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Probing Molecular Adsorption and Mechanics at the Atomic Scale: The Nanocar Family of Molecules

By

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ABSTRACT

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Molecular machines, typically thought to be only the fanciful imaginings of speculative fiction, have taken great strides in recent years towards real-world viability and usefulness. Under variable temperature scanning tunneling microscopy, (STM) one family of these nascent devices is characterized with atomic resolution, and probed and manipulated with sub-angstrom precision, adding to the growing body of knowledge of how molecular devices behave and react at nanometer scales. Evidence of temperature-dependent rolling of wheel-like fullerene constituents on the Nanocar is discussed in light of newly developed image analysis techniques. Additionally, charge-transfer mediated behavior at step edges, both static and dynamic, is investigated on a Au(111) surface for a more complete understanding of translation and surface diffusion. Molecular flexibility is thought to aid in this three-dimensional atomic-step-crossing diffusion, and is explored and discussed across many species in the Nanocar family of molecules. In all, many similar molecules have been characterized and explored via STM with an eye towards their dynamic capabilities and surface behaviors, in the hopes that future, more complex versions can build on the nascent knowledge base beginning to be established here.
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Chapter 1

Introduction

Scanning tunneling microscopy, or STM, mainly focuses on the extremely small – from the range of microns down to Ångstroms. The work covered by this thesis, then, seems to be of appropriately small focus, given the methods and tools on which it is based. While only a single molecule, the nanocar (as seen in Figure 1.1,) is the focus of much of the work presented here, there is a wide range of disciplines encompassing the breadth of knowledge to be gained from its studies. Surface science, surface chemistry, quantum mechanics and electronics, molecular modeling, and synthetic and organic chemistry are only a few of the regimes where nanocar knowledge may be classified. The structure of the molecule itself at first appears deceptively simple. Fullerene wheels are connected by freely rotating alkyne bonds to an oligo (phenylene ethynylene), or OPE central structure. Parallel OPE axles allowing for paired axial rotation of the fullerenes are connected at 60° angles by a similar OPE chassis structure. These basic components make up the majority of the molecular systems studied in these pages.

The main focus (which will be discussed in detail in the coming chapters) - the nanocar - has covered a lot of ground since its inception in 2003. Among its many firsts - first molecule purposefully and successfully designed for nanoscale surface transport, first evidence of rolling-assisted molecular translation, first step-crossing of a designed molecular machine – it has also spawned a number of similarly synthesized spin-off molecules from its core set of molecular building blocks and techniques. Fullerene- and carborane-terminated dimers, azo-dimers, trimers and their variations, nanotrucks and
nanocars and their myriad models, and porphyrin-based quadrimer fullerene pinwheels have all been put under the scanning tunneling microscope (STM) tip on different surfaces under a number of different conditions. These investigations have shown that the rolling of the fullerenes plays a large part in their surface diffusion under both direct tip-manipulation and indirect thermal activation via substrate heating. They’ve also shown much more significant interactions of these fullerenes with the gold surface than originally expected, producing a flexion in the OPE constituents of many similarly constructed molecules. Additionally, the nanocar molecules have elucidated the importance of the electronic interactions of molecules at step edges – the Smoluchowski effect - in their step-crossing and straddling abilities.
Fig. 1.1: The nanocar molecule in space-filling (with alkane chains absent for clarity) and schematic forms. Alkane chains are OC_{10}H_{21} and included for solubility during synthesis and deposition.
Constituting what could be called a precursor to useful molecular machines, these molecules can provide both a conceptual and hierarchical stepping stone to more complex and useful nanoscale chemomechanical systems. But while they have yielded great amounts of information under five years of laboratory investigation, there is still much that isn’t known about this completely new class of nano-devices. How, exactly, does intramolecular charge transfer and distribution affect surface mobility? Is it responsible for the lack of internal resolution in STM images, as seen in Figures 1.2 (A) and (B), or is it more due to the electronic effects of the OPE structures and their interplay with the fullerene constituents? What keeps the carborane wheels on the smaller models from rolling like their larger fullerene cousins? The task of answering these and many other difficult questions will fall to future researchers, who will hopefully find this initial work useful and enlightening in their quest to further the knowledge and understanding of this promising new class of molecular devices.
Fig. 1.2: A three-dimensional representation of the nanocar molecule is seen in (A) (vertical axis is exaggerated.) A typical distribution and surface coverage is illustrated in (B), showing the nanocar on a Au(111) surface decorated with monatomic step edges. Both images acquired at $-0.8$ V, 15 pA.
The content of this body of work is organized to lead the reader on a general progression through the research as it was roughly completed. A referral to the previous work covered in the author's Master's thesis will offer a more thorough background from which to understand some of the original principles upon which many of the conclusions reached here were built. In other words, this work builds upon the research completed and summarized for the Master's degree - it may be a useful reference. In these pages, there follows a brief summation of the background and basic principles of the experimental work – basic STM and UHV theory, and the specific experimental setup, including substrates, surface conditions, deposition methods and variable temperature methods, among other experimental specifics are discussed in Chapter Two. Chapter three discusses the nanocar's behavior at step edges in both static and dynamic regimes. Chapter Four introduces a self-devised method of automated image processing for molecule detection and measurement. Variable temperature results are discussed to elucidate the roll of temperature on nanocar fullerene rotation. Chapter Five looks at rigidity and flexibility in some of the nanocar family of molecules, exploring conformational changes by both alkyne rotation and OPE flexion. Chapter Six takes a look at some of the less-extensively-studied molecules of the nanocar family, and Chapter Seven includes a brief summary and a look at possible future directions for related research.
Chapter 2

Background

2.1 Basic STM Background and Theory

A scanning tunneling microscope consists of five main elements: the piezoelectric scanning elements, the tip, the sample itself, a set of control electronics that includes a feedback loop back to the scanning elements, and a computer to process the signals and run the accompanying interpretive software. The tunneling microscope gains its imaging strength from the quantum mechanical phenomenon of electron tunneling: the ability of a lower energy electron to cross a classically impassible higher energy barrier. The transmission current’s exponential dependence on the thickness of that barrier theoretically allows sub-Ångstrom vertical and lateral resolution, and when controlled by a feedback loop to the actuating piezo scanning elements, allows the tip to maintain a constant tip-surface separation of less than tenths of an Ångstrom. In constant-current mode, the STM data is inherently a mix of both electronic and topographic information, which makes precise interpretation of the subsequent images more challenging than for a purely topographic device, such as an atomic force microscope, or AFM.

The tunneling microscope is one of the only tools capable of real-space imaging of both electronic and topographic information, and of in-situ manipulation, both on the atomic scale. Information on the electron density of states can also be obtained in the form of current versus voltage (I-V) spectra, illuminating electronic interactions and transitions at a surface interface. For appropriate systems, ambient STMs can offer a
“quick and dirty” approach to these types of investigations, with lower cost and simpler preparation procedures than their ultra high vacuum (UHV) counterparts, which offer a much more controlled environment. Low monolayer adsorption rates and sample purity are the main advantages to UHV work, but many systems also offer variable temperature and various input/output connections for a wide range of possibilities in control and measurement. Of course both ambient and UHV systems can be tailored to almost any degree of complexity, but remain, in essence, mechanically and conceptually simple – though precise – tools. Preparation of an existing system can be relatively simple, as well, with scanning tips cut from appropriate metal wire. Tip apex diameter is not as important in STM as in other scanning probe microscopies, as discussed below, which allows for such mechanically cut tips.

The key to STM’s sub-Ångstrom z-scale resolution is the tunneling current’s dependence on the width of the tunneling gap. Looking at elastic one-dimensional tunneling through a rectangular potential as a simple model illustrates the basic idea. The barrier transmission coefficient – ratio of transmitted current density to incident current density – for a strongly attenuating barrier ($\chi_s \gg 1$) illustrates a tunneling current’s exponential dependence on barrier width, as seen in Equation 2.1.[1]
Equation 2.1

\[ T \approx \frac{16k^2 \chi^2}{(k^2 + \chi^2)^2} \cdot e^{-2\chi s} \]

\[ \chi = \left[ \frac{2m(V_0 - E)^{1/2}}{\hbar} \right] \]

Figure 2.1

Fig 2.1: A schematic of a one-dimensional rectangular potential barrier of height \( V_0 \) and width \( s \), with a representative wavefunction based on the time-independent Schrödinger equation.
The transmission coefficient is dominated by the exponential, $e^{-2\chi s}$, where $s$ is the width of the potential, or insulating barrier, and $\chi$ is the decay constant. This means that for every Ångstrom closer to the surface the tip moves, the tunneling current increases roughly by an order of magnitude. Even with small tunneling currents, subtle changes in surface topography can be easily detected in the form of a change in current, which is then run back through the feedback loop to the z-piezo for constant current scans. It is that extreme sensitivity to lateral and vertical signals that allows the STM to produce such high-resolution images of surfaces.

2.2 UHV Conditions

While the fundamental concepts of STM remain the same, the capabilities and restrictions of a UHV STM are much different from those of an ambient scope. Both have their strengths and weaknesses, and are used to attain goals better suited to one environment over the other. Ambient scopes – STMs with the scanning tip and sample in the open air – are generally much easier to work with; a new sample can be loaded and scanning can start in a matter of minutes. However, while an ambient scope may be best for quickly assessing the coverage or other properties of a new sample, ambient STM also has its drawbacks. Because of this atmospheric contamination, imaging with ambient STM is limited to chemically inert surfaces. More importantly in manipulation experiments, however, is the fact that this surface contamination can alter adsorption and diffusion dynamics, making clear identification of tip-sample physical interaction difficult if not impossible. With a monolayer of moisture and atmospheric particulates on
the sample surface, it cannot be assumed that a molecule or system is acting as it would on a clean surface.

To maintain a clean substrate surface, a vacuum system is employed. In the case of these experiments, a turbomolecular pump attached to the load-lock area is backed by a roughing pump. In the main chamber, an ion pump is used to maintain a pressure in the range of $10^{-10}$ Torr. A titanium sublimation pump (TSP) compliments the ion pump for brief periods of operation, and is often used to lower the main chamber pressure after a contaminating event. The UHV regime is generally considered to be from $10^{-9}$ Torr and below, while high vacuum is generally $10^{-4}$ to $10^{-9}$ Torr. UHV conditions are desirable for STM because of the desire to maintain a clean surface. At atmospheric pressures, a monolayer forms on any exposed surface almost instantaneously. At $1 \times 10^{-10}$ Torr, there are approximately $3.3 \times 10^{-6}$ molecules per cubic centimeter. This translates to a mean free path (MFP) of approximately $4.8 \times 10^{-7}$ centimeters, meaning that there are roughly $3.9 \times 10^{10}$ molecules incident on one square centimeter of surface every second. At this rate, and with a monolayer considered to be approximately $2 \times 10^{15}$ molecules per square centimeter, it takes 51,282 seconds, or nearly 14.25 hours for a monolayer to form on a sample in a $1 \times 10^{-10}$ Torr environment – assuming every incident molecule adheres to the surface. Comparing this to a high vacuum pressure of $1 \times 10^{-8}$ Torr, where it takes just over 8 minutes to form a monolayer, it's obvious the advantage UHV conditions provide for a surface analysis method such as STM.
Fig 2.2: Schematic of RHK UHV 300 variable temperature STM chamber and pumps. The gate valves are positioned at 90° to each other: one between the load lock and main chamber, and another between the load lock and turbomolecular pump. Not pictured are ion and roughing gauges, viewing windows and other ports, various electrical feedthroughs, and the wobble stick for transporting samples and tips inside the chamber.
Working with a UHV STM, however, also means extra preparation and precautions. No adhesives or material that will outgas can be placed into the chamber. Normal rubber in UHV conditions constantly emits enough vapor and particles to significantly raise the pressure of a chamber. Even a single fingerprint, while it won’t necessarily ruin the vacuum, is noticeable in a UHV environment. Because of this sensitivity to out-gassing materials, particular care must be taken in sample preparation and modification of any internal mechanisms or parts. No significant internal modification was necessary for these experiments, however, as the UHV chamber, scan head, controls and software are all from RHK Technology.[2]

2.3 Experimental Setup

2.3.1 Surface Preparation

Unless otherwise noted, all of the samples used for experiment were Au(111) on mica obtained from Molecular Imaging.[3] New Au(111) substrates have large, atomically smooth terraces with monatomic 2.4 Å high step edges clearly visible in the STM. The surface of a clean Au(111) substrate reconstructs to form both hexagonally close packed (hcp) and face centered cubic (fcc) configurations with a [(22±1) x √3] surface unit cell, forming a paired-row pattern known as a herringbone reconstruction. This energetically favorable surface reconstruction differs from the bulk fcc configuration, and is difficult to resolve with STM if the surface is not clean. With a periodicity of 6.3nm, the herringbone surface reconstruction can act as a reliable scale for surface measurements. This substrate is not only chosen for cost and convenience, but additionally it is able to be imaged in both ambient and UHV conditions.
Substrates used for ambient experiments were subjected to hydrogen flame annealing before deposition. Individual sample-sized gold on mica sections framed and backed by cleaned quartz were subjected to multiple brief, sub-second exposures to the tail end of a hydrogen flame. This was found to be successful in guaranteeing an acceptable surface for ambient work. UHV samples were often prepared in the same manner when ambient deposition procedures were used. With the introduction of a cleaner high vacuum deposition method (to be discussed in section 2.3.3) UHV sputtering and annealing became the surface preparation method of choice. Three to five alternating cycles of argon ion sputtering in a range of 1-2 keV for 4-5 minutes and annealing at 800 to 1000 K for 3-4 minutes were found to reliably and reproducibly achieve large, flat, and clean atomic terraces suitable for manipulation and dynamic experiments.

2.3.2 Molecular systems

The molecules discussed in these pages that have been subjected to various experiments via scanning tunneling microscopy are all quite similar in their main components, but quite varied in how those components are arranged. It has been said that the synthesis team under Dr. James Tour at Rice University has come up with a type of molecular tinker toy set in which relatively simple components can be joined together to form myriad more complex systems. The cores of nearly all of this family of molecules are made up of varying structures of oligo (phenylene ethynylene) (OPE) moieties, often with attached alkane chains for solubility. OPE segments are essentially phenyl rings joined by alternating single, triple, single carbon bonds, where the triple alkyne bonds allow for axial rotation. In the case of the titular nanocar, there are three basic OPE sections – two that are aligned parallel to each other, but slightly offset, and one
connecting the two parallel sections at 60° angles. To the four ends of the parallel
sections (dubbed axles for obvious reasons) are attached through freely rotating alkyne
bonds four C\textsubscript{60} fullerene molecules that act as wheels. (See Figure 1.1.)

2.3.3 Molecular solutions

The molecules being studied were always obtained after synthesis in a dry,
powder form. To keep the powder dry and to reduce exposure to ultraviolet light (that
seemed to break apart some of the fullerene-based structures) the glass sample vials were
wrapped in aluminum foil and stored in a desiccator. UV-filters were also used on lights
in the laboratory for sample preparation and transfer. To disperse the molecules being
studied onto the Au(111) on mica substrates, the pure powdered sample was dissolved
into a solution. Toluene was used as the primary solvent for nearly all deposition
techniques, though ethanol, CS\textsubscript{2} and CS\textsubscript{2}/ toluene combinations were tested.
Fig 2.3: Clean Au(111) with visible herringbone surface reconstruction in upper right inset, atomic detail in upper left inset, and three-dimensional representation of the Au(111) atomic lattice in the main image rendered from the original data from the upper left inset image. The periodicity of the alternating bcc-fcc regions of the herringbone surface reconstruction is approximately 6.3 nm. All images acquired at -0.5 V, 5 pA.
Grains or flakes (depending on the exact synthesis procedure) of pure molecules were placed in a cleaned dry vial before the solvent was added. Often sonication was necessary to break down the pure sample and disperse it in the solution. The typical judgment of acceptable dispersion was based on a lack of sedimentation or particulate matter being visible in the solution. Sonication times varied depending on the solubility of each sample, with times ranging from one or two seconds to over an hour. Working with such small amounts of each pure sample, solution molarity was rarely accurately known as a balance sensitive enough for such low-weight measurements was not available. Acceptable solution concentration was judged by – and through trial and error based on – the degree of color tint or intensity of the various solutions.

2.3.4 Deposition

Once in a solution, the molecules were initially dispersed onto a Au(111) substrate by drop-casting or spin-casting the solution onto the substrate for ambient STM studies. Drop-casting consists of depositing a drop of solution onto a substrate and letting the solvent evaporate away. This method was usually used for low-concentration solutions where consistent surface coverage had proven difficult, or in situations where monolayer or greater surface coverage was desired. Spin-casting consists of depositing a drop of solution onto a substrate held in a chuck spinning at the desired rate. In this particular configuration, the exact rate of rotation was not precisely known, only the same approximate rate was used for each successive deposition process. By controlling the drop volume with a micropipette, the deposition process for each solution was fine-tuned through trial and error to achieve the desired coverage.
Fig. 2.4: (A) A cross section shows the mechanisms of the dosing valve mounted on the high vacuum load lock area of the chamber and used for deposition in the majority of UHV experiments. (B) The home-built control box used to quickly actuate the dosing valve was connected to a constant current, low voltage power supply (LVPS), the valve itself, and received its trigger signal from the walker control box from the RHK electronics.
When in UHV, however, a cleaner surface is easier to maintain, with the difficulty arising from the introduction of liquid sources in a high vacuum environment. To perform liquid deposition in the UHV STM, an electromagnetically-actuated solenoid valve[4] was used[5] by mounting the valve vertically over the sample on the load-lock area of the UHV chamber where it could be opened to the high-vacuum ($10^{-8}$ torr) load-lock for as few as 3 milliseconds. The resulting vapor deposition bypassed the need for vacuum sublimation of the molecules which was not possible due to thermal decomposition of the alkynyl bonds.

2.3.5 Annealing

To perform variable-temperature UHV STM experiments, the samples were annealed by means of resistive heating of a silicon wafer element placed directly under the gold on mica substrates. The sample holders in the RHK system allow for up to five points of contact aside from the tunneling tip. Typically two contacts were used to pass current through a slender piece of silicon beneath the Au(111) on mica substrate, with the mica in direct contact with the silicon, while a third occasionally applied the bias to the sample itself. A K-type thermocouple in direct contact with the gold substrate allowed for real-time, accurate temperature measurements of the surface, and often applied the bias voltage. A low-voltage, high-amperage power supply was used to resistively heat the Si element, and could be roughly controlled to within +/- 25°C.

2.3.6 Low Temperature

A Lakeshore cryostat attached to the chamber was used to flow liquid nitrogen and liquid helium to cool the sample holder. Difficulties arose, however, when a sample-
mounted silicon diode only noted temperatures around 250K. The cryostat diode and sample stage thermocouple noted appropriate temperatures during cooling, however, as did the sample holder silicon diode when immersed directly in liquid helium prior to mounting. This lead to the conclusion that thermal contact between the sample stage and the sample itself was extremely poor, or there is some unknown heat leak into the sample. Initial data was collected at the relatively high temperature of 250K, but further studies were delayed until a fitting solution could be found to lower the sample temperature. The silicon diodes in the cryostat and self-mounted on the sample holder were also both from Lakeshore with an accompanying controller.
Chapter 3

Nanocar Step Crossing Facilitated by the Smoluchowski Effect

Many recent studies have demonstrated the ability to manipulate individual molecules in a variety of unique configurations including along surfaces via rolling [6-10], stick-slip or sliding motions [11], chemically restricting them to 1-dimensional paths [12], and rotation in place along axis both perpendicular [13] and parallel [14, 15] to a surface, as well as creating and breaking chemical bonds [16]. Most of these studies utilize the atomic resolution and clean surface conditions allowed by the ultra-high vacuum (UHV) scanning tunneling microscope (STM), which is also the only tool currently capable of simultaneously inducing motion and gathering data on a single molecule. The motion in these systems as described has been mostly restricted to an individual terrace. However, to strive towards real-world applications, dynamics in the vicinity of step edges must also be taken into account, especially considering that even the flattest surfaces have atomic terraces only a few microns wide. Individual fullerenes have shown the ability to facilely cross the barrier of atomic steps, however, this was achieved with direct manipulation by the STM tip [17].

We have previously described [7] a family of fullerene-based molecules with alkyne linkers that have been synthesized showing directional preference in both STM tip-manipulation and thermally excited motion. These structures have been termed nanocars. Looking at the different models of these fullerene nanostructures [12], the type of motion depends on how the fullerene subcomponents are oriented relative to the overall molecular structure. Of particular interest is the 4-fullerene nanocar molecule
where the fullerenes are grouped in pairs and arranged to directly convert the C\textsubscript{60} rolling motion about each alkyne into lateral translation of the entire molecule, as shown in the inset in the upper right of Figure 3.1. With the synthesis of the nanocar molecule that contains a chassis composed of a oligo (phenylene-ethynylene) (OPE) moiety, we have discovered a molecular design that is capable of crossing single Au(111) steps under thermal excitation as observed by UHV STM. We attribute this behavior to a favorable combination of both mechanical and electronic structure of the molecule.

The nanocar samples were synthesized as previously described [18] and sonicated from powder into a toluene solution (~5 \textmu M.) The solution was dosed through a fast-actuating solenoid dosing valve into vacuum [5] onto the previously argon sputtered and annealed Au(111) on mica substrates at room temperature, before being brought into the UHV area of the chamber for scanning. All results were obtained in UHV with a commercially available variable temperature STM (RHK UHV-300) [19], and scanned with mechanically sharpened Pt/Rh (90/10 – 85/15) tips. Annealing was achieved through resistive heating a piece of silicon placed directly below the Au(111) on mica samples in the sample holder, and temperatures were measured by K-type thermocouple wire directly on the Au(111) surface.
Fig. 3.1: (A) Chemical model of the nanocar. (B) STM image ($V_b = -0.8$ V, $I_t = 10$ pA, 58 x 58 nm) of nanocars deposited on Au(111) by the dosing valve. Bright features are fullerene wheels; intramolecular OPE and alkyl groups are not visible.
Typical deposition parameters lead to low sub-monolayer surface coverage of nanocars with effectively uniform distribution of the molecules both near step edges and on open terraces. Even though the fullerenes “wheels” dominate the appearance of the nanocars when imaged by STM, the orientation of each molecule can be determined even lacking intramolecular detail by analyzing peak-to-peak measurements between the fullerene wheels [2]. When compared to the expected size, measurements in both directions in UHV conditions tend to be slightly shorter suggesting a slight bowing in the OPE axles and chassis, but the ratio of the axle to chassis length is nearly the same as predicted except for cases of extreme deformation. Even though the OPE moieties throughout the nanocar are expected to be fairly rigid [20], the overall flexibility can accommodate a surprising range of structural distortion as will be discussed later, thus sometimes affecting the determination of their orientation.

As described previously [7], the nanocar samples on Au(111) were annealed to approximately 200 °C and scanned at a frame rate of roughly one image per minute. At these temperatures and with moderate surface coverage, it was sometimes difficult to unambiguously track a particular molecule between terraces due to the thermal motion, tendency to cluster, and the time-lapse nature of STM images. On a particular surface with incidentally formed 2 –10 nm diameter monatomic Au(111) mesas, nanocars were seen to cross onto and back down from the small plateaus as seen in the series of time-lapse images in Figure 3.2. This shows the ability of thermally-activated nanocars to diffuse across step edges.
Fig. 3.2: STM image ($V_b = -0.95$ V, $I_t = 200$ pA, 25 x 25 nm) of a nanocar crossing a monatomic step. Series of key images (A-F) taken from a movie during annealing at ~200 °C. From (A) to (B), a single nanocar crosses over a Au(111) step edge to sit atop an island for frames (B) and (C), then returns to the main plateau in (D), and a different (or the same) nanocar moves back onto the island for another frame (E), before returning again to the main plateau in frame (F).
Typically, when the molecules were traversing steps on larger terraces under heating conditions, the transit of the step occurred in between imaging frames. In the case of the smaller gold islands, it is obvious that the presence of a nanocar appearing on top must have originated from the surrounding lower terrace. Figure 3.3 contains a sequence of consecutive images during an instance where a nanocar crosses up a step and onto a higher terrace and the overall motion is captured by multiple STM images. In this case, it is difficult to know the initial and final position of the nanocar on each terrace, however, it is clear from the middle frames that the molecule traverses the step beginning with a single fullerene wheel and oriented with its axles parallel to the step edge. Due to these problems of unambiguously identifying and tracking a single molecule between multiple consecutive images, these captured instances of identifiable step crossing are rare, though we believe their incidence must be much higher than observed in a given area for the same reasons. We hope to better elucidate the surface interactions that facilitate the step-crossing and thereby reduce or eliminate some of the ambiguity of the associated dynamic observations by further studying these molecules in static conditions at room temperature both near and straddling the step edges.

Monatomic step-edge adsorption in molecular systems has been studied for a number of different molecular species, including benzene [21, 22] and C_{60} [23]. Most molecules adsorb preferentially at the top or bottom of the step due the particular charge acceptance or donation characteristics of the molecule coupled with the local density of states (LDOS) perturbations at the steps of the specific crystalline surface [21, 24]. The most dominant charge-transfer mechanism for conjugated organic molecules adsorbed at
metal surfaces is the Smoluchowski effect [25]. The Smoluchowski effect describes the spreading and smoothing of surface electron wavefunctions in metals, specifically at step edges. The effect imparts a slight net positive charge at the top of the edge, and a slight net negative charge at the bottom. This usually leads conjugated molecules with their specific charge donating or accepting characteristics to adsorb preferentially above or below a step [22, 26]. For example, benzene molecules can readily donate charge on Ag(110) and therefore they adsorb preferentially on the top of step edges [21]. The nanocar molecule, with its four fullerene wheels and connecting OPE axles and chassis, has shown the ability to adsorb at both the upper and lower portions of the gold steps. In addition, it also demonstrates a unique ability to straddle the monatomic Au(111) step edge at room temperature, which presages the dynamic step crossing observed during the annealing experiments.

The nanocars have been observed at step edges in six different configurations: above, below, and straddling a step edge, with each position having the OPE axles either parallel or perpendicular to the step edge direction. Step-straddling nanocars are described by having two fullerenes on the upper edge, and two fullerenes on the lower edge of a monatomic step. Occasionally there will be a single fullerene wheel straddling in either direction across the step. Of all these straddling types, a clear majority are oriented with axles perpendicular to the step-edge direction. Of those isolated molecules at step edges (not straddling), there is no clear preference in orientation or position either above or below the step.
Fig. 3.3: A sequence of STM images ($V_b = -0.2$ V, $I_t = 150$ pA, 33 x 33 nm, ~ 200 °C) illustrating a nanocar crossing a monatomic step edge between two terraces on Au(111).
Cross-sections of nanocars in proximity to step edges were analyzed across the fullerene wheels on images acquired. Over the range of tunneling parameters (-820 mV to +400 mV, 5 to 30 pA), a negligible variation in fullerene height correlated to scanning parameters was observed for terrace-isolated nanocars. The apparent height of the fullerenes attached to the nanocars was found to vary greatly according to positions relative to the step edges, however. An example of a step straddling nanocar with its corresponding cross-sections is shown in Figure 3.4A and B. This apparent height difference of the fullerene wheels located at step edges roughly follows that of previous findings of C_{60} on Au(111) [27]. Fullerene wheels at the top of a step edge appear smaller than both the terrace-isolated wheels and those at the bottom of step edges. To simplify the analysis for the purposes of step-crossing, we excluded effects due to the orientation of the molecules relative to the step.

Using the fullerenes of a terrace-isolated nanocar as a reference, molecules with all four wheels away from any step edges demonstrate an average apparent fullerene height of 2.89 Å, as illustrated by the first bar in chart Figure 3.4C. In comparison, the height of any top-edge fullerene (both red and blue fullerenes as marked in Figure 3.4C) averages 1.82 Å, yet the difference between the two types of top-edge fullerenes is approximately 10% of the larger measurement (1.93 Å for a top fullerene on a flat nanocar and 1.71 Å for a top fullerene that is on an edge-straddling nanocar.) Fullerenes not directly against a step-edge show a 13% difference between the two positions, 3.41 Å for an away fullerene on a bottom flat nanocar, and 2.95 Å for an away fullerene on a top flat nanocar. When the fullerene wheels adsorb along the bottom of a step edge they
demonstrate a difference of 20%: 3.42 Å for a bottom-edge fullerene on a flat nanocar and 2.72 Å for a bottom-edge fullerene on a straddling nanocar. Through comparisons of the six near-edge configurations shown in Figure 3.4C, it is clear that fullerene position relative to the step has an influence on apparent height, especially considering the difference between top-edge fullerenes and the average plateau-isolated nanocar. Top-edge fullerenes, regardless of the position of the rest of the molecule, are similar, as are bottom-edge fullerenes and away fullerenes, respectively. As expected, the general trend of these results is that the fullerene at the top of the step over the net positive charge cannot draw as much surface charge donation as typical on the plateau, (0.8 electrons per molecule for bare C$_{60}$ [28]) while those at the net negative bottom edge of a step are able to draw a greater charge donation.
Fig. 3.4: (A) STM image ($V_b = -0.8$ V, $I_t = 14$ pA, 9 x 12 nm) of a nanocar straddling a single gold step with the accompanying cross-sections (B) which highlight the change in the apparent height of the upper fullerenes due to charge-transfer from the Smoluchowski effect. (C) Average fullerene height by both fullerene and molecule position. The white bar signifies the height of the fullerene wheels when they are far from a step edge, while the other colored bars correspond to the heights of the wheels at locations commensurate with those shown in the colored figures below the plot.
Still more significant are the differences due to the precise position of the step edge relative to the entire molecule. These results indicate that the charge transfer that leads to adsorption at step edges is not isolated to the position of individual fullerenes, but instead involves the positioning of the molecule as a whole and the resultant intramolecular charge redistribution. The straddling of the steps and the accompanying change in apparent fullerene height is likely due to the electron donation and acceptance properties across the whole molecule, but manifests in the appearance of the strongly-bound fullerenes [27, 29]. Further investigation of nanocars containing subtle variations in chassis and axle structure and incorporating edge-relative orientations will better elucidate the intramolecular charge transfer and its corresponding role in the adsorption and diffusion of these molecules across the surface.

In addition to the charge-transfer effects seen at step edges, the physical structure of the nanocar molecule also plays a role in its step-edge behavior. As seen in Figure 3.5 (A) and (B), the nanocar molecule on the left changes conformation, bringing two fullerenes much closer together and the other two much further apart while the structure of the molecule on the right remains unchanged. Coupled with the axle’s rotational abilities made possible by the prevalent alkyne bonds, this flexibility aids in dynamic step crossing as well. The flexibility of alkyne bonds in the chassis of the nanocar is additionally demonstrated by alternate configurations of the molecule on the surface as seen in Figure 3.5 (C), with the corresponding cross-section shown in Figure 3.5 (D). Here we highlight the most extreme case where an axle is rotated nearly 180° from its
normal position, after which one fullerene is located effectively on top of another on the surface, creating an image that appears to be of a 3-wheeled nanocar with one large wheel. While this type of alternate configuration has been found on the surface, it is not very common.

In conclusion, we have studied both passive and thermally active step-edge behaviors of nanocar molecules on Au(111). Apparent height differences between static fullerene wheels at different locations near step edges illustrate active charge redistribution governing the adsorption dynamics of the molecules. Fullerene position alone does not dictate the apparent height of the wheels. Instead, the position of the whole molecule determines the charge distribution of each fullerene, indicating that there are yet-unknown electronic effects across the inner OPE structures. This charge transfer influenced by the Smoluchowski effect, coupled with the physical flexibility and rotational characteristics of alkyne-facilitated fullerene rolling and axle pivoting, seems likely to aid the nanocar with a step-crossing ability at elevated temperatures.
Fig. 3.5: (A) and (B) (same scale) illustrate the flexibility of the nanocar with consecutive scans of two molecules at $V_b = 0.4$ V, $I_t = 10$ pA. Front and rear fullerenes on the same side of a molecule can show a large discrepancy in peak to peak distance measurements, while fullerenes along an axle maintain a much smaller range of measurements. (C) Alternate possible conformation of the nanocar molecule (-0.92 V, 15 pA) with one fullerene on top of another with the corresponding schematic inset illustrating the flexibility of the axles with respect to the chassis. (D) The cross-section highlights the difference in height of the crossed wheels.
Chapter 4

Temperature Dependence of Spinning Fullerenes Probed by Tunneling Microscopy

4.1 Introduction

As simple molecular machines evolve into more complex and useful devices, the question arises as to how to best impart energy so that they may perform their designed tasks. In the case of the nanocar, mechanical energy was directly applied to a single molecule in the form of a scanning tunneling microscope (STM) tip, inducing rolling motion perpendicular to the Oligo phenylene (ethynylene) (OPE) axles. Additionally, thermal energy applied to the entire substrate induced rolling motion in many molecules simultaneously. As methods for controlling these devices change to suit specific circumstances and goals, it is important to evaluate and understand the mechanisms of energy exchange.

Recently we have analyzed the Nanocar, whose structure is illustrated in Figure 4.1. Towards this end, it has been shown that the four fullerenes act as wheels, analogous to their macroscopic counterparts, allowing the Nanocar to primarily move in a direction perpendicular to their connecting alkyne “axles,” both under direct tip-manipulation via STM, and on a heated surface in a UHV environment.[7] In addition, the Nanocar has demonstrated interesting dynamic behaviors in the vicinity of Au(111) step edges, illustrating step straddling and crossing which is believed to be enabled by the rotation of the wheel-like fullerenes.
Fig. 4.1: The Nanocar molecule's alkyne connections to the wheel-like fullerenes allows rolling motion of each individually.
While these results are intriguing in their own right, the important question still remains as to how, exactly, the rotating mechanism of the fullerenes interacts with the surface to enable directional rolling motion. Under high-temperature conditions, specifically, there is the question of how thermal energy is translated into directional motion. Tracking and analyzing a single moving molecule at high temperatures is not a practical way of discerning the intricacies of the fullerene-substrate interactions, due partly to the high relative speed at which the Nanocar is capable of moving and the necessarily slow raster speed of the STM tip. In addition, obtaining intramolecular resolution has so far proven elusive, especially under high temperature conditions, leaving single molecule study short on details needed for further understanding.

With this in mind, it has proven useful to study the statistics of a large number of molecules at elevated temperatures. Through analysis of a large set of data it has become apparent that at higher temperatures, on average the fullerene wheels of the Nanocars appear noticeably larger than at room temperature. Often there was a discrepancy in size within the molecule itself, wherein only some fullerenes displayed this larger apparent size. These larger fullerenes are shown in Figure 4.2 at approximately 200 °C, with a cross section in 4.2 (A) showing a 1 Å height difference between the larger and normal-sized fullerenes. Previous STM studies of C₆₀ on various surfaces note that in comparison to molecules with clear molecular orbital detail, those with no detail appear higher, and are interpreted as rotating on the surface.[30] It follows, then, that these larger fullerene wheels on the nanocar molecules are themselves rotating. If this is the case, it would be expected that at
higher temperatures more fullerenes should be spinning – appearing larger than non-rotating fullerenes – than at room temperature.

To obtain an accurate picture of whether or not this initial observation is correct, we have developed and automated a process by which thousands of nanocar fullerenes can be detected, extracted, and analyzed from STM data. This automation allows for a statistically significant sample size which would be much more difficult and time consuming if performed manually.
Fig. 4.2: High temperature data of nanocars on Au(111) at approximately 200 °C (-0.94 V, 180 pA) illustrate the larger apparent height of rolling fullerenes, as shown by the cross section of (A).
4.2 Experimental Setup

For this analysis, all images were acquired via UHV variable temperature STM in a commercial RHK system.[19] Nanocars were deposited via a dosing valve[5] onto argon sputtered and annealed Au(111) on mica substrates in high vacuum. Tips were mechanically cut Pt/Rh 80/20 or 87/13. Once in the chamber, high temperatures were achieved through resistive heating of a silicon element directly beneath the substrate, while temperatures were recorded via a K-type thermocouple on top of the sample surface.

Room and high temperature images were obtained at a range of scanning parameters from 4 to 160 pA, and -1.3 to 0.8 V, with no significant direct correlation between parameters and feature height. High temperature measurements were performed on samples heated to approximately 200 °C. To obtain accurate results during the processing, image sizes used for analysis ranged from 51 to 120 nm for both room and high temperature scans with sampling rates of 512 x 512 pixels per image.

4.3 Background Subtraction / Fullerene Detection and Analysis

The strength of probe microscopy lies in its ability to image individual atoms and molecules, however, this property makes acquisition of ensemble information about such systems quite challenging. A significant problem in batch height analysis of STM data at atomic scales lies in the strong likelihood that multiple different atomic terraces reside in the same image. This is especially significant in the case of the nanocar, which tends to straddle Au(111) monatomic step edges. Common background plane subtraction is not sufficient to remove the influence of these steps on the underlying substrate from height
analysis – which is the most effective method to determine size due to known tip-convolution effects. Background plane subtraction removes the overall pitch, or slope of an image, but can significantly distort the z-range data. This method also cannot remove the true background – such as step edges or abrupt changes in height – and is most effective in correcting a planar slope.

To accurately remove the background and level the measurements of every molecule across each image, we have developed a new method of background selection. Illustrating this process, we will discuss the various steps using a representative room temperature STM image as it is shown in its original state in Figure 4.3 (A). Initially, a median line filter is run on the original image in the fast-scan direction to remove any major line artifacts or noise spikes. (Figure 4.3 (B)) Next, in our method, the background is determined by the average value of pixels using a sliding block processing technique with a pre-defined two dimensional shape. (All processing is done in Matlab with a combination of standard, in-built functions and self-written routines for the specific purpose of this investigation.) A structured element (strel) is created to be convolved around each pixel – in this case we applied a disk with a radius that is linked to the image size in such a way that it is always larger than the C₆₀ wheels, yet small enough not to significantly blur step-edge detail. (We’ve found that a disk radius of approximately 15 Å is the best compromise, accounting for a wide range of surface features and step densities.) Each center pixel in a structuring element is then given the average value of all the pixels in the element, creating a uniform background devoid of sharp features smaller than the size of the structuring element itself. The choice of sample size and shape determines what size features are effectively removed – in this case the fullerences on the
nanocar molecules - and which are chosen to make up the overall background – the step edges and plateaus. Figure 4.3 (C) illustrates how this method, accounting for the size of the features that are to be analyzed, can effectively create an accurate background with sharp step edges and changing slope. This background is then subtracted from the original image, effectively removing the height differences due to step edges and any inherent slope in the image (Figure 4.3 (D)) While there can be slight fluctuations at step edges in this background subtraction routine, and peak fullerene heights may be slightly decreased from the original image, these effects are universal across all the measurements and still yield valid relative information as discussed below.

Detecting and measuring individual fullerenes still requires further processing. The background subtracted image is first run through a median filter function to remove any remaining significant noise spikes that could be mistaken for fullerene features. This is preferred to a mean filter, since significantly high noise spikes can still remain in the latter. Figure 4.3 (E) illustrates the results from this step, as well as the slight improvement in contrast gained by removing noise spikes. Since this image has already been background subtracted, all fullerene features will appear above a certain minimum height. This allows a cutoff height to be chosen, ignoring everything below, and effectively thresholding the image to the desired level. As represented in Figure 4.3 (F), the cutoff was set to 2 Å. From this thresholded image, a binary mask is then created with zero values for everything below the cutoff, and ones for everything above the cutoff. (Figure 4.3 (G)) The binary image is then run through another “strel” function. This time, a disc size is chosen such that it is smaller than the fullerenes (we’ve found that a radius of about 5 Å is a good compromise for a wide range of data, though individual cases may
respond better to slightly larger or smaller sizes) to keep the overall information of each feature. As shown in Figure 4.3 (H), this removes most remaining noise spikes or lines smaller than the disk size, and also serves to better separate individual features for individual analysis. In typical fashion, this binary image is then used to find a center region for each feature, or fullerene, by applying a morphological erode operation, which computes the regional maxima of the Euclidian distance transform on the binary image. Pixels in each feature that are equidistant maxima from an edge are kept, while all others are set to zero, resulting in only the center regions of each feature remaining. This resultant binary image (Figure 4.3 (I)) is then multiplied by the background subtracted image, producing an effective mask (Figure 4.3 (I)) where only the center regions of each feature are kept. While the peak of each feature is not always in the center, this is an accurate method for batch measurement of feature height, accounting for varied data collected over a long period of time, with numerous tips and tip states. This method of location-biased height measurement is also effective at accounting for noise spikes over the fullerenes themselves.
Fig. 4.3: Major processing steps used to isolate and measure individual fullerenes are performed on the original image (A) and illustrated sequentially (B) – (I) representing only the upper left quadrant of the image. Blue dots in (J) mark individual measurement points over fullerenes. Original image acquired at -0.8 V, 16 pA, 98 x 98 nm.
The resultant working image now has each fullerene isolated and reduced to a few center pixels in each feature. Most features have more than one pixel remaining. To avoid multiple sampling from the same fullerene, each isolated cluster of central pixels for each feature is then individually labeled according to the number of features in the image. This labeling operation, then, lets the routine run through each labeled feature and record the maximum height of each fullerene only once. Other mid-processing images can also be displayed, including an overlay of measurement points on the original image, as in Fig. 4.3 (J), in order to diagnose any problems and double check the measurements. In its current form, this routine handles thousands of feature measurements with remarkably few missed and even fewer misidentified features. The former is more forgivable as it may represent (very few) missed data points, but the latter actively distorts data, and has been more of our focus to eliminate in this work. To obtain a perspective on the error in this process, ten randomly selected images were investigated manually where approximately 6% of definitively identifiable fullerenes were missed, and 2% misidentified, out of a total of 887 data points collected. These percentages seem acceptable given the overall collection of over 10,000 points for each temperature in the resultant histogram comparisons.

4.4 Results / Data

A total of 10,000+ measurements were performed for both elevated and room temperature samples. With this many measurements, we obtain an accurate picture of the statistical distribution of apparent heights, and how temperature modifies this. As seen in
Figure 4.3, which overlays both high and room temperature histograms, there is a noticeable shift of 0.8 Å in the peak bin for the two temperature-dependant histograms. This clearly shows a prevalence of larger (higher) fullerene wheels on Nanocars at high temperatures when compared to room temperature. When taken in light of previous research, this indicates a greater degree of spinning fullerenes at elevated temperatures, as expected.

The distribution of these two histograms follows a similar trend. The sharper drop from the peak occurs on the high side of the high temperature histogram, and on the low side of the room temperature histogram. This could be indicative of a the histograms approaching a height limit of the fullerenes independent of adsorption sites, meaning that further increasing or decreasing the temperature may not drastically alter the histogram peak position. Preliminary data at temperatures below 297 K (represented by the line in Figure 4.4) shows that the peak of the distribution can still shift slightly downward at lower temperatures. This is to be expected since it is well known that fullerenes freely rotate in bulk samples at room temperatures and that it is only their strong interaction with the underlying gold substrate that slows and halts this rotation as seen in previous STM studies.
Fig. 4.4: The apparent height distribution of nanocar fullerenes is displayed according to temperature. The high temperature measurements show a higher distribution peak than the room temperature measurements, as well as a change in line-shape. The preliminary low temperature data displayed by the blue line highlights this trend, as the steeper side of the line-shape occurs on the low temperature side for lower temperature measurements, compared to higher temperature measurements where the steeper side of the line-shape is on the higher side. This illustrates a kind of upper and lower bound for apparent height measurements as correlated with temperature.
The dispersion of the histogram shapes for the various temperatures can be
tentatively explained as a result of the various adsorption sites of the fullerene wheels. As
seen in Chapter 3, a nanocar fullerene's location relative to a Au(111) step edge
significantly influences its apparent height due to charge transfer with the surface
influenced by the Smoluchowski effect. Step edges are not the only effect that can
influence apparent height, however. A wide range of apparent fullerene heights has been
seen at both high and room temperatures — from approximately 1.5 to 4 Å — away from
any step edges or other appreciable surface features. These observations and data sets
lead to the conclusion that the distribution of heights for both spinning and stationary
fullerenes is approximately Gaussian.

When applied to the apparent height histograms at room and high temperatures,
we can roughly fit each temperature-dependent histogram with a convolution of two
Gaussian line shapes — one that accounts for those fullerenes that are stationary, and one
that accounts for the higher rolling fullerenes. The peak positions for each type of
Gaussian are the same for both room and high temperature conditions; only their widths
and intensities change. These initial findings can be interpreted as the intensity of each
Gaussian depicting the relative amounts of stationary vs. rolling fullerenes in each case,
while the width reflects the dispersion of adsorption sites. (More accurately, it is the ratio
of the integrals of the Gaussians that represents the relative amounts of stationary vs.
rolling fullerenes.) Figure 4.5 illustrates a graphical interpretation of the convolution of
Gaussian line shapes for the room and high temperature histograms.
Fig. 4.5: Dotted Gaussian line shapes representing spinning and non-spinning fullerenes convolute to roughly fit (solid blue line for room temperature, solid black line for high temperature) the overall shape of the histogram data from Figure 4.4, which is represented by the open circles.
4.5 Conclusions

In conclusion, we have developed an automated method to account for complex backgrounds including monatomic steps, noise, and feature separation in the height analysis of large numbers of the fullerene wheels of the Nanocar. From initial STM observations of changes in apparent height accompanying variations in temperature, this process has allowed the collection of a large ensemble of molecules to confirm the trend. When viewed in light of previous work on surface-bound fullerenes, it is hypothesized that higher temperatures induce more rolling fullerenes, as portrayed by an increase in the peak height of the resulting height and temperature-dependent histograms. This also agrees with our previous work showing the increased mobility of nanocars at high temperatures, and suggests a driving mechanism for mobile nanocars derived from the rolling fullerenes.

The rotational energy imparted to the fullerenes, then, is hypothesized to be the main cause behind the thermal diffusion of the nanocars. While the motion of the fullerenes may not always be in lock-step with their translation across the gold surface, their rotation is directly tied to the nanocars' surface mobility at high temperatures. Since the fullerenes are the only strongly interacting parts of the nanocar in direct contact with the gold surface, their behavior relative to that surface dictates the motion of the whole molecule – not the other way around. It seems, however, that the induced rotation of all four fullerenes is not necessary for whole-molecule motion. Figure 4.2 (A-D) illustrates the motion of a nanocar with two large fullerenes and two average-sized fullerenes, indicating that not all are rolling at the time the images were acquired. It is possible to hypothesize as to the mechanisms involved – perhaps the rotation of some fullerenes increases the nanocar energy enough to overcome Au(111)-nanocar interaction.
Chapter 5

Probing Molecular Flexibility with Tunneling Microscopy

Molecules like the nanocar are often graphically represented by chunky, space-filling chemical models, or squat, rounded shapes in SPM images that, to everyday intuition, can belie their dynamic and conformational range. For instance, Lander[31] and porphyrin[32] (Cu-TBPP) molecules specifically appear rather stocky and immobile, but have both been shown to exhibit conformational changes due to flexibility of their protruding appendages (four 3,5-di-tert-butyl-phenyl (TBP) legs on both molecules.) Some molecular structures, on the other hand, intentionally use flexibility or the ability to change conformation to their advantage or purpose. Azobenzene, for example, has been extensively studied for its ability to change between stable cis and trans conformations.[33]

Additionally, many relatively simple molecular systems have shown interesting dynamic capabilities under the right conditions. A study of a monolayer of hex-tert-butyl-decadiyne (HB-DC) on Cu(100) illustrates how a single molecule can act as a rotor within a supramolecular bearing.[13] All these examples emphasize that the dynamic range of even simple molecules can run counter to our initial impressions - often based on chemical schematics or scanning probe images. When characterizing or studying new molecular systems, especially via scanning tunneling microscopy (STM), specific attention needs to be paid to their possible conformational and dynamic behaviors if proper conclusions or observations are to be reached. In the case of the following work,
experimental observations varied rather significantly from the expected results, necessitating a more flexible approach to how we thought about the systems.

We have characterized by scanning tunneling microscopy (STM) a number of molecular systems based upon varying arrangements of fullerenes and oligo (phenylene ethynylene) (OPE) constituents with an eye towards understanding their single molecule mechanics. One of the major difficulties in imaging these molecules revolves around the interplay between the electronic characteristics of the OPE elements when covalently bound to the fullerenes. It is this combination that seems responsible for the resulting transparency of the inner molecular structures of these molecules to tunneling currents.

Over a wide range of tunneling parameters (-2 to 2 V, .03 to 1.5 nA), the OPE intramolecular elements remain unresolved even in the case of a variation that possesses a metalized porphyrin core. However, with the benefit of molecular models and dynamic observations via ultra-high vacuum (UHV) STM, there is still much to be inferred about and learned from the unseen interior of these molecules. As discussed below, our investigation of this family of molecules has shown that in every OPE-based, fullerene-wheeled molecule studied so far, the core structures have proven surprisingly flexible – allowing for widely varying molecule configurations and unique surface adsorption characteristics.

Based on their previous uses in conducting polymers and single molecule electronics, it is generally agreed that OPE-based molecular elements are fairly rigid. Our research illustrates that as integral parts of the various molecular structures in these studies, they possess an unexpected degree of flexibility. A key factor to this flexibility is the relatively strong chemisorbed $C_{60} - Au(111)$ interaction.[28] While the 1.87 eV
desorption energy is lower on Au(111) than for other noble metals (specifically copper, which also yields a 1.6 electron per C\textsubscript{60} surface-to fullerene charge transfer to only 0.8 for Au(111)) it is still strong enough to significantly influence the form or conformation of most C\textsubscript{60}-based molecules we’ve studied. On clean gold surfaces (for instance one prepared by repeated cycles of argon sputtering and annealing with deposition performed by fast-actuating dosing valve, compared to ambient hydrogen flame annealing followed by spin-casting for deposition) a higher flexibility is inferred by comparisons of molecule length. A stronger interaction between the fullerenes and a cleaner Au(111) surface (UHV versus ambient conditions) leads to greater flexing of the OPE sections, and smaller apparent size of the entire molecule.

The simplest molecule for which we will highlight this flexibility is the OPE-fullerene dimer as seen in Figure 5.1. Inner OPE structures of varying length and characterized by the number of phenyl groups were synthesized, and subsequently characterized on Au(111) on mica via STM in both ambient and UHV environments. For ambient scanning, the Au(111) substrates were hydrogen flame annealed prior to spin-casting toluene solutions of the dimer molecules. For UHV scanning, the Au(111) substrates were prepared in the same way before introduction to the UHV environment. Molecular models were used to calculate the expected length from fullerene peak to fullerene peak of a straight molecule. For the dimer with one phenyl group (referred to as a P1 dimer) the expected peak to peak length is 1.85 nm. The average measured length in ambient conditions is about 5% shorter, at 1.75 nm. In UHV conditions this difference jumps to nearly 20%, with average measurements showing only 1.43 nm between
fullerene peaks. This discrepancy between ambient and UHV observations is most marked in the P1 molecule, though still seen in both P2 and P3 dimers as well.

Generally, except for the case of the P1 dimer in UHV conditions, the longer molecules show a greater percentage mismatch between the modeled lengths of a straight dimer and the actual observed peak-to-peak measurements. This is likely explained by the additive properties of flexibility in general. While each OPE segment may have a flexibility constant or relation to the force applied, more segments together increase the overall flexibility. For instance, in a study on covalently linked porphyrins arrays, a diphenylethynyl linker was found to flex $26^\circ$ out of plane with the porphyrins, while a diphenylbutadiyne linker was found to flex $31^\circ$.[34] For the former to be joined with other diphenylethynyl-porphyrin groups and complete a full $360^\circ$ loop, it would require 14 porphyrin-linker groups joined together, while the latter would only require 12. (Essentially, in a long enough chain of any elements with limited flexibility, the ends will eventually be able to touch, making a closed loop.)

The case of the P1 in UHV conditions, however, seems to contradict this idea. (See Chart 5.1.) One possible explanation of the much shorter conformation may entail a strongly favored surface adsorption arrangement and a restriction of other adsorption possibilities due to the initial length limitations of the shorter molecule. (e.g. There are more possible adsorption arrangements for longer molecules that don’t as strongly distort the relaxed, straight conformation.) Whether this flexibility is typically in plane with the surface, normal to it, or some varying degree between the two is still unknown. However, the repeatedly observed shorter lengths of these dimers indicates that some sort of curvature or flexibility is certainly occurring.
Fig. 5.1: Fullerene – OPE dimers of varying length (denoted by the number of phenyl groups) were studied in both ambient and UHV conditions. (B: -1 V, 30 pA, C: -1 V, 90 pA, D: -1 V, 90 pA, all 11.4 x 11.4 nm)
Table 5.1

<table>
<thead>
<tr>
<th>Dimer</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
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<tr>
<td>Calculated (nm)</td>
<td>1.85</td>
<td>2.56</td>
<td>3.27</td>
</tr>
<tr>
<td>Ambient</td>
<td></td>
<td></td>
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<tr>
<td>Measured Ave. (nm)</td>
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<td>2.33</td>
<td>2.89</td>
</tr>
<tr>
<td>% Dev. from Model</td>
<td>-5.40</td>
<td>-8.98</td>
<td>-11.62</td>
</tr>
<tr>
<td>UHV</td>
<td></td>
<td></td>
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<tr>
<td>Average (nm)</td>
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<td>2.25</td>
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<tr>
<td>% Deviation from Model</td>
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<td>-12.11</td>
<td>-13.76</td>
</tr>
</tbody>
</table>

Table 5.1: Peak-to-peak lengths for three types of C_{60} dimer molecule (denoted by the number of phenyl groups between fullerenes) are compared for calculated, ambient measurements, and UHV measurements.

Another molecular variation to exhibit this effect, and which has been the recent focus of a great deal of study is the nanocar.[7] Again, the interior structure remains unresolved, and so flexibility is mainly inferred by peak to peak measurements versus modeled expectations. The nanocar, however, has the advantage of four points of reference versus only two for the dimer. As seen in Figure 5.2, this makes the flexibility of the OPE structures readily apparent in the difference between two images of the same molecule. In this case, nanocars were scanned at high temperature (approximately 200°C) and observed to not only roll across the surface and cross monatomic step edges, but also to readily change conformation as seen in Figure 5.2 (A) and (B). Numerous instances of conformational change have been observed in these molecules at both high and room temperatures, including images acquired both before and after those in Figure 5.2, the frequency of which alone rules out piezoelectric hysteresis or thermal drift as sole explanations. While a single loose fullerene adsorbed in the vicinity of a three-wheeled
nanocar may produce the same visual effect by moving relative to the attached fullerenes, in many cases this planar flexibility was observed with all four fullerenes moving in concert either before or after the observed change. One obvious illustration of this is again data acquired at high temperatures. These highly mobile nanocars undergo frequent and often drastic conformational changes while all four fullerenes move in concert – obviously attached to the central OPE portion of the molecule. However, even at room temperature such conformational changes have been observed, induced inadvertently by interaction with the STM tip.

An added characteristic from the alkyne bonds that allows the fullerenes to roll as wheels in the nanocar comes in the form of another type of flexibility. Due to the low rotational barrier of the alkyne, each OPE “axle” directly joining the fullerenes can pivot in relation to the other, and the connecting OPE “chassis.” This can lead to an alternate surface conformation as seen in the inset to Figure 5.2 (C), with one fullerene on top of another due to a nearly 180° rotation of an axle. While this is a rare occurrence, Figure 5.2 (C) and its cross section in Figure 5.2 (D) illustrate this extreme situation. A less extreme usage of this rotational freedom is thought to help in atomic step crossing and straddling in conjunction with the apparent flexibility of the OPE structures of the nanocar.
Fig. 5.2: The nanocar has exhibited two different types of conformational change. (A) and (B) illustrate the flexibility of the OPE segments connecting the fullerenes (at 500 K, -0.94 V, 180 pA), while (C) (-0.92 V, 15pA) and its cross-section (D) illustrate rotation about the alkyne connecting the chassis and axle OPE segments, resulting in one fullerene stacked on top of another, giving a 3-wheeled appearance.
Another similar molecule in this family displays additional surface conformations due to the rotation of the alkyne bond. Figure 5.3 (A) shows the kinked chassis nanocar in its most common conformation, while 5.3 (D) illustrates this conformation as observed in UHV. The combination of this rotational pivoting of the OPE axles, and the flexibility of the OPE components themselves makes unequivocal identification of the other two other conformations (B) and (C) extremely difficult. While it is likely that Figure 5.3 (E) captures conformation 5.3 (B), it cannot be stated with certainty, and could simply be a distorted version of conformation 5.3 (A). While many other apparent formations have been observed, the lack of resolution of the inner OPE structure and their previously observed flexibility indicates that it is possible that the conformations in figure 5.3 (B) and (C) are not naturally occurring on the Au(111) surface, or are simply indistinguishable from each other, and possibly from formation (A) as well.
Fig. 5.3: The kinked or bent-chassis nanocar and its three possible conformations due to alkyne rotation are modeled in (A) through (C). (D) illustrates conformation A as seen in UHV, while (E) could be either conformation A or B. (Both (D) and (E) acquired at -0.7 V, 4 pA.) The additional flexibility of the OPE constituents complicates definitive labeling.
To better understand the mechanisms behind the transparency of the central structure in the above molecules, a slightly different type of molecule, dubbed the nanotruck, is seen modeled in the inset to Figure 5.4 (A), and was imaged on a Au(111) sample in UHV as seen in Figure 5.4 (A). With much shorter axles that contain no OPE constituents, not only is the flexibility reduced, but more obviously, and in a reversal from the rest of the molecules discussed here, the inner structure of the molecule appears brighter than the surrounding fullerenes. Aside from a different type of central structure, the main difference between this and other molecules is that the four fullerenes are directly attached with a simple alkyne bond lacking the phenyl ring. To further understand the interactions occurring here, another similar molecule was synthesized with the exact same central chassis structure, but with longer, OPE-based axles, as modeled in the inset to Figure 5.4 (B) (leaving off the alkane chains again for clarity. Coincidentally, the additional alkane chains also increased solubility during synthesis and made solution-based deposition much easier and more reliable in comparison to the shorter axle version.) As seen in Figure 5.4 (B), the inner structure – OPE axles and central chassis – is no longer resolved, with the conclusion that the added phenyl constituents between the fullerenes and central chassis must be responsible.
Fig. 5.4: Two different nanotruck versions were examined to explore the role of the OPE constituents in the resolution of interior structures on fullerene-based molecules. The smaller version with axles lacking the phenyl rings saw a central structure resolved more brightly than the surrounding fullerenes, while the addition of phenyl groups saw a complete lack of resolution of the internal structures. (A) acquired at 1 V, 100 pA, (B) acquired at -0.4 V, 40 pA. (Additional images at a wide range of both positive and negative bias failed to resolve the inner structure in (B).
One of the most intriguing and flexible molecules characterized so far is seen in Figure 5.5 - a porphyrin core with four biphenyl OPE arms each capped with C\textsubscript{60}. The first characteristic to become immediately apparent is the continuing lack of resolution of the inner structure, even with the addition of the copper-based porphyrin core. Traditionally porphyrins are readily imaged by STM, though the central structure is generally overshadowed by taller TBPP or similar legs,[32] making this lack of resolution more intriguing, even given the observed characteristics of other OPE-based molecules. The next most apparent characteristic is the molecule’s incredible affinity for straddling step edges. Almost no molecules were found to be stable on open terraces, and the vast majority was found in areas where steps were close enough together to allow two fullerenes to adsorb at an upper edge, and two fullerenes to adsorb at the next lower edge, as seen in Figure 5.5 (A) and (B). From investigation of numerous samples and images, it is apparent that the preferred adsorption site has all four fullerenes at the top of two different step edges. This incredible affinity for step edge adsorption is also, perhaps, partly responsible for the great degree of flexibility exhibited by this porphyrin-based molecule. A stronger interaction with the surface at the step edge could potentially create a greater flexing force, which, coupled with the relatively long OPE length, may induce greater flexibility in the whole molecule.
Fig. 5.5: A porphyrin center with four biphenyl, C$_{60}$-capped legs is still unresolved on the Au(111) surface (-0.3 V, 3 pA). Strong affinity for step edges may be partly responsible for the increased flexibility observed.
In conclusion, we've characterized a number of different types of molecules with similar OPE-based inner structures. The OPE constituents, typically treated as particularly rigid, have shown a great degree of flexibility when coupled with their fullerene counterparts on a Au(111) surface. Scanning tunneling microscopy results compared over ambient and UHV conditions show that greater flexibility comes with a cleaner surface, suggesting that the flexing effect is a result of the relatively strong fullerene-gold interactions. In addition, the alkyne bonds in these OPE-based molecules allows for rotation of the axles of certain types of the molecules, resulting in varying possible surface conformations, some of which have been directly observed. When paired with the inherent flexibility seen in these molecules, however, identification can be uncertain. In addition, comparison between molecules with fullerenes attached to OPE structures and those attached directly to a central core show that the OPE plays a central role in the inability to resolve the inner molecular structure.

The implications from these studies may prove useful in future designs of molecular electronic or dynamic devices. Flexibility will not only have to be accounted for in design, but could also be incorporated to have an active roll in the functionality of varied devices. The effect of flexibility on areas such as molecular and polymer electronics would have to be considered, as the deformation of molecular structures has shown to have an effect on conductivity. It could also be a benefit, however, to have flexible molecular wires in self-ordered systems, as a lack of fine spatial coordination between systems is not readily available in self-assembled environments. In all, small-scale molecular flexibility – often counterintuitive at first approach – may prove to be
both an advantage and a challenge for future electronic and mechanical molecular devices, and it must be accounted for from design to implementation.
Chapter 6

Other Work

One of the advantages to the experience built up over the years in the Tour lab as they developed and created the nanocar, is that it helped them to create a kind of molecular tinker toy set, allowing for myriad molecular variations composed of the same basic components, and using many of the same synthesis techniques.[35-40] Many of these molecules share similarities with the nanocar, and have been characterized and studied via STM: often as a complement to work on the nanocar itself, but sometimes based on their own merit. Though often not as extensively studied as some of their more prominent counterparts in the earlier pages of this thesis, many of these molecules show great promise for future experiments - some of which are already being carried out by other researchers in the Kelly lab.

One thing shared by all of the molecular variations studied by STM in this work is that all are, in some way, wheeled molecules. Fullerenes, with their spherical, cage-like structure are most frequently used, and have been shown to roll under both direct tip-manipulation and thermal motion. The other type of wheel structure used is the carborane molecule – a similarly cage-like structure of carbon and boron that creates a much smaller wheel with triangular segments, as opposed to the fullerene’s hexagons and pentagons. In this discussion, variations on the nanocar can be categorized by the number and type of wheels. There are alternate versions of nearly every fullerene-based molecule that instead utilize the carborane, though dynamic experiments have so far been inconclusive as to whether or not they roll in a manner similar to the fullerene versions.
The first alternate molecule in this discussion is a variation on the basic fullerene dimer concept: a two-wheeled, fullerene-based molecule. The great difference, however, comes in the form of a photoactive azo compound (characterized by the N-N double bond) in the middle of the molecule, which would allow the molecule to bend and straighten between the cis and trans conformations under illumination or electric field pulses[33, 41]. Ideally, these conformations would measure 2.0 nm for the folded cis form, and 4.3 nm for the extended trans form (using peak-to-peak measurements to circumvent tip convolution effects.) Previous STM studies[33] of the azobenzene and derivative molecules illustrate its dynamic abilities, with trans to cis photoisomerization occurring at ultraviolet wavelengths, and cis to trans occurring at blue wavelengths. Azobenzene molecules have also been isomerized with voltage pulses from an STM tip.[41] Initial studies in UHV on Au(111) have suggested that photoisomerization of the azofullerene dimer can occur on the surface, as seen in Figure 6.2. The previously exhibited flexibility of the OPE-fullerene combination means that these measurements fall well within the range of possible surface conformations for their respective isomers, though the wide range of other measured peak-to-peak lengths and lack of resolution in the interior of the molecule makes absolute certainty impossible without further experimentation. In fact, preliminary studies performed by the Tour group suggest that the quenching effects of the fullerenes on either side of the azo-OPE combination greatly reduce isomerization efficiencies to the point that further study in the hope of reaching a useful photo-molecular device is questionable. However, more thorough experimentation and analysis are required before a definitive conclusion is reached.
Fig. 6.1: Model of the azo-OPE fullerene dimer in the *trans* form
Fig. 6.2: A space-filling model shows the azo-OPE fullerene dimer in both the trans (A) and cis (B) forms, with modeled fullerene peak-to-peak distances of 4.3 nm and 2.0 nm, respectively. STM images at 10 pA and -1 V highlight a dimer that isomerizes between images from trans to cis, though gold-fullerene interactions appear to distort the dimer from the expected lengths.
The second alternative molecule in this discussion is a variation on the nanocar molecule, and replaces the fullerenes with carborane wheels.[36] This is a four-wheeled, carborane-based molecule. The actual molecule, with the much smaller carboranes, has a much smaller chassis and axle interior structure, as seen in Figure 6.3, doing away with all but three phenyl groups that make up the backbone, or chassis of the molecule. A six-wheeled version was also characterized by Jun Zhang in the Kelly group. Initial characterization studies for both versions ran into difficulties with contamination by the much larger nanocar molecule, but eventually provided a stark contrast of the molecules, especially their large size difference. A “nano traffic jam” is seen in Figure 6.4, which serves as a stark comparison of the sizes of the six-wheeled carborane nanocar and the four wheeled fullerene nanocar. Similar studies were carried out on these carborane-based molecules as on the original nanocars, but it was found to be much more difficult to induce motion. This leads to the initial conclusion that the carborane-based molecules do not employ the same rolling mechanism as found in their larger fullerene-wheeled counterparts. Again, however, more thorough experimentation and analysis is required before definitive conclusions are reached.
Figure 6.3

Fig. 6.3: A space filling and wire model of the carborane nanocar
Fig. 6.4: Six-wheeled carborane nanocars, (schematic in lower right inset) highlighted in blue trapezoids, decorate the Au(111) surface in aggregates of > 1 monolayer. Contamination of the original fullerene nanocar (schematic in upper left inset, and two sets of four bright lobes in the main image) during deposition allows for a side-by-side comparison of the significant differences in both height and width of the two similarly structured nanocars. (Image acquired at -1 V, 10 pA)
The recurrent issue with the lack of resolution of the inner structures of the fullerene-based molecules of all types has led to attempts at circumventing and further understanding this problem. Alternate dimer models with fewer alkane chains attached to the OPE segments, and intentionally one-wheeled versions (Figure 6.5 c) have failed to enlighten the issue. No intramolecular resolution was achieved with any dimer variants, leading to the initial conclusion that an interaction between the fullerene and OPE segments (specifically the phenyl groups) inhibits the visualization of these structures. Additionally, experiments were carried out using self assembled monolayers, or SAMs, as dielectric barriers between the nanocars and the Au(111) surface. This was done with the intention of exploring the roll of the interplay between the gold surface and fullerenes in the continuing lack of intramolecular resolution. Unfortunately, no internal structures were observed, and the nanocars appeared similarly to that which was previously seen on bare Au(111) surfaces – only the four lobes of the fullerenes were visible through a wide range of tunneling parameters, as seen in Figure 6.5 (a) and (b). (Also interesting in its own right is the relative mobility of the molecules on the SAM surface, highlighted by the highly deformed conformation of the nanocars in Figure 6.5 (b), and additional instances of nanocars moving on the surface at room temperature. It appears in many cases that the assumed interdigitation of the alkane chains with the SAM is not as strong or as prevalent as originally assumed.) When taken in light of the discussion in Chapter 5, where even porphyrin-bound copper amidst the fullerene-OPE legs is unresolved, it lends further credence to the theory that the interplay between the OPE and fullerene components is mostly responsible for this characteristic.
Fig. 6.5: (A) and (B) (-0.6 V, 3 pA) show the fullerene nanocar on a C₆ SAM, still with a lack of resolution of the inner OPE structure. The flexibility is still notable, as seen in B), indicating that direct interaction of the fullerenes with the Au(111) substrate is not necessary for significant deformation of the OPE constituents.
Another interesting point in the discussion on the lack of internal resolution in the nanocar and other molecules comes from studies of the original nanotruck, as briefly discussed in Chapter 5 and seen in Figure 5.5 (A). The nanotruck, without the typical OPE segments attaching the fullerenes to the central structure, actually resolves the inner structure. As seen in the image, the central chassis actually appears brighter than the surrounding fullerenes. A molecule with the exact same chassis and OPE-joined fullerenes, as seen in Figure 5.5 (B), again does not allow for resolution of any internal structures. This addition of OPE constituents between the chassis and fullerenes effectively masks the chassis structure entirely to the tunneling electrons.
Fig. 6.6: (A) (-1 V, 30 pA) and (B) (-1 V 80 pA) show two different dimer variation attempts at intramolecular resolution, with their accompanying models, though images still showed no internal structure on either version.
Chapter 7

Future Directions / Conclusion

From the myriad studies of numerous molecules described in these last few chapters, much has been learned – perhaps nothing more poignantly than the fact that there is still much we don’t know. What we do know, however, is quite significant. The nanocar and its family of molecular machine precursors have illustrated a number of interesting behaviors and effects that may be utilized in future, more complex molecular devices, among them: fullerene rolling-facilitated surface mobility under direct tip manipulation and surface annealing, a strong fullerene-Au interaction, a high degree of OPE flexibility, a number of different surface conformations, an interesting OPE-fullerene electronic effect leading to essentially “invisible” intramolecular structures, dynamic monatomic step crossing and a number of stable step straddling positions, and accompanying strong electronic surface interactions at step edges. While these discoveries may prove useful in future nanomachines, they all reveal more questions than they answer. To cover only a few of the potential research avenues open to those who may be carrying on similar work in the future, the nanocar serves as viable platform from which to launch a brief discussion of important unanswered questions.

One of the first questions directed towards useful applications for the nanocar and its ilk is whether and how a group of nanocars could be directionally controlled in concerted motion. Towards this end there are a few different approaches. The first involves surface modification to affect tracks or guides for nanocar and -truck variations across flat surfaces. Various self-assembled monolayers, or SAMs, could create such
structures, as, potentially, could the already periodically ridged surface structure of any (110) fcc lattice structure, or perhaps those with higher Miller indices, such as fcc (775), for instance. These routes, however, lead to the realization that the nanocar’s behavior has only been extensively studied on Au(111), and that drastically different behaviors and characteristics could be found on other surfaces. Since the strong interaction between the Au(111) surface and fullerene wheels appears to play a significant part in the nanocars’ rolling surface translation, a significant question is whether the nanocar would roll in a similar manner on different surfaces. This is an important question to be answered before other surfaces and surface patterns are attempted for strict directional control.

Other experimental concerns, however, also arise with the introduction of varied surfaces for nanocar or similar molecule studies. As mentioned in Chapter 2, most deposition of these molecules occurs through the dosing valve on the high-vacuum load lock area of the chamber. This is not a problem with Au(111) as a substrate, as it is inert and is not readily influences by the introduction of solvents and higher pressures. Many other surfaces, however, must be kept in inert environments after preparation or their desirable surface characteristics will be lost. Silicon, for instance, would prove an interesting substrate on which to explore the rolling of nanocar fullerenes, since previous studies have seen fluorinated fullerenes rolling on that surface.[42] The method of deposition, however, would have to be changed to a dry, UHV-compatible technique in order to maintain the surface state. Oxidation of other surfaces such as tungsten or platinum would also need to be addressed in a new method of deposition. Evaporation is not an option for the nanocar and similar fullerene-based molecules, as the desorption temperature for the fullerenes from their alkyne bonds is below the temperature needed to
evaporate the molecule. Attempts were made at dry deposition w/ direct contact of a nanocar-laden fiberglass weave to a Au(111) sample surface, as has been shown to work with nanotubes, but led to areas of either exceedingly high or non-existent surface coverage. Appropriate sub-monolayer coverage will be a difficult challenge with these molecules, though the idea of flash deposition holds promise. A single monofilament covered with the desired molecule and surrounded by a slightly opened envelope of tantalum or other foil could perhaps achieve the desired deposition effect. While still using thermal desorption to eject the molecules, a much shorter subjection to high temperatures could be achieved with the proper materials and techniques.

The other main approach to strict concerted directional control is to implement the directional constraint into each molecule itself – to vary the structure to contain a dipole manipulable by external fields. Efforts are already underway in the Tour lab to implement just such a mechanism into a nanocar variant, with varying degrees of success. If implemented, this would theoretically allow numerous molecular devices to be directionally controlled by external field to move in a controlled manner across a surface. This possibility, of course, leads to numerous further questions beyond synthetic concerns to those of appropriate field strength, long range molecular surface mobility, precise transport mechanisms, ideal surface density, and many others to be uncovered along the way. When coupled with active sites for molecular or atomic adsorption on the molecule itself, useful applications truly start to arise.

More fundamental questions still remain to be answered, however, before a thorough understanding of the nanocar can be claimed. While electronic effects at step edges are visible through position-dependent differences in apparent height, the exact
nature of these effects are still unknown. A more thorough study of these step edge electronic effects, including spectroscopy and low temperature analysis may help elucidate the nature of step edge interactions in both static and dynamic situations, leading to better predictions of behaviors on varying surfaces. Also towards that end, theoretical calculations would prove a boon to experimental studies in that they could allow for more precise probing of specific theoretical behaviors. For instance, differing surface adsorption sites could be probed at low temperatures and more easily interpreted, allowing for a more thorough analysis of fullerene rolling and overall molecular transport. The relative complexity of the molecule has proven a barrier to detailed atomic-scale modeling so far, but new methods and motivations will undoubtedly spur more work towards this end in the future.

Additional fundamental questions remain as to the exact strength and roll of the Au(111)-fullerene interactions, the exact degree and method in which the rolling fullerenes allow for directional motion, the range of angles from perpendicular to the OPE axles that the nanocar can roll, and the exact cause of the lack of intramolecular resolution, to name a few. But new molecules are constantly being synthesized, begging to be examined by STM. For instance, nanocar variants with an inherent dipole, a light-actuated “motor,” or functionalized ends that could allow for train-like attachments of multiple molecules inherently attract attention with their possibilities. It is therefore important to grasp the basics on the simpler systems that can be applied to more complicated future versions.

This thesis and the work before it has just scratched the surface (in some cases literally, a fact many a ruined STM tip could attest to) of the expanding body of
knowledge to be gleaned from the nanocar and its family. Low temperatures, spectroscopic and microwave analysis, varied surfaces and new experimental applications are just some of the possible directions for future work on the nanocar alone. Alterations in wheels, body composition, deposition, scanning and analysis techniques, and even synthesis and overall purpose of the molecules will inevitably follow - in some cases must follow - on the way to real-world viability and usefulness. While the current generation isn’t there yet, the possibility doesn’t seem far off, and I appreciate all that I’ve learned and the opportunity to contribute to this small first step in that direction.


[34] A. A. BothnerBy et al., Journal of Physical Chemistry 100, 17551 (1996).


