monolayer of C₈ thiol. The lower area highlighted by the arrow represents an etch pit as seen in Figure 1.

This lab focuses on both imaging SAMs with STM and making measurements that reveal both their physical and electronic properties.

Goals

1. To obtain STM images of a SAM.
2. To measure the topographic height difference between a mixed C_8/C_x ($x > 8$) SAM.
3. To calculate the expected height difference between a mixed C_8/C_x ($x > 8$) SAM.
4. To reconcile why these two values are not the same.

Background

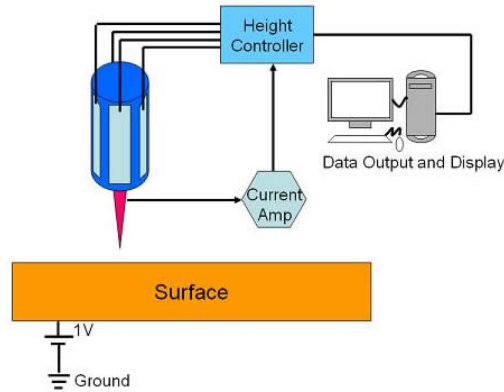


Figure 2. STM schematic. The red triangle is an atomically sharp tip that approaches within 1 nanometer of the surface.

Figure 2 shows the typical layout of a STM. An atomically sharp tip, most commonly made from a cut platinum/iridium or chemically etched tungsten wire, is brought within a nanometer of the surface under investigation [1]. Classically, no current should flow between the tip and the surface as they are not in metallic contact. However, at small tip-surface separations the wavefunctions of the atoms in the surface and the single atom at the very end of the tip overlap and electrons can *tunnel* across the barrier when a voltage is applied between tip and surface [2]. The exponential dependence of the tunneling current I on the distance between the tip and the surface imparts exceptionally high resolution to the technique, i.e. a very small change in surface-tip separation leads to a large change in tunneling current:

$$I \propto \exp(-2\kappa d) \quad (1)$$

where d is the distance between the surface and tip and

$$\kappa^2 = \frac{2m}{\hbar^2}(eV_B - E) \quad (2)$$

where \hbar is Planck's constant ($h/2\pi$), E is the energy of the state from which tunneling occurs, and eV_B is the barrier height.

The STM tip is mounted on a piezoelectric tube scanner. Piezoelectric materials are unique in that when a voltage is applied across them, they expand or contract. The piezoelectric tube is most often built in three parts such that the application of voltages to each part individually gives the possibility of very accurate movement in the x, y, and z directions [2].

A more detailed explanation of electron tunneling involves looking at the Fermi energies (the energy of the highest occupied electronic state) of the tip and the surface [1]. When the tip and the surface are brought close together but are not connected electrically, the offset in the Fermi energies of the sample, E_F^S , and tip, E_F^T , is equal to the difference in the work functions ($\Delta\phi$) of the two metals.

$$\Delta\phi = E_F^S - E_F^T \quad (3)$$

The following figure illustrates how a current can flow between the tip and the surface when a potential difference is applied between the two. In Figure 3 the sample is biased positively with respect to the tip. This lowers the Fermi energy of the sample by eV , where e is the elemental charge and V is the potential difference. The occupied states of the tip now lie at the same energy as some of the unoccupied states of the sample, and thus electron transfer will occur from the tip to the sample since the unoccupied states of the sample are at a lower energy [1].

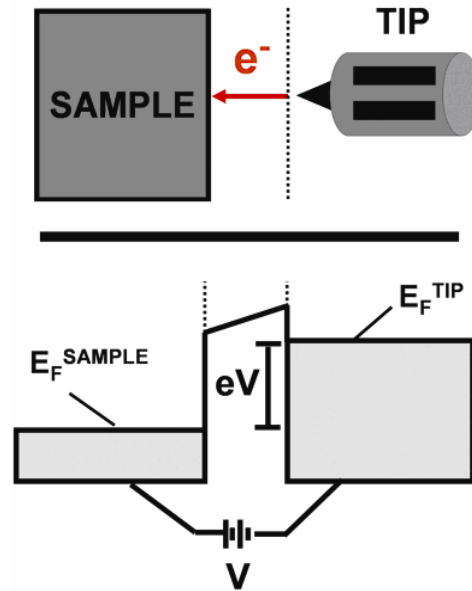


Figure 3. Illustration of the electronic energy levels of the tip and sample and electron tunneling across the barrier. The right hand side of the schematic shows the energy level of electrons in the tip and the left shows those of the electrons in the sample.

STM imaging is commonly performed in two modes of operation. In *constant height mode* the tip is scanned across the surface in the xy-plane of the surface without any adjustment of the z-piezo [2]. Since the tunneling current is dependent on the distance between the tip and the surface, variations in the tunneling current are recorded

and a current image is displayed. Features in this image can be correlated with either the topography or electronic structure of the surface. While images can be acquired very fast in this mode it is rarely used as scanning over any surface features larger than the tip-sample distance will lead to a tip “crash” in which the atomically sharp tip is lost. In *constant current mode* the tunneling current is kept constant by a feedback loop that continually adjusts the tip height using the z-piezo. An image is generated by plotting the z-piezo height versus lateral position and contains information about both sample topography and electronic structure. The corresponding current image will be featureless, as the tunneling current in this mode is always constant.

The height of a molecule as measured by the STM, h_{STM} , is typically not the same as the actual physical height of the molecule, h_{film} , because the tip-sample interaction combines both physical and electronic properties of the surface. When imaging a SAM, the tip hovers just above the film (SAM), meaning that the STM tip does not penetrate into the monolayer (see Figure 4), thus creating two distinct regions: the vacuum gap (d_{gap}) and the actual film or SAM (h_{film}). The transconductance (reciprocal resistance) of the tip-film gap (G_{gap}) is adjustable and depends on the separation between the tip and the SAM, d_{gap} . This separation is controlled by the STM. While scanning in the constant-current mode, the imaged topography includes height contributions from both the film and the tip-film gap since the tip does not touch the top of the SAM.

$$h_{STM} = h_{film} + d_{gap} \quad (4)$$

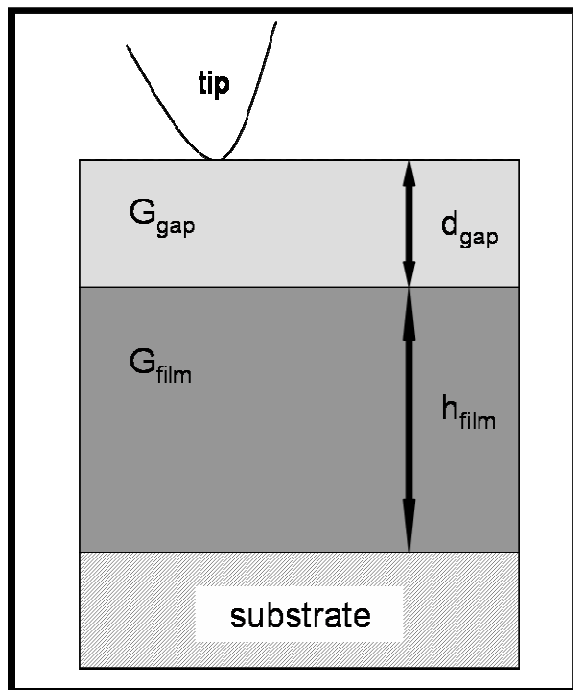


Figure 4. Schematic showing how imaging of a SAM involves electron tunneling through two distinct layers: the vacuum gap and the film. Each region has its own transconductance ($G = I/Resistance$), which depends on the physical thickness of the layer.

In this lab, a two-component SAM comprised of regions of a C_8 SAM intermixed in regions of a C_x SAM, which is longer than the C_8 component, will be used for measurements. The transconductance of a molecule decreases exponentially with increasing length, as increasing length results in the molecule becoming more insulating. As the STM scans from a region of the SAM that contains alkyl chains with eight carbons to a region in which the chains contain more carbons, h_{film} increases by a distance of x CH_2 units (Each CH_2 unit is 1.1 \AA in length.) while the transconductance decreases, since the longer chain is more insulating. In order to compensate for this decrease in measured tunneling current, the STM decreases d_{gap} by some amount to increase the tip-film gap transconductance (G_{gap}), which allows for a constant overall transconductance. This is explained visually in Figure 5.

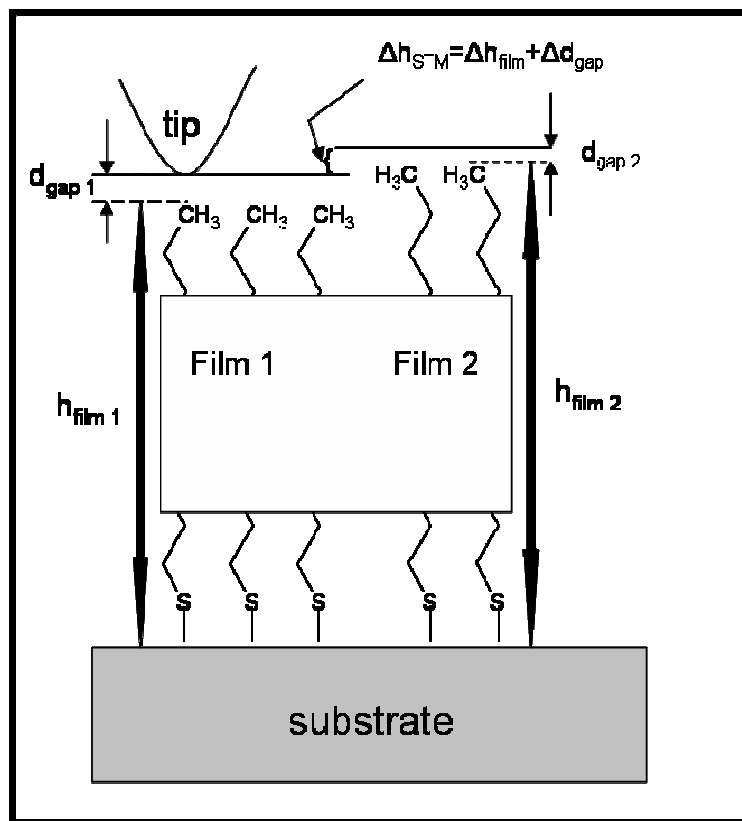


Figure 5. Schematic showing the STM tip trajectory over a multi-component SAM and how differences in chain lengths are compensated for by changes in the tip-film gap, d_{gap} , to maintain a constant overall current.

The relationship between the physical height as measured by the STM and the actual height difference between two SAM regions with different alkyl chain lengths can also be explained through various quantum mechanical equations. As stated previously, the tunneling current used by the STM to image is exponentially related to the tip-substrate separation. The tunneling current is related to resistance according to Ohm's Law ($V = IR$) and transconductance (G) is reciprocal resistance ($G = 1/R$). Thus, it can be derived that G is also exponentially related to the tip-substrate separation. The tip-

substrate separation can be broken down into two portions as represented in Figure 4. The transconductance of these two regions can then be described as:

$$\text{vacuum gap: } G_{gap} = Ae^{-\alpha d_{gap}} \quad (5)$$

$$\text{film: } G_{film} = Be^{-\beta h_{film}} \quad (6)$$

where α and β are decay constants and A and B are contact conductances. The transconductance of the system is the product of the two individual transconductances.

$$G_{tot} = G_{film} \times G_{gap} \quad (7)$$

Taking into account Ohm's Law and the fact that images are produced in constant current mode, G_{tot} is constant over the image, regardless of the presence of different chain lengths in the SAMs.

$$G_{tot} = G_{film1}G_{gap1} = G_{film2}G_{gap2} \quad (8)$$

According to Ohm's Law and the fact that transconductance is reciprocal resistance,

$$G_{tot} = I/V \quad (9)$$

As stated previously, the height measured by the STM contains contributions from both the film and the tip-film gap (see equation 4). Since STM does not directly measure h_{STM} , but rather the change in height between two different films, Δh_{STM} , the following is true:

$$\Delta h_{STM} = h_{STM2} - h_{STM1} \quad (10)$$

where h_{STM1} represents the height of the C_8 SAM film and h_{STM2} represents the height of the C_x SAM film. According to equation 4,

$$\Delta h_{STM} = (h_{film2} + d_{gap2}) - (h_{film1} + d_{gap1}) = \Delta h_{film} + \Delta d_{gap} \quad (11)$$

It is now possible to make some approximations that make the math easier to solve. Since the characteristics of the vacuum gap do not change significantly from C_8 chains to C_x chains, the vacuum decay constants (from equations 5 and 6) can be set equal to each other, $\alpha_1 \approx \alpha_2$ and $\beta_1 \approx \beta_2$. The same is true of the contact conductances ($A_1 = A_2$). With these assumptions and some algebraic manipulation, the following equation can be derived:

$$\Delta h_{STM} = \Delta h_{film} (1 - \beta / \alpha) + (1 / \alpha) \ln(B_2 / B_1) \quad (12)$$

Since it can also be approximated that $B_1 = B_2$, as C_8 is quite similar to C_x , the last term can be neglected to obtain,

$$\Delta h_{STM} = \Delta h_{film} (1 - \beta / \alpha) \quad (13)$$

According to theory, the values for α and β are 1.2 \AA^{-1} and 2.3 \AA^{-1} [4], respectively. It is therefore possible to say,

$$\Delta h_{STM} = 0.5 \Delta h_{film} \quad (14)$$

Thus, a mathematical relationship between the measured height differences and the actual height differences of two thiol molecules can be obtained.

Procedure

List of Chemicals

None

List of Materials

- Au substrate with coadsorbed C_8/C_x SAM which has been attached to a metal plate
- Pt/Ir wire
- Tweezers
- Wire cutters (to make the end of the tip atomically sharp)

Instructions

1. Preparing the STM tip
 - a. Hold the end of the Pt/Ir wire firmly with the tweezers.
 - b. At an angle of 45° with respect to the wire, close the fine wire cutter until you can feel the wire, but **do not** cut the wire.
 - c. In order to prepare an atomically sharp tip, as you close the wire cutters pull up at an angle with the cutters. Listen for a clean snap sound, which tends to indicate a good cut.

Do not touch the end of the tip with anything!!! Ensure the tip wire is straight.

2. Mounting the tip in the STM
 - a. Place the tip wire into the tip holder parallel to the groove in the holder so that it crosses below the tip clamp.
 - b. Move the tip wire sideways until it is in the groove in the tip holder.

The tip should be securely held under the clamp and extend approximately 2-3 mm beyond the tip holder.

3. Installing the sample into the STM

a. Place the prepared Au sample onto the magnetic end of the sample holder using a pair of tweezers.

b. Clean the sample holder with a Kimwipe to remove any fingerprints or contamination that may be on the holder. It is now important that you do not touch the metal part of the sample holder with your fingers. Put the sample holder **carefully** in the scan head so that it does not touch the tip. Be careful that the sample is not pulled from the sample holder by the magnet that holds the sample holder in place.

c. Place the sample holder down on the sample holder guide bars and carefully push it towards the tip without crashing the sample into the tip.

d. Using the magnifying glass on the STM cover, make sure that the sample is close to the tip (~1 mm), but not touching.

4. Entering the parameters in the control panels

a. If the software is not loaded, double click on the EasyScan icon on the desktop.

b. Click the icon with a crank to open the Z-Controller panel. Activate the appropriate parameter by clicking it with the mouse pointer.

c. The set-point should be set to 0.02 nA .

d. The tip voltage should be set to 1.0 V.

e. The P gain should be set to 10,000. The I gain should be set to 1,000.

5. Approaching the tip to the sample

a. The piezo motor is operated using the Approach Panel in the Positioning window. Click the Positioning icon (box with 4 arrows).

b. Watch the distance between the tip and sample with the help of the magnifier on the STM cover. Click the advance icon in the Approach Panel to move the sample towards the tip to a distance of a fraction of a millimeter. This is the manual operation of the piezo.

You should just be able to see the gap between the tip and its mirror image in the magnifier.

c. For the final approach, the tip approaches the sample until the set point is reached. Check that the parameter settings are correct and then click the approach icon in the Approach Panel.

d. If the approach was finished successfully, the message box 'Approach done' appears. Click the 'OK'-button.

If the probe status as indicated by a light on the STM controller turns from green to red, then the tip has crashed into the sample. Click the withdrawal icon to remove the tip and reapproach. If the tip does not approach after 20 sec, try to decrease the tip-sample distance a little more with the manual operation of the piezo motor.

6. Collecting images

a. Once the tip has approached the sample, imaging of the sample immediately begins. Click the tip icon to open the Imaging window. If the image appears black, then the tip has false approached. If this occurs, click the stop icon in the imaging tool bar and click the approach icon again.

b. If the preparation of the tip and sample and the approach was successful, images will show a more or less straight line in the Line Graph and a plane in the Color map.

c. A line that jumps around in the Line graph indicates an unstable tunneling current. Usually this is caused by the tip being too blunt or instable. If this is the case, then you should stop scanning and cut a new tip.

d. To stop the scan, click the 'Stop' icon in the imaging tool bar. Then click the 'Withdraw' icon in the approach panel. Carefully, take the sample holder out of the STM. To remove the tip, move the tip parallel to the clamp with the tweezers without touching the end of the tip. Then, cut the end of the tip as explained above.

An example of what type of image to expect can be seen below. The arrow indicates a transition between a C_8 and C_x SAM.

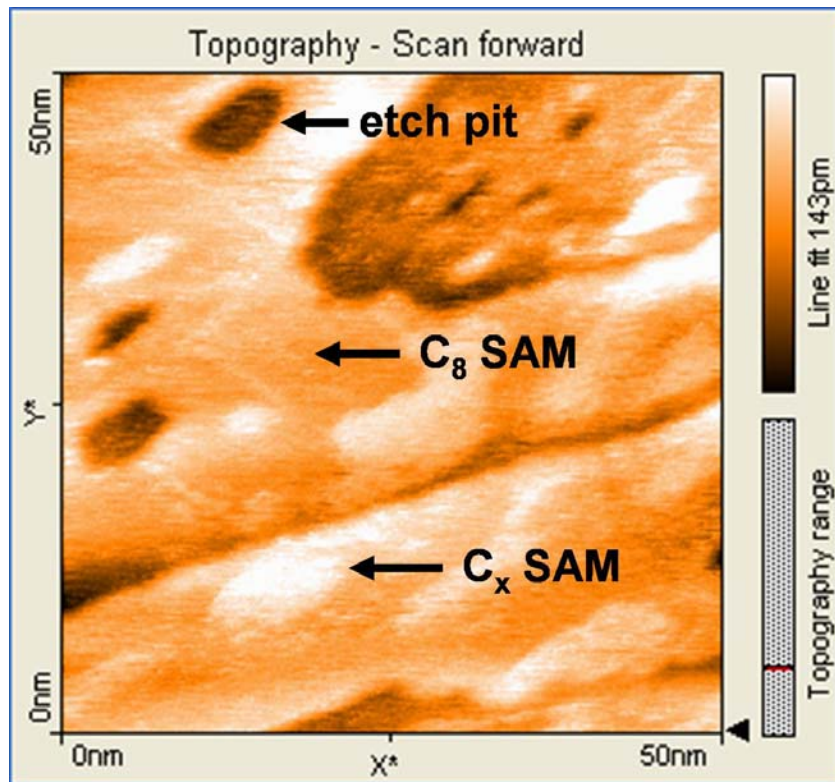


Figure 6. STM image of a coadsorbed C_8/C_x SAM.

d. In order to obtain the best image possible, it is necessary to change the gain values which change how fast the tip responds to changes in the surface. To begin with, try $P = 10,000$ and $I = 1,000$. After initial imaging, change these values up and down to

optimize image quality. If the image is too grainy or pixilated, bring both gain values down. If the image is too streaky or undefined, increase both gain values. The proportional gain (P-gain) should be larger than the integral gain (I-gain) by a factor of 10.

e. You may also want to slightly change the values for the setpoint and tip voltage to optimize image quality.

7. Changing the scan size

a. Scan size is controlled by the Imaging Panel. To change the scan size, type the desired size into the Image width box. To begin with, start with an image size of 250 x 250 nm² and work down to a size of 25 x 25 nm².

b. A good scan size to record height measurements would be 50 x 50 nm² or 25 x 25 nm².

8. Moving around on the sample

a. It is helpful to move around on the sample if good images do not appear after the initial approach of the tip. It is also a good idea when taking measurements to get a measurement from different areas of the surface in order to see if the measured values are truly representative of the entire surface.

b. The 'Move' icon in the imaging tool bar moves the position of the imaged area. The change in position is indicated by an arrow. The start of the arrow is defined by the mouse cursor position where the left mouse button is clicked, and the end of the arrow by the position where the button is released. The image is moved by double clicking in the scan area.

9. Recording an image in order to take measurements

a. Click the icon with the word 'Photo' in the imaging tool bar. If the button is clicked when a scan is in progress, the image will be generated in a separate window when the scan is finished. During the scan, the button should remain pressed.

b. Once the image has been recorded, click on the icon a second time to stop the capture process.

c. Record ~5 images at different areas of the surface.

10. Collecting height measurements

a. After recording ~5 images, perform the following measurements.

b. Open the Tool Results panel by clicking on the icon with an image of a pocket knife.

c. Click on the icon with a curved line displayed relative to two axes in the imaging tool bar; this is the icon to create a cross section of a particular area on the surface. The line is displayed in Tool Results panel.

d. The line is defined by drawing an arrow. The start of the arrow is created by the mouse cursor position where the left mouse button is clicked, then end of the arrow by the position where the button is released. The cross section is displayed by double clicking in the image.

e. Click on the icon that displays the letter “D” next to an arrow separated by two lines in the imaging tool bar. This icon is used to measure the distance between two parallel lines. The result of the measurement is displayed in the Tool Results panel.

f. The distance (height) is measured by drawing two lines on the graph displaying the cross section. The first point of the first line is defined by the mouse cursor position where the left mouse button is clicked, and the second point position is determined when the button is released. After releasing the mouse button, a second parallel line sticks to the mouse cursor, which is positioned by clicking in the desired location. The direction of the parallel lines can be adjusted by dragging their end markers, and they can be moved by dragging the center marker. The distance is displayed in the Tool Status window.

g. An example of where to place the lines on the image is displayed below. Notice that you should not place the lines at the extreme high or low points of the line scan, but in the middle in an effort to avoid measuring noise rather than actual surface features.

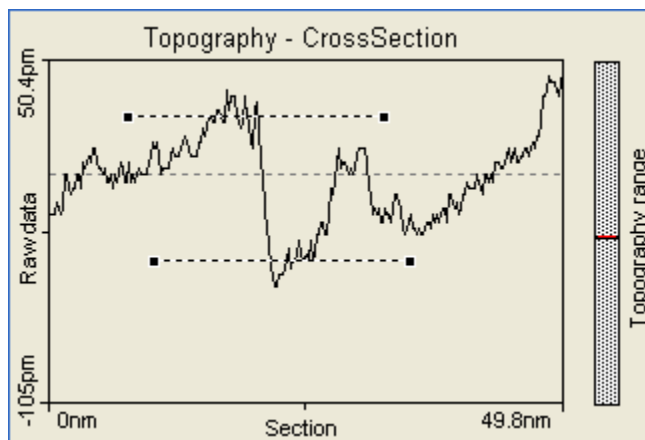


Figure 7. A line scan of the surface showing where to place the lines to take a height measurement.

11. Calibrate measurements

Because every STM scanner measures surface features slightly differently, it is necessary to calibrate the scanner in the z-direction. This can easily be done by measuring certain surface features of known height with the STM and comparing those measured values to the known values. For this lab, we will compare the measured values for the height of Au steps on the surface to their known values. The height of a Au step is 0.235 nm.

- Using the above instructions, determine the heights of Au steps on the surface.
- Create an excel table with these measurements.
- After moving around on the sample and recording height measurements (~5) in a variety of areas, find the average value and standard deviation for these heights.
- The gain, which corrects for the errors in the scanner, is calculated as follows:

$$Gain = \frac{\text{known height}}{\text{measured height}}$$

- This calculated gain should be used for the subsequent measurements.

12. Collect data

a. Record the measured height difference between a C₈ SAM and a C_x SAM. Get ~5 measurements, and using excel find the average and standard deviation for these data points. (Don't forget to use the gain calculated in the previous step to obtain the STM height difference.)

Questions

1. What is the topographic height difference between a C₈/C_x SAM as measured by the STM?
2. What is the expected height difference between a C₈/C_x SAM based on the actual physical height difference of the molecules?
3. How can the difference between these values be explained?
4. How many carbons are in the C_x SAM?

Fundamental scientific questions

1. How is it possible for electrons to move from the tip to the substrate if they are not in physical contact?
2. Why does the tip have to be atomically sharp?
3. What other systems can be imaged using STM?

References

- [1] K. W. Kolasinski, *Surface Science: Foundations of Catalysis and Nanoscience*, John Wiley & Sons, West Sussex (2004).
- [2] G. Attard and C. Barnes, *Surfaces*, Oxford University Press, New York (2004).
- [3] L.A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara and P. S. Weiss, *J. Phys. Chem. B* **103**, 8122 (1999).
- [4] M. Salmeron, G. Neubauer, A. Folch, M. Tomitori, D. F. Ogletree, and P. Sautet. *Langmuir* **9**, 3600 (1993).