Lateral Force Needed to Move a Molecule on a Surface

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Sushila Kumari Khadka

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This thesis titled
Lateral Force Needed to Move a Molecule on a Surface

by
SUSHILA KUMARI KHADKA

has been approved for
the Department of Physics and Astronomy
and the College of Arts and Sciences by

Saw Wai Hla
Professor of Physics and Astronomy

Robert Frank
Dean, College of Arts and Sciences
Abstract

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Lateral Force Needed to Move a Molecule on a Surface

Director of Thesis: Saw Wai Hla

Diffusion processes of atoms and molecules on surfaces are vital for the formation of thin films. This thesis is devoted to the data analysis of the molecular manipulation experiments to compare lateral forces required to move a sexiphenyl molecule on a Ag (111) surface in two different directions; along the long molecular axis and along the sideways directions of the molecular axis. By finding the force angles as functions of lateral distances from the manipulation signals, the fit parameters of a Morse potential between the tip-apex atom and the sexihenyl molecule is determined. Comparison between the lateral forces to move the sexiphenyl along two surface close-packed directions reveals the preferential diffusion direction of the molecule as along its long molecular axis. This finding provides an important basis for understanding molecular diffusion processes on surfaces.
I would like to dedicate this work to my husband and family members who encouraged me for the higher education.
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Chapter 1- Introduction

1.1 Background of Instrumentation

This thesis is contributed to analyzing the data taken in nano science lab of Ohio University by Prof. Saw W. Hla. The data is based on the lateral manipulation of Sexiphenyl molecule on Silver Substrate using STM tip. The analysis of the data is done with the purpose of understanding the manipulation processes and lateral forces required to move a molecule along different directions on Ag (111) surface.

As we know, new technology has always stimulated researchers to put innovative ideas to replace complex devices with a simpler one. As a consequence, in a few decades the discoveries of transistors, light emitting diodes etc. have taken technology to a new level. The organic light emitting diodes have made it possible to design the most efficient devices with the cutting edge research in nano science. Moreover, the blue light emission diode that awarded a noble prize for physics in 2014 has provided scientists a new vision to develop research areas in organic semiconductors as well. So, nanotechnology is emerging on developing organic devices that are lighter, have flexible displays, and are low cost [1, 2]. In this thesis, the study of various features of sexiphenyl molecule to move on a substrate, gives a new dimension in understanding and fabrication of better organic electronic devices in thin film process.

For the analysis work performed in this thesis, it is essential to understand the experimental technique used in imaging and manipulation of individual molecules on surfaces which is explained below.
1.1.1 Brief History of STM (Scanning Tunneling Microscopy)

The STM was first introduced by Binning, Rohrer, Gerber and Weibel in 1983 [3, 4] who used it to obtain an atomic resolution of Silicon (111) surface. Ever since then, this instrument has been an essential tool for nano and atomic scale surface imaging, local tunneling spectroscopic measurements, and determining surface electronic structures of various conducting materials [5]. With advancements in STM, researchers can now image adsorbates on surfaces such as individual atoms, organic molecules, and even biological molecules such as DNA with atomic or sub-molecular resolutions [5, 6]. In addition, the STM can be used as a tool to manipulate individual atoms and molecules adsorbed on surfaces and thus making it a nano engineering tool as well [7, 8].

1.1.2 Operation of STM

An STM consists of an atomically sharp probing tip made up with a conducting material such as Tungsten (W). The tip is connected to a piezo drive. The piezo drive can have three mutually perpendicular piezoelectric transducers, i.e. piezo-x, piezo-y and piezo-z, to monitor the movement of the tip along the respective directions as shown in Fig.1.
The piezo drive moves in specified directions by the contraction and expansion of the piezo tube with the application of a voltage. For quantum tunneling in STM, tip and surface are essential to be less than 1 nm apart. Electrons tunneling between the tip and sample produce a tunneling current when a bias voltage is provided.

The tunneling current needs to be amplified and converted into a voltage. The current is then compared to a reference value. The z-piezo moves up and down depending on whether the tunneling current is greater or smaller than the reference value. This process, known as the STM feedback loop, controls the signal in STM and it is also used by the data acquisition system to produce an image of a surface. The STM components should be made as rigid as possible to reduce mechanical vibration which is improved by additional vibration isolation such as pneumatic suspensions.
1.1.3 Quantum Tunneling in STM

Quantum mechanically, a particle is considered to have a dual nature; as a particle and a wave [9]. A potential barrier is formed by a vacuum gap between two metal surfaces. Classically, the electrons cannot tunnel through the barrier. However, according to quantum mechanics, there is a probability of finding the particle on the other side of the potential barrier if the width of the barrier is small enough. Fig.2 illustrates the tunneling process in an STM.

\[ \frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} (U - E) \psi(x) = 0 \]  

\[ \psi(x) = Ae^{kx} + Be^{-kx} \]

*Figure 2: One dimensional quantum tunneling in vacuum.*

The barrier has a potential of “U” and the energy of electrons is “E”, where E<U.

The Schrodinger equation in the vacuum region (rectangular barrier) is written as [10]:
where, $k = \sqrt{\frac{2m(U-E)}{\hbar^2}}$ is the decay constant. Considering the exponential decay for positive x-direction only, $\psi(x) = Be^{-kx}$ and at $x=0$, $\psi(0) = Be^{-k \cdot 0}$ which gives $B = \psi(0)$. Therefore we can write $\psi(x) = \psi(0)e^{-kx}$.

Now the probability density of finding a particle at any distance $x$ in the potential barrier is

$$|\psi(x)|^2 = |\psi(0)|^2 e^{-2kx} \quad (3)$$

At $x=d$,

$$|\psi(d)|^2 = |\psi(0)|^2 e^{-2kd} \quad (4)$$

The work function for a metal is, $W = E_{vacuum} - E_f \quad (5)$

![Diagram](image)

*Figure 3: Work function for metal.*

Here, $E_f$ is the Fermi Energy of the surface and $E_{vacuum}$ is the energy of the vacuum level. For this case, the vacuum level in considered to be the height of the potential barrier or the gap between the two metal surfaces. If we consider the vacuum level as the reference level (i.e.$E_{vacuum} = 0$), then the work function can be written as,
$W=-E_f$. The work functions for all the metals have predetermined values, such as alkali metals have work function values from 2-3 eV [11].

Initially, the sample and the tip are considered to be in the same Fermi level resulting in no electron flow from the tip to the sample and vice versa. When a bias voltage is applied between the tip and the sample, the Fermi level is changed, i.e. either raised or lowered. For a positive bias polarity of the sample, $V_{bias} > 0$, the Fermi level of the tip attains a higher position and electrons tunnel from the tip to the sample. For $V_{bias} < 0$, the process is reversed.

In this experiment, the tip is in floating ground and the sample has been provided with $+V_{bias}$ so that the tunneling of electrons is from the tip to the sample. Consider the sample states $\psi_n(x)$ with energy level $E_n$ are located between $E_f$ and $E_f - eV$. For the case, $eV<<W$, the electrons having the energy close to the fermi level are taken into account. Then, 

$$W \approx E_n$$

And

$$k = \frac{\sqrt{2mW}}{\hbar}$$

Now the tunneling current is directly proportional to the number of states on the surface of sample.

$$I \propto \sum_{E_n=E_f-eV}^{E_f} |\psi_n(0)|^2 e^{-2kd}$$

(6)

### 1.1.3.1 Local Density of States (LDOS)

The number of electrons per unit energy per unit volume known as the density of states of the sample influences induction of tunneling current. It is defined for sample surface at $x=0$ as [3]:

$$D(0,E) = \frac{1}{eV} \sum_{E_n=E_f-eV}^{E_f} |\psi_n(0)|^2$$

(7)
\[ D(0, E) \times eV = \sum_{E_n=E_f-eV}^{E_f} |\psi_n(0)|^2 \] (8)

From equations (6) and (8),

\[ I \propto eV D(0, E) e^{-2kd} \] (9)

Equation (9) shows that the tunneling current decays exponentially with the increase in vacuum gap between two metal surfaces.

1.2 Background of the Materials Used

1.2.1 Silver Substrate

We use a single crystal silver substrate, Ag (111), in the current measurements. Silver is a transition metal and has an electronic configuration [Kr].4d\textsuperscript{10}5s\textsuperscript{1}. It has an FCC crystal structure, and the (111) plane in the FCC crystal of silver forms a closed pack structure as shown in Fig. 4(a). The hexagonal closed packed structure in the (111) plane has three closed packed row directions, [110], [101] and [011], and they are oriented at every 60° with respect to each other Fig.4 (b).

![Figure 4: a) (111) plane in fcc silver crystal, b) directions in hexagonal closed packed structure.](image-url)
1.2.2 Sexiphenyl

Sexiphenyl \((\text{C}_{36}\text{H}_{26})\) is an organic molecule which has a linear chain shape formed by connecting 6 \(\pi\) rings \([12]\) and it is \(\sim 2.79\) nm long. The electrons from the \(\pi\) bonding in alternate carbon atoms form a ring shaped pattern in this aromatic molecule which is shown in Fig. 5. Sexiphenyl molecule is weakly adsorbed on the Ag (111) surface and due to steric repulsion, every alternate \(\pi\) rings of the molecule is twisted. In case of a free standing molecule, the twisting angle between the two nearest \(\pi\)-rings can be over 40 degrees \([13]\). On Ag (111) surface, however, the alternate \(\pi\)-rings are still twisted but the twisting angle is reduced to \(\sim 11\) degrees \([14]\) due to adsorption to the substrate. The molecule adsorbs on the surface due to weak potential barriers or the surface force however no chemical bonding with the surface molecules have been observed. Fig. 5 presents the molecular structure of Sexiphenyl molecule where the rings are connected by carbon- carbon sigma bonding.

\[\text{Figure 5: Molecular structure of sexiphenyl.}\]
Organic materials are popular to be used as flexible electronic devices. Moreover, the process for the device fabrication is also cheaper than their inorganic counter parts, which motivates the wide use of organic molecules in electronic devices such as photovoltaic cells, light-emitting diodes, lasers, field effect transistors and also in organic integrated circuits [15]. Sexiphenyl is a wide band gap organic semiconductor, and therefore has possible applications in opto-electronic devices such as organic field effect transistors, solar cells and also in light emitting diodes [16, 17].

Almost all the organic electronic devices formed by molecular films, can be grown using various techniques such as Vapor Deposition Process (VDP), Molecular Beam Epitaxy (MBE), Chemical Deposition Process (CDP) and so forth [18]. Unlike inorganic materials, organic molecules may not have chemical bonding between the molecules in the films, thereby requiring only the physisorbed process (less strongly bound to the surface) for the epitaxy growth [19]. The study of organic semiconducting molecular alignment and their features on a metal is useful to check the efficiency of charge transfer in electronic devices as well [20].

This study is based on realizing the features of a sexiphenyl molecule movement on Ag (111) surface at liquid Nitrogen temperature. The fundamental idea derived at this low temperature provides an idea about how the different parameters can be controlled for the fabrication of electronic devices at room temperature.
1.3 Background of Mechanical Processes

1.3.1 Diffusion

The process of movement of atoms or molecules on a surface is known as diffusion. The diffusion process is fundamental for thin film formation and it controls the quality of the film grown. Fig.6 describes the movement of an atom along various regions on a substrate.

The energy associated with diffusion along terrace, step, kink, 1D, 2D and 3D barrier varies depending on the forces required to move the atom on those areas. These diffusion barriers at the step edge are termed as Ehrlich Schwoebel Barriers [21].

![Figure 6: Atom movement along various landscapes of a substrate surface.](image)

Basically, during a thin film formation, molecules or atoms emitted from the source impinge on the substrate surface first and undergo diffusion processes resulting in formation of deposited layers ranging from a few nanometers to micrometers thick films.
The quality of thin films cannot be controlled unless the physics behind how the molecules tend to align on the surface and how they diffuse is known. Unlike inorganic materials growth, which involves diffusion of individual atoms on surface, the diffusion processes of molecules on surfaces are not known. Unlike single atoms, which have roughly symmetric round shapes, molecules have asymmetric shapes and thus sophisticated diffusion processes may be involved in their diffusion. Moreover, the molecules are formed by multiple atoms and they can conform different structures based on the surface geometry underneath. This further complicates the diffusion processes of the molecules as well. To investigate diffusion processes of a long molecule on a two dimensionally symmetric surface, we choose sexiphenyl adsorbed on Ag (111) as an archetype.

In this thesis, we perform a qualitative analysis on how much force is required to move a single sexiphenyl molecule on an Ag (111) surface. Since the growth of thin film is highly dependent on the diffusion processes along different directions on substrate as well as orientation and ordering of the molecules on the surface, this study provides single molecule diffusion processes at the ultimate atomic limit for the first time.

1.3.2 Morse Potential

One of the handy models to study the interatomic interaction of diatomic molecule is Morse Potential. This is also of practical use to study the potential energy between an atom and a surface. The expression for the Morse Potential can be written as [22]:

$$U(r) = D_e \left[ 1 - e^{-\beta(r-r_e)} \right]^{2}$$

(10)
Where \( r = r_t - r_e \) is the tip-atom distance; \( r_t \) is the total distance between the atoms from their center, while \( r_e \) is the equilibrium bond distance; ‘\( D_e \)’ is the potential well depth, which is related to dissociation energy (or binding energy), and ‘\( \beta \)’ is the parameter that controls the width of the potential well. The Morse potential due to tip-atom interaction is shown in Fig.7

\[ U(r) = A\left(1 - e^{-Br}\right)^2 \]  (11)

By expanding the above equation,

\[ U(r) = A + Ae^{-2Br} - 2Ae^{-Br} \]  (12)
Here the second term is considered to be a short range potential called repulsive potential and the last term is a long range potential, which is attractive. The attraction between the atoms is observed at long range of distance whereas the repulsion between the two atoms is defined for a short distance only. This attractive part of potential is mainly used for atom and molecule manipulation experiments.

In our experiment, the Morse potential arises only from the tip-molecule distance. This potential energy has no association with lateral manipulation of the molecule. At a very close tip-atom distances, i.e. less than an atomic distance (< 3Å), the interaction between the tip apex atom and the manipulated atom on the surface become dominant over the background surface and the tip. Then a two-atom potential can be assumed. The total force due to the tip-molecule interaction at the distance ‘r’ is obtained from the equation,

\[ F = -\frac{dU}{dr} \]

The force of interaction is inversely proportional to the tip-molecule distance, and it can be obtained from the slope of the Morse potential curve.
2.1 Atom Manipulation Processes on a Surface

The STM tip can be used to manipulate atoms and molecules for the construction of quantum structures, to understand their movements on various conducting surfaces, and for the study of electronic and dynamical properties of atoms and molecules on a substrate [23]. This is done by manipulating atoms and molecules one by one using the STM tip. There are mainly two schemes for atom manipulation; lateral and vertical manipulations [24].

2.1.1 Lateral Manipulation

In this process, the atoms or molecules are moved parallel to the surface, which involves three experimental steps; moving the tip towards the atom or molecule, lateral motion of the tip along the surface, and withdrawal of the tip back to the image height. Fig. 8 shows this process.

![Figure 8: Lateral Manipulation of an atom by STM tip.](image)
As the tip is brought near to the sample, it increases the interaction force between tip and the surface atom, which we will label from now on as the ‘total force’, $F_T$. When the force required for manipulating atom due to the interaction between the tip atom and adsorbed atom on surface is obtained, the tip-atom distance is kept fixed at the constant current mode. The required force for displacing the molecule is determined from the bias voltage and tip- height value is supposed to be determined from lateral manipulation process. These particular values are obtained from a series of trials for manipulating a single molecule/atom by changing bias voltage and recording the tunneling current in an automated computer system. Then, the tip is moved parallel to the surface. During this, the atom moves along with the tip and hence it is relocated to the desired position. After reaching to the destination, the tip is retraced back to the normal imaging height thereby leaving the atom on the surface.

The tip height signal recorded during the lateral manipulation gives us information about the atom movement. Based on the forces involved in the manipulation and the nature of atom movement, the lateral manipulation process can be grouped into three regimes; pulling, sliding and pushing [25, 26]. The signals for each case are shown in Fig.9. The manipulation curves shown are signals that appear similar to the lateral manipulation curves of tip height versus lateral displacement in STM images. The atom is supposed to be moving beneath the signals at a distance equal to the constant tip-surface atom distance (r). The signals are the path of the tip that the atom follows laterally on the sample surface.
2.1.1.1 Pulling

In the pulling process, the magnitude of total force is kept constant by fixing the tip-atom distance constant. So, the tip follows the contour of the manipulated atom in a circular path. By doing so, the lateral force component of the total force changes with the path. The lateral component \( F_L \) increases as the tip moves along the contour. As the lateral force just exceeds the surface force \( F_S \), the atom then hops to the next lattice site following the tip. At this point, the surface atom is so close to the tip and thus the feedback loop system pulls the tip back to keep the current constant and also to maintain the same tip-atom distance. This phenomenon appears as if the tip is moving abruptly up and gradually down throughout the atom manipulation. The manipulation curve shows the tip height signal during the atom movement is like a saw tooth wave as in Fig.10.
2.1.1.2 Pushing

In the pushing process, the tip slowly moves upward of the manipulated atom which is at rest initially. When the lateral force exceeds the hopping barrier, the atom is pushed to the next lattice site due to a repulsive force between the tip and the manipulated atom. This causes an abrupt increase of tip-atom distance. The tip height is again lowered by the STM feedback system to maintain the constant current. The manipulation signal of pushing is also like saw tooth wave but it looks opposite to that of pulling process as shown by blue curves in Fig.9.

2.1.1.3 Sliding

In this case, the tip is relatively closer to the surface atom than that of the pulling mode. Thus the manipulated atom is trapped between the tip and the surface, and moves smoothly along with the tip. There is no immediate retraction of the tip like that of pulling and pushing mode. This is shown by red curves in Fig.9.
For the manipulation of a molecule adsorbed on a surface, similar three manipulation regimes as in atom manipulation can be involved. Moreover, due to flexibility of the molecule, more complicated manipulation mechanisms than the ones observed on single atom manipulation can also occur. For this thesis, only simple pulling manipulation curves are selected for the analysis.

The atoms/molecule rest on the sample surface at a very low temperature therefore reduces the thermal agitation. For this experiment, the sexiphenyl molecule is manipulated at liquid nitrogen temperature (77K). This low temperature enables the molecules to remain on the Ag corrugated surface in the absence of any external force. Thus the molecule has to overcome the surface force to diffuse on the sample surface. The study of molecule movement force on an adsorbate at a low temperature enhances the prospects to control the room temperature phenomenon for the molecular movement as well,

2.1.2 Total and Lateral Forces in Atom Manipulation

The lateral force in atom manipulation can be described as [26, 27]:

\[ F_L = F_T \cos \phi \]  \hspace{1cm} (13)

\[ F_L = -\frac{dU(r)}{dr} \cos \phi \]  \hspace{1cm} (14)

Where “r” is the tip-atom distance, U(r) is the potential energy between tip-atom and \( \phi \) is the angle between total force and the lateral force. At the time of hopping, the lateral force Fs is just enough to overcome the surface binding force \( F_{Lth} = F_S \).
Figure 11: Atom movement to the next lattice site and threshold lateral force for the transition.

At the point of atom hopping, considering a discrete case, the lateral force can be described as:

\[ F_{Lth} = \left| \frac{U(r)}{r} \right| \cos \Phi \]  

(15)

\[ \frac{F_{Lth}}{r} = \frac{U(r) \cos \Phi}{r} \]  

(16)

\[ \frac{r}{r} F_{Lth} = \frac{U(r)}{r} \]  

(17)

Here, \( \Gamma = \frac{r}{\cos \phi_{th}} \) and \( \phi_{th} \) is the threshold force angle. Since for a small tip atom distance, a change in \( F_{Lth} \) is considered to be constant for atom movement along a particular direction. Then from (17),

\[ \frac{r}{r} F_{Lth} = \frac{U(r)}{r} \]  

(18)

Thus the nature of \( \Gamma \) versus \( r \) plot is similar to that of \( U(r) \) versus \( r \) plot, which can be obtained from either a Lennard Jones Potential or a Morse Potential curve.
Lennard Jones potential for two non-bonded atoms or molecule is defined with an expression as,

\[ U = \frac{A}{r^m} - \frac{B}{r^n} \]  \hspace{2cm} (a)

The first term is considered as a repulsive term and the second term as attractive term. A and B are the constants. Typically, 12-6 Lennard Jones Potential (i.e. \( m=12 \) and \( n=6 \)) are used to study the interaction due to Van der Waals forces. However, the values of ‘m’ and ‘n’ can be extracted for some cases depending upon the type of molecules involved in the interaction. This has been previously studied [27] to obtain the force required to manipulate a single Bromine and Silver atom separately on a silver surface. Using (18) and (a), it was proposed that,

\[ \Gamma \propto \frac{A}{r^m} - \frac{B}{r^n} \]  \hspace{2cm} (b)

The \( \Gamma \) equation (b) was fitted with the Lennard Jones potential (a) to get the values of \( n \) which represents the attractive part. Thus the values of \( n \) obtained provided the strength of the interaction of silver and bromine atoms with the silver atom on the surface. However in the Morse potential, we make a qualitative comparison for the lateral forces to move a molecule by producing the \( \Gamma \) curves for molecular axis direction and molecular side direction movement on a silver surface. This is further explained in the result analysis part.

The use of Morse potential in this thesis to study the two atom interaction in order to compare the lateral forces for moving an atom on a substrate using STM tip provides a new approach in understanding the nano science.
Chapter 3 - Results and Discussions

3.1 Adsorption of Sexiphenyl on Ag (111)

Sexiphenyl appears as an elongated shaped molecule that preferentially aligns its long molecular axis along the surface closed packed directions on Ag (111), (Fig. 12). In this adsorption geometry, each π-ring of the sexiphenyl is located on top of the three fold hollow sites of the Ag (111) surface.

The interatomic distance on Ag (111) surface is 2.89 Å, which is almost lattice, matched with the molecule’s long axis length (2.79nm). Since the molecule-surface bonding is weak, there is a high tendency of the molecule being easily displaced during the imaging process [28].

![Alignment of Sexiphenyl along closed packed row on Ag (111) Surface](image)

*Figure 12: Alignment of Sexiphenyl along closed packed row on Ag (111) Surface*
3.2 Lateral Force Measurement of Sexiphenyl on Ag (111)

To understand the molecular diffusion processes of sexiphenyl on Ag (111) terrace, two different lateral forces are required. The question here is how the molecule diffuses along its long molecular axis and along the sideways. These two directions are indicated with arrows in Fig.12. For the diffusion, lower or higher diffusion barriers will require smaller or larger lateral forces, respectively. Therefore, a direct measurement of lateral forces into different directions of the surface will highlight the molecular diffusion processes on this surface. As shown in equation (18) in previous chapter, the $\Gamma/r$ plot should have a similar shape as the $U/r$ plot. $\Gamma$ is dependent on the threshold force angle, $\varphi$, and the tip-molecule distance, $r$. Both, ‘$\varphi$’, and ‘$r$’ are measurable quantities.

Therefore, in order to determine the lateral forces, the threshold force angles for molecule
movement parallel to the long molecular axis direction and sideway to the long molecular axis direction are measured for different tunneling resistance values, i.e. different tip-molecule distances.

As mentioned earlier in chapter 2, during the lateral manipulation process, the tip-molecule distance is kept constant by the STM feedback control system. Only pulling manipulation signals are chosen for the analysis. In the pulling mode, the movement of the tip initially follows the circular trace of the top part of a π-ring of the sexiphenyl while the molecule remains stationary on the surface. This kind of motion changes the total force direction while maintaining the same magnitude. The change in the direction induces its lateral force component (Fig.14 and Fig.15). The lateral force increases as the tip moves along the contour of the molecule, like in the case of atom manipulation. After the STM tip covered a certain arc path, the lateral force components of the total force overcomes the surface binding force of the sexiphenyl enabling the molecule to hop to the next lattice site. The tip now becomes close to the sexiphenyl molecule and it suddenly pulls back to maintain the same tip-molecule distance by the STM feedback-loop. This produces an abrupt increase in the tip-height. The lateral force component corresponding to this particular point, denoted here as the threshold lateral force ($F_{Lth}$) thus exceeds the surface force.

The drawing in Fig.14 illustrates the concept of a lateral manipulation signal. The arc like tip-paths here are the motion of the tip above the sexiphenyl molecule while the vertical lines are the retraction traces of the tip soon after the molecule jumps to the nearest lattice sites. This produces typical saw-tooth like signal similar to the one
observed in atom manipulation. In this process, the molecule is displaced along the horizontal line. Although we cannot image the tip-apex atom, the total force direction between the tip-apex atom and a part of the sexiphenyl will be along the shortest distance between them. If we assume circular shapes for the tip-apex atom and the part of the π-ring of sexiphenyl, then the shortest distance will be the distance along the radial line of a circle of π-ring. Thus the arcs here are extended to make a complete circle, and the total force direction is considered to be along the direction of the radius of the circle produced.

![Diagram](image)

*Figure 14: Measurement of threshold force angle constructing circles.*

For the threshold force angle, ‘φ’, the total force direction is measured between the center of the circle and the point where the sudden rise in manipulation signal occurs. The lateral movement of the molecule is parallel to the surface and therefore it is in the horizontal direction. Thus, the angle between the total force direction and the horizontal gives the force angle, ‘φ’. This process is explicitly illustrated with a diagram below.
Figure 15: Lateral force measurement. The change in total force direction as the tip-apex atom traces the arc like manipulation path. The total force direction can be known by finding the radius of the arc. The threshold force angle $\phi$ is the angle between the horizontal line representing the lateral movement direction, and the total force direction along the radius drawn at the point of molecule hopping.
Here, we are basically focused only on finding the threshold angles for manipulation as the exact total force cannot be determined. As in the figure above, if $F_T$ is the initial total force magnitude at a tip-molecule distance $r$, this value remains constant throughout the path. The change in direction of the force changes the lateral force magnitude. Thus choosing the circles is a useful tool to analyze the lateral manipulation for the calculation of force angle. An example for the measurement of threshold force angles is shown in Fig.16

![Figure 16: Measurement of force angles at a resistance value.](image)

For the analyses, a set of average data points for each tunneling resistance value are selected. The tip-height distance corresponding to each resistance is determined from an average I-Z spectroscopy. This standard spectroscopy is obtained experimentally by scanning the surface for different resistance values and the tip height was recorded as
shown below. This I-Z spectroscopy is used to convert the tunneling resistance to the vertical tip-height.

![I-Z spectroscopy graph](image)

*Figure 17: I-Z spectroscopy*

### 3.3 Manipulation of Sexiphenyl Molecule along Molecular Parallel Direction.

In STM experiments, lateral manipulations of sexiphenyl have been performed along the long molecular axis direction on Ag (111) surface using different tunneling resistance values. In order to get precise analysis results, the data showing fine manipulation curves with clear images are selected. For this case, 0.3 MΩ, 0.6 MΩ, and 2MΩ resistance value for the finest data are picked up.

An example of data selected for the analysis is presented in Fig.18. Fig.18a. shows an STM image of sexiphenyl on Ag (111) before manipulation event. After the lateral manipulation, the molecule has been moved as shown in Fig.18b. Thus, the
sexiphenyl molecule at the left is moved along its long molecular axis direction as indicated with an arrow for about 2.79 nm distance, which is about 10 surface Ag atomic distances. An example of tip-height signal recorded during such manipulation is shown in Fig. 19.

Figure 18: Manipulation of sexiphenyl molecule on Ag (111) along closed packed direction. [Tunneling parameters: 8 nm x 7 nm scan area, V = 0.43 V, and I = 1.3 nA].
Figure 19: An example of manipulation curve for long molecule parallel direction.

From the experimental data used for the analysis, it can be explained how the molecule moves during the manipulation; the sexiphenyl moves by hopping onto single atomic lattice sites of the silver surface. The arc-like shapes of the manipulation curve in Fig.19 are the paths of the STM tip along the sexiphenyl molecule contour at each lattice site, during which the molecule remains at rest before hopping to another site. The vertical lines at the end of the arcs are the sudden pulling of the tip when the molecule jumps to the next lattice sites. From the experimental manipulation data recorded at different tunneling resistance values (table 1), analyses are performed to determine the threshold force angles using the technique discussed in the previous section. The measured average threshold force angles are given in table 1 below. For the tunneling
resistance values the corresponding tip heights are then calibrated using the I-Z spectroscopy (Fig.17).

Table 1: Force angles, tip height values at a given resistance for parallel manipulation

<table>
<thead>
<tr>
<th>Tunneling resistance (MΩ)</th>
<th>Tip-height (Å)</th>
<th>Force angle(degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1.89</td>
<td>85.05±1.42</td>
</tr>
<tr>
<td>0.6</td>
<td>2.25</td>
<td>83.25±2.84</td>
</tr>
<tr>
<td>1.0</td>
<td>2.58</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2.99</td>
<td>82.12±2.99</td>
</tr>
<tr>
<td>100</td>
<td>5.32</td>
<td>76.81±1.12</td>
</tr>
<tr>
<td>200</td>
<td>5.71</td>
<td>73.68±1.09</td>
</tr>
</tbody>
</table>

Fig.20 shows the tip-height and force angle plot obtained using table 1. The linear relationship between these two quantities shows that in lateral manipulation of sexiphenyl molecule along a closed packed direction, the force angle gradually decreases with the increase in tip-molecule distance as expected. This also signifies that for small change in tip height if the threshold lateral force is the same, then the force angle has to decrease with the decrease in tip-molecule interaction. The value of slope of the line and intercept on the y-axis from the linear fit was found to be -2.673 and 89.949 respectively. These values are further used to find $I'$ versus $r$ relation.
3.4 Manipulation of Sexiphenyl Molecule along Molecule Sideways Direction.

An example manipulation sequence used for the current analysis is presented in Fig. 21. Here, a sexiphenyl molecule at the right side of the left image Fig. (21a) has been moved along the direction indicated with an arrow by 6 nm, which is ~ 20 atomic sites of Ag (111) surface. For the analysis, only the manipulation signal containing single atomic site hops of molecule are selected.

Next, the data for the manipulation of sexiphenyl molecule along a sideways direction of their long molecular axis are analyzed. The experimental data reveals that the manipulations have been performed along the directions 60 degrees deviated from the long molecular axis with various tunneling resistances.
Figure 21: STM images of lateral manipulation of sexiphenyl molecule along sideways to molecular axis. [Tunneling parameters: 14 nm x 10 nm scan area, $V = 0.5.5$ V, $I = 1.4$ nA].

Fig.22 depicts an example of tip height signals for sideways manipulation of the molecule. It is seen that the molecule at each hopping, has moved by single silver atom (2.89 Å) distance along the sideways direction.

Similarly, table 2 summarizes the different resistance values used for manipulation, the calibrated tip-heights and the measured force angles.
Figure 22: An example of manipulation curve for sexiphenyl along molecule side direction

Table 2: Force angles, tip height values at a given resistance for sideways manipulation

<table>
<thead>
<tr>
<th>Tunneling resistance (MΩ)</th>
<th>Tip-height (Å)</th>
<th>Force angle (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.2</td>
<td>83.80 ± 0.56</td>
</tr>
<tr>
<td>0.15</td>
<td>1.45</td>
<td>79.64 ± 0.86</td>
</tr>
<tr>
<td>0.3</td>
<td>1.89</td>
<td>76.93 ± 0.33</td>
</tr>
<tr>
<td>0.6</td>
<td>2.32</td>
<td>72.03 ± 1.125</td>
</tr>
<tr>
<td>0.8</td>
<td>2.45</td>
<td>71.57 ± 0.41</td>
</tr>
<tr>
<td>1.2</td>
<td>2.62</td>
<td>69.41 ± 1.39</td>
</tr>
<tr>
<td>3.0</td>
<td>2.99</td>
<td>66.21 ± 0.65</td>
</tr>
</tbody>
</table>
Figure 23: Force angle versus tip-height plot for molecule-sideways direction

The plot of the threshold force angle as a function of the distance for the sideway direction manipulation is presented in Fig.23. It shows the expected inverse linear dependence of force angle to the distance, i.e. the decrease in the angle as the tip-molecule distance increases. Likewise for parallel manipulation, the slope and intercept for the best fit line related to the sideway manipulation was found to be -9.456 and 95.102 respectively.
The force angle vs. distance plots for the parallel and sideway manipulation events are summarized below in Fig.24.

![Figure 24: Force angle versus tip-height plot for molecule-parallel and sideways direction.](image)

These plots show a linear relationship between force angles and tip height. Moreover, the sideway manipulation gives a much deeper slope than the parallel manipulation direction. The observed decrease in the threshold angle with increase in tip height which satisfies the equation (13) given as $F_L = F_T \cos \phi$.

As $F_L$ is constant for a particular surface direction, the increase in tip height ($r$) decreases the total force interaction between two atoms, so the force angle $\phi$ should also decrease.
Now using the values of slopes and intercepts from the best fit data, the \( \Gamma \) (Gamma) versus tip height curves are generated using the expression:

\[
\Gamma = \frac{r}{\cos \phi_{th}}
\]  \hspace{1cm} (19)

The parameters then obtained from gamma best fit are plugged in the Morse potential equation (12).

\[
\Gamma(r) \propto A + Ae^{-2Br} - 2Ae^{-Br}
\]  \hspace{1cm} (20)

![Morse potential fit curve](image)

**Figure 25: Morse potential fit for terrace-parallel direction**

This is Morse potential fit curve for the parallel manipulation. First, the \( \Gamma \) versus \( r \) values were generated using slope (m) and intercept (c) from Fig.20 in the equation
ϕ = mr + c and $\Gamma = \frac{r}{\cos \phi_{th}}$ and fitted with $\Gamma(r) \propto A + Ae^{-2Br} - 2Ae^{-Br}$. Only few points for tip-molecule distance ranging in our manipulation regions are plotted. These points are chosen at the equal spacing that lies almost within the range of parallel manipulation tip-molecule distance for our data. Therefore, the curve is for the tip height used for the manipulation range of 1.89 Å- 5.71 Å which is also the attractive interaction part of the Morse potential. The curve shows that $\Gamma$ decreases rapidly with decrease in r. From this curve we obtained the parameters A and B for plotting Morse Potential curve shown in Fig.26.

![Figure 26: Morse potential curve for terrace-parallel direction](image)

As expected, the $\Gamma$ versus tip height curve shown above is similar to the Morse potential curve. Both the attractive and repulsive parts are included in this potential
curve. At \( r = 0 \), the tip-molecule are in contact and this is an equilibrium point. For \( r < 0 \), there is repulsive potential whereas for \( r > 0 \) (attractive potential), we have our tip-molecule distance for moving molecule along terrace-parallel direction.

![Figure 27: Morse potential fit for molecular sideways direction.](image)

Similarly, The Morse potential fit for side- direction is obtained using the constants and slope from the best fit line Fig.23. In the Fig.27, seven different values of tip-molecule values at equal spacing were considered to show the Morse potential fit.

Our tip-height ranges from 1.2 Å- 2.99 Å which is again an attractive region in Morse potential curve. This range accommodates the \( r \)-values for the experimental data. While comparing the Morse fit of the two directions, we observe that \( \Gamma \) fit for side direction is falling much faster than the parallel direction. So, it can be understood that the curve has a greater slope. Here, parameter \( A \), in this graph is associated with the
potential depth and B controls the width of the potential well that is considered to be the same values as that of parallel direction Morse fit. Using this values in equation, $\Gamma(r) \propto A + Ae^{-2Br} - 2Ae^{-Br}$, we get the Morse potential curve as shown in Fig.28.

![Figure 28: Morse potential curve for terrace sideways](image)

The above $\Gamma$ versus r curve illustrates the nature of Morse potential for molecule sideways movement. All three regions (attractive, equilibrium and repulsive) are demonstrated for $r<0$, $r=0$ and $r>0$ respectively. In our experiment, the manipulation region is less than 3Å for which there is attractive interaction till the tip and surface molecule do not come in contact.

It is important to note that although different lateral forces are involved in the relocation of the sexiphenyl into the two different directions on Ag (111) surface, the
total force at a given tip-height should be the same. This means that the U versus r curve for both manipulation events are the same. This is because both cases uses similar STM tip (assumed Ag coated W tip) approaching toward a sexiphenyl molecule adsorbed on Ag (111) surface. And hence, the fit parameter, B, which controls the width of the potential, has to be the same. As expected, both experimental fits to $\Gamma$ vs. r curves give the same value of ‘B’.

3.5 Qualitative Comparison of Lateral Forces for Sexiphenyl Molecule

Manipulation using Morse Potential Curves.

The comparison of lateral forces can be made using the Morse potential curve. Fig.29 illustrates the $\Gamma$ versus tip-molecule distance for two molecule manipulation directions.

Figure 29: Comparison of gamma versus tip height curve
These curves are proportional to the Morse potential according to equation (18) as mentioned below.

\[
\frac{r}{r} \alpha \frac{u(r)}{r}
\]

or,

\[
\frac{r}{r} \times F_{Lth} = \frac{u(r)}{r}
\]  

(18)

Where, \(F_{Lth}\) is the proportionality constant called threshold lateral force (assuming it is constant for a small tip-molecule distance variation). Thus from equation (18), the \(U(r)\) versus \(r\) can be obtained by multiplying \(\Gamma\) versus \(r\) curve with the threshold lateral force required for the manipulation of sexiphenyl molecule along that particular direction.

Then, we can write,

\[\Gamma \times F_{Lth} = U(r)\]

(21)

Let, \(\Gamma_1\), \(U_1\), \(F_{L1}\) and \(\Gamma_2\), \(U_1\), \(F_{L2}\) be the gamma, potential energy and threshold forces for molecule parallel and molecule sideways directions respectively. Then, using above equations we get,

\[
\frac{\Gamma_1}{\Gamma_2} \times \frac{F_{L1}}{F_{L2}} = \frac{u_1}{u_2}
\]  

(22)

As explained before, the Morse curves here are based on the interaction between tip atom and sexiphenyl molecule. In this experiment, in both types of manipulation, the tip atom and surface molecule are the same; the tip atom has a silver atom (tip has been crashed in silver cluster to make a silver atom tip) and surface atom is sexiphenyl. So, the interaction for silver atom and sexiphenyl molecule in either case will produce a similar
Morse potential curve. Moreover, the two Morse potential curves should coincide if the interaction nature is identical ($U_1 = U_2$). Therefore equation (22) can be written as,

$$\frac{r_1}{r_2} = \frac{F_{L2}}{F_{L1}}$$

From equation (23), it can also be understood that the ratio of the $\Gamma$ values for the two directions is same as that of the ratio of their lateral forces. Thus in fig (29), displaced gamma curve from the other gamma curve provides us the strength of the threshold lateral force difference for pulling the sexiphenyl molecule along its long molecular axis and to the sideways direction of its axis.

Now, putting the values from experimental data, $\frac{r_1}{r_2}$ was found to be 2.25.

Thus we interpret that $\Gamma_1$ curve is obtained by multiplying $\Gamma_2$ with factor~2.3. Also, putting this value in (24), we obtain,

$$F_{L2} = 2.3 \times F_{L1}$$

Thus, the threshold lateral force required for the side direction manipulation is nearly 2.3 times the lateral force for the parallel direction.
Chapter 4 - Conclusion

The study of lateral manipulation of sexiphenyl molecule along two different directions using STM resulted in significant observations [29]. Based on the manipulation of sexiphenyl in each direction by its hopping to silver atom lattice site (2.89Å) at each manipulation, a comparison of the lateral forces was made. We found that the force angle versus tip height slope for side direction was greater in magnitude than the parallel direction. We calculated the threshold lateral forces for the movement of molecule along its long molecular axis direction (closed packed direction) and along the direction sideways to the molecular axis using the Morse potential. From our result, it was observed that the $\Gamma$ curve for side direction was much shallower than the parallel direction curve and that could be fitted to the parallel direction curve by multiplying with a constant factor of 2.3. From this, we can also conclude that greater lateral force is needed for the molecule to move sideways of its molecular alignment. Thus the threshold force for manipulating sexiphenyl molecule along the different angled directions from a closed packed direction was almost 2.3 times greater than the threshold lateral force for the side direction of the molecular axis. This is an intriguing finding because for the case of a single atom manipulation on the same surface, movement along all the three symmetric directions along the surface close-packed rows will require the same lateral force. This is simply due to the two dimensional symmetric nature of the surface. Surprisingly, on the same surface, the lateral forces required to move the sexiphenyl are totally different, and it is greatly dependent on the direction of the long molecular axis, rather than the symmetric close-packed row directions of the surface. We propose that the observed
effect is due to the symmetry breaking by the molecule. Unlike single atoms, which have roughly a symmetric shape on Ag (111), sexiphenyl is asymmetric, i.e. is a 1-D shaped molecule.

Thus, in this thesis we found that, sexiphenyl molecule diffuse more easily along its long molecular axis direction on Ag (111) surface than other directions. Normally, surfaces having atomic troughs such as Ag (110) or Ag (211) surfaces are used for directional diffusion of adsorbates. The finding in this thesis introduce a new paradigm: a directional diffusion of adsorbates on a two dimensionally symmetric surface can be achieved if adsorbate itself has a 1-D structure.
References


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