



LUND UNIVERSITY
Faculty of Science

Radical Adsorption onto CO Intercalated Graphene

David Linehan

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Supervised by Jan Knudsen and Foteini Ravani

Department of Physics
Division of Synchrotron Radiation Research
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Abstract

This project studies with scanning tunneling microscopy (STM) if radicals can adsorb onto the surface of graphene flakes which had been intercalated with CO. To obtain CO intercalated flakes of graphene, flakes of pristine graphene are formed, and subsequently intercalated by a super dense “water” phase. This water phase allows for the intercalation of CO, where it is observed that flakes are intercalated digitally; either fully intercalated or not at all. After dosing radicals, it is observed that, while radicals readily adsorbed onto bare flakes of graphene, flakes of CO intercalated graphene are nearly universally adsorbate free. Following a new round of annealing and CO dosing, it is found that the sample possessed flakes with CO intercalation channels and other forms of non-digital intercalation. Previously CO intercalation channels could only be found during very brief (several seconds) exposure to CO. This information suggests that the intercalation of CO somehow precludes the adsorption of these radicals, and vice versa.

Contents

1	Introduction	3
2	Background.....	4
2.1	Freestanding Graphene.....	4
2.2	Graphene on Ir(111)	4
2.3	Intercalation and Adsorption.....	6
2.4	STM.....	6
3	Experiment.....	9
3.1	Setup.....	9
3.2	Preparation of Sample	10
3.3	Analysis of Sample.....	12
4	Results and Discussion	13
4.1	Graphene and Intercalate Substrate.....	13
4.2	Radicals on Intercalated Graphene.....	15
5	Conclusion	17
6	Outlook	17
7	References	19

Acronyms

STM	Scanning Tunnel Microscopy
UHV	Ultra High Vacuum
L	Langmuir
FCC	Face Centered Cubic
HCP	Hexagonal Close Packed
TPG	Temperature Programmed Growth
CVD	Chemical Vapor Deposition

1 Introduction

Graphene is a uniquely marvelous material. Graphene is composed entirely of carbon in a two-dimensional grid, meaning that the structure is only one atom thick. Among graphene's many impressive qualities are near transparency to visible light, astoundingly high conductance of both electricity and heat, and being far stronger than steel despite being far lighter. These properties made the discovery of graphene merit the Nobel Prize in 2010. Graphene's high electrical conductance is due to being a semi metal; a zero-gap semiconductor. As a semi-metal, graphene has an electron mobility several orders of magnitude greater than that of silicon, making graphene a potentially indispensable material in the future of the technological age. Despite the current expense in developing graphene, the fact that graphene is made entirely of carbon (a relatively cheap material) gives hope for graphene being available in all potential future applications.

Currently graphene can be made in several ways. While initially graphene was formed through the mechanical exfoliation of graphite, in this thesis graphene is grown directly on the surface of a single crystal of iridium cleaved along the (111) plane. With graphene formed on Ir(111), it could be studied how inserting molecules beneath the graphene would affect the ability to bind atoms on top of the graphene.

More specifically, it is studied how the intercalation of CO beneath flakes of epitaxial graphene would affect the adsorption of radicals onto the surface of the graphene. To this end, CO was intercalated by first intercalating an OH-H₂O phase, and then exposing the surface to CO. The CO entered beneath the flakes of graphene through points intercalated by OH-H₂O. After this, radicals were formed. Formation of radicals was done by dosing C₂H₄ around the sample and disassociating it by use of a current carrying filament. Ideally disassociation would produce complex carbon hydride radicals, but without a chemical analysis, the type of radicals cannot be verified. As the effect of CO intercalation on the adsorption of radicals has never been studied before, there are numerous potential applications, such as in the manipulation of the electronic properties of graphene, or the detection of intercalants or radicles on graphene. The primary instrumentation used to conduct this study was the scanning tunneling microscopy technique (STM) which can provide an atomic scale picture of the studied surface.

2 Background

In this chapter, background information of the sample, how it can be modified, and how it can be studied is provided. Regarding the sample, the concepts of freestanding graphene and Ir(111) supported graphene are discussed. Modification background entails the growth of graphene on Ir(111) and a brief description of intercalation and adsorption. Finally, the principles of the scanning tunneling microscopy (STM) technique will be also provided.

2.1 Freestanding Graphene

Graphene is a monolayer structure composed entirely of carbon arranged in a honeycomb lattice; a grid of hexagons. In each carbon atom, the s , p_x , and p_y orbitals hybridize and form sp^2 bonds ($\delta_{1,2,3}$ in Figure 1). The unaffected p_z -orbital forms a π band oriented perpendicular to the plane of graphene. The π band is half full, and can bind covalently with neighboring atoms [1]. Graphene's structure consists of a repeating unit cell of two carbon atoms, shown in Figure 1, with a periodicity of $2.45 \pm 0.04 \text{ \AA}$ [2].

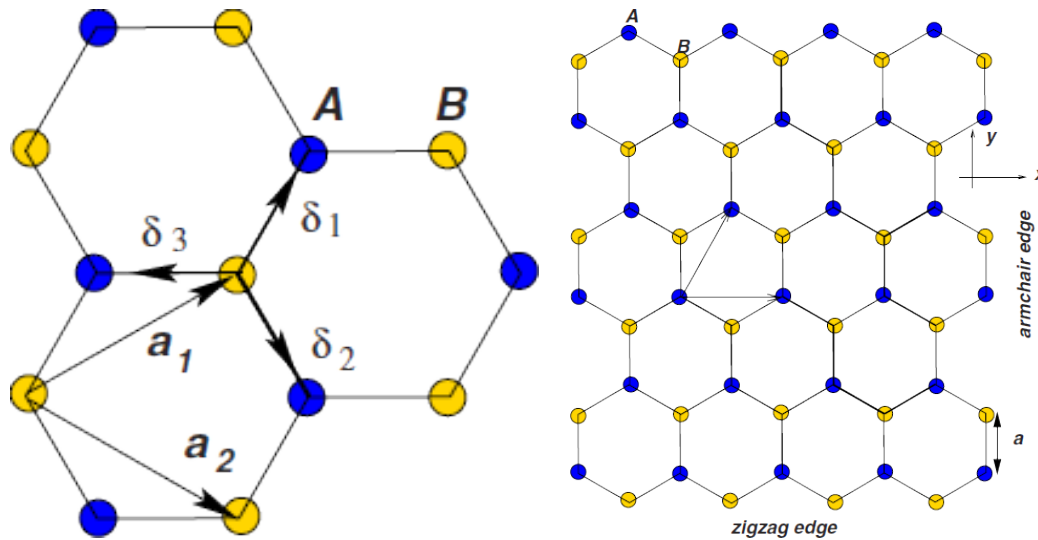


Figure 1: left: Lattice structure of graphene, where $\delta_{1,2,3}$ are the sp^2 hybrid bonds, and $a_{1,2}$ are the lattice vectors. right: Graphene's honeycomb structure on a larger scale. Both images utilized from Neto et al. [1].

2.2 Graphene on Ir(111)

Iridium is a so called Noble Metal which reacts poorly with most substances. Graphene can be grown on a variety of metal surfaces, such as (but not limited to) Cu, Rh, Pt, and Ir. Iridium's low activity makes it a particularly good substrate for the growth of graphene with an almost undisturbed linear Dirac-like dispersion characteristic, like that of isolated graphene [3, 4]. Iridium crystallizes in an FCC structure and, as such, the (111) plane of iridium has a hexagonal structure which has an interatomic distance of 2.715 \AA [2].

Graphene Structure on Ir(111)

Graphene and Ir(111) both have hexagonally based structures, though their lattice constants vary slightly. The lattice constant of Ir(111) is 11% larger than that of graphene. This means that no matter how the two materials are aligned, there will always be a mismatch, leading to a so-called moiré pattern, illustrated in Figure 2.

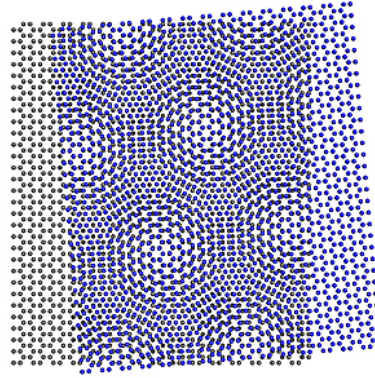


Figure 2: Illustration of a hexagonal moiré pattern due to overlapping honeycomb structures. This is quite similar to how graphene will look on top of Ir(111). Image credit to NIST [5].

As one can see in Figure 2, the moiré is substantially larger than the structure of the initial honeycomb structures. In the same way, the moiré structure formed due to the lattice mismatch of graphene and Ir(111) has a periodicity with a $25.2 \pm 0.4 \text{ \AA}$ unit cell. [2]; approximately a factor of ten larger than the initial structures. The unit cell being far larger not only aids in quick detection (compared to looking for graphene's unit cell) when using STM, but it also gives information about how graphene's atoms overlap with Ir(111).

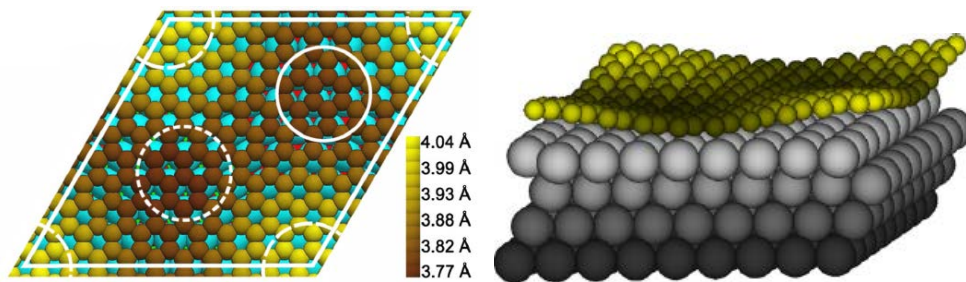


Figure 3: left: Schematic illustration of 10x10 carbon (in the form of graphene) on top of 9x9 iridium. Image taken from N'Diaye et al. [6]. right: Side view of the topographical differences (which leads to the moiré pattern) between graphene and the iridium under it. Taken from Lazić et al. [7].

Figure 3(left) shows an HCP-type region (enclosed with a full circle), an FCC-type region (enclosed by a short-dashed circle), and an atop-type region (enclosed by dashed circle segments). The color bar denotes the distance between the carbon and the iridium surface [7]. In the FCC and HCP sites, every second atom is located above a threefold hollow site, while the remaining atoms are located directly above an iridium surface atom. In the atop regions, an iridium surface atom is centered within a graphene honeycomb [2]. The overlap in FCC and HCP regions leads to an increased bond strength between the carbon atoms and the iridium atoms, causing a lower interatomic distance, as seen in Figure 3(right).

Graphene Growth Methods

Two methods are used to grow graphene in this project: TPG (Temperature Programmed Growth) and CVD (Chemical Vapor Deposition). The TPG process consists of adsorption of hydrocarbons at room temperature (RT), in this case Ethylene, followed by pyrolysis at elevated temperatures. This leads to the formation of graphene islands on the surface of a metal. CVD consists of hydrocarbons being dosed onto an already hot substrate, where the hydrocarbons disassociate directly upon adsorption. This extends the graphene islands to a size proportional to the exposure time and pressure between the sample and the hydrocarbons.

2.3 Intercalation and Adsorption

Intercalation is the process of inserting a substance between two distinct compounds, in this case the layers of Ir and graphene, as illustrated in Figure 4. From a practical standpoint, intercalation allows for the modification of graphene properties. These properties include the potential to increase the bandgap or reduce its reactivity, for example with the substrate surface. In order to intercalate materials such as carbon monoxide, oxygen, and hydrogen, they must first adsorb on clean Ir(111) patches. O₂ and H₂ molecules dissociate directly upon adsorption, while the CO molecule remains intact. Subsequently the adsorbed atoms or molecules diffuse under the graphene flakes from their edges; adsorption through graphene is impossible. For this reason, in this work, it was important to have a coverage ratio noticeably lower than 1; there should be flakes of graphene instead of a full monolayer. Flakes, thusly, have the obvious advantage of possessing a high edge to area ratio.

While intercalants are molecules beneath the graphene, adsorbates are the molecules above it. Though Figure 4 shows intercalation and adsorption coexisting, this is not necessarily possible in all cases, and it can be studied in what sense adsorption and intercalation can coexist, and in what ways adsorption can influence properties of graphene.

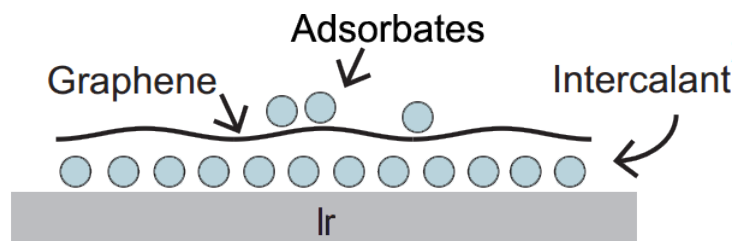


Figure 4: Illustration of graphene intercalation modified from Gr  n  s [8].

2.4 STM

STM (Scanning Tunneling Microscopy) is a high-resolution scanning probe technique which gathers surface information by raster scanning a tip over a surface while maintaining a constant quantum tunneling current. In this experiment, the tungsten tip was scanned forward and back along an x axis, after which the position along the y axis was increased by one. This process was repeated until a maximum y value was achieved, after which the process repeated, but with decreasing y values. Since x and y represented directions along the sample, this provided a

pixel map of the surface. Therefore, four images were created by each scanning cycle. A constant voltage can be applied between the tip and the surface, and then the current can be influenced by the distance, d , between the tip and the sample. The current can be expressed by the equation:

$$I(d) = K \cdot V \cdot e^{-2\kappa d}$$

Where $I(d)$ is the current as a function of the gap between the tip and the sample, K is an arbitrary constant, V is the voltage between the tip and the sample, and κ describes the decay of the electron wavefunction within the gap. This signifies why there would be a lower current with a greater gap length, or greater current with a greater voltage difference. An increase in κ would also lead to a decrease in current, and, since κ is affected by the work function for the sample, the current would also depend upon the material being studied. Consequently, impurities may appear to be lower than they actually are, since, depending on the material, the change in κ can be compensated by a decrease in d [9].

Given the relation between current and distance, STM can operate in either a constant current mode, or a constant displacement mode. The constant displacement mode will record varying currents along the sample, and will save time by not needing to constantly readjust its position normal to the sample. This has the advantage of scanning more quickly, but the significant disadvantage of potentially running into a raised area of the sample, potentially leading to irrecoverable damage of the tip. Instead, constant current mode can be used to prevent unintentional contact between the sample and the tip. As such, constant current mode is the mode used in this work.

When scanning, the system will store the x/y/z coordinates and display them as pixels with a color code. The x and y bounds will be user specified depending on what image resolution is desired, while the z coordinate is determined by the distance needed to maintain the constant current. To maintain the current, a feedback loop continuously adjusts the distance between the tip and the sample. These positions are manipulated by applying voltages to three piezo crystals, allowing the atomic resolution that the STM is capable of. Since the tip displays the total current traveling through the whole tip, an ideal tip would have one sharp point with a head of one atom, illustrated in Figure 5.

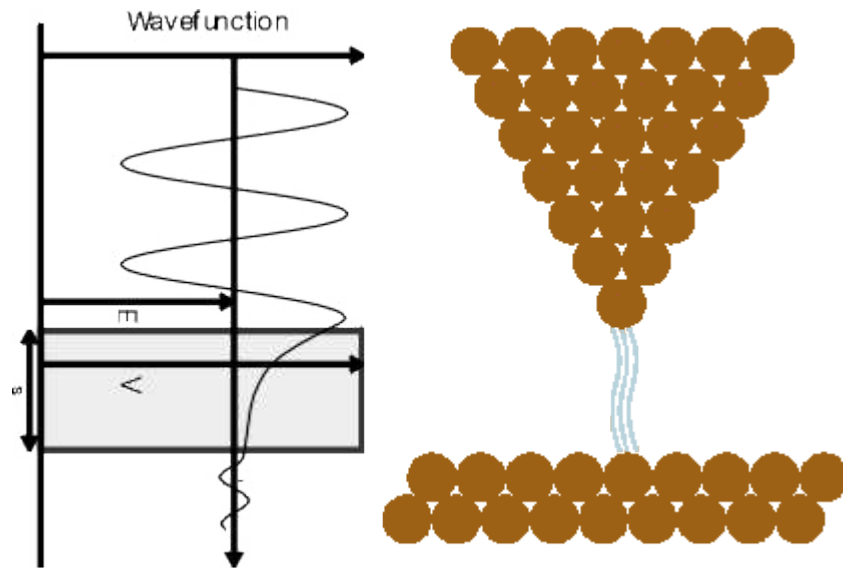


Figure 5: An illustration of an atomically sharp tip, along with a demonstration of how tunneling plays a role. Image modified from Tufts University [10].

An atomically sharp tip, however, is difficult to achieve, due to deformations from collisions, or unintentional binding of loose atoms from the sample. Practical methods for achieving a sharp tip are briefly mentioned in section 3.3.

3 Experiment

These experiments intend to study the effects of radicals on CO intercalated graphene flakes. The following section will provide an overview into the experimental setup, as well as the processes used to clean the sample and develop structures of interest upon the sample. Finally, tools used to analyze these structures will be described.

3.1 Setup

Figure 6 shows the UHV (Ultra High Vacuum) setup, located at Lund Universities Physics Department. The UHV setup is essentially divided into three main chambers: an analysis chamber, a preparation chamber, and a load lock system.

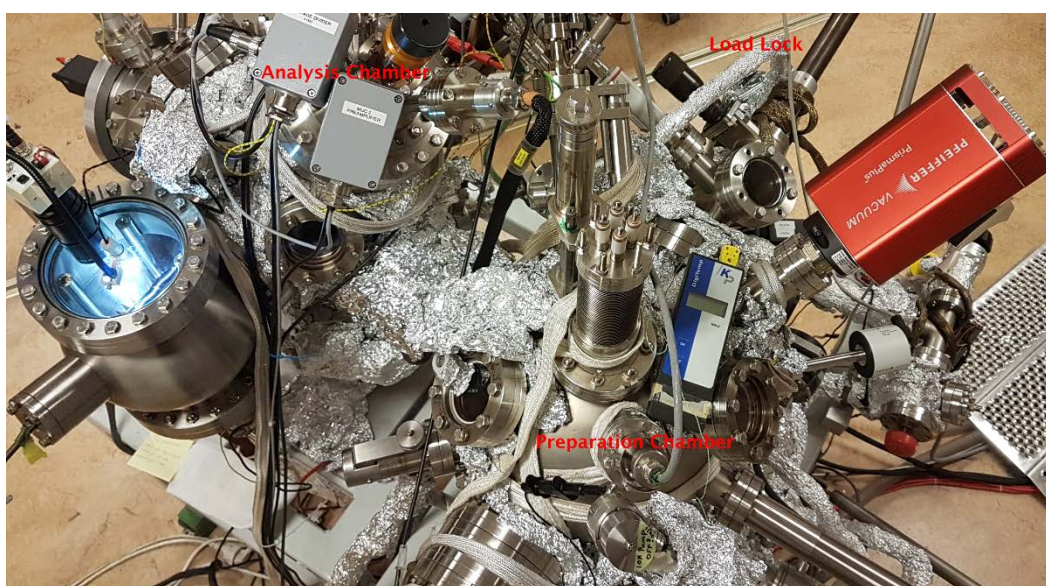


Figure 6: Picture of experimental setup, with the analysis chamber in the upper left, the preparation chamber in the lower middle, and the load lock system at the window in the upper right.

The preparation chamber is where the sample can be prepared using a variety of methods. These methods include sputtering, electron beam heating, and physical vapor deposition using evaporators. Of notable use for this study, a home designed cracker, Figure 7(left), is used to facilitate energy dependent reactions, while leak valves are used to dose gases.

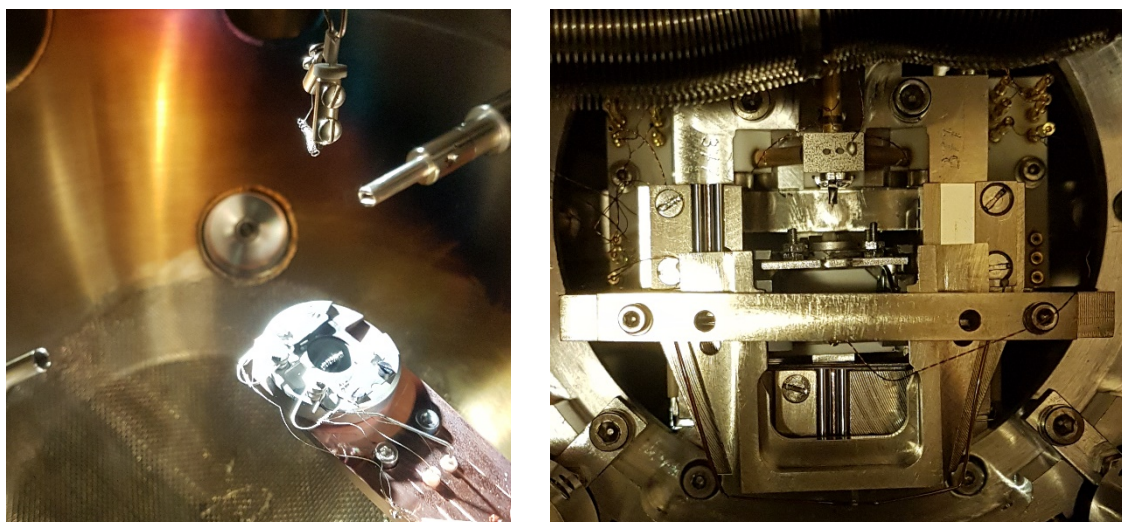


Figure 7: left: The homemade cracker (the upper most object) located in the preparation chamber. On the right middle is a transfer arm, and in the bottom half is a manipulator. right: the STM table located in the analysis chamber.

The analysis chamber contains the apparatuses necessary to perform LEED (low energy electron diffraction), Auger spectroscopy and STM. The preparation chamber contains the necessary pumps to bring the chambers from atmospheric pressure to UHV conditions, though both are capable of maintaining a UHV in the order of 10^{-10} mbar. The load lock system provides fast entry of the sample from atmospheric pressure to UHV without venting the preparation chamber. The sample can be transferred from load lock to preparation's manipulator, and from preparation's manipulator to analysis' manipulator using transfer arms. To transfer the sample from the manipulator in the analysis chamber to the STM table, a wobble stick is used.

3.2 Preparation of Sample

Sample Cleaning (Ir(111))

Before graphene is grown, the Ir(111) substrate is cleaned; a necessity for most surface science studies. To clean Ir(111), first a sputtering process is performed, which consists of bombarding the sample with Ar^+ ions. Ar^+ is used because, as an ion, it is easy to both direct and accelerate. Ar, as a heavy atom, is very effective at sputtering the surface, and, as a noble gas, can easily be removed by thermal annealing. These ions collide with surface atoms and kinetically eject them. Sputtering is done for 15 minutes, at 2×10^{-5} mbar of Ar, with an accelerating voltage of 1.5 keV.

Subsequently, the sample is annealed in 5×10^{-7} mbar of O_2 for 5 minutes at 900°C . Firstly, annealing removes carbon from the sample, and, secondly, annealing smoothes out the surface. Following annealing, the temperature is increased to 1200°C for several seconds to remove remaining oxygen.

These two techniques are repeated until the sample is sufficiently cleaned; as judged by STM images.

Graphene Growth (Gr/Ir(111))

Graphene flakes are produced on the clean Ir(111) surface through the use of both TPG and CVD. During the TPG process, the sample is exposed to 10^{-6} mbar of C_2H_4 (Ethylene) at room temperature. After 200 seconds, the sample is flashed at $1100^\circ C$ for several seconds. In the following CVD process, the temperature is kept at $1000^\circ C$ while exposed to C_2H_4 at a pressure of 10^{-7} mbar for 60 seconds.

CO Intercalation (Gr/CO/Ir(111))

In order to intercalate CO in a UHV environment, a super dense “water” phase (OH- H_2O) must first be formed beneath graphene. The specifics of this process are provided in the results section; 4.1. Atomic oxygen can be intercalated by allowing the sample to cool to just under $200^\circ C$, and then dosing the sample with 10^{-6} mbar of O_2 for 200 seconds [11]. The relatively high temperature allows for dissociated oxygen to intercalate beneath graphene [12]. The sample is then cooled to room temperature before 10^{-6} mbar of H_2 is dosed for 100 seconds. The hydrogen and oxygen then bound together under the graphene to create the “water” phase [13].

To intercalate CO, the sample is dosed with 10^{-6} mbar of CO for 100 seconds (100L; where L stands for the unit Langmuir [$\mu Torr \cdot s \approx 1.33 \text{ nbar} \cdot s$]).

Radical Dosing (R•)

5×10^{-7} mbar of C_2H_4 is dosed at room temperature for 10 minutes with a filament carrying 3.0 A and 4.9 V placed near to the surface of the sample. While it is unknown what occurs with CO intercalated graphene, it is expected that, as in previous work, non intercalated graphene will be functionalized.

Annealing (of R•/Gr/CO/Ir(111))

With the goal of removing intercalates, the sample is flashed first for 1 minutes at $300^\circ C$ and then, after scanning with the STM to observe changes, again at $400^\circ C$.

CO Intercalation (of R•/Gr/CO/Ir(111))

To see if previously intercalated flakes had their edges modified by radicals, a further round of CO dosing is performed at 300 L.

3.3 Analysis of Sample

To analyze the samples surface, the STM in the analysis chamber is used. The STM is connected to a system of hardware and software, MATRIX, which could control various parameters of the microscope. These parameters consisted most notably of the coarse and fine position of the tip along the sample, the distance between the tip and the sample, and the voltage gap and current between the tip and the sample. The position along the sample determined which section of the sample would be studied by the STM while the parameters between the tip and the sample affected image quality. To further aid image quality, it is possible to apply short voltage pulses to the tip or even to crash it into the sample surface. The voltage pulses served to dislodge foreign atoms from the tip, while crashing could intentionally deform a blunt or otherwise poor tip into a sharp point. The files obtained from this system are then analyzed using the image processing program “ImageJ”.

4 Results and Discussion

Throughout the following section, the data gathered during this project will be analyzed. To begin, the components of the images will be described; which parts are made up of bare iridium, graphene, water, or CO. Finally, the interaction of radicles with CO intercalated flakes of graphene will be discussed.

4.1 Graphene and Intercalate Substrate

Possessing flakes of graphene on the Ir(111) surface was essential for this experiment, as adsorption occurs from the edges. Direct intercalation of CO between pristine graphene flakes and Ir(111) is impossible at UHV conditions [11]. While it is possible to intercalate CO in a mbar regime [11], at UHV pressures, a super dense “water” phase (OH-H₂O) must first be formed [13]. To do this, a heated sample is exposed to a relatively high pressure (specifics provided in section 3.2 above) of molecular oxygen. The oxygen disassociates into atomic oxygen, which then intercalates. Following this, the sample is allowed to cool before exposing the surface to molecular hydrogen. This hydrogen forms a water phase both on the Ir(111) surface, and beneath graphene. While the water formed on the bare Ir(111) regions desorbs directly, the water formed beneath graphene becomes trapped [13]. Much like with O₂ [12], the water phase aids in the intercalation of CO at UHV pressures. With the flakes now intercalated by CO, the properties of radical adsorption on CO intercalated flakes can be studied.

In Figure 8, images of water bubbles beneath graphene flakes are shown. Figure 8(middle) presents a colormap of the STM image in Figure 8(left). The water bubbles, graphene flakes, and Ir are colored blue, gold, and shades of purple, respectively. Graphene flakes of various sizes are clearly observed. One can also see that graphene flakes predominantly form along step edges, though flakes disconnected from edges can also be seen. On the bare graphene flakes, a clear moiré pattern is visible, denoting a mismatch between the lattice structure of the graphene and Ir(111), as is discussed in section 2.2. In particular, the dark regions correspond to areas with stronger bonding (FCC and HCP sections) while the brighter spots are atop regions. Analysis of several images reveals that the graphene flakes cover 45% of the Ir(111) surface.



Figure 8: left: an 80nm x 80nm overview of a section of graphene flakes, some intercalated with a water phase. middle: colored image where blue corresponds to water intercalation, gold corresponds to graphene formed along step edges, orange corresponds to graphene disconnected from step edges, and purple corresponds to bare Ir(111), with the brightest purple being the highest step, and the darkest being the lowest step. right: a 27nm x 27nm zoom in with a “water” intercalated flake of graphene.

As can be seen in Figure 8 and Figure 9, the water phase forms primarily along the edges of graphene flakes. Intuitively, intercalation is also more common for large flakes, as there is more area to trap water. When water is intercalated, one can notice a decrease in bond strength between graphene and Ir by the blurring of the moiré pattern. With the bonds between graphene and Ir inhibited, it can be studied how further properties are affected. Figure 8(right) gives a clear example of how the water phase can blur the moiré pattern, similar to O intercalation [12]. Figure 9 presents an overview of a region containing CO intercalation. The water phase is also visible and is located near step edges, suggesting that graphene near step edges may possess an increased susceptibility to water intercalation. On average, intercalated water phases account for 18% of the surface.

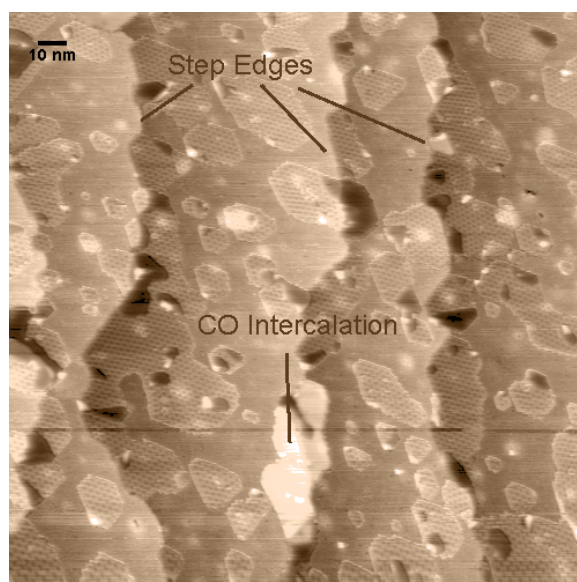


Figure 9: a 200nm x 200nm overview displaying the low levels of intercalated CO, where the brightest flake is CO intercalated. The iridium step edges and the CO intercalated flake are labeled accordingly.

As stated above, CO intercalation can only occur where a water phase exists in ultra-low pressures. Like water, CO has an increased chance of intercalating along a step edge, and, after examining multiple images of CO intercalated graphene, is more likely to intercalate larger flakes, possibly due to there being more water intercalation points on a larger flake. In general, CO intercalation occurs digitally (fully intercalated, or not at all), as shown in previous experiments [11]. When examining flakes that are CO are intercalated, one can again notice a decrease in bond strength between graphene and Ir(111) by the complete lack of a moiré. Upon the analysis of multiple images, the CO coverage is found to be 3%, indicating a low level of CO intercalation.

4.2 Radicals on Intercalated Graphene

While radicals readily adsorb on bare flakes of graphene, CO intercalated graphene was almost completely adsorption free. This limited adsorption is pictured in Figure 10; the adsorbates are the relatively bright rings (with darker centers) upon the flakes. As a reference to the radical adsorption on non-intercalated flakes, the lower left flake in Figure 10(left) and the lower left and lower right flakes in Figure 10(right) are well populated with radical adsorbates. In contrast Figure 10(left) has only a handful of radicals on the large CO intercalated flake, while Figure 10(right) has just two on its CO intercalated flake. Other CO intercalated flakes possessed no radical adsorption. The fact that some flakes possess radicals confirms that radicals are not present, yet simply disguised. This leads to the clear conclusion that these radicals, in general, “avoid” CO intercalated flakes.

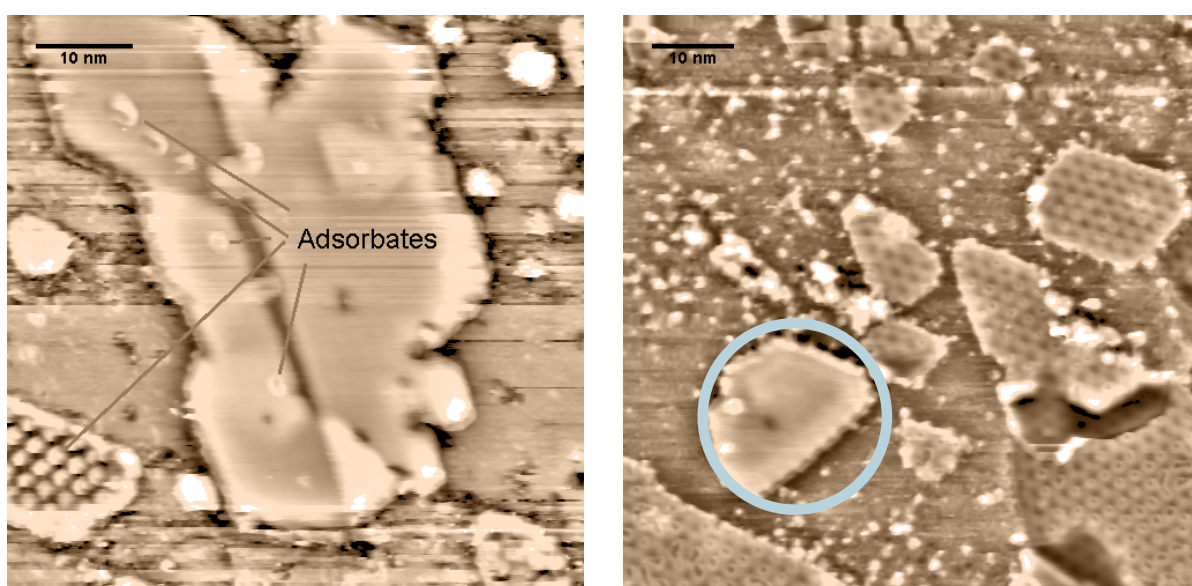


Figure 10:left: a 60nmx60nm STM image of a CO intercalated graphene flake. right: a 70nm x 70nm image of radical dosed flakes; intercalated in the lower left quadrant (circled), and non-intercalated flakes elsewhere.

The knowledge that these radicals do not readily adsorb on CO intercalated graphene allows for the potential study of the radical's effect on CO intercalated graphene flakes. This study was carried out by first annealing the sample to remove CO, and then dosing CO in an attempt to intercalate flakes again.

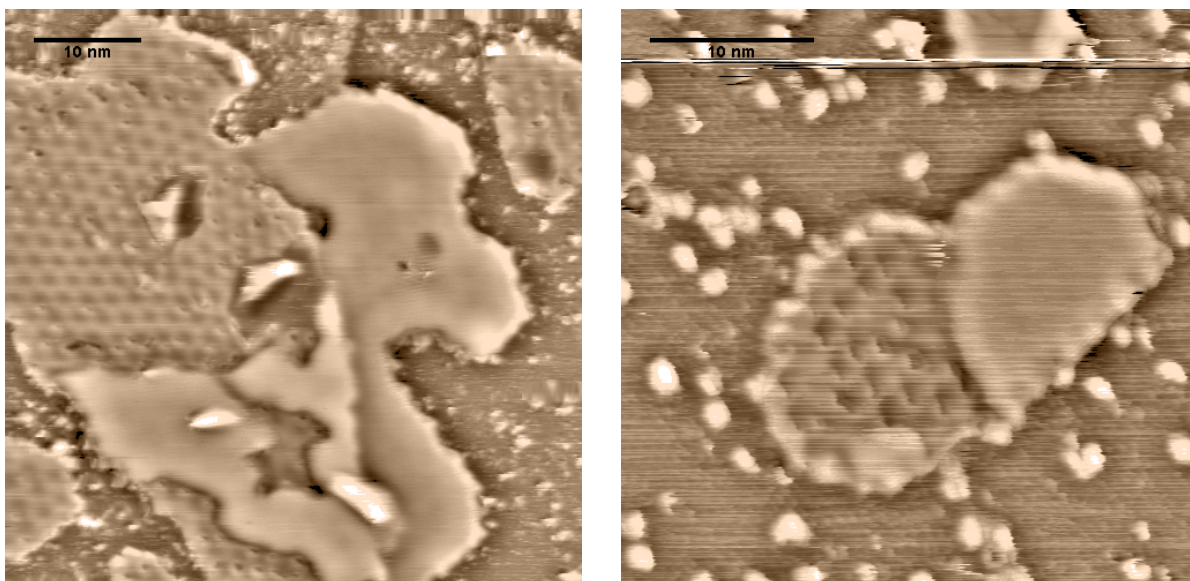


Figure 11: left: a 53nmx53nm image of a CO channel beneath graphene, surrounded by bare graphene. right: a partially intercalated graphene flake, half of which is covered by radical adsorbates.

As displayed in Figure 11, after annealing CO intercalation was no longer digital. Instead of fully intercalated flakes, a large proportion (90%) were partially intercalated, either in the form of channels, or in bubbles, much like those observed for the water phase. The channels seemed to appear on larger flakes, while bubble intercalation seemed to appear on smaller flakes. Furthermore, while the channel intercalated flakes were surrounded by patches of bare graphene, the bubble intercalated flakes contained very little bare graphene.

A possible explanation for the partially intercalated graphene surrounded by bare patches (75% of partially intercalated graphene) is that these bare regions had been intercalated previously, as radicals would not have adsorbed due to the presence of CO. This is supported both by the observation that intercalated flakes are less likely to contain adsorbents, but also by the observation that most intercalated flakes had been relatively large. It is conceivable that the remaining channels had somehow been trapped by radical adsorption along the edges, though more study would be needed to confirm this theory.

The bubble intercalated flakes (25% of partially intercalated graphene) were exclusively found in small flakes. An obvious explanation of this is that a flake must have a certain size in order for a channel structure to appear. Less easy to explain is the fact that all of these flakes were, as opposed to channel intercalated flakes, in close proximity to heavily radical adsorbed flakes. It is possible that these flakes had been populated with water intercalation before the annealing, and were subsequently intercalated with CO. Though most of the water phases had been removed during the annealing process, it is possible that this CO entered by aid of the water phase, though it seems clear that further study into this phenomenon is warranted.

5 Conclusion

Through this study, it was found that when a flake of graphene was intercalated by CO, adsorbates were placed atop intercalated flakes very rarely. In contrast, flakes of bare graphene readily adsorbed the radicals which they were exposed to. As no chemical analysis was performed, it cannot be certain what form of radical was preset upon intercalated and non-intercalated flakes, and differences may be caused by differing radical species. It was also found that the presence of radicals on a flake seems to influence the intercalation of CO; the presence of radicals either slows down, or inhibits entirely the intercalation of CO.

6 Outlook

To further the understanding of these results, a lengthier study could be performed. With such a brief time, it was difficult to obtain a wide variety of images, and there was little time to collect many panorama shots, to truly examine the sample as a whole. As mentioned above further chemical analysis (such as XPS) could allow for a more comprehensive study of the nature of the adsorbates, and whether differences here lead to certain CO flakes containing radicals. Future studies would also allow for the closer study of the edges of CO intercalated flakes, and if they had been altered by the presence of radicals.

Though these results need continued analysis, these findings could potentially have an impact on the manipulation of graphene. If a method could be devised to direct radicals onto graphene, certain patterns could be created which could be intercalated (for example a circuit of CO intercalation channels could be formed). From an analysis standpoint, this information could be used to determine whether a sample of graphene has adsorbates on it; if it cannot be intercalated, there could be radicals, even if STM is unable to image them.

Acknowledgments

To close out, I'd like to thank the people who have helped me all throughout this project. Firstly, I would like to thank Jan Knudsen for giving me the opportunity to work under his guidance, and for showing a passion for his work that is so rare to see. Secondly, I want to thank Foteini Ravani for patiently teaching me the necessary skills to work in a lab, and always helping me to understand the concepts at play. I can honestly say I've never learned more in such a short time than I have working in this lab. Finally, I'd like to thank my coworkers David Johansson and Virginia Boix for providing companionship both in the lab and behind the keyboard, and for being ready ears during the occasional stresses of this project.

7 References

- [1] C. a. A. H. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics*, vol. 81, pp. 109-162, #jan# 2009.
- [2] A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse and T. Michely, "Structure of epitaxial graphene on Ir(111)," *New Journal of Physics*, vol. 10, p. 043033, #apr# 2008.
- [3] Z. Sun, S. K. Hämäläinen, J. Sainio, J. Lahtinen, D. Vanmaekelbergh and P. Liljeroth, "Topographic and electronic contrast of the graphene moiré on Ir(111) probed by scanning tunneling microscopy and noncontact atomic force microscopy," *Physical Review B*, vol. 83, #feb# 2011.
- [4] A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F.-J. Meyer zu Heringdorf, R. van Gastel, B. Poelsema and T. Michely, "Growth of graphene on Ir(111)," *New Journal of Physics*, vol. 11, p. 023006, #feb# 2009.
- [5] NIST, "Moiré Patterns Created by Overlaid Sheets of Graphene," [Online]. Available: <https://www.nist.gov/image-20517>. [Accessed 21 March 2017].
- [6] A. T. N'Diaye, S. Bleikamp, P. J. Feibelman and T. Michely, "Two-Dimensional Ir Cluster Lattice on a Graphene Moiré on Ir(111)," *Physical Review Letters*, vol. 97, #nov# 2006.
- [7] P. Lazić, N. Atodiresei, V. Caciuc, R. Brako, B. Gumhalter and S. Blügel, "Rationale for switching to nonlocal functionals in density functional theory," *Journal of Physics: Condensed Matter*, vol. 24, p. 424215, #oct# 2012.
- [8] E. Grånäs, "Above and below graphene: nanoparticle chemistry and interface reactions," Lund, 2014.
- [9] G. Binnig and H. Rohrer, "Scanning tunneling microscopy," *Surface science*, vol. 126, pp. 236-244, 1983.
- [10] Tufts University, "How the Scanning Tunneling Microscope Works," [Online]. Available: <https://ase.tufts.edu/chemistry/sykes/Tutorial%20Group%20Presentations/Theory/how%20STM%20works.html>. [Accessed 21 03 2017].
- [11] E. Grånäs, M. Andersen, M. A. Arman, T. Gerber, B. Hammer, J. Schnadt, J. N. Andersen, T. Michely and J. Knudsen, "CO Intercalation of Graphene on Ir(111) in the Millibar Regime," *The Journal of Physical Chemistry C*, vol. 117, pp. 16438-16447, #aug# 2013.

- [12] E. Grånäs, J. Knudsen, U. A. Schröder, T. Gerber, C. Busse, M. A. Arman, K. Schulte, J. N. Andersen and T. Michely, "Oxygen Intercalation under Graphene on Ir(111): Energetics, Kinetics, and the Role of Graphene Edges," *ACS Nano*, vol. 6, pp. 9951-9963, #nov# 2012.
- [13] E. Grånäs, U. A. Schröder, M. A. Arman, M. Andersen, T. Gerber, K. Schulte, J. N. Andersen, B. Hammer, T. Michely and J. Knudsen, "Water Chemistry Beneath Graphene: Formation and Trapping of a super-dense OH-H₂O Phase".