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Buckminsterfullerene on KBr studied by High Resolution NC-AFM: Molecular nucleation and growth on an insulator

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Abstract

Non-contact atomic force microscopy (NC-AFM) has been applied to the prototypical molecule-insulator system C_{60} on KBr. Both contact and non-contact imaging modes were used to characterize the KBr(001) surface. C_{60} molecules were deposited on UHV-cleaved KBr(001) surfaces and imaged with NC-AFM. Surveys of the surface revealed an island growth mode with a tendency towards nucleation at step edges. A long diffusion length was also estimated (600-800nm) from survey images. Molecular resolution images were also obtained revealing a coincident epitaxy between the C_{60} molecules and the substrate. Also, a 20 ± 3pm height difference is observed between some first layer molecules, closely corresponding to the geometrical height difference between two orientations of C_{60} . Nucleation of C_{60} at kink sites was directly observed by NC-AFM and a calculation of the electrostatic forces on a C_{60} molecule at a kink in a KBr step confirms an additional contribution to the substrate-adsorbate interaction.

Résumé

La microscopie à force atomique hors-contact (NC-AFM) a été appliqué à l'étude du systême C_{60} sur KBr, qui est un example d'un systême de molécules sur substrat isolant. Des modes en contact et hors-contact on été utilesés pour charactériser la surface du KBr(001). Des molécules de C_{60} furent déposées sur une surface de KBr(001) fendue sous UHV et furent imagées par NC-AFM. Une étude révéla la croissance d'îlots de molécules sur las surface et une tendance de nucléation aux bords de terrasses atomique. Une grand longueur de diffusion de molécules (600–800nm) fut estimée à partir des image obtenues. Des images á résolution moléculaire furent obtenues et une différence de hauteur de $20 \pm 3pm$ entre certaines molecules de la première couche, ce qui correspond à la différence géométrique de hauteur entre deux orientations de C_{60} . La nucléation à des sites "kink" fut observée directement par NC-AFM, et un calcul des forces électrostatiques au site de la molécule confirme une contribution additionelle à l'interaction entre le substrat et la molécule.

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List of Abbreviations and Symbols

AFM	Atomic Force Microscopy/Microscope
CPD, V_{CPD}	Contact potential difference
C_{60}	60 carbon cage molecule, "Buckminster Fullerene"
EFM	Electrostatic Force Microscopy/Microscope
FIM	Field Ion Microscopy/Microscope
LEED	Low energy electron diffraction
LD	Laser diode
LF-AFM/FFM	Lateral-force AFM /
	Friction Force Microscopy/Microscope
MFM	Magnetic Force Microscopy/Microscope
NC-AFM/FM-AFM/DSFM	Non-contact AFM / Frequency modulation AFM /
	Dynamic Scanning Force Microscopy/Microscope
QPD	Quadrant Photodiode
RHEED	Reflection High Energy Electron Diffraction
SEM	Secondary Electron Microscopy/Microscope
STM	Scanning Tunneling Microscopy/Microscope
TEM	Transmission Electron Microscopy/Microscope

A	Amplitude of cantilever oscillation
a_i	Substrate lattice constant
b_i	Overlayer lattice constant
$[\mathbf{C}]$	Matrix describing overlayer relation to substrate lattice
c_N	Normal mode spring constant of cantilever
c_L	Lateral or torsional mode spring constant of cantilever
δf	Error in frequency measurement
Δf	Measured/set-point frequency shift
f_0	Natural/free resonant frequency of cantilever
F_N	Normal force/load
F_L	Lateral/friction force

Chapter 1

Introduction and Background

1.1 Introduction and Motivation

The development of scanning probe microscopy as a tool for exploring a wide variety of surface science systems has helped to open up the nanoscale world for scientific investigation. The invention of the Scanning Tunneling Microscope in 1982 by Binnig and Rohrer [1] has since lead to a variety of different tools for imaging, characterizing, and even influencing the properties of surfaces and nanostructures. The field of scanning probe microscopy (SPM) has had an influence on a wide range of fields from biology to chemistry to physics and engineering.

One key area of study to which STM and AFM have been valuable assets, is the study of molecules on surfaces. The ability to image, electronically probe, and manipulate molecules on surfaces has lead to a better understanding of these systems with applications ranging from catalysis to molecular electronics. Indeed, the ability to study these systems and *control* the environment of the molecule with the tip has lead to a revival [2] of the idea of molecular electronics first proposed in 1974 by Aviram and Ratner [3]. The pursuit of a working single molecule electronic device is ongoing with many different approaches being explored [4].

The construction of a planar, three-terminal molecular device would be desirable from an integration standpoint. Since current silicon based technologies rely on planar structures, a molecular device would be more easily integrated into current architectures if a planar geometry could be achieved. However, the resistance of a molecule ~ 1 nm in size is of the order of 1G Ω , which is large compared to the resistance of a typical semiconductor on the same scale. This leads to currents running through the substrate as well as the molecule, making the effect of the molecule on the properties of the device difficult to interpret and predict. To eliminate this problem, an insulating surface would ideally be used in the construction of a planar molecular device.

Additionally, the use of a planar geometry would allow the influence of the substrate on the molecule to be studied. Effects such as charge transfer and steric hinderance to conformations could be studied in a planar device where the molecule is in direct contact with the surface. Electronic properties of two terminal devices can be measured by STM, especially where the tip is atomically characterized by field ion microscopy (FIM), however, only the contacts interact with the molecule in this geometry. Similarly, break-junction experiments have been performed in electrolyte solutions to allow gate voltages to be applied to the molecule *without* these substrate interactions [5].

The design and implementation of a molecular device on an insulator would be difficult at this point in time as there is currently very little known about surface science on insulating surfaces. The majority of traditional surface science tools, including STM, are electron based. This makes the study of insulating surfaces difficult at best, due to charging effects and damage caused by the measurement process. Previous studies of molecular systems on insulating substrates have been performed using contact mode AFM, TEM of released films, and/or RHEED [6, 7, 8, 9]. However, these techniques provide either low resolution information (as in contact mode AFM), may be destructive (as may occur with contact AFM, or electron techniques), or examine structures which may have been altered by the process or sample preparation (as in the case of released films which may relax from the structure on the substrate, or the use of RHEED during growth which could create charge defects and alter the growth). The addition of atomic resolution non-contact atomic force microscopy (NC-AFM) nearly a decade ago [10, 11] to the surface science toolbox has made the high-resolution, non-destructive, real-space imaging of insulating surfaces possible. As this tool is developed and applied to a wider variety of systems, it has the potential to provide similar information about surface surface of insulators, including about molecular systems deposited on insulators, as STM was able to provide for conducting surface systems [12].

As more is learned about insulating surfaces with NC-AFM, and how deposited molecules and metals will interact with them, it may become possible to design and implement a planar molecular device on an insulating surface. The NC-AFM technique can then be applied to image the device with high resolution to determine the atomic positions of the leads, molecule, and substrate. This detailed information can then be used as input to model the device and compare to experimental results, thus closing the loop between theory and experiment. In this way, such a device will hopefully increase our understanding of the processes involved in transport through nanoscopic structures, contacts and molecules, as well as having potential technological applications.

The aim of this thesis is to describe the use of NC-AFM as a tool for studying molecular systems on insulating surfaces, as well as some of the relevant background concepts, through the example of C_{60} on KBr.

1.2 Overview of Atomic Force Microscopy

Originally intended to locally probe thin oxide layers on the micron scale for IBM corporation to improve gate oxides in transistors, the STM was instantly a much more powerful tool than expected. Atomic resolution on $Si(111)7 \times 7$ was obtained within the first year of its reported use [13]. Atomic force microscopy (AFM) was invented on a similar principle in 1986 by Binnig, Quate and Gerber [14], and the development of lateral force, or friction force microscopy (LF-AFM or FFM) followed one year later [15]. The first lattice image was obtained on graphite with contact



Figure 1.1: Key events in Scanning Probe Microscopy: STM to now. The invention of STM in 1982 [1] was not long proceeded by the invention of AFM [14]. However, unlike STM which yielded atomic resolution on the Si(111)-7 \times 7 surface within a year [13], true atomic resolution followed nearly a decade later [10, 11].

mode AFM in the same year [16]. The development of FM detection for AFM in 1991 [17] lead to the non-contact AFM family, including magnetic force microscopy (MFM) and electrostatic force microscopy (EFM). Using FM detection in NC-AFM, the first "true" atomic resolution including single atom defects was obtained in 1995 on Si by two groups [10, 11]. As the development of high resolution AFM has lagged that of STM there remains a great deal of potential to learn about systems which were inaccessible to STM, as well as provide complementary information for those systems which have already been studied by STM due to the differing contrast origins of the two techniques.

1.2.1 Contact-mode atomic force microscopy

Contact-mode AFM is much like the sense of "touch" in that the shape and texture of surfaces is determined by measuring local forces. In contact mode AFM, a sharp tip is raster scanned over a surface, usually using a piezo-electric scanner, much as a blind person moves their hands across a page to sense the patterns of raised bumps which constitute words in braille (see fig. 1.2). The tip is attached to a force sensor



Figure 1.2: Comparison of contact mode AFM with reading of braille. (a) Image of person reading braille by sensing the patterns of raised bumps on a page [18]. (b) Schematic of AFM tip scanning across a surface sensing the variations in force over the atoms.

which responds to proximity to the sample surface as well as other interaction forces between the tip and surface. Most often, the force is used as a feedback parameter and the piezo-electric scanner will retract or extend in the z-direction to maintain a constant force. The z-piezo response is considered the AFM "topography" although in reality it is a convolution of the actual topography of the sample and the interaction forces between the tip and sample.

There are several types of force sensors in common use now, all of which are based on a sharp tip attached to a cantilever. This is a convenient method as the force exerted on the tip is then directly proportional to the deflection of the cantilever. To measure the deflection of the cantilever, often an optical method or a piezoresistive cantilever is used. The latter is simpler in terms of the amount of instrumentation required, however the fabrication of such cantilevers with built in piezoresistive detection with the sensitivity required for many applications remains a challenge for microfabrication technologies. For some applications this method is sufficiently sensitive, and the advantages of the reduced instrumentation and flexibility of the technique can outweigh any loss in sensitivity. Optical detection methods are more common and usually employ either interferometry or a beam deflection system. Interferometers can be designed to make highly sensitive measurements of the deflection of the cantilever, and are often employed in ultra-high vacuum and low temperature systems where it is advantageous to introduce a single optical fiber and house the rest of the detection system externally. However, problems with the optical alignment and approach of the fiber over the small cantilever can be inconvenient. Beam deflection systems operate by focusing a laser on the back of a cantilever where it is reflected into a split or quadrant photodiode. As the cantilever bends, the position of the reflected beam on the photodiode will change, and thus give a measure of the deflection of the cantilever. Beam deflection systems require more "onboard" instrumentation, ie, a laser, a photodetector, and some scheme of aligning both, and are thus more commonly found in ambient and liquid AFM systems, though many vacuum systems also now employ this technique.

A major advantage of a beam deflection system over an interferometer for measuring the deflection of the AFM cantilever is the ability to measure lateral forces as well as normal forces when a quadrant photodiode is used. Lateral-force AFM (LF-AFM), or friction force microscopy (FFM), is of great interest in the field of nano-tribology, or the study of friction on the nano-scale. Of recent interest is the study of atomic stick-slip motion under ultra-high vacuum conditions [19, 20] in the hopes that it will advance our understanding of friction mechanisms on the atomic scale. Manipulation experiments have been of significant interest as a method of building prototype molecular devices, and the information obtained from LF-AFM could greatly improve understanding of the underlying mechanisms involved in these processes. It has been proposed that frictional effects between an adsorbate (a single asperity contact) and an atomically flat surface may play a role in single molecule manipulation experiments [21]. Also, a variation of LF-AFM was recently used to measure forces exerted on and by the tip *during* a single molecule manipulation [22].

Applications of contact and intermittent contact, or "tapping" mode, AFM appear in a growing number of fields. AFM is now frequently used in the imaging and probing of mechanical and electrical properties of biological system ranging from large cells down to single bio-molecules. It is also used in chemistry and engineering to characterize the quality of thin films and the roughness of surfaces.

1.2.2 Non-contact atomic force microscopy

Unlike the previous section where a static mode of imaging is described, an oscillating cantilever may be used in a dynamic imaging mode. As in contact mode imaging, a sharp tip is raster scanned over the surface and the recorded signals provide feedback and mapping of the specimen of interest. There are two such methods of force detection for AFM, relying on amplitude modulation (AM) or frequency modulation (FM) detection. The first, more common, is often referred to as "tapping" or intermittent contact mode. In this mode the cantilever is excited at a fixed amplitude and oscillation frequency at or near the resonant frequency of the cantilever. A reduction in the amplitude indicates an often repulsive interaction between the tip and sample and is used as a feedback parameter. Alternatively, a frequency detection mode can be used where the cantilever is similarly excited at or near its resonant frequency, but the change in frequency of the cantilever and tip-sample interaction system is measured (see fig. 1.3). The excitation is altered to track the resonance of this combined system. Additionally, the tip is generally maintained at a distance such that it remains in the attractive regime of the tip-sample interaction, hence the term "noncontact". Since NC-AFM remains in this attractive regime it is less destructive than tapping mode. However, because the cantilevers must have high Q-factors, NC-AFM is usually performed in a vacuum or low temperature environment making it unsuitable for most biological applications. This frequency modulation AFM (FM-AFM) has also been coined dynamic scanning force microscopy (DSFM), or most commonly non-contact AFM (NC-AFM).

In NC-AFM mode, the sharp tip is oscillated over the surface and as the interaction between the tip and sample changes, the resonant frequency of the cantilever and tipsample interaction system changes. This is analogous to a coupled spring system in which the spring constant of one of the components is variable, altering the resonance frequency of the system (see fig. 1.3). In this way, the frequency shift of the system is a measure of the tip-sample interaction. This frequency shift is proportional to the force gradient in the small amplitude limit, where the amplitude of oscillation is small compared to the tip-sample separation. For large amplitude oscillations, the frequency shift is related to the interaction in a more complex way [23]:



Figure 1.3: Schematic of a typical NC-AFM. The sample, represented by the close-packed spheres, is scanned by an xyz-piezo electric scanner. The oscillation of the cantilever is excited by a separate piezo, and the AC-deflection of the cantilever is sensed by an optical beam-deflection scheme. The magnified area gives a representation of the tip-sample system with the interaction between tip and sample shown as a spring. The cantilever and tip-sample interaction can be thought of as a coupled spring system. As the spring constant of the interaction changes, the resonant frequency of the entire system shifts. It is this frequency shift which is measured in NC-AFM.

$$\frac{\Delta f}{f_0}kA = \int_0^{2\pi} \frac{d\phi}{2\pi} F(\bar{z} + A\cos(\phi))\cos(\phi) \tag{1.1}$$

where Δf is the frequency shift, f_0 is the resonant frequency of the cantilever, k is the spring constant of the cantilever, A is the amplitude of the oscillations, and the variable of integration, ϕ , is the angular position of the cantilever at any given time, ie. the force is integrated over one full cycle of the cantilever oscillation. There are several methods which have been developed to convert frequency shift to force [24, 25] which will not be discussed here, though it is necessary for detailed quantitative analysis of many results.

As in contact mode AFM, NC-AFM is sensitive to a combination of forces. The three main contributions are electrostatic (long-range), van der Waals (long/intermediate-range), and chemical (short range). The electrostatic contribution to the frequency shift can be expressed as [23]:

$$\frac{\Delta f_{elec}}{f_0} kA = -\frac{\pi \epsilon_0 R (V_{bias} - V_{CPD})^2}{\sqrt{2\bar{s}A}}$$
(1.2)

where Δf_{elec} is the electrostatic contribution to the frequency shift, f_0 is the resonant frequency of the cantilever, k is the spring constant of the cantilever, A is the amplitude of oscillation, R is the radius of the tip, V_{bias} is an applied bias between the tip and sample, V_{CPD} is the contact potential difference, and \bar{s} is the distance between the sample and the macroscopic portion of the tip. The contact potential difference is a property of both the tip and sample materials and is related to the difference in work function of those two materials, and is defined as [26]:

$$V_{CPD} = \frac{1}{e} (\Phi_{tip} - \Phi_{sample}) \tag{1.3}$$

where Φ_{tip} is the work function of the tip material, and Φ_{sample} is the work function of the sample material.

Note that by applying a bias voltage, the electrostatic contribution to the frequency shift can be minimized. This is often advantageous as long range electrostatic forces can make small features difficult or impossible to resolve as the forces measured are not local on the atomic scale [27]. Also note that there is a $\bar{s}^{-1/2}$ dependance of the frequency shift on distance between the macroscopic tip and the sample indicating that the effect is long range, as well as a quadratic relationship between frequency shift and bias voltage.

Similarly, the van der Waals contribution to the frequency shift can be expressed as [23]:

$$\frac{\Delta f_{vdW}}{f_0}kA = -\frac{HR}{12\bar{s}\sqrt{2\bar{s}A}} \tag{1.4}$$

where Δf_{vdW} is the van der Waals contribution to the frequency shift, H is the Hamaker constant and can be taken as the geometric mean of the Hamaker constants for the tip and sample. Note that there is a $\bar{s}^{-3/2}$ dependance of the frequency shift on the distance between the macroscopic tip and the sample due to the van der Waals contribution.

Taking the chemical interaction to be well modeled by the Morse potential, and assuming that the tip does not enter the repulsive regime of the chemical potential, an expression for the chemical contribution to the frequency shift can be derived from the attractive portion of the Morse potential [23]:

$$\frac{\Delta f_{chem}}{f_0} kA = -\frac{U_0}{\sqrt{\pi A\lambda}} \sqrt{2} e^{\frac{-s-s_0}{\lambda}}$$
(1.5)

where Δf_{chem} is the chemical contribution to the frequency shift, U_0 is the depth of the chemical potential, λ is the characteristic interaction length, s_0 is the position of the minimum of the chemical potential, and s is the distance between the microscopic apex of the tip and the sample. Here there is a much stronger, i.e. exponential, dependence on the tip-sample separation, but only at short range. For high resolution



Figure 1.4: Example of frequency shift vs. distance relation showing contrast inversion The images in (a) and (b) show the Au(111) herringbone reconstruction in both normal ($\Delta f = -85$ Hz, A=6nm) and inverted ($\Delta f = -98$ Hz, A=6nm) contrast respectively (images from [28]). The solid curve in (c) represents a typical Δf vs. distance relation according to the sum of the electrostatic, van der Waals, and Morse potential contributions to Δf . The dashed line is shifted in z a small amount representing a topographical height difference between two regions of the sample, and has a different CPD from the first. The cross-over between the two curves separates the regions of normal and inverted contrast. The arrows along the bottom axis of the graph point towards the solid curve, the direction indicating whether this region appears topographically higher (arrow pointing to the right) or lower (arrow pointing to the left).

imaging of many materials it is necessary to be in the regime where the chemical interaction dominates.

Due to the different contributing interactions, and the different length scales over which they dominate, it is possible to have an apparent inverted contrast over inhomogeneous regions of a sample depending on the relative strengths of the contributions to the frequency shift. For example see figure 1.4 where for two different regions, represented by different frequency shift vs. distance curves, the frequency shift vs. distance relations can have cross-over points resulting in an inversion of contrast in the image [29, 28].

NC-AFM has developed into a number of different tools for different applications including magnetic force microscopy (MFM), electrostatic force microscopy (EFM), and Kelvin probe microscopy (KPM). These different modes of imaging allow investigation of many different types of samples, giving NC-AFM additional functionality beyond its high resolution capabilities.

1.3 Brief theory of Growth and Epitaxy

Both the growth of deposited materials and the final structure of the overlayer depend on a delicate balance of energetics and kinetics. An understanding of the growth of a given material on a specific substrate, as well as a determination of the final structure, can provide information about the interactions between the deposited atoms or molecules and the deposit–substrate interactions. The field of scanning probe microscopy has opened a window into the microscopic world of growth allowing study of nucleation and the early stages of growth [12].

1.3.1 Nucleation and growth concepts

Nucleation and growth processes are governed by a combination of equilibrium thermodynamic processes and non-equilibrium kinetic processes. These occur both on an atomic scale, where nucleation takes place, and on the large scale where the island or layer morphology forms during continuing growth.

Atomistic processes during adsorption include arrival of the atoms at a flux F, reevaporation, surface diffusion and binding and nucleation (see fig. 1.5). Surface



Figure 1.5: Atomistic surface processes The dark grey represents the substrate material with the light grey representing the deposit material. Arrival occurs at some flux, F. Once on the surface, the atoms may diffuse, bind to a special site, bind to the substrate or each other, diffuse along an existing surface of the deposit material, or interdiffuse with the substrate material. (figure after Venables [30])

diffusion is an activated process requiring some energy, E_d , occuring on both the substrate surface and the different facets of the nucleated deposit material. Binding to the substrate, special sites on the substrate and nucleation of clusters of the deposit material are also activated processes, requiring some energy, E_b , to reverse the process. Additionally, interdiffusion can occur at the interface between the substrate and the deposit material. Although all of these processes occur, usually only one, or a combination of a few will be rate-limiting, and thus will be responsible for a nucleation barrier, and need to be incorporated into any quantitative model.

The energetics of cluster formation are governed by a balance of a surface term and a volume term which compete to disintegrate a cluster or create a cluster respectively. The **critical cluster size** is defined as the size at which the surface energy term and the volume energy term are equal. If the cluster is less than this critical size it will dissolve by the atoms or molecules diffusing away, and if it is larger than the critical size the island will continue growing. Nucleation of critical size clusters can be described in terms of the free energy of a cluster of j atoms. For 3D island growth, the free energy is given by [30]:

$$\Delta G(j) = -j\Delta\mu + j^{2/3}X \tag{1.6}$$

where $\Delta G(j)$ is the free energy of a cluster of j atoms, $\Delta \mu$ is the chemical potential, or in this case the supersaturation, and X is the surface energy term. The surface energy can be expressed as a sum of the surface energy of the deposit material island and the interface energy [30]:

$$X = \sum_{k} C_k \gamma_k + C_{AB} (\gamma^* - \gamma_B)$$
(1.7)

where the first term is a sum over the surface energies of all facets of the deposited island, and the second term corresponds to the interface energy. The maximum in the free energy (eqn. 1.6) corresponds to a nucleation barrier, and thus the cluster size corresponding to this maximum is the smallest possible stable cluster. Below this critical cluster size, the atoms will dissociate and diffuse away to reform clusters until a sufficient number of stable clusters exist to nucleate further growth. By differentiating the free energy, one can find the critical cluster size, j_{crit} [30]:

$$\frac{\partial}{\partial j}\Delta G(j) = -\Delta \mu + \frac{2}{3}j^{-1/3}X \tag{1.8}$$

$$j_{crit} = \left(\frac{2X}{3\Delta\mu}\right)^3 \tag{1.9}$$

The same process can be used to find the critical cluster size for 2D, or layer growth. In this case, the starting expression for the free energy is slightly different [30]:

$$\Delta G(j) = -j\Delta\mu' + j^{1/2}X \tag{1.10}$$

where $\Delta \mu'$ is now related to both the chemical potential, or degree of supersaturation, and the surface energies [30]:

$$\Delta \mu' = \Delta \mu - \Delta \mu_c \tag{1.11}$$

$$\Delta \mu_c = (\gamma_A + \gamma^* - \gamma_B) \Omega^{2/3} \tag{1.12}$$

where γ_A is the surface energy of the deposit material, γ_B is the surface energy of the substrate, γ^* is the interface energy, and Ω is the volume of the deposit. As a side note, $\Delta \mu'$ can also be expressed in terms of the adsorption isotherm: $\Delta \mu' = kT \ln(\frac{p}{p_0})$, such that the step height of the adsorption isotherm corresponds to the difference in surface energy in eqn. 1.12. That aside, differentiation of the free energy (eqn. 1.10) leads to a critical 2D cluster size given by [30]:

$$j_{crit} = \left(\frac{X}{2\Delta\mu'}\right)^2 \tag{1.13}$$

This thermodynamic description of nucleation is somewhat oversimplified as it leaves out some of the kinetic process which can effect nucleation, and applies *macroscopic* quantities on a *microscopic* system, especially since critical clusters can often be as small as one atom. As such, there are many atomistic models that deal with nucleation and subsequent growth which will not be discussed here.

It is worth noting at this point however, that the critical cluster size, as well as parameters related to the diffusion of the deposited material can be found experimentally through the expressions derived from mean-field nucleation theory for the density of islands. Starting from the rate equations describing the density of stable 2D islands and monomers with no re-evaporation, it can be shown that in the limit of saturation, the density of large stable clusters, n_x is given by [12]:

$$n_x = \eta(\theta, j) \left(\frac{D}{F}\right)^{-\chi} \exp\left(\frac{E_j}{(i+2)kT}\right)$$
(1.14)

where D is the diffusion rate, η is an exponential pre-factor dependent on coverage, θ ,

and cluster size, j. E_j is the binding energies of a cluster of size j_{crit} , and the exponent χ can be expressed in terms of the critical cluster size: $\chi = j_{crit}/(j_{crit}+2)$. In the saturation limit, the ratio D/F can also be expressed in terms of a characteristic length, l, which is the mean island distance and also the mean free path of diffusing adatoms [12]:

$$\frac{D}{F} \simeq \frac{l^6}{\ln(l^2)} \simeq l^6 \tag{1.15}$$

In this way, the ratio D/F can be found experimentally and a plot of $\log(D/F)$ vs. $\log(n_x)$ can be used to determine the exponent χ and subsequently the critical island size. Additionally, under conditions where dimers are stable, i.e. $j_{crit} = 1$, an Arrhenius plot can be used to extract the migration barrier and attempt frequency for diffusion of the adsorbate.

The time evolution of submonolayer growth proceeds from nucleation, where a supersaturated background is required, through diffusive growth, where the supersaturated background is depleted by the growing nuclei, to a **coarsening** stage at low supersaturation, where growth of some islands is at the expense of others which dissolve into the background. As the first nuclei begin to form they gather material from the surrounding area, and thus begin to deplete the initially uniform supersaturated background. The nucleation rate, and the distribution of the nucleation rate, will depend on the conditions of the growth, such as the supersaturation, the temperature, and other conditions which may effect the initial dispersion of the nuclei (eg. surface defects). As the initial nuclei continue to grow in the diffusive regime, the density of islands remains roughly constant, and the islands are similar in size. The supersaturated background provides the islands with material to continue growing at roughly the same rate continuing to give a narrow size distribution. Before growth can proceed into coarsening, or Ostwald ripening, the supersaturation must be depleted to a point where small islands begin to break apart and that material is available to diffuse through the supersaturated background to continue growth [31]. In the case where there is a constant flux of material deposited, this last stage does not necessarily occur without a further annealing process [12].



Figure 1.6: Energetics and growth modes. Fig. (a) shows the definitions of the surface energies of the overlayer, γ_a , the substrate, γ_b , and the interface free energy, γ^* . (b), (c) and (d) show the different growth modes resulting from different balances of the surface energies. (figure after Venables [30])

From a more macroscopic view, the balance of the surface energies of the substrate and deposit material, as well as the interface energy (see fig. 1.6) dictate the way the growth proceeds after nucleation. This can be broken down into three main growth modes [30]:

- Island/Volmer–Webber growth: (see fig. 1.6b) Atoms nucleate small clusters on the substrate surface which grow into islands of the condensed phase of the deposit material. In terms of the surface free energies: $\gamma_A + \gamma^* > \gamma_B$, ie, the atoms of the deposit material are more strongly bound to each other than the substrate. Thus, a supersaturation of deposit atoms is needed to induce nucleation.
- **Stranski–Krastinov:** (see fig. 1.6c) Deposited atoms initially form a layer-by-layer growth due to a strong interaction between the deposit atoms and the substrate, such that $\gamma_A < \gamma_B + \gamma^*$. However, as more material is deposited, the interface energy, γ^* , increases making subsequent layer growth *unfavorable*. At this point, the condition for Island growth is satisfied, and the material continues to deposit only if there is a supersaturation of the deposit atoms. Typically the increase in the interface energy is due to strain in the first few layers.
- Layer-by-Layer/Frank-van der Merwe: (see fig. 1.6d) Atoms are more strongly bound to the substrate than each other and first condense to form a complete layer. Provided the binding energy of subsequent layers decreases monotonically with coverage approaching the bulk crystal value, the deposit material will continue to grow layer-by-layer. In terms of the surface free energy: $\gamma_A < \gamma_B + \gamma^*$.

Thus the growth mode observed can also give a relative measure of the surface energies.

Although most of the concepts discussed here are described within an equilibrium framework, kinetic processes can also have a major impact on the growth. One striking example of this is dendritic and fractal growth which can occur in both heterogenous and homogeneous systems. The formation of these types of structures is dictated by a balance of diffusion parameters [32].

1.3.2 Epitaxy of organic molecules

Standard discussions of epitaxy generally refer to simple atomic systems where the deposited material is similar to the substrate material in size, symmetry, and interaction strength and stiffness. Where the symmetry and the size of the overlayer lattice is similar to the substrate, the degree of epitaxy is usually given in terms of the 1D lattice mismatch parameter:

$$f = \frac{(b-a)}{a} \tag{1.16}$$

where b is the overlayer lattice constant, and a is the substrate lattice constant. However, this 1D parameter is only meaningful for lattices with the same symmetry. For molecular overlayers, this is often not the case as many molecular films have a low symmetry and large lattice constants compared to most substrates.

Additionally, the structural arrangement of organic molecules on surfaces is determined by a complex interplay of molecule-molecule interactions, substrate-overlayer interactions, and lattice geometries. The "soft" (often Van der Waals in origin) interactions between molecules gives the overlayer a relatively small elastic constant as compared to typical inorganic materials, allowing the overlayer lattice to deform in order to accomodate the substrate. Similarly, the interactions with the substrate may be weak (especially in the case of insulators which are examined here), and also "soft". This often leads to structures which are not commensurate (molecule A, sticks to specific site on substrate B), but coincident where there is a distinct lattice *registry*, but the substrate-overlayer interaction is *not* necessarily minimized. As it is this balance of competing interactions which dictate the structure of the overlayer, determination of the structural relationship between the overlayer and substrate can also reveal information about the relative strengths and stiffnesses of the interactions in the system without knowledge of the detailed forms of the interaction potentials.

The relationship between any two lattices can be given as the matrix which transforms the set of substrate lattice vectors into the set of overlayer vectors as given by:

$$\begin{bmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{bmatrix} = [\mathbf{C}] \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{bmatrix} = \begin{bmatrix} p & q \\ r & s \end{bmatrix} \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{bmatrix}$$
(1.17)

Where the symmetry of the two lattices is the same, a short-hand version of this matrix is often used. Wood's notation takes the multiplying factor required to transform the each of the substrate lattice vectors to each of the supercell lattice vectors, and follows this with a rotation angle if required. For example, the matrix:

$$\left[\begin{array}{cc} 2 & 2\\ 2 & 2 \end{array}\right] \tag{1.18}$$

would be written as $\sqrt{2} \times \sqrt{2}R45^{\circ}$, since each of the supercell lattice vectors is $\sqrt{2}$ times longer than the substrate lattice vectors, and the supercell lattice is rotated by an angle of 45° from the substrate lattice. This particular cell can also be written as $c2 \times 2$, where a supercell that has the same orientation as the substrate lattice, and edges that are two times the length of the substrate lattice vectors, but has one extra overlayer atom in the *center* of the cell. Wood's notation is a very convenient way of stating an overlayer structure, however, since there is no way of defining a different angle between the overlayer lattice vectors from the substrate lattice vectors, it can only be applied to systems which have the same basic symmetry. Since molecular systems often have a different symmetry from the substrates they are deposited on, matrix notation *must* be used to define an epitaxial relation.

The matrix elements p, q, r, s can also be found in terms of the lattice constants of the two lattices a_1, a_2, b_1, b_2 , and the angles between the lattice vectors (α, β) , and θ , the rotation angle between the overlayer and substrate lattices (as shown in fig. 1.7) [33]:

$$p = \frac{b_1 \sin(\alpha - \theta)}{a_1 \sin(\alpha)} \tag{1.19}$$


Figure 1.7: Definition of epitaxial lattice parameters. The lattice vectors a_1 and a_2 and the angle α define the substrate lattice. Similarly, the lattice vectors b_1 and b_2 and the angle β define the overlayer/deposit lattice. The angle θ defines the rotation of the overlayer with respect to the substrate.

$$q = \frac{b_1 \sin(\theta)}{a_2 \sin(\alpha)} \tag{1.20}$$

$$r = \frac{b_2 \sin(\alpha - \theta - \beta)}{a_1 \sin(\alpha)} \tag{1.21}$$

$$s = \frac{b_2 \sin(\theta + \beta)}{a_2 \sin(\alpha)} \tag{1.22}$$

Using the matrix \mathbf{C} , the type of structural relationship can be easily classified according to the "grammar of epitaxy" put forth by Hooks et al. [33] as follows:

- **Commensurism** (also referred to as point-on-point coincidence): All matrix elements of **C** are integers, indicating that each overlayer lattice point lies on a substrate lattice point. For inorganic systems, this is the most common case where an "epitaxial" relationship is described. Energetically, a commensurate lattice leads to a minimization of the substrate–overlayer interaction. Since this situation usually arises when the substrate–overlayer interaction dominates, the positions of the deposit lattice points will be determined by the surface potential.
- Coincidence-I (also referred to as point-on-line coincidence, or "quasi-epitaxy" [34]): At least two of the matrix elements of C are integers confined to a

single column of the matrix. This defines the situation where every overlayer lattice point lies on at least one primitive lattice line of the substrate, hence the alternate terminology of "point-on-line (POL)" coincidence. Coincidence-I can be subdivided into two catagories:

- **Coincidence-IA** : All matrix elements are rational numbers. In this case a supercell can be constructed, defining a phase coherent registry with the lattice, even though some overlayer lattice points do not lie on lattice points of the substrate. In inorganic systems this is typically referred to simply as "coincidence". In terms of the substrate-overlayer interaction, the situation of coincidence-IA is energetically less favorable than commensurism as some of the overlayer lattice points will be out of phase with the substrate lattice, even though a longer range phase coherence still exists. Of course, when the full set of interactions is considered, this may still be an energetic minimum for the system.
- **Coincidence-IB** : At least one of the matrix elements of **C** is an irrational number. Although every overlayer lattice point lies on one primitive lattice line of the substrate, the irrational matrix element produces an incommensurate relationship in one direction. Due to this incommensurate relation in one direction, a finite supercell *cannot* be constructed. (Note: If the supercell size exceeds the area investigated experimentally, coincidence-IA will be indistinguishable from coincidence-IB.)
- **Coincidence-II** (also called "geometrical coincidence"): All matrix elements are rational, but no column consists of integers. In this case a supercell can still be constructed, but not all of the lattice points of the overlayer lie on at least one substrate lattice line. Although this case violates the reciprocal space criterion $(\mathbf{b}_1^* = m\mathbf{a}_1^*, \text{ where } m \text{ is an integer})$, it is still considered coincidence due to the presence of a lattice registry (supercell can be constructed). Again, coincidence-II is less energetically favorable in terms of the overlayer–substrate interaction than the aforementioned cases.
- **Incommensurism** : The matrix **C** has at least one irrational element and neither column consists of integers. In this case there is no finite size supercell which can

be constructed, and hence no distinct lattice registry between the overlayer and the substrate. Incommensurism is the least favorable in terms of the interface energy and will occur in the absence of an available phase-coherent structure.

The type of geometrical arrangement as described above that is actually present in a given system will depend upon the relative strengths and elasticities of the overlayer–substrate interaction and the intralayer interaction, as well as the availability of a lattice matching geometry. In many cases for molecular systems, the relatively soft intralayer and overlayer–substrate interactions (ie. small elastic constants, or potential wells with low curvature) lead to coincident structures that are indeed energetically favorable.

1.4 C₆₀ on KBr: prototypical system

KBr is an ionic salt (alkali halide) with a cubic NaCl structure (fcc with a basis). The conventional unit cell has a lattice constant of 6.60 Å, which is maintained at the surface with insignificant rumpling [35] (see fig. 1.8). KBr is easily cleaved along the {100} planes. It is relatively inert, and is primarily sensitive to water and CO contamination at step edges. KBr is considered an insulator, and has a dielectric constant of 5.65 at 25°C over a frequency range of $100-1 \times 10^9$ Hz [36].

 C_{60} , the third elemental form of carbon (after graphite and diamond in abundance respectively), was disovered by Kroto and Smalley in 1985 [37]. Sixty carbon atoms form a spherical cage with each of the atoms located at the vertices of a truncated icosahedron, or the shape of a soccer ball (see fig. 1.8). The C₆₀ molecule owes its nickname "buckyball" to its resemblance to the geodesic domes designed by R. Buckminster Fuller. The van der Waals radius of a single C₆₀ molecule is ~ 7 Å[37], and in bulk, C₆₀ forms an fcc crystal with an intermolecular spacing of 10.2 Å[38]. Previous results from STM have shown that the binding energy of C₆₀ depends a great deal on the substrate, interacting strongly with metal and semiconducting surfaces, and much more weakly with oxide (insulating) surfaces [38]. Both KBr and C_{60} are well studied systems within the NC-AFM and STM communities respectively. Atomic resolution was achieved on an alkali halide in 1997 by Bammerlin et. al. [39] and the sample preparation of these substrates is well documented. The ability to achieve atomic resolution on the substrate is important both for understanding the growth of the molecular species on the surface as well as for future molecular electronics experiments where the substrate may influence the electrical properties of the molecule. C_{60} was chosen both for its potential application in molecular electronics [40, 41], as well as its simple geometry. The spherical geometry of C_{60} makes ab initio computations involving the molecule more tractable. Such calculations may be used in understanding the interaction between the molecule and the substrate in understanding growth, as well as modeling electrical properties to compare to the measurement of a future molecular device. Additionally, the relatively large size, and spherical shape of the C_{60} molecule makes it potentially easier to image as it is expected to have a larger corrugation, when considering geometry alone, than a large flat molecule such as a porphyrin, metal-pthalocyanine, or perylene derivative.

Although literature on growth of molecules on insulating surface is scarce, there have been some studies of C_{60} on various insulators, including alkali halides [9, 42, 43]. These studies were performed with a variety of techniques including contact mode AFM (and lateral force AFM) and electron microscopy. However, as discussed previously, these techniques often do not provide high resolution information, or are destructive to the sample surface being investigated. NC-AFM offers the possibility of both non-destructive and high spatial resolution investigation of both films and nanostructures of these molecular systems on insulators. The simplicity of the C_{60} on KBr(001) system and wide range of existing literature on each of the selected substrate and the selected molecule make this a reasonable candidate for a prototypical molecule-insulator system to which the NC-AFM technique can be applied to the study of molecular nucleation and growth on an insulator.



Figure 1.8: Approximately to scale model of C_{60} molecules on a KBr surface. A KBr(001) surface is shown exposed here with the bromine ions shown as small dark grey spheres, and the potasium ions shown as larger light grey spheres. The lattice constant of the bulk conventional cell of this cubic NaCl structure, $a_1 = a_2 = 6.6$ Å, is shown on the side. The ions are represented by close-packed spheres with the ratio of the radii approximately equal to that of the ionic radii of K and Br. The C_{60} molecules are shown on top of the KBr(001) surface with a lattice constant of ~10Å, close to the bulk close-packed spacing.

Chapter 2

Experimental Methods

The instrument used for the experiments which are described herein is based on a commercially available variable temperature, ultra-high vacuum AFM/STM/SEM JEOL JSPM 4500a. Additional instruments and electronics have been added to the system. Unless otherwise specified, major components were supplied by JEOL.

2.1 The Ultra-High Vacuum system

All of the experiments discussed were performed in an ultra-high vacuum (UHV) environment. The entire vacuum system including chambers and pumps (with the exception of a roughing pump) are mounted on an air table for vibration isolation (see fig. 2.1). The lab floor is on a separate foundation further reducing issues of building vibrations (see fig. 2.2). For example, a lab on the fourth floor of the adjacent building measured vibrations with an accelerometer of $1.4 \times 10^{-3} m/s^2/Hz^{1/2}$ for a frequency range of 10–100Hz, which is roughly an order of magnitude larger than measured in the JEOL instrument lab of $2.4 \times 10^{-4} m/s^2/Hz^{1/2}$ for a smaller range of frequencies frequencies, 60–100Hz, and even less for lower frequency.

The UHV system consists of two primary chambers, a transfer arm to move speci-



Figure 2.1: Photograph of UHV apparatus. Labels identifying the various instruments available on the UHV system. The two large arrows on the bottom indicate the imaging chamber and preparation chamber sides of the vacuum system. The entire apparatus is mounted on an air table. The TSP/Ion pumps and turbo pump are not visible but are suspended beneath the table. The pump control box is to the bottom left, and the electronics are located on a rack to the right. Each of the elements labeled is described in the text.



Figure 2.2: Plot of floor vibrations measured by accelerometer in JEOL instrument room. The magnitude of vibrations measured on the separate foundation in the range of 60–100 Hz were $\sim 2.4^{-4}m/s^2/Hz^{1/2}$, roughly an order of magnitude less than the 4th floor of the adjacent building.

mens between them, and a fast load-lock to introduce specimen to the UHV system without breaking vacuum in the primary chambers. The load-lock is pumped on by a magnetically levitated turbo pump, and reaches an adequate pressure for transfering specimen into the primary chambers ($\sim 5 \times 10^{-6}$ Pa) after approximately 30 minutes. Each of the primary chambers is pumped on at all times by a combination titanium-sublimation pump (TSP) and ion-pump. The primary chambers are baked by a combination of internal heating coils and external heating tapes for about 4 days to achieve ultimate pressures. Typical base pressures after bake-out and outgassing of filaments and evaporation sources are 1×10^{-8} Pa and 3×10^{-8} Pa for the preparation and main chambers respectively. Pressures are measured with hot cathode ion gauges.

The preparation chamber contains a carousel to store and manipulate specimen. Items mounted on special parent holders can be transfered into the preparation chamber via the load-lock transfer arm, and can likewise be transfered into the main observation chamber via a second transfer arm. The carousel can be rotated and tilted for coarse alignment with the various preparation and characterization tools available, and has micrometer screws for additional fine alignment.

The main observation chamber has a linear manipulator to allow specimen, ie, samples and tips, to be transfered from the parent holders to the observation stage. The manipulator can be moved back and forth along a track as well as up and down to lift specimen out of the parent holders and place them on the stage. The specimen are picked up by means of a pin which can be opened and closed by a solenoid. This pin can only be released again when a downward force is applied as achieved when placing a tip or sample in the tip or sample positions of the stage, or in a parent holder. This ensures that the specimen are securely in place before the manipulator can be disengaged. Also, to prevent excessive force from being applied to the piezo when placing samples into the stage, there is a force meter on the side of the manipulator, and the pin is designed to release before a damaging force would be applied.

2.1.1 Description of removable elements

There are several removable elements of the system which have some built-in functionality, and require description. The first of these is the sample holder and parent holder designed specifically for cleaving crystalline samples in situ. The **cleaving sample holder** has the same exterior dimensions as the other sample holders to enable transfers and allow compatibility with the other parent holders. However, unlike the other sample holders where the sample is clamped flat to the front of the holder, the cleaving holder has a rectangular cut-out in the sample position allowing a block of the desired material to be placed in this space and protrude a distance out from the face of the holder. The sample is then clamped in place by two small screws which push a metal plate against the bottom edge of the crystal (see fig. 2.3). The **cleaving parent holder** has two solid machined fingers holding the sample holder in place. A spring pushing against the back of the sample holder provides tension so that the sample holder does not fall out. This is in contrast to the normal parent



Figure 2.3: Crystal cleaving holder and cleaving station. The cleaving holder (a) shown in front and side view with crystal in place. The parent holder is shown in (b) with the sample holder in place. The cleaving station is advanced over the cleaving parent holder. Once in place, a moveable arm pushes on the protruding crystal, causing it to snap off.

holder which has two spring clips, electrically isolated from one another, pushing the sample holder against a solid back. This different design is necessary as a great deal of force is exerted on the sample, sample holder, and the arms which hold the sample holder during the cleaving process. Other specialty sample holders are designed for both direct current, and indirect heating of samples, as well as a specially designed indirect heating parent holder.

The second key removable element is the **cantilever holder** for AFM measurements (see fig. 2.4). The microfabricated cantilevers (described below) are held in place against a small piezo-electric actuator by a spring clip which can be released by pushing up the spring clip using a special platform with a protruding pin. There are three electrical contacts to the cantilever holder, two of which are for the piezo-electric actuator made via the two protruding pins on the bottom of the cantilever holder. The third contact is used to apply a voltage between the tip and sample through the spring clip which holds the cantilever chip, and is made via a contact pad on the side of the cantilever holder.



Figure 2.4: Photograph of cantilever holder for AFM measurements. The cantilever chips are held against the pizeo actuator by the spring clip which also provides an electrical contact to the tip. Electrical connections for the piezo are made through the pins on the bottom, and for the spring clip by the contact on the side. For scale, cantilever holder is ~ 2 cm wide. (Photograph courtesy of S. Fostner.)



Figure 2.5: SEM image of a typical Nanosensors cantilever. Image of a typical microfabricated cantilever (Nanosensors NCLR type) by *in situ* SEM. The AFM tip is at the end of the cantilever on the underside. Scale bar: $50\mu m$.

	Mikromasch NCSC12 "E"	Mikromasch CSC12 "E"	Nanosensors NCLR
l	$350\pm5\mu\mathrm{m}$	$350\pm5\mu\mathrm{m}$	$225\pm10\mu\mathrm{m}$
w	$35\pm 3\mu m$	$35\pm 3\mu m$	38 (20–45) μm
t	$2.0{\pm}0.3\mu\mathrm{m}$	$1.0\pm0.3\mu\mathrm{m}$	$7\pm1\mu\mathrm{m}$
f_0	21 (17-24) kHz	10 (7-14) kHz	190 (146–236) kHz
k	0.30 (0.1–0.4) N/m	0.03 (0.01 - 0.08) N/m	48 (21–98) N/m
ρ	$0.01-0.05\Omega \mathrm{cm}$	$0.01\text{-}0.05\Omega\mathrm{cm}$	$0.01-0.02\Omega \mathrm{cm}$

Table 2.1: Manufacturer's specifications for types of cantilevers used.

The **cantilevers** used are commercially available microfabricated highly doped ntype silicon cantilevers with integrated pyramidal tips (see fig. 2.5). Rectangular cantilevers were used, rather than triangular cantilevers, as spring constants are more easily calculated for this shape. All cantilevers used had reflective back coatings to improve the signal to noise of AFM measurements. Three different types of cantilevers were used which had the manufacturer's specifications indicated in table 2.1.1. All cantilevers used were baked for \sim 7 hours in situ to remove surface contaminants. No other processing was applied to the tips. As the tips were not heated sufficiently to remove the native oxide layer, it is assumed that all tips were initially coated with an SiO₂ layer.

2.1.2 Description of preparation chamber instruments

The preparation chamber has a number of surface science instruments mounted directly on the UHV system for in situ sample preparation and characterization. The instruments used in the experiments described in this thesis will be given some basic description here, and their use will be discussed elsewhere as appropriate.

- **Crystal cleaving station** The crystal cleaving station consists of two pieces, a specialized sample holder and a movable arm which can be advanced and docked with the carousel. Once docked, a block of stainless steel is lowered against the protruding crystal until the crystal snaps off (see fig. 2.3).
- **Crystal heater** A tungsten heating filament was built into a parent holder [44], such that the sample holder sits in front of the filament and is heated radiatively and through contact with the surroundings of the holder. This allows heating of cleaved insulating samples.
- Molecule Evaporator A three-source thermal evaporator with temperature feedback, commercially available from Kentax, was used to deposit molecules on surfaces. Molecules are evaporated from quartz crucibles surrounded by resistively heated coils. Water cooling prevents adjacent crucibles from being heated, and a specially designed shutter allows for all possible combinations of sources to be opened for co-evaporation if multiple power supplies are used. For the experiments performed only one molecule was evaporated, and thus the shutter was positioned so that only the desired source was open to further reduce the possibility of contamination from adjacent sources. The evaporator was mounted on a set of retractable bellows and can be isolated from the preparation chamber by a valve and connected to a separate pumping line. This allows the replacement of the molecular sources without breaking vacuum in the preparation chamber.
- **Quartz Microbalance** An Inficon bakeable sensor was used to monitor deposition rates and coverages. The sensor was mounted on a set of retractable bellows to allow for positioning at the sample location to measure the rate, and then

retraction for deposition of the desired material. For C_{60} a density of 1.700 g/ml³ [45], a z-factor of 1.000 and tooling of 1.000 was used.

LEED/AES A rear-view low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) system built by SPECS is mounted on the top of the preparation chamber facing the carousel. The carousel could be rotated and adjusted with the micrometer scews to carefully position a sample for observation from any of the electrically contacted specimen positions. For both LEED and AES observation modes, the carousel was set to ground by the electrical feed throughs corresponding to the appropriate sample position. Since the experiments described herein deal with insulating substrates, only preliminary LEED results will be discussed.

Also mounted on the preparation chamber were a four-source metal evaporator from Oxford Applied Research, and a scannable ion-sputtering gun from SPECS. These instruments were not used prominently in the experiments discussed.

2.1.3 Description of main imaging chamber

The main imaging chamber contains all of the real-space imaging tools of the system, the STM/AFM and the field-emission SEM (FE-SEM). For all of these modes of imaging the sample is positioned on the sample stage, which sits on stacks of alternating metal and viton discs to minimize vibrations. The stage (shown in fig. 2.6) can be locked to prevent damage to the vibration isolation when being removed from the vacuum system for maintenance, or for high resolution SEM observation. The samples are mounted vertically, using the linear manipulator described previously, onto an xyz piezo-electric scanner by two spring clips. The piezo-electric scanner has a 5μ m range in the x and y directions, and 1.4μ m in the z direction at room temperature. A separate calibration is used for low temperature experiments. The AFM cantilever or STM tip is mounted opposite the sample, approximately 10 mm away when the tip is manually retracted. For AFM and/or STM observation a coarse approach can be made with a mechanical lever which locks the tip mounting into the



Figure 2.6: Top view photograph of AFM/STM/SEM stage. Labels identify different parts of the stage described in the text. The alignment screws are used to position the laser, mirror directing laser beam to QPD, and the QPD. The tip and sample are mounted vertically (looking down from this view). The scanner is not visible here. The metal foils are connected to a cold finger inside the measurement chamber.



Figure 2.7: Beam deflection optical system with quadrant photo-diode. A laser beam is focused onto the back of a reflective cantilever. As the cantilever bends, the beam is displaced on the QPD. The differing intensity is measured as a voltage difference which gives a measure of the deflection.

stage. A motor approach can then be made, first visually, and then with computer controlled feedback. The sample can also be moved with x and y motors each with a range of approximately 300μ m. For SEM observation the STM or AFM tip may be either fully retracted or approached. In the approached position, the SEM can also be used to image the AFM or STM tip.

For AFM observation a beam deflection system is used. A laser diode is located in situ behind the tip. The focus of the laser is set during installation (see appendix A for details on laser diode replacement) by means of a lens on an adjustable mounting in front of the laser diode. The alignment of the laser on the back of the cantilever is adjusted by two rotary feedthroughs which control the up/down and left/right position of the laser via a series of gears and levers. A video camera allows an initial alignment of the laser on the end of the cantilever, and fine adjustments can be made after by maximizing the total intensity on the photodiode. The laser light reflects off of the back of the cantilever into a mirror, which reflects the beam into the quadrant photodiode (QPD). Three signals are read from the QPD: the total intensity, or "SUM" signal, the difference between the two halves of the QPD corresponding to the normal deflection of the cantilever, or "A-B", and the difference between the two halves rotated 90° corresponding to the lateral deflection of the cantilever, or "C-D" (see fig. 2.7). The mirror rotates to adjust the position of the beam on the QPD in the "A-B" direction, and the QPD can be adjusted up and down to center the beam in the "C-D" direction. For beam deflection AFM systems, "A-B" is typically used to denote the normal deflection of the beam by the cantilever, and "C-D" is typically used to denote the lateral deflection of the beam by the cantilever.

The FE-SEM consists of two parts, the electron column containing the gun and optics, and the detector. The electron column consists of a hot cathode Zr coated W(100) field emission tip, and the electron optics for focusing and aligning the beam. The electron column can also be valved off from the main chamber, and pumped independently by a small ion pump. This helps maintain a good vacuum in both the main imaging chamber, and the electron column.

The electron column is mounted at an angle of 45° from horizontal, and 45° from the vertical plane of the sample position. The cantilever is at an additional 16° angle from the vertical plane of the sample position, as shown in fig. 2.8. These angles must be taken into consideration when making detailed size measurements of objects as the image seen is a projection onto a plane at these angles. For example, when measuring the dimensions of a cantilever as seen in the image as l_i and w_i , where these are the length and width, respectively, as measured from the image, the following transformation must be used to obtain the real length and width of the cantilever, l_0 and w_0 respectively:

$$l_i = l_0 \sin(\alpha + \delta) \tag{2.1}$$

$$w_i = w_0 \sin(\beta) \tag{2.2}$$

Where α is the angle of the electron column from the vertical plane of the sample position, β is the angle from horizontal, and $-\delta$ is the angle of the cantilever from



Figure 2.8: Schematic of SEM view angles. The electron column is represented by the dark grey rectangle. The cantilever is represented by the light grey box in the center of the chamber outline. The dotted lines give the orientation of the sample and the perpendiculars to the sample plane as a reference for the measured angles (given here in degrees).

the plane of the sample position.

The sample stage can also be cooled for observation by means of a cryotstat in thermal contact with the sample stage via a cold finger and bundled silver foils. The inner dewar can be filled with either liquid nitrogen ($T_B = 77$ K) or liquid helium ($T_B = 4$ K) resulting in estimated sample temperatures of approximately 100K or 30K respectively. An outer dewar provides a cold jacket and is always filled with liquid nitrogen when the cryostat is in use. With the outer dewar filled, the holding time for liquid nitrogen is approximately 30 hours, and for liquid helium is 1.5-3 hours.

2.2 Description of imaging modes used

Two primary modes of atomic force microscopy imaging were employed herein, "contact" mode, and "non-contact" mode, or frequency detection AFM. The STM mode was also tested, but not used here as all of the sample substrates were insulating.

2.2.1 Contact-mode AFM imaging

As discussed briefly in the previous chapter, contact mode AFM creates an image of a surface by raster scanning a sharp tip attached to a force sensor across a surface and recording the force related signals. There are different methods of sensing the force between the tip and a surface, however, the beam deflection approach with a quadrant photo-diode (QPD) is used here. In this case, as the tip is scanned over the surface, the static deflection of the cantilever is measured by the deflection of the laser beam on the QPD as a voltage in the "A-B" direction, or V_{A-B} . This voltage is used as a feedback parameter to minimize the deviation of V_{A-B} from the desired set-point. For greatest sensitivity, the QPD should be aligned such that V_{A-B} is close to zero during normal imaging conditions. The piezo-electric scanner moves in the z direction, ie. changes the separation distance between the tip and sample to maintain this constant deflection, and thus a constant force. The z-movement of the piezo is recorded as a function of the x and y positions of the piezo producing a topography which can then be displayed by the computer.

A quantitative calibration of the normal force can be performed by finding the relationship between V_{A-B} and the deflection of the cantilever, and by calculating the spring constant of the cantilever. The former can be found by performing a force vs. distance measurement which moves the piezo at constant rate towards and away from the sample and measures the deflection of the cantilever. This gives a relation between distance and voltage on the QPD, which we will call the sensitivity, s_z , of the combined cantilever and photo-diode system. It should be noted that both the approach and retract directions are usually measured, so that any adhesive effects are observed and excluded for the purpose of calibration. In this way, the normal force exerted on and by the cantilever can be expressed in the following way [46]:

$$F_N = c_N s_z V_{A-B} \tag{2.3}$$

where F_N is the normal force, c_N is the spring constant of the normal mode of the cantilever, s_z is the aforementioned sensitivity in V/m, and V_{A-B} is the voltage on the QPD in the "A-B" direction. It should be noted here, that for proper calculation of the force V_{A-B} as used in the equation above should be the difference between the voltage during imaging, and the "zero" force voltage, i.e. the QPD voltage when the tip is retracted. The spring constant associated with the normal bending mode of a rectangular cantilever can be expressed as [46, 47]:

$$c_N = \frac{Ewt^3}{4l^3} \tag{2.4}$$

where E is the elastic modulus of the cantilever material, w is the width of the cantilever, t is the thickness of the cantilever, and l is the length of the cantilever. Generally, the length and width of the cantilever specified by the manufacturer are sufficiently accurate to calculate the spring constant, but can be measured with an SEM to obtain greater accuracy. However, the thickness of microfabricated cantilevers can vary widely, and as c_N goes as the cube of the thickness, it should be obtained to greater accuracy. The simplest method of determining the thickness of the cantilever is from the resonance frequency [48]:

$$t = \frac{4\sqrt{3}\pi l^2}{1.873^2} f_0 \sqrt{\frac{\rho}{E}}$$
(2.5)

where f_0 is the resonance frequency of the cantilever, l is again the length, ρ is the density of the material, and E is again the elastic modulus of the material. For silicon, the values of the elastic modulus and the density are $E_{Si} = 1.69 \times 10^{11} N/m^2$ and $\rho = 2.33 \times 10^3 kg/m^3$ respectively [49].

A secondary mode of contact mode imaging is lateral force AFM (LF-AFM), or friction force microscopy (FFM). This mode is possible with a QPD as the lateral deflection of the cantilever can be recorded simultaneously with the normal mode information. Other optical detection schemes cannot measure lateral or friction forces. In LF-AFM mode, the scan direction is rotated by 90° from the usual scanning direction to maximize the lateral forces on the cantilever (see fig. 3.5). The same contact mode imaging as described above is performed, but now the "C-D" signal on the QPD is also recorded corresponding to the lateral forces exerted on and by the cantilever. As with the normal forces, the lateral forces can be quantified. The lateral, or torsional, force can be expressed as [46]:

$$F_T = \frac{3}{2} c_T \frac{h}{l} s_z V_{C-D}$$
 (2.6)

where F_T is the torsional force, c_T is the torsional spring constant, h is the height of the tip, l is the length of the cantilever, s_z is the sensitivity of the QPD as above, and V_{C-D} is the voltage signal of the QPD in the "C-D" direction. The factors of 3/2 and h/l compensate for the twisting of the cantilever and that the laser is not focused on the pivot of this motion (the tip apex) but on the back of the cantilever above the position of the tip. For a rectangular cantilever, the torsional spring constant can be expressed by the following [46]:

$$c_T = \frac{Gwt^3}{3h^2l} \tag{2.7}$$

where G is the shear modulus of the material of the cantilever, w is the width, t is the thickness, h is the height of the tip, and l is the length of the cantilever. For silicon, the value of the shear modulus is $G_{Si} = 0.68 \times 10^{11} N/m$ [49].

As the lateral forces measured can be quite small, an amplifier (by Stanford Applied Research) was used on the V_{C-D} output signal before recording it with the computer software. Gain settings of $20\times$, $50\times$, and $100\times$ were used depending on the total range of the signal, and a low pass filter was used.

2.2.2 Non-contact AFM imaging

As described briefly in the previous chapter, non-contact AFM (NC-AFM) operates in a similar manner to contact mode AFM, whereby a sharp tip is raster scanned over a surface and a parameter related to the interaction between the tip and sample is measured. As opposed to contact mode, where a static deflection is measured, the tip is made to oscillate and a shift in the resonance frequency of the tip-sample system is measured. An oscillatory drive signal is applied to the small piezo under the cantilever chip (as described previously) causing the cantilever to oscillate. The same beam deflection system used for contact mode imaging is used to measure the oscillation of the cantilever in the "A-B" channel, and the "C-D" is centered to zero and is not expected to show much variation. Both the excitation of the cantilever, and the frequency measurement are performed by a phase-locked loop (PLL).

A simplified block diagram of the frequency detection and excitation signal production electronics of the NanoSurf PLL used for the experiments described herein can be found in fig. 2.9 [50]. The PLL takes the oscillating "A-B" signal of the QPD as the input frequency. The phase of this signal is then compared to the phase of the output signal of the voltage controlled oscillator (VCO). The multiplier and low-pass filter act as this phase comparator, as indicated in the figure by the grey dotted line. The output of the phase comparator, U_{phase} is given by [50]:

$$U_{phase} \propto \cos(\phi_{in} - \phi_{ref}) \tag{2.8}$$

where ϕ_{in} is the phase of the input signal, and ϕ_{ref} is the phase of the VCO output signal. A proportional-integral (PI) gain controller provides feedback on this phase comparison such that the VCO has the same frequency as the input signal, and thus there is a constant 90° phase shift between the input signal and the VCO output. The PLL is then in the "phase-locked" state, hence the term "phase-locked loop". While in the locked stated, the PLL can measure small changes in the input frequency in the same way by adjusting the VCO output to accommodate the shift in frequency. The output is a DC representation of the difference between the measured frequency and



Figure 2.9: Simplified Block diagram of frequency detection of NanoSurf PLL The input of the frequency detection circuit is an oscillating signal of some frequency (ω_{in}) and constant phase offset (Φ_{in}) . This is compared to a reference signal produced by the voltage controlled oscillator (VCO) with some frequency (ω_{ref}) and constant phase offset (Φ_{ref}) . The "phase comparator", outlined in the dotted grey box, consists of a multiplier and a low pass filter to reduce noise on the input of the PI controller. The PI controller adjusts the output of the VCO until it matches the input signal, such that the PLL is "phase-locked". The DC input of the VCO is a measure of the frequency shift. The output of the VCO can also be used as an excitation signal.

the center frequency (the free resonance frequency of the cantilever). Additionally, the NanoSurf PLL maintains a constant amplitude of the cantilever oscillation by means of a second feed-back loop which determines the excitation amplitude. The PLL provides the cantilever excitation signal from the VCO with the appropriate amplitude as determined by the amplitude controller. The use of a PLL for frequency detection is preferred to other methods of dynamic mode AFM as it is highly sensitive to small deviations in the resonant frequency, allows control over the amplitude of the cantilever oscillation, and is insensitive to changes in the Q-factor of the system [50].

A schematic diagram of the JEOL electronics and software with the NanoSurf PLL

for NC-AFM imaging is shown in fig. 2.10. A bundled cable caries most of the information to and from the measurement chamber, represented by the thick grey arrow, and is fed into the JEOL AFM controller electronics, or "black box". From the AFM controller, each of the signals indicated can be accessed. Feedback parameters, ie. gain and filter settings, as well as the frequency shift set point are set from within the control and acquisition software (WinSPM for Windows '98). The AFM controller feedback circuit uses the NanoSurf frequency shift output as the feedback parameter and moves the piezo in the z-direction to maintain the frequency shift set-point, such that images are acquired at constant frequency shift. Up to three auxiliary channels can be recorded in addition to the topography. These channels have been omitted from the diagram for the sake of clarity, but could be used to record the error signal (δf) , the amplitude, and/or the dissipation.

An additional mode of imaging, called Kelvin Probe Microscopy (KPM) was used in NC-AFM mode. KPM measures electrostatic differences, or differences in the contact potential difference (CPD), over different areas of the surface [51]. In short, KPM minimizes the the electrostatic forces at each point. Recalling from the previous chapter, the electrostatic contribution of the frequency shift, Δf , has a quadratic dependence on an applied voltage:

$$\Delta f \propto (V_{bias} - V_{CPD})^2 \tag{2.9}$$

where V_{bias} is the applied voltage, and V_{CPD} is the contact potential difference. During KPM imaging, an oscillating bias voltage is applied between the tip and sample, at a frequency that is much less than the resonant frequency of the cantilever, and thus outside the lock range of the PLL, with an amplitude which would provide a measurable change in the frequency shift. A lock-in amplifier is used to provide the oscillating voltage signal and detect the amplitude of the frequency shift response at the voltage oscillation frequency. An additional feedback circuit uses the lock-in output as input to minimize the frequency shift response at the voltage oscillation frequency by changing the DC bias applied between the tip and sample. In this way, the electrostatic contribution to the frequency shift is minimized, and the DC



Block Diagram of NC-AFM imaging mode with nanoSurf™ PLL

Figure 2.10: Block diagram of NC-AFM imaging mode with external PLL and KPM feedback Above is a representation of the electronics used for NC-AFM and KPM imaging. The measurement chamber is represented by the "Measurement" block. The JEOL AFM controller accesses most of the signals going to and from the measurement chamber, including QPD readings, xyz-scanner control, and motor control. The NanoSurf easyPLL consists of two boxes, one for frequency detection, and one for producing the drive signal for the cantilever. Most of the parameters are set directly through the computer acquisition and control software. The additional electronics and connections required for KPM imaging are shown in the grey box.



Figure 2.11: Illustration of Kelvin Probe imaging. The top left image is an illustration of a topographic AFM image of two materials, A and B, B being of greater height (white) than A (dark grey). The top right image shows what the Kelvin Probe image might look like if the CPD of B was less than the CPD of A, as can be seen in the frequency shift vs. voltage relation for each plotted below.

bias used to achieve this is a measure of the contact potential difference between the tip and the different sample areas (see fig. 2.11). It has also been put forth that the topography obtained while the KPM feedback is active is the "true" topography of the sample as the electrostatic forces are minimized over heterogeneous samples [52]. A schematic of the KPM electronics is included in fig. 2.10, with the additional electronics for KPM inside the grey box, and the additional connections for the lock-in amplifier and Kelvin Probe feedback circuit shown with dashed lines.

Chapter 3

KBr substrate preparation and characterization

3.1 Preparation of the KBr(001) surface

Blocks of pure, optical quality, unpolished KBr crystal were obtained from Korth Krystalle. The pieces were cleaved along the {100} directions to the appropriate size for use in the cleaving holder described in the previous chapter. Air-cleaved samples were cleaved using a sharp, clean razor blade, with the sample mounted in the cleaving holder. The cleaved surface was exposed to air for no longer than 30s before introduction to the load-lock and pumping. Once inside the preparation chamber, samples were heated for 1-2 hours using a quartz lamp directed at the surface through a window to remove any surface contamination that may have accumulated. For vacuum cleaved samples, the crystal was mounted in the sample holder and a line was lightly scribed in the <100> direction with a clean razor blade. The crystal was then introduced to the vacuum system through the load-lock. Once in the preparation chamber, the sample was cleaved using the cleaving station described in the previous chapter. The sample was then heated with the heating parent holder (described in the previous chapter) for 1 hour at $\sim 150^{\circ}$ C to remove residual charge from the



Figure 3.1: Atomic resolution with NC-AFM on KBr(001) surface – typical features. One of the ionic species is visible in the image making the lattice appear rotated by 45° (the crystal is oriented with < 010 > pointing up). The enhanced contrast at the step edge and kink sites is due to increased reactivity and electrostatic interactions. (image courtesy of J. Mativetsky.)

cleaving process.

Atomic resolution NC-AFM imaging of the KBr(001) surface is expected to produce an image of the cubic lattice with one of the species appearing bright, or topographically high, and the other appearing dark, or topographically low. Which of the ionic species, K^+ or Br^- appears bright depends on the charge and chemical sensitivity of the tip [48]. Also, due to an increased chemical reactivity (low coordination) and electrostatic interaction, the step edge appears topographically higher than the upper terrace and has a larger corrugation than atoms on the flat terraces in the NC-AFM images (see fig. 3.1)[27].

It was observed that KBr(001) surfaces had a high concentration of defects when exposed to the hot-cathode ion gauges (see fig. 3.2). This is likely caused by a low dose of charged particles incident on the sample which desorbs a small number of ions from the surface. This could be used purposely to create samples with randomly distributed defects. However, for the majority of the samples examined, the gauges were turned off for the duration of the experiment to prevent such damage.

Although it is difficult to study insulating surfaces with electron-based probes, LEED is possible on various alkali halides [35, 53]. Generally, to obtain good results, special precautions are taken, such as heating of the substrate, and the use of low beam currents with correspondingly sensitive detectors. However, as long as the exposure time is short to avoid damaging the surface studied, and the energy is maintained at a sufficiently large value to overcome the insulating gap and prevent charging, LEED images can be obtained with a typical apparatus on the KBr(001) surface (see fig. 3.3). Here the KBr surface was found to have the expected four-fold symmetry. As the image was somewhat out of focus, no quantitative analysis was attempted.



Figure 3.2: Defects created by electron damage on KBr(001) surface. A schematic diagram (a) shows a single vacancy (left) and an irregularly shaped pit (right). An NC-AFM image (b) shows two types of defects, one area of defects appears to have halos around the vacancies (upper left of image) likely due to some unbalanced charge, and the other type appears simply as depressions in the surface (lower half of image). Image size: 15×15 nm, $\Delta f = -37.4$ Hz, A=7nm, $V_{bias} = 0V$.



Figure 3.3: LEED images of KBr(001) surface. LEED pattern in (a) from Vogt et al. [35] under low primary current conditions. (b) LEED pattern acquired with ER-LEED system described previously and digital camera.

3.1.1 Comparison of air-cleaved and UHV-cleaved surfaces

NC-AFM was used to characterize both air-cleaved and UHV cleaved surfaces. Large scale images showed some differences in the size and structure of the terraces produced by both methods. Typically, air-cleaved samples had terraces that were 50-100 nm wide, and were generally aligned in the $\langle 010 \rangle$ direction (see fig. 3.4c). The terrace sizes for air-cleaved samples tended to be consistent for different areas of a given sample. UHV cleaved samples typically had areas with terraces of $\simeq 1\mu$ m or larger. However, areas of the sample tended to vary greatly, some terraces being only a few tens of nm wide (see fig. 3.4d and inset). The difference in large scale features is likely due to the different methods used to cleave the sample. Air-cleaved samples were cleaved by striking a sharp razor blade with a hammer (see fig. 3.4a). UHV-cleaved samples were cleaved by pressing down on a protruding piece of the crystal (see fig. 3.4b), which is more like a breaking or tearing mechanism than the cutting mechanism in air.

Atomic resolution was obtained on both air-cleaved and UHV-cleaved samples. This seems to indicate that the samples are well-ordered and free of contamination in



Figure 3.4: Comparison of air cleaved and vacuum cleaved KBr surfaces Figures (a) and (b) show the method of cleaving in air, and in UHV respectively. (c) and (d) are images of the resulting (001) surfaces of the KBr for air cleaving and UHV cleaving respectively. The inset of (d) shows how some areas of the UHV cleaved sample have narrow terraces, and irregular structure. Atomic resolution was achieved on both air and vacuum cleaved surfaces, (e) and (f) respectively. Image (c): $\Delta f = -13.6$ Hz, A=7nm, $V_{bias} = 0V$, size: 600 nm, image (d): $\Delta f = -2.63$ Hz, A=7nm, $V_{bias} = 0V$, size: 600nm, inset: $\Delta f = -5.27$ Hz, A=7nm, $V_{bias} = -0.5V$, size: 400nm, image (e): $\Delta f = -30.3$ Hz, A=7nm, $V_{bias} = +9V$, size: 6nm, image (f): $\Delta f = -20.2$ Hz, A=7nm, $V_{bias} = +2V$, size: 6nm,

both cases, and that either method is acceptable. However, due to the possibility of contamination at step edges in air-cleaved samples, as well as the possibility of finding larger terraces on UHV-cleaved samples, the majority of the KBr substrates used were prepared by *in situ* cleaving, and should be assumed so unless otherwise specified.

3.2 Contact mode imaging of the KBr(001) surface

Although NC-AFM is able to provide more high-resolution information about the surface, contact mode imaging can sometimes allow access to different information. Here some contact mode imaging was performed both to test the instrument and attempt to gain some further understanding of processes on the KBr(001) surface.

3.2.1 Preliminary results from variable temperature friction measurements

Contact mode AFM was used to find a suitably flat area of the surface to perform lateral force measurements. Once over a flat area, the scan size was reduced to 5-10 nm, and the z-piezo feedback was set very low to maintain a constant average load without cross-talk between the normal force and the lateral force. Two different cantilevers were used, both of the type Mikromasch CSC12 "E". The normal and lateral spring constants were calculated as previously described, and were found to be: 0.044 N/m and 28.6 N/m respectively for the first, and 0.031 N/m and 20.39 N/m for the second.

Resolution of atomic stick-slip in the lateral force channel (see fig. 3.5) was achieved at room temperature (~ 21°C, 294 K), as well as liquid nitrogen (sample temperature: ~ 100 K) and liquid helium temperature (sample temperature: ~ 30 K). Figure 3.5 shows sections of lateral force images, 5×1 , nm at each temperature with both



Figure 3.5: FFM images at liquid He, liquid N, and room temperature. Partial mirror images at top show forward and backscan on each line. Selections are 1×5 nm each. Starting from top: room temperature (21°C), $F_N = 0.39$ nN, liquid nitrogen temperature (~ 100K), $F_N = -0.45$ nN, liquid helium temperature (~ 30K), $F_N = -1.00$ nN. Friction loops shown below taken from cross-section marked on each partial image above for corresponding temperature and load.

the forward (left half) and back (right half) scan, ie. when the tip is moving to the right and to the left respectively. The marked cross-sections are also shown, displaying clearly the stick-slip motion of the tip over each atom. Hysteresis was also observed, indicating that some energy is dissipated into the surface, particularly for the low temperature traces. Note, however, that the loads for the low temperature images are increasingly strong in the "pulling" direction (cantilever is bent towards the surface due to an attractive force). This was due to an observed increase in the adhesion of the tip to the surface at these temperatures. However, since the loads were ill-defined due to drift in the z direction, especially at low temperatures, statements regarding the temperature dependence of the friction force will be reserved for further experiments. Drift was also apparent in the slow scan direction (y-direction) as can be seen by the "squashed" appearance of the KBr lattice in the images in figure 3.5, however, this could be corrected during the scan process, and does not effect the ability to define the forces, and is thus of less importance than the drift in the normal force.

Despite the problems encountered, the variable temperature measurements could be obtained, and the forces measured are on the order of tenths of nN, demonstrating that the instrument functions over a temperature range of 30–300 K with a sufficient sensitivity for this type of measurement. Further investigation of friction phenomena at variable temperature should be performed to confirm the functional dependance of atomic scale friction forces on temperature [54]. Although quantitative friction measurements were made difficult by drift, the ability to measure the small lateral forces involved in atomic stick-slip motion points to the possibility of measuring lateral forces during molecular manipulation investigations.

3.2.2 Preliminary results of ESD modification of KBr by SEM

Recent NC-AFM measurements of Sub-PC on electron irradiated KBr have suggested that the nanometer size pits produced by electron exposure could be used as a "nanopatterning" technique to confine small numbers of molecules [55]. Here, the possibility of using the in-situ SEM to expose a small area of the KBr surface is investigated for potential patterning applications.

Contact mode imaging was used to characterize the air-cleaved KBr surface prior to exposure to the SEM electron beam. Figure 3.6 shows the contact mode topography (a) and lateral force (b) images before electron irradiation. The tip was then retracted with the piezo and the shutter to the SEM column opened slightly to aim the electron beam near the tip position. Once the electron beam was positioned and switched to a high magnification to reduce the exposure area, the shutter was opened completely for a short period of time. The electron beam produced by the SEM had an emission current of 84μ A at an acceleration voltage of 10 keV. The sample was at room temperature and was not heated after irradiation.

After electron irradiation, the same area of the surface was imaged by re-approaching the tip. Although large scale features of the surface were still visible, the general appearance of the surface became much more rough and irregular after electron exposure as seen in both the topography (fig. 3.6c) and lateral force image (fig. 3.6d). Depressions in the surface are 10-20 nm deep, indicating that many layers of the KBr were affected by the electron beam. The general appearance of the surface seems consistent with images from electron stimulated desorption experiments on KBr where approximately half a monolayer of the surface is removed (transition between pits and islands) [56, 57, 58]. However, in these previous experiments, desorption occured layer-by-layer such that the pits were only a single atomic layer deep. The more rounded appearance of the structures imaged here are likely due to tip convolutions. To determine whether the effects were localized or not, the tip was retracted and moved $\sim 10 \mu m$. This new area was imaged and appeared unaffected by the previous irradiation (see fig. 3.7a and b). The irradiation procedure was repeated on this area giving similar results (see fig. 3.7c and d). The damaged surface was repeatedly imaged causing a rearrangement of the surface into rows perpendicular to the fast scan direction. This "ripple" formation has been observed in polymer systems [59] and was recently observed on atomically flat KBr(001) surfaces, i.e. surfaces that were not previously modified [60]. The wavelength of the ripple pattern on KBr has been found to correspond to the radius of the AFM tip [60], indicating here that the tip



Figure 3.6: ESD modification of KBr surface by SEM. Before images (a) and (b) of an air-cleaved KBr surface, and after (c) and (d) electron irradiation (of same area). SEM parameters: Acceleration voltage: 10,000V, Emission current: 84μ A, exposure time: ≤ 2 minutes, corresponding to an electron dose of $\sim 6 \times 10^{13}$ electrons. Contact mode topography image (a) with lateral force image (b) before electron irradiation, $F_N \simeq 20.4$ nN, topography image (c) with lateral force image (d), imaged immediately after electron irradiation in same location at $F_N \simeq 20.4$ nN.

radius was approximately 60 nm. The onset of ripple formation on the ESD modified surface was almost immediate. After only one or two scans the ripple pattern became evident, and became more pronounced with further scanning. It seems reasonable that the ripple formation process occurs readily on a damaged surface as there are many atoms which are unstable to initiate the process. These measurements show that localized surface modification with the SEM is possible. With further experimentation, it seems likely that less drastic changes could be obtained by using lower energy, and that by controlling the focus of the beam, an isolated area can be exposed allowing this technique to be used for patterning.


Figure 3.7: Ripple formation on ESD modified KBr surface. Before (a) and (b), and after (c) and (d) electron irradiation, (e) and (f) after imaging. SEM parameters: Acceleration voltage: 10,000V, Emission current: 84μ A, exposure time: ≤ 1 minute, corresponding to an electron dose of $\sim 3 \times 10^{13}$ electrons. Contact mode topography image (a) with lateral force image, $F_N \simeq 20.7$ nN, topography image (c) with friction image (d), imaged immediately after electron irradiation at $F_N \simeq 20.7$ nN, topography (e) with friction image (f), $F_N \simeq 21.6$ nN, after several scans, more pronounced vertical lines correspond to area imaged on smaller scale.

Chapter 4

C_{60} on KBr – imaging and growth characteristics

4.1 Deposition of C_{60} molecules on the KBr(001) surface

The KBr(001) surface was prepared as described in the previous chapter and characterized prior to the deposition of molecular material. The C₆₀ molecules were obtained from Alfa Aesar and had a specified purity of 99.9+%. Additional purification is achieved by outgassing the source in UHV at 220°C for a period of ~14 hours. C₆₀ molecules were deposited via thermal evaporation by the molecule evaporator described in chapter 2 on to a room temperature substrate. Typically, the deposition temperature was 330°C. A temperature dependence plot of the deposition rate, measured with the quartz microbalance described previously, is given in figure 4.1, though the deposition rate was also dependent on the source and shutter position. Adjustment of the shutter to reduce the rate of evaporation was chosen rather than altering the temperature to avoid also changing the kinetic energy of the deposited material. Rates used ranged from 0.0015 ML/s to 0.0077 ML/s. A list of rates, deposition times and coverages used for different samples is given in table 4.1.



Figure 4.1: **Temperature dependance of deposition rate.** Quartz microbalance readings showing the dependence of the deposition rate on source temperature. Rates determined from best fit of each data set are included in the legend.

In the case of a few preliminary samples, the rate was unknown and assumed to be approximately 0.1 ML/s from the quartz microbalance reading taken most closely to the experiments in question.

4.2 General growth characteristics and structure

NC-AFM imaging of the C_{60} structures on KBr(001) reveal clusters with an overall hexagonal shape which are often internally branched. Even for the submonolayer coverages used, the C_{60} clusters were ~ 2 nm or more in height, corresponding to two

Sample	Rate	Dep. Time	Coverage
KBr14	0.010 ML/s	2s + 14 s	0.10 ML
KBr16	0.0046 ML/s	44 s	0.20 ML
KBr18	0.0045 ML/s	11 s	0.05 ML
KBr19	0.0077 ML/s	14 s	0.11 ML
KBr24	0.0015 ML/s	67 s	0.10 ML
KBr27	0.0040 ML/s	25 s	0.10 ML

Table 4.1: Rates and coverages of C_{60} on KBr samples used

or more layers of C_{60} . This indicates an island, or Volmer–Webber growth mode, also implying a weak interaction between the C_{60} molecules and the KBr substrate. Also, an estimate of the diffusion length from the minimum distance between islands on flat terraces gives a value of 600–800 nm, which is consistent with contact AFM studies of C_{60} on alkali halides [9], but much longer than that of metals on alkali halides (from island densities [61]). Likely due in part to the fact that terraces are typically smaller than the diffusion length, the C_{60} islands are observed predominantly at step edges. Since the island density and size distribution of the islands are heavily influenced by the presence of steps on the surface, sufficient statistics could not be obtained to further analyze the growth on terraces.

Both the coverage and deposition rate of the C_{60} molecules were varied (see fig. 4.2). The general appearance of the islands does not seem to change significantly with coverage. The structures formed at a deposition rate of 0.0045 ML/s are typically two layers high with internal branching, and an outer rim (see fig. 4.3). At low coverage, the islands are close in size to the branch width, and therefore appear less branched. Disconnected regions were also observed in some islands, perhaps indicating the presence of multiple domains. At higher coverages, the structures become somewhat larger, but appeared to keep the same structure.

Varying the rate seemed to have more of an effect on the structures. A higher rate appeared to result in more compact structures, though some compact islands, and some evidence of branching are observed to co-exist at all rates and coverages examined. The compact islands are always hexagonal in shape and vary in height from two to five layers, with taller islands typically observed at step edges. The



Figure 4.2: Island appearance as a function of deposition rate and coverage. The above images are of similar areas on different samples where different rates and/or coverages of C_{60} were deposited. All depositions were on room temperature substrates with an evaporation temperature of 330°C.



Figure 4.3: Branched, two layer C_{60} island Area displayed in 3D is shown in the grey box in the image on the right. Arrows indicating the heights of different parts of the island have been added to the 3D image, showing the second layer rim (2) at the edge of the island and the inner part of the island which is 1 layer high (1). The image on the left shows a typical hexagonal, branched island as observed on large KBr terraces. The structure has three separate parts in this case, (3) is separate, possibly indicating different domains, and exhibits both branching, and hexagonal symmetry. Image size: 600×600 nm, $\Delta f = -2.2$ Hz, A=7 nm, C₆₀ coverage: 0.2 ML @ 0.0045 ML/s.



Figure 4.4: Compact C_{60} island with incomplete top layer. 3D and 2D image of a compact island with incomplete top two layers. Several features to note are the roughly hexagonal shape of the island, the beginning of subsequent layers in the center of the island growing out towards the edge, and the small difference in height between the portion of the island on the top edge of the step and the bottom edge of the step. $\Delta f = -5.8$ Hz, A=7nm, $V_{bias} = +0.75V$, Image size: 150×150 nm. (0.1ML $C_{60} @ \sim 0.01$ ML/s).

upper layer is usually incomplete, and appears to grow outward from the center of the island to the edges (see fig. 4.4). The dependance of the island morphology on the deposition rate indicates that the structures observed are *not* in equilibrium, and although more branched structures are observed at lower deposition rates, it is not certain at this time if this is the equilibrium structure. To confirm this, an annealing study should be performed, although the low evaporation temperature of KBr in UHV will provide an upper limit for the annealing temperature.

Branched islands are typically two C_{60} layers high and often have a rim, where the inner part of the island is one layer high, and the edges of the structure are two layers high (see fig. 4.3). These branched structures differ from typical dendritic growth as the outer perimeter of the island maintains a hexagonal shape, unlike fractal or



Figure 4.5: Comparison of C_{60} growth at step edge to "seaweed" growth. Approx. $2.4\mu m \times 1.4\mu m$ composite of 600×600 nm images patched together showing how the C_{60} structures formed at step edges exhibit some degree of branching and tip splitting similar to "seaweed" growth, as well as the large terraces without C_{60} islands $(0.2ML C_{60} @ \sim 0.0045ML/s)$. (inset) typical calculated seaweed growth structure from Provatas et. al. [64].

dendritic structures which extend fingers out and do not turn back inward to create a well defined outer perimeter. At step edges, the growth takes on an appearance similar to "seaweed" growth, so named for its resemblance to seaweed (see fig. 4.5). This seaweed growth occurs in the presence of a weak surface tension anisotropy and temperature gradient forming branches that semi-periodically split, similar to fractal growth, but lacking an overall fractal dimension. This type of growth is observed in a number of systems including directional solidification of binary alloys [62], bacterial colonies, electrodeposition, and drying water films [63].

4.3 Structure determination of C_{60} overlayer



Figure 4.6: Molecular and atomic resolution on C_{60} on KBr The above image has been processed using an alternating black and white greyscale to give contrast on both the substrate and molecular overlayer since the corrugation on each is much smaller than the step height. The region on the right is a C_{60} overlayer and the step in the middle of the image is ~8 nm high. The region on the left is the square KBr lattice. The image is 11 × 11 nm, and was obtained with $\Delta f = -11.3$ Hz, and A=7nm.

One of the advantages to studying molecular systems on alkali halides with NC-AFM is the ability to perform high resolution imaging on both the molecular overlayer and the ordered, atomically flat substrate. This allows a determination of the relation between the overlayer and the substrate, ie. the epitaxial relation if one exists. Even from STM data, there are few molecular systems for which the epitaxial relation to a given substrate is known [33]. Since obtaining both molecular resolution on the C_{60} overlayer and atomic resolution on the KBr(001) surface is highly dependent on the quality of the tip, only a few images like this were obtained. Here, one particular image (shown in fig. 4.6) will be examined, and compared to the edge orientations of other islands observed to determine the generality of this structure. This particular image is of the edge of an island located over a step. The island formed in such a way that the upper KBr terrace had only one layer of C_{60} making resolution of both structures less difficult than an area that was two C_{60} layers high. Ideally, these results would be compared with another technique for surface structure determination, for example LEED. This was attempted but yielded inconclusive results (see appendix B).

The first conclusion that can be drawn from both the large scale morphology previously discussed, and molecular resolution imaging, is that the C_{60} molecules form a hexagonal arrangement on the KBr surface, despite the four-fold symmetry of the substrate. This mismatch in symmetry is one of the factors which often leads to coincident structures in molecular systems.

4.3.1 Structure determination from overlayer rotation angle

Recalling from chapter 1, the matrix elements describing the relation of the overlayer lattice to the substrate can be determined from the lattice parameters of both lattices, and the orientation of the overlayer with respect to the substrate lattice. Measurements taken from a drift corrected version of the image in fig. 4.6 indicate that there is only a small, if any, deformation of the C₆₀ overlayer lattice, and an alignment with the < 010 > direction of the KBr surface. Using the lattice parameters for the conventional cell of KBr: $a_1 = a_2 = 6.6$ Å, $\alpha = 90^{\circ}$, and the equilibrium lattice spacing of C₆₀ : $b_1 = b_2 = 10$ Å, $\beta = 60^{\circ}$, and an overlayer rotation angle of: $\theta = 30^{\circ}$ corresponding to an alignment in the < 010 > direction, the matrix **C** is:

$$\mathbf{C}_{calc} = \begin{bmatrix} 1.31 & 0.757\\ 0 & 1.52 \end{bmatrix} \simeq \begin{bmatrix} 4/3 & 3/4\\ 0 & 3/2 \end{bmatrix}$$
(4.1)

Since no column consists of integers, this structure is either coincidence-II or incommensurate. Since the overlayer lattice may be slightly distorted from the values used, it is possible that the matrix elements can be rounded to fractions.

Although atomic/molecular resolution was not achieved everywhere, it is possible to extract information from large scale overview images about the number of rotational domains. Three families of angles were found by measuring the relative orientations of the edges of the C_{60} islands found on terraces. The three hexagonal angles $(30^{\circ}, 60^{\circ}, 120^{\circ})$, as well as the 90° angles are expected from the symmetry of the C_{60} and the KBr lattices respectively. However 20° and 80° angles were also measured and most likely indicate two rotational domains 20° apart (note that 80° is the same as an additional 20° rotation from 60°). It should also be noted that neither of these orientations correspond to the same < 010 > orientation observed in figure 4.6.

4.3.2 Structure determination by Image addition method

An image clearly displaying both the substrate and overlayer lattice, in principle, contains all of the information needed to determine the structure in that area, i.e. the lattice parameters of each lattice and the relative orientation of the overlayer to the substrate. Similar to overlaying the two lattices on transparencies, addition of the two lattice images by computer software can be used to look for points where the two lattices overlap in the same way. If these points repeat in a periodic fashion, a supercell can be defined.

From a molecular/atomic resolution image, an equally sized section of the substrate and the overlayer is cut out. An averaged unit cell image of the same size is created by averaging over all unit cells (as defined by a selected area) in the image, and re-tiling the unit cell (see fig. 4.7). This unit cell averaging reduces noise on the image, allows re-tiling of a larger area than perhaps is clear in the original image, and if defined correctly, improves the accuracy of the lattice spacing. The averaged unit cell images are then added:

$$(KBrAvgUnitCell + C60AvgUnitCell) \times 0.5 = CombinedImage$$
(4.2)

The result is a combined image that represents the relationship between the overlayer and the substrate. The combined image is used to look for any features which may repeat. An irregular diamond shape is outlined in the combined image in figure 4.7 which was used to visually identify periodicities. Any periodicity in this image will represent a periodicity in the overlayer–substrate geometry, and will thus define a supercell.

To test for the correct choice of a supercell, the supercell is cut out and re-tiled, without rotation or mirror operations, to recreate the combined image. The difference of the two images is then taken compare the choice of supercell:

$$(CombinedImage - RetiledImage) \times 0.5 + 128 = DifferenceImage$$
 (4.3)

If the difference image is featureless (at a grey-scale level of 128) the re-tiled image is identical to the original combined image. (Note: A Moiré pattern may appear if some of the supercells are not placed exactly during retiling. Striking features will appear if the wrong unit cell is chosen, including a large amplitude Moiré pattern and/or pieces of the combined image showing through.)

Using this method, two different supercells were identified, shown in fig. 4.8, with respect to the KBr lattice. The first can be defined with respect to the conventional cell of the KBr lattice in matrix notation as:

$$\mathbf{C}_{1} = \begin{bmatrix} 11/8 & 3/4 \\ 0 & 3/2 \end{bmatrix}$$
(4.4)

This corresponds to the primative cell of the $c11 \times 3$ structure, as it would be defined in Wood's notation.

The second supercell can be defined with respect to the conventional cell of the KBr lattice as well. In Wood's notation this is an 8×3 superstructure, or with respect to the primitive cell of the KBr, a $\sqrt{8} \times \sqrt{3}R30^{\circ}$. Or in matrix notation, with respect to the KBr conventional cell:

$$\mathbf{C}_2 = \begin{bmatrix} 4/3 & 3/4 \\ 0 & 3/2 \end{bmatrix}$$
(4.5)



Figure 4.7: Example of Image addition method of supercell determination Average unit cell images are created of both the molecular overlayer lattice and the atomic substrate lattice. These average unit cell images are added together to create the combined image. Within this combined image, if a periodicity can be distinguished, it is representative of a periodicity in the overlayer structure with respect to the substrate, i.e. this periodicity represents a supercell. The supercell can be cut out and used to create a retiling of the original combined image. The difference between these two represents the error in the retiling. A faint Moiré pattern may appear due to small offesets in the retiling process. If the wrong unit cell is chosen the difference image will contain more striking features.



Figure 4.8: Possible C_{60} on KBr supercells. The two possible supercells determined from the image addition method are shown. The $c11 \times 3$ supercell primative cell is shown in (a) over the KBr average unit cell image, and in (b) over the C_{60} average unit cell image. The 8×3 supercell is shown in (c) and (d) over the KBr and C_{60} average unit cell images respectively.

This unit cell, defined in matrix notation agrees well with the structure predicted from the lattice constants and overlayer rotation determined from the image (see eqn. 4.1). Although the first supercell identified has a smaller primitive cell, the 8×3 both agrees better with the calculated matrix, as well as appearing to be a slightly better fit to the C₆₀ lattice. However, both will be considered as the size of the C₆₀ molecules makes a precise determination of their location difficult.

Both of these structures fit the description of a coincidence-II structure as all of the matrix elements are rational, but no column of the matrix consists of integers. Hence, a supercell can be constructed and there is a distinct registry and phase coherence between the two lattices, though only *some* of the overlayer lattice points lie on lattice lines of the substrate. The presence of a coincidence-II structure also implies that the cost of deforming the overlayer is greater than the energetic gain of finding an phase coherent registry with the lattice. A prediction algorithm, outlined by Hillier et al. [65], and described in appendix C was used to search for commensurate and coincidence-I structures. As no structures were found within a reasonable range of C_{60} lattice constants, it will be assumed that any possible C_{60} structures will be either coincidence-II or incommensurate. In this case, the lack of available lattice geometries will be the primary reason for the coincidence-II structures. However, the presence of these out-of-phase structures still suggests that the cost of deforming the overlayer to an in-phase configuration is greater than the energetic gain of forming a structure which satisfies the overlayer-substrate interaction. This implies that the C_{60} – C_{60} intralayer interaction is stronger than the C_{60} –KBr interaction, which is also consistent with the observation of an island growth mode.

The image addition method described here is a relatively simple way of determining structures. It does however have some limitations as multiple unit cells may be apparent if the difference between them is small and/or the positions of the lattice points are ill-defined due to a significant extent of the atom or molecule. The major advantage to this method, besides its simplicity, is that two parts of the *same* image are compared such that any drift and/or non-linearities in the piezos are automatically excluded and drift correction is not needed.



Figure 4.9: Model structures from image overlay. Model shown above created by overlaying circles on lattice identified in molecular resolution image. The two supercells identified by the image addition method can be identified here also. (a) primitive cell of $c11 \times 3$ and (b) 8×3 .

4.3.3 Model structures from image overlay and reconstruction

A model of the C_{60} on KBr structures was created by overlaying a lattice of circles on the original molecular resolution image (see fig. 4.9). The two unit cells identified by the image addition method can also be identified in the model structure (fig. 4.9a,b). However, the slight shifts in position of the molecules defining the supercells in figure 4.9a,b may be due to errors in re-creating the lattice structure. Thus it should not be taken as an indication that these supercells are invalid. Rather, this method is more useful in determining the *translational* position of the overlayer molecules with respect to the KBr, and as a first look at the symmetry of the supercells.

From the information provided by the image overlay, a model of the structure seen in the molecular resolution image can be reproduced (see fig. 4.10). For either of the proposed structures the C_{60} molecules sit on alternating top sites, i.e. top K⁺ then top Br⁻, in the < 010 > direction for some rows. The number of out of phase and symmetry equivalent molecules depends on the exact structure, and this cannot be well determined from the image overlay method.



Figure 4.10: Reconstruction of molecular resolution image and models of 8×3 and $c11 \times 3$ supercells. (a) Reconstruction of molecular resolution image in fig. 4.6 based on an 8×3 structure and the translational position of the overlayer determined from the image. The second row of molecules (marked by the arrow) are located on top sites of alternating K⁺ and Br⁻ ions. (b) and (c) show exact models of the 8×3 and $c11 \times 3$ superstructures respectively.

4.3.4 Comparison of possible structures

Since more than one structure could be determined from the image, a comparison of the energies of each of the possible $n \times 3$ structures can help ascertain the most likely structure.

The overlayer energy can be estimated by a harmonic approximation of the C_{60} – C_{60} potential between each of the nearest neighbours for a given structure. In this case, the Girifalco potential [66] is used for the C_{60} – C_{60} interaction, which approximates the C_{60} molecule as a spherical shell of uniform density when integrating the C–C interactions over the molecules. This approximation is valid in the temperature range where the C_{60} molecule is rotating ($T \ge 300^{\circ}$ K for bulk C_{60}). Although it is not known whether the C_{60} molecules are rotating on the KBr surface, it is a reasonable approximation for the purpose of this calculation. The functional form of the potential is:

$$\phi(r) = -\alpha \left[\frac{2a}{r(r/2a-1)^3} + \frac{2a}{r(r/2a+1)^3} - 2\left(\frac{2a}{r}\right)^4 \right] +\beta \left[\frac{2a}{r(r/2a-1)^9} + \frac{2a}{r(r/2a+1)^9} - 2\left(\frac{2a}{r}\right)^{10} \right]$$
(4.6)

where α and β are constants with units of energy, a is the position of the energy minimum, and r is the separation distance between the two molecules. The values of all constants are given in table 4.2. From this potential, an effective elastic constant between two molecules, $c_{C_{60}}$, can be calculated:

$$c_{C_{60}} = \left. \frac{\partial^2 \phi}{\partial r^2} \right|_{r=r_0} \simeq 15.94 N/m \tag{4.7}$$

Using this harmonic approximation (see fig. 4.11) an estimate of the energy required per molecule to deform the lattice from its equilibrium structure can be made:

$$E_{cost}/molecule = \frac{1}{3} \sum_{i=1}^{3} c_{C_{60}} (b_i - r_0)^2$$
(4.8)

Binding Energy	1.4 eV [38]	
Equilibrium separation (r_0)	10.06 Å[66]	
α	$74.94 \times 10^{-22} J$ [66]	
β	$135.95 \times 10^{-25} J$ [66]	
2a	7.1 Å[66]	

Table 4.2: C_{60} parameters for Girifalco potential and energy calculation

where the b_i are the deformed lattice constants in each direction, r_0 is the equilibrium separation between molecules, *i* runs from 1 to 3 summing the energies for each uniquely displaced nearest neighbour, and the factor of 1/3 reduces the energy to be comparable to the binding energy between two molecules, i.e. the energy cost/molecule.

A relative estimate of the interface energy can also be obtained by determining the ratio of "out of phase" to the total number of molecules. These "out of phase" molecules, which do not sit on lattice points, will have some increased energy compared to molecules which *do* sit on lattice points. Although each "out of phase" molecule will have a different contribution to the total interface energy depending on the exact position of the molecule with respect to the substrate potential, this ratio can give a rough estimate of the relative energies.

A number of possible structures were determined by looking at the equilibrium lattice of the C_{60} molecules overlaid on the KBr(001) lattice. Structures which visually appeared to be a close fit were considered. The overlayer lattice constants to make each structure conform to the KBr lattice were calculated and used to determine the energy cost per molecule for each. The ratio of "out of phase" to total number of molecules was also calculated for each structure. The results are tabulated in table 4.3. It should be noted that the harmonic approximation will underestimate the energy required for compression of the lattice, and overestimate the energy for expansion of the lattice. From the relative energies as well as the image addition method, the 8×3 overlayer structure seems the most probable structure for this area.



Figure 4.11: Girifalco potential and harmonic approximation for C_{60} – C_{60} interaction. The plot shows the Girifalco potential (in solid line) with the corresponding harmonic approximation (in dashed line). The harmonic approximation is reasonably good very close to the equilibrium separation. Inset, is a schematic of the C_{60} lattice showing the three unique directions, and the central molecule which is considered.

•

Structure	Lattice Parameters	E _{cost}	$rac{\#out-of-phase}{total\#molec}$
$c5 \times 3$	$b_1 = 9.62 \text{\AA}$	0.068 eV	0.75
	$b_2 = 9.90 \text{\AA}$		
	$eta=59.0^\circ$		
8×3	$b_1 = 10.10 \text{\AA}$	$0.005 \ \mathrm{eV}$	0.92
	$b_2 = 9.90 \text{\AA}$		
	$\beta = 60.7^{\circ}$		
$c11 \times 3$	$b_1 = 10.34 \text{\AA}$	0.030 eV	0.88
	$b_2 = 9.90 \text{\AA}$		
	$\beta = 61.4^{\circ}$		
13×3	$b_1 = 9.90 \text{\AA}$	0.012 eV	0.95
	$b_2 = 9.90 \text{\AA}$		
	$\beta = 60.0^{\circ}$		
18×3	$b_1 = 9.82 \text{\AA}$	0.023 eV	0.96
	$b_2 = 9.90 \text{\AA}$		
	$eta=59.73^\circ$	ļ	
$c21 \times 3$	b ₁ =9.98Å	$0.017 \mathrm{~eV}$	0.94
	$b_2 = 9.90 \text{\AA}$		
	$eta=60.3^\circ$		

Table 4.3: Comparison of different possible $n \times 3$ C₆₀ overlayer structures



Figure 4.12: First layer bright and dim C_{60} molecules Image in (a) shows the first layer of a C_{60} island with molecular resolution. Image size: 20 nm × 20 nm, $\Delta f = -11.3$ Hz, A=7 nm. The line in (a) is represented in cross-section in (b) with the height difference of ~20 pm indicated by the arrow, and dashed lines. The molecular models in (c) show a small height difference between a C_{60} molecule with a pentagonal face in contact with the surface (left) and a hexagonal face in contact with the surface (right).

4.4 First layer C_{60} – Bright and dim molecules

Molecular resolution of the first layer of C_{60} revealed two different effective heights in the AFM topography (see fig. 4.12a), giving the appearance of "bright" and "dim" molecules. Measurement of the height difference between these "bright" and "dim" molecules yielded a value of 21 ± 3 pm (see fig. 4.12b). It should be noted that the ability of the instrument to measure height difference and corrugations on the order of 10's of pm indicates that the instrument is very stable, and the electronics contribute very little noise to the measurement.

The geometrical height difference between two different orientations of the C₆₀ molecule, namely the five-fold ring, and the three-fold ring in contact with the surface (see fig. 4.12c), can be calculated. The expressions for the center to centroid distances for both the pentagonal and hexagonal faces of a truncated icosahedron, based on an icosahedron of edge length a = 1, are respectively given by [67]:

$$r_5 = \frac{1}{2}\sqrt{\frac{1}{10}(125 + 41\sqrt{41})} \tag{4.9}$$

$$r_6 = \frac{1}{2}\sqrt{\frac{3}{2}(7+3\sqrt{5})} \tag{4.10}$$

The ratio of the height difference to the taller of the two orientations can be used to give an estimate of the height difference that would be observed in the AFM image:

$$\Delta h_o = \frac{|r_5 - r_6|}{r_5} \times h_o \tag{4.11}$$

where h_o is the height of the taller species measured in the image, and Δh_o is then the expected height difference. This geometrical height difference was found to be 21.7 pm, which is in very good agreement with the measured height difference. The close correspondence of the apparent height difference in the AFM topography to the geometrical height difference between these two orientations indicates that this is a likely origin of the observed "bright/dim" phenomenon.

Additionally, the "bright" and "dim" molecules were not observed to change contrast (ie. from "bright" to "dim" or vice-versa) on a time scale of > 30 minutes, indicating under this interpretation that the molecules are not rotating out of the plane of the substrate in the first layer on KBr at room temperature. Sub-molecular resolution imaging of the C₆₀ molecules would show whether or not there is an in-plane rotation, and hopefully confirm the proposed orientations for both the "bright" and "dim" molecules. This has not yet been achieved, but may be possible at low temperature. Also, the lack of rotation implies a strong interaction either between the C₆₀ molecules or between the molecules and the substrate. However, the growth and structure of C₆₀ on KBr has indicated a *weak* interaction between the molecule and the substrate. One possible explanation for this is that the molecules are sterically hindered from this rotation due to the slight deformation of the lattice as discussed in the previous section. A similar phenomenon of "bright" and "dim" molecules has been observed on C_{60} on noble metals by STM on C_{60} monolayers [68, 69, 70]. On the noble metals, the molecules have been observed to change contrast, and this frequency is inversely related to the strength of the interaction between the molecule and the substrate [69]. In the case of C_{60} on metals, the mechanism of the "bright" and "dim" contrast is often attributed to a difference in the local density of states over different orientations of the molecule [71, 72]. This could also lead to a difference in charge transfer between the molecule and the substrate, and an electrostatic difference which NC-AFM may also image differently. Although it seems likely that the difference in contrast is due to the geometrical height difference between the two orientations mentioned previously, another mechanism such as an electrostatic difference between the two species may be responsible. At this time, there is no way to distinguish these different mechanisms. In principle, high resolution Kelvin Probe imaging (similar to that demonstrated by Kitamura et. al. [73]) should show any electrostatic differences between the "bright" and "dim" molecules, however, data of this type could not yet be obtained.

4.5 Nucleation of C_{60} on KBr at kink sites

High resolution NC-AFM imaging of monatomic KBr steps has shown streaky, or noisy areas localized around kink sites only after C_{60} deposition (see fig. 4.13). These streaky areas typically have an amplitude of ≤ 1 nm, and an approximate radius of 2 nm. The observation of this kind of streaky pattern in STM data has often been associated with mobile species on the surface [74, 75]. In this case, the streaky patches observed at the kink sites in the KBr are likely one or a few C_{60} molecules loosely bound which cannot be imaged properly due to both thermal motion of the molecule and forces exerted by the tip. Since they are bound to the kink site, the streaky patches are localized to this area. It should be noted that these streaky patches occasionally disappear from one image to the next as can be seen in figure 4.13(b), indicating that the molecules can be removed from the kink site with the small forces exerted under normal NC-AFM imaging conditions. This also confirms that the streaky patches are not due to an interaction between the tip and the surface



Figure 4.13: Direct observation of C_{60} nucleation at kink sites. Atomic resolution images of the KBr(001) surface with kinks in < 010 > steps. The streaky areas are likely C_{60} molecules loosely trapped at the kink sites. In (b) one of these fuzzy areas has disappeared between images, revealing the underlying KBr structure. (a) Image size: 18×18 nm, $\Delta f = -7.1$ Hz, A=7 nm, (b) Image size: 18×18 nm, $\Delta f = -7.4$ Hz, A=7 nm.

in this area. Combined with the observation in overview images that C_{60} islands preferentially form at step edges, the observation of loosely bound C_{60} molecules at kink sites strongly indicates that this is one of the initial nucleation sites.

One can argue that the binding energy is likely to be stronger at the kink site as it is more highly coordinated, and thus a more likely nucleation site than a position on a terrace, or at a straight step edge. Additionally, because KBr is an ionic crystal, there are increased electrostatic forces at the kink sites due to an inbalance of charge, making these sites more reactive with many species. A numerical calculation of the electrostatic potential for a KBr(001) surface with a kink site was performed by approximating the ions of the crystal as point charges. A sheet of alternating charges was produced (see fig. 4.14a), and a top layer was created with a step half way across the array in x, and a kink half way down in y (ie. to the right of the step, all charges were set to zero). The thickness (ie. number of layers with alternating charge below the surface) could be adjusted, as well as the size of the lattice (ie. number of ions). For the calculation shown in figure 4.14, a system of $30 \times 30 \times 10$ ($l \times w \times d$) ions was



Figure 4.14: Calculated electrostatic potential at a kink site. The model system is shown in (a), and consists of a series of alternating point charges. The top layer is partially removed to produce a step with a kink site one atomic row in size. The potential is calculated at a constant height above the surface (ie. following the contour of the step as indicated by the dashed line), in this case 0.5 l.c. or 1.65Å, on a mesh that is $10 \times$ finer than that of the lattice. The resulting potential map is shown in (b), with dark areas representing more negative values, and light areas representing more positive values. The cross-sections marked by the dotted line in (b) for the < 100 >, < 010 >, and < 110 > directions are shown in (c), (d) and (e) respectively.

used. The potential was then calculated on a mesh finer than the lattice at a constant height above the surface (see dashed line in fig. 4.14a) by summing the contribution from all charges at each point [76]:

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{M} \frac{q_{ijk}}{\sqrt{(x-x_i)^2 + (y-y_j)^2 + (z_0 - z_k)}}$$
(4.12)

where i, j, k are the indices of the summation corresponding to the positions of the charges, the lattice is a size $N \times N \times M$, the q_{ijk} are the charges at the given positions, x_i, y_j , and z_k are the coordinates of the charge, x and y correspond to the position on the mesh where the potential is calculated, and z_0 is the constant height above the surface where the potential is calculated. The 2D result of the potential at a constant height of 0.5 l.c. is shown in figure 4.14b. As the primary mechanism for atomic resolution on alkali halides is suggested to be due to electrostatics [27], it is perhaps interesting to note that the general features of the electrostatic potential correspond quite closely to atomic resolution images of similar structures (refer back to fig. 3.1).

The calculated potential shows a minimum (or a maximum depending on the sign of the charges) at the kink site. This can be seen in center of figure 4.14b, as well as in each of the cross-sections (fig. 4.14c,d,e) passing through the kink site. The minimum extends ~ 0.4 mV below the minima located over the negatively charged ions.

Although the C_{60} molecule is not polar, its relatively large polarizability [77] indicates that it will be attracted to this minimum (or maximum) in the electrostatic potential through an induced dipole in the molecule. The depth of the attractive potential due to this induced dipole can be estimated using the polarizability. Assuming a perfect dipole [76]:

$$U = -\vec{p} \cdot \vec{E} \tag{4.13}$$

where U is the energy, \vec{p} is the polarization of the dipole and is given by $\vec{p} = \alpha \vec{E}$, and \vec{E} is the electric field. By numerically differentiating the potential in the x-y plane along the constant height trace to find the electric field, and taking $\alpha = 522.78 \text{Å}^3$ for a single molecule [78], the potential well created by the electrostatic interaction with the induced dipole is ~ 0.44 meV, or less than 2% of the thermal energy at room temperature. Although the attraction produced by the electrostatic interaction at the kink site is not sufficient to bind the molecule at room temperature, it is an additional contribution to the interaction at a site which is already expected to be more reactive.

4.5.1 Preliminary results of defect induced nucleation

KBr samples cleaved in air were exposed to electron irradiation from the hot ion gauges creating defect structures in the KBr(001) surface. As discussed previously, the defects caused by low doses of electron irradiation form square or rectangular pits. These defects seemed to have provided nucleation centers for the C₆₀ molecules, altering the growth somewhat. The pits created by electron damage will have at least four sites similar to the kink site that was found to be one of the nucleation sites for the C₆₀ molecules. In this way, the presence of these defects can both increase the density of islands and move the system towards a defect induced nucleation rather than nucleation dominated by critical cluster formation.

The islands formed under these conditions were observed to have compact structures with *no* evidence of branching as opposed to the previous case where some branching was always observed in the absence of defects on the surface. Figure 4.15 shows a typical image of the surface with two island sizes, all compact hexagonal structures, with a histogram of the island size distribution. The standard deviation of the island size is somewhat small for each size grouping, 20–30% of the average size, indicating that each size grouping was nucleated at approximately the same time and subsequently grew at the same rate.

The lack of a significant shift in the average island size with a second deposition



Figure 4.15: Island sizes of C_{60} on KBr surface with defects. (a) Image of compact islands of two sizes on KBr with defects. Image size: 650×650 nm, $\Delta f = -5.8$ Hz, A=7nm. (b) Histogram of island radii for initial deposition (solid line) and second deposition (long dash line). Calculated average value and standard deviation from first deposition used to plot gaussians for large and small islands to guide the eye. Inset is a plot from Sagui and Grant [31] of the time evolution of 2D growth for zero nucleation rate width, ie. uniform nucleation rate.

(equivalent to longer time), as well as the slight shoulder on the left-hand side of the small size island distribution, compares well with the steady-state homogeneous nucleation theory result for a constant nucleation rate with a narrow, or zero-extent (δ -function) distribution [31]. In the case of defect induced nucleation one might expect the critical nucleus size, and thus the nucleation rate width, to approach zero, ie. a single molecule bound to a defect can nucleate island growth. As the nucleation rate distribution width is related to the critical nucleus size, and thus temperature, the behaviour of these distributions as a function of the substrate temperature should confirm whether this is defect induced nucleation.

The two sizes of islands, one with an average diameter of 26.6 nm, and the other with an average diameter of 109 nm for this sample, may be caused by two different types of defects, or a combination of defect induced nucleation and critical cluster formation. In the possible case of two different types of defects, one may have a longer ranging interaction, for example a net electrostatic charge, resulting in an attractive potential well around the defect, and thus a greater probability of collecting a larger number of molecules. This difference in range of forces from a defect seems quite likely, especially considering atomic resolution of defects formed by electron irradiation showed two types of defects, one with a halo and one without (see fig. 3.2). The observation of a halo in NC-AFM indicates the presence of such a long range interaction.

The ability to create defects using electron bombardment and subsequently deposit molecules which have a preferred nucleation site at these defects presents an interesting way to direct growth. In principle, the growth of molecules could be directed by using a focused electron beam to produce localized defects. The facility to direct growth in this way could be quite useful in developing molecular electronics devices.

4.6 Preliminary results with Kelvin Probe imaging of C_{60} on KBr

Kelvin Probe imaging was used to measure the difference in electrostatics between the C₆₀ molecules and the insulating KBr substrate. Frequency shift vs. voltage curves were performed on both the C₆₀ islands as well as the neighbouring substrate. The minima in the parabolic Δf vs. V measurements showed a consistent trend for the contact potential difference of the C₆₀ molecules to be larger than the contact potential for the KBr substrate. However, the difference between the two CPD values was not found to be consistent, typically varying from ~ 0.07 - 0.3V from sample to sample, and sometimes even measurement to measurement. Likely due to this variability in the CPD difference, kelvin probe measurements on pure C₆₀ on KBr samples often were unsuccessful, or of poor quality.

Kelvin probe images were obtained after gold was deposited on the surface (see fig. 4.16a,b), with a contrast of ~ 1V, corresponding well to frequency shift vs. voltage measurements on the same sample. This difference in the CPD is larger than that measured on samples without gold clusters, which likely contributed to the improved kelvin probe contrast. One possible explanation for the larger CPD contrast observed on the sample with gold is a shift in the work function of the C₆₀ molecules resulting from a charge transfer between the molecules and the deposited gold atoms.

The successful application of Kelvin probe microscopy to this and other heterogeneous systems would be useful for chemical species differentiation. Since the material of the tip is often uncertain, as interactions with the sample can often cause material to move to or from the tip, chemical identification using this technique would be difficult. However, as can be seen from figure 4.16b, the area covered by C_{60} molecules can be clearly distinguished from the KBr substrate. This could become increasingly important as systems with larger numbers of components are used. However, further understanding of the contrast mechanism for kelvin probe on an insulating substrate is needed, as well as further experimentation to understand the effect of the added metal atoms on the CPD contrast.



Figure 4.16: Kelvin Probe image of C_{60} on KBr (with Au deposited). (a) NC-AFM topographic image with simultaneously acquired Kelvin probe image in (b). $\Delta f = -7.8$ Hz, A=7nm, Image size: 500 × 500nm. (c) Δf vs. V measured on KBr substrate and on C_{60} island on same sample. Minima of parabolas are separate by $\sim 1V$ giving this as the difference in CPD between the two materials.

Chapter 5

Conclusions and Outlook

As the NC-AFM technique is applied to wider range of problems in surface science, it is becoming increasingly clear that NC-AFM has the potential to add to the field of surface science on insulators in a similar way as STM was able to provide for surface science on conducting substrates. The non-destructive, high-resolution imaging that both tools are capable of allows investigation of the nucleation and growth processes and structure of deposited materials. As the growth and structure of the deposited material depend on a careful interplay of interactions between the substrate and overlayer, especially in molecular systems, there is a wealth of physical information that can be obtained about the driving forces and relative energetics dominating these processes. The results presented here are an initial step towards uncovering these physical processes. Further experimental work on different combinations of molecules and insulating substrates will be needed to make generalized statements about the interactions between molecules and insulators.

The imaging capabilities of the JEOL SPM system were tested in a variety of modes including atomic scale imaging with the AFM. The sample preparation instruments were used to prepare clean insulating substrate surfaces on which to study the growth of molecules. The KBr(001) surface was characterized using LEED, contact mode AFM, and NC-AFM. Atomic resolution of the KBr surface was obtained for both air-cleaved and UHV-cleaved samples. Atomic stick-slip was also imaged in LF-AFM mode at variable temperature leading to the possibility of studying temperature dependance of friction effects as well as measuring forces involved in molecular manipulation.

The growth of C_{60} on KBr was studied, revealing an island growth mode of both branched and compact structures. An epitaxial relation for the C_{60} overlayer was determined to be an 8×3 supercell for one area. This appears not to be a general structure as the orientation of crystallites not formed on KBr steps have a different edge orientation. However, from calculations performed, all epitaxial structures within a reasonable range of overlayer deformations are of the type coincidence-II. Thus the presence of any of these structures indicates that the cost of deforming the overlayer lattice is larger than the energetic gain of forming a more phase-coherent registry with the substrate lattice. This implies, as does the island growth mode observed, that the C_{60} intralayer interaction is stronger than the C_{60} -substrate interaction for the KBr(001) surface. To confirm this, ab initio calculation should be performed to determine the strength and stiffness of the C_{60} -KBr interaction potential to then compare to the C_{60} - C_{60} interaction. Additionally, theoretical work on the growth mechanisms will be required to understand more thoroughly the driving forces behind the unusual, branched structures observed in the C_{60} on KBr system. The kink sites in the KBr steps were identified as one of the initial nucleation sites of the C_{60} molecules through NC-AFM imaging. A calculation of the electrostatics of this type of surface morphology indicated that there was a small, but additional contribution to the binding potential through the polarization of the C_{60} molecule at the kink site. Although this is not a significant effect for the non-polar C_{60} molecule, it may be significant for molecules with permanent electrostatic moments. The preliminary work performed on the modification of surfaces indicates that the SEM could be used to produce ESD-type defects on the KBr surface. Growth of C_{60} on surfaces with these kinds of defects show that the growth is modified by the presence of defects. In future, the SEM may be used to create localized defects to steer the growth to areas where molecules are desired, for example between deposited electrodes. High resolution images of monolayer areas of C_{60} revealed an apparent height difference of 21 ± 3 pm between some molecules. This height difference corresponds very closely to the geometrical height difference of the C_{60} molecule in two different orientations, namely with the hexagonal ring and the pentagonal ring in contact with the substrate. Kelvin probe imaging of the C_{60} structures on KBr was attempted with limited success, though in principle it could be used as a method of distinguishing different species on samples of this kind.

Greater understanding of the interactions between molecules and insulating surfaces will be crucial to the future design and implementation of a planar single molecule electronic device. Without this information, the engineering of such a device would be left to trial and error, and understanding its behaviour would be difficult. From the device engineering perspective, the C_{60} on KBr system seems less than ideal as the deposited material forms widely spaced clusters containing many molecules. There are two main solutions to this problem. Subtractive manipulation should be possible with an AFM tip, whereby molecules are removed from an electrically contacted cluster by a physical probe. It has recently been shown that semiconductor atoms can be manipulated by NC-AFM [79, 80] which brings STM-like manipulation of atoms and molecules a step closer to the AFM community. This method would be slow however, and thus unsuited for technological applications, and may also damage a tip which otherwise could be used to carefully image the completed device and/or act as an additional electrode. The second, is to design a system where the interactions between the molecule, electrodes, and substrate are such that the molecule "self-assembles" into a device when the contacting structures are already in place. This requires the study of an additional set of interactions, those between the molecules and the material comprising the electrical contacts, be it a metal or another conducting molecule, and work in this area is ongoing. As our understanding of a wide variety of molecular systems on insulators expands, it may become possible to engineer self-assembled, or partially self-assembled device systems through the selection of molecular, metallic, and insulating materials according to the relative interactions between each.

Appendix A

Replacement of Laser Diode for AFM beam deflection system

The laser diode used for the beam deflection system of the AFM is situated in UHV on the sample stage. A cylindrical assembly containing both the laser diode (LD) and a focusing lens (see fig. A.1) is situated in an aluminum block which facilitates heat dissipation from the LD as well as allowing positioning of the laser through connections to rotary feed-throughs. Three connections are made to the LD from electrical feed-throughs for the source, drain, and internal photodiode (PD). The source and drain power the LD, while the internal PD monitors the intensity. The internal PD is used by a feedback circuit in the laser power supply to maintain a constant intensity.

After approximately one year the LD began degrading, and in good UHV conditions, the sum signal fell to below usable levels after being left on for several hours. This is in contrast to new laser diodes which do not vary significantly in intensity after being left on for several days. Additionally, the voltage across "VR15" in the laser power supply electronics increased to above 11 V indicating that an abnormally large current was needed to power the LD. The likely cause of this failing intensity is an inability of the laser diode to dissipate heat during operation due to some internal damage. Replacement of the first and second LDs were deemed unsuccessful as the problem


Figure A.1: Schematic of laser diode assembly for AFM beam deflection system. The lens and LD are held into the cylinder by threaded rings. For coarse focusing of the laser on the cantilever, the position of the entire assembly can be shifted. For fine tuning, the position of the lens can be adjusted by turning the front portion of the cylinder.

re-occured only a few months later. These first two attempts were performed by following the JEOL instructions to solder the laser diode to the co-axial connectors to the feedthroughs. A UHV compatable AgSn 95%-5% solder was used for this purpose. However, to achieve good mechanical and electrical contact to the leads with this high melting point, flux-free solder, the pins of the LD had to be raised to high temperature which may have damaged the laser diode. To avoid this problem, the third laser diode was installed using small crimp connectors which were soldered to the co-axial connectors, but not directly to the laser diode pins. The LD pins were then connected to the co-axial cables using the crimp connectors to form a good mechanical and electrical contact. After connecting the laser diode to the electrical feedthroughs and placing the assembly on the stage, the focus of the laser is adjusted by moving the lens. A triangular cantilever is placed in the normal tip position for this purpose. At focus, no image of the cantilever will be visible (perhaps some diffraction), whereas on either side of focus an image of the triangular cantilever will be visible on a screen placed somewhere past the cantilever (filter paper is clean and works well). On each side of focus the image of the cantilever will point in opposite directions, opposite the direction of the cantilever if the lens is too far from the cantilever, and in the same direction as the cantilever if the lens is too close to the



Figure A.2: Focusing of the laser beam on the cantilever. Light obstructed by the cantilever if it is placed inside focus will block rays which pass through focus and appear on the screen on the opposite side as the cantilever producing and up-sidedown shadow image of the cantilever. Similarly, a cantilever placed outside focus will block rays which hit the screen on the same side as the cantilever producing a right-side-up shadow image of the cantilever. At focus, most of the light will be blocked by the cantilever, and no image will be produced, though there may be some diffraction effects visible.

cantielver (see fig. A.2). This replacement has functioned at full capacity since April, 2004, nearly 5 months to date.

Appendix B

LEED of C_{60} on KBr(001) surface

The sample was prepared in the same manner as the samples investigated by NC-AFM. A coverage of 0.2 ML was deposited on a fresh KBr(001) surface cleaved in vacuum at a rate of ~ 0.004 ML/s. Electron beam energies which were sufficiently large to prevent charging of the surface were used. Exposure to the beam was minimized as much as possible. The sample had no visual indications of damage (eg. colour change or cloudiness) after being removed from the vacuum system.

Although only a few spots can be seen in the images acquired due to both camera focus and possibly LEED focus, also resulting in some broadness of the LEED spots, there seems to be a two-fold symmetry in the diffraction pattern. Due to the poor quality of the LEED results combined with the expected complexity of the structures formed by C_{60} on the KBr(001) surface further analysis was not attempted. However, the ability to acquire *any* LEED pattern on this type of sample indicates that with greater attention to the special considerations required to perform LEED on insulating samples, a determination of the C_{60} structure on KBr should be possible.



Figure B.1: LEED images of C_{60} on KBr(001) at various energies

Appendix C

Prediction Algorithm for Epitaxy of Molecular systems

By modelling the two lattices as plane waves, a real-space analytic expression can be obtained to describe the degree of epitaxy, or phase coherence, between the overlayer and substrate (ie, commensurism vs. coincidence vs. incommensurism). The following expression produces a dimensionless energy which returns the values 0 (-0.5 on hexagonal substrates), 0.5, and 1, for commensurism, coincidence I, and incommensurism respectively [65].

$$\frac{V_{interface}}{V_0} = 1 - \left[\frac{\sin(M\pi p)}{\sin(\pi p)}\frac{\sin(N\pi r)}{\sin(\pi r)} + \frac{\sin(M\pi q)}{\sin(\pi q)}\frac{\sin(N\pi s)}{\sin(\pi s)}\right] \left[\frac{1}{2NM}\right]$$
(C.1)

Where p, q, r, s are the matrix elements of **C** as described previously, and $N \times M$ (where M and N are odd numbers) defines the size of overlayer lattice examined. This expression can be used to classify known structures, as well as predict possible commensurate and coincidence I structures based on expected overlayer lattice constants. Note that the function cannot discern coincidence II structures as there is no column of the matrix **C** which consists of integers, and hence $V_{interface}/V_0$ will take on the same value as for an incommensurate structure. In this case the matrix elements p, q, r, s must be examined.

A plot of $V_{interface}/V_0$ as a function of angle, or lattice constant or both will show where the function reaches the values 0 and 0.5 revealing where commensurate and coincident structures (respectively) are possible. A program was written in Fortran77 to find commensurate and coincidence-I structures in a similar way varying both θ , the overlayer rotation angle, and the overlayer lattice constant (where $b_1 = b_2$, and both change at the same time and β is held constant, exploring an isotropic deformation of the overlayer lattice). The "figure-of-merit" function $V_{interface}/V_0$, and the matrix elements p, q, r, s were calculated for a range of overlayer rotation angles for varying lattice constatns. To avoid numerical difficulties around the regions of the function where 0/0 occurs, L'Hopital's rule is applied within the code, replacing the expression which produces 0/0 with the appropriate limit:

$$\frac{\sin(N\pi p)}{\sin(\pi p)} = \frac{0}{0} \longrightarrow N \tag{C.2}$$

To access the full range of variable lattice parameters, the program was modified to include separately varying lattice constants b_1 and b_2 , as well as the angle between the overlayer lattice vectors β , and again the overlayer rotation angle θ . Since four parameters are now being varied, only incidences of commensurism ($V_{interface}/V_0 = 0$), and coincidence-I ($V_{interface}/V_0 = 0.5$) are recorded along with the values of b_1, b_2, β and θ where these instances occur, the matrix elements p, q, r, s and the actual value of $V_{interface}/V_0$.

All versions of the code were tested with an input of two identical hexagonal lattices, returning commensurism for all values of θ which are multiples of 60° and identical lattice parameters.

The prediction algorithm was applied to the C₆₀ on KBr system. Lattice constants of the KBr were input as: $a_1 = a_2 = 4.6669 \text{\AA}$ for the primitive cell, and $\alpha = 90^\circ$. The C₆₀ lattice was varied over: $9.600 \text{\AA} < b_1, b_2 < 10.400 \text{\AA}$ varied independently in steps of 0.004 Å, with β varied from 57.00° to 63.00° in steps of 0.04°. The overlayer rotation angle was varied from 0.0° to 90.0° in steps of 0.18°. A tolerance of 1×10^{-7} was used to record commensurism and coincidence-I cases. The code was also run with smaller step sizes and returned multiple results around the same peak. Only once instance of coincidence-I, and no instances of commensurism were found. The lattice constants and overlayer rotation for the coincidence-I structure are: $b_1 = 9.740$ Å, $b_2 = 9.768$ Å, $\beta = 57.16^\circ$, $\theta = 61.38^\circ$. This leads to a matrix:

$$\mathbf{C}_{coin-I} = \begin{bmatrix} 1.00 & 1.83\\ -1.00 & 1.83 \end{bmatrix}$$
(C.3)

The plausibility of this structure can be determined from the energy required to deform the overlayer to these lattice parameters (as described in section ??). For this particular structure the energy calculated from within a harmonic approximation of the intermolecular interaction is 0.36 eV or 25% of the binding energy between C_{60} molecules. Such an extreme deformation of the C_{60} overlayer seems unlikely, and as such, it is not expected that this structure would appear.

Appendix D

Lattice structure prediction algorithm code

Source code written in FORTRAN77, compiled in UNIX. Standard input file below.

PROGRAM LATTICE_STRUCTURE_v3

```
******
!
Ţ
    Calculates the value of the analytic "figure of merit" function
Ţ
    (dimensionless interface potential Vint)
Ţ
ł
    version 3 adds independantly variable overlayer lattice parameters
1
       (including beta)
L
Ł
I
    Defualt input file is lattice5.in
    Input angle values are in degrees
ţ
1
    Program contains subroutines: (none)
1
    I.
    IMPLICIT DOUBLE PRECISION (a-h, o-z)
    PARAMETER (pi=3.141592654)
```

```
PARAMETER (nptsx=10)
PARAMETER (nptsy=5000)
DIMENSION xrecord(nptsx,nptsy)
read(5,*) a1, a2, alpha
read(5,*) b1, b2, beta
read(5,*) delb1,delb2,delbeta
read(5,*) mm, nn
read(5,*) thstart, thend
read(5,*) nb, nbeta, ntheta
read(5,*) tol
read(5,*) nout
open(6, file="lattice4.ERR", status='unknown')
thstartr=thstart*pi/180
thendr=thend*pi/180
thstep=(thendr-thstartr)/ntheta
if (nb.eq.0) then
  b1step=0.0d+00
  b2step=0.0d+00
else
  b1step=(2*delb1)/nb
  b2step=(2*delb2)/nb
end if
den1=a1*sin(alpha*pi/180)
den2=a2*sin(alpha*pi/180)
alphar=alpha*pi/180
betar=beta*pi/180
delbetar=delbeta*pi/180
if (nbeta.eq.0) then
  betastepr=0.0d+00
else
  betastepr=(2*delbetar)/nbeta
end if
do i=1,(nb+1)
  xb1=(b1-delb1)+b1step*(i-1)
  do j=1,(nb+1)
    xb2=(b2-delb2)+b2step*(j-1)
```

```
do k=1,(nbeta+1)
            xbeta=(betar-delbetar)+betastepr*(k-1)
            do l=1,(ntheta+1)
              xtheta=thstartr+thstep*(1-1)
! [calculate matrix elements p,q,r,s]
              p=xb1*sin(alphar-xtheta)/den1
              q=xb1*sin(xtheta)/den2
              r=xb2*sin(alphar-xtheta-xbeta)/den1
              s=xb2*sin(xtheta+xbeta)/den2
! [to avoid the discontinuties in Vint, find where denomonators are 0 and
! replace with expression from L'Hopital's rule]
          iptest=sin(pi*p)*1000
            if (iptest.eq.0) then
              yp=mm
            else
              yp=sin(mm*pi*p)/sin(pi*p)
            end if
          iqtest=sin(pi*q)*1000
            if (iqtest.eq.0) then
              yq=mm
            else
              yq=sin(mm*pi*q)/sin(pi*q)
            end if
          irtest=sin(pi*r)*1000
            if (irtest.eq.0) then
              yr=nn
            else
              yr=sin(nn*pi*r)/sin(pi*r)
            end if
          istest=sin(pi*s)*1000
            if (istest.eq.0) then
              ys=nn
            else
              ys=sin(nn*pi*s)/sin(pi*s)
            end if
```

! [evaluate the function Vint and record values for commensurate and

```
! coincidence I cases (ie, Vint=0,0.5)]
            vint=1.00d+00-(yp*yr+yq*ys)/(2*mm*nn)
            vtest1=abs(vint-0.0d+00)
            vtest2=abs(vint-0.5d+00)
            if (vtest1.lt.tol) then
              xrecord(1,irecord)=xb1
              xrecord(2,irecord)=xb2
```

```
xrecord(3,irecord)=xbeta*180/pi
 xrecord(4,irecord)=xtheta*180/pi
 xrecord(5,irecord)=p
 xrecord(6,irecord)=q
 xrecord(7,irecord)=r
 xrecord(8,irecord)=s
 xrecord(9,irecord)=vint
else if (vtest2.lt.tol) then
 irecord=irecord+1
 xrecord(1,irecord)=xb1
 xrecord(2,irecord)=xb2
 xrecord(3,irecord)=xbeta*180/pi
 xrecord(4,irecord)=xtheta*180/pi
 xrecord(5,irecord)=p
 xrecord(6,irecord)=q
 xrecord(7,irecord)=r
 xrecord(8,irecord)=s
  xrecord(9,irecord)=vint
```

irecord=irecord+1

end if

end do end do end do end do

&

! [write out data file for all xrecord entries]

```
write(nout,'(9a15)')("b1","b2","beta","theta","p","q","r","s",
   "Vinterface")
do m=1,irecord
  write(nout,'(9g15.6)')(xrecord(n,m), n=1,9)
end do
```

END

Standard input file:

```
4.6669,4.6669,90
10.0,10.0,60
0.4,0.4,3.0
155,155
0.0,90.0
200,150,500
1.0d-07
52
INSTRUCTIONS FOR INPUT FILE:
The variables are to be entered in the following order:
                   *lattice parameters for substrate
a1,a2,alpha
                   *lattice parameters for overlayer
b1,b2,beta
delb1,delb2,delbeta *range of variation of overlayer lattice param
                   *size of overlayer mm x nn
mm,nn
                   *overlayer rotation angles (thstart.. thend)
thstart, thend
                   *number of samples in b, beta, and theta resp.
nb,nbeta,ntheta
tol
                   *sensitivity of coincidence detection
                   *number of output file (fort.nout)
nout
NOTES:
*alpha, beta, thstart, thend are input in degrees
*mm and nn must be odd numbers
```

Appendix E

Code for electrostatic kink site potential calculation

Source code written in FORTRAN77, compiled in UNIX. Standard input file below.

PROGRAM KINKPOTL_V3

```
! Program calculates the electrostatic potential at a kink site in a cubic
! ionic crystal.
! Returns 3 cross-section <100>, <010>, <111>, and the potential at all
! points in an array.
! Returns the energy landscape for a polarized C60 molecule
I
      IMPLICIT DOUBLE PRECISION (a-h, o-z)
      INTEGER z1,z2
      PARAMETER (nptssm=500)
     PARAMETER (nptslg=1000)
     DIMENSION z1(nptssm,nptssm)
     DIMENSION z2(nptssm,nptssm)
      DIMENSION vt(nptslg,nptslg)
      DIMENSION energy(nptslg,nptslg)
      DIMENSION xcross(10,nptslg)
      read(5,*) nn, nmesh
```

```
read(5,*) height, ithick
     read(5,*) rscale
     read(5,*) alpha
     read(5,*) nout
     read(5,*) nprint
     open(6, file="kinkpotl0.err", status='unknown')
     qscale=1.6d-19
     ck=9.0d+9
! [initialize arrays z1, z2, vt, energy]
     do i0=1,nn
       do j0=1,nn
         z1(i0,j0)=0
          z2(i0,j0)=0
        end do
      end do
     do ix=1,nn*nmesh
        do iy=1,nn*nmesh
         vt(ix,jy)=0.0d+00
          energy(ix,jy)=0.0d+00
        end do
      end do
! [create z2 array -- flat sheet of ions]
      print *, "z2 array, first 6 columns:"
      do i=1,nn
        do j=1,nn
          z2(i,j)=(-1)**(i+j)
          print *, "i=",i, " j=",j, " z2=",z2(i,j)
!
        end do
      end do
!
       do ip1=1,nn
         print *, z2(1,ip1), z2(2,ip1), z2(3,ip1), z2(4,ip1), z2(5,ip1),
!
ļ
      +z2(6,ip1)
!
       end do
! [create z1 array -- kink layer]
```

```
print *, "z1 array, first 6 columns:"
     do i=1,nn
       do j=1,nn
          if ((j.le.(nn/2)).and.(i.le.(nn/2))) then
            z1(i,j)=-z2(i,j)
          else if ((j.ge.(nn/2)).and.(i.le.(nn/2-1))) then
            z1(i,j) = -z2(i,j)
          end if
        end do
      end do
!
       do ip2=1,nn
!
         print *, z1(1,ip2), z1(2,ip2), z1(3,ip2), z1(4,ip2), z1(5,ip2),
Ţ
      +z1(6,ip2)
ł
       end do
! [calculate the potential on a mesh of nn*nmesh]
       do ix=1,nn*nmesh
         do jy=1,nn*nmesh
           do i=1,nn
             do j=1,nn
               do k=1,ithick
                 x=dble(ix)/dble(nmesh)
                 y=dble(jy)/dble(nmesh)
                 xdel=(x-dble(i))*rscale
                 ydel=(y-dble(j))*rscale
                 if ((j.le.(nn/2)).and.(i.le.(nn/2))) then
                   z0=-1.0d+00+height
                 else if ((j.ge.(nn/2)).and.(i.le.(nn/2-1))) then
                   z0=-1.0d+00+height
                 else
                   z0=-2.0d+00+height
                 end if
                 xk=dble(k)
                 zdel=(-xk-z0)*rscale
                 r=sqrt(xdel**2+ydel**2+zdel**2)
                 if (k.eq.1) then
                   qijk=z1(i,j)*qscale
                 else
                   qijk=z2(i,j)*qscale*(-1)**k
                 end if
```

```
vt(ix,jy)=vt(ix,jy)+ck*qijk/r
               end do
             end do
           end do
         end do
       end do
! [calculate derivative and find energy for polarized C60]
     do ix=1,(nn*nmesh-1)
        do jy=1,(nn*nmesh-1)
          dx=(vt(ix,jy)-vt((ix+1),jy))/(rscale/nmesh)
          dy=(vt(ix,jy)-vt(ix,(jy+1)))/(rscale/nmesh)
          energy(ix,jy)=-alpha*(dx**2+dy**2)
        end do
      end do
! [create cross-section arrays for <100>,<010>,<111> el potl, and energy]
      do i1=1,nn*nmesh
        xcross(1,i1)=i1*rscale/nmesh/1.0d-06
        xcross(2,i1)=vt(i1,((nn+1)/2*nmesh))
        xcross(3,i1)=energy(i1,((nn+1)/2*nmesh))
        xcross(4,i1)=vt(((nn+1)/2*nmesh),i1)
        xcross(5,i1)=energy(((nn+1)/2*nmesh),i1)
        xcross(6,i1)=sqrt(2.0)*i1*rscale/nmesh/1.0d-06
        xcross(7,i1)=vt(i1,i1)
        xcross(8,i1)=energy(i1,i1)
        xcross(9,i1)=vt(2,i1)
      end do
! [print out full array if specified]
      if (nprint.eq.0) then
        do ll=1,nn*nmesh
          write(nout+1,'(1000g15.6)')(vt(kk,ll), kk=1,(nn*nmesh))
        end do
        do ll=1,(nn*nmesh-1)
          write(nout+2,'(1000g15.6)')(energy(kk,ll), kk=1,(nn*nmesh-1))
        end do
      end if
```

! [print out cross-section (always)]

```
write(nout,'(10a15)')("x1/ang","V100", "energy100", "V010",
+"energy010", "x2/ang","V111", "energy111",
+"1col")
do ll=1,nn*nmesh
  write(nout,'(10g15.6)')(xcross(kk,ll), kk=1,9)
end do
END
```

Standard input file:

30, 10 0.5d+00, 10 3.3d-06 522e-30 54 0

INPUT FILE FOR KINKPOTL_V2:

nn, nmesh height, ithick rscale alpha nout nprint

*number of ions, integer, must be EVEN number, max 500 nn *multiplier of nn to determine number of mesh points for potential, nmesh integer, even, max to give nn*nmesh=10 000 (10 recommended) height *dble, height above surface in l.c. *integer, number of layers in calculation ithick rscale *dble, interionic distance in meters *integer, gives first file name as fort.nout nout *if 0, full array of potntial is printed as fort.(nout+1) nprint if 1, only cross-sections are printed in fort.nout ************

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