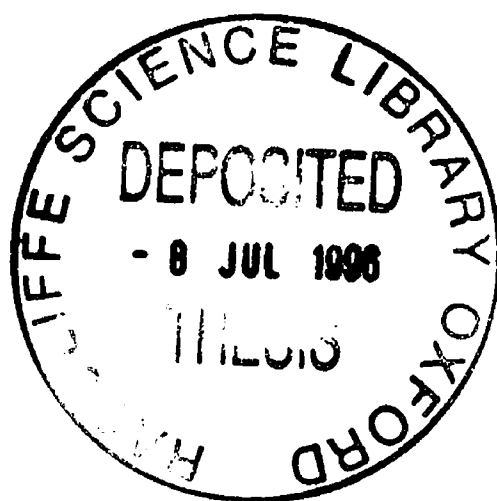


QUANTITATIVE STM IMAGING OF METAL SURFACES

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A Thesis submitted for the degree of Doctor of Philosophy at the University
of Oxford

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ABSTRACT

Many deductions made about STM images are based upon the model of Tersoff and Hamann, in which images are given in principal by a combination of surface atomic positions and local charge density. There is now a need for a fuller understanding of this technique in order to explain experimental evidence which indicates that the tip and sample can interact strongly during normal imaging.

In order to investigate the fundamental STM imaging process, a method for deducing the tunnel barrier height has been developed which is based on corrugation height measurements of constant current topographs. From experiments on clean Cu(100), values of the tunnel barrier height have been shown to be somewhat below the workfunction ($\sim 1\text{-}2.5\text{eV}$) but are in good agreement with other reports of atomically resolved barrier height data.

At large values of the tunnel conductance ($\sim 1\mu\text{S}$), a fall-off (based upon extrapolation of large separation data) in the corrugation heights is observed with increasing conductance. This effect is quantitatively explained using a Molecular Dynamics simulation of the tip approaching the sample. The simulation gives a good estimate of both the absolute tip-sample separation and site-dependent tip-surface forces.

Distributions of corrugation heights indicate that variations in both tip geometry and chemistry are likely to occur in practice and strongly influence the phenomena described above.

Similarly, it is found that increased local tunnel barrier heights are measured when the Cu(100) surface is modified with small numbers of single halogen atoms. This data has been used to estimate the contributions to the increase in local barrier height of both adsorbate induced dipoles and geometric topography. Values for the charge transfer between the surface and adsorbate have been established. The process of tip-induced adsorbate manipulation has also been demonstrated at room temperature.

To my Parents

Preface

This Thesis is an account of the work carried out by the author between October 1992 and September 1995, under the supervision of Dr J. B. Pethica. Apart from brief visits to other laboratories, this work was carried out in the Wolfson Research Laboratories in the Department of Materials, University of Oxford and the Center for Atomic Scale Materials Physics (CAMP) at the Institute of Physics, University of Aarhus, Denmark. The work was supported by the Engineering and Physical Science Research Council (UK) through studentship number 927004811.

This Thesis has not been previously submitted for a degree at this or any other University. The work of others has been freely drawn upon and is duly acknowledged in the text. Lists of references are given at the end of each Chapter and pertain to the Chapter in question. I am happy to acknowledge that the Molecular Dynamics (M.D.) calculations which led to the results presented in Chapter Six were performed by Dr J.A. Nieminen¹ using the M.D. code developed by Dr A.P. Sutton of the Department of Materials, University of Oxford.

Parts of this work have already been published in Scientific Journals:

(i) A.R.H. Clarke and J.B. Pethica, "Scanning Tunnelling Microscopy at Atomic Resolution: Quantitative Information from Corrugation Height", *Inst. Phys. Conf. Ser.* No. **146**, 671 (1995).

(ii) A.R.H. Clarke, J.B. Pethica, J.A. Nieminen, F. Besenbacher, E. Lægsgaard and I. Stensgaard, "Quantitative STM at Atomic Resolution: Influence of Forces and Tip Configuration" *Phys. Rev. Lett.*, **76**, 1276 (1996).

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"It was the best of times, it was the worst of times". I am sure that has meant something different to my family, friends and colleagues over the last three years or so. There are so many locations, experiences, stories, happenings, and joyful moments which for me will always be inextricably linked to this piece of work. In this woefully short statement, I should like to thank the people who have helped to make these memories all the more vivid.

I am indebted to John Pethica for the informal yet nevertheless caring nature of his supervisory role. It has been great fun to be a small part of the JBP "Empire" and I have emerged much the better for a spell under his direction. John offered me a mountain of good advice and it was at his suggestion that I spent 4 months between February and May 1994 at the Institute of Physics, University of Aarhus. Flemming Besenbacher generously allowed me to join his STM group and gave me freedom of movement within his lab for which I am grateful. A special vote of thanks is due to the Aarhus Aardvarks! - Phil Sprunger, Lars Olesen, Lars Pleth Nielsen, Erik Lægsgaard, Like Ruan, Ivan Stensgaard and the irrepressible Peder-Christian Tange Noergaard for making my stay so pleasurable.

Back in Oxford I was lucky to have on hand the calm experimental expertise and no nonsense attitude of my golf playing partner, Monsieur André Mayne. My long standing Tetris rival, Chris Goringe never let things get out of control and adopted a "*soft-hands*" (*limp wrists?*) approach to all the problems we encountered :-). James Owen (formerly of *Dulwich College*) subjected us all to fearful PUNishment :-(. Dave Bowler patched up many of my *self-inflicted* computer *injuries* without resorting to the "... *now there are two ways we can do this ...*" ultimatum. I am indebted to my fellow JBP group siblings for their support and especially from Suzi Jarvis and Syed Amanulla Asif during the sabbatical year. With Adrian Mann I spent literally hundreds of hours discussing the minutiae of our three mutual interests - cricket, politics and convergent beam electron microscopy!

Outside the laboratory, I was lucky to have the close friendship of Lisa, Mike and Jon, particularly in the somewhat tense final stages of this project when I was always dashing between Oxford and Bristol.

Finally I should like to thank my parents for all their love, support and continuous backing of me over so many years.

Abbreviations

AES	Auger Electron Spectroscopy.
CMA	Cylindrical Mirror Analyser.
FEM	Field-Emission Microscope.
FIM	Field-Ion Microscopy.
LDA	Local Density Approximation.
LDOS	Local Density of States.
LEED	Low Energy Electron Diffraction.
SEM	Scanning Electron Microscopy.
STM	Scanning Tunnelling Microscope. or Scanning Tunnelling Microscopy.
UHV	Ultra-High Vacuum.
m m	10^{-3}m (metres).
μm	10^{-6}m .
μS	10^{-6}S (Siemens).
$\text{\AA}$	10^{-10}m .
m V	10^{-3}V (Volts).
eV	$1.6 \times 10^{-19}\text{J}$ (Joules).
nA	10^{-9}A (Ampère).
mBar	10^{-3}Bar .

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Chapter 1

Introduction

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1.1Opening Remarks:

Scanning Tunnelling Microscopy (STM) is a tool used in surface science to produce real-space, atomic-scale resolution images of electrically-conducting surfaces such as metals, doped-semiconductors and certain metal-oxides [1.1, 1.2, 1.3]. Since its invention in the early 1980s, STM has been tremendously successful in investigating problems such as the atomic configuration of complex reconstructed surfaces [1.4]. A large body of work has also been concerned with the behaviour of adsorbates on surfaces [1.5], and has developed along several different directions, such as for example, the characterisation of equilibrium adsorption-sites [1.6]. There have been a number of investigations of dynamic phenomena [1.7, 1.8], as well as studies to elucidate two and three-dimensional epitaxial-growth mechanisms [1.9, 1.10]. By carefully controlling the imaging conditions, it has even been demonstrated that STM can be used as a deliberate atomic manipulation tool [1.11].

However, in spite of all the information gleaned to date using STM, quantitative understanding of this technique is surprisingly under-developed. Many of the deductions about STM images have been based upon the early model of Tersoff and Hamann [1.12, 1.13]. In their work, STM images are interpreted as maps of the Local Density of electronic States (LDOS) at the Fermi level, measured 5-10Å above the surface by a nominally point tip. From

the LDOS theory, the key result obtained is that the properties of the tip do not determine variations within the final image, which is simply a reflection of the underlying surface crystallography.

The LDOS of a surface is simply the energy resolved density of states at a particular point. In STM of metal surfaces, tunnelling is usually confined to states at or near the Fermi level. We are thus interested in the charge (per unit energy) derived from states at the Fermi energy, as measured physically at the centre of curvature of the tip. This quantity, $\rho(r_t, \mathcal{E}_F)$, is usually written:

$$\rho(r_t, \mathcal{E}_F) = \sum_v |\Psi_v(r_t)|^2 \delta(\mathcal{E}_v - \mathcal{E}_F) \quad (1.1)$$

where r_t is the centre of curvature of the tip
and Ψ_v is a surface wavefunction

Note that the summation in equation (1.1) does not take account of interference effects between contributing wavefunctions and hence we cannot strictly equate $\rho(r_o, \mathcal{E}_F)$ with the total charge density above a surface at a particular point. Such interference effects are purely quantum mechanical in nature, but they are important as they lead directly to the formation of chemical bonds [1.14]. Tersoff and Hamann note that for systems where directional bonding is minimal such as is the case for noble metals, contours of $\rho(r_o, \mathcal{E}_F)$ almost coincide with contours of total surface charge and so it is sometimes useful to think of an STM image of a metal surface as a contour map of surface charge density. The LDOS approach has shown to be effective in describing experimental data for metallic surfaces such as the (1x2) and (1x3) reconstructions of the clean Au(110) surface [1.15].

Despite this helpful picture, there is a large body of evidence indicating that the tip and sample interact more strongly than is suggested by this simple theory. Moreover, when taken collectively, these results serve to demonstrate that if the full benefits of Scanning Tunnelling Microscopy are to be enjoyed, it is essential to have a full quantitative understanding of this technique. The purpose of this opening Chapter is to outline some of the more unusual STM studies, and to suggest areas in which an improvement in understanding the STM imaging process is desirable.

1.2 Bizarre Imaging Phenomena:

The total surface charge density above metallic surfaces has been investigated using helium-atom diffraction. In experiments on Al(111) [1.16] and on other metal surfaces [1.17], corrugation heights - defined as the vertical distance between the highest point (maxima) and the lowest point (minima) of the total surface charge density measured along a periodic surface direction (see **figure 1.1** below), have been shown to be $\sim 0.05\text{\AA}$.

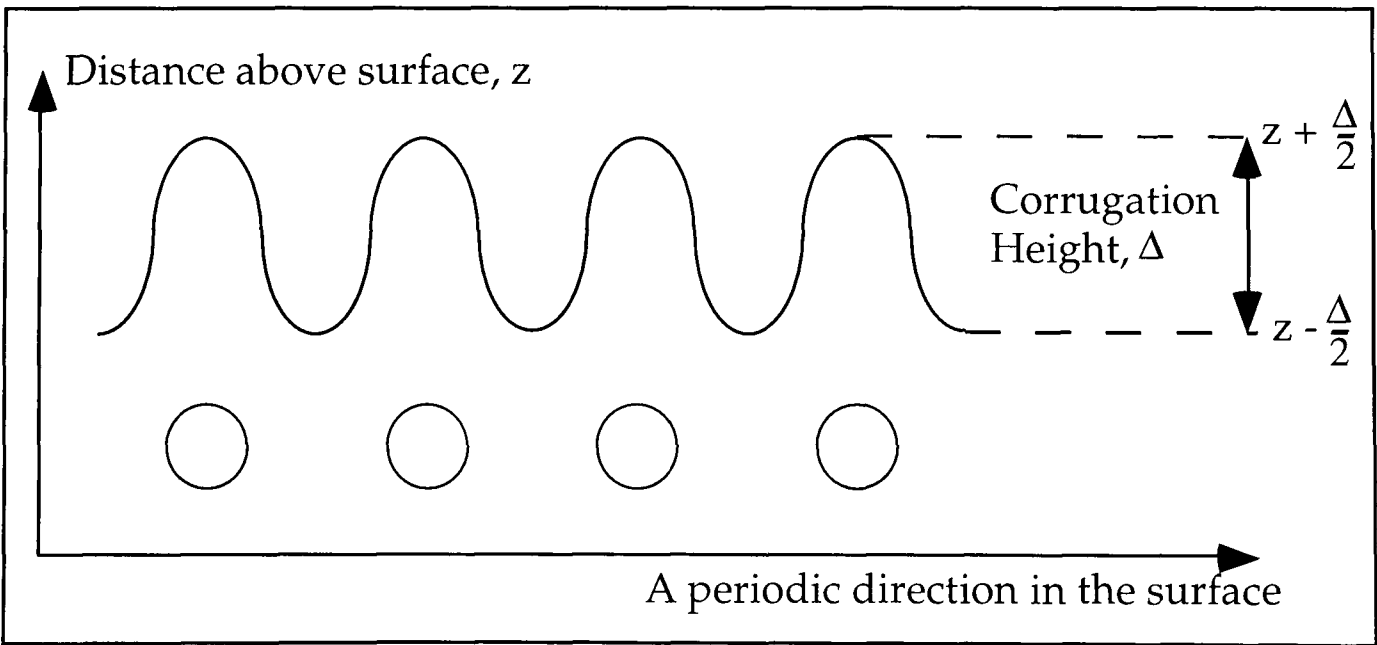


Figure 1.1: A schematic diagram illustrating the corrugation height, Δ , in the surface charge density, a mean distance, z , above a metal surface.

The theory of Tersoff and Hamann [1.12, 1.13] predicts STM corrugation heights for clean metallic surfaces under normal STM operating conditions of less than $0.1\text{\AA}$ (see **figure 1.2** below). However, helium atoms, are thought to approach the surface closer than an STM tip and it is therefore surprising to find experimental reports of STM corrugation heights in excess of $0.1\text{\AA}$ for many different low-index metallic crystal surfaces [1.18, 1.19, 1.20]. In one extreme example, the corrugations have been reported to vary from $0.1\text{-}0.8\text{\AA}$ over a $2\text{\AA}$ change in tip-sample separation [1.21]. Such experimental findings cannot be explained solely in terms of LDOS.

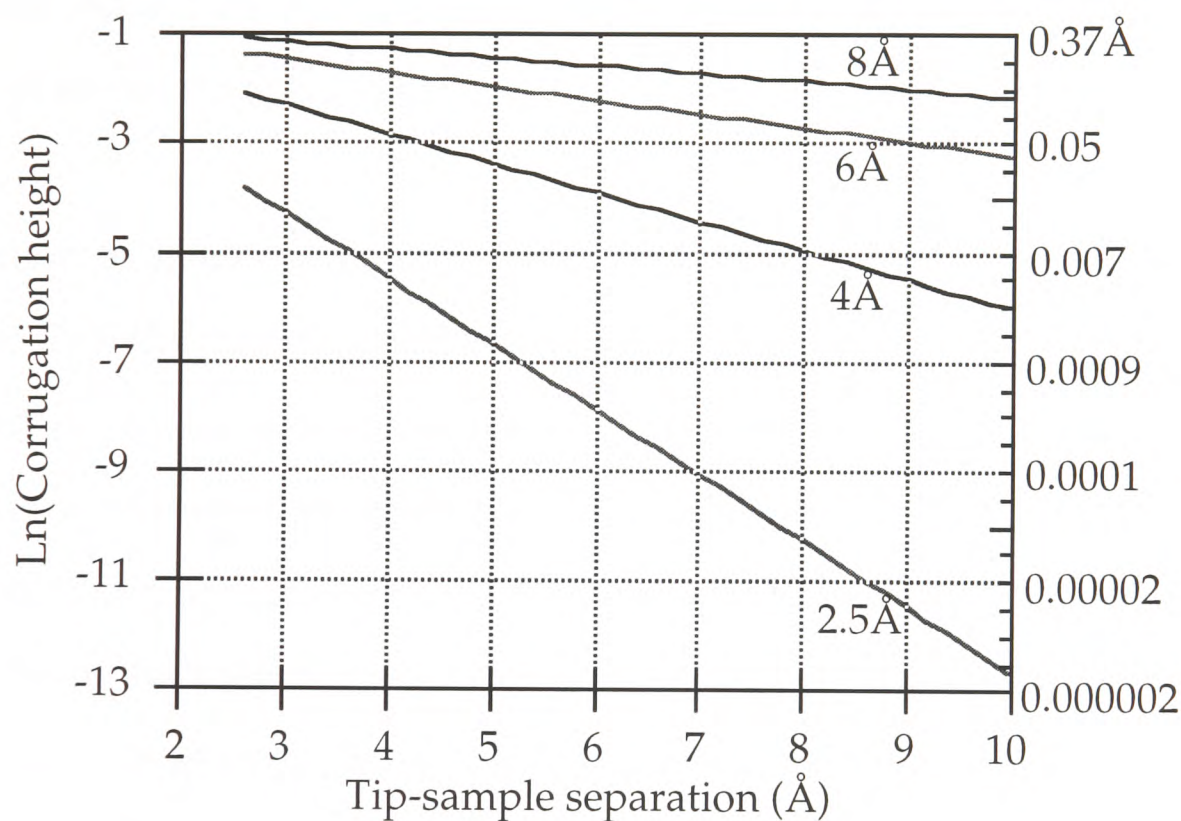


Figure 1.2: A graph illustrating the corrugation height theory of Tersoff and Hamann. This figure shows a plot of Ln(Corrugation Height) vs. tip-sample separation for a number of differently-spaced rows of atoms. The wavelength of these rows is indicated for each line of the graph.

Some workers [1.22-1.26] have explained their observations by proposing mechanical interactions between the tip and the sample. Good experimental evidence for such interactions can be found in the work of Dürig [1.24], who has deduced the existence of nano-Newton sized forces acting between an iridium tip and an iridium sample in the normal mode of STM imaging. In the special case of layered materials such as graphite, Pethica [1.25] has argued that

an image can be formed as the result of the tip becoming embedded in the uppermost layers of the substrate. The scanning needle shears the surface and this gives rise to a periodic fluctuation in the tunnel gap conductivity.

The effect of tip-surface forces is not always agreed upon. Ciraci et al. [1.26] have shown that site-dependent elastic strains resulting from tip-surface interactions can cause the measured corrugation to *decrease* with decreasing separation at small tip-sample separations ($<5\text{\AA}$). This result contradicts the experimental work of Winterlin et al. [1.21] who explain giant corrugations measured above the Al(111) surface in terms of an elastic deformation of a cluster of atoms at the tip apex.

In addition to giant corrugations and mechanical interactions, other findings indicate that the present level of understanding of STM is incomplete. In a study of silver adsorption on Si(111), Tromp et al. [1.27] have observed a dramatic asymmetry in filled-states images (atomic-scale resolution) and empty-states images (low resolution). These images were taken simultaneously and were tentatively explained by proposing the adsorption of a strongly electronegative atom at the tip. More recently, when investigating the clean Pt(25at%)Ni(75at%)(111) surface, Schmidt et al. [1.28] have been able to distinguish between the different chemical species of the alloy by observing a $0.3\text{\AA}$ difference in the corrugation heights of Pt (low corrugation) and Ni (high corrugation) when imaging the surface using small values for the tunnel gap resistance ($\sim 300\text{k}\Omega$). Ruan et al. [1.29] have noted that by reversibly manipulating the chemical species at the apex of the tip, either the metallic or non-metallic species in the Cu(110)-(2x1)O reconstruction is highlighted in the image. This effect has also been reported for the equivalent nickel reconstruction.

In a study of the deposition of gold on Ni(110), Pleth Nielsen et al. [1.30] have shown that at small gold coverages, the clean metal surface becomes populated with shallow dimer holes of depth $0.25\text{\AA}$ located at the nickel atom lattice sites. The number of holes increases linearly with increasing gold exposure. These holes are sometimes spontaneously transformed into small protrusions (two protrusions per dimer hole), from which it can be inferred that the holes are actually gold atoms substituted into the first nickel layer. In an investigation of the growth of iron layers on Cu(100) [1.31], patches of iron on a single terrace are usually seen as small monolayer islands $20\text{-}40\text{\AA}$ in diameter with an inter-island spacing $80\text{\AA}$; occasionally such patches are seen as $\sim 2\text{\AA}$ deep depressions within the surface. Such contrast reversals are not just limited to multi-element systems and have also been reported for the clean Au(111)- $(22\times\sqrt{3})$ reconstructed surface [1.32]. A contrast reversal was observed in this work when imaging a Cu(111) surface, see **figure 1.3** below.

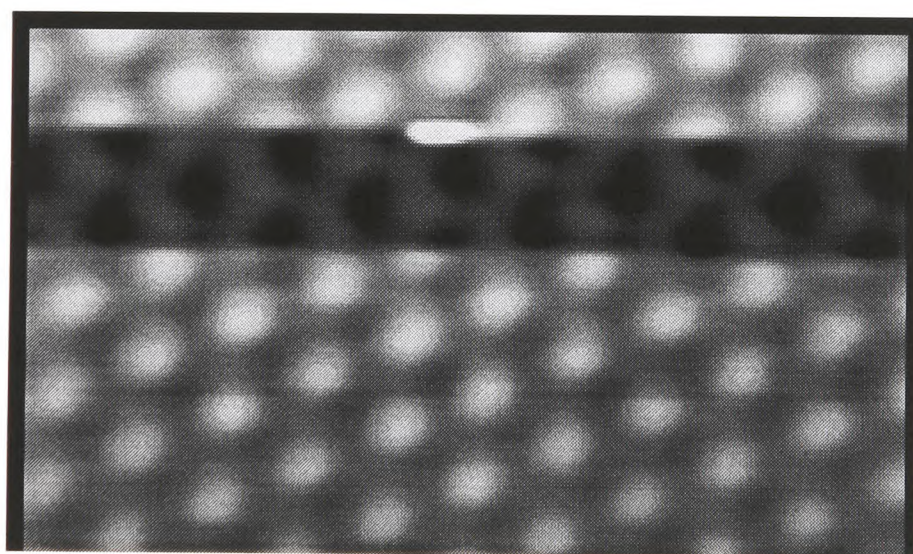


Figure 1.3: A $30\times 18\text{\AA}$ (vertical scale $0.6\text{\AA}$) STM image taken by the author showing a contrast reversal for the Cu(111) surface. The tunnelling parameters used were $I = 9.4\text{nA}$, $V = -7\text{mV}$.

The key point arising from these observations is that while the surface remains unaltered, the tip undergoes some as yet unknown metamorphosis. It was with such occurrences in mind that Sautet et al. [1.33] embarked upon a series of calculations to describe the imaging behaviour of metal + adsorbate systems. This work has concentrated on a limited class of systems in which the tip is

made of the same metal as the substrate. However, these calculations correctly predict features in the topographic image, such as the shape of adsorbates as a function of tip geometry and chemistry. Interference effects between the tip and surface wavefunctions have also been shown to play an important role.

1.3 Motivation for this study:

In response to the observations of bizarre imaging phenomena, this Thesis attempts to reverse the current trends in Scanning Tunnelling Microscopy, and regards STM itself as the system under investigation. Quantitative modelling of STM is a difficult problem, for it relies upon the knowledge of parameters such as the tip geometry and chemistry as well as the tip-sample separation. These factors are not usually known experimentally, but nevertheless have a direct effect on the final image. This lack of knowledge also makes it difficult to perform well-characterised experiments with the aim of understanding STM. However, I hope to demonstrate that some progress in this direction is possible.

As Chapter Four will show, even a basic parameter such as the tunnel barrier height, ϕ , is not always well understood. This parameter plays an important role in determining the image, as “barrier-height” images taken simultaneously with topographic images have shown [1.34]. The normal method to measure the tunnel barrier height is to oscillate the tip-sample separation and use the resulting changes in tunnel current to form an approximation for the derivative $\frac{\partial \text{Ln}(I)}{\partial s}$, which is proportional to the square root of the tunnel barrier height [1.35]. In practice, such measurements are difficult. At low oscillation frequencies, thermal drift can be a problem when comparing topographic and barrier-height images. At higher frequencies, calibration of the piezo motion is complex as it becomes a non-linear function of the bias voltage applied to the z-

piezo element. Any errors in $\frac{\partial \text{Ln}(I)}{\partial s}$ are especially severe as they are doubled in the value calculated for the barrier height.

In this Thesis, a new method of deducing the tunnel barrier height is presented. The basic technique employed to calculate this quantity is to measure the decay in corrugation heights of topographic images as the tip-sample separation is increased. In practice, the tip-sample separation can only be varied by changing the tunnel gap conductance, σ . Thus a sequence of images are taken using the same tip, each image taken at a larger value of the tunnel conductance. From systematic measurements of corrugation heights, Δ , along the principal directions of the topographic images a $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot for each data set can be made. The linear region of such a graph gives a direct measure of the tunnel barrier height. By making use of the constant current mode of imaging, uncertainties in the z-calibration (as deduced from measurements of step heights) are minimised.

The imaging behaviour of semiconductors in STM can be complex and strongly dependent upon the tunnelling parameters selected [1.2]. Moreover, the LDOS of such surfaces often varies rapidly between different sites in the surface. When all these factors are combined, it becomes difficult to model semiconductor surfaces in order to establish useful facts such as the tunnel current-distance relationship. Therefore, in this thesis, the experimental work experimental work has concentrated on unreconstructed metallic surfaces. Metals, unlike semiconductors, are especially useful for quantitative investigations, because they have a high LDOS at the Fermi level. Moreover, their STM images do not change very much as a function of the imaging parameters selected, except for the change in corrugation heights, which is a product of the tip-sample separation anyway.

The results presented here show that the tunnel barrier height is substantially lower than the surface workfunction when imaging using normal tunnelling conditions. The distribution of corrugation heights measured for the Cu(100) surface show that independent variations of the tip geometry and chemistry are likely in practice, leading to difficulties in data interpretation when using simple models.

Somewhat surprisingly, this work indicates that different tip species give rise to only small changes in the deduced tunnel barrier height ($\sim 0.5\text{eV}$) above clean metal surfaces. Small changes ($\sim 0.2\text{eV}$) in the local tunnel barrier height have also been found in preliminary studies of metal surfaces modified by small numbers of halogen atoms. It is likely that the tip-sample separation is a factor at least as important as the tunnel junction chemistry in determining the value measured for the tunnel barrier height. Variations in the tunnel barrier height measured as a function of the tunnel gap conductance have been explained using a model adapted from the apparent barrier height theory of Lang [1.36].

At large values of the tunnel gap conductance ($\sim 1\mu\text{S}$), a decrease in the corrugation height with increasing tunnel gap conductance has been observed. This effect has been quantitatively modelled using a Molecular Dynamics simulation which describes a site-dependent attractive-interaction on a sub nano-Newton scale acting between the tip and the surface. This has the effect of causing the change in true tip-sample separation to outstrip the extension of the z-piezo element leading to the measurement of an apparently reduced corrugation height. It is shown how this corrugation reduction leads to an estimate of the absolute tip-sample separation without recourse to the tunnelling parameters.

The material presented in the remainder of this Thesis is organised as follows: In Chapter Two, some of the basic concepts behind STM are introduced. This Chapter has a literature review which discusses the imaging behaviour of clean metal surfaces as well as metal + low-coverage single-atom adsorbate systems. Chapter Three provides a description of the surface-science equipment used to obtain the experimental data presented in this Thesis. A new method of deducing the tunnel barrier height is presented in Chapter Four which is based upon a corrugation height measurement and interpreted using a simple model. The implications for the nature of the tip apex are discussed on the basis of the results obtained. Analysis of the tunnel barrier height is continued in Chapter Five using a more complete model. The conditions for which the corrugation method of calculating the tunnel barrier height is strictly valid are discussed and illustrated experimentally. The roll-off in the corrugation heights observed at large values of the tunnel gap conductance is the subject of Chapter Six and is investigated using a Molecular Dynamics simulation of an STM tip approaching a Cu(100) surface. In Chapter Seven, the tunnel barrier height measurements are extended to the case of a surface modified by a small number of single atom halogen adsorbates. Tip-induced adatom manipulation is also demonstrated.

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Chapter 2

Scanning Tunnelling Microscopy

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2.1 Introduction:

In this Chapter, a broad overview of Scanning Tunnelling Microscopy (STM) is presented. The discussion here is aimed in particular at new workers in this field. In Section 2.2, STM is set in an historical context and is compared and contrasted with other microscopic techniques which similarly make use of quantum tunnelling or achieve a high level of lateral resolution. After an outline of the basic STM ideas in Section 2.3, the remainder of this Chapter is devoted to a literature survey. The review is divided into two sections and concentrates upon the imaging of both unreconstructed and reconstructed clean metal surfaces (Section 2.4), and the imaging of simple metal + adsorbate systems (Section 2.5). A discussion centred on the tunnel junction can be found in Sections 4.2 and 4.3 of Chapter Four.

2.2 Tunnelling and the Basic Principles of Operation of STM:

STM makes use of a bizarre feature of quantum mechanics - the tunnel effect. This phenomenon has been shown to be important in processes such as alpha-decay of proton-rich nuclei and the auto-ionisation of hydrogen in a static electric-field [2.1]. The basic idea behind electron tunnelling stems

from the fact that by assigning wave-like properties to an electron and using the Schrödinger equation, it can be shown that the electron has a finite probability of entering a region of space to which it is classically forbidden. Provided this region is sufficiently narrow ($\sim 5\text{-}10\text{\AA}$), the electron wavefunction can penetrate through such a barrier, emerging with a measurable amplitude, see **figure 2.1** below.

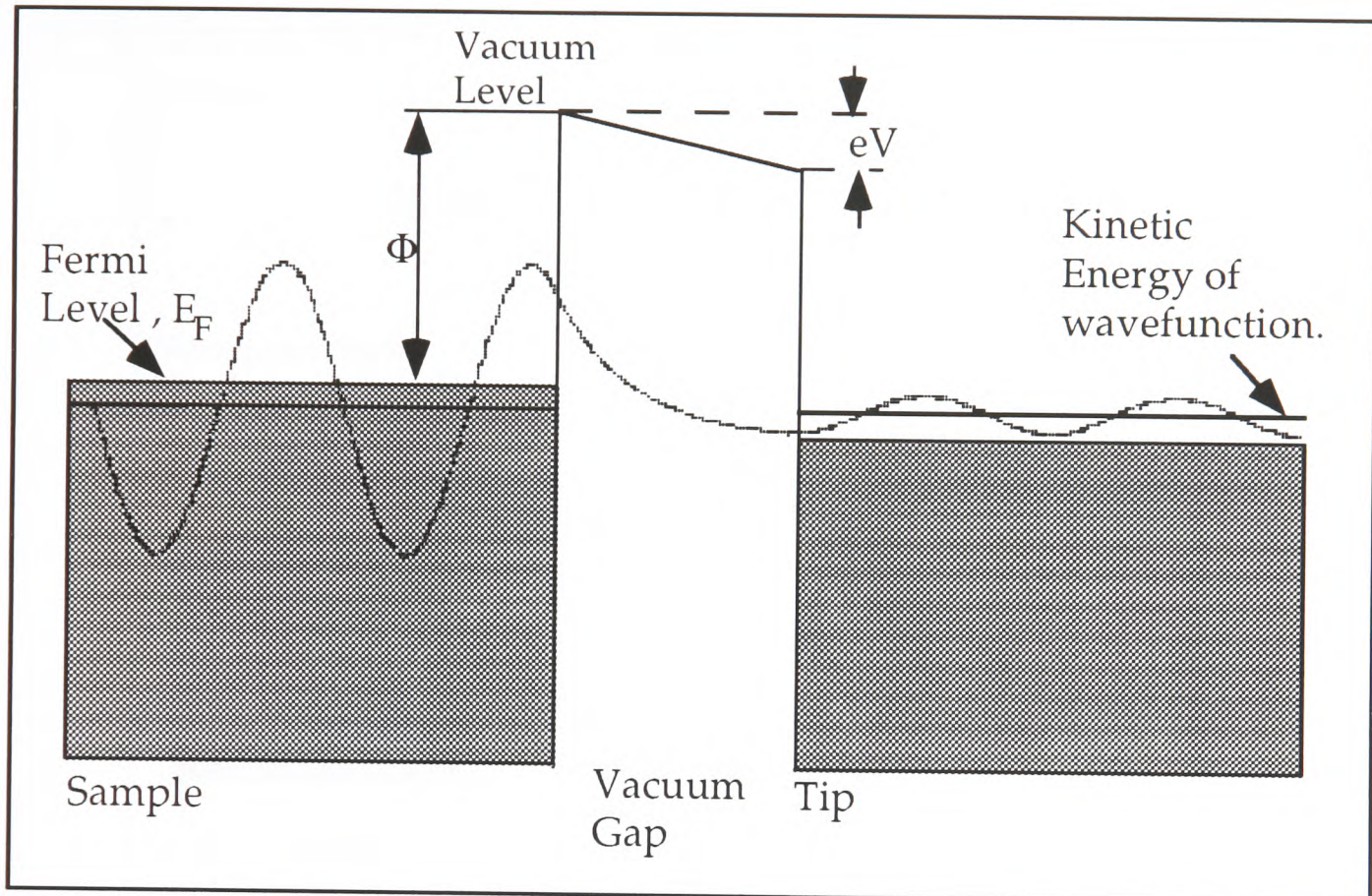


Figure 2.1: A schematic diagram showing a wavefunction tunnelling between two metallic electrodes (annotated here as 'Sample' and 'Tip') separated by a vacuum gap. Φ is the workfunction of the electrodes and V is the applied bias potential.

2.2.1 Historical Review:

The application of tunnelling to microscopy is not a new idea. Field Emission, which was discovered a few years after the First World War and later explained by Fowler and Nordheim [2.2], was developed into a microscopic technique in the 1930s by Müller. Field-Emission Microscopy (FEM) involves the application of a large negative potential (several thousand Volts) to a metallic sample in the form of a needle which has a hemispherical cap of approximate radius of curvature $100\text{\AA}$.

Above sharply curved regions of the specimen, the electric-field may reach values of $\sim 3\text{-}7 \times 10^9 \text{Vm}^{-1}$. Electrons can then tunnel through a surface potential barrier which arises from the combination of the potential applied to the sample and the image potential, see **figure 2.2** below. Emergent electrons are projected on to an earthed fluorescent screen surrounding the specimen so as to build up an image which corresponds to the underlying crystallography of the sample.

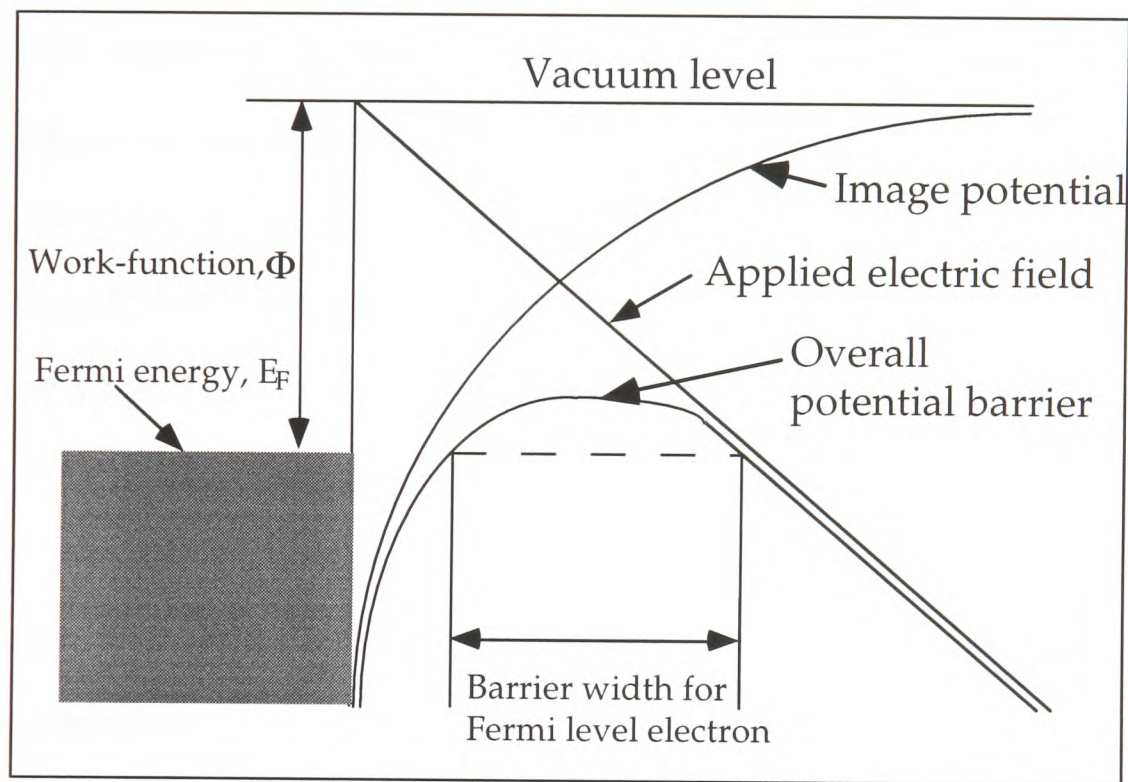


Figure 2.2: A schematic diagram showing how a large electric-field combines with the image potential to form a tunnel barrier for field-emitted electrons.

In 1971, Young et al. [2.3, 2.4] studied surfaces using field-emitted electrons from a tungsten needle mounted on a piezoelectric scanner which was positioned $1000\text{\AA}$ above a substrate. Typical resolution achieved with the *Topografiner* was $4000\text{\AA}$ in the plane of the surface and $30\text{\AA}$ perpendicular to it. By positioning the needle very close to the surface and varying the bias voltage from 8V down to a few milli- Volts, they were able to observe the transition between field-emission and metal-vacuum-metal (MVM) tunnelling. The significance of this study was that it suggested the possibility of MVM tunnelling combined with scanning facilities. Low-voltage experiments were plagued by both mechanical and thermal vibrations, and it was not until a decade later that Binnig and co-workers at IBM, Zürich

[2.5] overcame this problem by developing an elaborate method of magnetic-levitation using superconductors working at liquid helium temperatures.

Field-Ion Microscopy [2.6] (which was developed from FEM) is also a technique which can resolve detail on an atomic-scale. Again the sample takes the form of a metallic needle with a hemispherical cap of radius $\sim 100\text{\AA}$. The specimen is kept at cryogenic temperatures ($< 77\text{K}$) and raised to a high positive potential (3-30kV). A low pressure (10^{-5} mBar) of an inert gas, usually helium, is admitted to the microscope chamber. When the potential on the specimen is increased further, gas atoms in the vicinity of the specimen apex are polarised by the strong electric-field and are drawn towards the specimen surface. Field-ionisation of the gas atoms is caused by electrons tunnelling through the field-adsorbed gas atoms and into the metal. The positively charged image gas ions are then radially repelled from the specimen and strike a fluorescent screen giving rise to a field-ion image, see **figure 2.3** below.

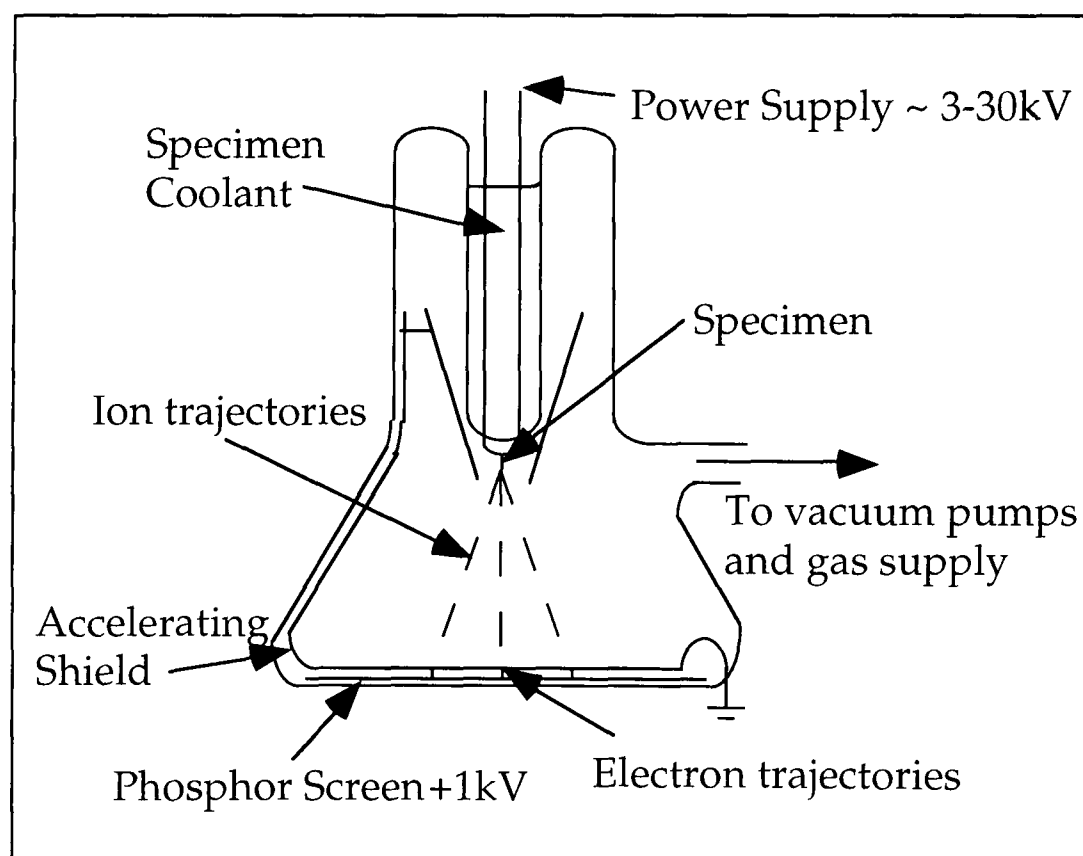


Figure 2.3: A schematic diagram showing the principal features of a Field-Ion Microscope.

Tsong [2.7] has compared and contrasted Field-Ion Microscopy with Scanning Tunnelling Microscopy. The main differences are summarised below in the table of **figure 2.4** below:

Characteristic	STM	FIM
Sample size and shape	No limitation in principle to size and shape of sample. However, it should basically be flat.	Sample limited to apex of needle (imaging area $<80\text{\AA}^2$)
Temperature of operation	Can be performed for temperatures between a few milli Kelvin up to 1200K.	Needs to operate at either liquid nitrogen or liquid helium temperatures.
Surfaces studied	Surfaces examined are basically thermal equilibrium structures.	Surfaces prepared reflect the field evaporation process.
External conditions required	Experiment can be performed in a variety of media: e.g. air, water, gaseous media, UHV.	Experiment must be performed in vacuo.
Chemical Information	Little chemical information available from topographic images; atoms in compound semiconductors can usually be distinguished.	By combining with a time-of-flight atom probe, FIM can provide detailed information about chemical species on a surface.

Figure 2.4: A table comparing and contrasting Scanning Tunnelling Microscopy and Field-Ion Microscopy.

2.2.2 Basic Ideas of Scanning Tunnelling Microscopy:

STM itself comprises an electrically conducting substrate, the sample, and an atomically sharp metallic needle, the tip, made of tungsten or sometimes iridium. If the tip is positioned in close proximity to the sample (separation $\sim 5\text{-}10\text{\AA}$), the wavefunctions in both electrodes begin to overlap. By applying a small bias voltage, V , between the two electrodes (typically $\pm 1\text{mV}$ - $\pm 3\text{V}$), the two Fermi levels are offset by an energy, eV . This enables electrons occupying filled states in one electrode to tunnel into unoccupied states in the other electrode, see **figure 2.5** below. A current (typically $1\text{-}20\text{ nA}$) then flows across the junction, from which it is possible to deduce the electronic structure and geometric topography of the sample at that point. By scanning the tip over the sample, it is possible to gather surface data over a large area (relative to the lateral resolution of the STM) of up to $5000 \times 5000\text{\AA}$.

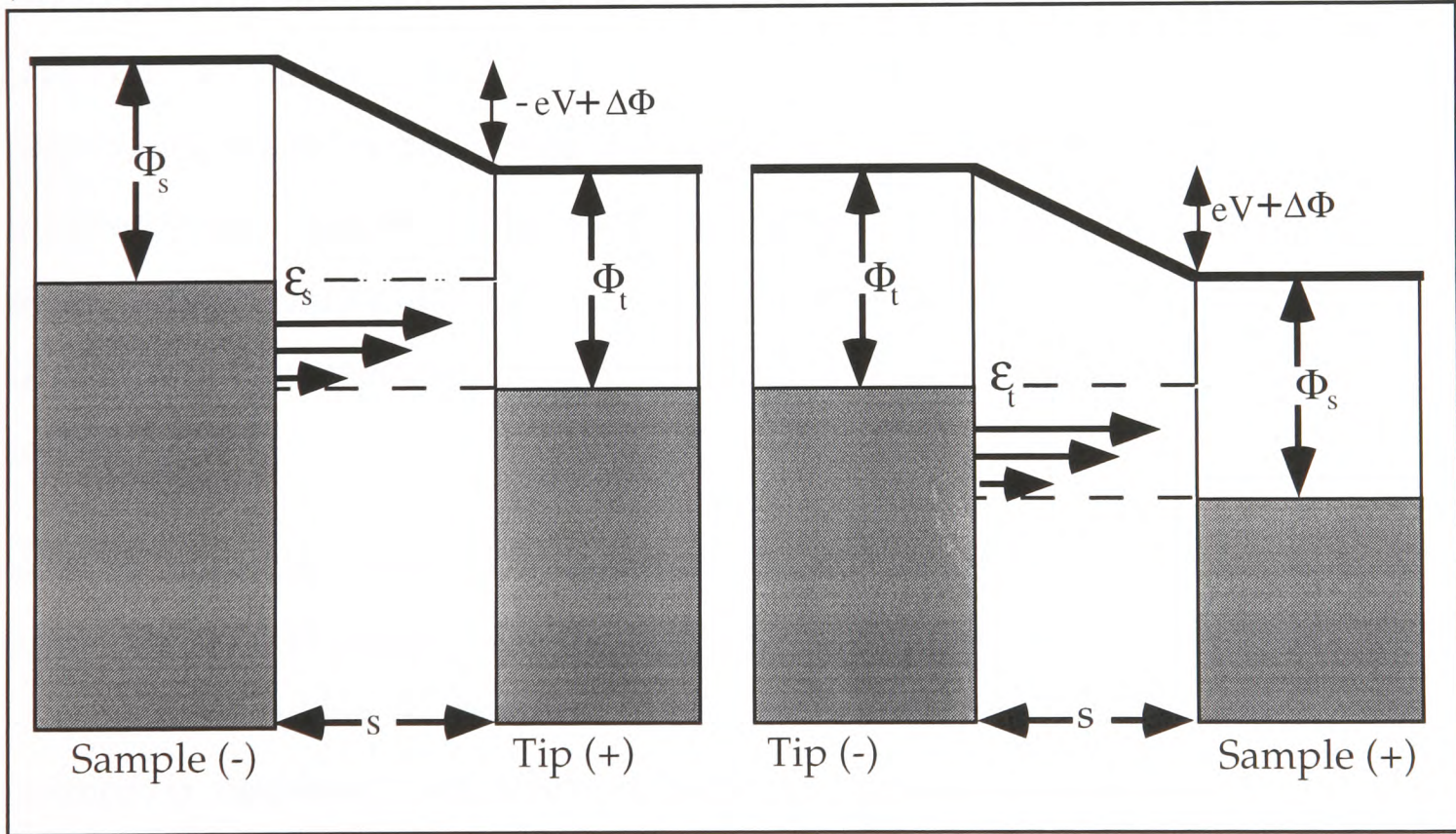


Figure 2.5: Two schematic diagrams showing electron tunnelling out of and into a sample. In this figure, the use of a positive sample bias, V , corresponds to the imaging of the empty sample states and the use of a negative sample bias to the imaging of filled sample states. s is the tip-sample separation; $\Phi_{s,t}$ are the workfunctions, $\epsilon_{s,t}$ are the Fermi levels. The arrows qualitatively show the probability of electrons tunnelling through the tunnel gap.

Good evidence for the fact that electronic structure can dominate STM images comes from studies of compound semiconductors. Feenstra et al. [2.8] simultaneously imaged the GaAs(110) surface using bias voltages of +1.9V and -1.9V. The former image samples the semiconductor's empty states; the latter image shows the semiconductor's filled states. A superimposition of these two images shows a spatial offset in the respective positions of the maxima and minima in each image, in this case due to the fact that the occupied states are mostly located on the arsenic atoms while the unoccupied states are mostly on the gallium atoms.

The scanning tip is mounted on three mutually perpendicular voltage-driven piezoelectric transducers which control its motion over the surface. Throughout this work, the convention is adopted that the x-and y-piezo elements are aligned parallel to the surface, while the z-piezo is oriented perpendicular to the surface. In order to scan the tip over a region of interest, a voltage applied to the x-piezo causes the tip to move some pre-determined distance along this direction. At the end of the line scan, the tip returns to the start of the line-scan and a voltage ramp is applied to the y-piezo, which causes the tip to be displaced slightly in this direction. This sequence is then repeated so that an image is taken as a series of parallel line scans.

STM is normally used in a constant-current imaging mode. In each line scan, the vertical position of the tip is controlled by the z-piezo which itself is contained within a feedback loop, see **figure 2.6** overleaf. The tunnel current is amplified and then compared against a reference value. The difference between these terms is used to determine the voltage applied to the z-piezo, so that the tunnel current remains at a constant value. The final image is a plot of tip position above the surface as a function of lateral surface position, $z(x,y)$, and is typically displayed as a series of contours using a grey scale shading (black usually corresponding to the lower parts of the image and white to higher parts).

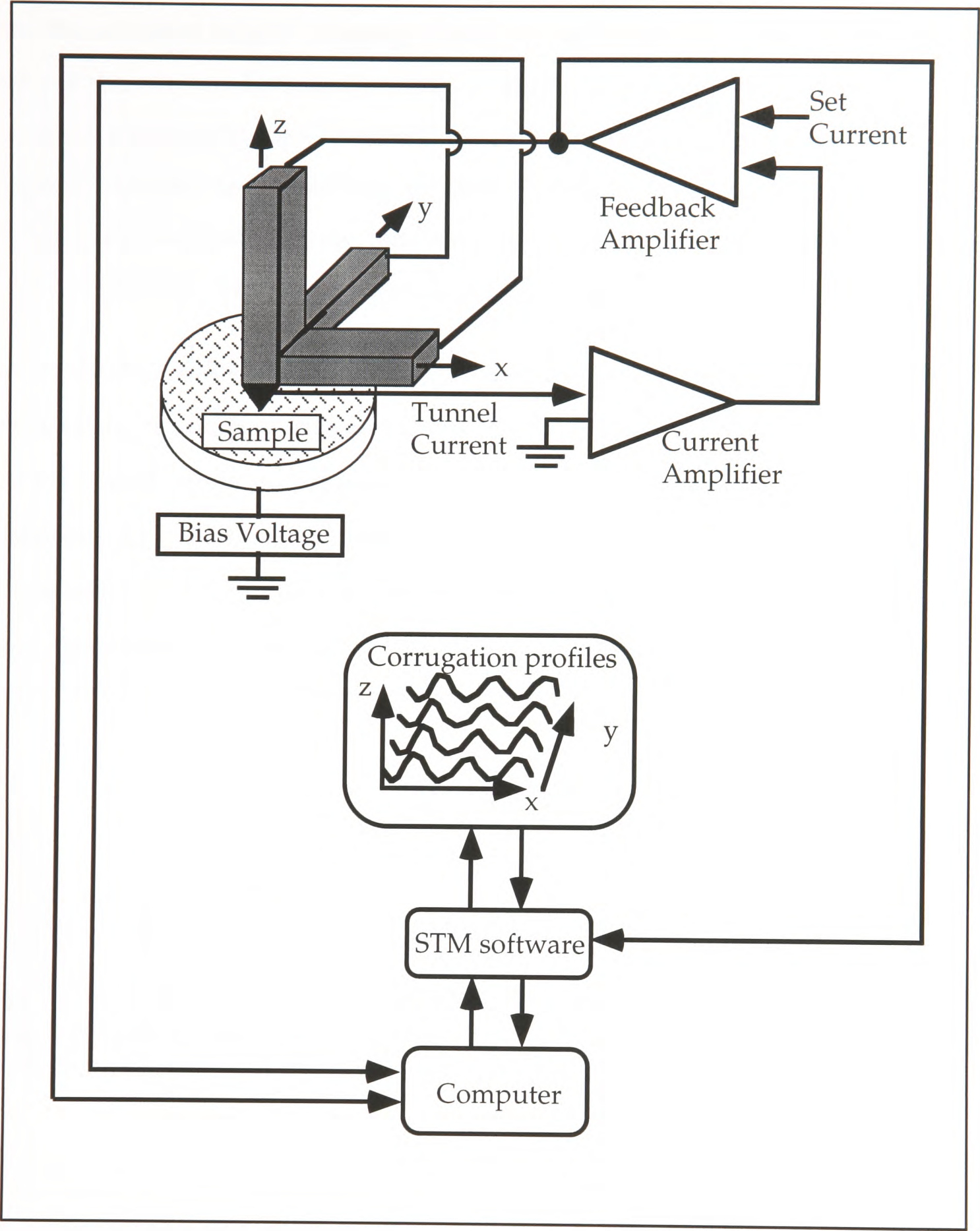


Figure 2.6: A schematic diagram showing the STM constant current mode of operation.

In the constant-height imaging mode, the tip is held at a constant distance above the surface. During scanning, changes in current due to variations in surface topography are detected, so that the final image is a plot of the tunnel current as a function of lateral surface position, $I(x,y)$. This data acquisition method is rarely used except in cases where the sample is known to be atomically-flat over a large area.

A qualitative understanding of STM can be obtained from a simple model of tunnelling published 20 years prior to the invention of STM. Using the WKB mean barrier approximation [2.1], Simmons [2.9, 2.10] derived a one-dimensional relationship relating the tunnel current I , and the electrode separation, s , for tunnelling between two flat, parallel free-electron metals, see equation (2.1).

$$I \propto \frac{\phi_M^{1/2} V}{s} \exp(-A \phi_M^{1/2} s) \quad (2.1)$$

where $A = \frac{4\pi}{h} (2m_e)^{1/2} = 1.025 \text{ eV}^{-1/2} \text{ \AA}^{-1}$

ϕ_M is the mean tunnel barrier height between tip and sample in the tunnel gap (typically 2.5-4eV; $1\text{eV} = 1.6 \times 10^{-19} \text{ J}$), V is the applied bias voltage, h is Planck's constant and m_e is the mass of an electron.

It is the exponential dependence of the tunnel current upon the tip-sample separation which is responsible for the high vertical resolution ($\sim 0.01 \text{ \AA}$) of STM. Assuming a tunnel barrier height of 4eV, then a one order of magnitude change in the tunnel current changes the tip-sample separation by about $1 \text{ \AA}$.

2.3 STM Imaging of Clean Metallic Surfaces:

The LDOS theory of Tersoff and Hamann [2.11, 2.12] (see the discussion of sections 1.1 and 2.3.1) predicted an lateral resolution of 5-6Å when imaging metallic surfaces, and so resolution of individual atoms within the surface was not expected. There have subsequently been numerous reports of atomic-scale resolution for many different low-index metallic faces, demonstrating that this phenomenon is not restricted to the occasional freak surface. The reader will no doubt be relieved to learn that such studies have confirmed the predictions of simple "billiard-ball" stacking models, when applied to the crystallographic structure of unreconstructed metallic surfaces, see **figure 2.7** overleaf.

Atomic-scale resolution of a metallic surface - a thin film of Au(111) prepared by epitaxial deposition of gold onto a cleaved mica surface was first reported by Hallmark et al. [2.13]. In this study, corrugation heights measured using the constant-current mode of STM varied between 0.05 and 0.5Å; and specifically, the corrugation was found to be 0.3Å at a tip bias of +30mV and $I = 3\text{nA}$. A surface state 0.4eV below the Fermi level seen in both tunnelling spectroscopy and photoemission data [2.14] was proposed to be responsible for these corrugation heights.

A most important study is that of Winterlin et al. [2.15, 2.16] who imaged Al(111). By varying the tunnel current in the range 1-40nA ($V=-110\text{mV}$), the exponential decay of the corrugation in the charge density above the surface was verified. Corrugation heights ranging from 0.8Å down to 0.1Å were measured over a 2Å change in tip-sample separation. By varying the bias voltage in the range $-1\text{V} < \text{Bias Voltage} < 1\text{V}$, while keeping the tip-sample separation constant, the possibility of surface states being responsible for the imaging mechanism was ruled out as there was no change in corrugation height. This also demonstrates that there was no electric-field induced distortion of the electronic surface.

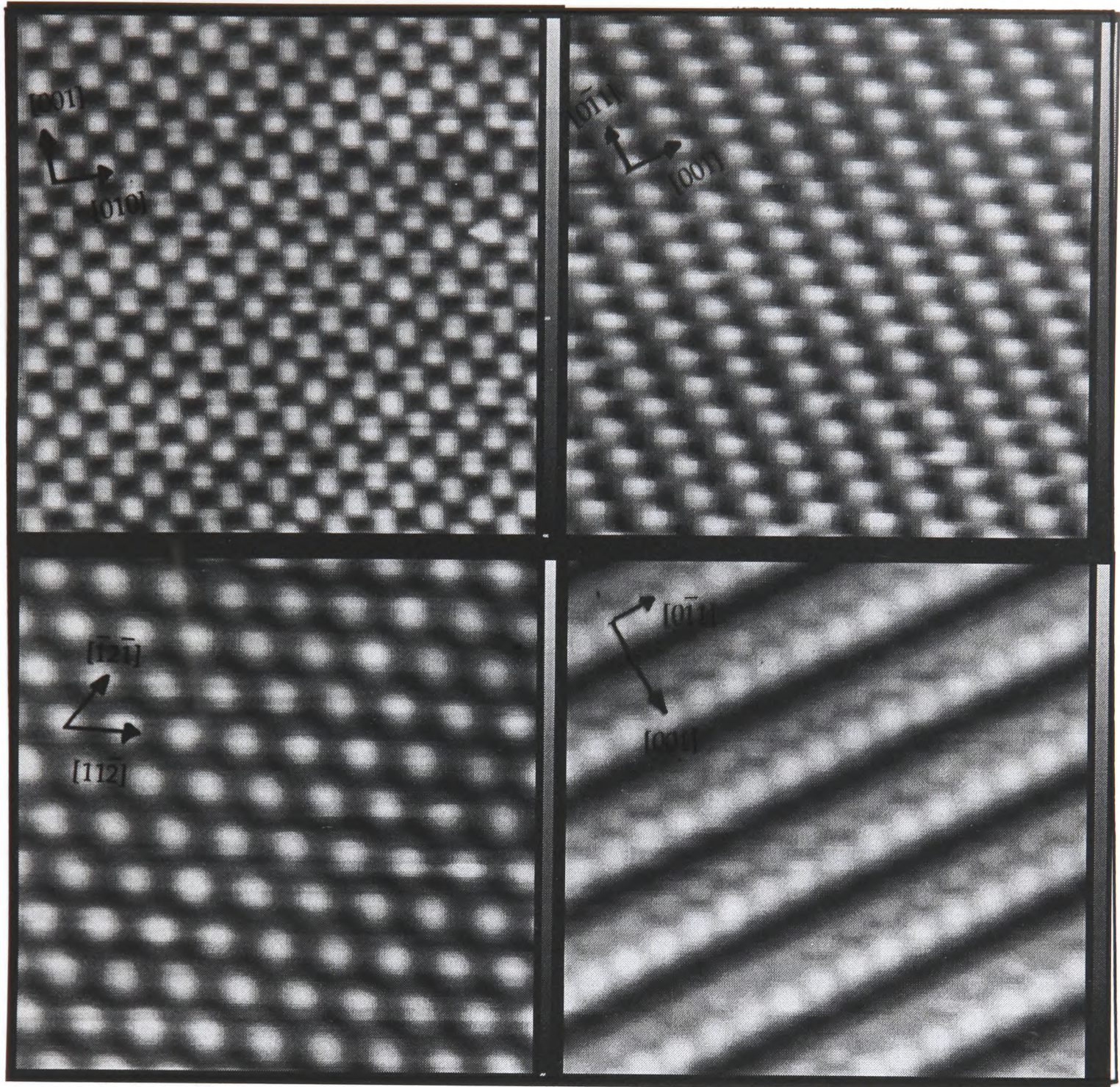


Figure 2.7: A selection of STM images showing the different crystallographic surfaces of copper.

- (i) Top left corner, $50 \times 50 \text{ \AA}$ (vertical scale $0.25 \text{ \AA}$) - Cu(100), tunnelling parameters $I = 7.6 \text{ nA}$, $V = -5 \text{ mV}$.
- (ii) Top right hand corner, $50 \times 50 \text{ \AA}$ (vertical scale $0.6 \text{ \AA}$) - Cu(110), tunnelling parameters $I = 1.8 \text{ nA}$, $V = -23 \text{ mV}$.
- (iii) Bottom left hand corner, $30 \times 30 \text{ \AA}$ (vertical scale $0.4 \text{ \AA}$) - Cu(111), tunnelling parameters $I = 11.1 \text{ nA}$, $V = -20 \text{ mV}$.
- (iv) Bottom right hand corner, $50 \times 50 \text{ \AA}$ (vertical scale $0.7 \text{ \AA}$) - Au(110) (1x2) reconstruction, tunnelling parameters $I = 19.3 \text{ nA}$, $V = +8 \text{ mV}$.

The same authors [2.15, 2.16] found that a 'tip zap' (that is to say applying a large bias voltage $\sim -7.5\text{V}$ to the sample while it is scanning over a region of the surface for a few line scans) can reproducibly transform the tip in to a high resolution mode. The tip responds to this voltage pulse by withdrawing from the sample surface by about $30\text{\AA}$. When the bias is restored to its original value, the tip does not return to its former position, but is displaced from it by about $25\text{\AA}$ and so has *elongated* as a result of this process. This fact suggests that a field evaporation process such as that exploited by Fink [2.17] cannot be responsible for this type of tip reconfiguration. The lengthening of the tip is either the result of restructuring of the tip itself or due to the transfer of material from sample. This sharpening mechanism has been applied to tips when imaging a number of different close-packed metal surfaces and so this phenomenon is not surface chemistry specific. It is thus thought that diffusing tungsten atoms on the surface of the tip are polarised by the electric-field between the tip and the sample, and are attracted to the tip-apex where the electric-field is strongest with the resultant formation of a small cluster of atoms at the apex with a protruding tip orbital [2.18], see **figure 2.8** overleaf.

Samsavar et al. [2.19] have reported observing an emergent dislocation on Cu(111), but did not discuss details of their imaging. Berndt et al. [2.20] have investigated the tunnelling characteristics necessary to produce atomic-scale resolution of close-packed metal surfaces. On both Cu(111) and Ag(111), corrugation heights of $0.05\text{-}0.3\text{\AA}$ were measured over a wide range of bias voltage (100mV - 1.4V). However no reproducible relationship between bias voltage and corrugation height could be established. This shows that the characteristics of the tip can vary significantly despite the use of identical tunnelling parameters.

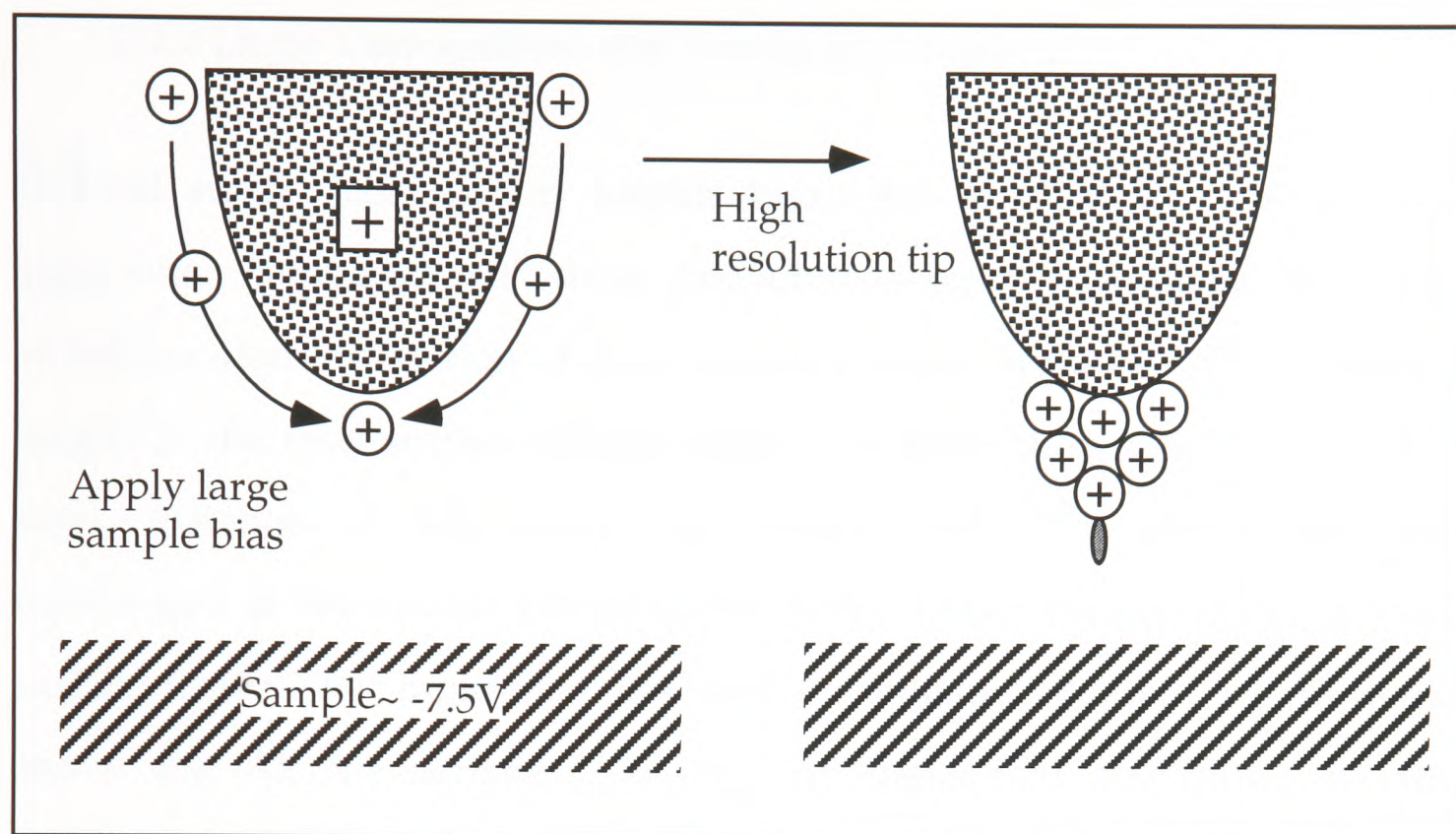


Figure 2.8: A schematic diagram showing the possible mechanism for the formation of a high-resolution tip as a result of the application of a large potential bias while scanning. Atoms on the surface of the tip walk to the apex in response to the high electric field (electro-migration) leading to the formation of a cluster with a dangling orbital in a favourable orientation for imaging the surface.

Ni(100) has also been used to investigate corrugation heights. Alan Partridge et al. [2.21] have measured heights of $0.12\text{\AA}$ and $0.08\text{\AA}$ along the [001] and $[0\bar{1}1]$ directions respectively. These values are a little larger than those measured by Kopatski and Behm [2.22] on the same surface (Corrugation heights $< 0.05\text{\AA}$). This discrepancy is at least partly due to the different tunnelling parameters used in the two experiments. A magnetic surface state at the surface Brillouin zone boundary has been identified just below the Fermi level [2.23]. This may be the source of the 'enhanced' corrugation heights as it occurs in the same energy region as the reported optimum imaging conditions ($I = 2\text{nA}$ $V = -15\text{mV}$).

Other unreconstructed metallic surfaces which have been imaged with atomic-scale resolution include Ag(110) [2.24], Cu(111) [2.25], Cu(110) [2.26], Cu(100) [2.27], Ni(111) [2.28], Ni(110) [2.29], Pt(111) [2.30], Ru(0001) [2.31], $\text{Pt}_{25}\text{Ni}_{75}$ [2.32] and $\text{Ni}_{50}\text{Al}_{50}(111)$ [2.33].

2.3.1 Large Corrugations and Anomalous Behaviour:

Metal surface corrugation heights measured by STM are unexpectedly large when compared with those measured by other techniques. In studies of helium-atom diffraction of close-packed metallic surfaces, the corrugation height in the total surface charge density has been shown to be $\sim 0.05\text{\AA}$ at small distances ($\sim 2\text{\AA}$) above the surface [2.34]. This result has been reproduced in theoretical calculations of the charge density above a metal surface [2.35, 2.36]. Inglesfield has also investigated the surface potential above the Al(100) surface [2.36], but site-dependent variations in this quantity only occur up to $0.75\text{\AA}$ above the geometrical surface, and it is most unlikely that an STM tip can approach this close to a surface.

The most likely explanation for the measurement of large corrugation heights above close-packed metal surfaces, has been provided in a series of papers by Chen [2.38-2.40]. The approach used here was essentially a fuller version of the method of Tersoff and Hamann [2.11, 2.12]. Using the transfer Hamiltonian method of Bardeen [2.37], they showed in the limit of zero temperature and small bias-voltage, that the tunnel current, I , is proportional to the sum of the squares of the tunnel matrix elements for the system. Each matrix element, $M_{\mu\nu}$, is a measure of the tunnelling probability between an occupied state μ , located predominantly on one electrode, and an unoccupied state ν , located predominantly on the second electrode.

Tersoff and Hamann only considered tunnelling events involving an s-state located at the centre of curvature of the macroscopic tip, and this leads to the well known LDOS result. Chen [2.38] has extended the analysis to take account of tunnelling events involving p- and d- tip orbitals. Using the delightfully simple derivative-rule, Chen has shown that the tunnel-matrix element is given up to a numeric factor by the amplitude of the sample wavefunction at the centre of curvature of the tip for a tunnelling event

involving an s- tip-state. For tunnelling into a p- tip-state, the matrix element is proportional to a similarly spatially-evaluated first-order partial derivative of the sample wavefunction, and proportional to a second order partial derivative (or linear combinations thereof) for tunnelling involving a d- tip-state. By making use of the condition of constant current, Chen [2.39] has demonstrated that the expected corrugation height for tunnelling between the surface and a d_{z^2} tip-state directed towards the sample surface is about one order of magnitude greater than that predicted from the s-wave model and is in good agreement with the experimental data of Winterlin et al. [2.15, 2.16].

Using the reciprocity principle [2.40], whereby the image remains unaltered by the *conceptual* exchange of tip and sample wavefunctions, this theory is also capable of explaining spontaneous corrugation reversals observed by Barth et al. [2.41] on Au(111). Tunnelling from this surface is dominated by s-states near the Fermi level and the high lateral-resolution images obtained suggests that the tip has a d_{z^2} state at its apex. From the reciprocity principle, we know the STM image remains unaltered as a result of the exchange of the orbitals involved in the tunnel process. It is recalled by returning to the s-wave model of Tersoff and Hamann [2.11, 2.12], the final image is independent of the properties of the tip. Thus the Au(111) image may be thought of as the tip LDOS measured at the centre of every gold atom. In addition to the d_{z^2} orbital, there are four other d-states to consider, defined by their angular momentum quantum numbers $l=2$, $m= \pm 1$ (d_{xz} and d_{yz}) and $l=2$, $m= \pm 2$ ($d_{x^2-y^2}$ and d_{xy}). Each of these $m \neq 0$ states exhibits a negatively-protruding LDOS, as opposed to the positively protruding LDOS of the d_{z^2} orbital. Thus, with an $m \neq 0$ tip-state at the tip apex, an inverted STM image is to be expected with the interstices highlighted at the expense of the atomic sites. However, because of the spatial arrangement of these five orbitals, the d_{z^2} state which is directed towards the surface usually has a much larger tunnel matrix element and so dominates the tunnel current most of the time. Occasionally, as a result of some fluctuation, an $m \neq 0$ state may contribute strongly to the tunnel current, causing the image reversal.

2.3.2. Spectroscopic Induced Contrast:

In general, it is difficult to obtain contrast between different metallic elements using STM because all metals have a high density of states at the Fermi level and valence electrons which are delocalised. In some systems, it is possible to utilise geometrical differences such as in the case of the growth of gold on Cu(100) [2.42], where a c(2x2) overlayer forms with two inequivalent atoms per unit cell which have different heights in the image. The higher sites were tentatively assigned as gold atoms which have a larger atomic radius when compared with copper atoms.

There has recently been some progress in distinguishing different metallic elements on a surface using a method which does not rely on the condition of the tip. Mo and Himpsel [2.43] have observed the spectroscopic signature of copper deposited on a W(110) surface. At low coverages, the copper decorates step edges. When imaging the filled sample-states ($V < 0$), the copper atoms are topographically lower than the tungsten terrace step height (the tungsten co-valent radius is about 10% larger than that of copper). When imaging the empty sample-states at an energy in excess of 0.6eV above the Fermi level, the reverse is true, see **figure 2.9** overleaf. Inverse-photoemission spectroscopy studies [2.44], explain this phenomenon in terms of an intense copper induced empty-state located 0.6eV above the Fermi level becoming available for tunnelling. Mapping of this state in momentum space indicates that it is s-p like and has a large spatial extension of the wavefunction. It is centred at zero parallel momentum and so ideal for STM imaging.

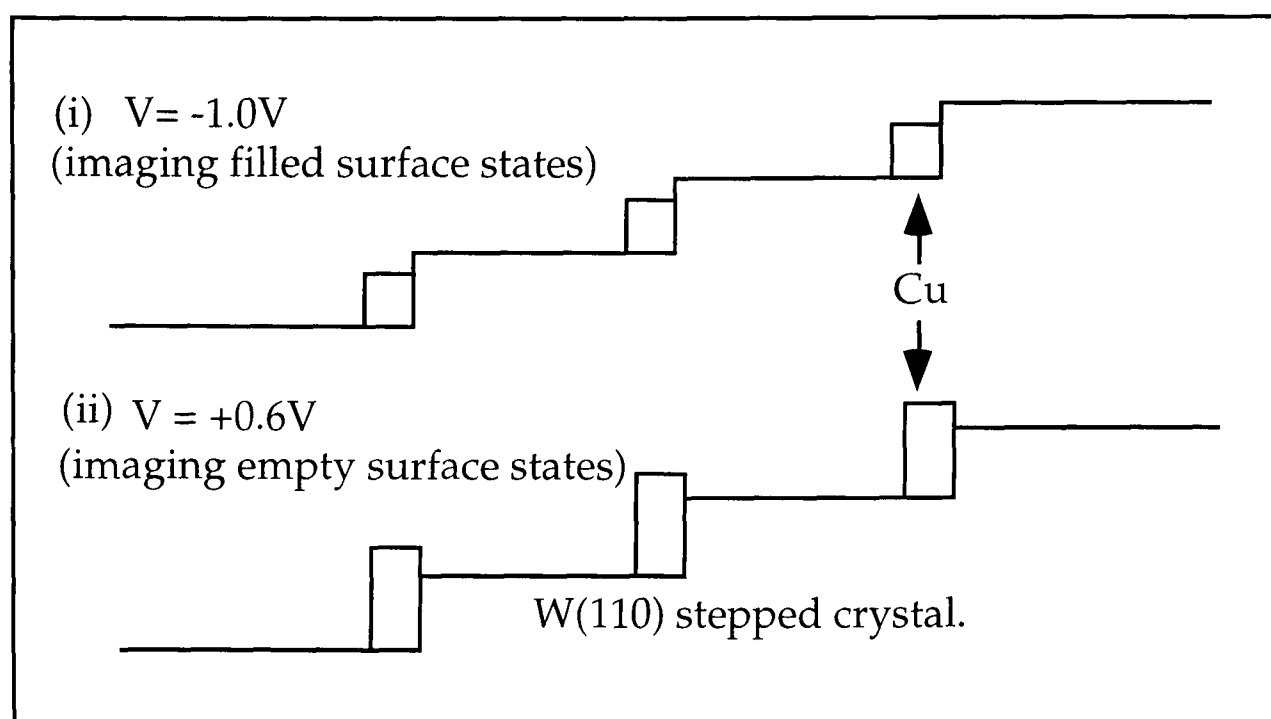


Figure 2.9: A schematic diagram to illustrate the image contrast observed by Mo and Himpsel [2.43] for copper deposited on a stepped W(110) surface. (i) When imaging the surface filled-states, the copper atoms at the step edge appear lower than the tungsten step height. (ii) An empty-states image taken using an imaging bias voltage in excess of 0.6V shows the reverse effect.

In a slightly different vein, Jung et al. [2.45] have noted that by using STM at high voltages ($> 4V$) in the transition region between tunnelling and field-emission, a series of sharp resonances become available for tunnelling. These are image-states and their energy is determined by the surface workfunction. They are induced by the combination of the image potential and electric field in the tunnel gap [2.46]. Evaporation of small amounts of copper on Mo(110) leads to terrace edges being decorated with copper. Increasing the sample bias continuously towards more positive bias voltages gives rise to an oscillatory reversal in the contrast of the two different surface species. Copper stripes appear substantially brighter than the molybdenum substrate at sample bias voltages of +5.3, +7.1 and +8.2V, but are slightly darker than the substrate in between these maxima. As with the case of copper on W(110), the deposition of copper on Mo(110) induces a state 0.8eV above the Fermi level that is available for empty-states tunnelling. By imaging the surface using bias voltages either side of the

the image state gives rise to the greater topographic contrast. Quantitative analysis (using the change in the copper step edge height between the two images) has shown that the image-state contrast corresponds to 60% of the Mo(110) step compared with 30% in the case of the copper-induced state. Note, that since large bias voltages are required to exploit the image states, lateral resolution in these images is low.

2.4 Reconstructed Surfaces:

In the previous section, the discussion of imaging clean metal surfaces was restricted to: (i) unreconstructed surfaces, in which the atoms are in crystallographic registry with the underlying crystal e.g. Cu(100), Pt(111) and Ag(111) and (ii) incommensurate surfaces, which exhibit the same basic crystallography within the surface but in addition have a different (usually smaller) spacing between the first and second layer compared with layers deep within the bulk crystal, e.g. Cu(110), Ni(110). The difference between these two types of surface cannot be distinguished using STM, nevertheless I refer the interested reader to the discussion of Kittel [2.47].

However, there is a third category to consider in which the surfaces are known as reconstructions. Here a radical reorganisation of surface atoms leads to the formation of a new layer which has its own distinct crystallographic arrangement that is quite separate from that seen in the bulk crystal. Surface reconstructions are characterised by an atomic density which is different from that of the underlying layers. The unit cells of such reconstructions, are described by the Wood notation [2.48], see **figure 2.10** overleaf:

Some reconstructions have large repeat distances, and because of this a reconstructed surface - the (1x2) Au(110) missing row structure, was one of the first periodic metal surfaces to be observed by STM [2.49], see **figure 2.7**.

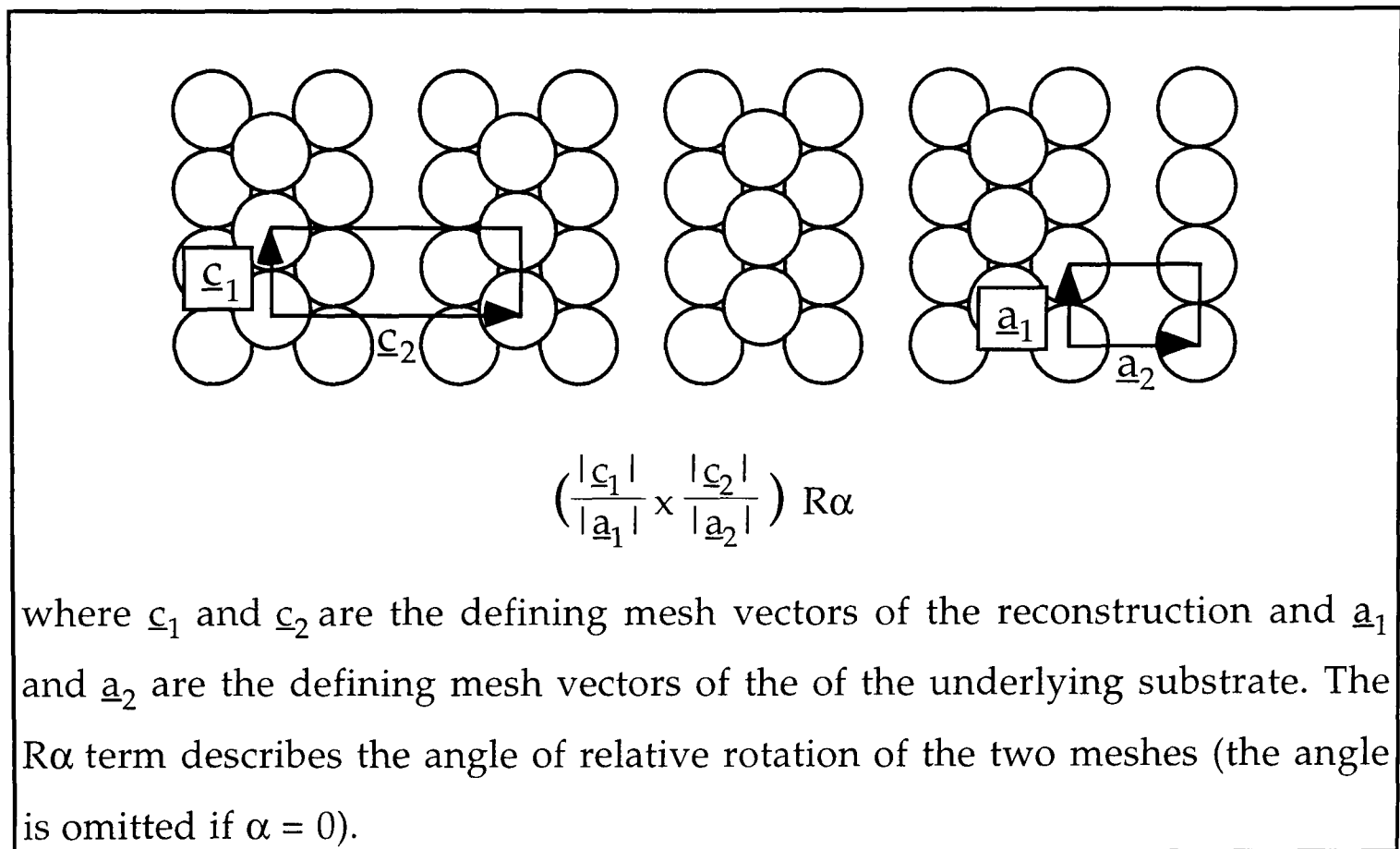


Figure 2.10: A diagram to illustrate the Wood notation using the example of the (1x2) reconstruction shown by a (110) surface such as occurs for gold.

Among the surfaces shown using other techniques to be reconstructed, are the (5x12) Pt(100) surface [2.50, 2.51] and the (5x20) Au(100) surface [2.52, 2.53]. STM has confirmed that the basic ingredient of both these reconstructions is a hexagonal close-packed layer superimposed upon the underlying square substrate. Six rows of metal atoms lie along the $[0\bar{1}1]$ direction, on top of five substrate rows or hollow sites. The resulting periodicity of $\sim 14\text{\AA}$ orthogonal to these rows corresponds to the main corrugation seen in the STM images. Each row has a slightly different adsorption site, and this results in a vertical displacement of atoms in the uppermost layer, giving rise to a “geometric” corrugation of $0.2\text{-}0.3\text{\AA}$. The top layer of both these surfaces is slightly rotated ($<1^\circ$) with respect to the substrate lattice as a result of a contraction of the $[0\bar{1}1]$ rows.

In the clean $(22\times\sqrt{3})$ Au(111) surface [2.54], a 4.2% uni-directional contraction along the $[0\bar{1}1]$ direction forces 23 surface atoms into a 22-atom bulk length. This gives rise to a stacking fault structure comprising regions of face-

centred cubic structure separated from narrower hexagonal close-packed regions by broad transition bands aligned along the $[11\bar{2}]$ direction in which atoms are displaced into less favourable vertical sites. The atoms in the transition region are also displaced in a direction orthogonal to the contraction in order to take up the offset between the fcc and hcp adsorption sites. Barth et al. [2.41] have shown that over large areas ($1000 \times 1000 \text{ \AA}^2$), this reconstruction has three-fold symmetry. The double-ridged superstructure changes orientation about every $280 \text{ \AA}$ and a regular herringbone pattern is observed. This structure is sensitive to local defects - near a step, the herringbone structure is often replaced by a U-shaped structure, which has a slightly different atomic configuration from the basic reconstruction.

Using a variable temperature STM, Wengelnik et al. [2.55] have imaged the W(100) surface at 80K and at room temperature. At 80K, the surface exhibits a $c(2 \times 2)$ reconstruction, characterised by zig-zagging $\langle 0\bar{1} \ 1 \rangle$ rows. A phase-transition occurs in the region 210-250K, and at room temperature the surface is seen as an ordered (1×1) structure. However at both temperatures in this study, the corrugation measured along the most closely-packed directions could not be resolved and was lost within the background noise.

The clean Pt(110) surface is known to exhibit a (1×2) reconstruction. Gritsch et al. [2.56] have shown that this reconstruction can be lifted by the adsorption of small quantities of carbon monoxide. The adsorbate displaces the metallic atoms with the formation of small patches of "bulk-terminated" (1×1) surface around a square depression in the surface where the CO is presumed to reside.

2.5 Metal + Adsorbate Systems:

Once the clean metal surface has been fully investigated, the next stage to consider is the modification to the STM image due to single-atom adsorbates. The discussion in this section is concerned with both metallic and non-metallic adsorbates. Where possible, examples of collaboration between theory and experiment have been included in order to describe and understand the imaging behaviour that can be expected from metal-adsorbate systems.

The easiest modification to conceptualise in the image is the superposition of the adsorbate's LDOS near the Fermi level. This was first suggested by Lang, who in an early set of theoretical papers [2.57-2.60] assessed the effect of single-atom adsorbates upon STM images. The theoretical experiment was modelled using two jellium electrodes, with a sodium atom adsorbed on one electrode acting as the tip. The tip was then scanned past various different chemical species and the corresponding tunnel current contours calculated [2.59] (see **figure 2.11** overleaf). These contours were found to be almost identical to the combined substrate + adatom LDOS at the Fermi level, thereby extending the range of validity of Tersoff and Hamann's original conclusion.

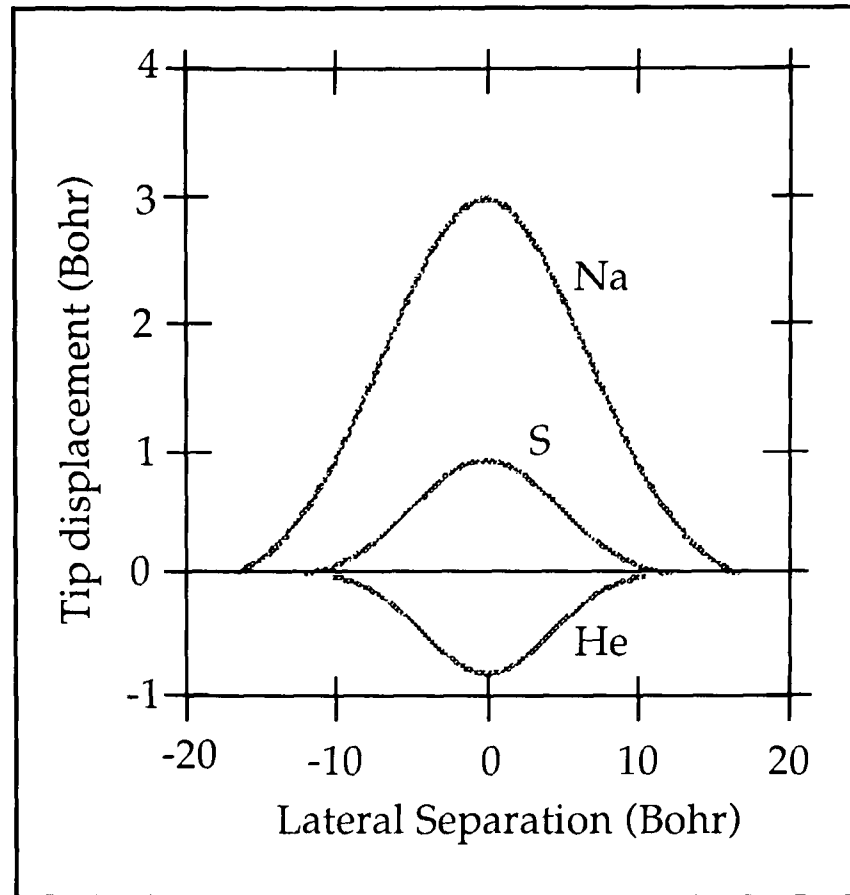


Figure 2.11: A graph taken from ref. [2.59] showing the tip-displacement required to keep a constant tunnel current calculated as a function of the lateral separation of the tip-apex atom for various different surface adsorbates. At an infinite lateral separation, the tip atom (sodium) is 16 Bohrs above the surface (1 Bohr = $0.529\text{\AA}$).

From **figure 2.11**, it is seen that the spatial extent of the sulphur atom contour is less than that of the sodium atom. This is explained by the fact that a sodium contributes more strongly to the Fermi-level state density than a sulphur atom (see **figure 2.12** overleaf), and that a sulphur atom sits closer to the surface than a sodium atom. The surprising result is that of helium: intuitively a topographic maximum is to be expected in the constant current contour, however, the filled valence-shell of helium is far below the Fermi level and does not contribute to the tunnel current. The only effect of helium is to polarise metal states away from the Fermi-level, thereby reducing the tunnel current and so producing a dip in the LDOS contour.

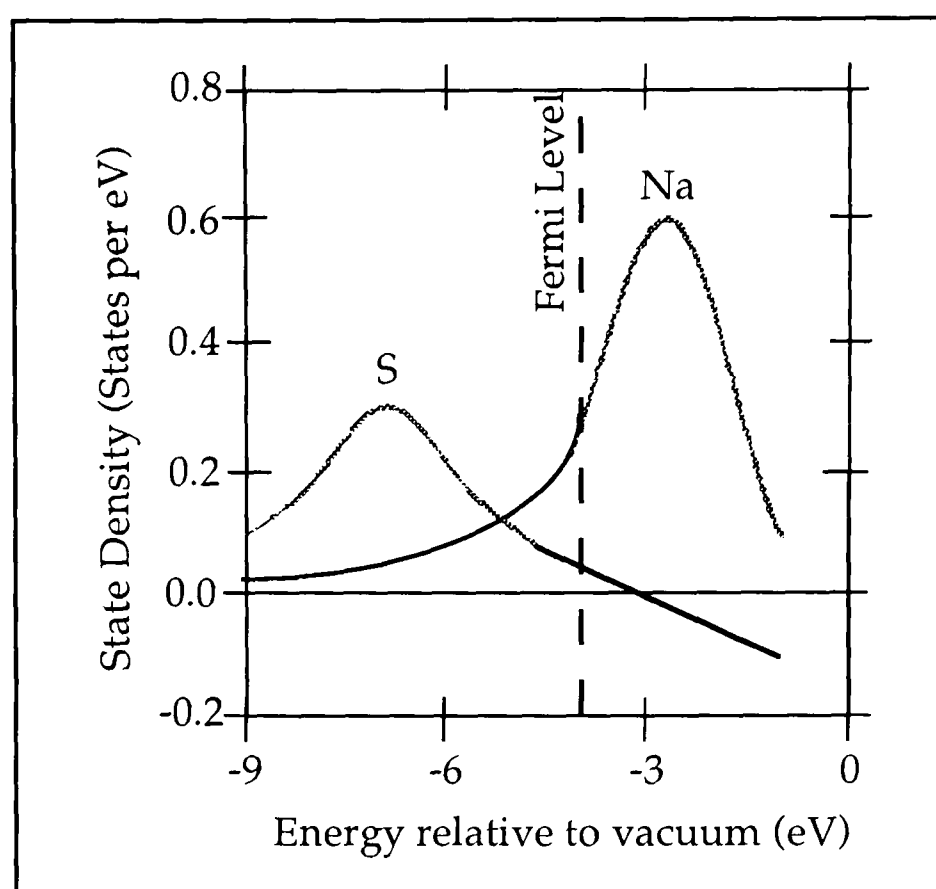


Figure 2.12: A graph taken from ref. [2.60] showing the difference in state density calculated as a function of energy between the metal + adatom combined system and the bare metal. The 3s resonance of sodium and 3p resonance of sulphur are displayed.

Later, the electronic size of the different adsorbates was calculated as function of applied bias in order to investigate the contribution of the adsorbate density of states to the topographic image [2.60]. In the case of sodium (see **figure 2.12** above), the unoccupied-state density above the Fermi level is dominated by the 3s resonance; and this was found to reflect accurately the calculated size of the adatom - a large positive protrusion in empty-state images. However, experimental work by Schuster et al. [2.61] found that single potassium atoms on Cu(110) are imaged as square holes of dimensions $7 \times 7 \text{ \AA}$ and $0.5 \text{ \AA}$ deep, independent of the tunnelling parameters used. Sodium and potassium are both simple mono-valent metals and would be expected to behave similarly under STM; it is therefore clear that at least in this case, the Lang analysis is not completely correct.

The observations of Doyen et al. [2.62] confirm the need of STM theory to take into account the structure of the tip. They imaged caesium atoms on Cu(110). In the majority of occasions, these atoms are seen as depressions of depth $0.3\text{\AA}$. After a sudden tip change, however, the atoms were imaged as protrusions with a height of up to $1\text{\AA}$. A short time later, the tip changed again and depressions were seen again in the image.

In the case of the sulphur adsorbate (see **figure 2.12**), the 3p resonance is a long way below the Fermi level and so only the tail of the resonance features in the unoccupied-state density. For small imaging bias voltages ($< +1\text{V}$), this atom is predicted to be seen as a protrusion, and this has been confirmed experimentally [2.63]. In a study of sulphur on Cu(11 1 1) - a vicinal surface to Cu(100), Rousset et al. [2.64] have seen sulphur atoms as protrusions of height $0.3\text{\AA}$. However, after a tip change, these atoms are seen as depressions of depth $0.9\text{\AA}$. This result is probably caused by the adsorption of a sulphur atom at the tip apex. **Figure 2.12** shows that sulphur has a lower Fermi-level state density than a metal. As a result of such a tip change, the tip apex has to approach the surface more closely in order to attain the same degree of wavefunction overlap for a given tunnel current, and hence larger corrugations are measured.

The interesting case is that of molybdenum, which has a prominent 4d resonance 0.3eV below the Fermi level. However, this orbital was predicted to contribute only marginally to the size of the adsorbate [2.59]. At a larger imaging bias of $+1\text{eV}$, the 5s resonance of molybdenum is predicted to give rise to a large protrusion in the image. Unfortunately there are no reports of the imaging of single molybdenum adatoms, however Mo, et al. [2.43] have not reported any anomalous behaviour in the imaging of the Mo(110) surface.

The work of Lang shows the importance of the characteristics of the tunnelling wavefunctions. The more delocalised s-states contribute more to the tunnel current than contracted d-states of the same energy. In addition, the relative spatial orientation of wavefunctions should also be considered: p_z orbitals oriented perpendicular to the surface will affect the tunnel current much more than p_x and p_y orbitals which are concentrated in a plane parallel to the surface.

A number of investigations have been made on metal + oxygen systems. Doyen et al. [2.65] have calculated tunnel current contours for an oxygen atom adsorbed on Ni(100), using a single tungsten atom adsorbed on W(110) to describe the tip. The method used here is an extension of that due to Tersoff and Hamann [2.11, 2.12] which explicitly allows for tip-sample interactions. At small separations ($< 6\text{\AA}$), a negative displacement is predicted at the site of the adsorbate in the contours of constant current (in contrast to the calculated maxima in both the total charge and Fermi-level state density contours). At larger separations a positive tip-displacement is predicted, leaving an intermediate separation of about $6\text{\AA}$ for which the tip is blind to the presence of the adsorbate. These findings are explained on the basis of the different parts of the surface wavefunctions that are sampled as the tip-sample separation is varied. At small tip-sample separations, an oscillatory part of the substrate wavefunctions arising from the mixing of the metal s-p functions and the oxygen 2p orbitals is sampled. The projection of this part of these wavefunctions at the tip is smaller than the projection of the unperturbed tails of the nickel substrate wavefunctions, and hence a negative tip-displacement is expected. At larger separations, the tip 6s orbital increasingly probes the exponentially decaying sample wavefunctions, and current contours are qualitatively similar to those of charge density result.

This calculation was followed up experimentally by Kopatski and Behm [2.22], who report that adsorbed oxygen atoms are seen as local square minima of depth $0.3\text{\AA}$ and width $4\text{\AA}$ located on four-fold hollow sites on the Ni(100) surface. This is in contrast to the results of a LEED study which deduced the binding geometry of oxygen to be $0.8\text{\AA}$ above the topmost Ni layer [2.66]. Unfortunately Kopatski and Behm were unable to find any imaging conditions for which the adsorbed atom was represented by a topographic maximum in the image.

Using the same Doyen model [2.65], Kopatski et al. [2.67] calculated constant current contours for an oxygen atom adsorbed on Al(111). Here the adsorbate was predicted to be seen as a protrusion extending $\sim 0.3\text{\AA}$ above the surface. The oxygen 3s orbital - which is empty in the free atom was predicted to be partially filled when chemisorbed onto Al(111), thereby increasing the LDOS at the Fermi level. However, it was found experimentally [2.68] that for small coverages of oxygen (surface coverage $< 5\%$) when using low tunnel currents ($I < 1\text{nA}$), islands of oxygen atoms of diameter $10\text{-}20\text{\AA}$ were in fact imaged as depressions up to $0.7\text{\AA}$ deep. In the same study, after ion-sputtering the surface at 300K and annealing it at 800K, some high-resolution images exhibited clusters of "hat-like" features. Each complex had a central protrusion surrounded by a ring-shaped depression. The entire diameter of such features was $8\text{\AA}$ and the height difference with respect to the surrounding aluminium surface was $\pm 0.4\text{\AA}$. The rings of depressed material are in fact six individual hollows arranged in a hexagonal-lattice, each hollow coinciding with the centre of a three-fold coordinated site of the underlying substrate, while the central protrusion was coincident with the seventh three fold site in the centre of the hexagon. These features were interpreted as oxide nuclei.

The (2x1) oxygen-Cu(110) reconstruction has been widely studied in STM. The reconstruction forms as a result of the diffusion of copper atoms at terrace edges into long [001] oriented added-rows, with one oxygen atom located in each long bridge position, see **figure 2.13** below. Coulman et al. [2.69] have noted that the apparent height of the copper atoms in individual Cu-O strands with respect to the underlying substrate is a function of the potential bias used. The copper atoms are seen as depressions of depth upto $0.3\text{\AA}$ when using an imaging potential bias voltage $> -1\text{V}$ and protrusions of height upto $0.4\text{\AA}$ when using a bias potential in the range $-1.4\text{V} < \text{bias voltage} < -1\text{V}$. Jensen et al. [2.26] have observed qualitatively similar results, although Chua et al. [2.70] claim that the island strands are a constant height $0.8\text{\AA}$ above the substrate, independent of the tunnelling conditions.

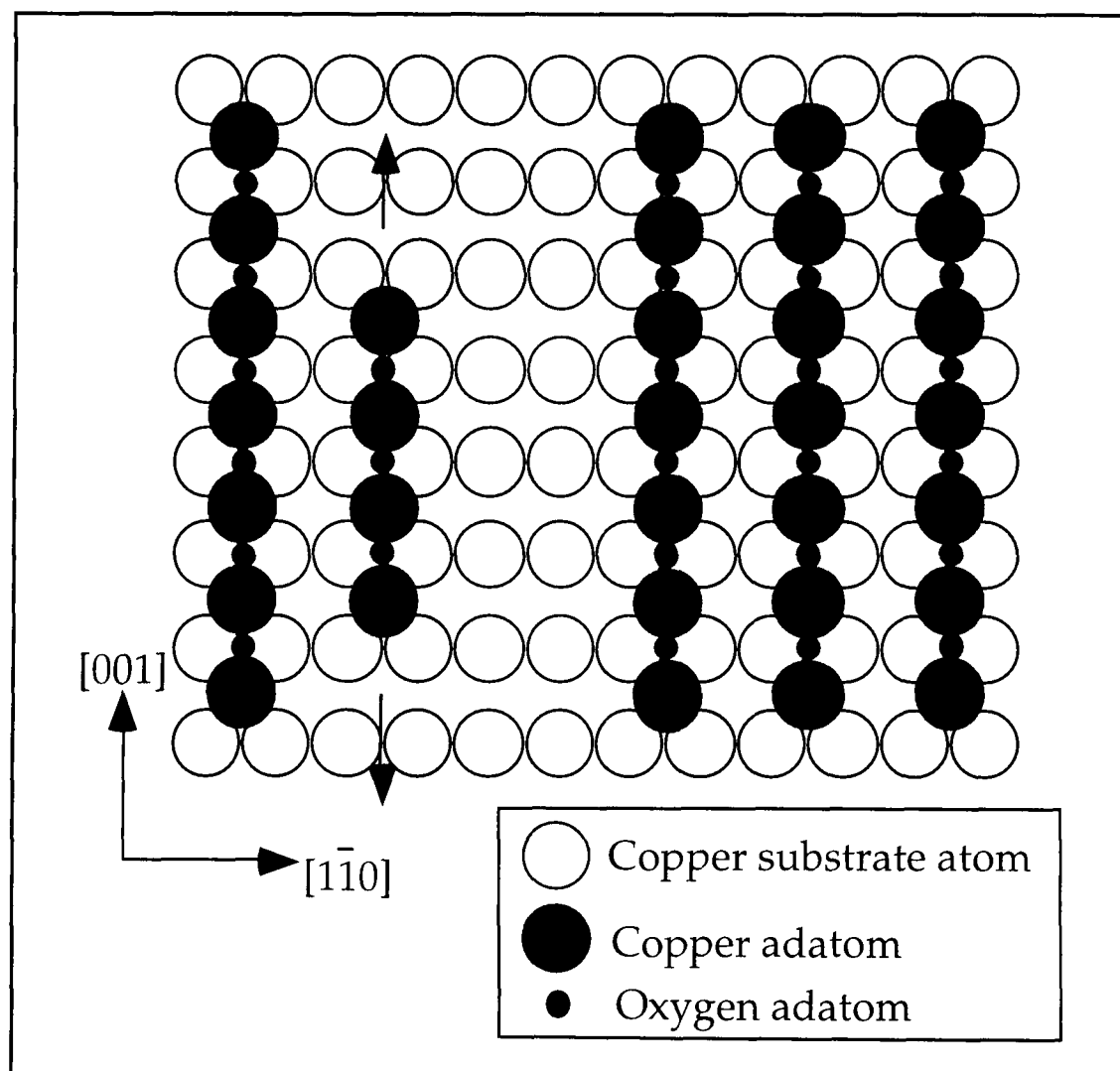


Figure 2.13: A diagram showing the (2x1) oxygen-Cu(110) reconstruction. Single strings of Cu-O adatoms grow along [001] to form added rows. The arrows indicate the predominant direction of growth of the reconstruction.

Figure 2.14 below shows an image in which the oxygen atoms are imaged in the Cu(110) (2x1)O reconstruction. This is deduced from the fact that the atoms in the reconstruction are “in-phase” with the underlying metal surface. Following the interpretation of Ruan et al. [2.71], this image is assumed to have been taken by a metal-atom terminated tip.

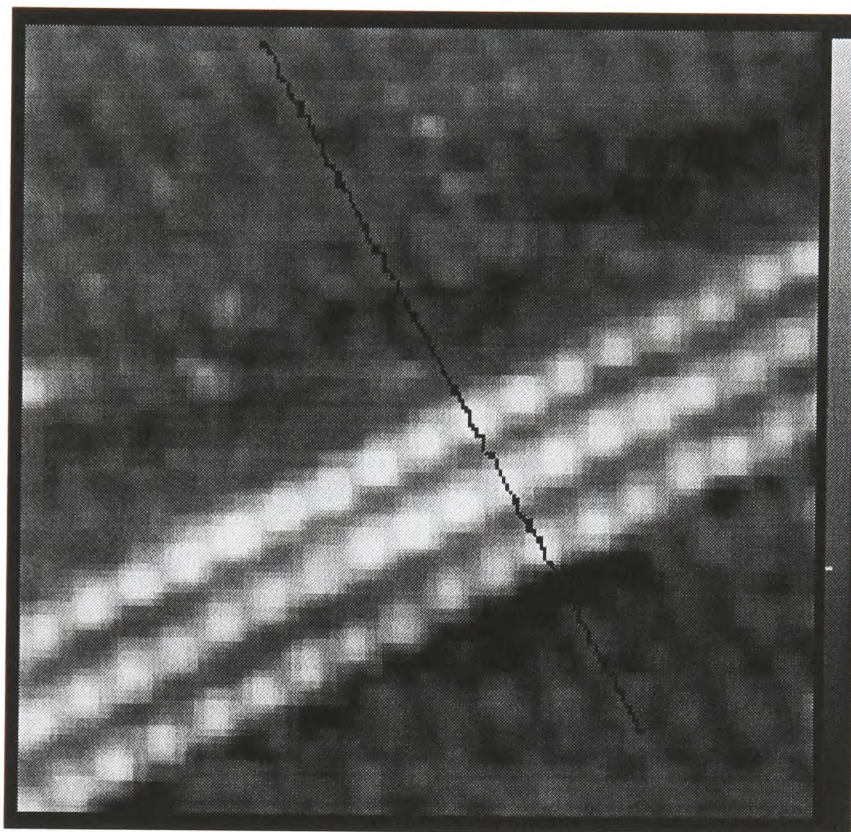


Figure 2.14: A $70 \times 70 \text{ \AA}$ (vertical scale $0.9 \text{ \AA}$) STM image showing a finger of the (2x1) oxygen-Cu(110) reconstruction. The predominantly one-dimensional nature of the formation of this reconstruction is apparent from this image. A line shows that the atoms are “in-phase” with the underlying substrate, a fact which identifies these species as oxygen. The tunnelling parameters used were $I = 8.2 \text{ nA}$, $V = -12 \text{ mV}$.

Brune et al. [2.72] have directly imaged the adsorption sites for carbon on Al(111). At a high tunnel gap resistance, $R_t \sim 10^9 \Omega$, carbon adatoms are imaged as protrusions of height $0.3 \text{ \AA}$ and diameter $4 \text{ \AA}$, surrounded by ring-like depression zones of depth $0.2 \text{ \AA}$ and diameter $5 \text{ \AA}$. However, by decreasing the tip-sample separation, on some occasions the underlying substrate was also resolved. By making a small change in the potential bias from $V = -20 \text{ mV}$ to $V = -70 \text{ mV}$ (tunnel current = 41 nA), an interesting change in the image could be effected. In the former case, the adatom is not seen

and its three nearest underlying substrate neighbours are observed to be displaced downwards by $\sim 0.3\text{\AA}$, although the three next nearest neighbours are shifted upwards by about $0.2\text{\AA}$. In the latter case, the image displays a protrusion of about $1\text{\AA}$ in height due to the carbon atom. The change in potential bias is not large enough to explain these observations on the basis of LDOS near the Fermi level. Rather this effect is interpreted as being induced by the change in tip-sample separation turning off a Friedel-oscillation like interaction. In studies of carbon adsorbates on Ni(100), Clink et al. [2.73] report the observation of Maltese-cross like features of depth $0.3\text{\AA}$ located on four-fold hollow sites.

When investigating some systems, tip-induced electric-field perturbations in the final image cannot necessarily be ignored as the problem of the non-observation of carbon monoxide at low surface coverages has shown [2.74, 2.75]. Ramos et al. [2.74] has demonstrated that this effect may be due to a rotation of the molecule towards the scanning tip which effectively switches the tunnel current off. However, it is also likely that surface diffusion plays a role in this problem, as Zeppenfeld et al. [2.76] have been able to image single carbon monoxide molecules at 4K.

It is important to distinguish between different adsorbates when using STM. Thus far little effort has been directed to this area of study, however, by taking advantage of the different electrical properties of adsorbates, Behm [2.77] has easily distinguished and identified oxygen and carbon atoms on Al(111) at low surface coverages ($< 0.1\%$). The situation may not be so straightforward for more complex adsorbates. Weiss and Eigler [2.30] found three distinct types of image of benzene molecules adsorbed on Pt(111). These images were the result of different adsorption sites taken up by benzene molecules. In contrast to these data, Hallmark et al. [2.78] claim it is

possible to use STM to identify a range of different organic aromatic molecules including naphthalene, azulene, monomethylazulene, dimethylazulene and tri methyl-azulene. The data presented in this study is not of the highest quality and so it is hard to assess the conclusions offered. This is an important area of study with surface defects in particular playing a major role. The discrimination of different species using STM is likely to become a major field of investigation in the years to come.

In general, STM images of adsorbate systems do not simply reflect ion -core positions and as is the case for STM of semiconductor surfaces, it is necessary to image a particular system over a wide range of experimental conditions in order to completely characterise its behaviour.

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Chapter 3

Experimental Apparatus

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3.1 Overview:

Much of the experimental work presented in this thesis was carried out at the Center for Atomic-Scale Material Physics (CAMP) at the Institute of Physics, University of Aarhus, Denmark. I have therefore decided to describe the apparatus available in that Department, a mixture of home-made equipment (including the STM itself) and commercially-available systems. The intention of this Chapter is to provide the reader with an understanding of a range of standard surface science tools and techniques. The surface science equipment available in Oxford is essentially identical to that discussed here. For details of the *Omicron* Ultra High Vacuum (UHV) system available in Oxford [3.1], I refer the interested research worker to the discussion of past and present colleagues [3.2-3.8].

3.2 The Scanning Tunnelling Microscope:

The Scanning Tunnelling Microscope used throughout this study was small and compact, easily fitting into an average-sized coffee cup [3.9, 3.10]. The microscope is based on a scanner tube and inchworm design (see **figure 3.1** below). The scanner comprises a piezoelectric tube, made from PZ-27, which is a hard lead-zirconate material [3.11] with a low mechanical Quality factor, Q , of 80 and a high Curie temperature of 623K. The scanner tube (6) is 6mm long, with internal diameter 3.05 mm and external diameter 4.4 mm. It is connected to the outside world via fine silver electrodes.

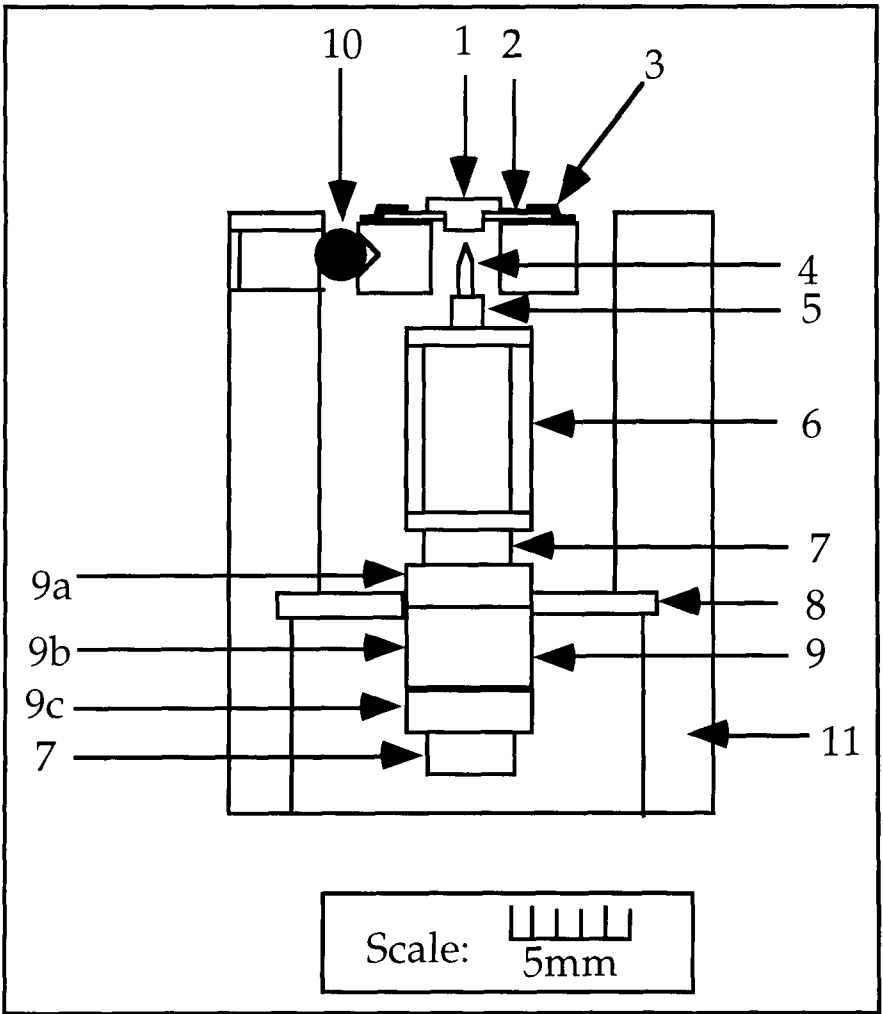


Figure 3.1: A diagram showing the principal features of the Scanning Tunnelling Microscope used in this work. (1) Sample, (2) Sample-holder, (3) Copper leaf spring, (4) Tip, (5) Tip-holder, (6) Scanner Tube, (7) SiC rod, (8) Macor disc, (9) Inchworm-linear piezoelectric motor, (9a) Inchworm Upper-Electrode, (9b) Inchworm Central-Electrode, (9c) Inchworm Lower-Electrode, (10) Quartz ball, (11) Invar Housing.

Motion of the scanner in a direction normal to the plane of sample surface is achieved by applying a bias voltage $\pm V_z$ to an electrode connected to the inner tube wall. Raster scanning of the tube parallel to the surface is achieved by applying bias voltages $\pm V_x$ and $\pm V_y$ to four electrodes mounted on the outer tube wall. A tungsten tip (4) is mounted in a Macor block (5) which is glued on top of the scanner tube [3.12]. Coarse approach of the tip towards the sample is effected via a linear motor, the inchworm (9). The inchworm comprises a second identical piezoelectric tube, through which passes a highly-polished cylindrical silicon carbide (SiC) rod of diameter 3mm (7). The scanner tube (6) is mounted on top of this rod. Bearings made of a soft solder (composition 10% Ag: 45% Sn: 45% Cu) sit between the SiC rod and the inside of the inchworm piezoelectric tube. The outer electrode of the inchworm is divided into three parts in the ratio 1:2:1, while the inner electrode is undivided and held at ground potential. By applying positive or negative voltages to the outer electrodes, they cause the tube to expand or contract circumferentially. The bearings respond by clamping or releasing the SiC rod from the piezoelectric tube.

In a typical approach cycle (see **figure 3.2** overleaf), both parts of the rod are initially clamped (i); the lower part unclamps the rod (ii); the centre is expanded by applying a negative voltage (iii); the lower part clamps the rod (iv); the upper part releases the rod (v); and finally the centre part is contracted (vi). The net effect of this cycle is to move the ceramic rod towards the sample, which is off the right hand edge of the diagram. The operator can determine the size of such jumps within the range 2-2000Å, depending on how far the tip is presumed to be from the surface. This approach is terminated as soon as a tunnel current is detected. At the end of an imaging session, the approach cycle is reversed and the tip is withdrawn from the sample, typically by a distance of 0.7mm. As **figure 3.1** shows, the

inchworm is held by a Macor disc (8) which itself is mounted in a cylindrical Invar housing (11). This housing reduces the effects of temperature change since Invar (composition ~ 36% Ni : 64% Fe) has an extremely low thermal expansion coefficient ($\sim 2 \times 10^{-6} \text{K}^{-1}$), which is close to that of PZ-27.

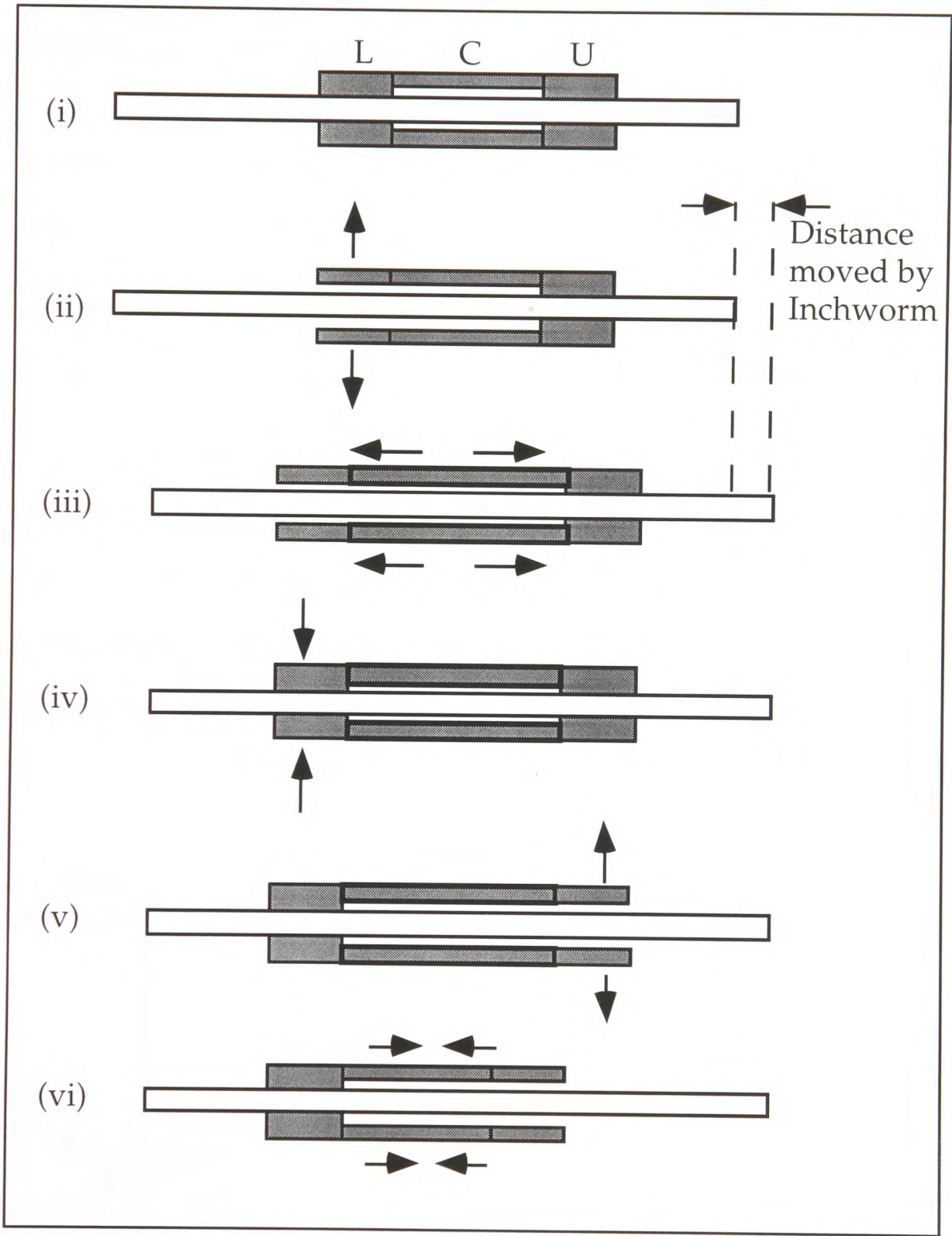


Figure 3.2: A schematic diagram showing the operation of the inchworm which is used to move the tip to and from the surface. The arrows show the direction of expansion or contraction of the inchworm at various points during its motion. In an approach cycle, the inchworm moves from the left to the right of this figure. The inchworm in this diagram is rotated 90° with respect to that shown in **figure 3.1**. Note that L refers to the lower part of the electrode, C refers to the centre part and U to the upper part of the electrode which are 9c, 9b and 9a respectively in **figure 3.1**.

Three quartz balls (10) are used to provide thermal insulation between the top of the microscope and the remainder of the STM to reduce the effects of temperature change still further. The samples are mounted on tantalum holders (see section 3.8) and are rigidly mounted directly on top of the STM housing, thereby minimising the need for external damping. The STM unit is mounted in the UHV system on a base plate resting on four Viton O-rings [3.13] which provide internal vibration damping. Samples can be freely exchanged in and out of the microscope by withdrawing the sample or by pushing it beneath a copper leaf spring (3) using the main chamber manipulator arm.

3.3 Tip preparation:

The tip used in this work was a 0.5mm diameter single-crystal tungsten wire with a $\langle 100 \rangle$ orientation. This orientation was chosen because low-energy (110) facets are revealed when the crystal is etched. The equipment used to etch a tip is shown in **figure 3.3** below.

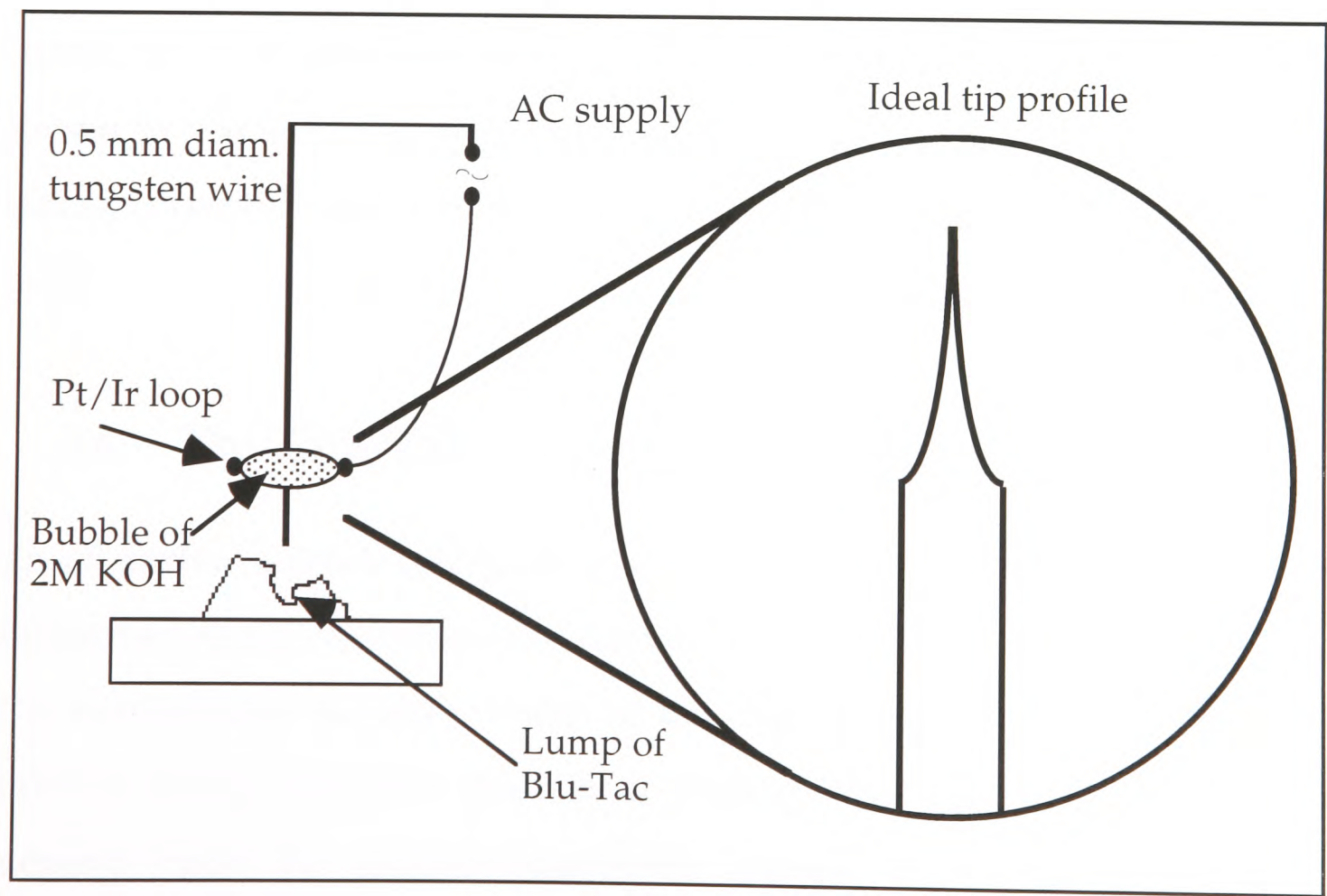


Figure 3.3: A diagram of the simple apparatus used for etching tips.

The tip wire was immersed in the centre of a meniscus of 2M aqueous potassium hydroxide solution formed in a horizontal wire loop (composition Pt90%, Ir10%) of 5mm diameter. An a.c. power supply (50Hz, 3V) was used to etch the crystal so as to prevent tungsten deposition at either electrode [3.14]. After a minute or so, the diameter of the tip in the meniscus is completely eaten away and the tip breaks off, falling into a lump of blue-tac held just below the Pt-Ir loop. This method produces sharp, facet-stabilised, whisker-free tips. Immediately prior to insertion into the UHV chamber, the apex of the tip was etched for 5-10 seconds in 4M aqueous hydrofluoric acid to remove any residual oxide layers.

Once the tip was in the microscope, the STM software allowed for modification of the apex. By opening the feedback loop, it was possible to apply a 10 milli-second bias voltage (10mV-10V) to the tip, which may desorb material from the apex; alternatively the tip could be deliberately indented into the surface to modify its chemical composition. This combination of electrochemical etching and *in situ* modification has been shown to produce a tip which is reliable over many months and capable of taking several thousand STM images of a wide variety of metallic surfaces [3.15].

3.4 The Ultra High Vacuum (UHV) Chamber:

In all surface science problems, it is important to be confident that surface properties alone are being investigated, uncomplicated by gases that form the surrounding medium. Many of the experiments we wish to perform involve firing electrons towards a surface. The results obtained often depend upon the incident electron's energy. It is thus important to minimise the possibility of inelastic scattering of these electrons prior to

their impingement on the surface. These two factors necessitate the performance of experiments in Ultra High Vacuum (UHV) conditions, which are usually thought of as a pressure of 10^{-10} mBar or lower.

Figures 3.4 (i) and 3.4 (ii) overleaf show photographs of the UHV system in which the STM was housed. **Figure 3.4 (iii)** shows the array of electronic devices used to control the surface science tools. **Figure 3.5** shows a schematic diagram of the UHV system. This is a single stainless-steel chamber, which contains the STM unit, reverse-view Low Energy Electron Diffraction (LEED) optics, Auger equipment (i.e. an electron gun and a Cylindrical Mirror Analyser (CMA)), a differentially-pumped ion-gun for sputtering surfaces, a tungsten filament for high-temperature electron-beam annealing, a mass spectrometer and a copper “garage” for parking up to ten different crystals. The chamber is pumped on by an ion-pump, an oil diffusion-pump, and a titanium-sublimation pump. An ion-gauge monitors the internal chamber pressure, and because of the multitude of pumping facilities a base pressure of $\sim 7 \times 10^{-11}$ mBar is easily obtainable. A main manipulator arm is mounted on top of the UHV chamber and can move in three dimensions by means of hand-driven translators; the manipulator can also be rotated through 360° about an axis aligned along its length. The sample grips at the end of the manipulator arm perform a second task; one is made from chromel, the other from alumel and together with the sample holder grips they form a thermocouple which can be used to measure the temperature of the sample (see **figures 3.5 and 3.14 (iii)**). A turbomolecular-pump is used to evacuate a bellows gas-line connected to the differentially-pumped ion-gun, and also to purge stainless-steel gas-handling lines through which gases are fed into the UHV chamber. The gases (e.g. hydrogen, oxygen, carbon monoxide) are admitted into the chamber via sapphire-seated leak valves.

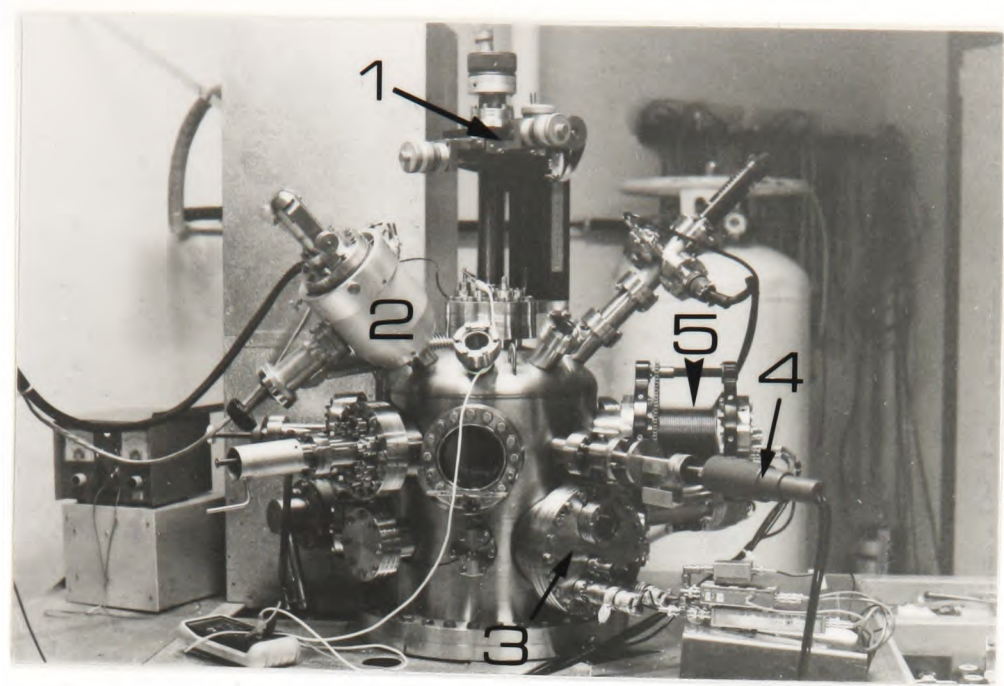


Figure 3.4(i): A photograph showing the main features of the UHV system used in this work. (1) Manipulator arm, (2) Ion-Gun, (3) STM-flange, (4) Electron-beam heater, (5) LEED apparatus.

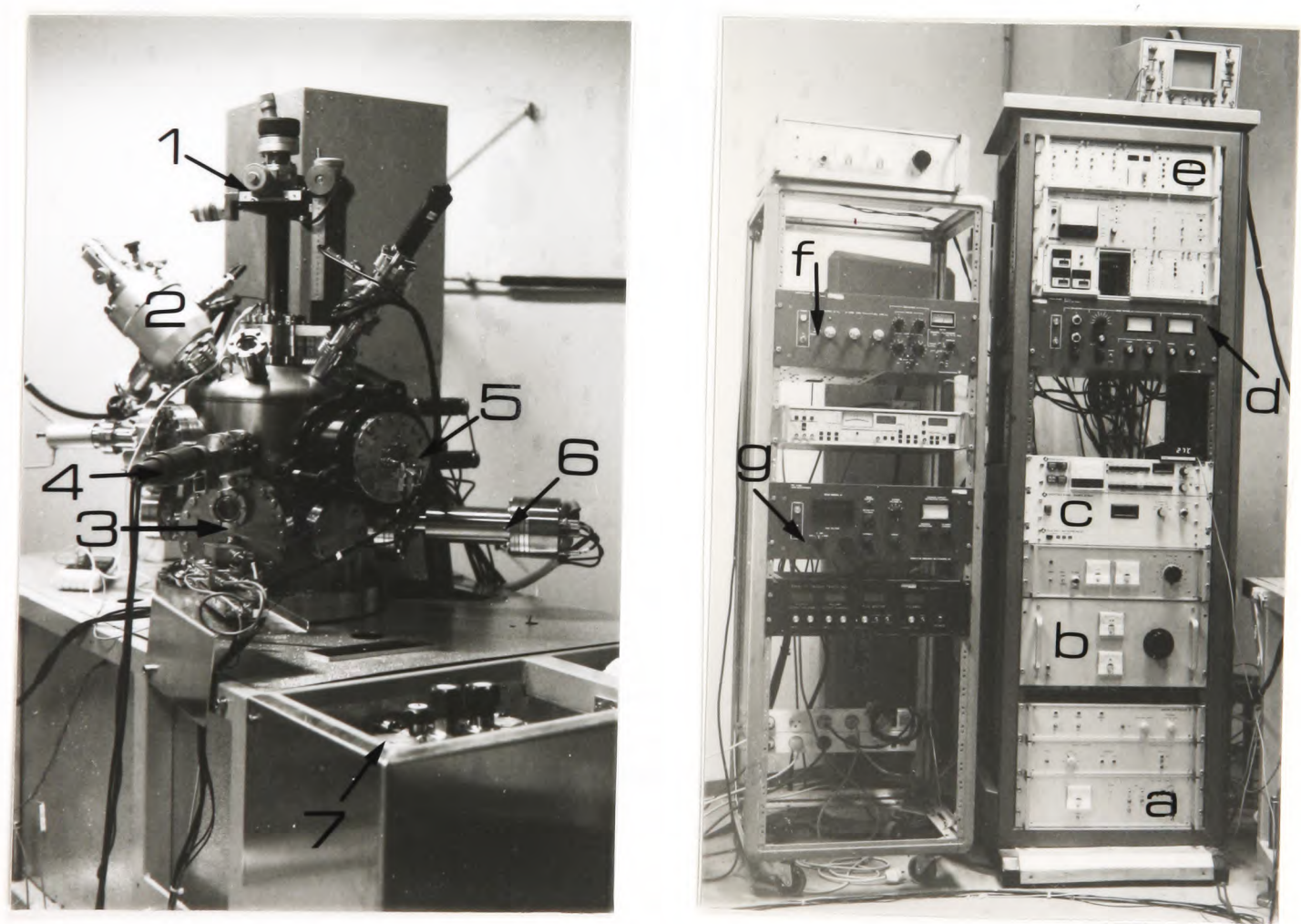


Figure 3.4(ii): (left) The same features are shown here as in figure 3.4(i). However also shown are: (6) Mass-Spectrometer, Gas Bottles (7).

Figure 3.4(iii): (right) A photograph showing the electronics stack from which the surface science tools are controlled. Units are shown for: (a) Ion-Pump, (b) Electron beam heater, (c) Mass-Spectrometer, (d) Cylindrical Mirror Analyser, (e) Ion-gauge, (f) Ion-gun and (g) LEED.

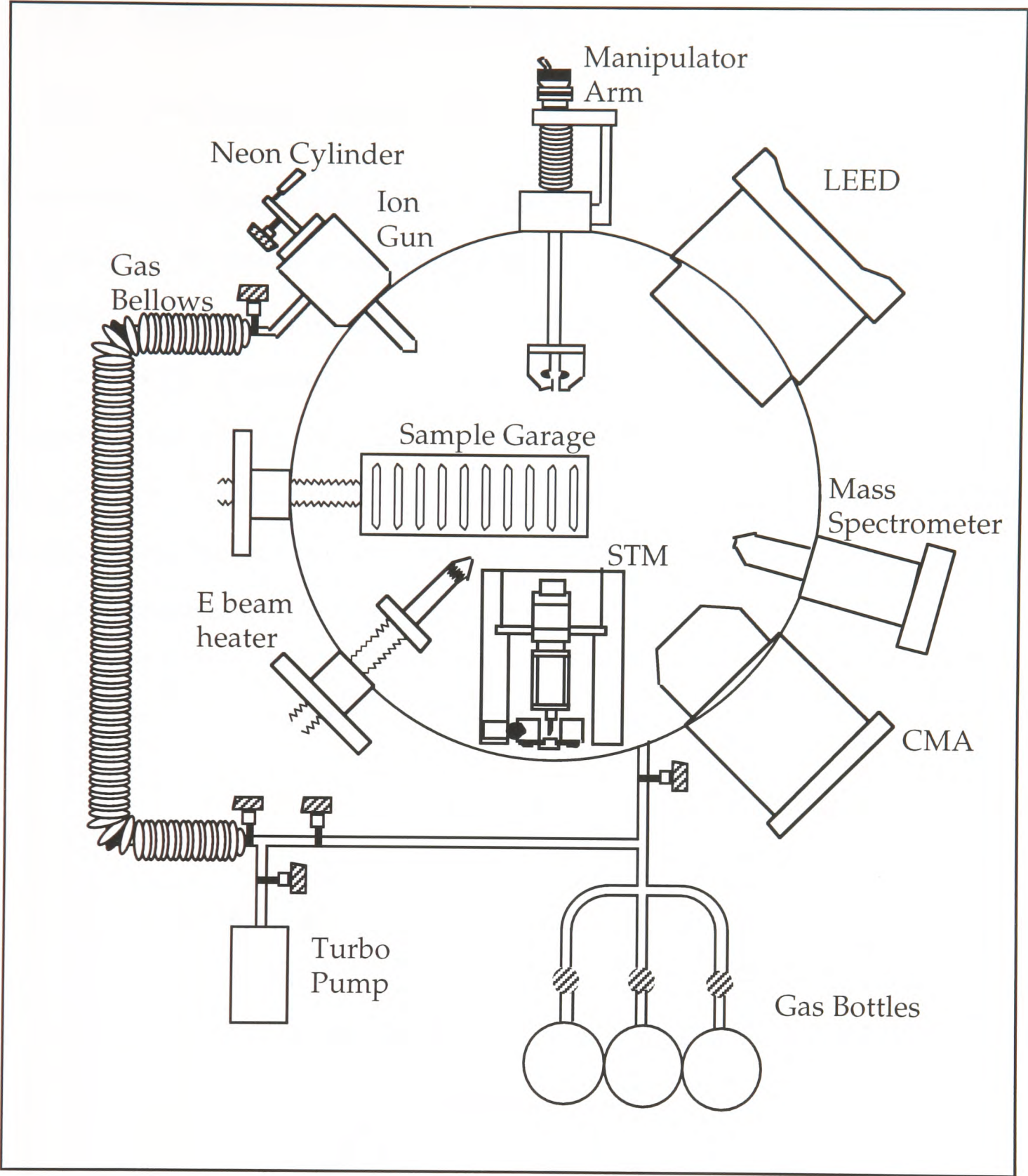


Figure 3.5: A schematic diagram showing the Aarhus UHV chamber and the instruments it houses.

3.5 Surface Analysis Techniques:

3.5.1 Low Energy Electron Diffraction (LEED):

Low Energy Electron Diffraction (LEED) is a surface-specific technique used as a tool to determine long-range surface order, which is a necessary prerequisite for obtaining good STM images. A focused, mono-energetic electron beam (typically $\sim 20\text{-}200\text{eV}$) from an electron gun strikes the grounded sample surface under investigation. About 1% of the incident electrons are elastically-backscattered, and a series of diffracted beams emerge from the sample and traverse the region between the sample and the hemispherical grid G1 (see **figure 3.6** below).

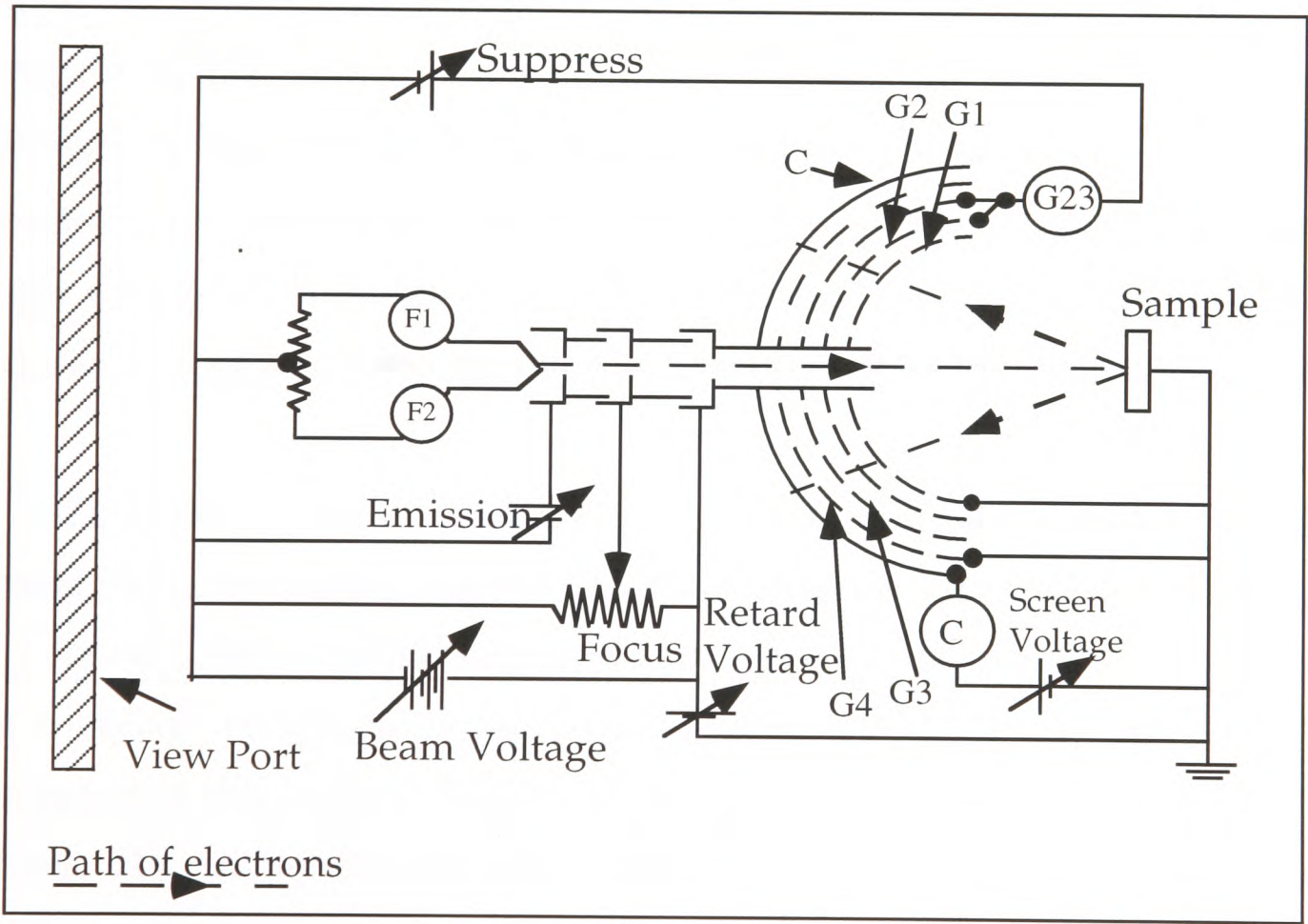


Figure 3.6: A diagram showing the principal features of the reverse view LEED optics used in this work.

The location and intensity of each beam on the collector screen varies according to the energy of the incident beam. The former can be easily determined by the use of the Bragg equation, while for the latter a

sophisticated calculation using kinematic (single scattering events) or dynamic scattering theory (multiple scattering events) is necessary [3.16].

The particular LEED optics discussed here have three extra hemispherical-grids. Voltages are applied to the inner grids, G2 and G3 (also known as suppressors), to allow only diffracted electrons to pass on to the fourth grid, G4. Varying the voltage G23 acts as a method of contrast adjustment and so the inner two grids effectively act as a high pass filter. The electrons that pass through the grounded fourth grid are then accelerated by a potential on the collector screen, C. These accelerated electrons cause a phosphorescence which results in a visible LEED pattern.

Diffraction patterns are viewed from behind the collector screen through a viewport in the centre of the mounting flange. The pattern is thus only obscured by the shadow of the electron gun; in order to see the specularly-reflected beam the sample can be tilted slightly so the surface normal is no longer parallel to the central axis of the electron gun. The Rear-View LEED optics in this system were supplied by Princeton Research Instruments Inc..

A LEED pattern is an image of the surface reciprocal-lattice net when viewed along the surface normal at a great distance above the crystal. **Figure 3.7** overleaf shows a LEED pattern for the clean Cu(100) surface. This surface has a square reciprocal-space lattice which is reflected in the four-fold symmetry of this pattern. **Figure 3.8** is a LEED pattern of the clean Cu(110) surface. The real-space unit cell of this surface is a primitive rectangle and so the corresponding reciprocal-lattice is also rectangular. In reciprocal-space, the distance between two points is inversely-proportional to their real space separation. Hence the long edge of the LEED rectangle in **figure 3.8** corresponds to the real space close packed $\langle 0\bar{1}1 \rangle$ direction, while the short edge corresponds to the $\langle 001 \rangle$ direction. This means that the real-space unit cell of the (110) surface and its reciprocal-space equivalent are rotated with respect to each other by 90° .

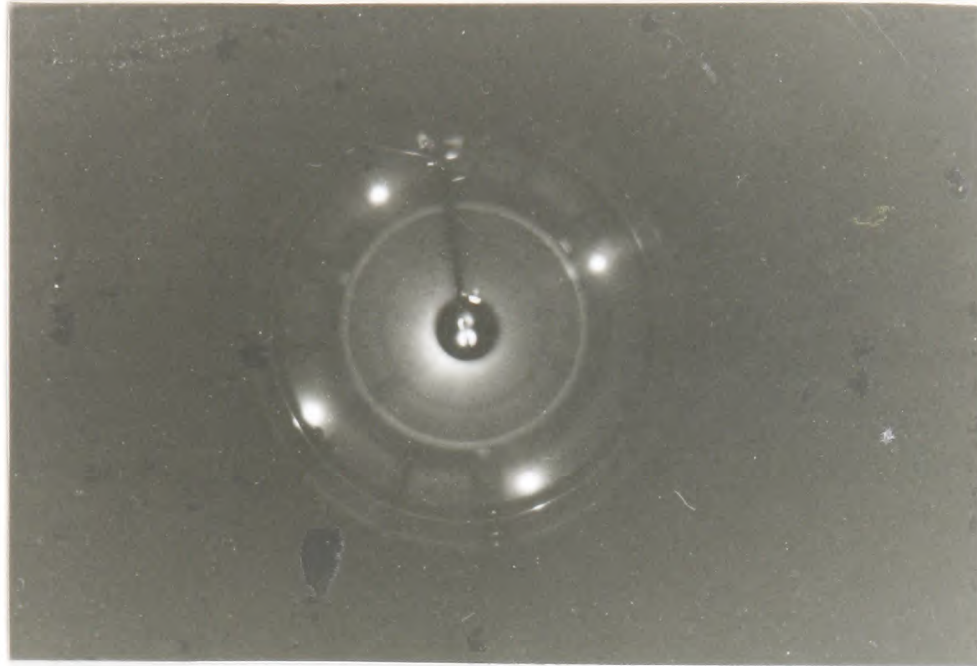


Figure 3.7: A Low Energy Electron Diffraction pattern taken from a Cu(100) surface at an incident beam energy of 47eV.



Figure 3.8: A Low Energy Electron Diffraction pattern taken from a Cu(110) surface at an incident beam energy of 73eV.

3.5.2 Auger Electron Spectroscopy (AES):

Auger Electron Spectroscopy (AES) is an analytical tool used to assess surface chemical composition at both a qualitative and quantitative level. In this work, AES was used for qualitative assessments for two reasons - as a check for the cleanliness of the sample surface; and to confirm the species present on a surface after dosing with a particular gas. Auger Electron Spectroscopy requires the use of relatively low-energy incident electrons, which have mean free paths of $\sim 5\text{-}15\text{\AA}$ in solid matter and thus are sensitive to the surface. However, it is also necessary to use somewhat higher energy incident electrons ($>1\text{keV}$) than in LEED. Incident electrons are used in a ballistic capacity to knock out core-level electrons of surface atoms. Less tightly bound electrons then drop down to fill the vacancies created, see **figure 3.9** below.

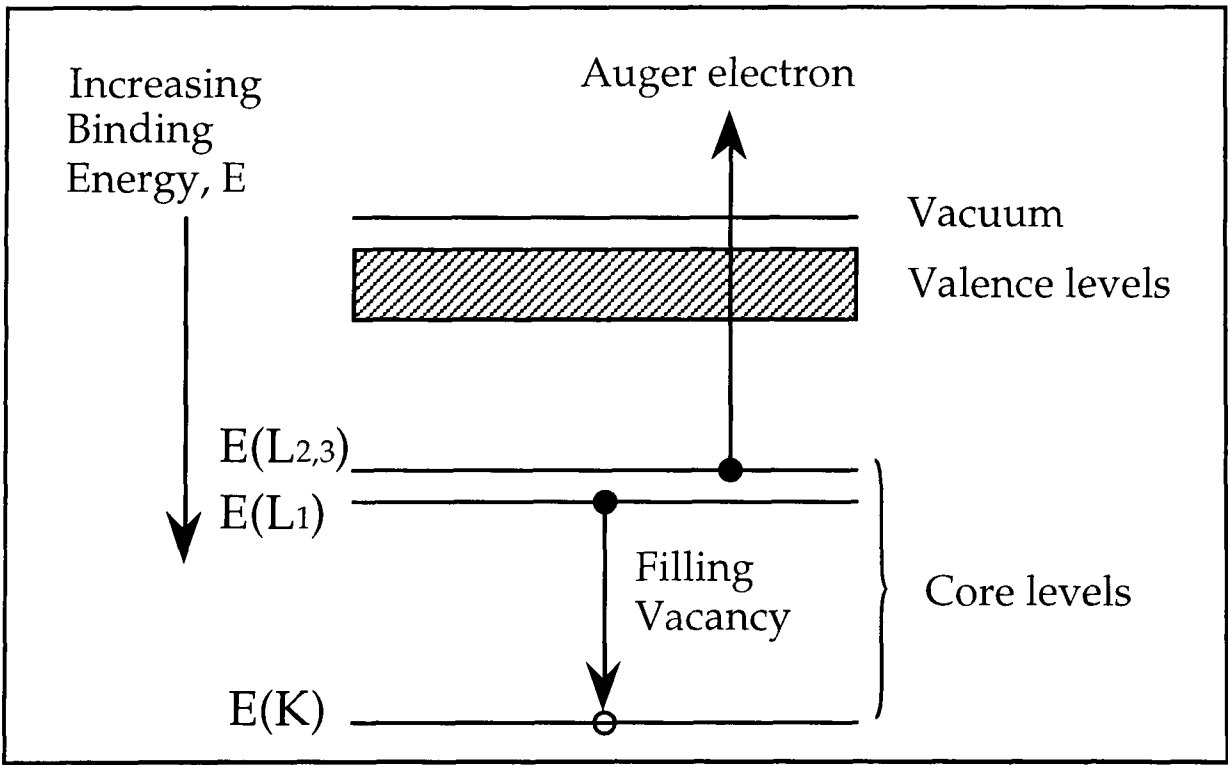


Figure 3.9: An energy diagram illustrating the KL_1L_2 Auger decay of a $1s$ core hole.

Energy can be conserved in one of two ways. In the first Auger mechanism, the energy $-(E_K - E_{L1})$ in **figure 3.9** is emitted as a photon. In the second Auger mechanism exploited here, a radiationless transition occurs whereby

an electron of comparable energy to the initial energy of the demoted electron is emitted and escapes from the surface atom. The kinetic energy, $-(E_K - E_{L1} - E_{L2})$ of such *Auger* electrons is characteristic of their atom of origin, and so by detecting the number of electrons emitted at each energy, $N(E)$, we can build up a profile of the surface chemistry. In practice, the spectrum that results is rather featureless except for a few deviations which show up much more strongly in the energy-derivative signal, $dN(E)/dE$. This second Auger mechanism is dominant for cases where the initial core electron has a binding energy of less than 10keV.

In Aarhus, a Princeton Research Instruments PHI 10-155 Cylindrical Mirror Analyser was used to detect Auger electrons ejected from specimens excited by an electron beam. A electron-beam of energy 3keV is generated by an electron gun contained within an inner cylinder and directed towards the sample (see **figure 3.10** overleaf).

The resultant Auger electrons pass through a gap around the grounded inner cylinder and approach the outer cylinder. This second cylinder is negatively-biased and thus repels electrons, forcing them through a second gap in the inner cylinder and into an electron multiplier. Here the number of electrons is multiplied prior to striking a collector plate. The deflection of the electrons by the outer cylinder is dependent upon the kinetic energy of the Auger electrons and the bias potential applied to the cylinder. Thus, by ramping the potential bias on the outer cylinder, it is possible to build up an $N(E)$ spectrum. After amplifying the output current from the electron multiplier and storing it digitally, the signal is differentiated in order to reveal a series of sharp peaks at specific energies which determine the chemical composition of the surface.

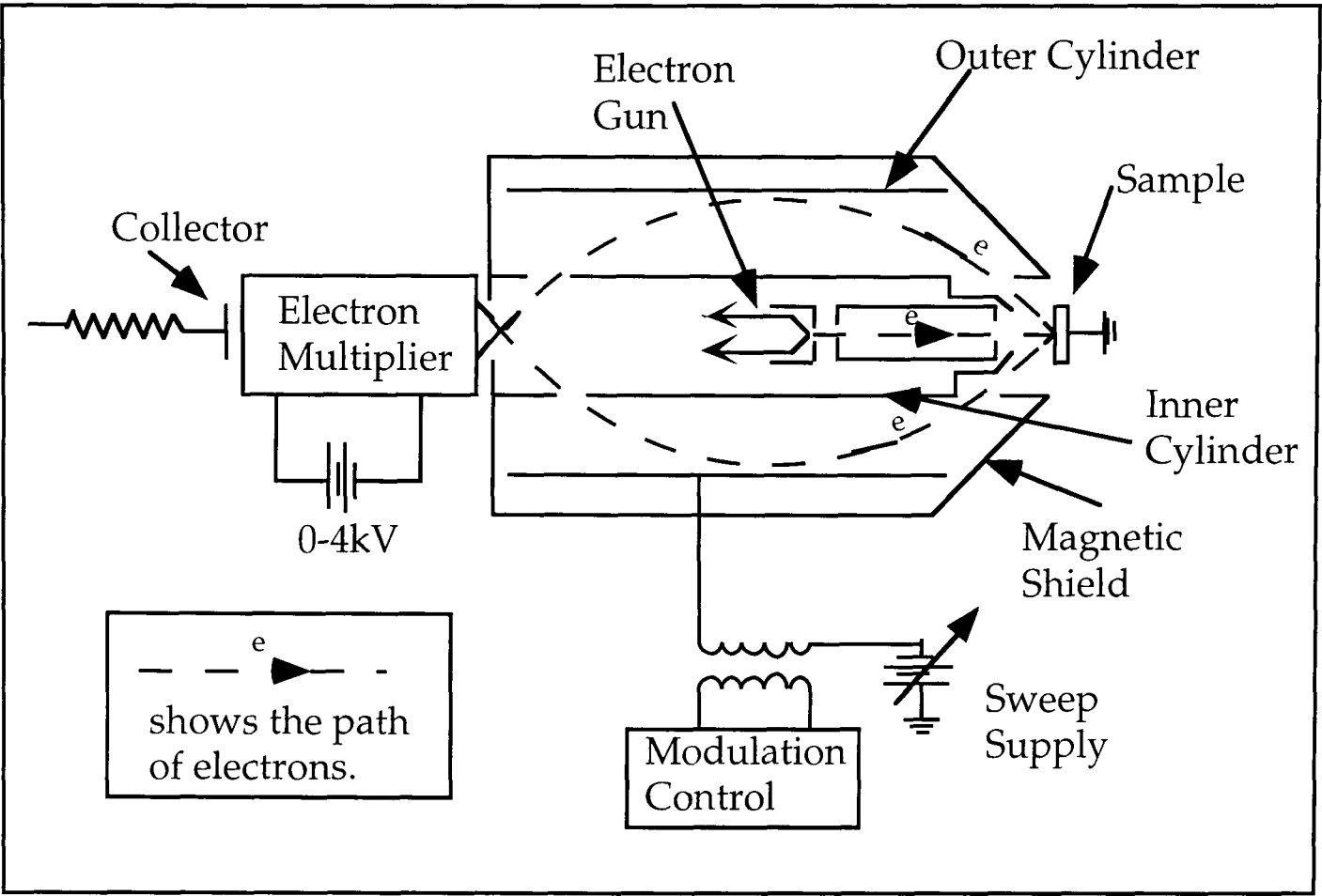


Figure 3.10: A diagram showing the principal features of the Auger equipment.

Typical Auger spectra are shown in **figures 3.11** (clean Cu(110)) and **3.12** (Cu(110) + 3 Langmuir oxygen) overleaf.

n.b. 1 Langmuir exposure of any gas is defined as an exposure of 1.32×10^{-6} mBar seconds.

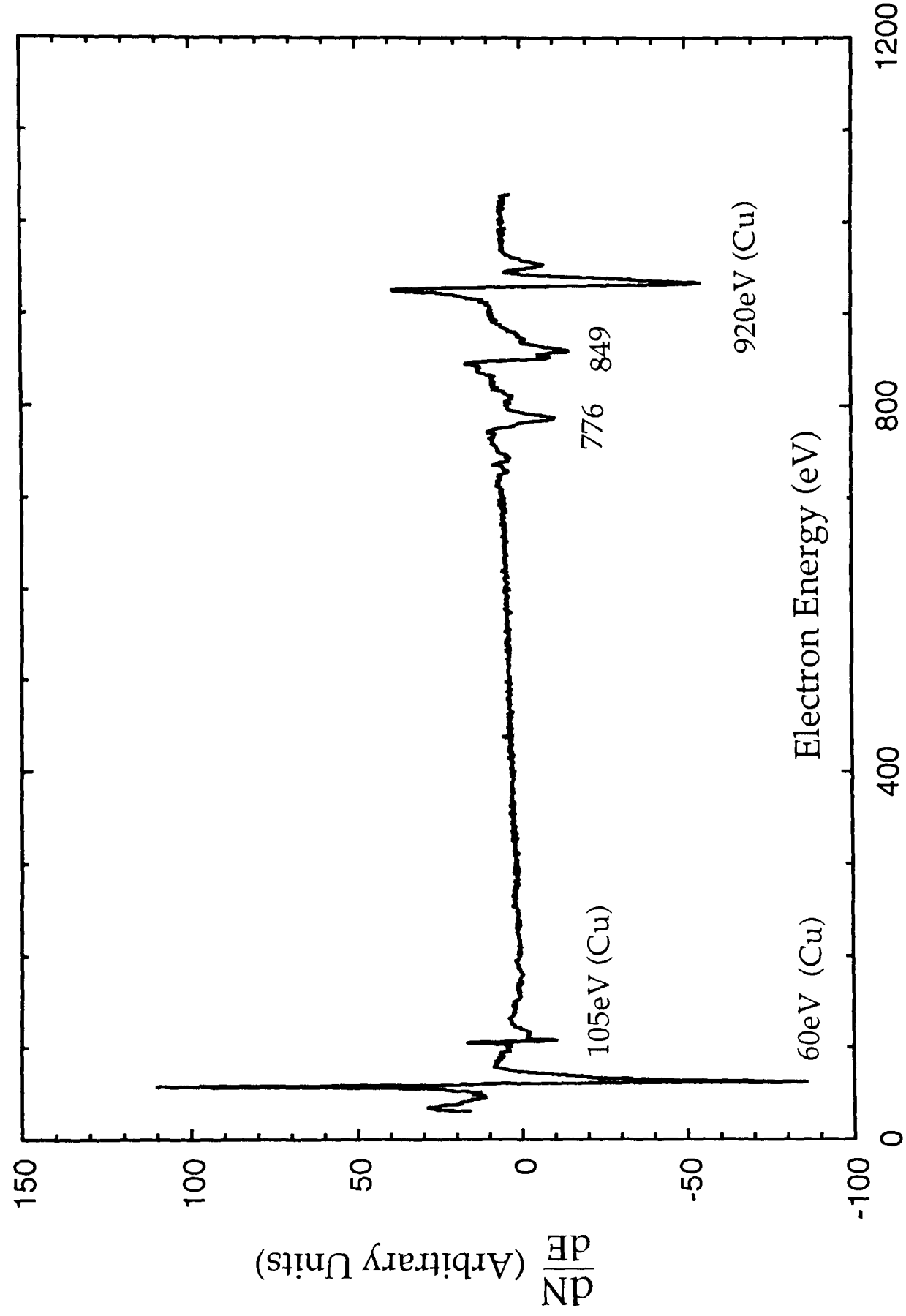


Figure 3.11: An Auger spectrum taken from a clean Cu(110) surface.

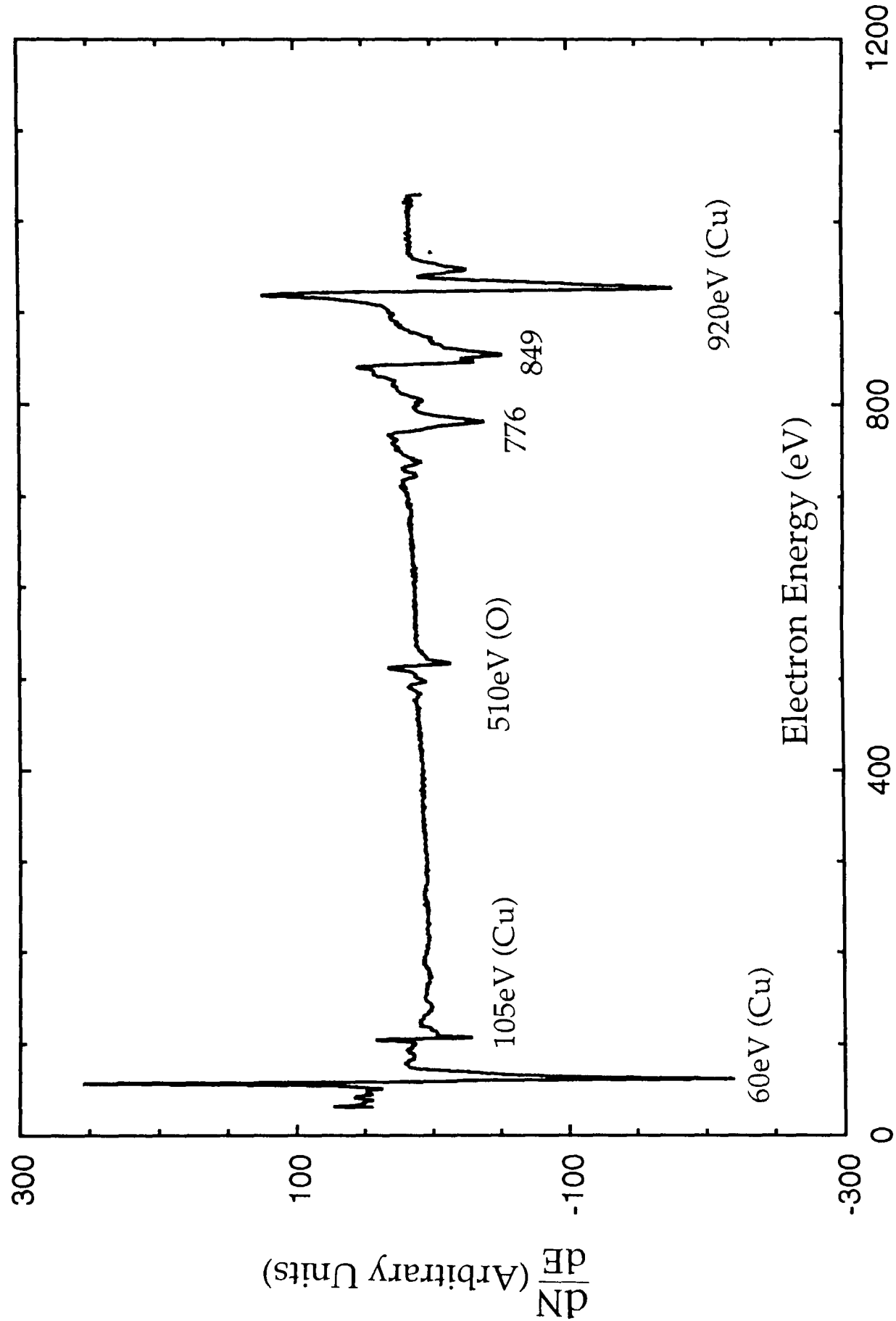


Figure 3.12: An Auger spectrum taken from a Cu(110) surface modified by the exposure of 3 Langmuir of oxygen.

3.6 Mass Spectroscopy:

It is always necessary to know the composition of an Ultra High Vacuum, especially where gas-dosing experiments are envisaged. When dosing with a particular gas, care should be taken to ensure that the dosing pressure is well above the largest single partial-pressure of any of the background gases. Equally, the dosing pressure should be not too high because with the proportionately shorter exposure time required for a given dose, errors due to the “switch-on” and “switch-off” times of the gas in the chamber become more significant. A mass spectrometer works by detecting ionised particles in the vacuum chamber. When dosing with a complex molecule, a number of ions of different mass:charge ratio are formed. It is important to check the characteristic “cracking-pattern” of the molecule, where the relative numbers of each different ionised species are noted down and compared against a reference pattern. The mass-spectrum cracking-pattern of an organic molecule 1-bromo 2-chloro ethane is shown in **figure 7.2** on page 168.

3.7 Surface preparations:

The metal crystals used in this thesis (see **Section 3.8**) were spark-cut from a single crystal rod. Because of the design of the sample holder, the crystals took on a top-hat like appearance with an inner diameter 6mm, an outer diameter 9mm and a total height 3mm of which the “brim” of the top hat accounted for 2mm. Prior to insertion in the microscope, the crystals were polished using progressively finer grade alumina paste (down to a particle size of 0.05 μ m). After ultrasonic-cleaning using ethanol and then distilled water, the crystals were inserted into the UHV chamber to commence sputtering and annealing.

3.7.1 Ion-Sputtering:

The commonest way to prepare a clean metal surface in Ultra High Vacuum is to subject it to a process known as ion-sputtering [3.17]. Energetic ions are fired at the surface of interest to strip away surface material via a momentum transfer process. Sputtering removes not only the major surface constituent but also any contaminants present. The sputter process causes considerable damage to the surface and so it is necessary to anneal the crystal to approximately three-quarters of its melting point in Kelvin for a few minutes to restore surface order. The annealing process may well cause bulk-impurities to move to the surface, necessitating subsequent sputter-anneal cycles; however after a few cycles of this nature it is possible to produce a flat well-ordered contaminant-free surface.

The UHV system in Aarhus made use of the Princeton Research Instruments PHI Model 04-303 differentially-pumped ion-gun. The basic principles of operation are as follows: Neon gas atoms enter an ionisation-chamber through a leak valve connected to a gas bottle. When the filament in the ion-gun is heated, electrons are emitted and they are attracted to a positively-biased grid (see **figure 3.13** overleaf). Most of the electrons pass through the grid and strike neon atoms in the ionisation-chamber. These collisions eject valence electrons, producing positively-charged ions, which are then withdrawn from the ionisation-chamber under the influence of a negatively-biased extractor lens. The ions are then focused by a lens-system into a 10 mm diameter spot on the sample. The ion-gun makes use of the principle of differential pumping. An aperture is placed in front of each lens, thereby creating a pair of mini “chambers” each of which is separately pumped by an external turbo-pump. This method lowers the necessary chamber-pressure of neon, which results in cleaner surfaces.

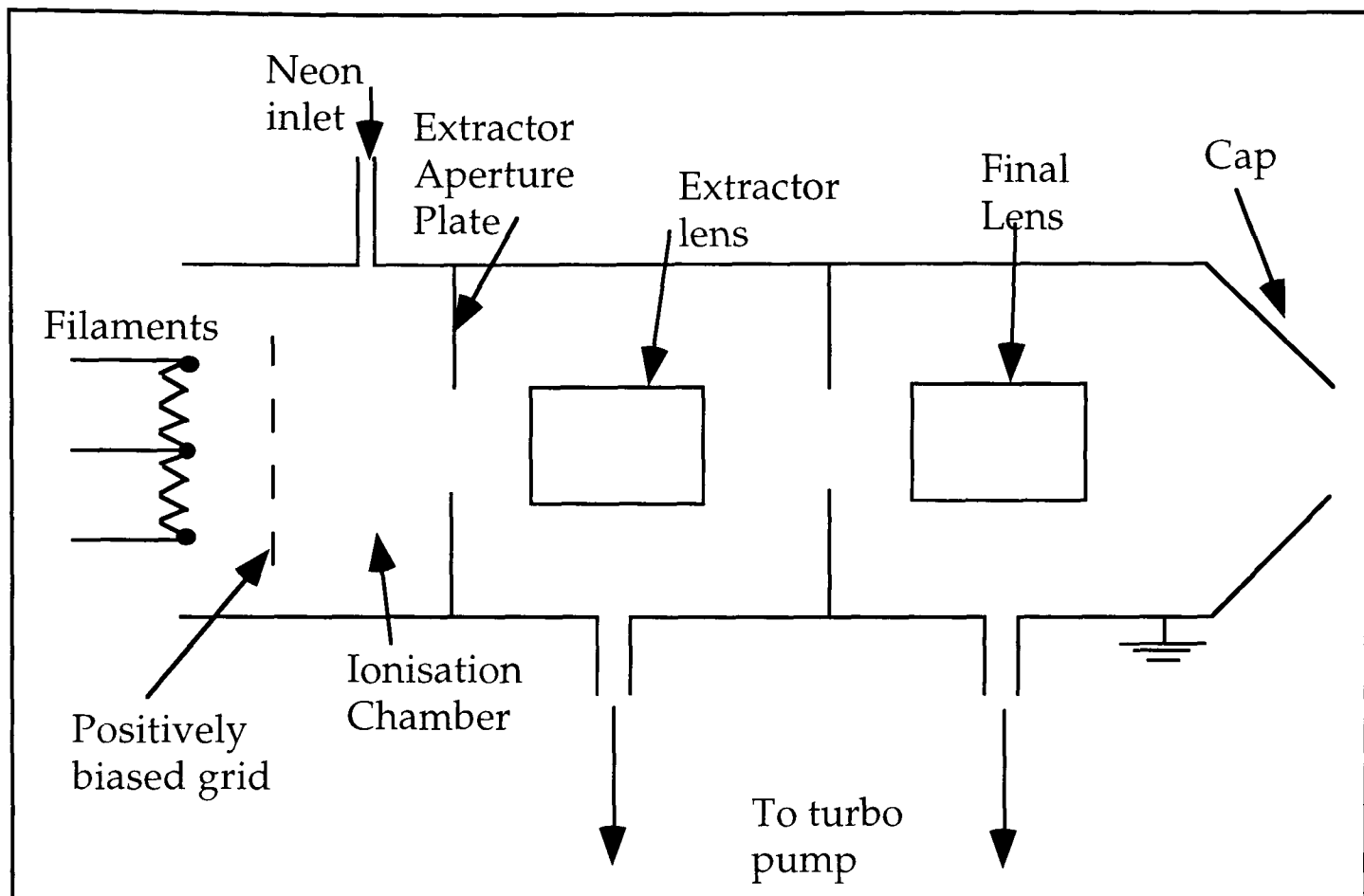


Figure 3.13: A schematic diagram showing the principals of a differentially-pumped ion-sputter gun.

In fact, it is a very laborious process to prepare a freshly-polished crystal for insertion into the STM with a realistic hope of acquiring some useful data. Even highly-polished crystals can still have significant surface contamination problems. The work in this thesis was centred around copper. Musket et al. [3.18] have shown that polycrystalline copper, the (100), (110) and (111) single crystals are contaminated by carbon, oxygen and sulphur. The (111) crystal also has traces of chlorine and nitrogen.

In order to prepare the Cu(100) surface used in this work, a series of Neon-ion sputter-anneal cycles were performed. These cycles were continued until sharp LEED spots indicated a well-ordered (1x1) surface, and no impurities could be detected by Auger Electron Spectroscopy (AES). Sputtering took place in a neon atmosphere (Pressure $\sim 1 \times 10^{-7}$ mBar) and lasted 15 minutes using ions of energy 4keV. The ion-current as measured at the sample was $\sim 10 \mu\text{A}$. The crystal was then annealed at 530°C for 15 minutes.

3.8 Sample Holders:

The metal crystals used in this work were mounted in holders shown in **figure 3.14** overleaf. The sample holders were constructed from a rectangle of tantalum sheet of thickness 1mm with a centrally located circular hole, of diameter 6mm into which the crystal face was inserted. The shoulders of the crystal were pressed down rigidly onto the back plate of the holder by a spot-welded tantalum-foil belt. The sample holder has two thin wire grips which pass through a Macor block, which is itself attached to the rear of the sample holder by two stainless steel screws. The grips allow the manipulator arm to move the sample through the chamber to all the different preparation and analysis tools. The thin wire grips also serve an additional role, as together with the wires shown in **figure 3.14(iii)**, they form a chromel–alumel thermocouple which measures the temperature at the back of the crystal. Ideally, the thermocouple should be located on the top surface of the crystal. However, since the crystals are relatively thin (3mm) and have a high thermal conductivity, it can be expected that the thermocouple readings are a good representation of the surface temperature. The crystals are electron-beam heated using a tungsten filament in close proximity ($\sim 2\text{mm}$) to the tantalum back-plate. The filament is held at -1kV with respect to the earthed sample in order to accelerate the electrons into the back-plate which increases the efficiency of their heating effect.

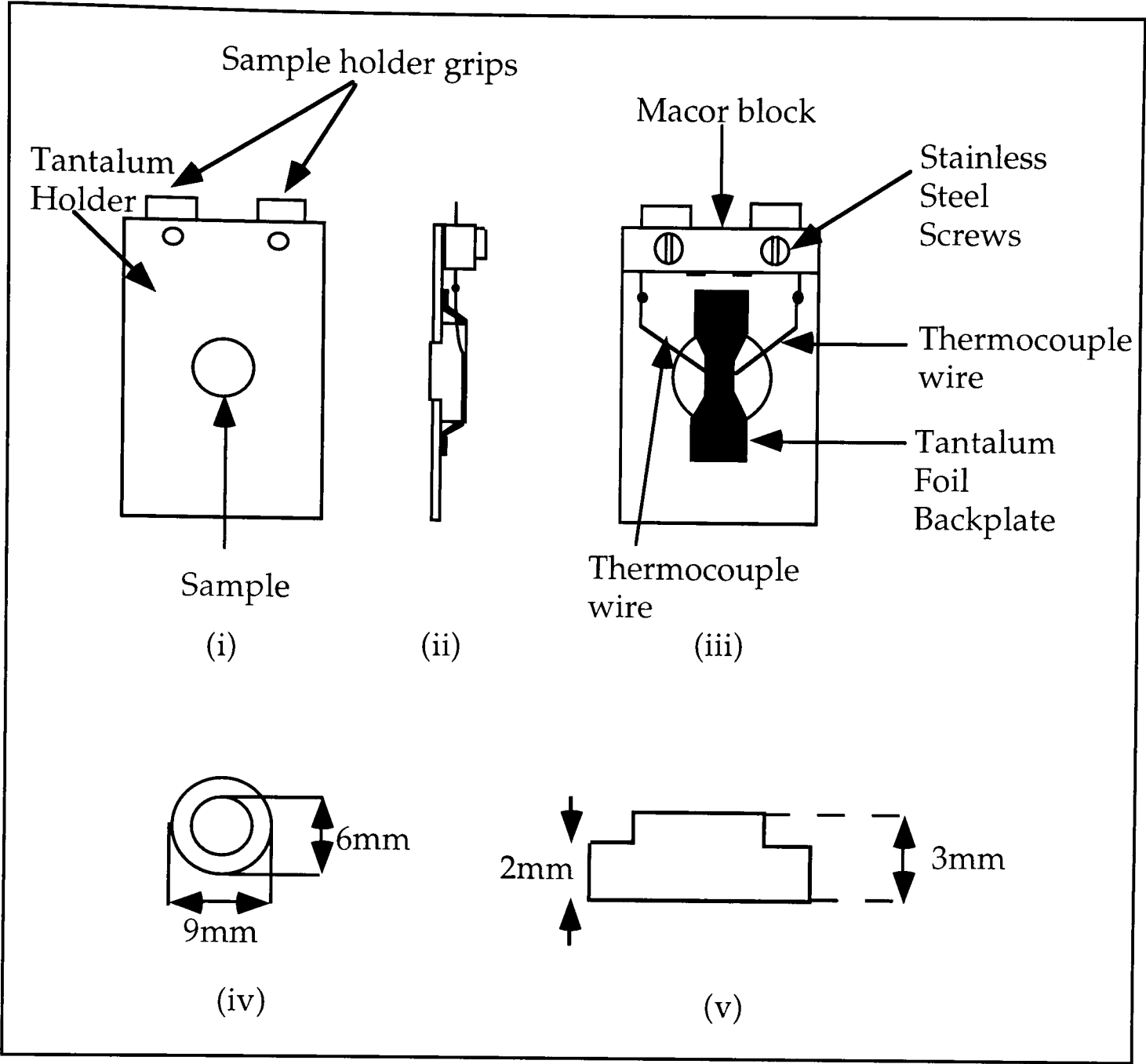


Figure 3.14: Three views of the sample holders used in this work: (i) front, (ii) side and (iii) reverse and two views of the crystals (iv) top and (v) side.

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- [3.10] E. Lægsgaard, F. Besenbacher, K. Mortensen, and I. Stensgaard, *J. Micros.*, **152**, 663 (1988).
- [3.11] PZ-27 piezoelectric elements were obtained from Ferroperm A/S, Trorod, Vedbæk, Denmark, DK 2950.
- [3.12] Macor is a machinable glass ceramic of approximate composition 46SiO_2 , $16\text{Al}_2\text{O}_3$, 17MgO , $10\text{K}_2\text{O}$, $7\text{B}_2\text{O}_3$. It is widely commercially available for example at Goodfellows of Cambridge, Cambridge Science Park, Cambridge, CB4 4DJ, U.K.
- [3.13] Viton is a fluoroelastomer (also known as poly (2-fluorobuta-1, 3-diene)), which is capable of withstanding baking temperatures of up to 150°C , it is manufactured by DuPont U.K. Ltd, Wedgwood Way, Stevenage, Hertfordshire, SG1 4QN U.K.
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Chapter 4

Tunnel Barrier Heights

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4.1 Introduction:

The workfunction of a clean metal surface is defined as the work done (in some infinitely slow, reversible thermodynamic process) to remove an electron at the Fermi level to a point well above the surface. The final ‘resting-place’ of the electron should be a position where the electric potential is uniform. This requires the electron to be placed at a large enough distance above the surface ($>100\text{\AA}$) for image forces to be negligible, but also at a distance that is small in comparison with the lateral extent of the emitting surface so that electric-field lines due to the removed electron do not extend beyond the rim of the surface [4.1]. However, STM operates at small tip-sample separations ($\sim 5\text{-}10\text{\AA}$) where the interface potential experienced by a tunnelling electron may well vary in directions both parallel and perpendicular to the sample surface [4.2]. Thus the tunnel barrier height should not necessarily be regarded as equal to the surface workfunction.

Most STM images are interpreted using the Tersoff and Hamann model [4.3, 4.4], in which the tip traces out contours of charge density above the surface. These contours are given in principle from a combination of atomic positions and the local density of states for the chosen imaging energy. Since the publication of their work, very few quantitative models of STM experiments have been presented. The primary reason for this is the uncertain nature of both the tip chemistry and its geometry. In addition, the variation of the decay length, κ , and hence the mean tunnel barrier height, ϕ_M , above the surface is not well understood ($\kappa \propto \phi_M^{1/2}$, see equation (4.1)). This relative weakness of quantitative modelling is not of serious concern when STM is used to determine lateral atomic geometry in cases where the surface electronic structure is not complex, such as is the case for metal surfaces. However, a better understanding of the factors involved in STM imaging is desirable, particularly for images of semiconductors, which show strong effects of surface-electronic structure and probably tip-electronic structure too.

In a quantitative, energy-dependent simulation of Si(113) images, Wilson et al. [4.5] have shown that site-dependent tunnel barrier heights are needed to account for the experimental images obtained when imaging the empty-states of this surface. The simulation indicates that except for special cases such as for example where the height variation of atoms normal to the surface is large or where local variations in LDOS are pronounced, local tunnel barrier heights are likely to be most important in determining what is seen in STM.

The main objective of this Chapter is to present an investigation of the tunnel barrier height. The material in the remainder of this Chapter is organised as follows: Section 4.2 describes earlier methods used to measure the tunnel barrier height, while previous experimental findings are presented in Section 4.3. A new method for deducing the tunnel barrier height, based upon the decay of vertical corrugation in a sequence of topographic images is presented in Section 4.4. In Section 4.5, a method of stabilising the scanning tip is discussed. The corrugation height data obtained for the Cu(100) surface is presented in Section 4.6. The implications of these data for the STM imaging process are discussed. Finally in Section 4.7 values for the tunnel barrier height deduced from the corrugation data are calculated.

4.2 Measurement of the Apparent Barrier Height:

Experimental values for the apparent barrier height, ϕ_{APP} , have previously been calculated by using the one-dimensional model of Simmons [4.6, 4.7]. Using the WKB mean barrier approximation, the tunnel current, I , between two free-electron like parallel electrodes is calculated as a function of their separation, s , and the bias voltage, V , see equation (4.1) below.

$$I \propto \frac{V\phi_M^{1/2}}{s} \exp(-2\kappa s) \quad (4.1)$$

where κ , the decay length = $\frac{(2m_e\phi_M)^{1/2}}{\hbar}$ (units of κ : $\text{\AA}^{-1}$)

m_e is the mass of an electron and $\hbar = \frac{h}{2\pi}$, with h being Planck's constant

When calculating the apparent barrier height, many research workers (for example see [4.8]) ignore the separation dependent pre-exponential factors in equation (4.1). These terms contribute a small amount to the variation in tunnel current compared with the exponential term and are partially self cancelling anyway. Hence the apparent barrier height is often calculated using equation (4.2) below:

$$\phi_{\text{Apparent}} = \frac{\hbar^2}{8m_e} \left(\frac{\partial \text{Ln}(I)}{\partial s} \right)^2 \quad (4.2)$$

In this work, the "apparent barrier height" refers to the result of an experiment to measure the quantity defined by equation (4.2). The term "mean" tunnel barrier height refers to an idealised model such as the multiple image-potential reduced tunnel barrier described in [4.17] and Section 5.2 of this Thesis.

It is possible to measure the apparent barrier height by systematically observing the decay in tunnel current as the tip-sample separation is increased [4.9]. However, it is generally quicker, to use a modulation method. Using this latter technique, a high frequency displacement, $\Delta s(\omega)$, is applied to the z-piezo so as to change the tip-sample separation. A current modulation is associated with the change in tip-sample separation. From the ratio of the "modulation" current and the "topographic" current, an approximation for the derivative $\left(\frac{\partial \text{Ln}(I)}{\partial s} \right)$ can be made. By repeating the measurement at every pixel in the topographic image, barrier-height images may be taken at the same time as topographic images. Both images have the same basic spatial features and some authors [4.10, 4.11] have argued that "barrier height" images are to be preferred as they have a higher signal to noise ratio.

In certain circumstances when measuring the tunnel barrier height, it may not be correct to equate the change in length of the z-piezo element with the change in tip-sample separation. When using the gap-width modulation technique to deduce $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$, care must be taken to ensure that the modulation frequency is kept well away from any mechanical resonances of the system. Near such resonances, there is a considerable enhancement of the actual tip motion over the calibrated motion. Any such errors are particularly severe as they are doubled in the measurement of the tunnel barrier height.

The choice of modulation frequency is crucial to the barrier height measurement. The frequency of modulation is usually above that of the feedback loop so as not to interfere with the basic topographic measurement. However, if an insufficiently high modulation frequency is used, then thermal drift may cause the tip to move to adjacent topographic sites during the measurement. Drift in the z-direction during a measurement can also lead to erroneous values for the modulation-induced tunnel current. When operating at excessively high modulation frequencies, the z-piezo does not exhibit a linear response as a function of applied voltage and it can be difficult to obtain a good calibration of its change in length. Generally a modulation frequency of about half the lowest mechanical resonance of the system is used for barrier height measurements.

In a pre-STM investigation of the current-distance characteristics of a variable-width vacuum tunnel-gap between two gold spheres, Teague [4.12] found it necessary to correct their measured separation for the effects of a minute deformation of opposing sphere faces when in close proximity.

More recently, Chen and Hamers [4.13] found it necessary to take account of tip-surface forces acting on the tip-apex in STM barrier height measurements above Si(111).

4.3 Measurements of the Tunnel Barrier Height:

In spite of the difficulties discussed in section 4.2, it is interesting to note that experimentally-measured values for the apparent barrier height above clean metal and semiconductor surfaces are usually close to their respective surface workfunctions [4.2, 4.13-4.17]. These results are in stark contrast to the reduction of the mean barrier height as deduced from the multiple-image-potential approximation, where at a separation of $5\text{\AA}$, the barrier is at least 2eV below its large separation workfunction ($\sim 4\text{eV}$) limit (see the discussion of Section 5.2 in Chapter Five).

It was with this paradox in mind that Coombs [4.17] examined the behaviour of the derivative $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ over a wide range of tip-sample separations. By explicitly including all the distance dependent pre-exponential terms of equation (4.1) when calculating the current-distance derivative, Coombs was able to show that the apparent barrier height remained almost equal to its workfunction limit down to separations of $\sim 5\text{-}6\text{\AA}$. This result was due to the variation of the multiple image-potential reduced tunnel barrier with tip-sample separation which caused the apparent barrier height to be overestimated at a given separation. Other workers in the field [4.18, 4.19] have reached similar conclusions about the behaviour of the apparent barrier height.

Using an iridium tip and polycrystalline iridium sample, Dürig et al. [4.20] have found that the apparent barrier height remains at a constant value of 5eV with decreasing tip-sample separation right down to the formation of a tip-surface point contact. Olesen [4.21] has reached similar conclusions, using a tungsten tip forming a point contact with Ni(100), Cu(100) and Pt(100) (the tunnel barrier height taking values of 2-3eV). However, Dürig et al. [4.20] argue that what they observed may have been caused by the accidental cancelling out of the opposing influences of tunnel barrier collapse and the increasing participation of iridium d-electrons in the conduction process at small separations. They found that the tunnel barrier did in fact collapse when this experiment was repeated for a polycrystalline aluminium surface.

Additional experimental evidence for the collapse of the tunnel barrier at very small tip-sample separations can be found in work by Gimzewski and Möller [4.22]. Using an iridium tip and a polycrystalline silver surface, the tunnel current was monitored as a function of tip-displacement towards the surface starting from a reference point taken as $I = 1.2\text{nA}$, $V = -20\text{mV}$. The apparent barrier height was observed to decrease from 3.5eV at a displacement of $1\text{\AA}$ to 1.5eV at a displacement of $3.5\text{\AA}$. At a tip displacement above $4\text{\AA}$, there was a discontinuity in the measured tunnel current which was assumed to correspond to the formation of a point contact and the collapse of the tunnel barrier. The major conclusions of this study have been reproduced in a calculation by Lang [4.23] who used a jellium model, where the tip is simulated by a single sodium atom adsorbed on one of the electrodes. Kuk and Silverman [4.24] have also observed the collapse of the tunnel barrier in studies of the Au(100) (5x20) surface .

The discussion of this and the previous section illustrates the general uncertainty about the tunnel junction, and the difficulties encountered in making accurate measurements to investigate this region. At least part of the reason for our poor understanding of the tunnel barrier height is that experiments still cannot be performed using tips of known, and more importantly reproducible, geometry and chemical composition. The use of polycrystalline surfaces in experiments only adds to the difficulty of data interpretation. Gomez-Rodriguez et al. [4.25] have recognised the problem of surface topography in barrier height measurements. They tried to separate topographic effects from potential variations by calculating the cosine of the angle between the local surface normal, ds , in the STM topographic image and dz , the tip-modulation direction, see **figure 4.1** below. Images of $\cos(s,z)$ were compared to $\left(\frac{\partial \text{Ln}(I)}{\partial z}\right)$ images; differences at equivalent points in each image were ascribed to changes in the surface chemical composition.

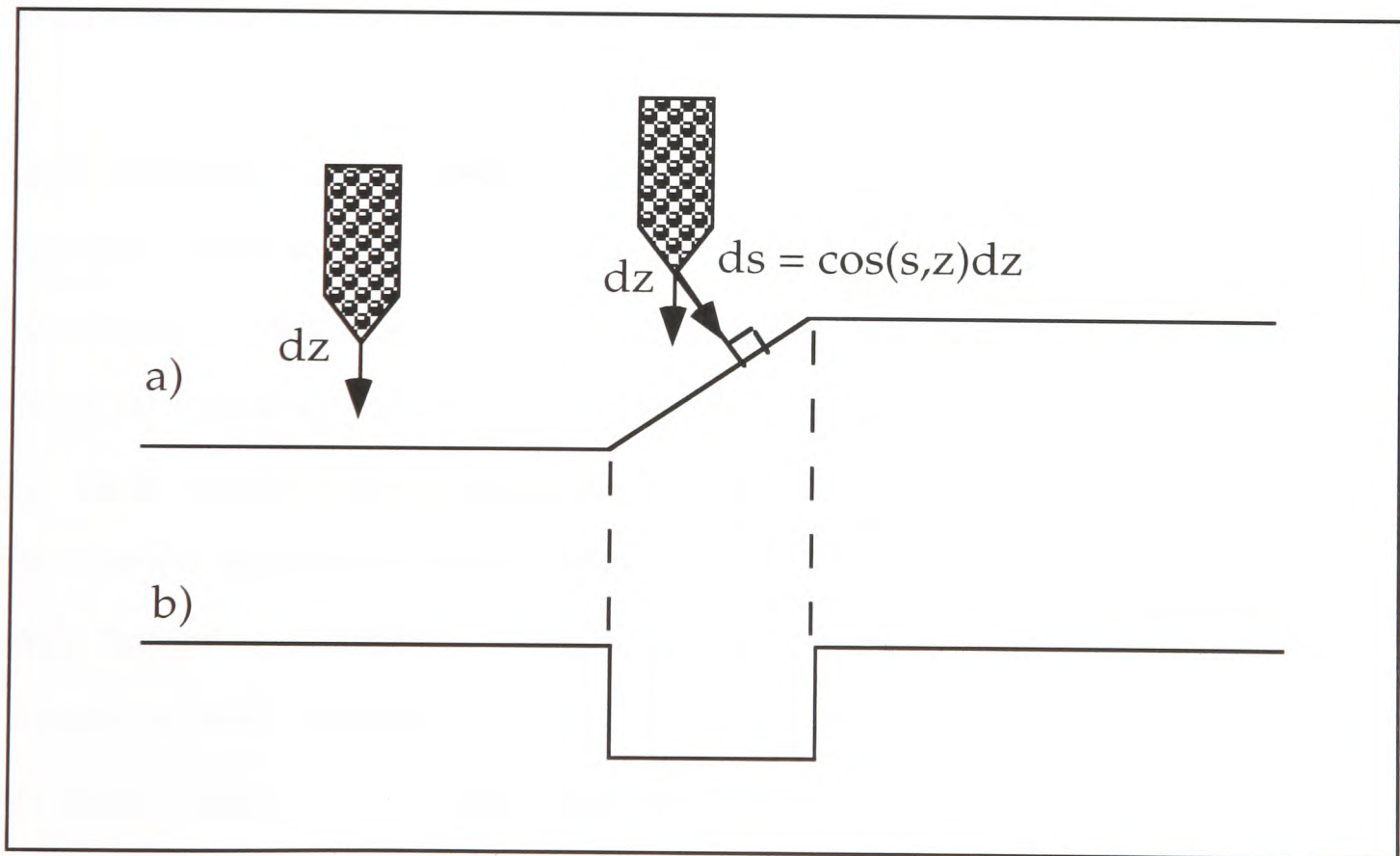


Figure 4.1: A schematic diagram illustrating the topographic contribution to the STM barrier-height images. a) A topographic profile, b) The corresponding $\cos(s,z)$ profile. (s,z) is the angle formed by the normal vector to the surface at each point (ds) and the modulation direction (dz). Note that a step in topography corresponds to a depression in the $\cos(s,z)$ image.

4.4 Corrugation Heights:

In this section, a new method for measuring the tunnel barrier height is presented. The key feature of this technique is that calibration difficulties are minimised because the measurement uses the normal constant current mode of STM which by design is most accurate. The z-calibration of the tip motion is well established from measurements of step heights so that accurate measurements of corrugation heights can be made. By using conventional STM images in this method, there is no need to complicate the experiment by sending additional electronic signals from for example, lock-in amplifiers to the constant current feedback loop. Because only one measurement is taken per image pixel, problems due to thermal drift of the tip are reduced as far as is possible. The avoidance of a tip-modulation in this measurement eliminates problems associated with resonance effects and interference with the constant current feedback loop.

The technique employed to calculate the tunnel barrier height is to measure the rate of decay of the vertical corrugation in the surface charge density as a function of decreasing tunnel gap conductance, $\sigma \left(= \frac{I}{V} \right)$. A series of topographic images are taken in quick succession using the same tip. Each image is of the same area of the surface, but is taken at a different tip-sample separation. Experimentally this parameter is varied by taking each image at a different tunnel current, while the potential bias on the sample is held constant. Systematic measurements of corrugation heights are made along the principal directions in each image. A $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot is then made for each data set which is used to deduce the parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \right)$ and hence the tunnel barrier height, via equation (4.4) overleaf. In principle, this experiment could be performed by varying the potential bias, while keeping the tunnel current constant. However, it was found to be easier to vary the separation by changing the tunnel current.

In this Thesis, the data obtained is interpreted using the model of Tersoff and Hamann [4.3, 4.4]. They assumed the simplest possible electronic structure for the tip, namely that it can be approximated as a spherically symmetric s-wavefunction located at the centre of curvature of the macroscopic tip. Contributions to the tunnel current due to tip-wavefunctions with angular momentum dependence (characterised by quantum number $l \neq 0$) were neglected as such wavefunctions are in comparison with s-waves not so spatially extended. By considering the limits of low temperature and small bias voltage, it was shown that the STM tunnel current was proportional to the Fermi level surface Local Density Of States evaluated at the centre of curvature of the tip. As noted in Chapter One, this result is independent of the assumed tip structure and implies that when imaging a metal surface in constant current mode, the data obtained can be loosely thought of as a contour map of surface charge density.

Using a one-dimensional model, with a plane-wave basis for the surface wavefunctions, Tersoff and Hamann [4.3, 4.4] were able to show that for periodic surfaces, the local density of states (LDOS) at the Fermi level had the periodicity of the underlying surface-lattice and could hence be Fourier analysed using surface reciprocal-lattice vectors as an expansion basis. At large distances above the surface, the STM image is dominated by the terms in the Fourier expansion with the smallest decay constants. By assuming the STM image to be well characterised by the zeroth order term and the first oscillatory term of the Fourier series and making use of the experimental condition of constant current, an expression was derived for the peak to trough amplitude, Δ , of the corrugations above the surface at an average distance, s , see equation (4.3) overleaf and **figure 1.1**:

$$\Delta \propto \frac{1}{2\kappa} \exp(-\beta(s+R)) \tag{4.3}$$

where $\beta = 2\left(\kappa^2 + \frac{G^2}{4}\right)^{1/2} - 2\kappa$ with $G = \frac{2\pi}{a}$ (a reciprocal lattice vector)

s = vertical height above the surface and R is the tip radius of curvature

Equation (4.3) implies that for a given mean tip-sample separation which corresponds to a particular value for the tunnel current, a tip with a larger radius of curvature will measure a smaller corrugation height than a tip with a small radius of curvature.

Although the theory of Tersoff and Hamann is by no means the last word in STM imaging theory, their model is used here because of the particularly transparent physical meaning it gives to STM images when imaging at small bias voltages. By combining the equations for the tunnel conductance (4.1) and corrugation height (4.3) but assuming the contributions of the pre-exponential terms of both equations to be constant, the "corrugation-height" deduced tunnel barrier, ϕ , is given by equation below (4.4):

$$\phi = \frac{\hbar^2 G^2}{8m_e X} \tag{4.4}$$

where $X=(b(b+2))$ and b is the gradient of a $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot.

Before starting a set of experiments, particularly after making some repairs to the STM, it is important to check the calibration of the piezo-elements. For the x- and y-piezo elements this procedure was undertaken by taking some atomic-scale resolution images and then measuring the inter-atomic

spacing along the principal directions in these images. By comparing these values against those obtained from X-Ray diffraction data [4.30], calibration factors could be added if necessary in the data acquisition software to correct the motion of the piezo-elements. It is harder to calibrate the z-piezo motion. This is because for an accurately cut crystal there are comparatively few steps in the surface and it also requires a high quality tip to image the terraces on either side of the step. Moreover, when imaging a material such as copper at room temperature, there is a lot of step-atom motion [4.31] which leads to rather fuzzy and ill-defined step edges in STM images, see **figure 4.2** below. Once a good image of a step has been obtained the same ideas discussed above apply to the calibration of the z-piezo motion.

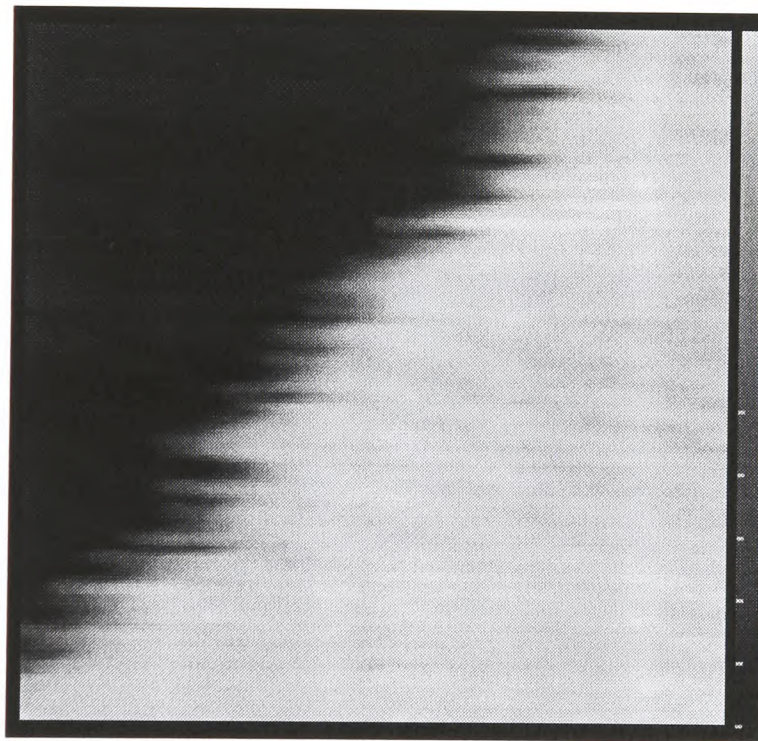


Figure 4.2: A 70x70Å (vertical scale 1.4Å) STM image of two terraces of Cu(100) separated by a step edge. A weak atomic corrugation can just be perceived on the right-hand terrace. This image shows that at room temperature there is considerable amount of step-edge atom motion.

4.5 Tip Stability:

At the beginning of many imaging sessions, the tip was rather unstable and susceptible to spontaneous changes. A requirement of the technique

developed in this work is that the tip is completely stable over a period of several hours. It was sometimes possible to stabilise the tip by making a number of indentations into the surface (~ 25 over a period of a few minutes). In this process, the feedback loop was switched off and the tip pushed a small depth (up to $10\text{\AA}$ as measured by the change in length of the z-piezo element) into the surface. Such an indent gives rise to the formation of a protrusion on the surface at the site of the indentation, see **figure 4.3** below. These indentations do not all have the same effect, a shallow indent may give rise to a much larger protrusion than a deeper indentation. Eventually though, a point is sometimes reached at which a stable tip is created. A stable tip is regarded as one which does not form a protrusion as a result of indenting the tip in to the surface five or six times in a row. It is then possible to start imaging with the probability of a tip change occurring being greatly reduced.

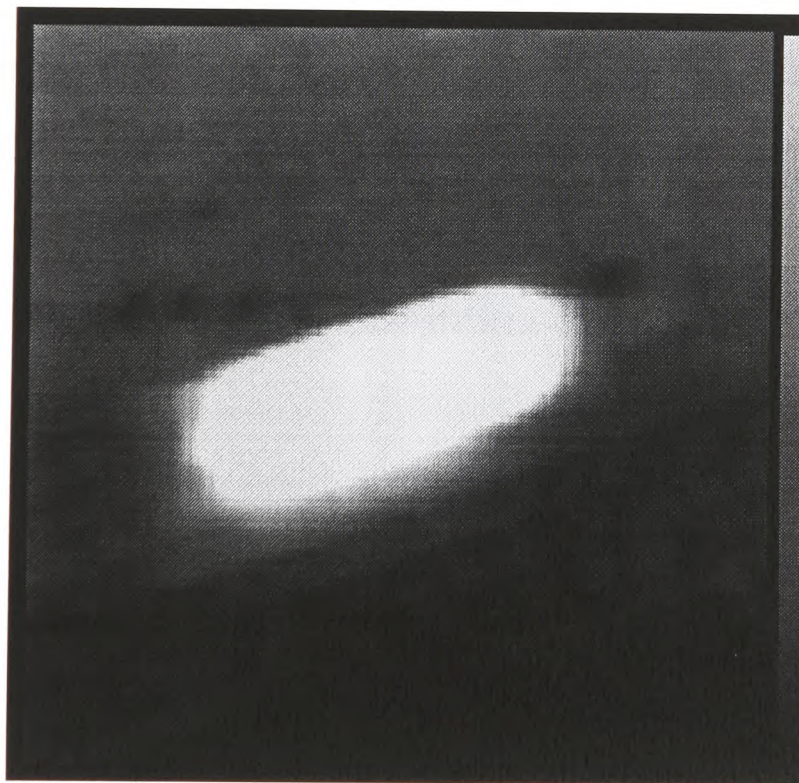


Figure 4.3: A $70 \times 70\text{\AA}$ (vertical scale $1.1\text{\AA}$) STM image of a Ni(110) surface showing an indentation-induced protrusion. The dimensions of this feature are approximately $40\text{\AA}$ long, $15\text{\AA}$ wide and $1.2\text{\AA}$ high. Although it is not clear from the background of this figure, the long axis of this protrusion is aligned along the $\langle 011 \rangle$ direction of the surface. This image has been slightly tilted in order to make the top half of the surface clearer to the reader.

During a sequence of indentations, it is likely that material transfer takes place across the tunnel junction. It is tempting to assume that the protrusions are tip-derived material. However, as can be seen in **figure 4.3** from the continuity in the shading scale of the image around the indentation, there is no abrupt change in the height of the surface at the point at which the tip made contact with the surface. In other words, the tip geometry does not change as a result of the indentation. The tip was made of tungsten which has a higher surface energy than either the copper or nickel substrates used in this work [4.26, 4.27] and so by plunging the tip into the surface, it is most likely that the tip needle becomes coated in a layer of surface material. Landman et al. [4.28] have investigated the process of a nickel tip indenting a gold substrate using a Molecular Dynamics (MD) simulation. Initially, there was a transfer of gold atoms from the surface to the tip in accord with the relative surface energies of the two materials. When the simulation was repeated using a gold coated nickel tip, no further transfer of matter was observed. A similar effect has been observed in an MD simulation of the indentation of an iridium tip into a lead substrate [4.29]. Such simulations could explain why the tip in these experiments becomes stable after performing a series of indents.

However, there is still the need to explain the protrusions. Olesen has investigated this phenomenon experimentally [4.21] and concludes that during an indentation, the tip acts as a drain for the flux of atoms diffusing over the surface. In **figure 4.3**, the anisotropy of this protrusion is clearly apparent and this reflects the ease of diffusion along different surface directions. During the time for which the tip is contact with the surface, not all these atoms can be transferred to the tip and as a result, a small cluster of atoms is left behind. Olesen has also observed the subsequent diffusion based annihilation of these protrusions.

4.6. Implications of Corrugation Heights:

The first extensive test of the method outlined in section 4.4 was on Cu(100). This is a surface with four-fold symmetry and there are two $\langle 0\bar{1}1 \rangle$ and two $\langle 001 \rangle$ directions along which to investigate the corrugation heights. Data obtained from this surface can thus be used to assess the effect of different surface reciprocal-lattice vectors upon the deduced values for the tunnel barrier height. A metallic surface was chosen for this experiment because under STM, metals do not usually exhibit strong voltage dependent imaging behaviour as they have a fairly high and comparatively uniform density of states near the Fermi level.

4.6.1. Experimental Method and Corrugation Height Data Analysis:

The method outlined in section 4.4 for deducing the tunnel barrier height relies upon taking good quality atomic-scale resolution STM images. This requires the use of small values for the tunnel gap resistance. Typical imaging conditions used in this work were in the range $I = 1\text{-}20\text{ nA}$ and $V = \pm 5\text{-}50\text{ mV}$, which corresponds to a tunnel gap resistance of a few Mega-Ohms (equivalent to a tunnel gap conductance $\sim 0.1\text{-}1\mu\text{S}$). By using lower values for the tunnel current and higher potential biases, the signal to noise ratio decreased and the corrugations in the image became much less consistent over the image. **Figure 4.4** overleaf shows part of a typical STM image.

The "raw" data obtained in experimental sessions was subjected to a rigorous series of tests before it was analysed in detail. The purpose behind these filtering procedures was to obtain final conclusions of as general validity as possible. This section outlines the way in which corrugation

height data sets were obtained experimentally and then explains the criteria used to accept individual data sets for a thorough corrugation analysis.

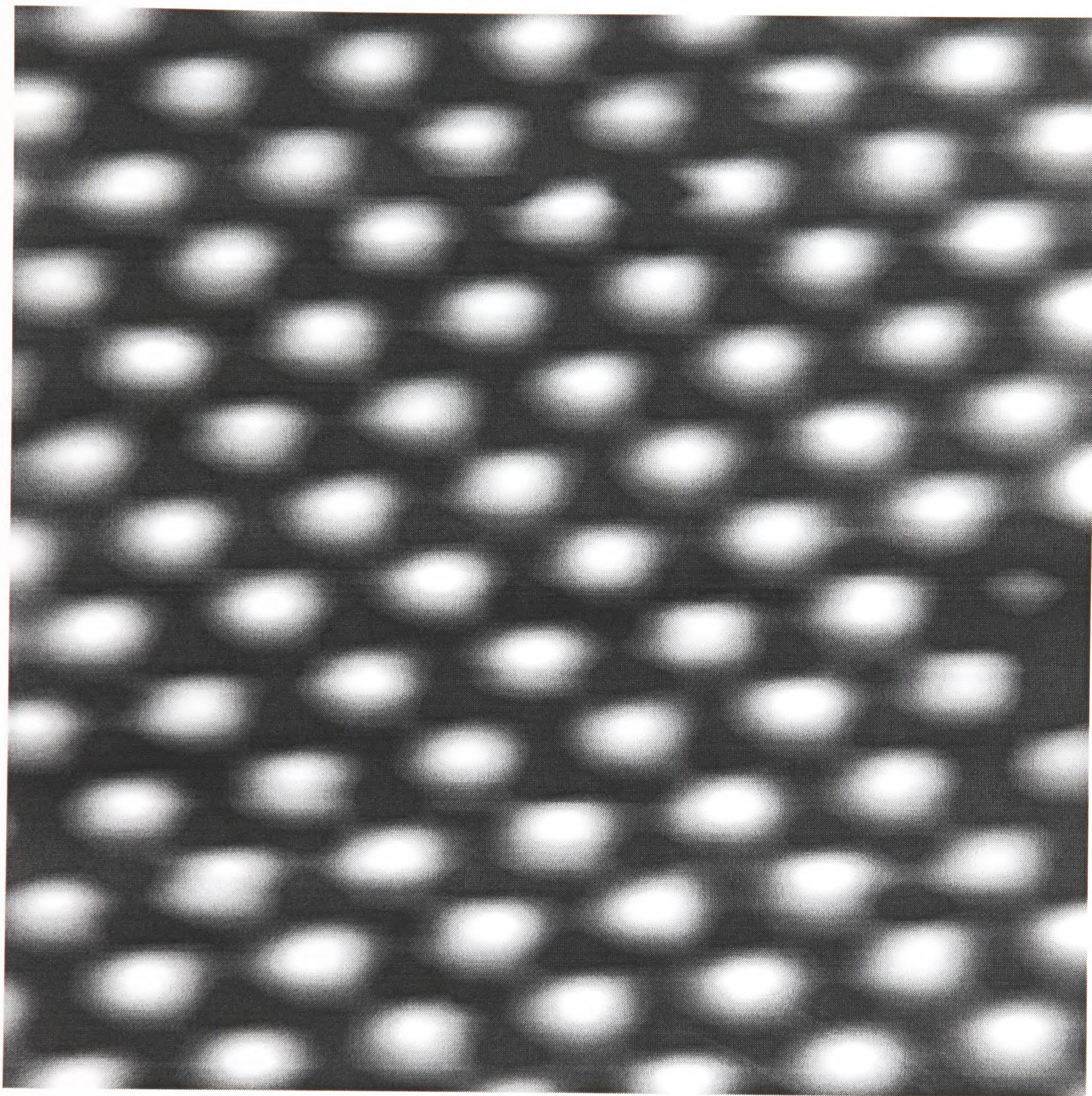


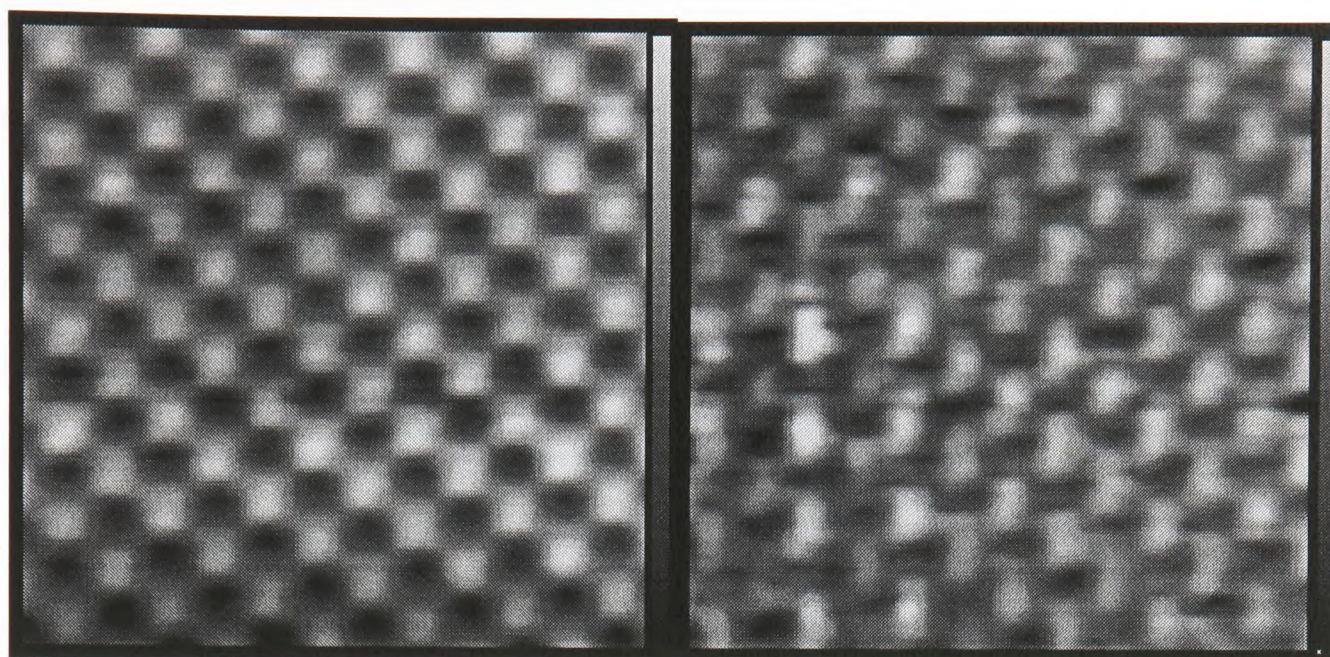
Figure 4.4: A $23\text{\AA} \times 23\text{\AA}$ (vertical scale $0.3\text{\AA}$) image of Cu(100), taken at $I=12.5\text{nA}$ and $V=28\text{mV}$. The single-atom defect on the right hand edge shows the tip is sharp.

In order to obtain a good straight line for each $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot, only data sets with images taken using at least five different sets of tunnel parameters were analysed in detail. After initial studies, it became clear that the

corrugation data did not behave linearly at large values of the tunnel conductance and so it also became important to take as many data points as possible in this latter region to investigate such behaviour.

During an individual experimental run, after adjusting the tunnel conditions until atomic resolution was obtained, five or six images were subsequently taken with each image taken at a larger value of the tunnel conductance. The next image in the series was taken using identical tunnelling parameters to the first image of the data set. After taking this second “initial tunnel-parameter” image, further images were taken using the same procedure as before and the tunnel conductance was increased in each successive image. However, typically after taking three or four more images, topographic resolution was completely lost. After such an occurrence the tip was radically altered and it was necessary to image a completely different part of the surface. As will be discussed in Chapter Six, it is thought that this loss in resolution corresponds physically to the on-set of mechanical instability with the tip crashing into the surface.

Prior to detailed corrugation height analysis, all the images in such a data set were checked to ensure that under a thorough examination they had the same basic symmetry and did not exhibit any peculiar structure indicative of a low symmetry tip. In **figures 4.5 and 4.6** overleaf, an example is presented where such an unusual structure was observed. These images were taken consecutively and only a few minutes apart. They are of the same area of the surface, the only difference being the tunnel parameters used in each case.



Figures 4.5 and 4.6: Two $30 \times 30 \text{ \AA}$ STM images. These images were taken consecutively. They are of the same area and differ only in that **figure 4.5** (left-hand image, vertical scale $0.3 \text{ \AA}$) was taken using a tunnel current, I , of 3.5 nA , while **figure 4.6** (right-hand image, vertical scale $0.45 \text{ \AA}$) was taken at 4.5 nA . The bias voltage in both cases was $+55 \text{ mV}$. It is clear that while the "atoms" are seen as squares in the left hand image, in the right hand image, not all the atoms have the same height and they take on a rectangular appearance in the image.

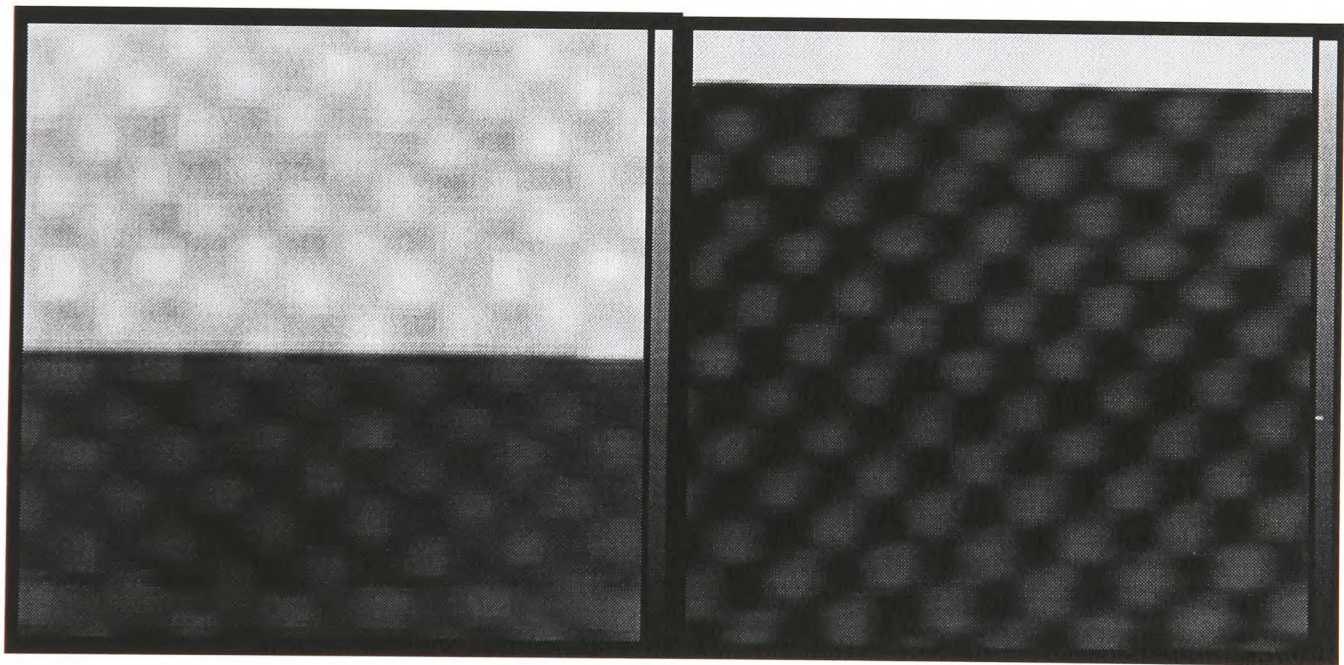
Some tip changes are by no means obvious, see **figure 4.7** overleaf and so to eliminate more subtle tip-effects, the corrugation heights for the two images in a set taken using the "initial-tunnel parameters" were analysed first. Providing these two "initial-tunnel parameter" images yielded similar values (within experimental error) for the corrugations heights, the remaining images in the data set were analysed in detail.

In a given data set, corrugation heights were separately measured for each principal crystallographic direction in each image. The length of the line traces used to measure the corrugation heights was necessarily limited by the size of the STM images taken (typically $50 \times 50 \text{ \AA}$). However, only line traces longer than five times the length of the particular surface periodicity under investigation were used in the corrugation height analysis. Starting from one end of each line trace, a vertical corrugation measurement was made between the first minimum and the adjacent maximum. The next

measurement was similarly made between this maximum and the next minimum in the sequence. This process was repeated all the way along the corrugation trace and then over all other parallel line traces in the image. An arithmetic mean value was evaluated for the corrugation height measured along this direction which took into account the different numbers of measurements made in each separate line trace.

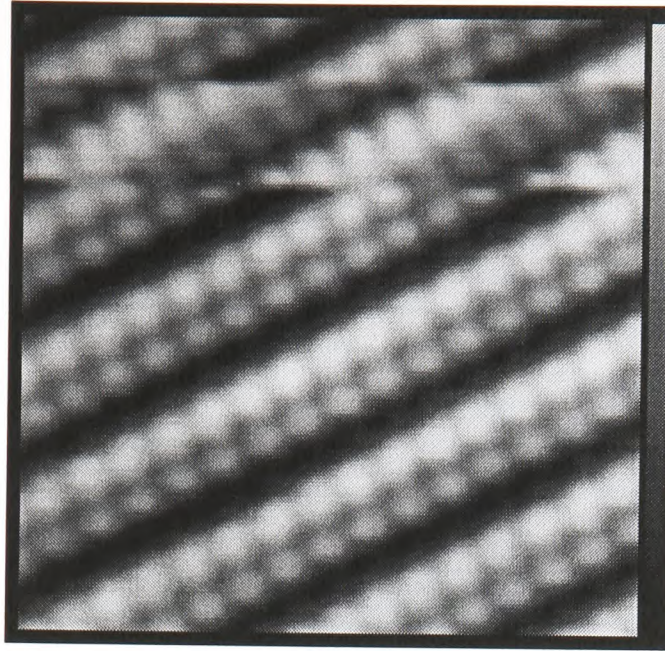
In this study, 36 sets of data taken from the Cu(100) surface were analysed in detail. For each data set, the individual corrugation data points had small standard deviations (<10% of their measured mean value).

The difficulty of obtaining these data sets should not be underestimated. At all times the operator is vulnerable to the spontaneous tip change as is illustrated in **figures 4.7, 4.8** below and **4.9** overleaf:



Figures 4.7: (left-hand image) A $30 \times 30 \text{ \AA}$ (vertical scale $0.6 \text{ \AA}$) STM image of the Cu(100) surface taken at $I=15.8 \text{ nA}$ and $V=+16 \text{ mV}$ which shows a spontaneous tip change in the centre of the image. The corrugation heights measured along the $\langle 001 \rangle$ direction change from $\sim 0.15 \text{ \AA}$ in the lower half of the image to $\sim 0.1 \text{ \AA}$ in the upper half of the image.

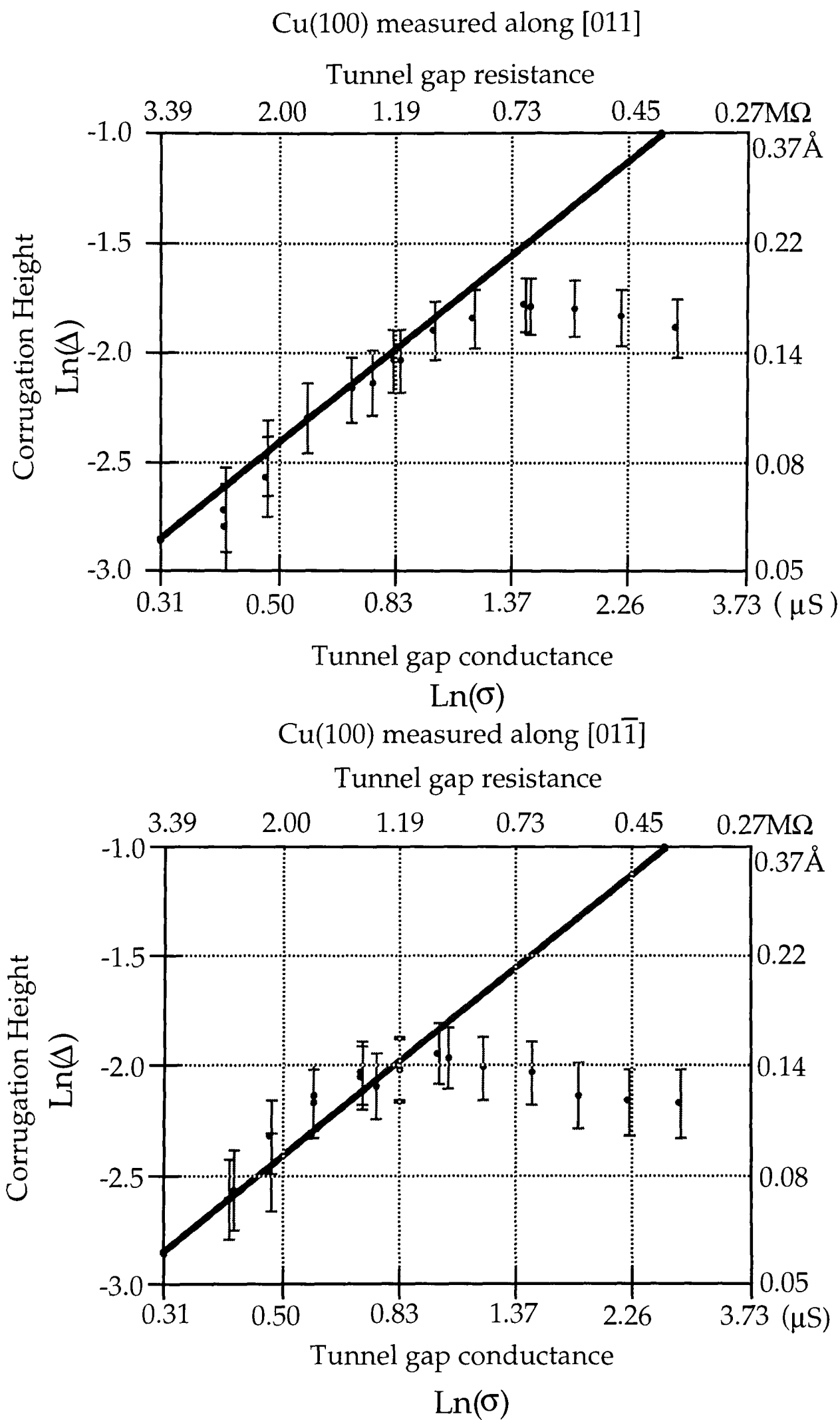
Figures 4.8: (right-hand image) A $30 \times 30 \text{ \AA}$ (vertical scale $1.4 \text{ \AA}$) STM image of the Cu(100) surface taken at $I=5.9 \text{ nA}$ and $V=+7 \text{ mV}$ which shows a spontaneous tip change leading to a complete loss in resolution in the topographic image.



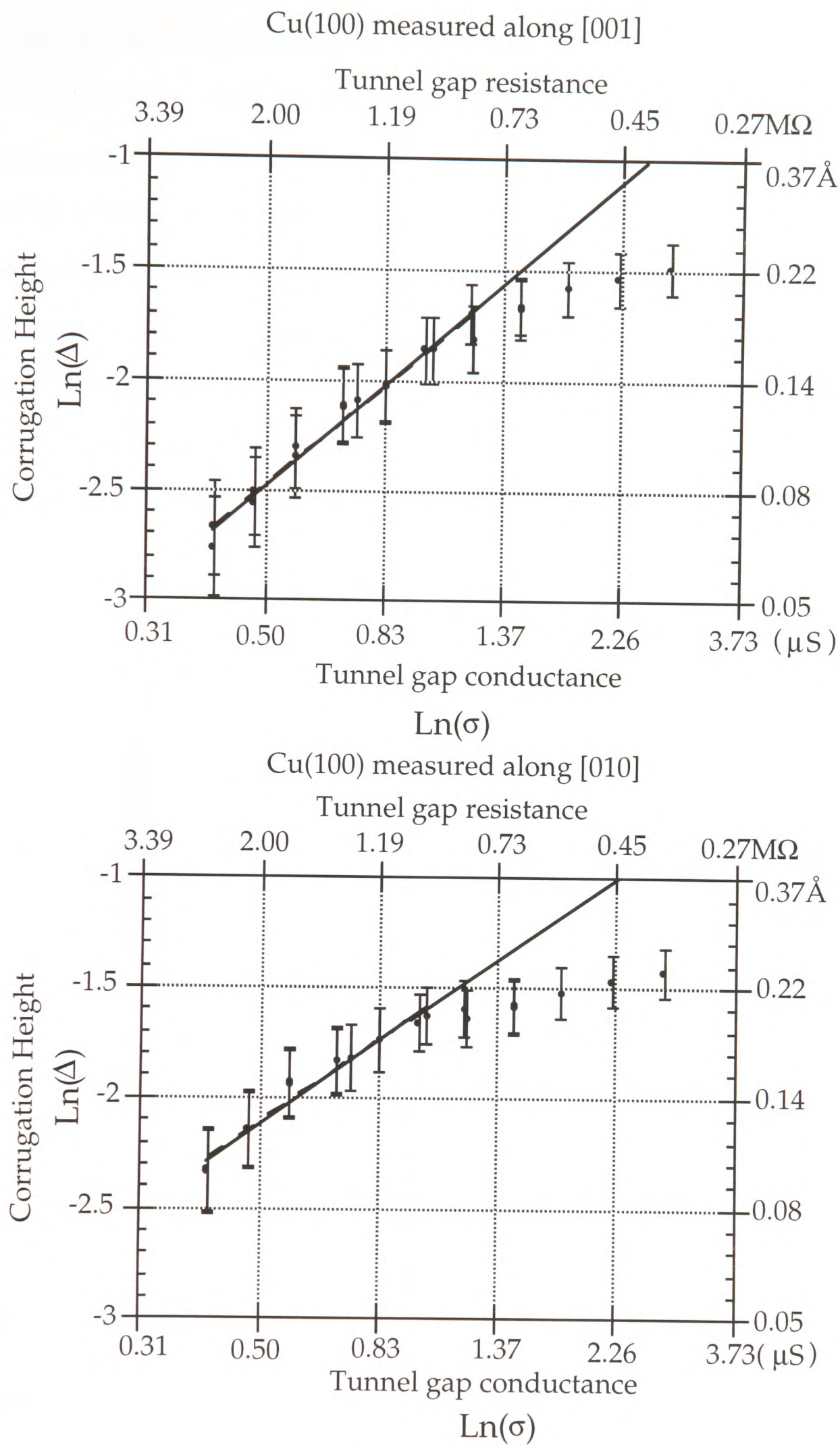
Figures 4.9: A $50 \times 50 \text{ \AA}$ (vertical scale $0.65 \text{ \AA}$) STM image of the Au(110) (1x2) reconstruction taken at $I=5.0 \text{ nA}$ and $V=-15 \text{ mV}$ which shows a short-lived jump in the lateral position of the tunnel junction.

4.6.2 $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots:

Typical experimental results are shown in **figures 4.10-4.13** overleaf. All four graphs are taken from a single experiment and show data measured along $\langle 0\bar{1}1 \rangle$ directions (**figures 4.10 and 4.11**) and $\langle 001 \rangle$ directions (**figures 4.12 and 4.13**). Data sets taken from crystallographically equivalent surface directions should ideally lead to identical corrugation measurements. The fact that there are slight differences between the two pairs of data shows that in this case the tip was not quite cylindrically symmetric about an axis perpendicular to the surface. Equation (4.3) shows how the local radius of curvature can affect the measured corrugation height. Nevertheless, each graph has two main regions to consider. At lower values of tunnel conductance, there is a linear region which is used to deduce the tunnel barrier height via equation (4.4). Beginning at a tunnel gap conductance of $\sim 1 \mu\text{S}$ (resistance $1 \text{ M}\Omega$) there is a "roll-off" region, where the corrugation height does not increase by as much as expected from a linear extrapolation of the data taken at lower values of the tunnel gap conductance. Eventually a point can even be reached at the which the corrugation heights are reduced compared with measured values at slightly lower values of tunnel conductance. As is discussed in Chapter Six, this phenomenon is interpreted as a mechanical tip-surface interaction.



Figures 4.10 and 4.11: $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots for the Cu(100) surface for corrugations measured along the $[011]$ and $[0\bar{1}1]$ directions respectively. In both figures, the right hand vertical axis shows the actual values of the corrugation height. The images were taken using a potential bias of -3mV .



Figures 4.12 and 4.13: as for figures 4.10 and 4.11, but these data were measured along measured along the [001] and [010] directions respectively of the Cu(100) surface.

When plotting the $\text{Ln}(\Delta):\text{Ln}(\sigma)$ data sets, it was necessary to take account of the finite resistance ($120\text{k}\Omega$) of the tunnel current pre-amplifier [4.16]. When imaging a surface using large tunnel gap resistances (many Mega-Ohms), the voltage drop in the tunnel gap is essentially equal to the bias potential on the sample. However, the data presented in this Thesis was often taken at small tunnel gap resistances ($\sim 1\text{M}\Omega$), and strictly the bias voltage is divided between the tunnel junction and the pre-amplifier, which in the sense of Ohm's law are aligned in series, see **figure 4.14**. The true voltage drop in the tunnel junction is given by equation (4.5) below:

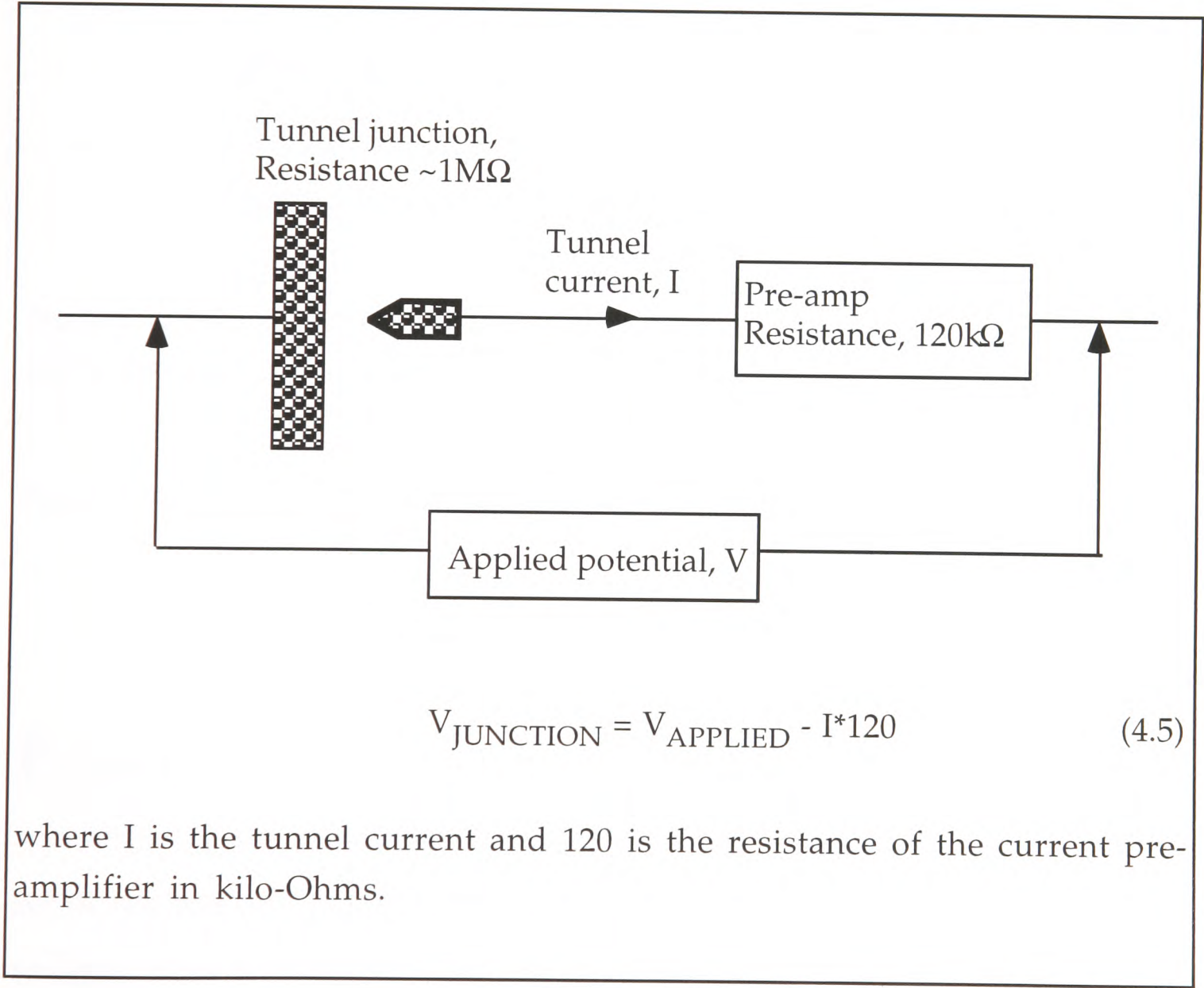


Figure 4.14: A diagram illustrating the need to take account the finite resistance of the current pre-amplifier when making $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots at large values of the tunnel conductance.

When calculating a best-fit line in data sets such as **figures 4.10-4.13**, from which to deduce $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$, it is important not to include "roll-off" data points, which could lead to an overestimated value for the tunnel barrier height. Thus for each data set, the best-fit line used to deduce the barrier height included points up to the data point at which the local gradient at each successive data point progressively decreased to zero.

A table of the barrier heights implied by the data of **figures 4.10-4.13** is shown below:

	Barrier height (eV)
Figure 4.10	1.9±0.1
Figure 4.11	2.4±0.2
Figure 4.12	0.9±0.1
Figure 4.13	1.0±0.1

Figure 4.15: A table showing the barrier heights implied by the experimental data of **figures 4.10-4.13**.

The implications of these results are discussed more fully in section 4.7.

4.6.3: Corrugation Heights and the Surface Inter-Atomic Spacing.

Figure 4.16 overleaf shows a frequency histogram for all the $\langle 001 \rangle$ data sets showing the maximum corrugation height measured prior to the onset of the roll-off. This figure exhibits an asymmetric distribution of values ranging from 0.09-0.27Å, with a peak in the distribution at $\sim 0.19\text{\AA}$. There are more data points on the low corrugation side of the peak. Similar observations were also noted for the $\langle 01\bar{1} \rangle$ data, see **figure 4.17** overleaf. In this latter case the corrugations are smaller, ranging from 0.03-0.16Å. The peak in the distribution occurs at $\sim 0.09\text{\AA}$. The "roll-off" point was selected

for this corrugation height analysis, rather than some arbitrary value of tunnel conductance because of its physical significance (see Chapter Six for further details). In the next section of this Thesis, the meaning of this corrugation height data is discussed further.

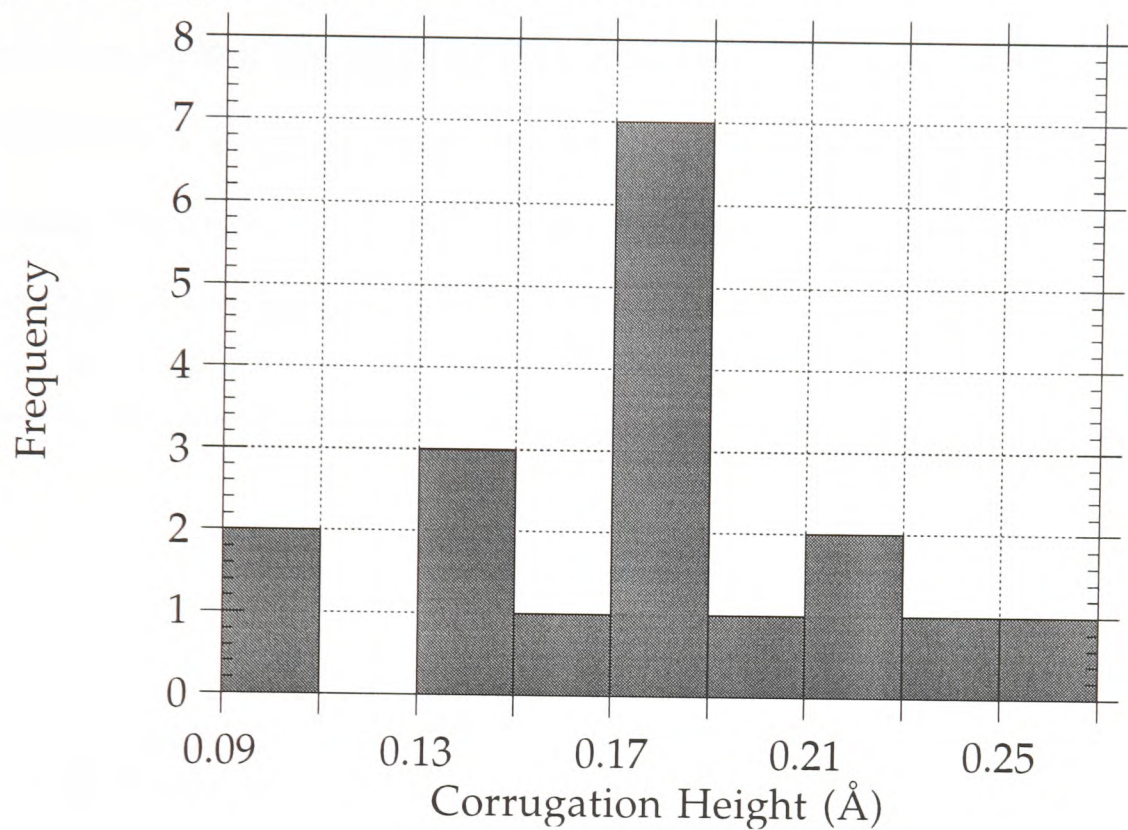


Figure 4.16: A frequency histogram for <001> data sets showing the distribution of the maximum corrugation heights measured prior to the on-set of the roll-off.

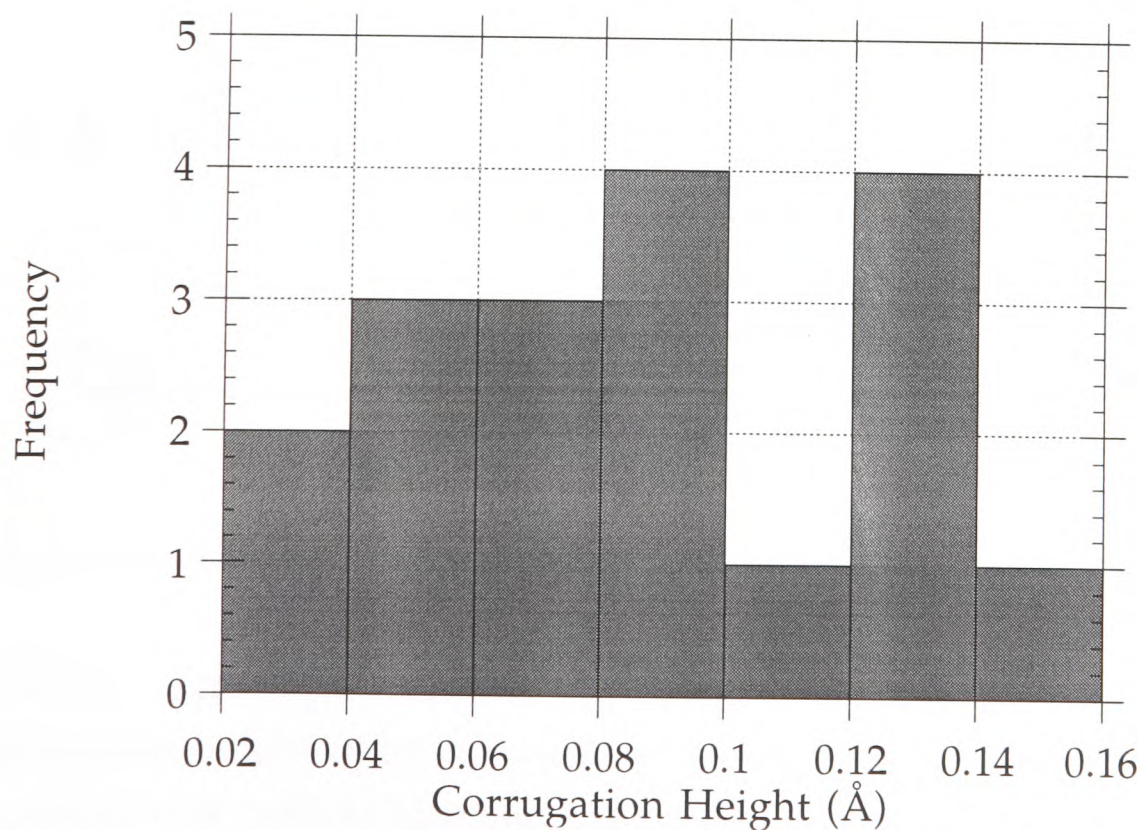


Figure 4.17: as figure 4.16 but for <011 > corrugation height data sets.

Figures 4.16 and 4.17 show that larger corrugation heights are to be expected along surface crystallographic directions for which the inter-atomic spacing is larger. Confirmation of the qualitative dependence of corrugation height upon the surface inter-atomic spacing can be obtained from a crude model in which the atoms are regarded as spheres of charge, see figure 4.18 below. The electronic charge, ρ , from one of these atoms decays exponentially with increasing separation, z , from the centre of the atom according to the relationship of equation (4.6):

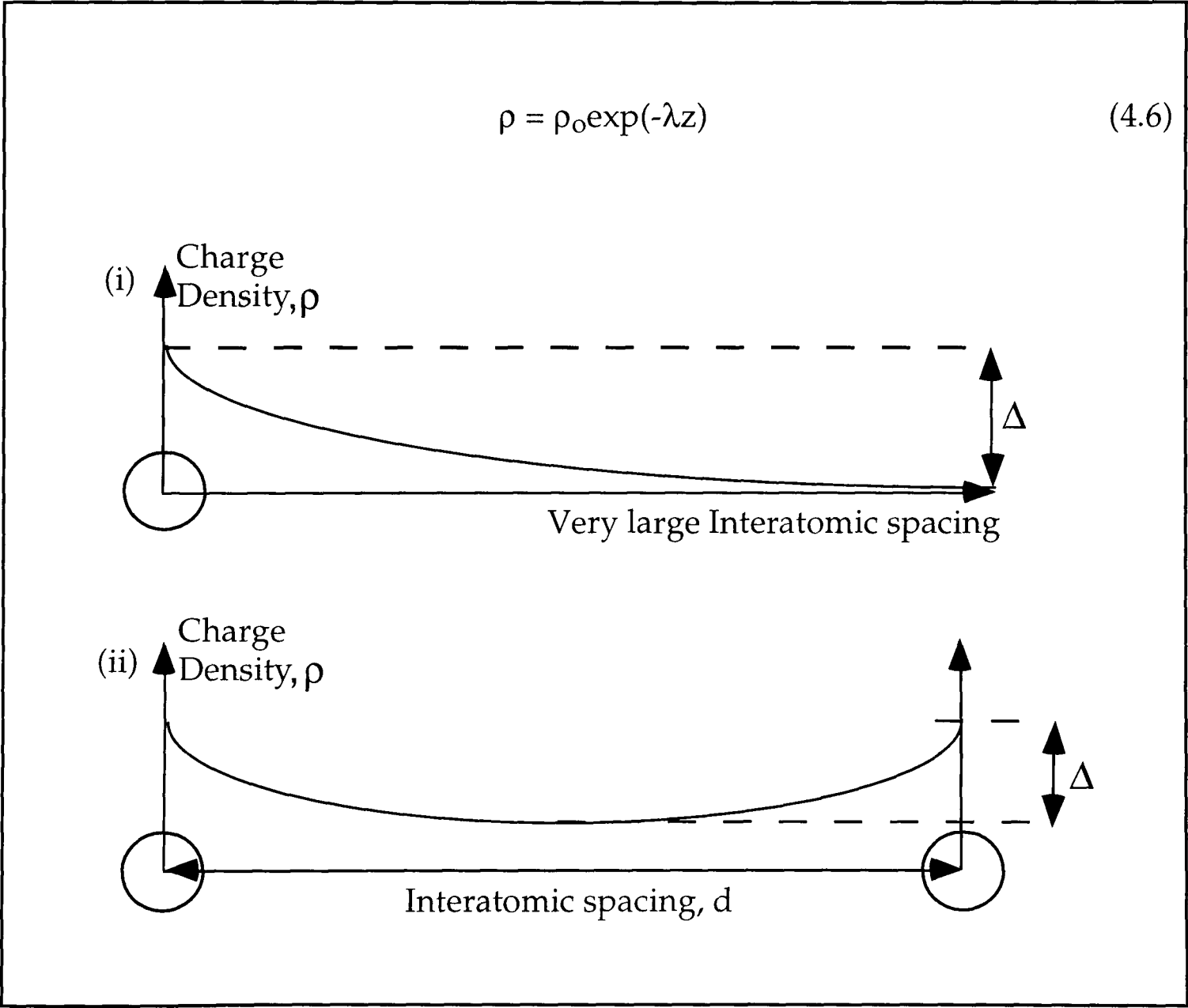


Figure 4.18: A schematic diagram to illustrate the qualitative dependence of the corrugation height upon the surface inter-atomic spacing. Two cases are shown, effectively infinite spacing and a finite spacing, d .

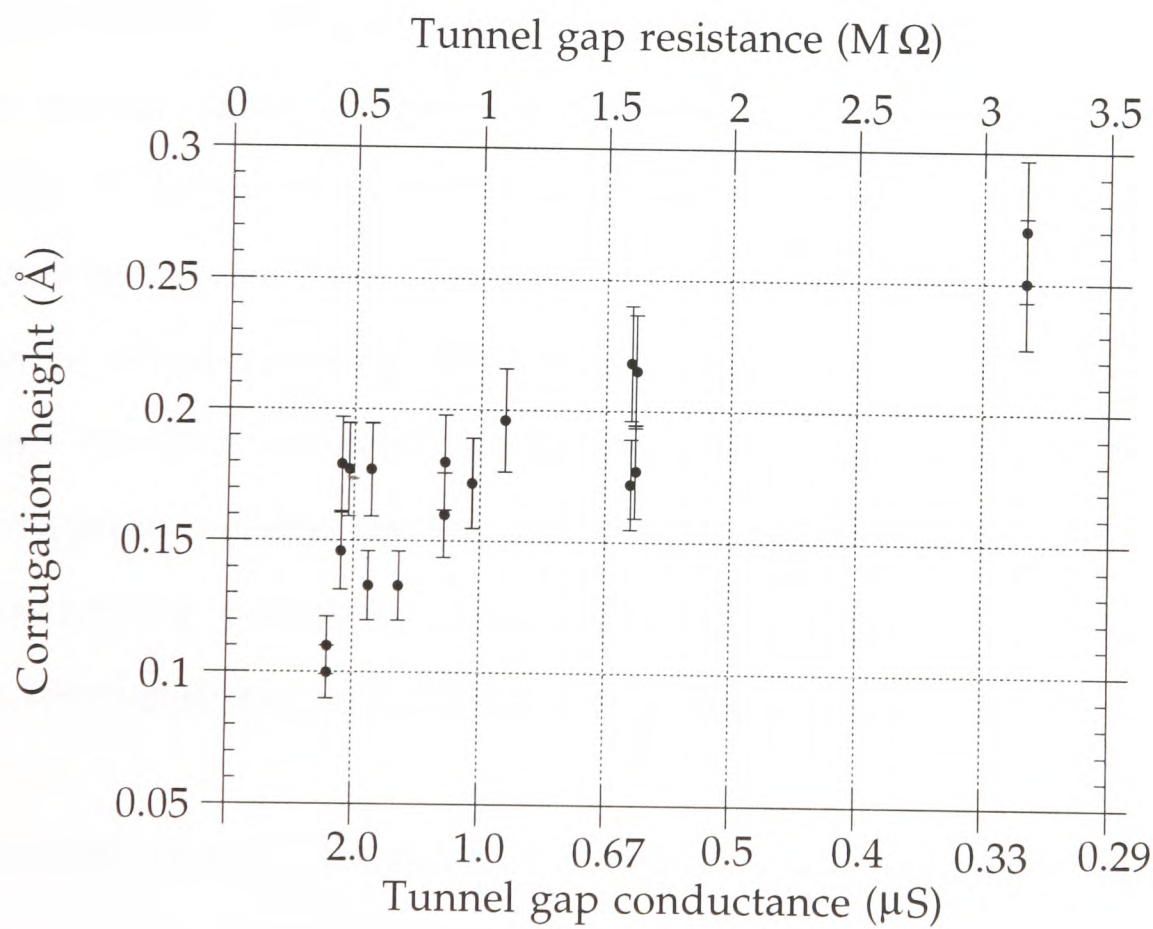
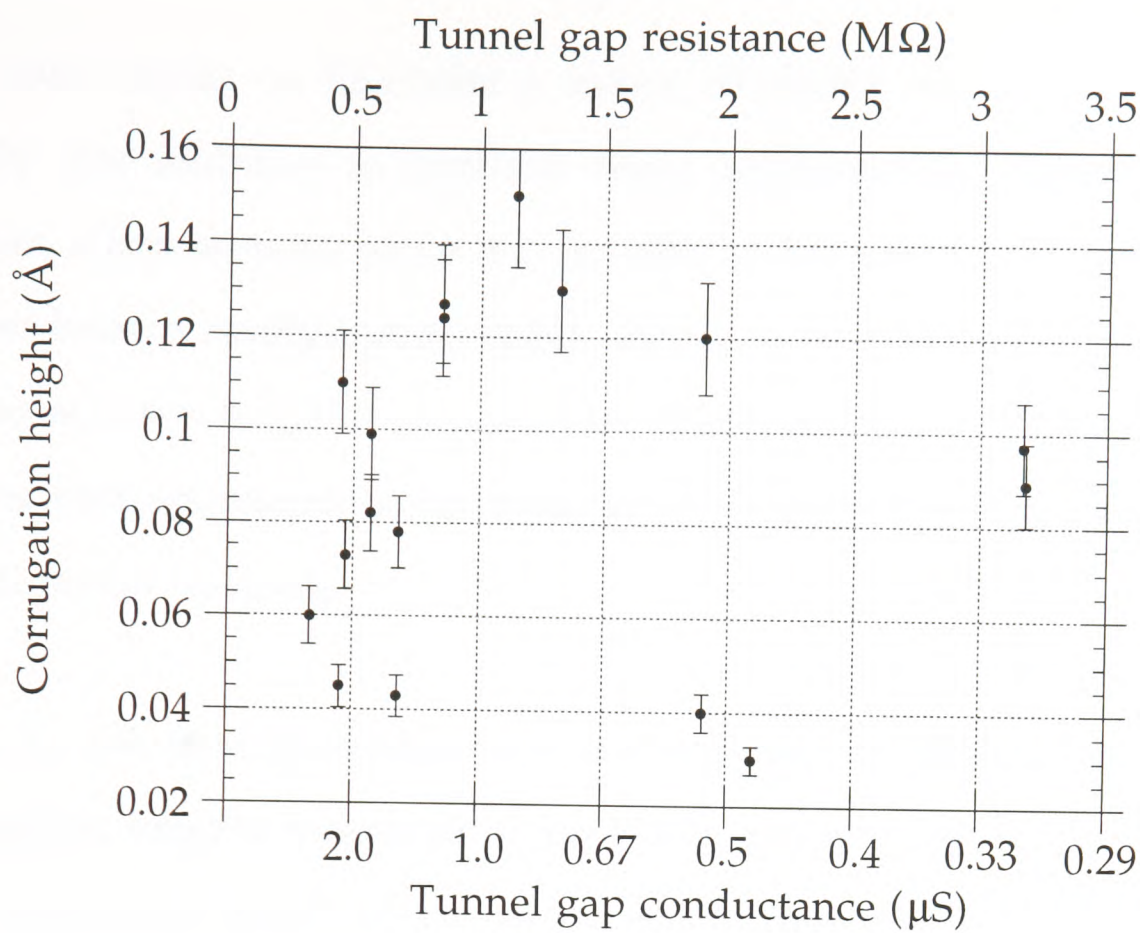
For a “metal” with a very large inter-atomic spacing, the measured corrugation height is equal to the height of the tip-apex atom above the surface. For metals with a smaller inter-atomic separation, d , the corrugation height, Δ , in the constant current mode of operation is given in this model approximately by equation (4.7):

$$\Delta \sim \frac{d^2}{8z} - \frac{1}{\lambda} \text{Ln}(2) \tag{4.7}$$

The relationship of equation (4.7) shows that this *very* simple model qualitatively predicts an increasing corrugation height as the inter-atomic spacing increases and also as the tip-sample separation decreases. Similar more quantitative trends have been demonstrated in the fuller treatments of this problem due to Tersoff and Hamann [4.3, 4.4] (see **figure 1.2**) and Stoll [4.32].

4.6.4: Corrugation Heights and the Tunnel Gap Conductance.

In **figures 4.19** and **4.20** overleaf, the maximum corrugation height measured prior to the on-set of the roll-off in each data set is shown as a function of the tunnel gap conductance.



Figures 4.19 and 4.20: Graphs showing the maximum corrugation height measured prior to the on-set of roll-off as a function of tunnel gap conductance. The graph at the top of the page is for $\langle 011 \rangle$ data, while the graph at the bottom is for $\langle 001 \rangle$ data.

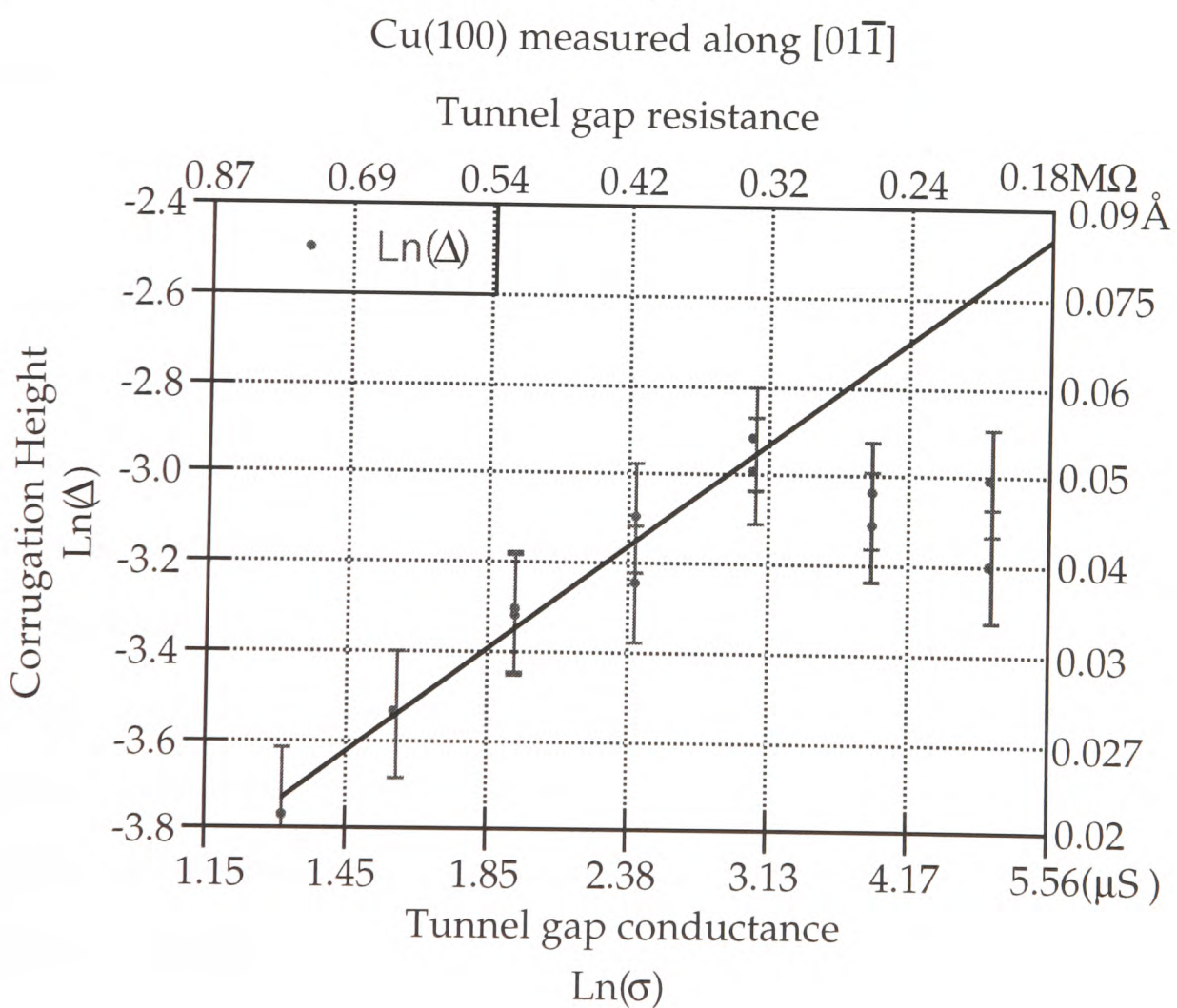
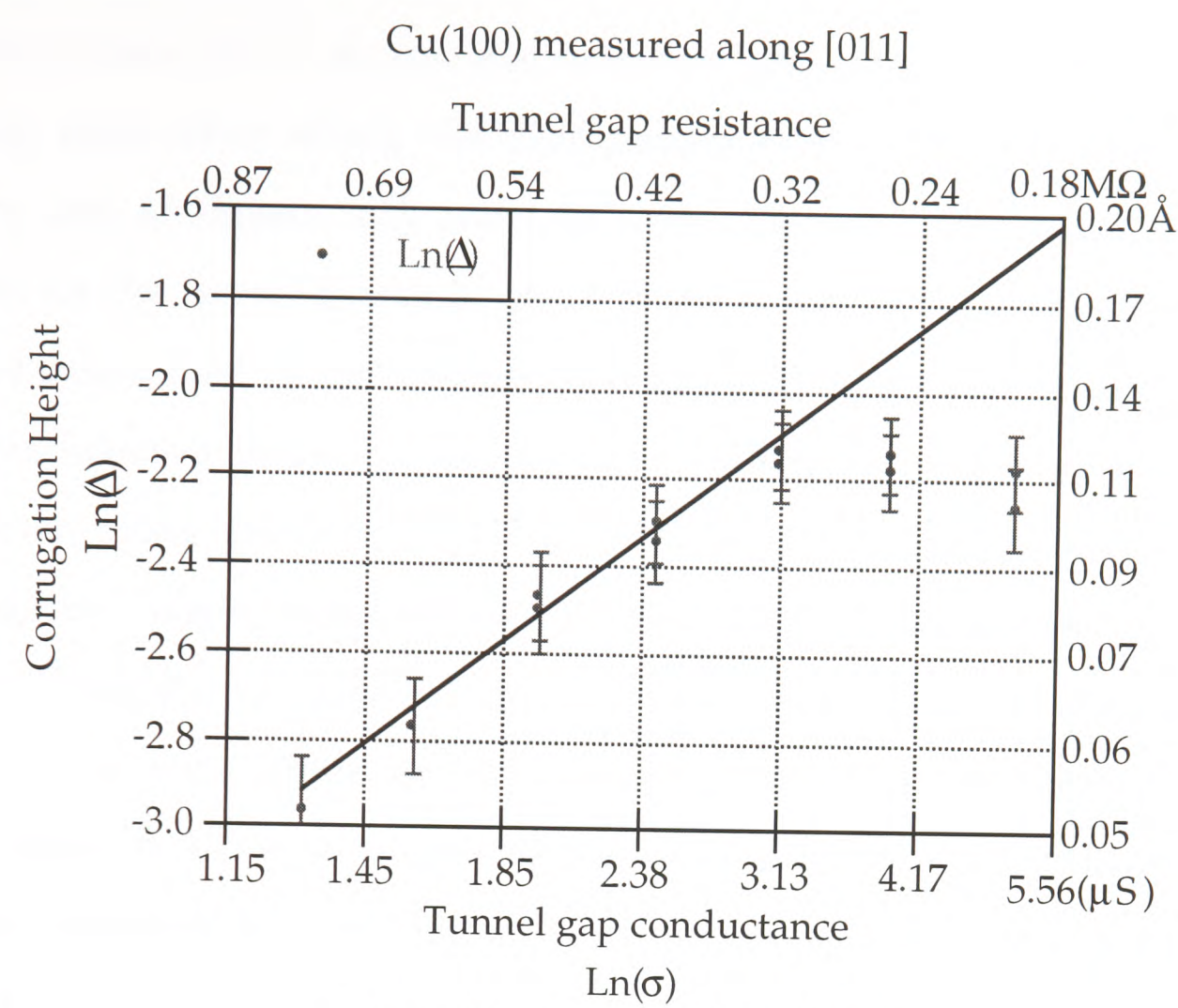
This data serves to illustrate a major difficulty within the STM field, namely the inability to perform truly reproducible experiments. This problem arises because while it is possible to invest a lot of time producing a tip of known configuration [4.24], once it is inserted into the microscope we lose all knowledge of its particular characteristics. Moreover, experience tells us that spontaneous tip changes are a frequent occurrence, even in normal mode imaging.

As far as the data presented here is concerned, in general, the maximum corrugation heights measured along $\langle 001 \rangle$ prior to roll-off are larger than those measured along $\langle 01\bar{1} \rangle$, as expected from the Tersoff and Hamann model [4.3, 4.4]. Nevertheless, there is an overlap between the two corrugation height distributions, which shows that the form of the scanning needle can vary significantly between different experiments in which atomic scale images were obtained. This is in accord with the findings of Berndt et al. [4.33] who were unable to find a reproducible relationship between the measured corrugation height and the tunnelling resistance when imaging the Cu(111) and Ag(111) surfaces. Note that although no clear-cut trend can be established for the $\langle 01\bar{1} \rangle$ data, the roll-off corrugation heights for the $\langle 001 \rangle$ data exhibit a weak trend to increase with increasing resistance. This trend is in opposition to that observed within individual experiments such as in **figures 4.12** and **4.13**.

One possible reason for this bizarre distribution of corrugation heights may be due to differences in tip chemistry at the apex. Support for this view comes from a study of the sulphur ($\sqrt{3} \times \sqrt{3}$)R30° overlayer on Pt(111) [4.34]. The corrugation heights measured above this surface have been observed to dramatically increase as a result of applying a large (~ 10 V) positive bias voltage to the tip. A small hole is seen in the overlayer beneath the site of

the tip during the voltage pulse and so this result is interpreted as being due to the transfer of a small number of sulphur atoms to the tip apex. Using the Electron Scattering Quantum Chemistry (ESQC) method [4.35], McIntyre et al. [4.34] have demonstrated that small corrugation heights are to be expected when a spatially extended 6s orbital, derived from a metal atom, is predominant at the tip-apex; while large corrugations are predicted from more the spatially confined 3s and 3p orbitals of a sulphur atom at the tip-apex. The application of this idea to the data in this Thesis would lead to the expectation that one would measure two main values for the corrugation height according to the chemistry of the tip apex. In practice, this is not observed and there must be additional factors to consider.

Figures 4.21 and 4.22 give some indication of what else is important. These figures show a pair of $\langle 0\bar{1}1 \rangle$ corrugation height: conductance graphs taken from the same set of STM images. These measurements were made along mutually perpendicular directions. The corrugation heights in **figure 4.21** are much larger than in **figure 4.22**. However, the slopes of each graph are almost equal. Using equation (4.4), the tunnel barrier heights are measured to be $1.5 \pm 0.1 \text{ eV}$ and $1.7 \pm 0.2 \text{ eV}$ respectively. In addition, the roll-off point in both data sets occurs at the same value of the tunnel conductance.



Figures 4.21 and 4.22: $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots for the Cu(100) surface for corrugation heights measured along the $[011]$ and $[01\bar{1}]$ directions respectively. These data lead to almost identical values for the tunnel barrier height although their respective corrugation heights are substantially different.

It seems reasonable to assume that only one chemical species was present at the tip apex when taking the STM images from which the corrugation height data of **figures 4.21** and **4.22** were obtained. This means that the values for the tunnel barrier height and the on-set of the corrugation roll-off are determined by the tip-apex chemistry. Differences in the corrugation heights between these figures are due to variations in the tip geometry projected along the two $\langle 0\bar{1}1 \rangle$ surface directions. The $[010]$ and $[001]$ corrugation height measurements for this data set were larger than the $\langle 0\bar{1}1 \rangle$ corrugation heights (as expected from the discussion of the previous section) and were almost equal to one another. The $\langle 001 \rangle$ measurements were made at 45° with respect to the $\langle 0\bar{1}1 \rangle$ corrugation measurements. This is consistent with an elliptically symmetric tip that in this instance is "blunt" when projected along the $[01\bar{1}]$ surface direction, "sharp" when projected along the $[011]$ direction and of intermediate radius of curvature when projected along the $\langle 001 \rangle$ directions.

Hence variations in the local tip radius may be responsible for the smearing out of an anticipated bimodal distribution of corrugation heights into a distribution where it is hard to pick out an obvious relationship. The data of **figures 4.19** and **4.20** seems to offer some support for this idea as in both figures there are many pairs of data points taken at the same value of tunnelling resistance but which have different corrugation heights. Moreover, different chemical species at the tip apex may result in observable differences in the tunnelling resistance at the on-set of corrugation roll-off.

4.7 Tunnel Barrier Height Analysis:

In the previous section, the distributions of the corrugation heights immediately prior to the roll-off were proposed to be the result of a combination of the independent variation of tip chemistry and tip geometry. In this section, the relationship of corrugation height with tunnel barrier height is examined. Equation (4.4) gives the relationship between $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ and the barrier height. In **figures 4.23** and **4.24** overleaf, frequency histograms are plotted showing the distribution of the corrugation height:slope function, $\frac{1}{(b(b+2))}$ which is directly proportional to the tunnel barrier height.

The similarity of the distribution of values in the histograms of **figures 4.23** and **4.24** suggests that the parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ is independent of surface direction chosen to measure the corrugation heights. Unfortunately, this assertion implies that equation (4.4) cannot be correct. Values of the tunnel barrier height measured from $\langle 001 \rangle$ data are predicted to be a factor of two lower compared with the values deduced from $\langle 01\bar{1} \rangle$ data, see the table of **figure 4.15**. Such an observation is not borne out experimentally as tunnel barrier height measurements based on the parameter $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ have clearly shown [4.15]. In Appendix B, a simple idealised theoretical model is presented which shows that the tunnel barrier height is in principle independent of the direction along which the corrugations are measured.

By treating every data point as an independent result, weighted arithmetic mean values for the function $\frac{1}{(b(b+2))}$ have been established for the two sets of data. A value of 0.35 ± 0.01 was obtained for the $\langle 001 \rangle$ corrugation data while a value of 0.28 ± 0.02 was calculated for the $\langle 01\bar{1} \rangle$ data. These values are close but not quite in agreement within the limits of experimental error.

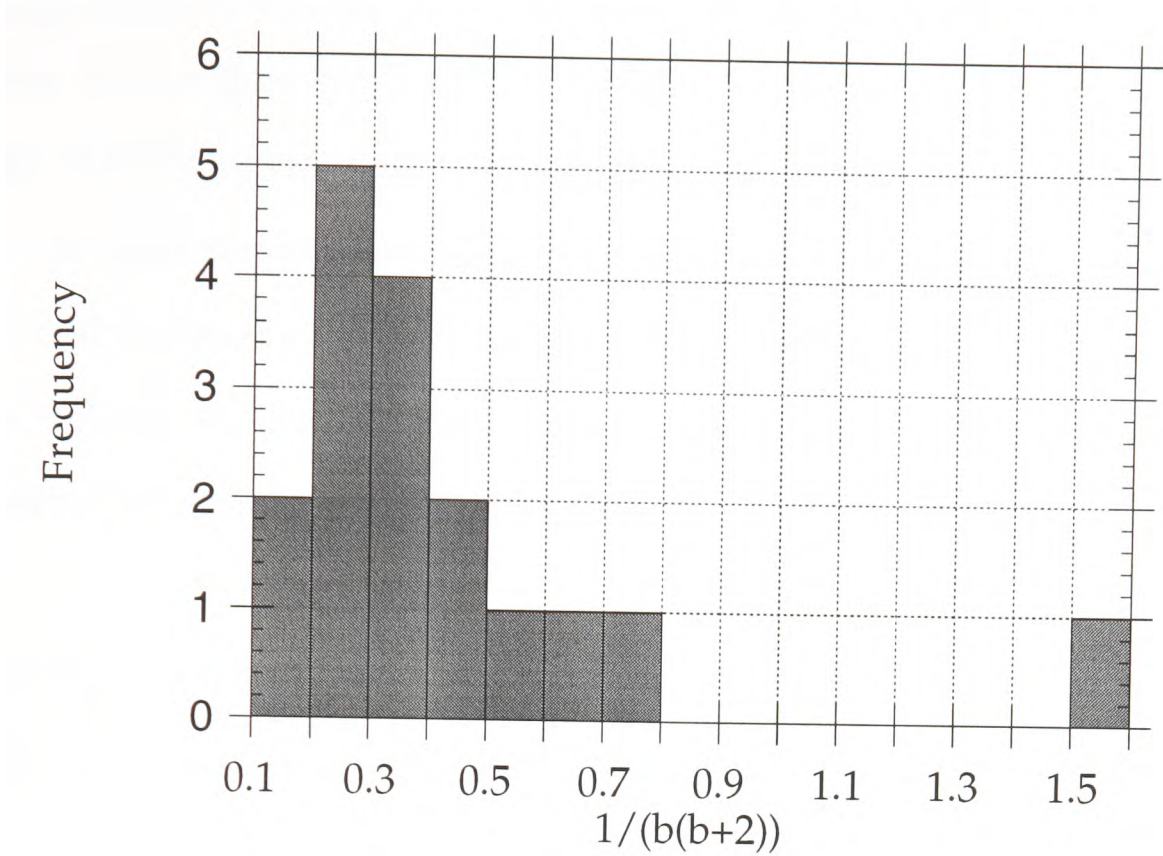


Figure 4.23: A frequency histogram showing the distribution of values of $1/(b(b+2))$, where b is the slope of a $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot. This figure is for $\langle 001 \rangle$ corrugation data.

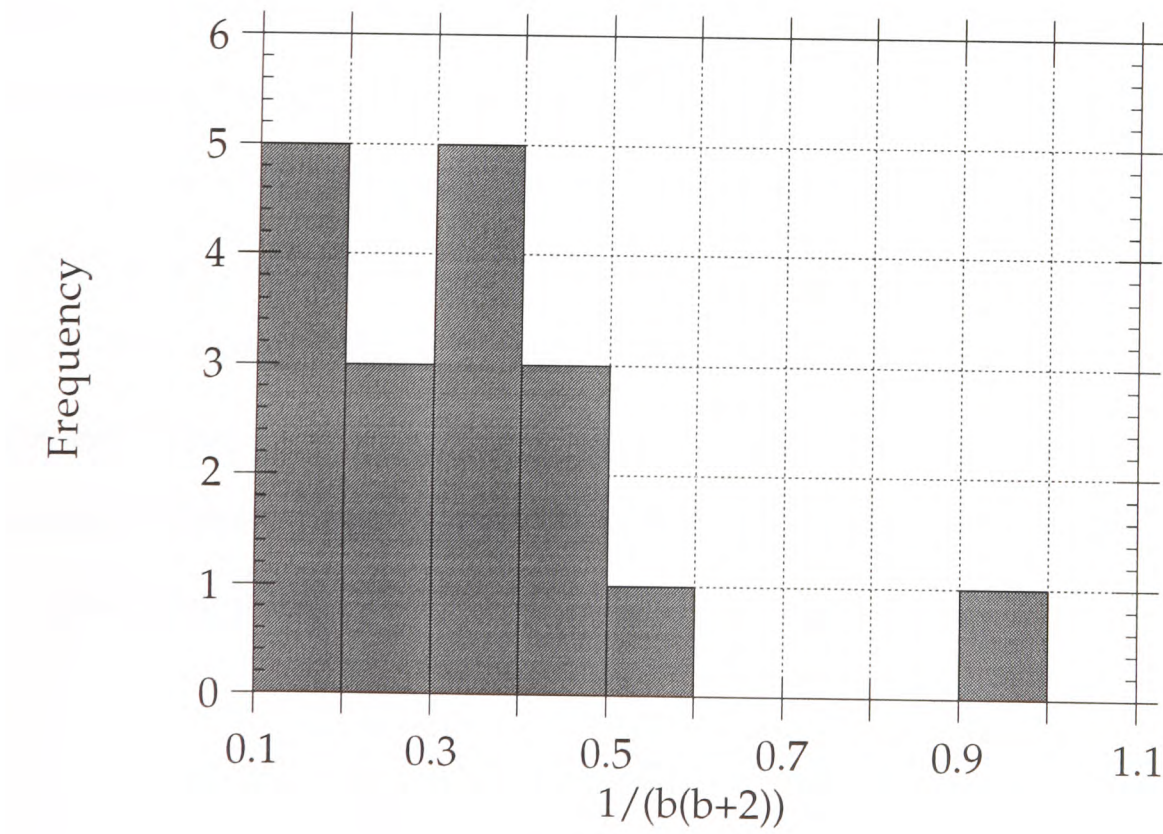


Figure 4.24: as figure 4.23 but for $\langle 011 \rangle$ corrugation data.

In order to deduce the tunnel barrier heights implied from this method, the $\frac{1}{(b(b+2))}$ function for the $\langle 001 \rangle$ data should be multiplied by 2.89eV and that for the $\langle 01\bar{1} \rangle$ data by a factor 5.78eV. Thus mean values for the barrier height of 0.97 ± 0.03 eV and 1.60 ± 0.12 eV respectively are calculated from these data. At least the higher value for the tunnel barrier height reported here is close to the values (~ 2 -3eV) reported by Olesen [4.16] who also took data at large values of the tunnel conductance ($\sim 1\mu\text{S}$) when investigating the formation of tip-surface point-contacts.

Figure 4.25 overleaf shows a plot of the data obtained for the tunnel barrier height as a function of the $\langle 001 \rangle$ maximum corrugation height measured prior to the on-set of the roll-off. Sadly, there is no obvious relationship between the corrugation heights and the tunnel barriers. This is slightly surprising in view of the fact that the workfunction of a metal surface has been observed to increase as the result of the adsorption of gaseous electronegative atoms [4.36]. Values for the tunnel barrier height are mostly confined to a range between 0.75-1.25eV, but occur over a rather large range of corrugation heights (~ 0.1 -0.25Å). This result is interpreted as a second indication that the combined effects of the independent variation in the tip-apex chemistry and geometry mean that it is difficult to pick out any clear trend in the data. “Sharp” and “blunt” tips terminated by a particular species are likely to measure similar values for the tunnel barrier height, but exhibit different corrugation heights, leading to a “horizontal smearing-out” of the distribution.

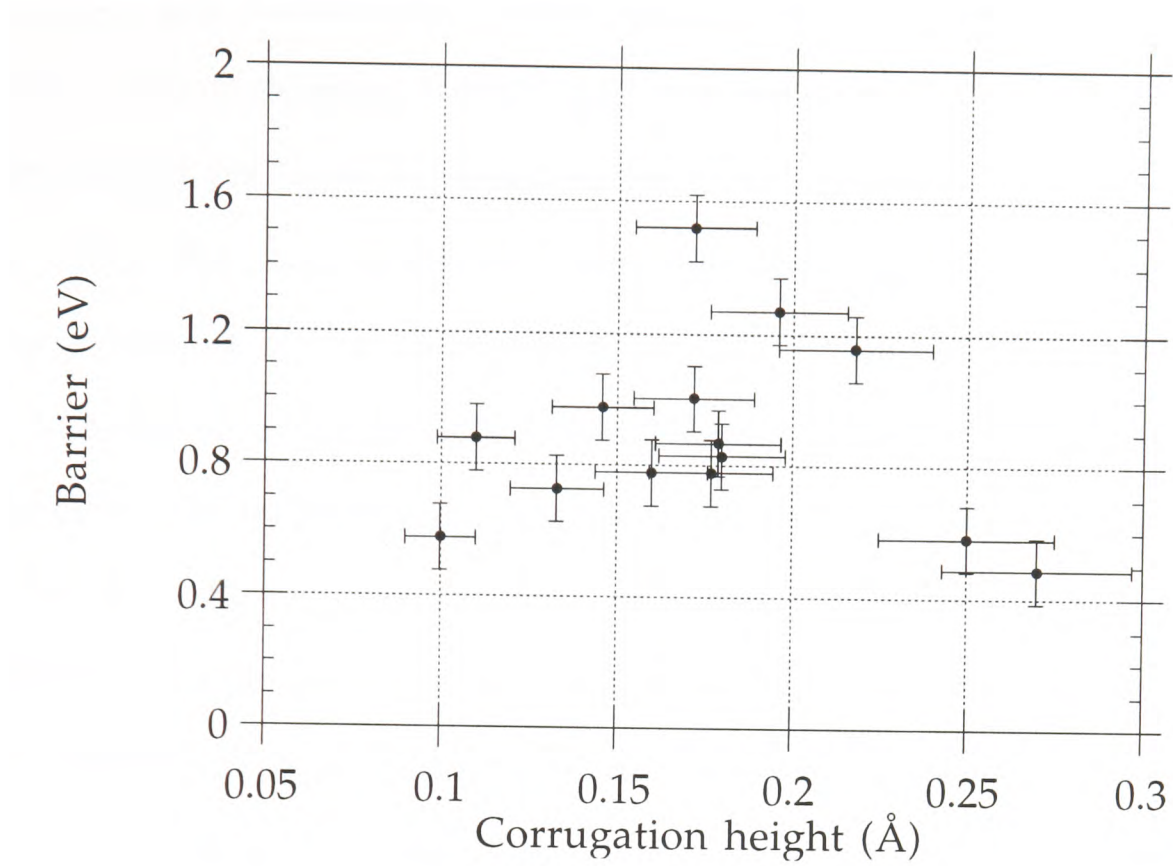


Figure 4.25: A graph showing the deduced tunnel barrier height as function of the corrugation height measured immediately prior to the roll-off. These data were measured along $\langle 001 \rangle$.

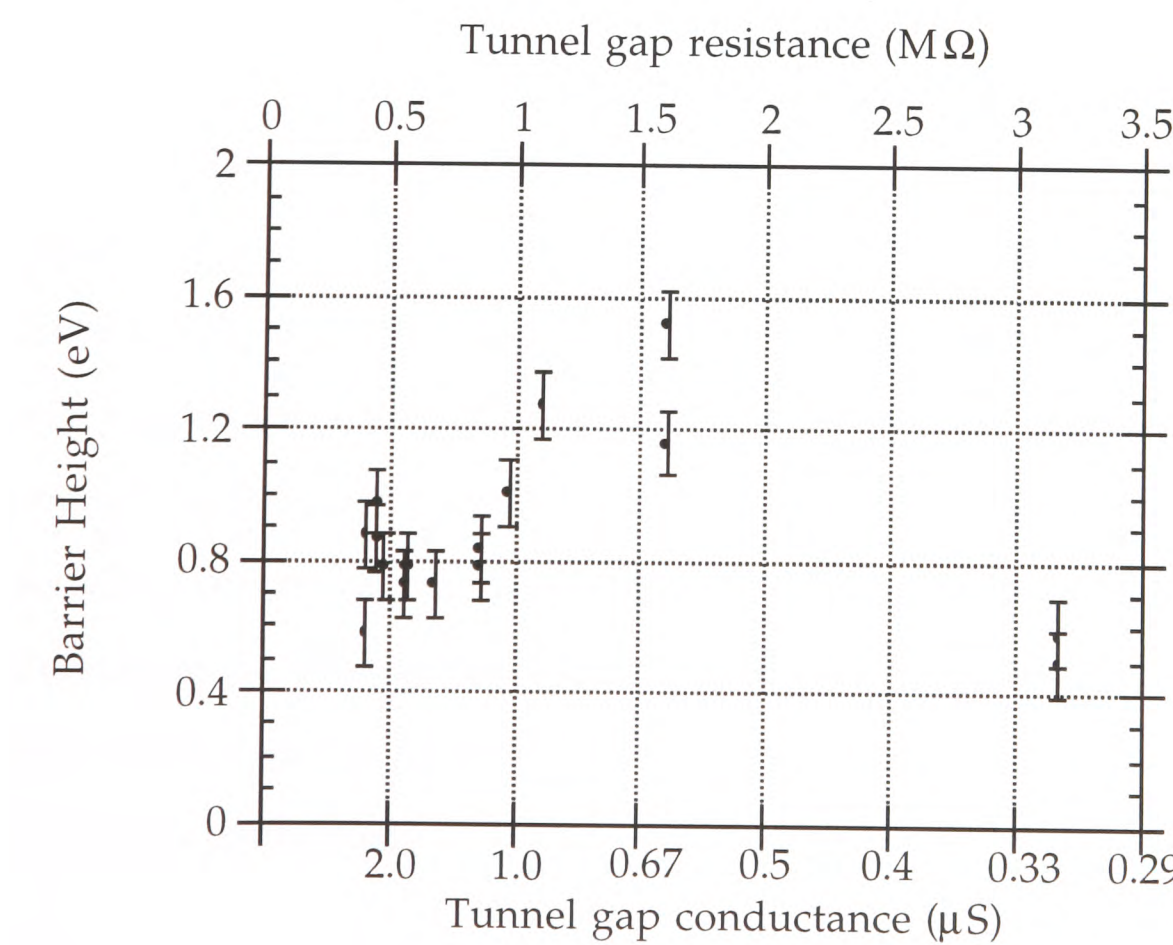


Figure 4.26: A graph showing the tunnel barrier height as function of the tunnel gap conductance. These data were measured along $\langle 001 \rangle$.

In **figure 4.26**, the tunnel barrier heights are plotted as a function of the roll-off tunnel gap resistance. These barrier heights show a slight trend to increase with increasing tunnel gap resistance. Since higher values for the barrier height are to be expected when a non-metallic atom is at the tip apex [4.36, 4.37]. The data presented here indicates that a non-metallic tip gives rise to a roll-off in the corrugation heights at larger separations compared with metallic terminated tips. Clearly sophisticated calculations are needed to confirm this hypothesis. However, such a notion would be expected to lead to a bimodal distribution of tunnel barrier heights. The actual distribution does not show this result and possibly highlights the need to take a realistic account of the local tip geometry together with the chemistry when calculating the tunnel barrier height as well as the on-set of the corrugation height roll-off [4.38].

For the sake of completeness, graphs equivalent to those shown in **figures 4.25** and **4.26** are plotted overleaf for the $\langle 0\bar{1}1 \rangle$ data. As with the $\langle 001 \rangle$ data, the values for the barrier height fall lie in a comparatively narrow range ~ 1 - 2.5 eV, while the values for the corrugation height at roll-off vary over a reasonable range (~ 0.03 - $0.16 \text{ \AA}$), see **figure 4.27**. The data is in accord expressed earlier that the properties of the tip can vary drastically between different experiments. Unfortunately the distribution of barrier heights as a function of tunnel resistance for the $\langle 001 \rangle$ data, see **figure 4.28**, is rather diffuse and I am unable to draw any conclusions from it, except that the understanding of the tunnel barrier height in STM is a rather difficult problem which appears to depend strongly upon variables which cannot be systematically controlled.

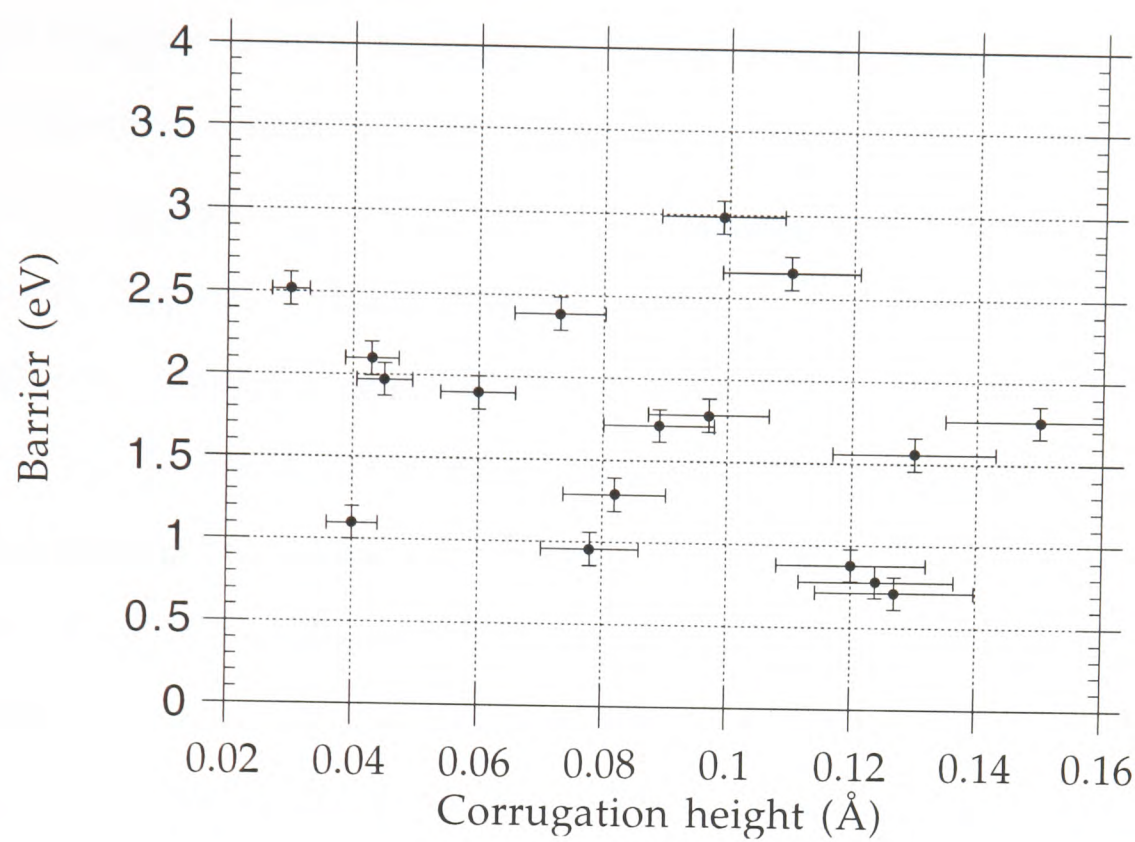


Figure 4.27: A graph showing the deduced tunnel barrier height as function of the corrugation height measured immediately prior to the roll-off. These data were measured along $\langle 0\bar{1}1 \rangle$.

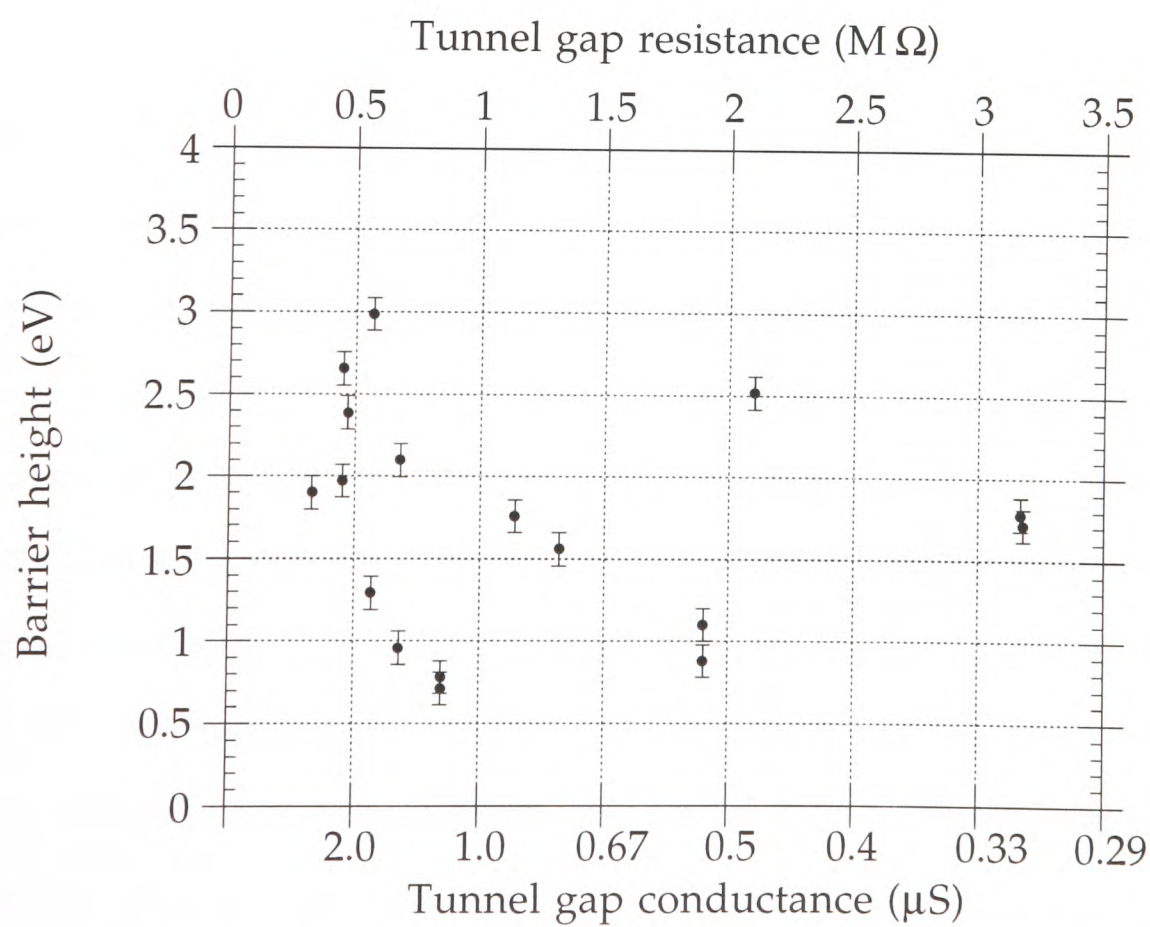


Figure 4.28: A graph showing the tunnel barrier height as function of the tunnel gap conductance. These data were measured along $\langle 0\bar{1}1 \rangle$.

4.8 Summary:

In this Chapter, a new method for deducing the tunnel barrier height has been presented which is based upon the measurement of the decay of the vertical corrugation in topographic images as the tip-sample separation is increased. Typical values obtained for the tunnel barrier height above Cu(100) are somewhat smaller than the workfunction and are in the range (~ 1 -2.5eV). In order to obtain atomic scale resolution data, the tip and the sample need to be in close proximity. At such small tip-sample separations, the effects of the exchange and correlation interactions are significant for tunnelling electrons and this results in a tunnel barrier height which is reduced well below its large separation workfunction limit. In individual data sets, at high values of tunnel conductance ($\sim 1\mu\text{S}$), the corrugation heights exhibit a “roll-off”, and do not increase by as much as would be expected from a linear extrapolation of the data taken at smaller values of conductance (i.e. as predicted by the unmodified Tersoff & Hamann model).

Nevertheless, it should be pointed out that these data are in good agreement with other reports of atomically resolved tunnel barrier height data obtained for both metal [4.15] and semiconductor [4.2] surfaces. Previous experimental studies have shown that atomic scale resolution data gives rise to a tunnel barrier height of $\sim 2\text{eV}$, while higher values for the tunnel barrier generally occur for topographic images with a lower level of lateral resolution [4.20-4.22]. Winterlin et al. [4.37] have measured a tunnel barrier height of $\sim 3.5\text{eV}$ above an atomically resolved Al(111) surface. However as they concede, it is likely that there are strong attractive tip-surface forces acting to produce this data. Moreover, Chen and Hamers [4.13] have conclusively demonstrated that attractive forces can be responsible for an increase in the tunnel barrier height of more than 1eV.

The relationship between the calculated values for tunnel barrier height and the distribution of corrugation heights appears to be complex and to depend upon a number of independent factors. Ideally one would expect a bimodal distribution of tunnel barrier heights, one value corresponding to a metallic atom terminated tip and the other to a non-metallic atom terminated tip. However, the experimental data was not so straight forward to interpret, leading to the idea that variations in the local tip radius are responsible for the observation of a "smeared-out" barrier height-corrugation distribution. A similar independent variation of both tip chemistry and geometry is also consistent with the distribution for the onset of roll-off in corrugation measured as a function of tunnel resistance.

These conclusions are somewhat unsatisfactory as they cannot as easily be verified experimentally within the present limitations of STM. Moreover there is no straightforward interpretative help at hand from any of the existing theoretical models. In short atomic resolution images can be taken using a wide variety of different types of tip which encompass significant variations in apex geometry and chemistry. The measured barrier heights are also likely to depend upon the values of tunnelling resistance selected.

Finally, an unfortunate drawback of the theory behind this method, is that although the parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ has been shown to be independent of the surface direction along which the corrugation heights are measured, the simple model used in this Chapter implies that the tunnel barrier height increases as the inter-atomic spacing of the corrugation measurement direction decreases. An elementary analysis, based upon the Principle of Conservation of Energy shows this conclusion to be incorrect. In the next Chapter, it is demonstrated how this difficulty can be removed and what "true" values for the tunnel barrier height are to be expected based upon a measurement of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$.

4.9 References:

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Chapter 5

The meaning of $\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}$

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5.1 Introduction:

When calculating the tunnel barrier height in Chapter Four, the pre-exponential terms in the equations for the tunnel conductance and corrugation height were assumed to be constant. In this Chapter, the tunnel barrier height is re-calculated using $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ when account is made of these pre-exponential factors.

Using equations (4.1) and (4.3), it is straightforward to derive an exact expression for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$, which can then be compared against experiment:

$$\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} = \left[-\frac{1}{2\phi_M} \frac{\partial \phi_M}{\partial s} - \frac{\kappa \Delta s}{\phi_M} \left(\frac{\kappa}{\left(\kappa^2 + \frac{G^2}{4}\right)^{1/2}} - 1 \right) \frac{\partial \phi_M}{\partial s} - \beta \frac{\partial \Delta s}{\partial s} \right] /$$

$$\left[\frac{1}{2\phi_M} \left(1 - A\phi_M^{1/2} \Delta s \right) \frac{\partial \phi_M}{\partial s} - \left(\frac{1}{\Delta s} + A\phi_M^{1/2} \right) \frac{\partial \Delta s}{\partial s} \right] \quad (5.1)$$

where Δs is the tunnelling width as distinct from the tip-sample separation, s ,
 and $A = \frac{4\pi}{h}(2m)^{1/2}$ ($= 1.025 \text{ eV}^{-1/2} \text{ \AA}^{-1}$).

The major unknown factors in equation (5.1) are the mean tunnel barrier height, ϕ_M , and its dependence upon the tip-sample separation, s . Thus the emphasis of section 5.2 is to present a tunnel barrier height function which is able to reproduce the observed behaviour of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$. This tunnel barrier height function is compared and contrasted in Section 5.3 with the more conventional multiple image-potential reduced tunnel barrier used by Coombs et al. [5.1]. In section 5.4, a simple approximate equation is derived which relates $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ and the tunnel barrier height. Finally in section 5.5, a set of experimental data is presented which satisfies the approximations made in section 5.4.

5.2 The Interface Surface Potential:

The aim of this Chapter is to show that the experimental data presented in this thesis are consistent with a model for the tunnel barrier adapted from the apparent barrier height theory of Lang [5.2]. Using the jellium model, Lang argues that the interface potential, V_{INT} , encountered by an electron above a metallic surface is given by the sum of two contributions; an electrostatic dipole-layer, V_{es} , and the exchange-correlation potential, V_{xc} .

The dipole term results because the “electron-fluid” in the bulk spills out a short distance beyond the positive background-edge of the metal, see **figure 5.1** overleaf. The electric-charge density, $n(z)$, in the transition region across the surface of a metal has been approximately described by Smith [5.3], see equations (5.2a and 5.2b) overleaf:

$$n(z) = n_o [1 - 0.5 \exp(\alpha z)] \quad (z < 0) \quad (5.2a)$$

$$\text{and } n(z) = \frac{n_o}{2} \exp(-\alpha z) \quad (z > 0) \quad (5.2b)$$

where n_o is the bulk electron density and z is measured in a direction perpendicular to the plane of the surface. For many metals $\alpha \sim 1.2\text{-}1.3 \text{ \AA}^{-1}$.

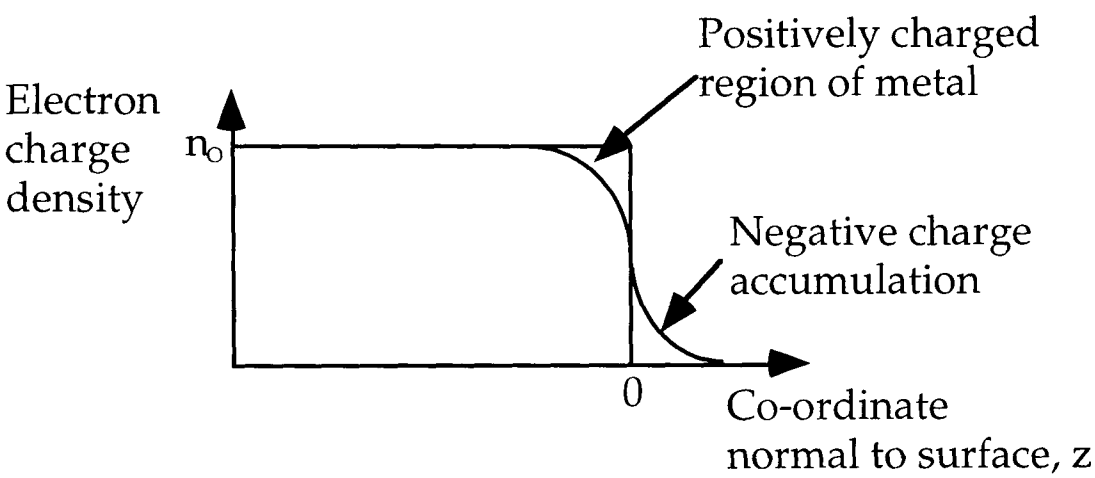


Figure 5.1: A schematic diagram showing the electric charge distribution normal to a metal surface

The fact that $n(z)$ decays exponentially above the surface implies that in this region, $V_{es}(z)$ tends exponentially towards the surface workfunction, i.e. $V_{es}(z) \sim \exp(-\alpha z)$ [5.4].

The second term of the surface potential, V_{xc} , describes the interaction between an electron and its exchange-correlation hole. This hole arises because each electron in a system lowers its energy because it repels all the other electrons in the system for two reasons. The first is the classic Coulombic repulsion and the second is the exchange-interaction which arises from the Pauli exclusion principle where electrons with parallel spins avoid one another. In this work, V_{xc} is evaluated in the Local Density Approximation (LDA) [5.5]. In the LDA, the effect of the exchange-correlation hole associated with a particular electron

is taken to be the same as that due to the hole that would surround the electron if it were embedded in a homogenous electron gas of density equal to that of the inhomogenous electron gas at the position of the electron. It can be shown [5.6] that the exchange-correlation potential, V_{xc} , is approximately proportional to the cube root of the local electron density, so that $V_{xc} \sim \exp\left(-\frac{\alpha Z}{3}\right)$.

It is appropriate at this point to sound a word of warning regarding the limitations of the LDA. The use of the LDA to calculate the exchange-correlation potential becomes increasingly invalid as the electron and its correlation hole become separated as they do when the electron moves into the region of space above the surface. As Bardeen [5.7] has shown, the classical image potential is an excellent approximation for this term right down to small distances, $\sim 1\text{-}2\text{\AA}$ above the surface. At small separations, the classical image potential diverges to minus infinity, whereas in a full quantum-mechanical calculation, the electron-metal surface interaction changes smoothly into the exchange-correlation potential as the image charge at the metal surface gradually becomes the exchange-correlation hole surrounding the electron [5.8]. Thus any agreement between experimental data and theoretical models of the tunnel barrier which use the LDA should be treated with some caution. Despite the unfortunate nature of the approximations outlined above, the functional form of the tunnel barrier used here is still nevertheless derived from the product of the overlap of two interface potentials, V_{INT} . The aim in proceeding in this manner is to attempt to explain the experimental data obtained in Chapter Four using a simple, analytic and approximate model, which does not require implementation via extensive computational effort.

Boundary conditions are needed for this model and here, the large separation limit of the surface potential is taken to be the workfunction of Cu(100) ($= 4.59\text{eV}$) [5.9]. Following Lang [5.2], a bulk base level for the surface potential of 12eV below the Fermi level is used. It is assumed that the surface potential takes this base level at the positive background edges of both metal electrodes.

The tunnel barrier, $\phi(z)$, takes the functional form of equation (5.3), and is shown in **figure 5.2** below:

$$\begin{aligned} \phi(z) &= \phi_o \left(1 - 1.81 \exp\left(-\frac{\alpha z}{3}\right) - 1.81 \exp(-\alpha z) \right) \left(1 - 1.81 \exp\left(-\frac{\alpha(s-z)}{3}\right) - 1.81 \exp(-\alpha(s-z)) \right) \pm \frac{Vz}{s} \\ &= \phi_o - 1.81\phi_o(-\alpha z) - 1.81\phi_o \exp\left(-\frac{\alpha z}{3}\right) - 1.81\phi_o \exp(-\alpha(s-z)) \\ &\quad - 1.81\phi_o \exp\left(-\frac{\alpha(s-z)}{3}\right) + 3.27\phi_o \exp(-\alpha s) + 3.27\phi_o \exp\left(-\frac{\alpha s}{3}\right) \\ &\quad + 3.27\phi_o \exp\left(-\frac{\alpha(s+2z)}{3}\right) + 3.27\phi_o \exp\left(-\frac{\alpha(3s-2z)}{3}\right) \pm \frac{Vz}{s} \end{aligned} \quad (5.3)$$

where s is the tip-sample separation, z denotes a co-ordinate perpendicular to the plane of the surface within the barrier, V is the applied bias voltage and ϕ_o is the workfunction of Cu(100).

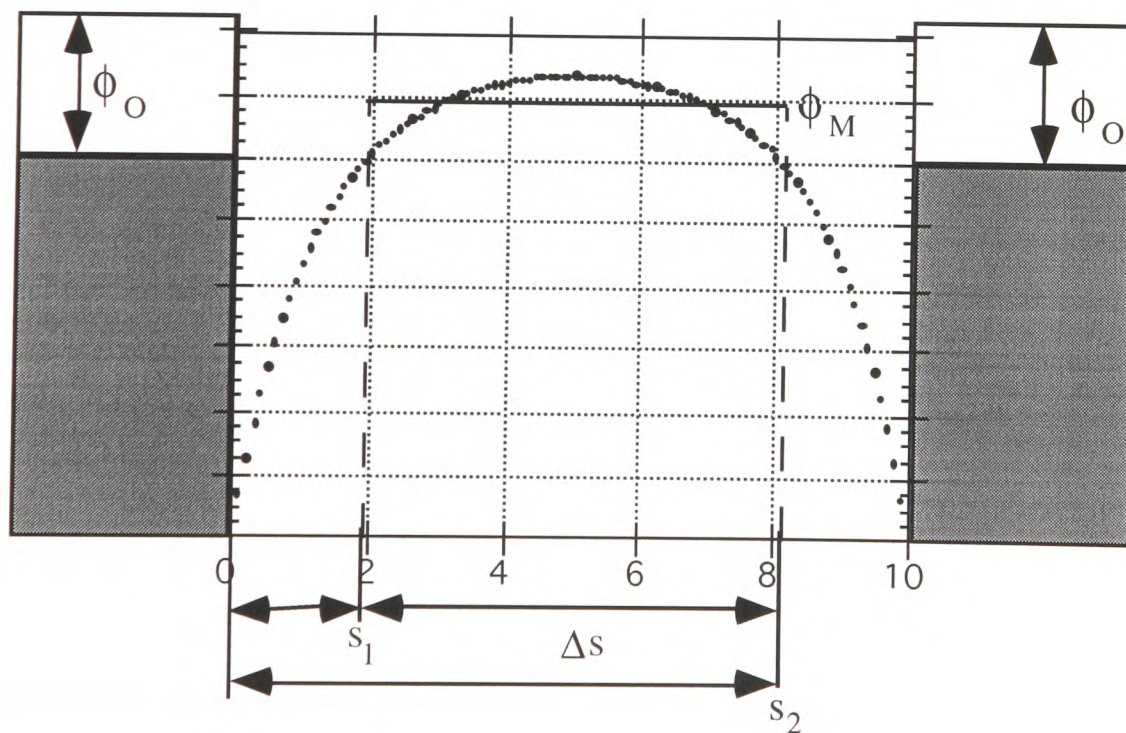


Figure 5.2: A diagram showing the form of the tunnel barrier between the tip and sample. A bias voltage of +10mV is used. The mean value of this tunnel barrier, ϕ_M , is calculated to be $\sim 1.8\text{eV}$. In this figure, the tip-sample separation is $10\text{\AA}$, s_1 and s_2 are the classical turning points. The barrier has a vertical scale of 2eV per large division.

At each tip-sample separation, an effective mean value for the tunnel barrier height, ϕ_M , was determined by integrating the barrier function between the classical turning points (i.e. the points at which the barrier function becomes equal to the Fermi energy). These points were found by solving equation (5.3) numerically by setting the tunnel barrier function equal to zero. To a good approximation, the classical turning points were found to occur at nearly invariant distances in the vacuum gap, taking values $s_1 = 1.95\text{\AA}$ (measured from the positive background edge of the one of the surfaces) and $s_2 = s - s_1$. In addition $\frac{\partial \Delta s}{\partial s} = 1$ (to a second order expansion in the tip-sample separation).

The effective mean tunnel barrier height, ϕ_M varies with tip-sample separation according to equation (5.4), see also **figure 5.3** overleaf:

$$\begin{aligned}
 \phi(s)_M &= \frac{1}{\Delta s} \int_{s_1}^{s_2} \phi(z) dz \\
 &= \phi_o + 3.27\phi_o \exp\left(-\frac{\alpha s}{3}\right) + 3.27\phi_o \exp(-\alpha s) \pm \frac{V}{2\Delta s} \\
 &\quad - \frac{3.62\phi_o}{\alpha \Delta s} \left[3\exp\left(-\frac{\alpha s_1}{3}\right) - 3\exp\left(-\frac{\alpha s_2}{3}\right) + \exp(-\alpha s_1) - \exp(-\alpha s_2) \right] \\
 &\quad + \frac{4.91\phi_o}{\alpha \Delta s} \left[\exp\left(-\frac{\alpha(3s-2s_2)}{3}\right) - \exp\left(-\frac{\alpha(3s-2s_1)}{3}\right) \right. \\
 &\quad \quad \left. - \exp\left(-\frac{\alpha(s+2s_2)}{3}\right) + \exp\left(-\frac{\alpha(s+2s_1)}{3}\right) \right]
 \end{aligned}$$

(5.4)

where Δs , the tunnelling width = $s_2 - s_1$

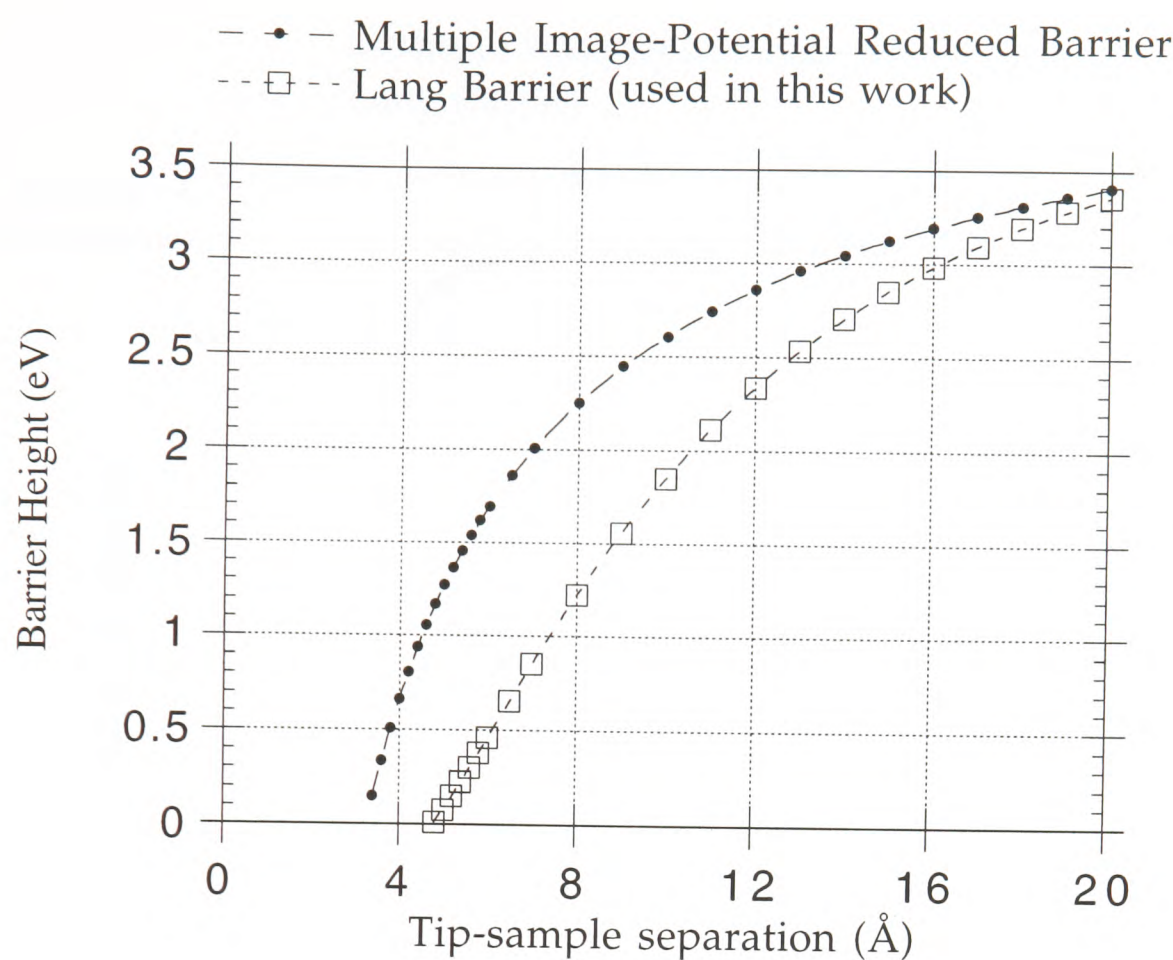


Figure 5.3: A graph showing the mean tunnel barrier height used in this work as a function of tip-sample separation. The multiple image-potential reduced tunnel barrier used by Coombs et al. [5.1] is included for comparison.

Using the multiple image-potential reduced tunnel barrier, Coombs et al. [5.1] have shown that measurement of the derivative $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ is not a good probe of the image potential. The apparent barrier height deduced using this method (see Section 4.2 of Chapter 4) is equal to the surface workfunction down to separations of $\sim 6\text{\AA}$. **Figure 5.4** overleaf shows the apparent barrier height deduced using the current-distance derivative for both the multiple image-potential reduced barrier and the tunnel barrier used in this work. The apparent barrier height deduced from the Lang model collapses from its large separation value $\sim 2\text{-}3\text{\AA}$ before the image-potential reduced barrier, but most of this off-set is due to the difference in effective gap tunnelling widths for the same tip-sample separation. In other words, the two models have different values for the classical turning points. The second feature worthy of comment is that at tip-sample separations $\sim 15\text{-}20\text{\AA}$, use of the Lang model leads to an apparent barrier height which is slightly above the workfunction.

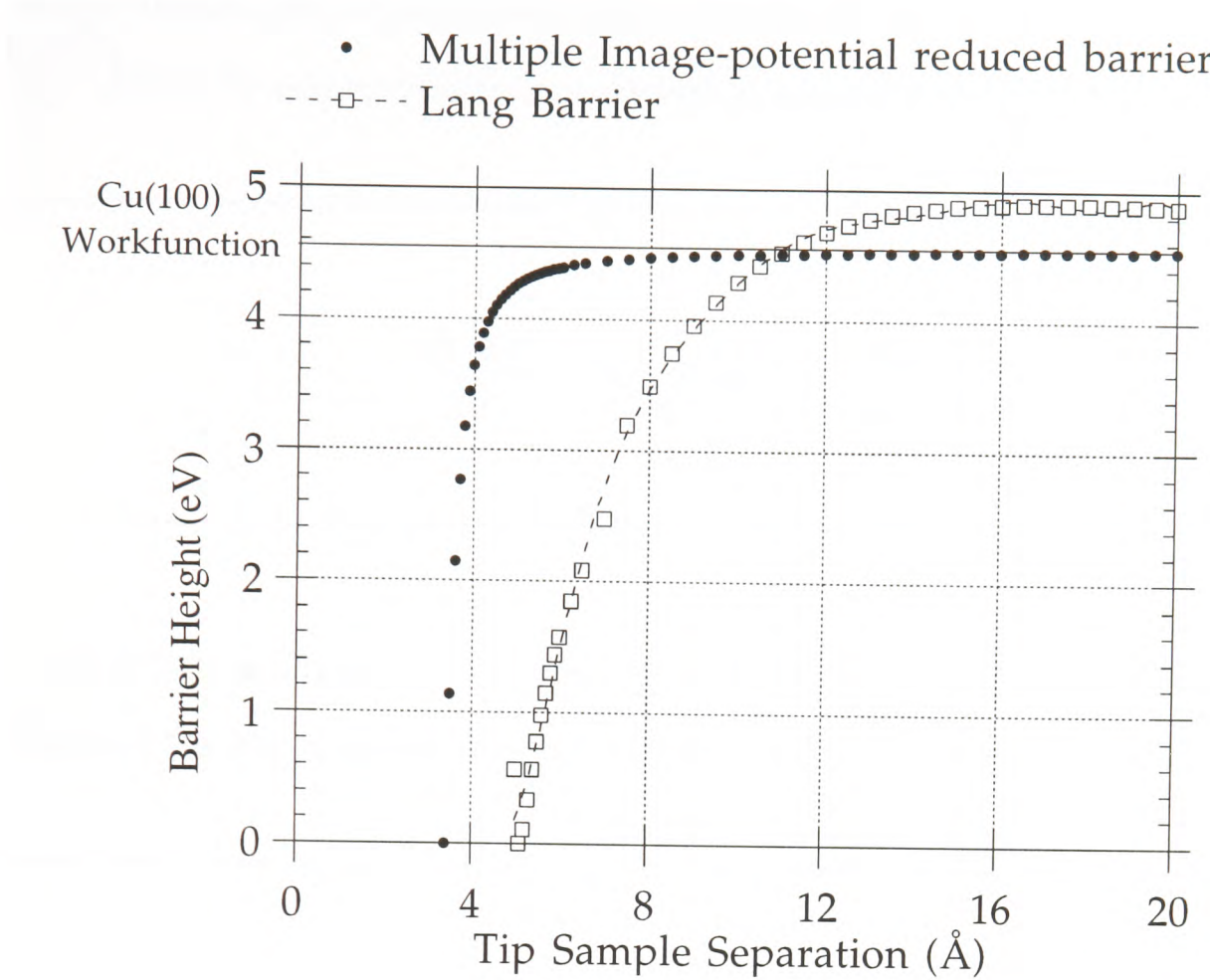


Figure 5.4: A graph showing the apparent barrier height calculated using the derivative $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ using the mean tunnel barrier described in this thesis and the more well known multiple-image-potential reduced barrier.

To see the reason for this behaviour, it is necessary to know what is being measured using $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$. Following the method of Coombs et al. [5.1], the apparent barrier height, ϕ_{APPARENT} , is deduced as:

$$\phi_{\text{APPARENT}} = \frac{\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)^2}{A^2} \tag{5.5}$$

where $\frac{\partial \text{Ln}(I)}{\partial s} = \left[\frac{1}{2\phi_M} \left(1 - A\phi_M^{1/2}\Delta s \right) \frac{\partial \phi_M}{\partial s} - \left(\frac{1}{\Delta s} + A\phi_M^{1/2} \right) \frac{\partial \Delta s}{\partial s} \right]$.

At large tip-sample separations, $(\Delta s)^{-1}$ tends to zero and $A\phi_M^{1/2}\Delta s \gg 1$, thus $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ may be approximated as shown in equation (5.6):

$$\frac{\partial \text{Ln}(I)}{\partial s} \sim -A\phi_M^{1/2} \left(1 + \left(\frac{\Delta s}{2\phi} \right) \left(\frac{\partial \phi_M}{\partial s} \right) \right) \tag{5.6}$$

When this approximation is substituted back into equation (5.5), an expression is obtained for the apparent barrier height:

$$\phi_{\text{APPARENT}} = \phi_M + \Delta s \left(\frac{\partial \phi_M}{\partial s} \right) + \left(\frac{\Delta s^2}{4\phi_M} \right) \left(\frac{\partial \phi_M}{\partial s} \right)^2 \tag{5.7}$$

Equation (5.7) shows that the apparent barrier height is strongly determined by the variation of $\left(\frac{\partial \phi_M}{\partial s}\right)$. At larger tip-sample separations $\sim 10\text{-}20\text{\AA}$, the gradient of the Lang barrier is roughly a factor of two larger than the multiple-image-potential reduced barrier, see **figure 5.5** overleaf. This leads to the result that in the former case, the sum of equation (5.7) is slightly more (a maximum of $\sim 0.4\text{eV}$) than the surface workfunction. At larger separations still, ($s \sim 50\text{-}100\text{\AA}$) the tunnel barrier gradient decreases and the sum of equation (5.7) approaches the expected workfunction limit.

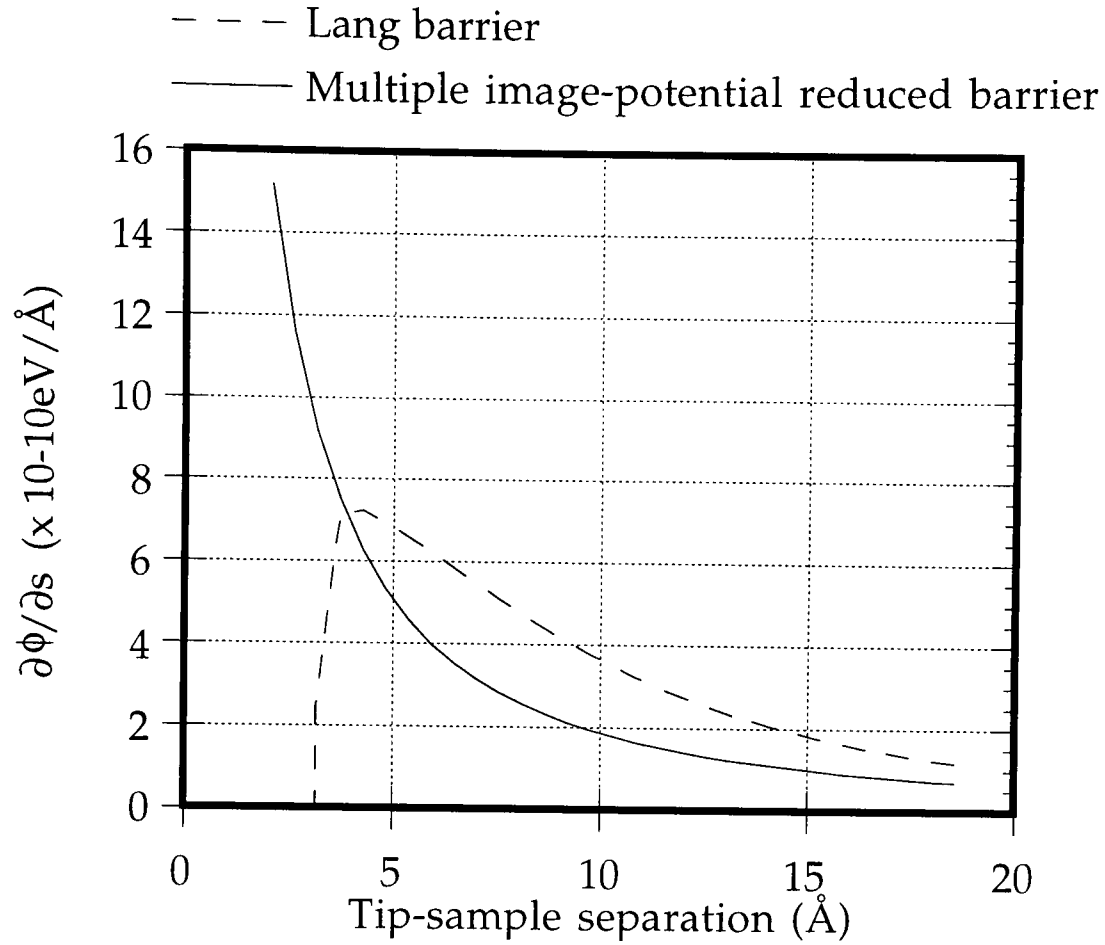


Figure 5.5: A graph showing the variation of the tunnel barrier gradient as a function of tip-sample separation for the two barrier models described in this work.

For completeness' sake and the requirement of equation (5.1) it should be noted that the gradient of the tunnel barrier introduced in this work takes the form of equation (5.8) below:

$$\begin{aligned}
 \frac{\partial \phi(s)_M}{\partial s} = & -3.27\alpha\phi_o \left[\frac{1}{3} \exp\left(-\frac{\alpha s}{3}\right) + \exp(-\alpha s) \right] \\
 & + \frac{3.62\phi_o}{\alpha\Delta s^2} \left[3\exp\left(-\frac{\alpha s_1}{3}\right) - 3\exp\left(\frac{\alpha s_2}{3}\right) + \exp(-\alpha s_1) - \exp(-\alpha s_2) \right] \\
 & - \frac{3.62\phi_o}{\alpha\Delta s} \left[\alpha\exp(-\alpha s_2) + \alpha\exp\left(-\frac{\alpha s_2}{3}\right) \right] \\
 & - \frac{4.91\phi_o}{\alpha\Delta s^2} \left[\exp\left(-\frac{\alpha(3s-2s_2)}{3}\right) - \exp\left(-\frac{\alpha(3s-2s_1)}{3}\right) - \exp\left(-\frac{\alpha(s+2s_2)}{3}\right) \right. \\
 & \left. + \exp\left(-\frac{\alpha(s+2s_1)}{3}\right) \right] \\
 & + \frac{4.91\phi_o}{\alpha\Delta s} \left[\frac{\alpha}{3}\exp\left(-\frac{\alpha(3s-2s_2)}{3}\right) + \alpha\exp\left(-\frac{\alpha(3s-2s_1)}{3}\right) + \alpha\exp\left(-\frac{\alpha(s+2s_2)}{3}\right) \right. \\
 & \left. - \frac{\alpha}{3}\exp\left(-\frac{\alpha(s+2s_1)}{3}\right) \right]
 \end{aligned} \tag{5.8}$$

5.3. The Effect of Including the Pre-Exponential Factors on the Tunnel Barrier Height:

By substituting the results of equations (5.4) and (5.8) into the expression for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$, the variation of this parameter can be assessed as a function of the tunnel gap conductance. Moreover the tunnel barrier heights implied by the slopes of experimental $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots can be deduced.

In figure 5.6 overleaf, experimentally determined values of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ are plotted. Each point is taken from a different $\langle 001 \rangle$ corrugation data set and plotted using the tunnel gap conductance of the final experimental image taken prior to the on-set of the corrugation roll-off. A series of theoretical curves showing $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ as a function of tunnel conductance (calculated using the $\text{Cu}\langle 001 \rangle$ surface reciprocal-lattice vector) are also included. These curves are able to successfully reproduce the experimentally observed change in $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ from 0.75 to 1.25 over roughly a factor of three change in tunnel conductance which corresponds to a change in tip-sample separation of $\sim 0.4\text{\AA}$.

Note that in order to calibrate the tunnel conductance, the theoretical curves plotted here require an estimate of the effective area of current emission. The curves shown in figure 5.6 were plotted using values of 0.1 (lowest curve in figure), 0.05, 0.03 and 0.02 (highest curve) times the area of a hemisphere of radius equal to a tungsten atom ($\sim 1.3 \times 10^{-19} \text{\AA}^2$). This figure shows that the current emission area is not constant between different experiments, although these curves are able to estimate upper and lower limits for this term.

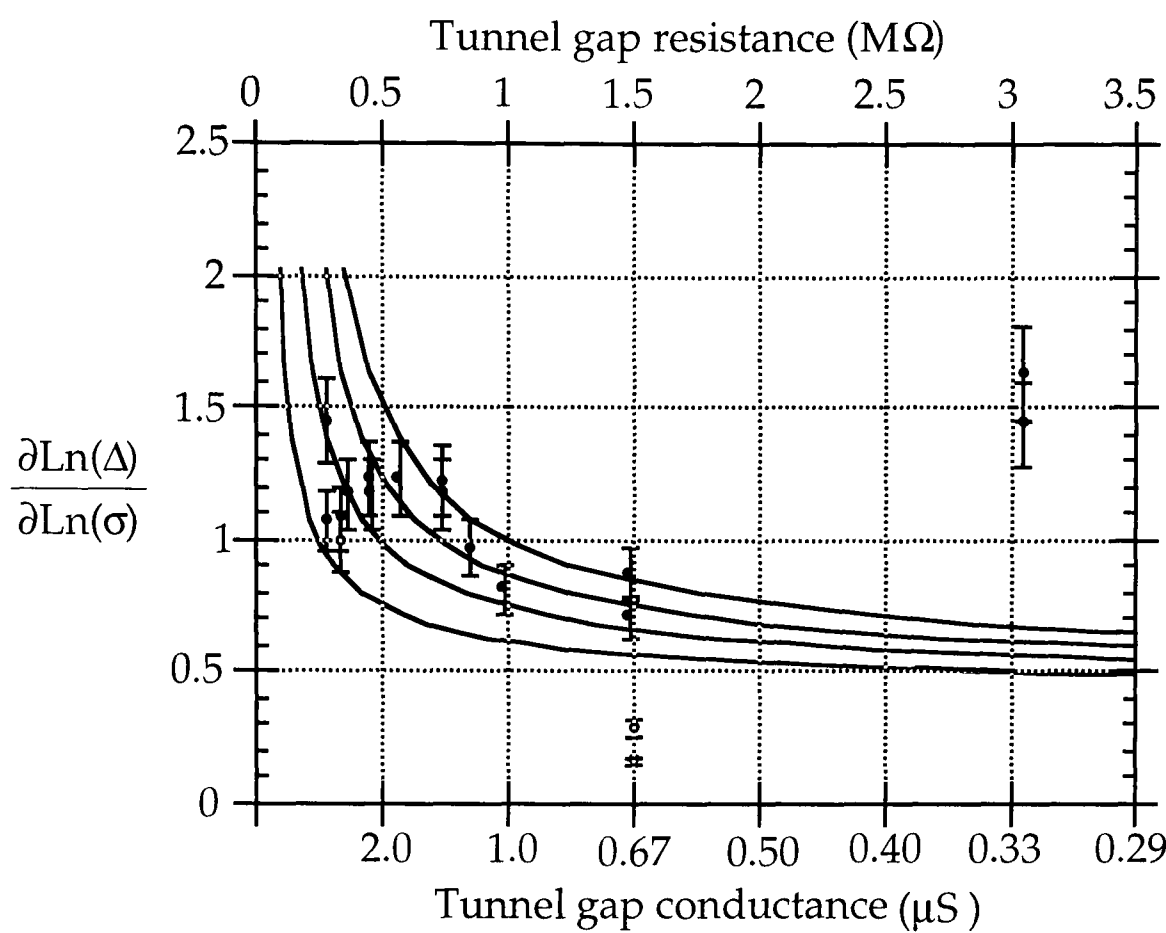


Figure 5.6: A graph showing a theoretical plot of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ calculated using equation (5.1). Experimental points taken from $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots for $\langle 001 \rangle$ corrugation height data are also included.

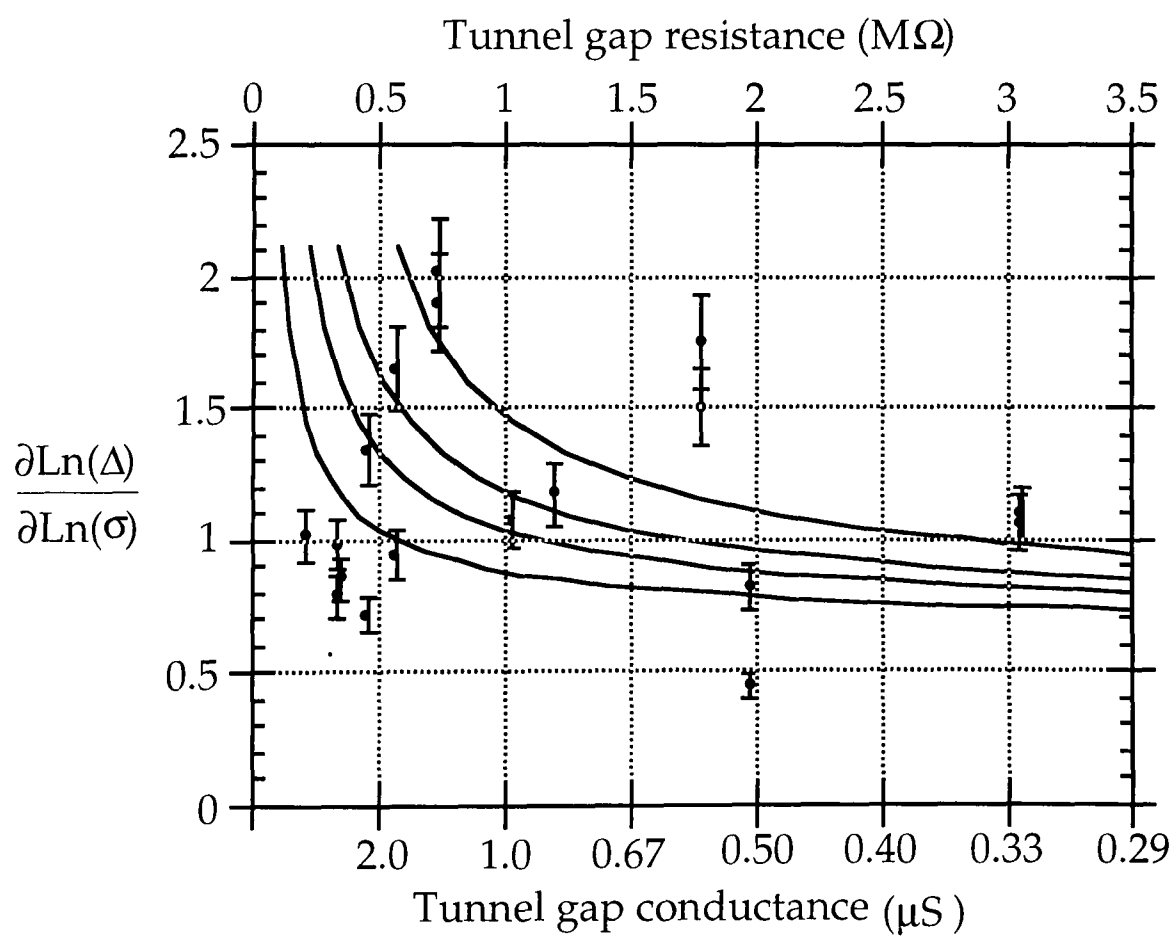


Figure 5.7: as figure 5.6 but for $\langle 011 \rangle$ data.

The equivalent experimental data and calculated curves for the $\langle 0\bar{1}1 \rangle$ corrugation height data are shown in **figure 5.7**. Once again, the corresponding experimental data points are mostly grouped in a fairly narrow band between 0.75 and 1.25. However, in this latter case, the theoretical curve falls off less rapidly with decreasing tunnel gap conductance. The change in $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ from 0.75 to 1.25 takes place over one order of magnitude change in tunnel gap conductance (equivalent to a change in tip-sample separation of $\sim 0.7\text{\AA}$). The theoretical absolute values of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ are larger at a given tunnel conductance in the case of the $\langle 0\bar{1}1 \rangle$ curve. Both of these observations are simple artefacts of the G-vector dependence of the corrugations in equation (5.1). The same four values for the current emission area used in **figure 5.6** were similarly used to calibrate the conductance in **figure 5.7**. These values do not so accurately describe the $\langle 0\bar{1}1 \rangle$ data, but they do confirm the area of emission to be of order $1 \times 10^{-20} \text{\AA}^2$.

The curves in **figures 5.6** and **5.7** are not terribly useful for deducing tunnel barrier heights unless the experimental points sit close to the appropriate theoretical curve. In fact it is more useful to replot these figures directly in terms of the implied tunnel barrier height, ϕ_M , which is after all the reason for performing these experiments in the first place.

Figure 5.8 overleaf shows a theoretical plot of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ calculated using the $\text{Cu}\langle 001 \rangle$ reciprocal-lattice vector as a function of the tunnel barrier height. The experimental points for the $\langle 001 \rangle$ corrugation height data are included in this figure so as to indicate the implied values of tunnel barrier height. **Figure 5.9** overleaf shows the equivalent curve for the $\text{Cu}\langle 0\bar{1}1 \rangle$ reciprocal-lattice vector together with the experimental points deduced from corrugation height measurements in that direction.

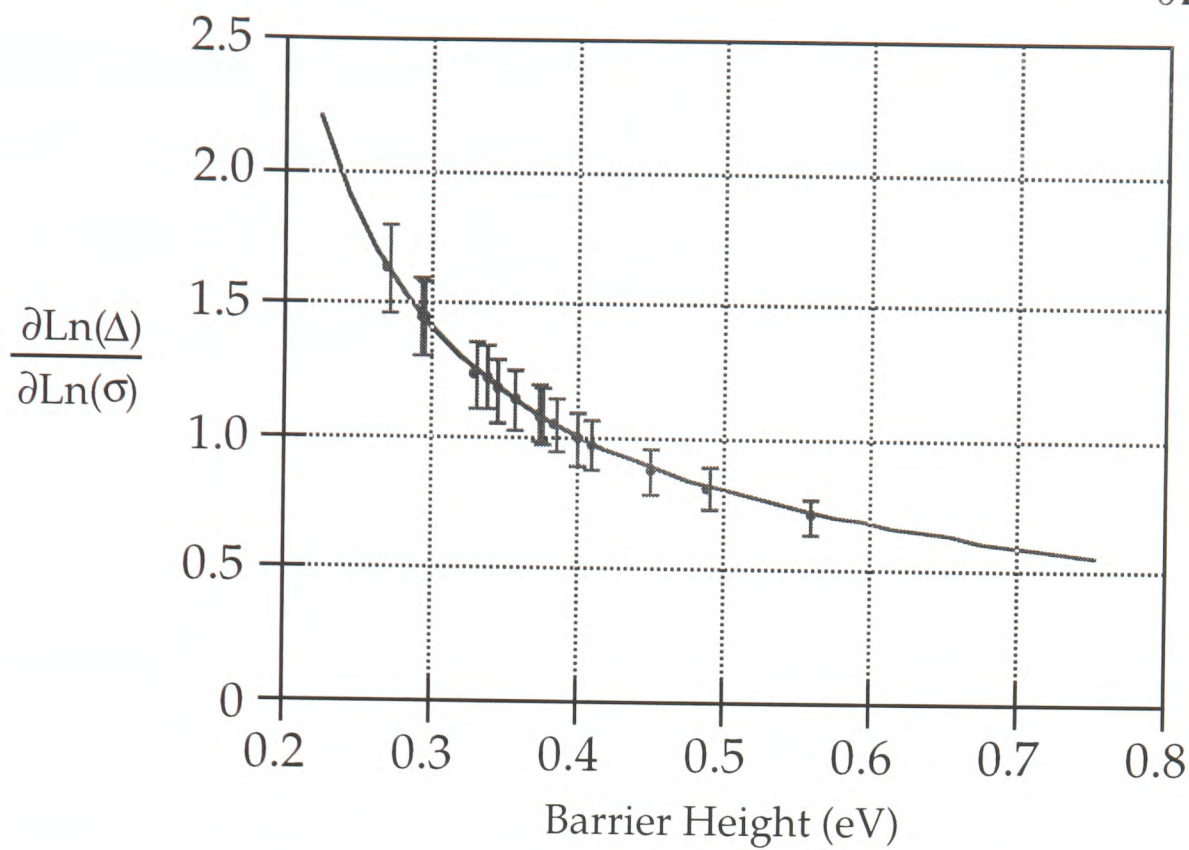


Figure 5.8: A graph showing $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ and the corresponding implied tunnel barrier heights. The data points are taken from $\langle 001 \rangle$ corrugation height data.

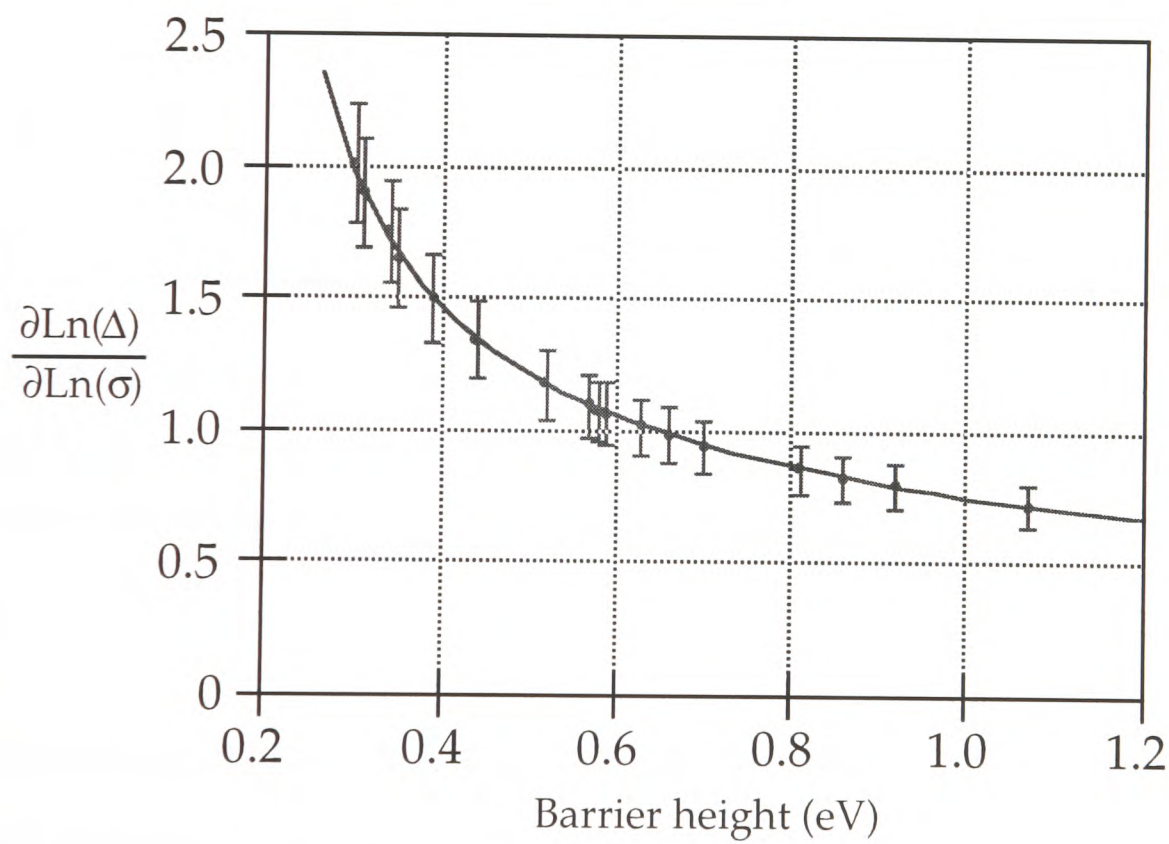


Figure 5.9: as **figure 5.8**, but the data points were taken from $\langle 0\bar{1}1 \rangle$ corrugation height data.

The implication of **figures 5.8** and **5.9** is that even when account is made of the pre-exponential factors, the deduced tunnel barrier heights are still strongly dependent upon the G-vector terms of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$. The data of **figure 5.8** shows a

spread of values for the tunnel barrier height ranging from 0.25-0.55eV, with a cluster of values in the range 0.3-0.4eV. The distribution of tunnel barrier heights in **figure 5.9** is more diffuse, ranging from 0.3-1.1eV. However, there is a preponderance of values at $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right) \sim 1$, corresponding to tunnel barrier heights ~ 0.5 -0.7eV.

Most of the values of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ in both figures fall in the range 0.75-1.25, which indicates that $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ is more or less independent of the surface direction along which the corrugation heights are measured. **Figure 5.10** below summarises the tunnel barrier heights predicted by both calculated curves for these defining values.

	$\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right) = 0.75$	$\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right) = 1.25$
Figure 5.8: ($\langle 001 \rangle$ data)	0.53	0.33
Figure 5.9: ($\langle 0\bar{1}1 \rangle$ data)	0.98	0.48

Figure 5.10: A table showing that corrugation measurements along different reciprocal lattice-vector directions lead to different values for the tunnel barrier height deduced using $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$. All tunnel barrier heights are quoted in units of electron volts (eV).

The tunnel barrier heights deduced from **figures 5.8** and **5.9** are approximately one order of magnitude lower than the workfunction of Cu(100). This result is an indication that the tip and sample were in close proximity when the STM data was taken. The values for the tunnel barrier calculated from the $\langle 0\bar{1}1 \rangle$ corrugation data are roughly a factor of two larger than those obtained from the $\langle 001 \rangle$ corrugation data. By recourse to equation (4.4), these differences are attributed to differences in the G-vector term in the parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$.

Finally in this section, it should be stated that these theoretical calculations were repeated using the multiple image-potential reduced barrier. However, in this latter case, the variation in $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ over the same range of experimental values was observed to occur over only a 20% change in the tunnel gap conductance. This corresponds to a very small ($\sim 0.15\text{\AA}$) change in gap width which does not seem physically plausible.

5.4 The interpretation of $\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}$.

The parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ has not been previously used to deduce tunnel barrier heights and so it is useful to have some idea of what is being measured physically in these experiments. As discussed in Chapter Four, the tunnel barrier height should be independent of the direction along which the corrugation heights are measured. Thus the following analysis is for a metal surface with large inter-atomic spacings.

When imaging such a metal surface using a large tip-sample separation, the condition $\kappa \gg \frac{G}{2}$ is realised. This enables the corrugation height decay constant, β , of equation (4.3) to be expanded using the binomial theorem:

$$\beta = 2\left(\kappa^2 + \frac{G^2}{4}\right)^{1/2} - 2\kappa$$

For $\kappa > \frac{G}{2}$

$$\beta \approx \frac{G^2}{4\kappa}$$

(5.9)

If a tunnel barrier height of 4eV is assumed to exist above a surface with large inter-atomic spacings, such as the Au(110) (1x2) reconstructed surface, then for

the 2x direction, which has a spacing of 8.2Å, the approximation of equation (5.9) introduces an error of ~ 15% into the decay constant, β .

Substituting equation (5.9) into the numerator of equation (5.1) gives:

$$\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \approx \left[-\frac{1}{2\phi_M} \frac{\partial \phi_M}{\partial s} - \frac{G^2}{4\kappa} \left(\frac{\Delta s}{2\phi_M} \frac{\partial \phi_M}{\partial s} - 1 \right) \right] / \left[\frac{1}{2\phi_M} \left(1 - A\phi_M^{1/2}\Delta s \right) \frac{\partial \phi_M}{\partial s} - \left(\frac{1}{\Delta s} + A\phi_M^{1/2} \right) \right] \quad (5.10)$$

In this equation, the good assumption $\left(\frac{\partial \Delta s}{\partial s} \right) \sim 1$ is implicitly made. The assumption of a large tunnel barrier height also implies a large tip-sample separation. This allows the denominator of equation (5.10), to be approximated as previously discussed in equation (5.6) of Section 5.2, leading to:

$$\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \approx \left[-\frac{1}{2\phi_M} \frac{\partial \phi_M}{\partial s} - \frac{G^2}{4\kappa} \left(\frac{\Delta s}{2\phi_M} \frac{\partial \phi_M}{\partial s} - 1 \right) \right] / \left[-A\phi_M^{1/2} \left(1 + \frac{\Delta s}{2\phi_M} \frac{\partial \phi_M}{\partial s} \right) \right] \quad (5.11)$$

However, equation (5.11), still has the difficulty of the G-vector term in the numerator. At very large separations ($>50\text{Å}$), the numerator approaches a value of $\frac{G^2}{4\kappa}$ as $\frac{\partial \phi_M}{\partial s}$ falls off to zero. In order to reduce the contribution of the G-term in the numerator, it is necessary to investigate this equation at smaller separations. Of course, this also has the unfortunate side effect that the condition $\kappa > \frac{G}{2}$ is not so well satisfied.

At moderate tip-sample separations $\sim 6\text{-}7\text{\AA}$, the first term in the numerator of equation (5.11) is approximately one order of magnitude larger than the second term. At such separations, the tunnel barrier gradient is steep and so $\left(\frac{1}{2\phi_M}\right)\left(\frac{\partial\phi_M}{\partial s}\right)$ takes a value close to one thereby cancelling out the second term in brackets. There is a price to be paid for the smallness of this second term, at these separations the tunnel barrier height is well below its workfunction limit and at a separation of $6\text{-}7\text{\AA}$ and $\kappa \sim \frac{4}{3} \frac{G}{2}$. If the second term in the numerator is neglected under these circumstances, the result is equation (5.12).

$$\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \approx \left[-\frac{1}{2\phi_M} \frac{\partial\phi_M}{\partial s} \right] / \left[-A\phi_M^{1/2} \left(1 + \frac{\Delta s}{2\phi_M} \frac{\partial\phi_M}{\partial s} \right) \right] \quad (5.12)$$

In order to obtain equation (5.12), it was noted that for separations $\sim 6\text{-}7\text{\AA}$, $\left(\frac{1}{2\phi_M}\right)\left(\frac{\partial\phi_M}{\partial s}\right) - 1 \sim 0$. This can also be used for an approximation in the denominator of equation (5.12), which leads directly to a simple expression for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$.

$$\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \sim \frac{1}{2A\phi_M^{1/2} \Delta s} \quad (5.13)$$

This final equation gives a physical interpretation of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$. Providing one assumes a particular model for the tunnel barrier as a function of tip-sample separation, then a measurement of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ allows for a simultaneous determination of the mean tunnel barrier height and the effective tunnelling width, that the barrier height corresponds to. This result is an important step

forward in STM as previous studies to measure the tunnel barrier height have concluded that in fact one measures a quantity which is proportional to the unreduced workfunction [5.1]. The complete generality of this result means that in principle it should be possible to investigate any model for the form of the tunnel barrier and to even assess effects such as variations in the local tip radius as well as tip chemistry. This result also implies that it should be possible to probe the image potential using this technique.

Figure 5.11 below shows a plot of the full theory (using the reciprocal-lattice vector for the 2x direction of the Au(110) (1x2) reconstruction) and the approximation of equation (5.13). Agreement between the approximate curve and full-theory curve is seen to be good at least at small values of the tunnel conductance. The two curves are not so close at large values of the conductance where $\left(\frac{1}{2\phi_M}\right)\left(\frac{\partial \phi_M}{\partial s}\right) \gg 1$. Making a better approximation for this term in the high conductance region would only alter equation (5.13) by a small numeric factor and would not change the basic result obtained.

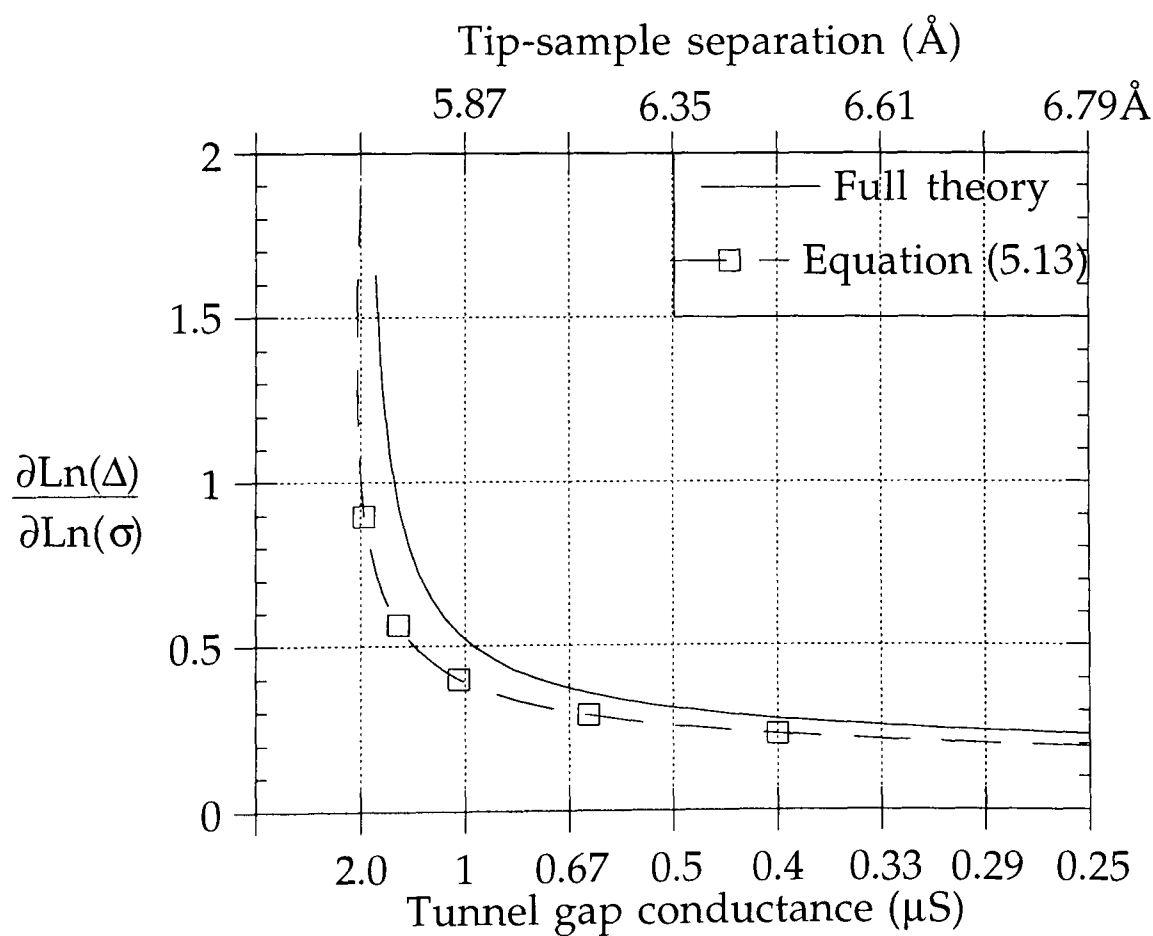


Figure 5.11: A comparison of the full theory used to calculate $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ with the approximate theory of equation (5.13).

Finally in this section, although equation (5.13) is not strictly applicable for atomic-scale resolution imaging, it nevertheless provides an insight into the reason for the difference observed in Section (5.3) in the behaviour of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ as a function of the tunnel conductance when comparing the Lang barrier and the multiple-image reduced tunnel barrier model.

By differentiating equation (5.13), the rate of change of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ is given as:

$$\frac{\partial^2 \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)^2} = \frac{-1}{2A\phi_M^{1/2} \Delta s} \left[\left(\frac{1}{2\phi_M} \right) \left(\frac{\partial \phi_M}{\partial s} \right) + \frac{1}{\Delta s} \right] \quad (5.14)$$

Over the region of interest, namely $0.75 < \left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right) < 1.25$, we know from equation (5.13) that the term outside the brackets of equation (5.14) does not vary significantly between the two tunnel barrier models. However, over the corresponding range of tip-sample separations ($\sim 3.55\text{-}3.7\text{\AA}$ in the case of the multiple image-potential reduced tunnel barrier and $\sim 5.6\text{-}6.05\text{\AA}$ for the Lang barrier), the former tunnel barrier height model exhibits a much larger gradient than the latter (see **figure 5.5**). This is the dominant reason for the rapid variation of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ when using the multiple image-potential reduced tunnel barrier.

5.5 Tunnel Barrier Heights Deduced from a Metal Surface With Large Inter-Atomic Spacings:

In the previous section, the physical significance of the parameter $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ was discussed. It is interesting to know what values for the tunnel barrier height are implied by the experimental data in circumstances where the simple relationship of equation (5.13) is valid. The analysis of section 5.4 is not strictly applicable to densely-packed metallic planes such as the Cu(100) surface. However by taking advantage of an experimental error, some progress in this direction can be made.

During an early set of experiments on the Cu(110) surface, the author annealed the crystal to 650°C over a series of sputter-anneal cycles. The recommended annealing temperature is only 550°C and as can be seen in **figures 5.12 and 5.13** overleaf, a bizarre reconstruction was seen using STM. Unfortunately no LEED or Auger data is available to provide any additional clues as to the nature of this surface and so analysis of this structure has had to be confined to the STM images themselves. The raw data was not consistent with any well known surface reconstruction. However by re-scaling the data via an 8% expansion along the Y-axis and a 3% contraction along the X-axis, this surface structure has been deduced as the c(6x2) reconstruction, usually seen as a result of high oxygen exposures on Cu(110) [5.10, 5.11]. The use of calibration factors may seem rather arbitrary, although the need for such factors in excess of 10% has been noted when examining other surfaces using an Omicron STM [5.12]. One possible reason for the unexpected observation of this reconstruction is that an unusual metal polish, Brasso, was used to prepare the crystal prior to insertion in to the vacuum system. Oxygen may have become embedded into the bulk crystal and only subsequently released as a result of the high temperature anneal.

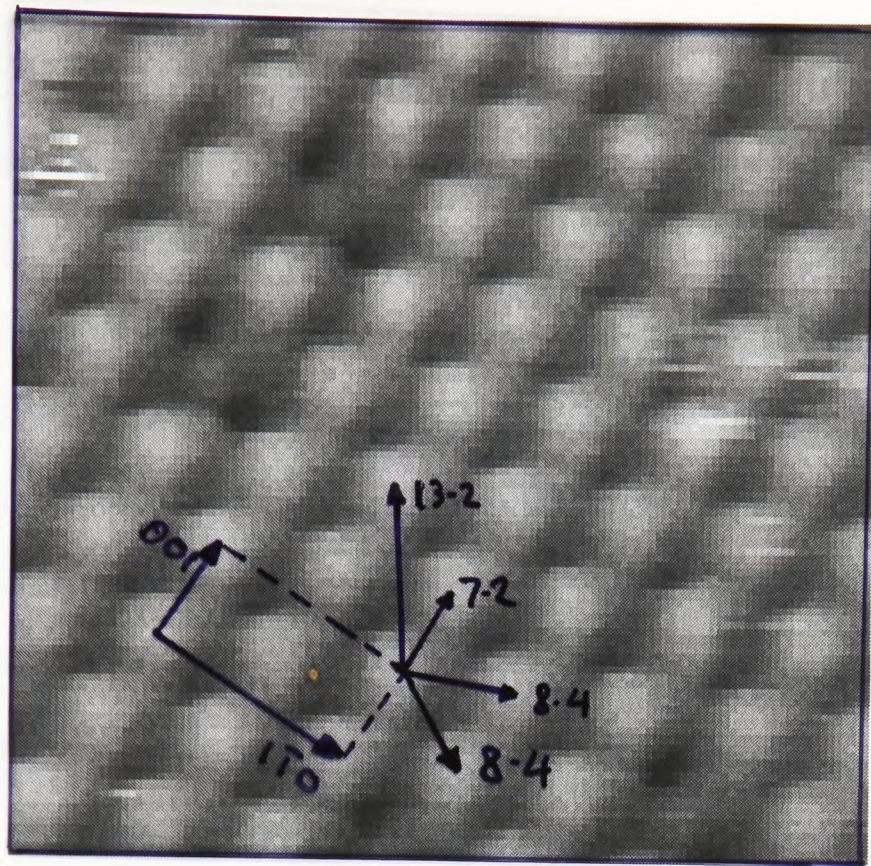


Figure 5.12: A 61x56Å (vertical scale 1.1Å) image of the c(6x2) reconstruction seen on Cu(110). The tunnel current was 10nA and the bias voltage -0.02V. The transparency shows a unit cell of the reconstruction together with the surface directions along which corrugation heights were measured; inter-atomic spacings are given in Ångströms. The defects in the top left hand corner show that the tip was sharp.

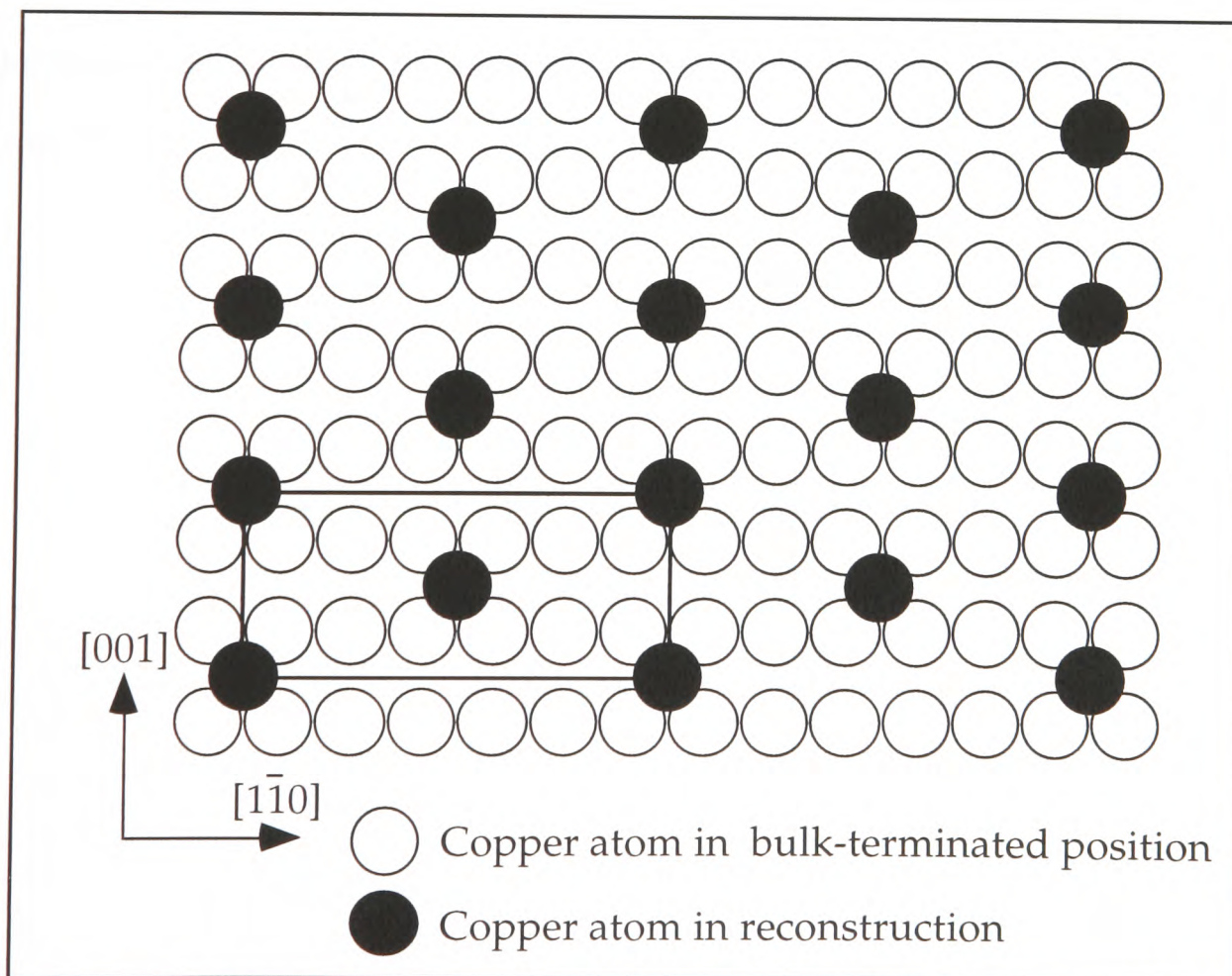


Figure 5.13: A diagram showing the atomic positions in the c(6x2) reconstruction seen in this work for Cu(110). A single unit cell is outlined in the bottom left-hand corner.

It was possible to image this reconstruction over a period of several hours. Moreover, the relative orientation of the surface was seen to rotate as a result of deliberate changes in the scan direction. Steps were also seen in this surface. These three factors give to support to the notion that the microscope was imaging a genuine surface structure. A large number of images were taken of this surface varying the tunnelling parameters in the manner described in Chapter Four. It was possible to vary the potential bias (while holding the tunnel current constant) over a larger range (V : 0.15 - 0.8V, $I = 5\text{nA}$) than was possible for the high resolution data presented in the previous Chapter. Images were also taken by holding the potential bias at a constant value and varying the tunnel current (I : 4-50nA, $V=+0.2\text{V}$). Corrugation height measurements were taken from these experimental images and are plotted in **figures 5.14 and 5.15** overleaf. Such data is important as far as the theory of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ is concerned. The combination of tunnelling parameters and surface structure successfully reproduce the conditions outlined in the previous section which are necessary to be able to accurately interpret $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ using the simple equation (5.13).

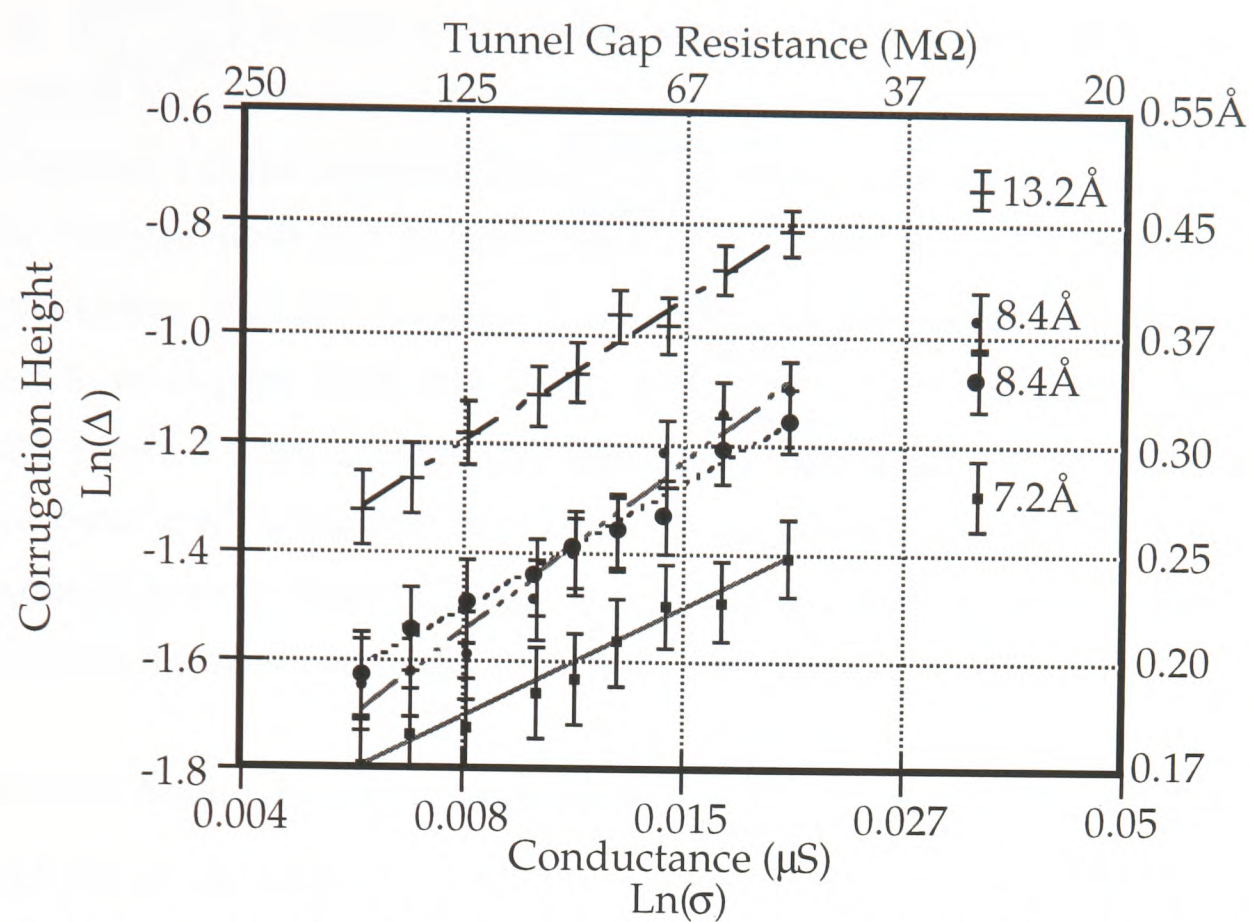


Figure 5.14: A $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot showing data taken from the $c(6 \times 2)$ reconstruction seen on a $\text{Cu}(110)$ surface. In this data set, the tunnel current was held constant at 5 nA , while the potential bias was varied between 0.15 and 0.8 V . The lengths $7.2\text{ \AA}$, $8.4\text{ \AA}$, $8.4\text{ \AA}$ and $13.2\text{ \AA}$ refer to inter-atomic spacings of the principle directions along which corrugations were measured. The right hand vertical scale shows the values of corrugation heights in this experiment.

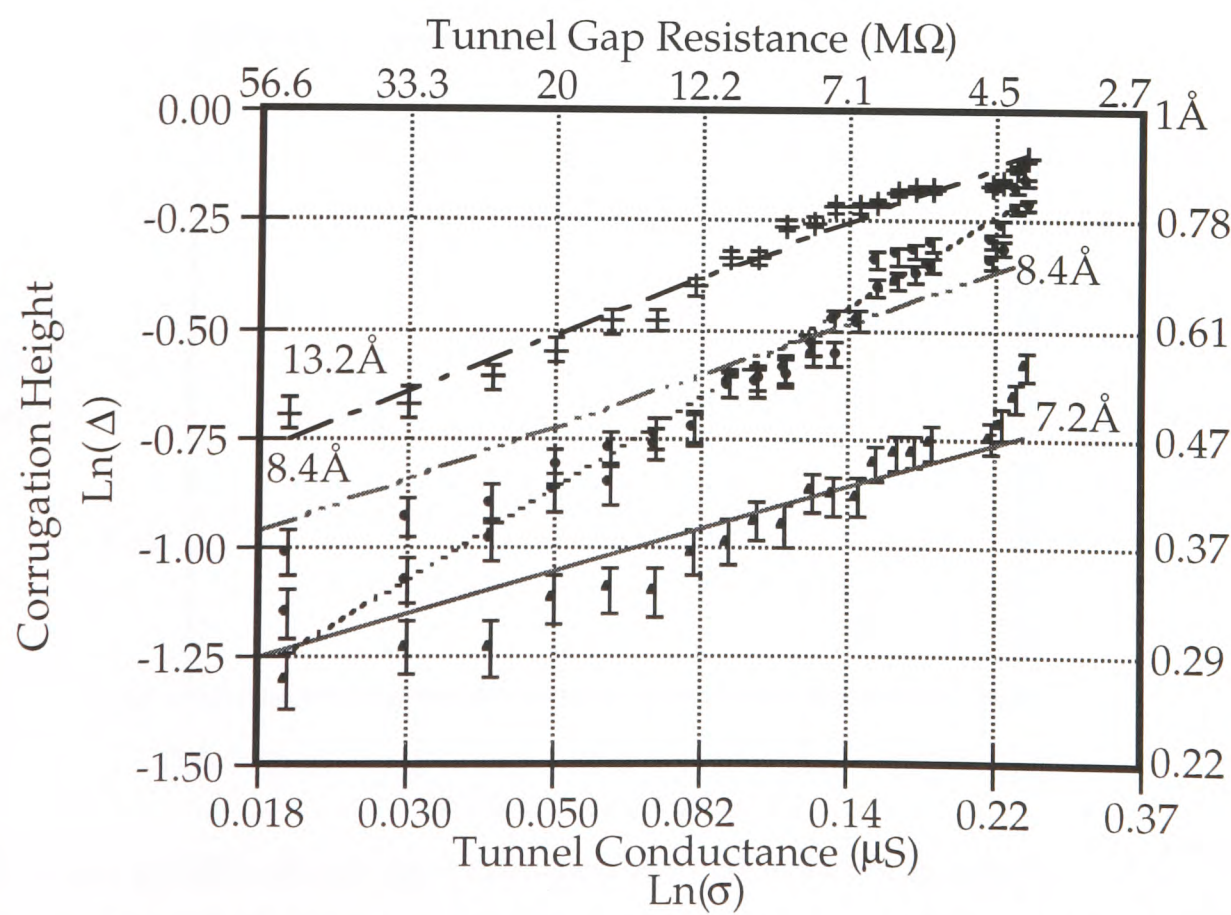


Figure 5.15: as **figure 5.14**, except that in this data the potential bias was held constant at 0.2 V , while the tunnel current was varied between 4 and 50 nA .

From the approximately parallel best-fit lines drawn through each data set, the value of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ is seen to be independent of the reciprocal-lattice vector along which the corrugation heights were measured. In order to deduce the tunnel barrier height implied by $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$, the value of the slope for the periodic feature with the largest inter-atomic spacing (and hence smallest reciprocal lattice-vector) was used. This optimises the approximations made in section 5.4. In **figure 5.14**, the value of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ for the 13.2Å feature is 0.44 ± 0.04 , while it takes a value of 0.26 ± 0.03 in **figure 5.15**. Note, however, that the data measured along the two unit cell diagonals, spacing 8.4Å, does not quite superimpose in these figures. This is further support for the notion that the tunnelling tip is not spatially uniform at the apex.

In **figure 5.16** below, the full theory for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ of equation (5.1) is plotted for the 13.2Å G vector together with the approximation of equation (5.13). The tunnel barrier heights implied by the data of **figures 5.14** and **5.15** can be immediately deduced by projecting the curves onto the x-axis at the appropriate values of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$, these results are tabulated in **figure 5.17**.

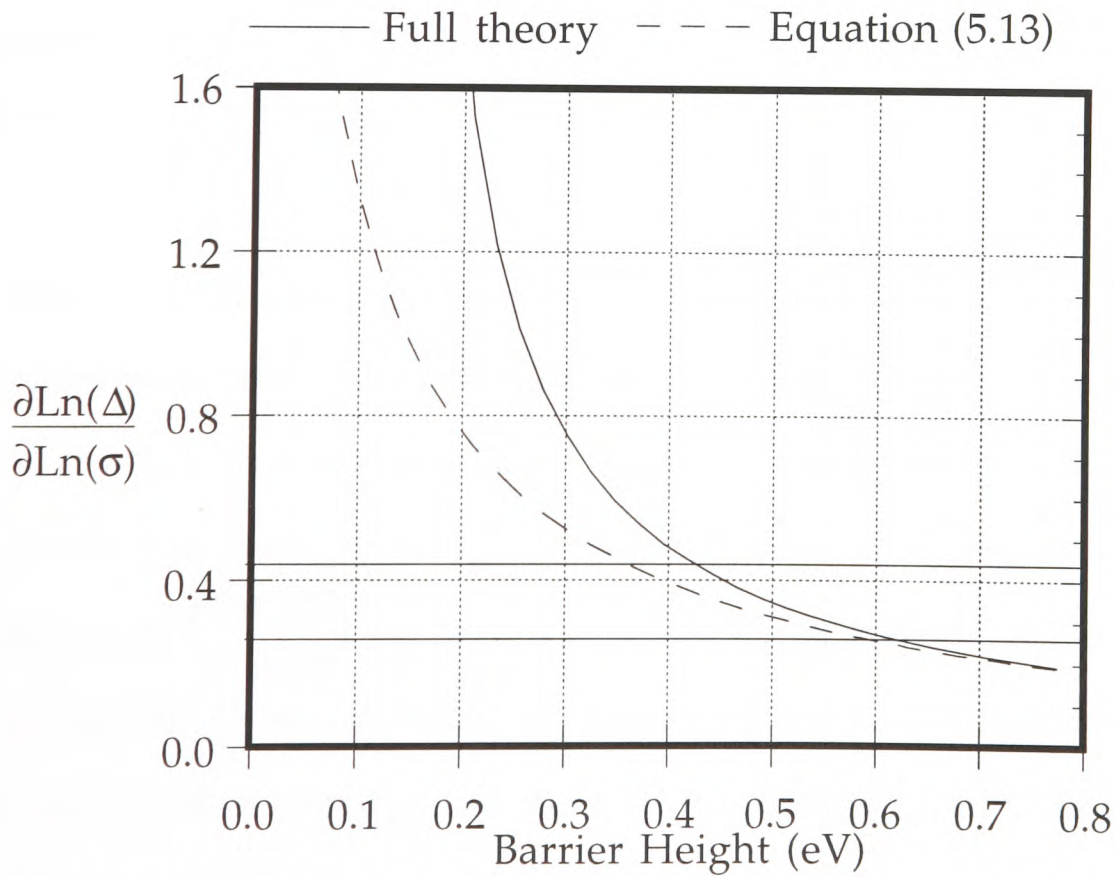


Figure 5.16: A graph showing a comparison of a full calculation of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ using a reciprocal-lattice vector for the 13.2Å feature of **figure 5.12** and the approximate result obtained using equation (5.13).

	Full Theory	Equation (5.13):
Figure 5.15	0.36	0.42±0.13
Figure 5.16	0.59	0.61±0.09

Figure 5.17: A table showing the tunnel barrier heights implied by the corrugation height data of **figures 5.14** and **5.15**, using different theoretical treatments. All tunnel barrier heights are quoted in eV.

These data show that use of the approximation of equation (5.13) works best to deduce the tunnel barrier height for surfaces with small reciprocal-lattice vectors when imaging at moderate values of tunnel gap conductance.

5.6 Summary:

In this Chapter, the tunnel barrier height has been investigated further by taking account of the separation dependent pre-exponential terms of the equations for the tunnel conductance and the corrugation height when deducing $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$.

The experimental data presented in this thesis has been shown to be consistent with a model for the tunnel barrier height in which there are two contributing factors: the first term is associated with the surface electrostatic-dipole layer and the second with exchange-correlation effects. Using this model, in the expression for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ leads to the deduction of tunnel barrier heights which are substantially lower than the workfunction of Cu(100) and usually ~ 0.5-1eV when using $\langle 0\bar{1}1 \rangle$ corrugation data. However, just as in Chapter Four, the tunnel barrier height values obtained for $\langle 0\bar{1}1 \rangle$ corrugation data are approximately a factor of two larger than those obtained from $\langle 001 \rangle$ data.

By considering a metal surface with large inter-atomic spacings and hence minimising the influence of surface reciprocal-lattice vectors, the tunnel barrier height has been shown to be proportional to $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)^2$. This approximation for $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ has been shown to give a good estimate of the tunnel barrier height above the Cu(110) c(6x2) reconstruction when using moderate values for the tunnel gap conductance. However even in this optimised case, the values obtained for the tunnel barrier height are still only $\sim 0.5\text{eV}$.

The conditions for which it is most appropriate to use $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ as a measure of the tunnel barrier are consistent with the ideas of Tersoff and Hamann. They cite the same criteria when deriving their equation for the distance dependence of corrugation heights above a surface, see equation (4.3) in Chapter Four.

5.7 References:

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Chapter 6

Tip-Surface Interactions

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6.1 Introduction:

The discussion of Chapter Four showed that at small values of the tunnel gap conductance, the extent of tip-sample interaction in STM is limited to the tunnel current flowing between the electrodes. However, as **figures 4.10-4.13** inclusive have shown, when the tunnel gap conductance is large ($\sim 1\mu S$), a "roll-off" in the corrugation heights is observed. In other words, the corrugation heights do not increase by as much as would be expected from an extrapolation of the linear low conductance region of a corrugation-conductance graph. Eventually a point can even be reached where the corrugation heights decrease when compared with data points taken at slightly smaller values of the tunnel conductance. This observation is indicative of the fact that under the normal mode of STM imaging, the tip and sample can interact strongly. The nature of this interaction is the subject of this Chapter.

The material presented in this Chapter is organised as follows. In section 6.2, I review the experimental work which indicates that the tip and sample can interact strongly. Details of the Molecular Dynamics simulations performed in

this work are presented in section 6.3, while a quantitative analysis of the corrugation roll-off is given in section 6.4. In section 6.5, the magnitudes and implications of tip-surface forces are investigated. Finally in section 6.6, the influence is discussed of perturbations in surface electronic structure upon the corrugation height.

6.2 Evidence For Tip-Surface Interactions in STM:

In principle, inter-atomic forces (magnitude $\sim 10^{-9}\text{N}$) can be investigated by measuring the deflection of a sample (in the form of a cantilever) in response to the presence of a probe tip. In practice, the direct measurement of such forces has been made difficult by the requirement in these experiments of stiff cantilevers with spring constants $\sim 100\text{Nm}^{-1}$; deflections in such levers are $\sim 0.1\text{\AA}$ and are hard to detect experimentally. More success has been had in measuring force gradients between the tip and sample [6.1, 6.2] by exploiting the dynamical properties of a sample in the form of a cantilever, see **figure 6.1** below.

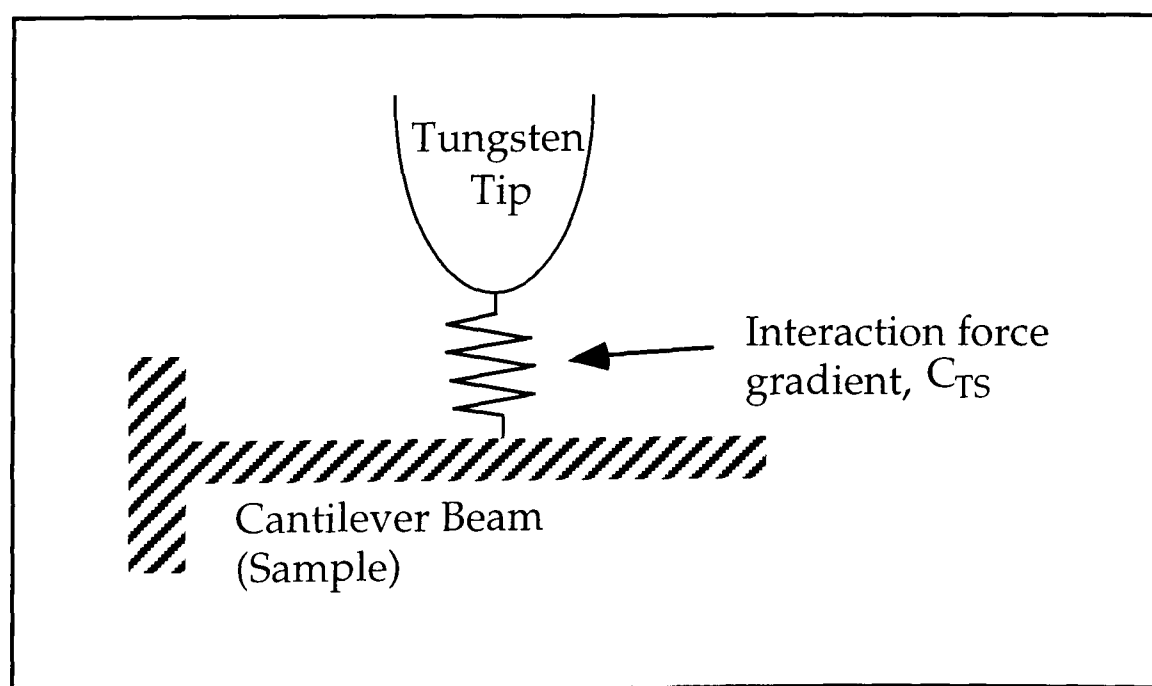


Figure 6.1: A schematic diagram illustrating the experimental set-up proposed by Dürig et al., [6.1] to investigate tip-surface interactions.

Dürig et al. [6.1] designed an experiment using cantilever-beams made of different materials including copper, stainless steel and tantalum. Silver films of thickness $\sim 2000\text{\AA}$ were then condensed on these beams. Even at room temperature, thermal vibrations cause the cantilevers to vibrate; the vibration frequency is dependent upon the tip-sample force gradient, and hence the tip-cantilever separation. By modelling the tip-sample force interaction as a spring of constant, C_{TS} , the resonance shift ($\omega_R - \omega_0$) can be related to the intrinsic properties of the beam using equation (6.1):

$$\omega_R = \omega_0 \left(1 + \frac{C_{TS}}{C} \right)^{1/2} \quad (6.1)$$

where ω_R and ω_0 are the resonance frequencies of the interacting and free lever respectively, C is the spring constant of the cantilever.

A number of important observations have emerged from Dürig's work. In investigations of clean samples, even at moderate levels of tunnel gap conductance, (σ : $\sim 0.1\mu\text{S}$) negative force gradients $\sim -10\text{Nm}^{-1}$ have been measured between the tip and sample, implying that attractive forces act between the tip and surface in this range. A maximum negative value for the force gradient of -15Nm^{-1} was measured at a tunnel gap conductance $\sim 1\mu\text{S}$. At higher values (σ : $\sim 10\mu\text{S}$), positive force gradients were frequently measured showing that the forces were becoming repulsive. By integrating the force-gradient curve, the strength of these tip-surface interactions has been shown to be on a nano-Newton scale [6.2]. The forces decay exponentially with increasing tip-sample separation and so cannot be interpreted as a Van der Waals interaction, although they are qualitatively consistent with the results obtained from metallic-adhesion theory [6.3].

This force-gradient measurement technique is also capable of giving information about the chemical nature of surfaces. On a clean polycrystalline aluminium surface, negative force-gradients (implying attractive forces) were measured. However, after exposing the surface to 1 Langmuir of oxygen, the tip experienced strongly negative force gradients (repulsive forces) [6.4]. It was also possible to detect single carbon atoms on a polycrystalline iridium surface by mapping short-range repulsive interactions [6.5].

Significant tip-surface interactions can also be found in experiments to measure the tunnel barrier height. In their pioneering work performed under moderate vacuum conditions ($\sim 10^{-6}$ mBar), Binnig et al. [6.6] used the derivative $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$ to measure a tunnel barrier height of 0.6 eV for a tungsten tip scanning over a platinum surface. After repeatedly cleaning the surface, this value increased to 3.2 eV. Coombs and Pethica [6.7] have explained the erroneously low values (< 1 eV) measured for the tunnel barrier height on “dirty” surfaces as the result of the tip penetrating through an oxide particle which acts as a spring between the tip and surface. The particle causes the true tip-displacement to become a fixed fraction of the change in length of the z-piezo element. Hence the modulation induced change in tunnel current is correspondingly reduced, leading to a low value for the tunnel barrier height. Similarly, Chen and Hamers [6.8] report tunnel barrier height measurements above Si(111) that vary with tip height above the surface. At large tip-sample separations, the tunnel barrier height is measured to be 3.5 eV, but as the tip approaches the surface the barrier height increases to 4.8 eV. Just prior to the formation of a mechanical contact, the barrier height decreases abruptly (< 1 eV). Using a simple Morse-type potential, these findings are accounted for by assuming that the tip-apex feels attractive interactions at large tip-sample separations and repulsive interactions at small separations.

Graphite has been extensively investigated using STM. A number of workers have measured giant corrugation heights for the basal plane of this material varying from 1-10 Å [6.9, 6.10, 6.11]. A theoretical analysis of graphite STM images by Tersoff [6.12] concluded that such giant corrugation heights could be explained as due to the peculiar electronic structure of this surface. The electron wavefunctions at the Fermi-level in graphite are characterised by an hexagonal array of nodes. Tunnelling is not permitted between such nodes and an s-state of the tip, and so it was argued that when the tip was positioned over a node, the absence of a tunnel current would cause the tip to move a large distance towards the surface. However, this analysis only took into account tunnelling into an s-like tip orbital. By extending Tersoff's method to include p_x (parallel to the surface) and p_z (perpendicular to the surface) orbitals at the tip, Lawunmi and Payne [6.13] showed the corrugation height above graphite to be independent of the tip height and to take a value of 0.23 Å. On the basis of this latter calculation, it seems unlikely that images of graphite can be explained solely in terms of its electronic structure.

A plausible explanation for the giant corrugation heights was proposed by Soler et al. [6.10]. They argue that during the experiment, the tip is actually in contact with the surface. By extending the z-piezo element, the tip moves relative to the base of the sample, but because the graphite is soft, the surface in the vicinity of the tip is deformed. This causes the true change in tip-sample separation as measured at the tip apex to be smaller than that measured at long-range by the z-piezo and so anomalously large corrugation heights can result.

An alternative explanation for STM images of graphite is the so-called "Pethica mechanism" [6.14], in which the tip becomes embedded in the uppermost layers of the surface. It is argued - all that is required to produce an image

when operating in the constant current mode is a periodic fluctuation in the conductivity between the tip and the sample. This is achieved by shearing of the top-most layers of the surface by the scanning tip. Support for this idea comes from the fact that STM graphite images are often characterised by a very low defect density.

6.3 Molecular Dynamics (MD) Simulations:

In a first principles calculation using a self-consistent pseudo-potential method, Ciraci et al. [6.15] investigated the Al(111)-Al tip system. They were trying to explain the giant corrugation heights measured by Winterlin et al. [6.16]. Ironically, however, it was concluded that site-dependent tip-surface forces actually worked to *reduce* the measured corrugation height at small tip-sample separations. A similar effect has been seen in the experiments presented in this Thesis. Following the spirit of the work of Ciraci et al., the interaction between the tip and the surface has been investigated using a Molecular Dynamics (MD) simulation. In the calculation described in this Chapter, the Sutton-Chen potential [6.17] was used to describe interatomic forces between atoms. This is an empirical potential based on the Finnis-Sinclair N-body potential [6.18] with the modification that the effects of long-range Van der Waals forces are included in the description of the atomic-interactions. The advantage of using an empirical potential in an Molecular Dynamics simulation is that large physical systems comprising thousands or even millions of atoms can be investigated. The Sutton-Chen potential is thus ideal for investigations of complex problems such as adhesion or friction [6.19]. The computational work presented in this Chapter was performed using the MD code written by Dr A.P. Sutton of the Department of Materials, University of Oxford. The simulations were run by Dr J.A. Nieminen during an extended visit to the same Institution.

The basic requirement of a Molecular Dynamics simulation is to integrate the equations of motion for the system under investigation over some period of time. The simulation performed here comprised a three-dimensional array of unit cells (see **figure 6.2** below).

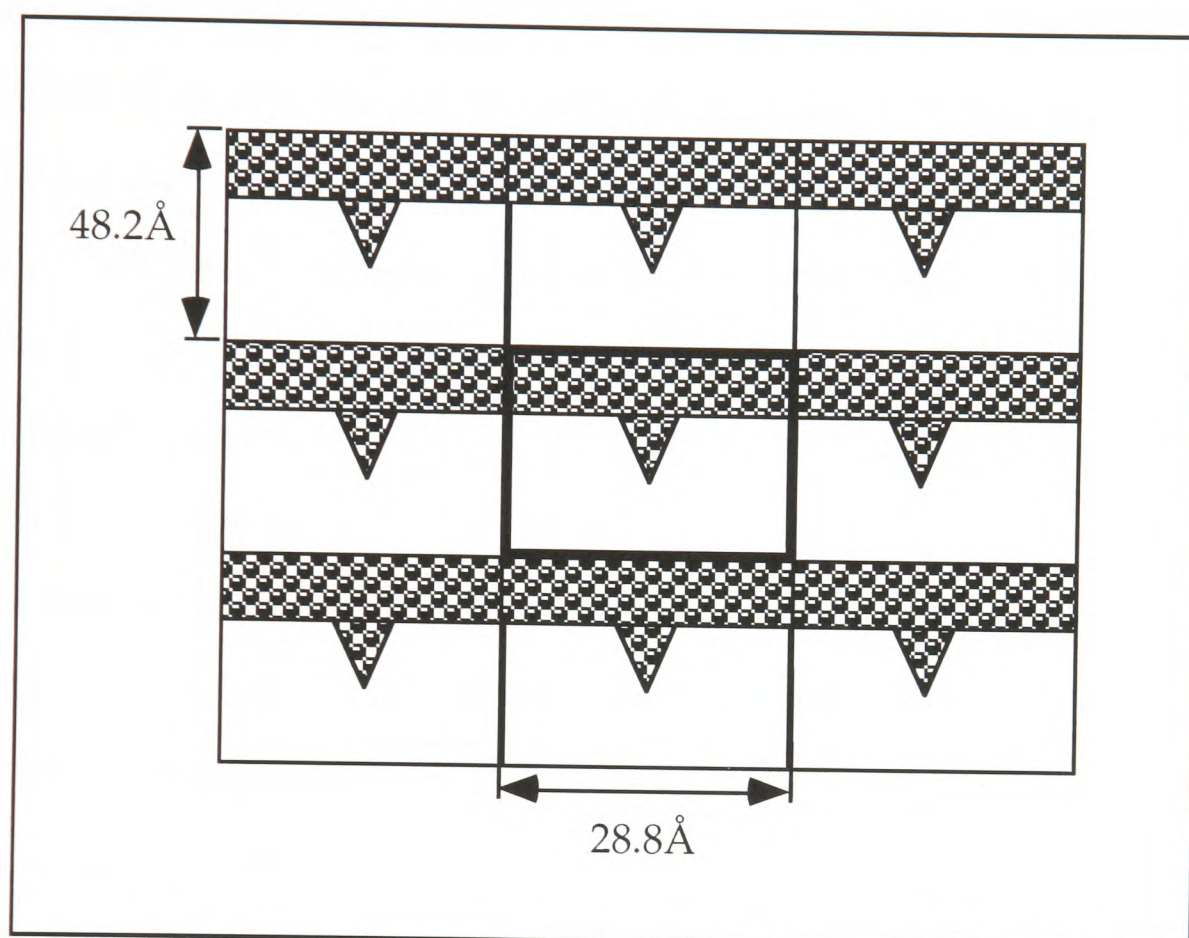


Figure 6.2: A schematic diagram showing the initial configuration of nine of the simulation unit-cells. This calculation makes use of periodic boundary conditions so that a single unit-cell (emboldened in the centre of the array) is effectively repeated *ad infinitum* in three orthogonal directions.

Every unit-cell in the simulation contained a total of 1444 atoms. The Cu(100) substrate was composed of 768 atoms arranged into a square-sided slab of width $28.8\text{\AA}$, which was six layers deep. To the underside of the substrate was attached the tip. This comprised 676 atoms and was a single atom terminated [100] oriented copper pyramid. The initial unit-cell height was $48.2\text{\AA}$, so that the tip apex atom was initially just over $7\text{\AA}$ above the top-most layer of the underlying substrate of the unit-cell beneath. In order to eliminate spurious "edge-effects" which result due to the finite size of the computational unit-cell, periodic boundary conditions were used in all three -dimensions. This means that an infinite array of unit-cells was used in this simulation.

In the present discussion, the problem under investigation is the approach of the tip towards a surface prior to the formation of a mechanical contact. During the MD simulation, the atoms in each unit cell were allowed to move under the restrictions imposed by the equations of motion. At the end of each simulation step (time length 2×10^{-15} seconds), the forces on each atom were calculated and the positions of every atom in the unit cell recorded. The positions and forces acting on all the atoms were then used as the initial co-ordinates for the next time step. 20000 such steps were used in this simulation. After every 50 time steps, the tip was moved incrementally towards the surface by decreasing the vertical height of each unit cell in the array by $0.011 \text{ \AA}$. This rate of motion of the tip towards the surface was sufficiently slow that between incremental movements, the system was able to come to mechanical equilibrium. In order to suppress the effects of thermal vibration in the MD data, this simulation was performed using a temperature of 25K.

6.4 Theoretical Calculations:

Although forces are usually the subject of interest in MD simulations, in this section it is the effects that such forces induce which are of interest and in particular the additional tip-displacements that result as the tip approaches the surface. In STM, the path of the tip is measured at long-range via the expansion or contraction of a piezoelectric crystal attached to the base of the macroscopic tip. However, if the apex of the tip is subject to short-range interactions, this may cause the true change in tip-sample separation to be different from that deduced from the change in length of the z-piezo element. An MD simulation should be capable of predicting the true tip-sample separation at which such interactions become significant. Moreover, the site-dependence of tip-surface interactions should give some important information about the observed

behaviour of the corrugation heights above a metal surface. The MD simulations in this work were performed for three different tip positions above the Cu(100) surface: (i) directly above a surface atom, (ii) directly above a bridge site, and (iii) directly above a hollow site, see **figure 6.3** below.

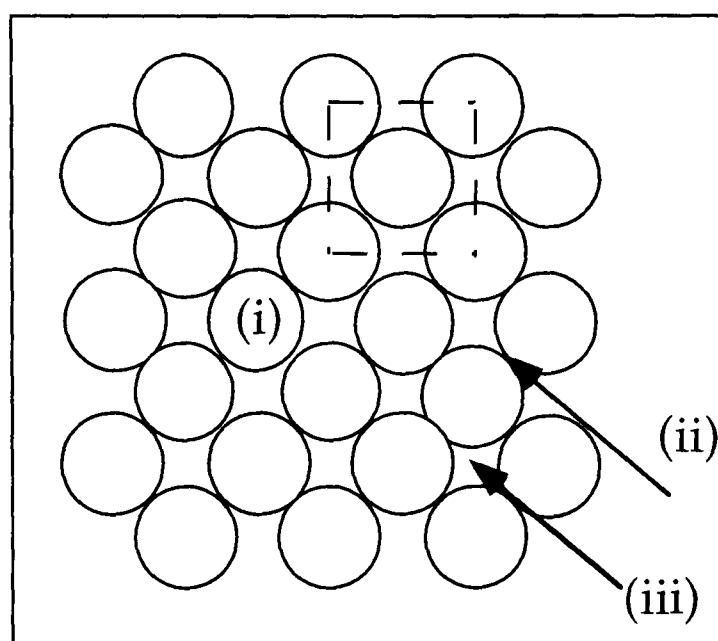


Figure 6.3: A diagram showing the three positions of the tip apex above the Cu(100) surface for which Molecular Dynamics simulations were performed. (i) An on-top site, (ii) A bridge site, (iii) A hollow site. A surface unit-cell is outlined by the dashed square.

6.4.1 Quantitative Analysis of $\langle 0\bar{1}1 \rangle$ Corrugation Height Data:

Figure 6.4 overleaf shows the results of performing MD simulations for the tip over the on-top and bridge sites. The graphs show the change in vertical supercell height (which is equivalent to the change in length of the z-piezo element perpendicular to the surface) as a function of the change in perpendicular separation of the tip apex atom from the nearest surface atom. All distances are measured between nuclear centres, the units used are Ångströms.

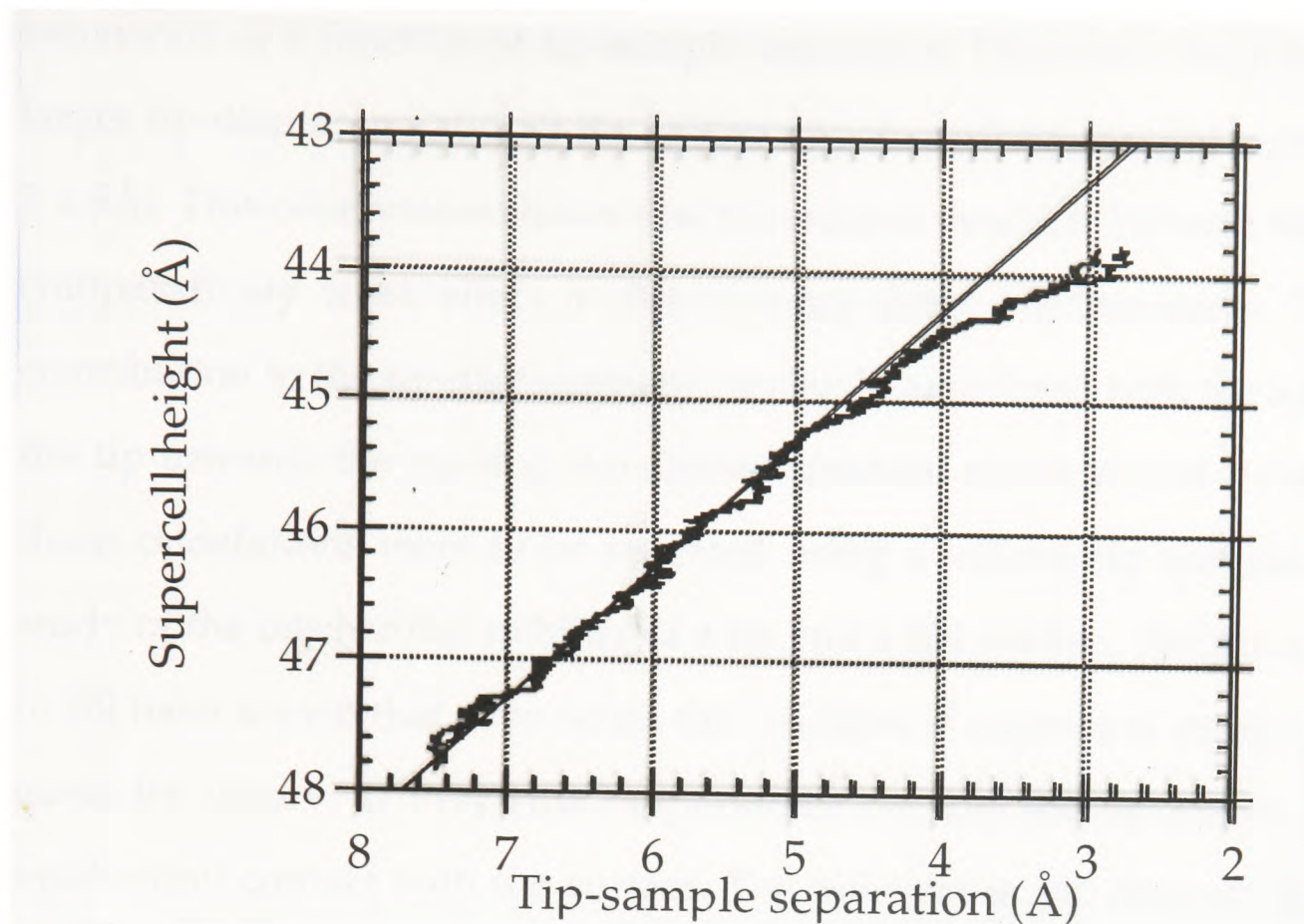


Figure 6.4: A pair of graphs showing the relationship between the change in vertical supercell height and the change in vertical distance between the tip apex and the nearest surface atom for the tip positioned over an atomic site (top sheet) and over a bridge site (on the printed page). Note that the tip-sample separation decreases from left to right along the abscissa and the supercell height decreases from bottom to top along the ordinate.

At relatively large tip-sample separations ($\sim 6\text{--}8\text{\AA}$), there is negligible interaction between the tip and sample; the change in length of the z-piezo element is an accurate reflection of the change in tip-sample separation. However, at smaller separations ($\sim 5\text{\AA}$ in the simulation), the tip begins to feel an attractive interaction due to the presence of the surface. This causes the tip apex to be strained towards the surface. The true change in tip-sample separation is now more rapid than the change in length of the z-piezo element, as shown from the fact that the MD curve bends away from the straight no-force line in **figure 6.4**.

The on-top and bridge site graphs show quantitatively extremely similar behaviour as a function of tip-sample separation. However, there is a slightly larger tip-displacement over the bridge site at small tip-sample separations ($\sim 3\text{-}3.5\text{\AA}$). This observation shows that the surface structure beneath the tip has a comparatively weak effect in determining these displacements. The major contribution to the tip-displacements is clearly associated with the approach of the tip towards the surface. An almost identical result would be obtained if these calculations were to be repeated using a jellium tip and sample! In a study of the mechanical stability of a tip and a flat surface, Pethica and Sutton [6.20] have shown that even when this problem is addressed using continuum elasticity theory, at very small separations ($\sim 1\text{-}2\text{\AA}$) the tip jumps to form a mechanical contact with the surface. The roll-over in the data of **figure 6.4** is simply interpreted as the precursor to this process.

As is shown in **figure 6.5** overleaf, the condition of constant *current* imposed upon the tip throughout these experiments acts to amplify the effects of tip-surface interactions upon the topographic images. The selection of a particular value of the tunnelling current, I , constrains the tip to trace out “true” surface contours (see **figure 1.1**) at a mean distance, s , above the surface. When the tip is over a bridge site, it is a distance $\frac{\Delta}{2}$ closer to the surface (where Δ is the corrugation height corresponding to that mean separation and surface feature spacing) and similarly over an atomic site it is a distance $\frac{\Delta}{2}$ further away. The next question to address is by how much less (as a result of tip-surface interactions) the z-piezo element is required to extend in order for the tip to detect the pre-set value of the tunnel current. In the schematic diagram of **figure 6.5** overleaf, the reduction in the z-piezo extension is given by the vertical distance between the no-force line and the appropriate interaction curve. In this figure, the site-dependent reductions in the extension of the z-piezo element are Δx_T and Δx_B over the on-top and bridge site respectively.

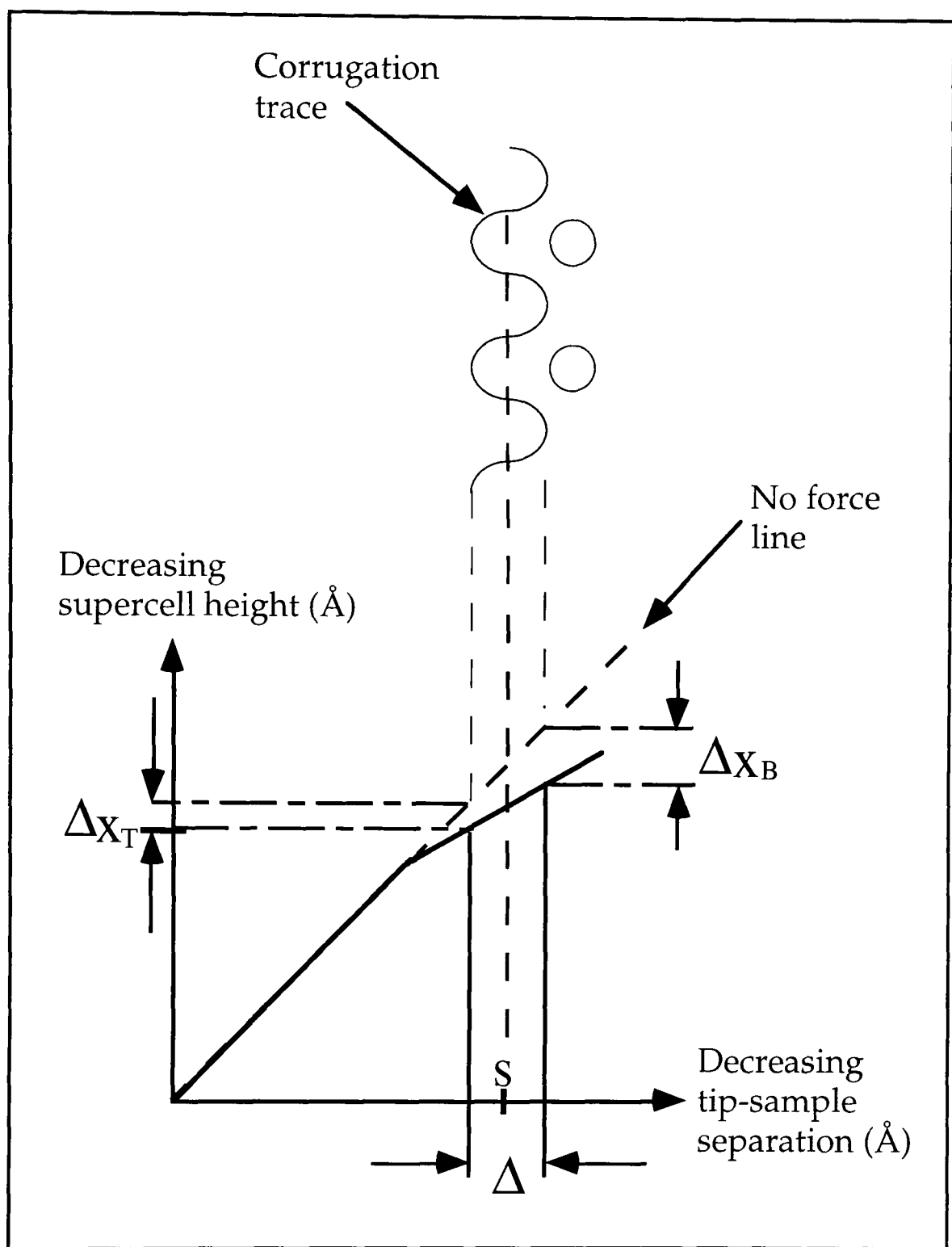


Figure 6.5: A diagram to show how to use the data of **figure 6.4** to deduce a reduction in the corrugation height. For the sake of clarity, the on-top and bridge site interactions have been assumed to be identical in this figure. The subscript 'T' refers to the tip position being directly above an on top site, while 'B' is for the tip over the bridge site.

When the tip is over an atomic site, the z-piezo extends until the apex detects the required value of tunnel current. However, the tip-sample interaction causes the tip to strain towards the surface a distance, Δx_T . Over the bridge site, the tip apex must move a distance, Δ , equal to the true corrugation height closer to the surface. Part of this distance is made up by the tip-surface

interaction over the bridge site which contributes a larger displacement, Δx_B , and the z-piezo element extends to make up the remainder of the true corrugation height. The site-dependence of the interaction means that the z-piezo measures a slightly reduced corrugation height compared with measurements made in the absence of tip-sample interactions. The corrugation reduction is given by the difference in the additional tip-displacements in the two tip-positions above the unit cell, namely $\Delta x_B - \Delta x_T$.

Finally in this discussion, it should be reiterated that this roll-off effect arises solely because of the use of the constant current mode of operation, in which the tip-sample separation changes slightly as the tip scans along a periodic feature, see **figure 1.1**. As noted earlier, the force experienced by a tip at a given height above a surface is essentially independent of whether the tip is directly above a surface atom, hollow, or bridge site. Thus a corrugation roll-off is not expected to be observed in similar corrugation height experiments conducted using the constant height mode of data acquisition.

Despite the use of a simulation temperature of 25K, the calculated MD data still shows a certain amount of "noise". In order to interpret the meaning of this data, it was necessary to fit a single curve to each MD simulation. A good description of both the on-top data and the bridge site data was given by the use of 8th order polynomials, see **figure 6.6** overleaf. The polynomials in each case were fitted to a range of tip-sample separations between 3 and 6Å. As the simulation temperature is fairly low anyway, the best way to further eliminate noise in the MD data, is to repeat the simulations using longer equilibration times during the approach of the tip towards the surface.

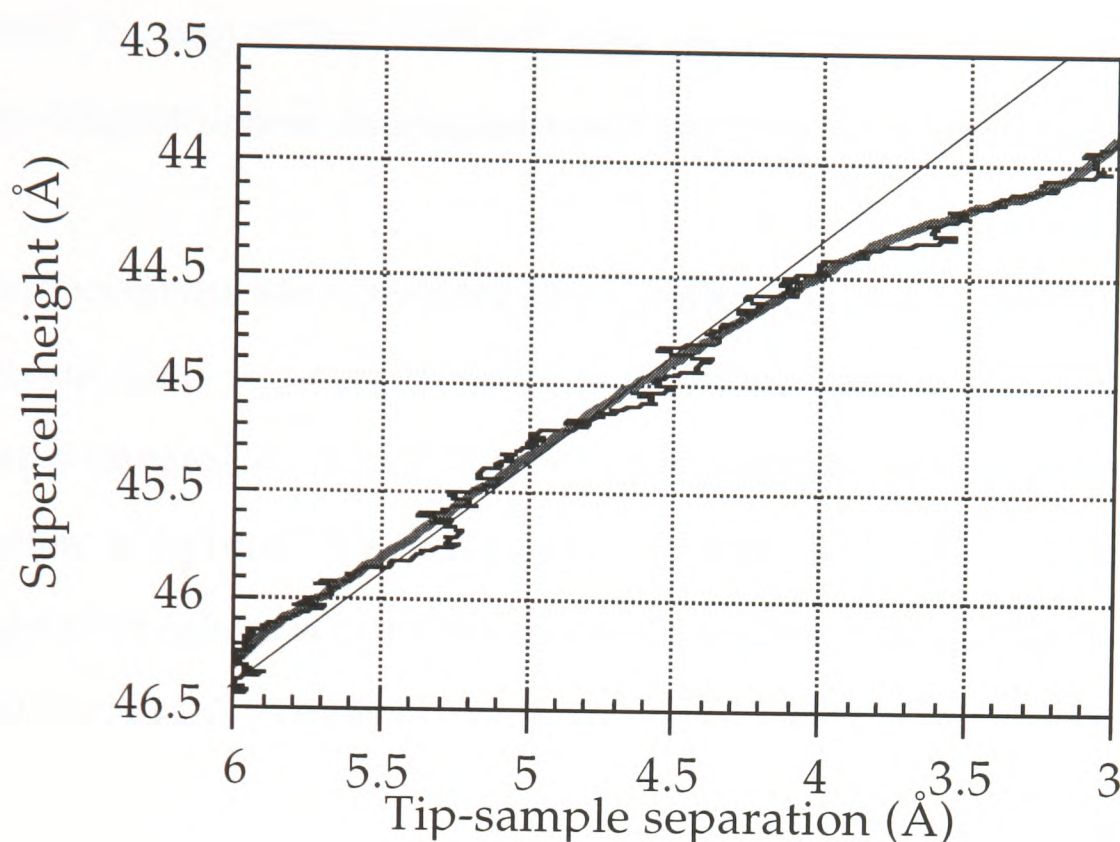


Figure 6.6: A diagram showing the 8th order polynomial (solid line) used to describe the MD data for the tip approaching the surface above an on-top site. The polynomial for the bridge data is quantitatively similar and is not reproduced here.

The true corrugation height determines the corrugation reduction as was illustrated in **figure 6.5**, hence it is necessary to know how the true corrugation varies as a function of the tip-sample separation. Experimentally, the true corrugation height is known as a function of tunnel conductance from the straight lines fitted to data sets such as **figures 4.10-4.13**. However, the MD simulations calculate tip-displacements as a function of the tip-sample separation and have nothing to say about the tunnel current flowing between the tip and the sample. There thus is a need for a method that allows for comparison between the MD theory and STM experiment.

The method adopted here is based upon trial and error and involves fitting an experimental plot to the theory. Starting with a data set such as **figure 4.10** which shows a corrugation roll-off, the "true" corrugation-conductance

relationship is calculated from an extrapolation of the linear part of the $\ln(\Delta):\ln(\sigma)$ graph. MD simulations are then used to calculate the corrugation reduction for one of the "roll-off" data points. Such a point was taken at a known value of tunnel conductance and hence its "true" corrugation is known.

Tip-displacements are systematically calculated above on-top and bridge sites at different mean separations using the true corrugation height appropriate to the experimental value of tunnel conductance. An absolute tip-sample separation is deduced for this data point when the experimentally measured corrugation height is equal to the difference in the true corrugation height and the MD-calculated reduction.

Simmons has calculated a one-dimensional expression for the tunnel conductance [6.21] as a function of tip-sample separation, see equation (6.2) below. But in order to use this relationship to deduce an absolute separation, it is necessary to know values for parameters such as the tip radius and the area of current emission which are not usually known experimentally.

$$\sigma = \frac{I}{V} \propto \exp(-A\phi^{1/2}s) \quad (6.2)$$

where $A = 1.025\text{eV}^{-1/2}\text{\AA}^{-1}$

By determining an absolute separation at a known value of the tunnel conductance using the MD data, the calibration difficulties are neatly avoided because pre-exponential terms required by equation (6.2) can be deduced. The significance of this result is that the entire range of separations used to deduce the absolute tip-sample separation of one corrugation-reduced data point can now be converted into equivalent values of tunnel gap conductance. Tip-

displacements can thus be calculated in terms of the tunnel gap conductance allowing a more direct comparison between theory and experiment.

The procedure outlined above was applied to the data of **figures 4.10** and **4.11**. In these corrugation experiments, the corrugation height is used to determine the tip-sample separation. However as noted in Chapter Four, the local radius of tip curvature determines the corrugation height along a particular direction. Moreover it is likely that the local radius of curvature varies when projected along different but nevertheless equivalent crystallographic directions. As the data of **figures 4.10** and **4.11** were taken simultaneously, it is necessary to determine a single conductance:separation relationship. This in turn requires a unique $\text{Ln}(\Delta):\text{Ln}(\sigma)$ relationship and so the *single* theoretical curve shown in **figures 6.7** and **6.8** was calculated using the mean of the $\text{Ln}(\Delta):\text{Ln}(\sigma)$ relationships for each experimental data set in order to minimise the effects of different local tip radii. A value of 2.12eV was used for the tunnel barrier height (calculated from equation (4.4)).

The mean value of corrugation heights for the three pairs of data points (one point from each figure) taken at the highest values of tunnel conductance were fitted to the MD data. The determination of the absolute tip-sample separation is rather sensitive to the choice of the pair of data points. In this instance, the values of absolute tip-sample separation deduced from the three different sets of data points differed from one another by approximately 0.1Å ranging between 3.58-3.74Å and increased as the tunnel gap conductance decreased. **Figures 6.7** and **6.8** overleaf show the full calculation of the tip-surface interaction corrected corrugation height as a function of the tunnel gap conductance. The absolute tip-sample separation scale in these figures was calculated using equation (6.2) and calibrated using the data points which are two from the right hand edge of each figure.

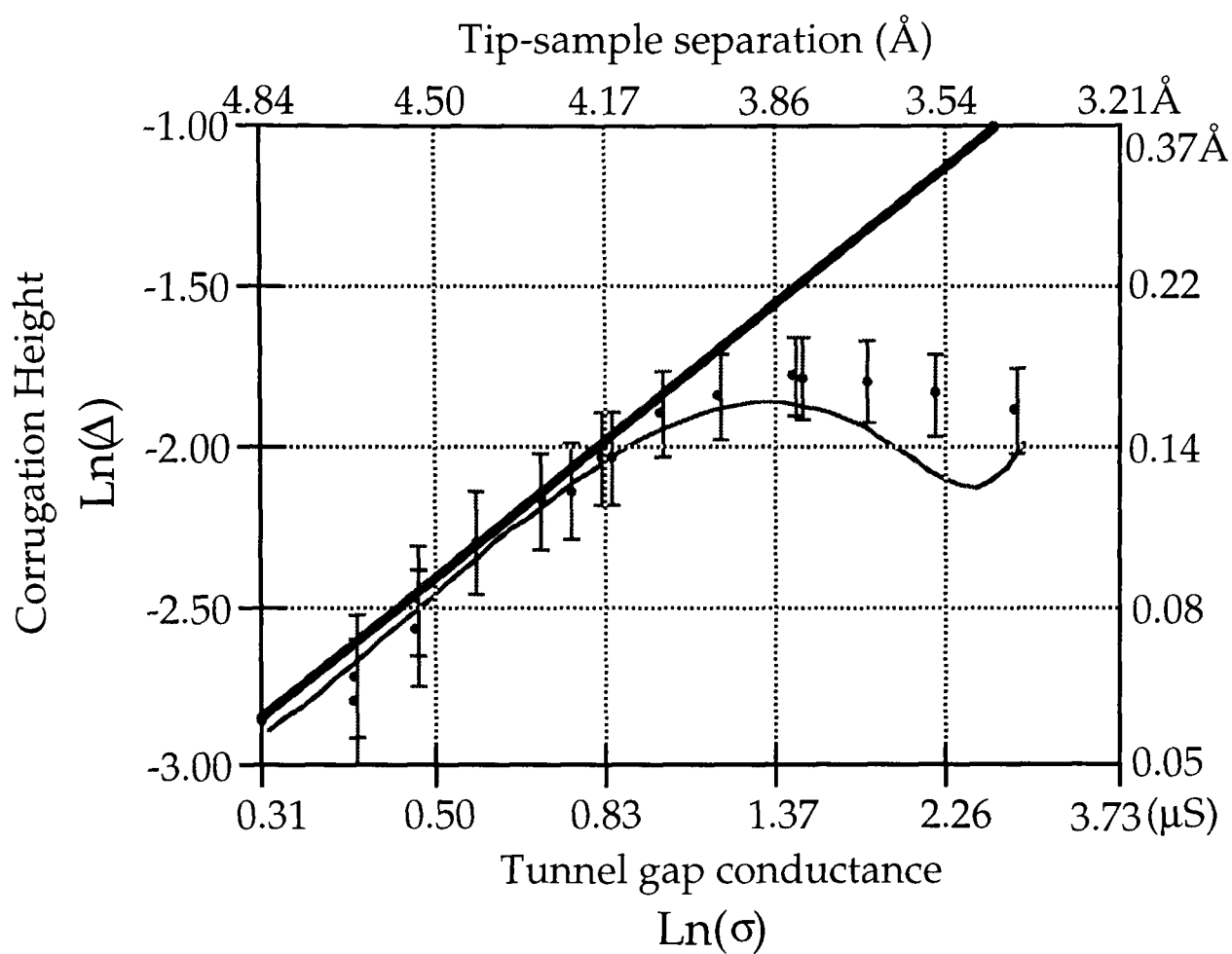


Figure 6.7: A graph showing the experimental data of **figure 4.10** and the theoretically calculated tip-surface interaction corrected corrugation height-tunnel gap conductance curve. The straight line gives the true $\text{Ln}(\Delta):\text{Ln}(\sigma)$ relationship.

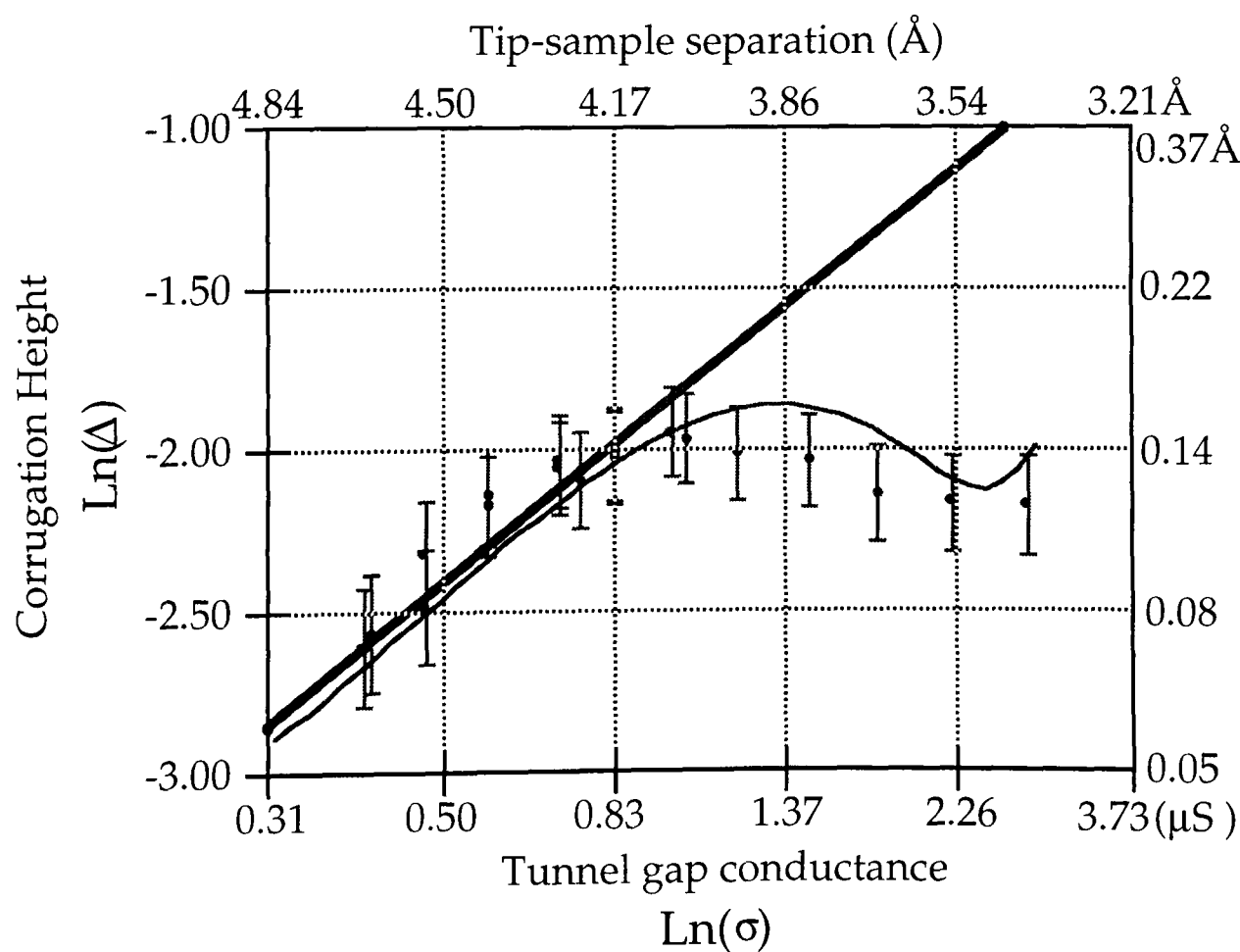


Figure 6.8: as **figure 6.7**, but the experimental data shown comes from **figure 4.11**.

By evaluating the form of the interaction corrected corrugation-conductance curve at small values of the tunnel conductance, the on-set of the roll-off could be established. This was defined to be at the mean separation for which the MD data first predicted the tip to be pulled towards both the on-top and bridge sites of the sample. It was found to occur at a tip-sample separation of $4.85\text{\AA}$.

The agreement between theory and experiment is seen to be good. In principle the anti-corrugating effect of these tip-displacements could ultimately lead to a reversal in the topographic image. However, with one exception which was thought to be due a change in the atomic configuration of the tip apex (see **figure 1.3**) such an effect was not observed experimentally in this work. **Figure 6.9** overleaf shows that the true corrugation function is well in excess of the calculated reduction for all values of mean tip-sample separation for which the data of **figures 6.7** and **6.8** was estimated to have been taken. However the corrugation reduction clearly approaches the true corrugation curve at small separations. Unfortunately in this region the polynomial of **figure 6.6** is not such a good description of the MD data. A better description of the data in this region may predict an image reversal at sufficiently small separations.

A corrugation reversal was not observed probably because of tip-surface mechanical instabilities. When imaging at very high values of tunnel conductance, resolution in the image was completely lost. This could be an exact cancellation of the corrugation by the displacement-induced anti-corrugating effect. However after losing resolution, the tip was always radically altered and rather unstable. It was then necessary to image a completely different part of the surface. This observation suggests that the tip was jumping into mechanical contact with the surface.

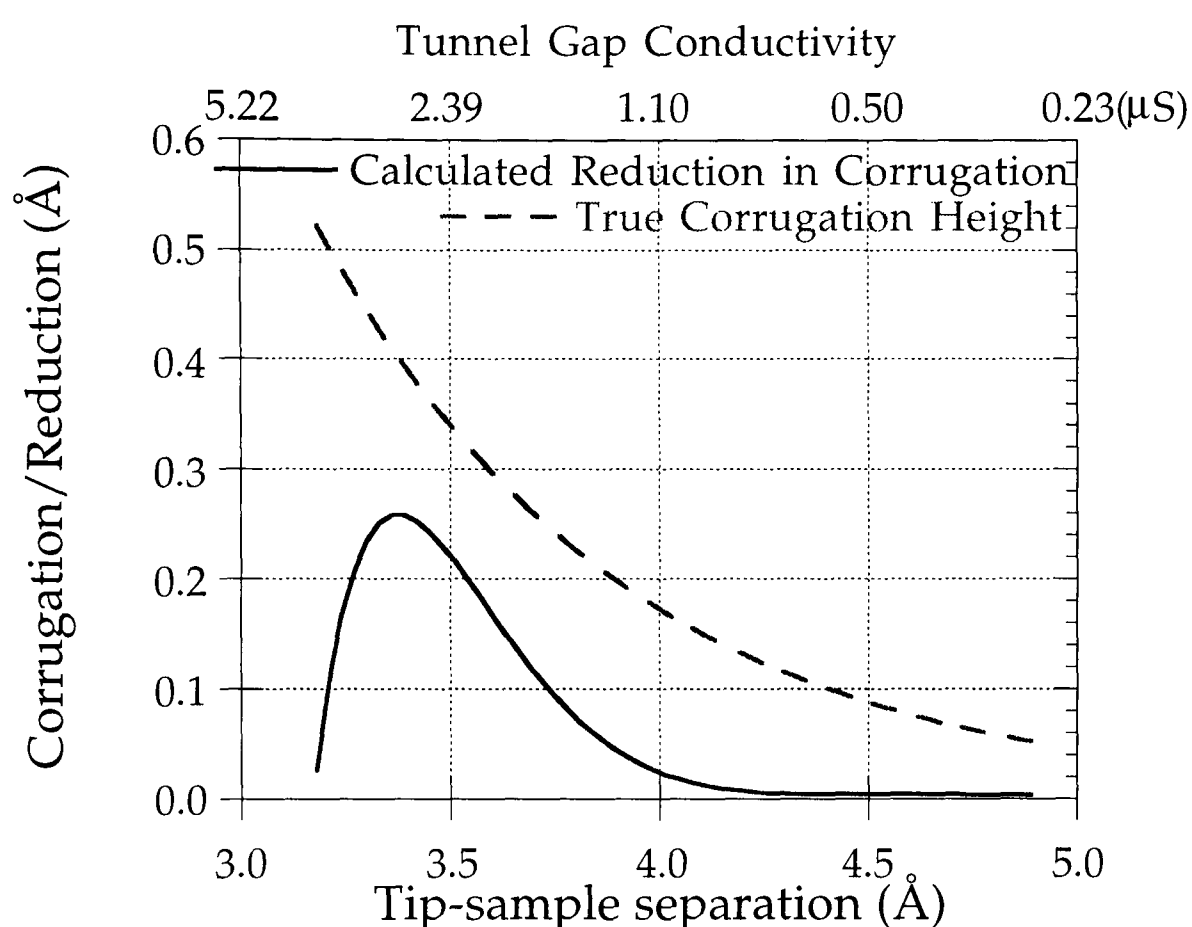


Figure 6.9: A graph showing the variation of the true corrugation height and the calculated reduction in corrugation height as a function of the tip-sample separation. This graph was based on the $\langle 011 \rangle$ data of **figures 4.4** and **4.5**.

The jump of a tip to contact with a surface has been widely studied theoretically. These investigations [6.19, 6.20] have reported that this phenomenon occurs at tip-sample separations of the order of one lattice parameter (in this case of copper this is a separation of $\sim 3.6\text{\AA}$). The jump is known to depend upon the homologous temperature ($= \frac{T}{T_M}$ where T is the simulation temperature and T_M is the melting point of the material) and the elastic properties of the materials used in the simulation. The tip-sample separations predicted in the Molecular Dynamic simulations of this work are consistent with the theory of the mechanical stability of a tip in close proximity to a surface.

6.4.2 Quantitative Analysis of $\langle 001 \rangle$ Corrugation Height Data:

There is a second major direction, namely $\langle 001 \rangle$ along which corrugation heights have been measured. The tip moves from an on-top site to a hollow-site during the course of a scan along this direction. Following the method outlined in the previous section, the differences in the tip-surface interactions over an atomic site and over the hollow site can be investigated. **Figure 6.10** below shows a superposition of MD data analogous to that presented in **figure 6.4** for the tip over the on-top and hollow sites. Just as in the previous case, there is no site-dependence in the interaction felt by the tip at large tip-sample separations ($> 6\text{\AA}$). However at smaller separations ($\sim 3\text{-}3.5\text{\AA}$), there is a marginally stronger tip-surface interaction when the tip is over the hollow site. This confirms the view that the surface structure is comparatively unimportant in determining the overall corrugation reduction.

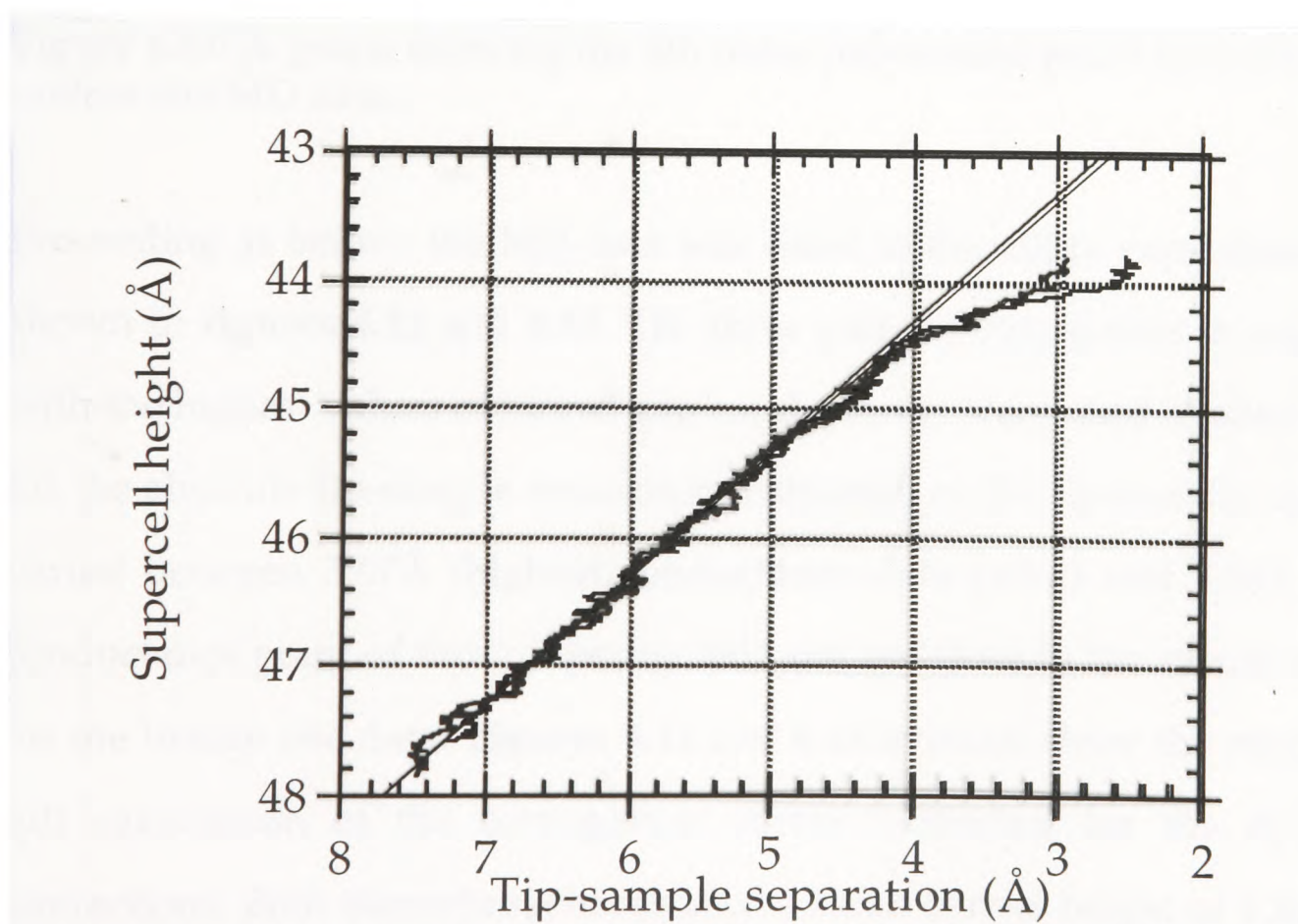


Figure 6.10: A Molecular Dynamics calculation showing the relationship between the change in vertical supercell height and the change in vertical distance between the tip apex and nearest surface atom for (i) the tip over an atomic site (top sheet) and (ii) the tip over a hollow site in the unit cell (printed page).

The corrugation reduction was calculated following the same method as for the $\langle 0\bar{1}1 \rangle$ corrugation height data, see **figure 6.11** below.

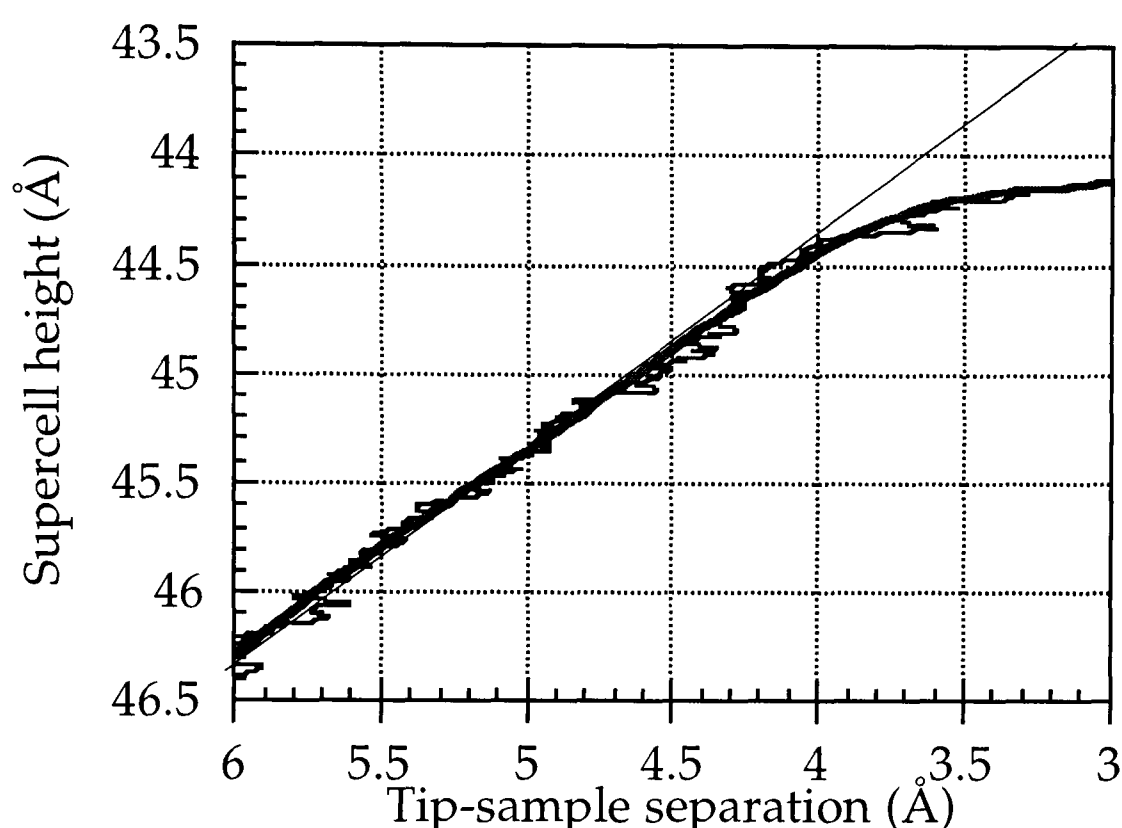


Figure 6.11: A graph showing the 8th order polynomial (solid line) fitted to the hollow site MD data.

Proceeding as before, the MD data was fitted to the $\langle 001 \rangle$ experimental data shown in **figures 4.12** and **4.13**. The three pairs of data points in each graph with the highest values of tunnel gap conductance, were used to obtain values for the absolute tip-sample separation. Estimates of the tip-sample separation varied between $3.67\text{\AA}$ (highest conductance data point) and $3.85\text{\AA}$ (lowest conductance point of those investigated) and are close to the values obtained for the bridge site data. **Figures 6.12** and **6.13** overleaf show the result of the full calculation of the corrugation curves corrected for the tip-surface interactions. Both theoretical curves used a mean barrier height of 1.26eV . The distance scale was calibrated from the corrugation reduction of the penultimate pair of data points. Changes in the tip-sample separation were deduced using equation (6.2).

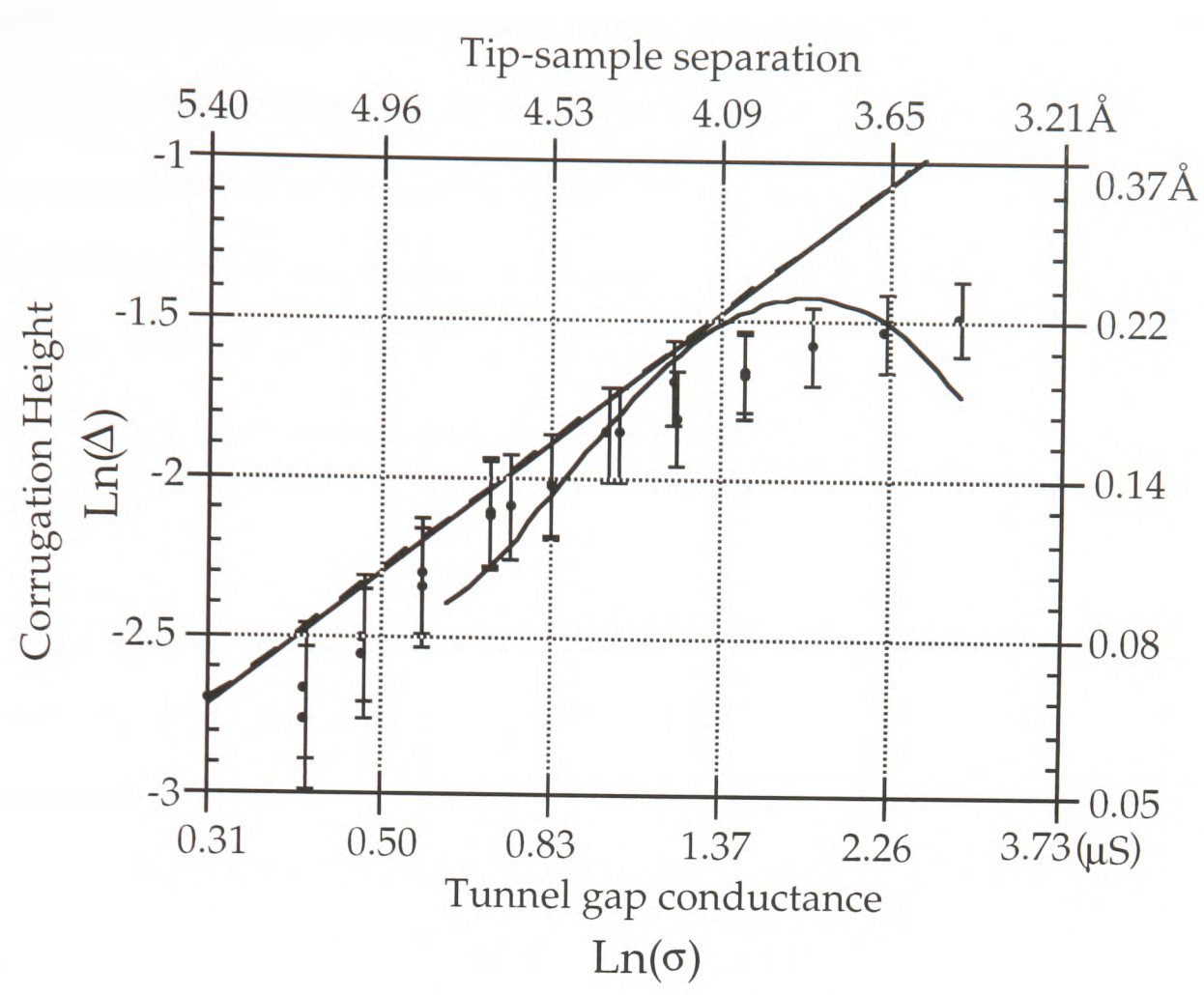


Figure 6.12: A graph showing the $\text{Ln}(\Delta):\text{Ln}(\sigma)$ experimental data of **figure 4.12** and the tip-surface interaction corrected corrugation-conductance curve based on the MD data of **figure 6.11**.

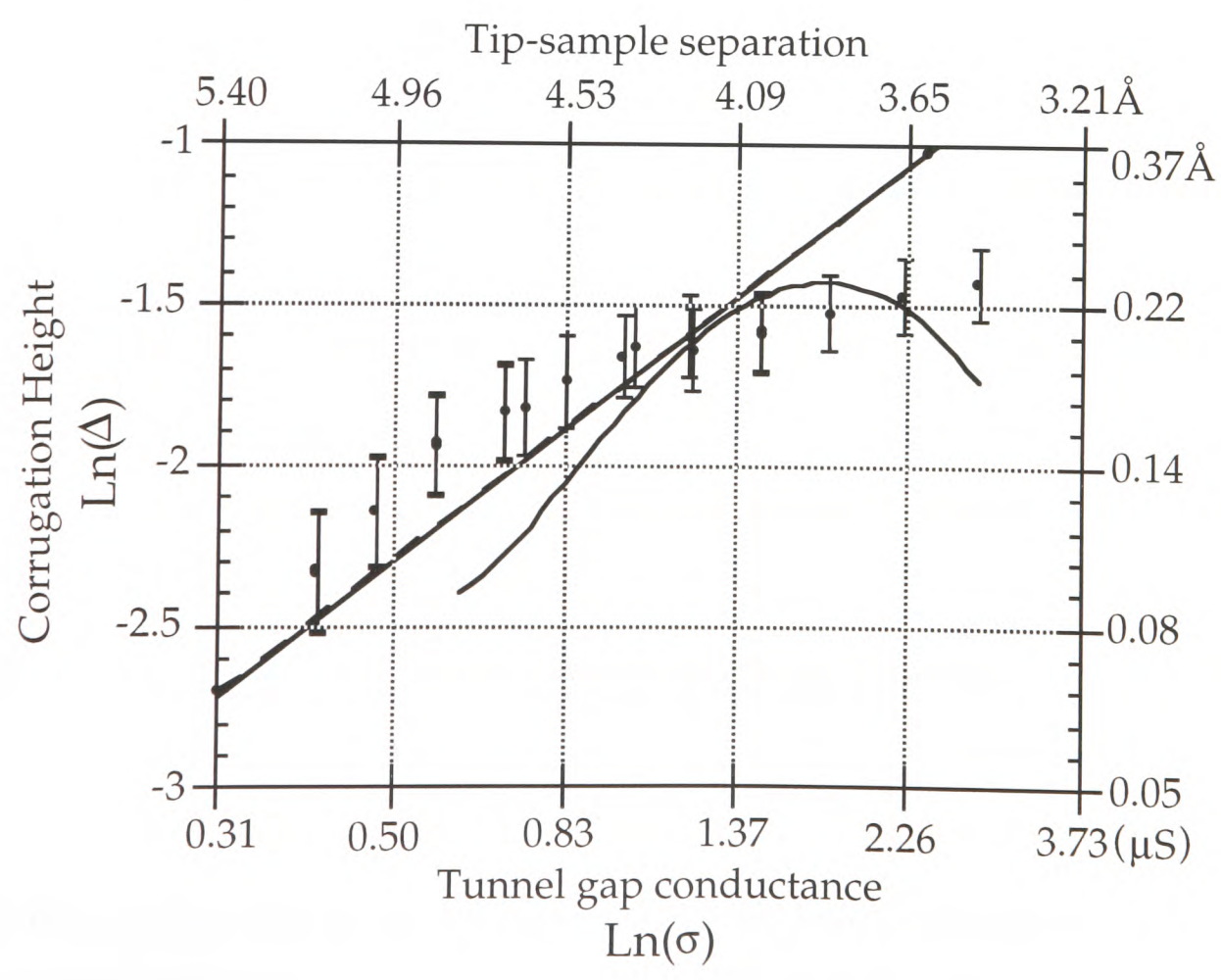


Figure 6.13: as **figure 6.12** but the experimental data is taken from **figure 4.13**.

Once again an adequate description of the experimental data was obtained using the MD simulations. The on-set of roll-off was calculated to be at $\sim 4.9\text{\AA}$ which is almost equal to the value obtained for the $\langle 0\bar{1}1 \rangle$ corrugation height data. Agreement between theory and experiment is not quite so good as was obtained for the bridge site data. This is attributed to the slightly small corrugation heights measured along $\langle 001 \rangle$ which were probably the result of a non-uniform tip.

Figure 6.14 below shows that for the $\langle 001 \rangle$ corrugation data, the true corrugation height is larger than the calculated corrugation reduction over the separation range ($3\text{-}6\text{\AA}$) for which the MD data was analysed. The polynomial fitted to the hollow site MD data was a good fit even at small tip-sample separations and so this result adds support to the view that the loss in resolution at high values of tunnel conductance is due to the tip-surface mechanical instability.

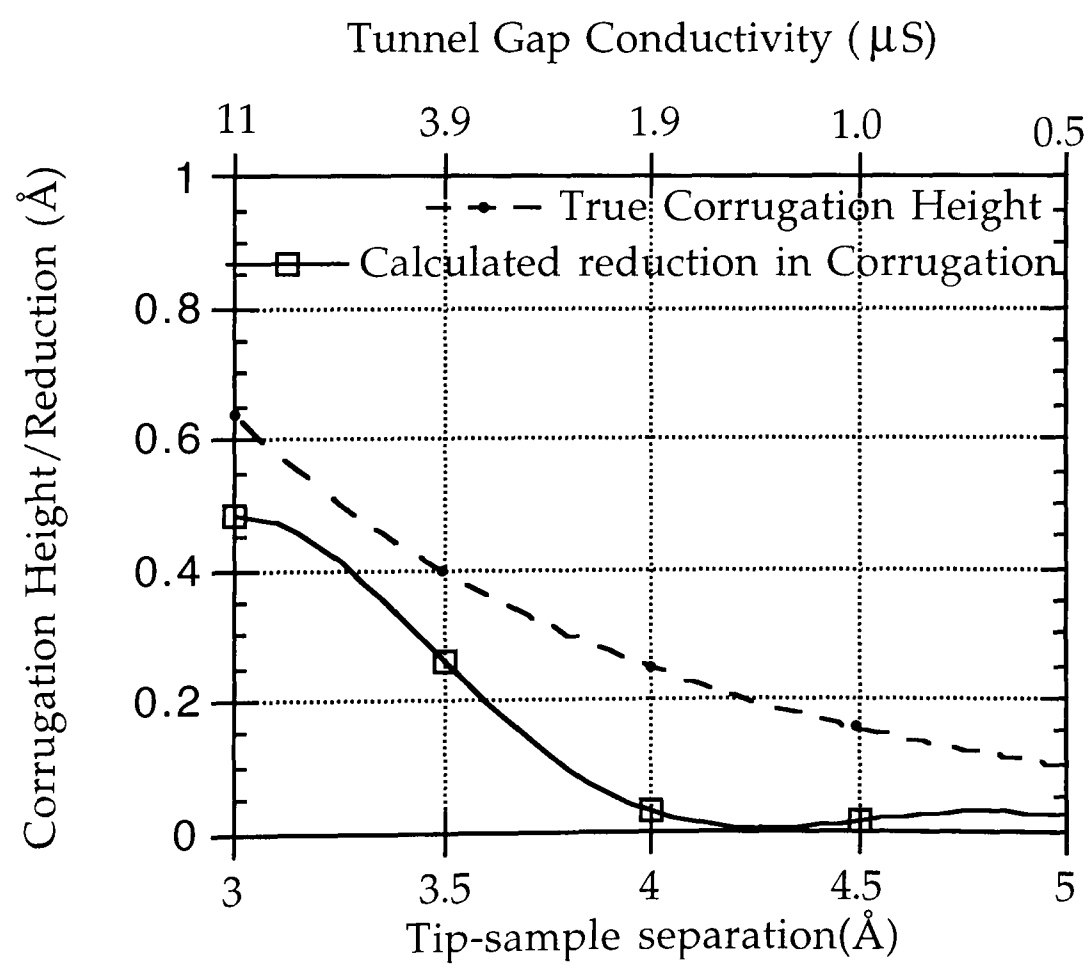


Figure 6.14: A graph showing the variation of the true corrugation height and the calculated reduction in corrugation height as a function of tip-sample separation. This graph was based on the $\langle 001 \rangle$ data of **figures 4.6 and 4.7**.

6.5 Tip-Surface Forces:

The discussion of the previous section has shown that the effect of forces in STM images can be significant leading to measurable consequences. However, thus far the question of the magnitude of the forces themselves has not been addressed. In the same MD simulation that was used to calculate tip-displacements, tip-surface forces were also calculated. **Figure 6.15** below shows a plot of the normal force acting between the tip and surface as a function of the absolute tip-sample separation for the tip positioned over the hollow site. The curves for the tip over the on-top site and bridge site are in close quantitative agreement.

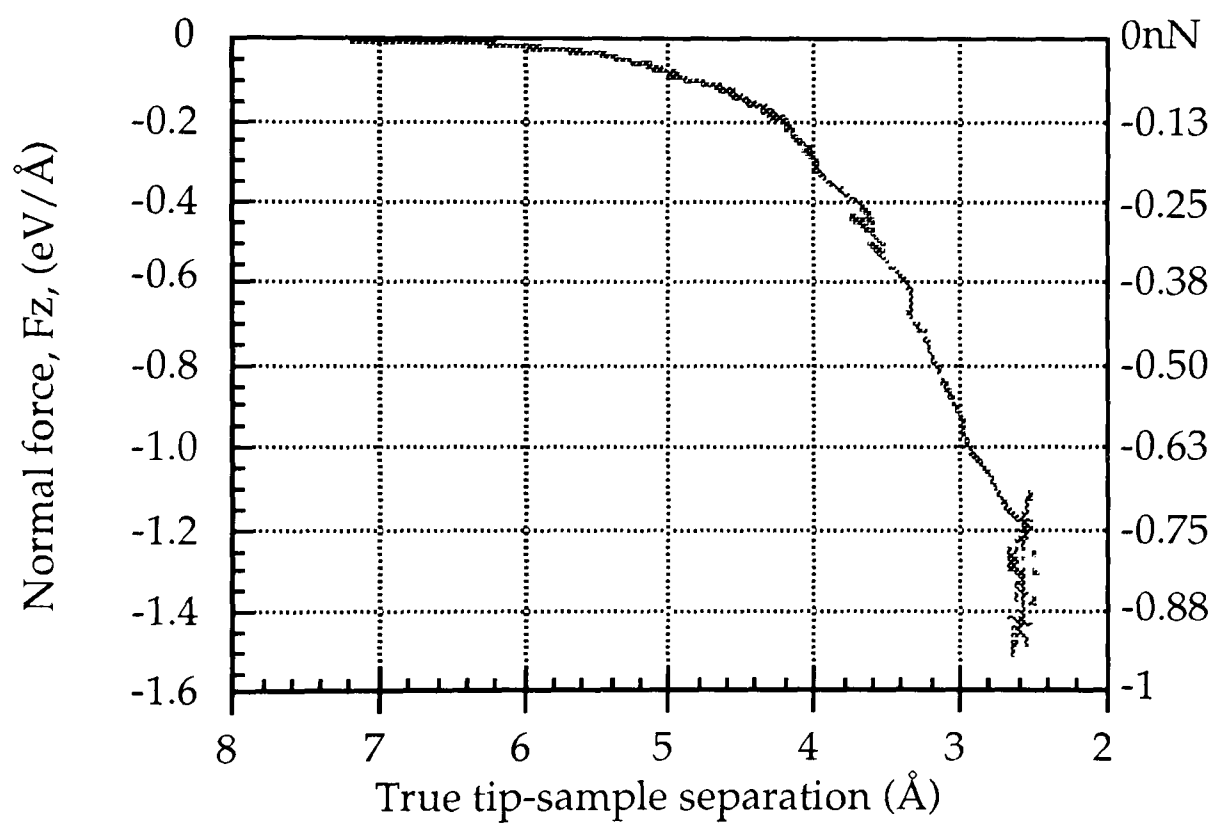


Figure 6.15: A graph showing the normal force acting between the tip and the sample as the absolute tip-sample separation is varied. The force is expressed in units of (eV/Å) on the left-hand scale, while the right-hand scale is in nano-Newtons. (1eV/Å = 1.6nN and 1nN = 10⁻⁹N)

From this large-scale graph, it can be seen that the normal force becomes more attractive as the tip-sample separation decreases and it starts to be a

measurable quantity at a separation $\sim 6\text{\AA}$. At the on-set of corrugation height roll-off described in the previous section (tip-sample separation $\sim 4.9\text{\AA}$), the normal force takes a value $\sim 0.06\text{nN}$ and increases to $\sim 0.3\text{nN}$ at a separation equal to the lattice parameter of copper, $3.6\text{\AA}$. The maximum normal force experienced by the tip over the hollow site in these calculations is $\sim 0.75\text{nN}$ at a separation of $\sim 2.6\text{\AA}$. These values are similar to those deduced by Dürig et al. [6.2] who integrated a force-gradient curve obtained for an iridium tip scanning over a polycrystalline iridium surface.

In this discussion, it is the corrugation height roll-off region which is of interest and so the forces are investigated in a narrow band defined as $4.25\text{\AA} > s > 3.25\text{\AA}$, where s is the *mean* tip-sample separation. **Figures 6.16** and **6.17** show the normal forces acting between the tip and sample for the tip over the on-top and bridge sites and the tip over the on-top and hollow sites respectively.

These data show that for a mean tip-sample separation (i.e. when imaging using a constant current), the tip-surface forces are largest when the tip is over the hollow sites and smallest when the tip is over the atomic sites. At large values of tip-sample separation, this result is simply illustrating the fact that because of the condition of constant current, the tip is closer to the surface over the bridge and hollow sites compared with when it is over the atomic sites.

At smaller tip-sample separations ($\sim 3.7\text{\AA}$), surface site-differences become more marked and tip-surface forces become substantially larger over the bridge and hollow sites. The divergence of the lines on each graph is an indication that the surface co-ordination experienced by the tip becomes important in determining the force acting on the tip at small separations. When the tip is over the on-top site, it has just one nearest surface atom neighbour, two in the case of the bridge site and four when it is over the hollow site.

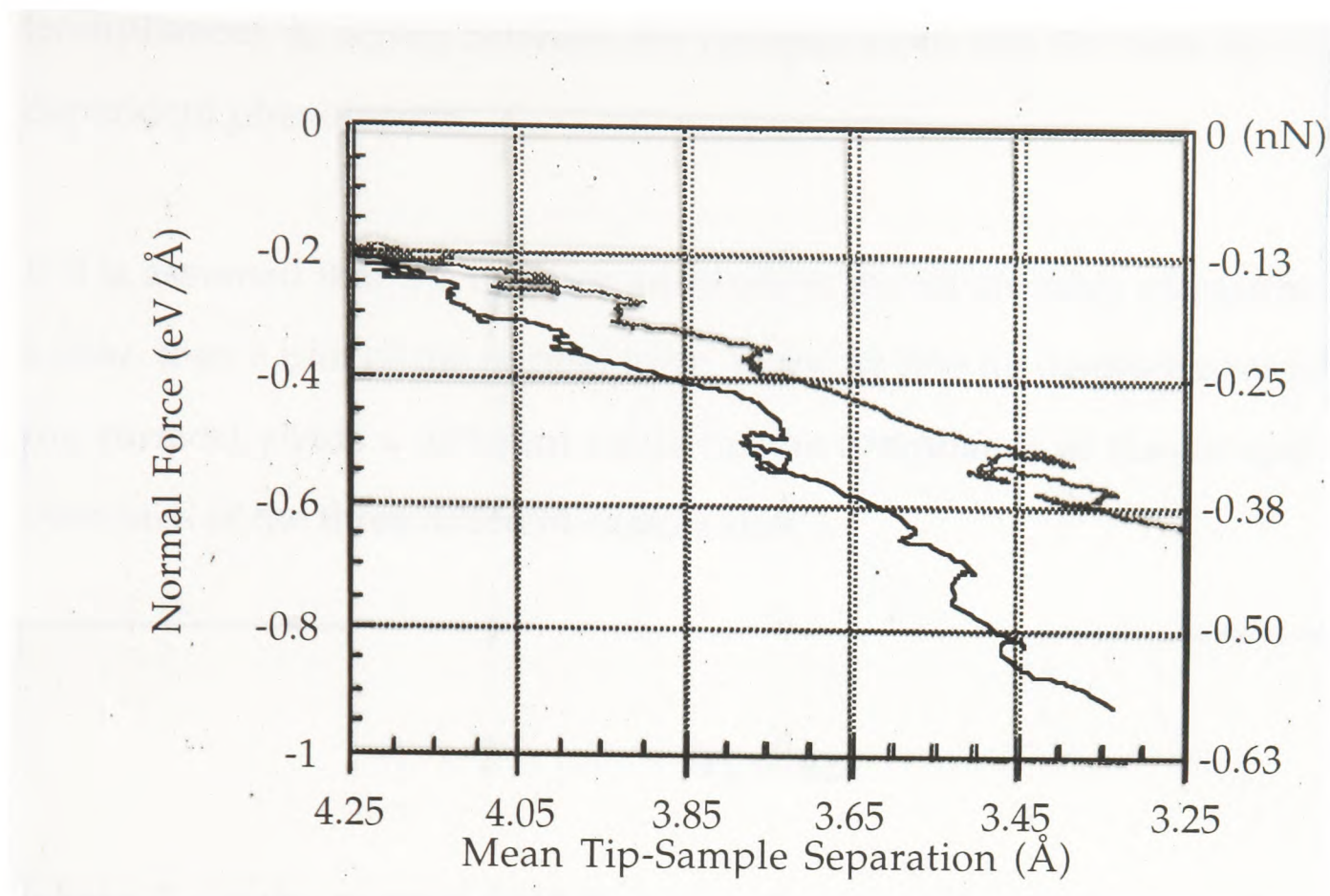


Figure 6.16: A graph showing the normal force acting between the tip and the sample as a function of the mean tip-sample separation. The graph on the transparency is for the tip above an atomic-site while the printed page graph is for the tip over a bridge site. The force is given in units of (eV/Å) along the left hand vertical scale and nano-Newtons along the right hand vertical scale.

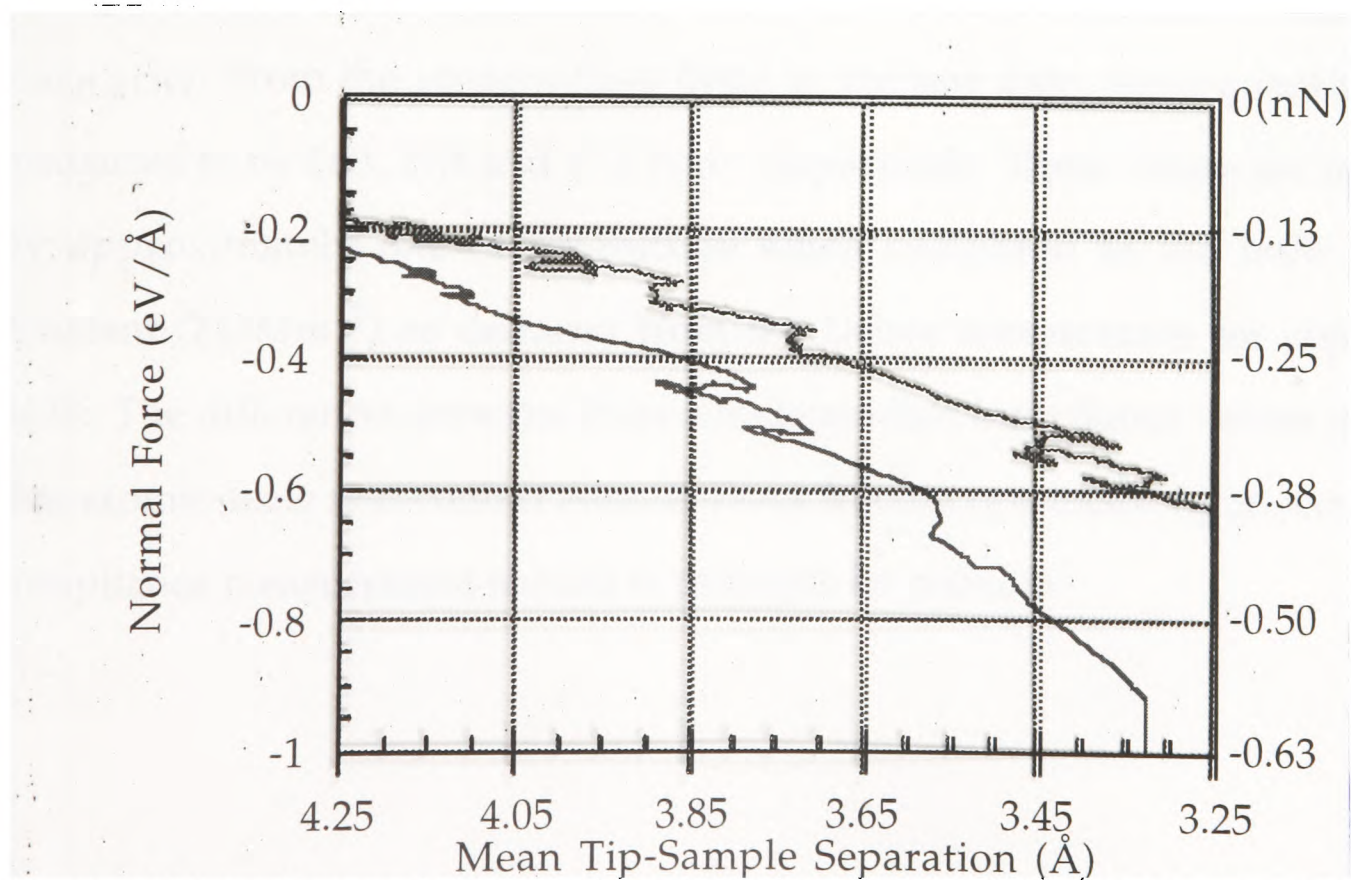


Figure 6.17: as figure 6.16, but the printed page graph is for the tip positioned above the hollow site.

A second interesting result of these data is that the effective spring constant (compliance), k , acting between the tip-apex atom and the bulk tip is a site-dependent phenomenon.

If it is assumed that the tip-apex atom obeys the relationship of equation (6.3) below, then a plot of the normal force, F_z vs. Δz (the tip displacement towards the surface) yields a different value for the compliance of the tip-apex atom over each of the three different surface sites.

$$F_z = -k\Delta z \quad (6.3)$$

where F_z is the normal force between the tip and sample, k is the spring constant (compliance) and Δz is the displacement of the tip-apex atom towards the surface from its large tip-sample separation equilibrium position.

In **figures 6.18 and 6.19** overleaf, it can be seen that $k_{\text{ON-TOP}} > k_{\text{BRIDGE}} > k_{\text{HOLLOW}}$. From the straight lines fitted to the raw data, these quantities are measured to be 21.3, 19.4 and 17.2 Nm^{-1} respectively. These values are reduced by approximately one of magnitude when compared to the bulk spring constant (213Nm^{-1}) as deduced from the Debye temperature for copper of 343K. The differences between these site-dependent compliance values indicate that atomic-scale non-contact Atomic-Force Microscopy based upon a constant compliance measurement should in principle be possible.

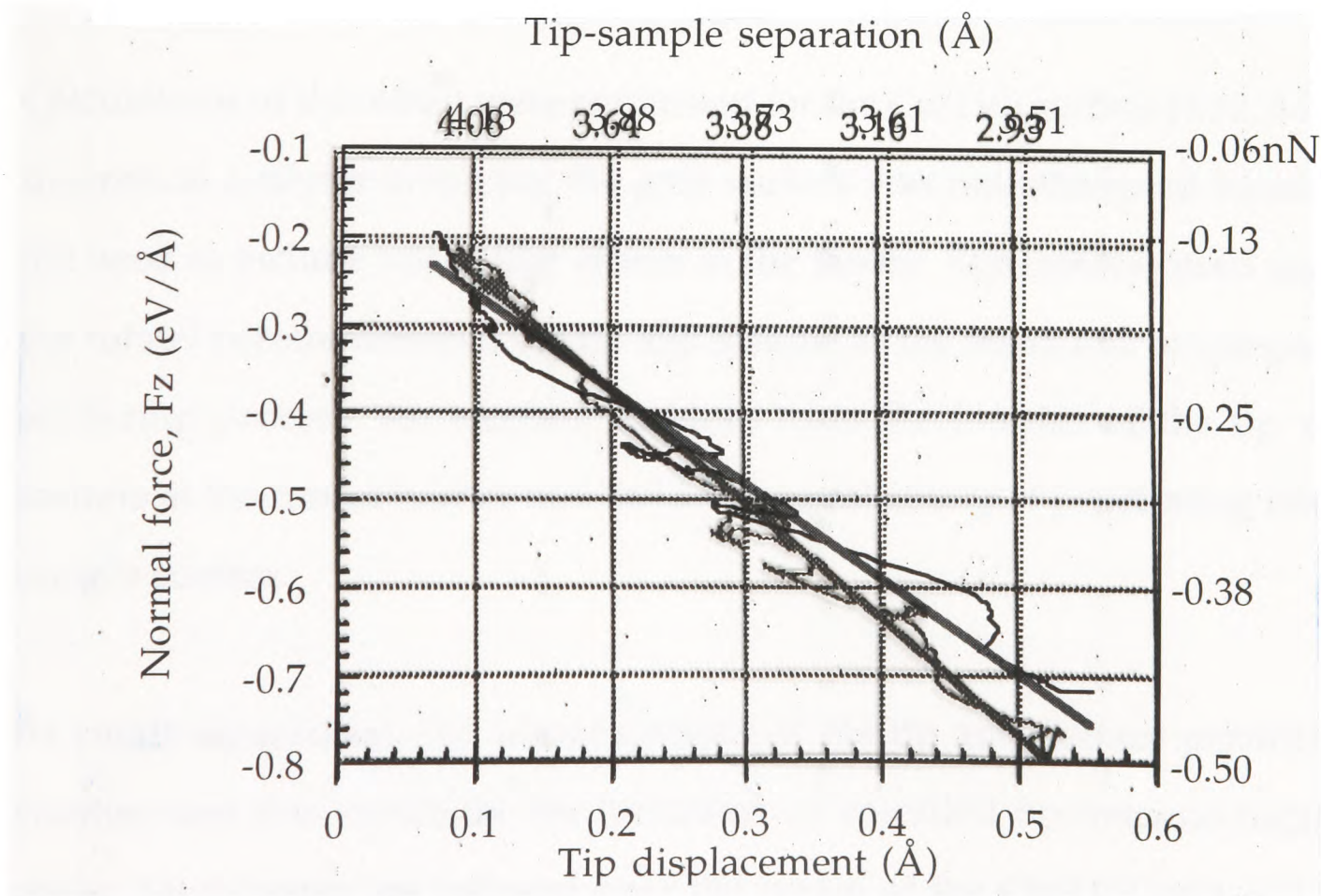


Figure 6.18: A graph showing the normal force acting between the tip and sample as a function of the displacement of the tip-apex atom towards the surface. The top graph is for the tip over an on-top site and the printed page graph is for the tip over a bridge site.

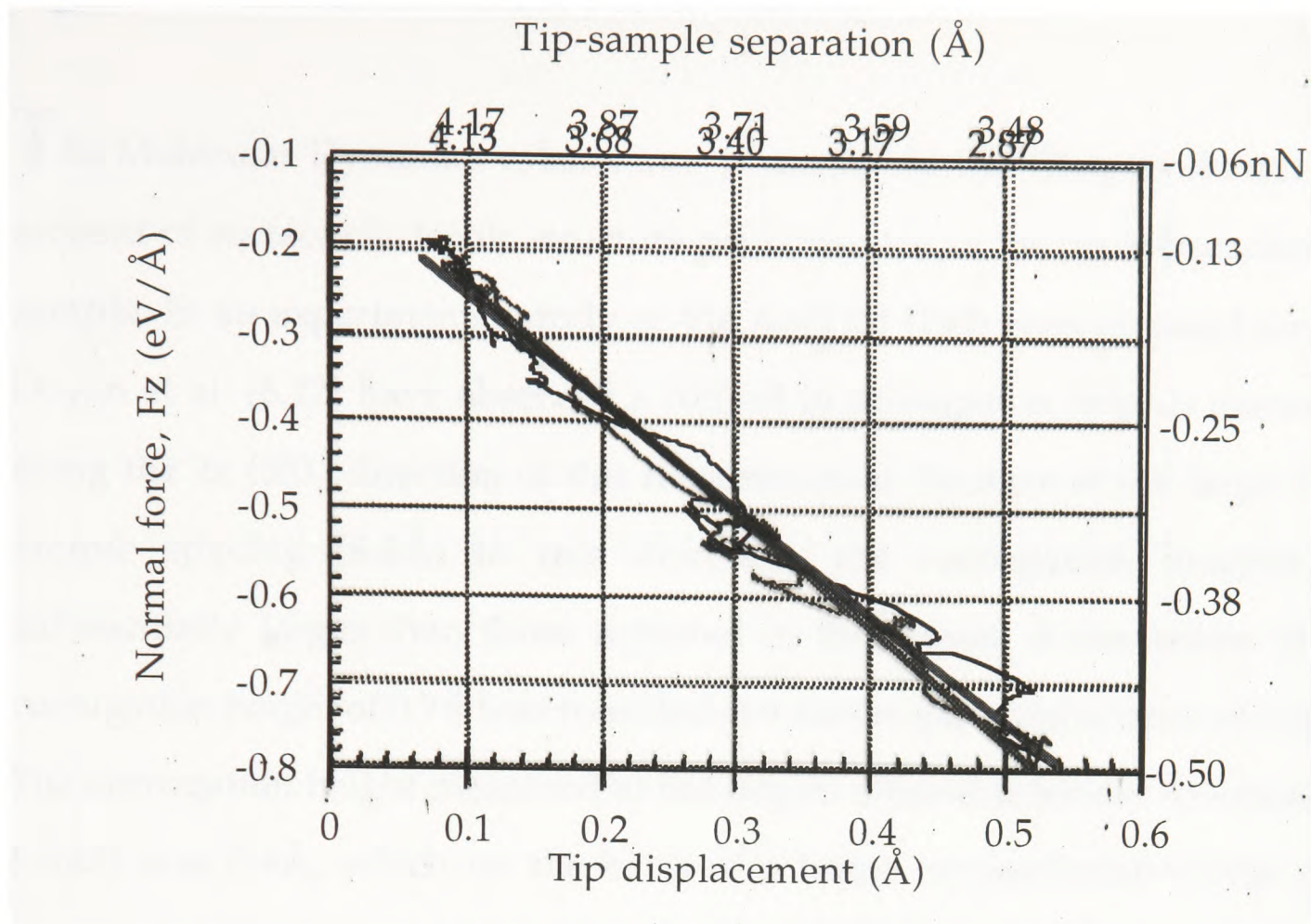


Figure 6.19: as figure 6.18 but for the printed page graph is for the tip over a hollow site.

6.6 Electronic Structure Perturbations:

The Molecular Dynamics calculations presented in this Chapter do not take account of surface electronic structure perturbations as the tip approaches the sample. In an experimental study of the Au(110) (1x2) reconstructed surface Doyen et al. [6.22] have observed a roll-off in corrugation heights measured along the $2 \times [001]$ direction of this reconstruction. Because of the large inter-atomic spacing ($8.2 \text{ \AA}$) in this direction, the corrugation heights are substantially larger than those reported in this thesis. A maximum in the corrugation height of $0.7 \text{ \AA}$ was recorded at a tunnel gap conductance of $0.18 \mu\text{S}$. The corrugation height measured at the largest attainable tunnel conductance ($\sim 1 \mu\text{S}$) was $0.4 \text{ \AA}$, which on the basis of a linear extrapolation of the data corresponds to a large reduction of $\sim 0.6 \text{ \AA}$. This roll-off is interpreted by Doyen et al. [6.22] as being due to a short-range interaction associated with the on-set of chemical bonding between the tip and sample.

Calculations of this effect were performed for the Cu(110) surface [6.22, 6.23]. A theoretical analysis involving the gold surface was not attempted because of the need to include relativistic effects in the theory. The method used regards the tunnel current between the tip and sample as the result of a single-particle scattering process. An electron incident from the interior of the tip metal scatters at the tunnel barrier and has a finite probability of penetrating into the sample surface.

At small separations, the wavefunctions of the tip and surface perturb one another and this results in the formation of so-called tip-induced localised states. More states are induced over the centre of the Cu(110) unit cell than over the atomic sites; when using the constant current mode of operation, the tip is closer to the surface over the former position where it experiences a

higher co-ordination. The relative enhancement in the local charge density over the centre of the unit cell compared with the atomic sites becomes larger at smaller tip-surface separations. Thus a decrease in the corrugation height is expected with decreasing tip-sample separation at very small tip-sample separations.

The LDOS perturbation corrugation reduction mechanism is predicted to begin at a smaller tip-sample separation ($\sim 3.7\text{\AA}$) than is calculated for the force-based mechanism presented in this thesis ($\sim 4.9\text{\AA}$). It is probably best to conclude that although the force-based mechanism appears to be the dominant one, electronic-structure perturbations may also be induced by the tip. However, they do not begin to become significant until the tip is rather close to jumping to contact with the surface. Moreover, the force-based mechanism is a universal phenomenon which should occur for all apex species, although different apexes may give rise to different values for the tip-displacements. The required LDOS changes may not easily occur for many crystal surfaces.

6.7 Summary:

In this Chapter, corrugation roll-offs measured at large values of the tunnel conductance have been successfully modelled using a Molecular Dynamics simulation. Using the change in length of the z-piezo element to deduce changes in the tip-sample separation becomes unreliable at small separations due to additional tip-displacements which can be as large as $0.5\text{\AA}$. There are two main contributions to such displacements. The dominant term is determined by the approach of the tip towards the surface. A second smaller term also exists which has been shown to depend upon the surface co-ordination experienced by the tip apex atom.

This force-based mechanism for corrugation height reduction is a universal mechanism and has been shown to be more important than Doyen's mechanism [6.22] which is based on electronic-structure perturbation. This latter mechanism may be responsible for a part of the reduction seen at very small separations ($< 3.7\text{\AA}$), although the well known effects of tip-surface mechanical instability would seem to place a limit on the usefulness of this theory. For example, the corrugation reversals predicted by Doyen et al. [6.22] at separations $\sim < 2.8\text{\AA}$ are not seen in this work.

By comparing theoretical predictions with experimental data, it has been possible to obtain a direct measure of the tip-sample separation. This is an important step forward in quantitative STM as the accurate measurement of this parameter has not been reported previously in the literature. The determination of an absolute tip-sample separation has enabled a tunnel current-distance calibration to be established which avoids the need for knowledge of parameters which are difficult to obtain experimentally.

Finally it has been shown that the forces acting under normal imaging conditions are substantial ($\sim 0.1\text{-}0.5\text{nN}$) and remain significant out to tip-sample separations of $\sim 6\text{\AA}$.

6.8 References:

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Chapter 7

Halogens

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7.1 Introduction:

In this Chapter, the effort towards a quantitative understanding of STM is continued with the presentation of some preliminary studies of a metal surface+halogen system at low adsorbate coverages. The idea behind these investigations is to see the change in the STM image as a result of making the simplest possible modification of a clean metal surface.

In the following section, a summary is given of the few previous STM metal+halogen studies. After the presentation of some basic surface science results in section 7.3, section 7.4 discusses the change in local tunnel barrier height induced by different adsorbates. Finally in section 7.5, the process of tip-induced atomic manipulation of surface adatoms is demonstrated.

7.2 Literature Review:

There are surprisingly few reports of metals-based STM studies involving halogen adsorption. The work that has been done to date has concentrated upon close-packed (111) faces of noble-metals. Motai et al. [7.1] studied the chlorine-Cu(111) system. At room temperature and 1/3 monolayer coverage of chlorine, a well-ordered ($\sqrt{3} \times \sqrt{3}$)R30° overlayer was seen in agreement with Low Energy Electron Diffraction (LEED) studies [7.2].

Hossick-Schott and White [7.3] have investigated overlayers of fluorine, chlorine, bromine and iodine on the Ag(111) surface. The iodine adlayer is consistent with a nearly perfect ($\sqrt{3} \times \sqrt{3}$)R30° structure, while the other halogens give rise to overlayers with a double-row structure of adsorbates aligned along the $[\bar{1}10]$ direction. Mixed-overlayer structures comprising two different halogens [7.4] have also been investigated. The surface morphology of such layers is quite different from those comprising one type of adsorbate. In the case of a 50:50 fluoro-chloro mixture, the double-row structure seen individually for both fluorine and chlorine is absent. A long range quasi-hexagonal Moiré-like pattern is observed in which the corrugation height in the topographic image varies from 0.3-0.8Å. There are a large number of vacancies in these mixed layers which result from stresses that occur as a result of the adsorbate-lattice mismatch. Similar results were observed for a 50:50 mixture of chlorine and iodine.

7.3 Surface Science Analysis:

The work presented in this Chapter is based upon the adsorption of 1-bromo 2-chloro ethane (BCE) on to a Cu(100) surface. This molecule has the interesting property [7.5] that upon contact with a copper surface, the halogen

atoms are adsorbed while the organic residue does not stick to the surface. I should like to thank Dr R.G. Jones of the Department of Physical Chemistry at the University of Nottingham for drawing my attention to this observation.

7.3.1 Gas-line Handling and Purification of BCE:

The BCE was used as supplied from the Aldrich Chemical Company [7.6]. At room temperature, BCE is a colourless liquid with a high vapour pressure. This vapour was introduced into a gas line via a Young's tap; this is a composite test tube made of glass at its base and stainless steel at its head. A short section of 6mm outside-diameter, stainless-steel pipe was bent into a right angle and welded on to the head of the Young's tap. A Nupro valve was welded onto the other end of this pipe in order to connect the Young's tap directly on to a gas line which fed into the main vacuum system, see **figure 7.1** below.

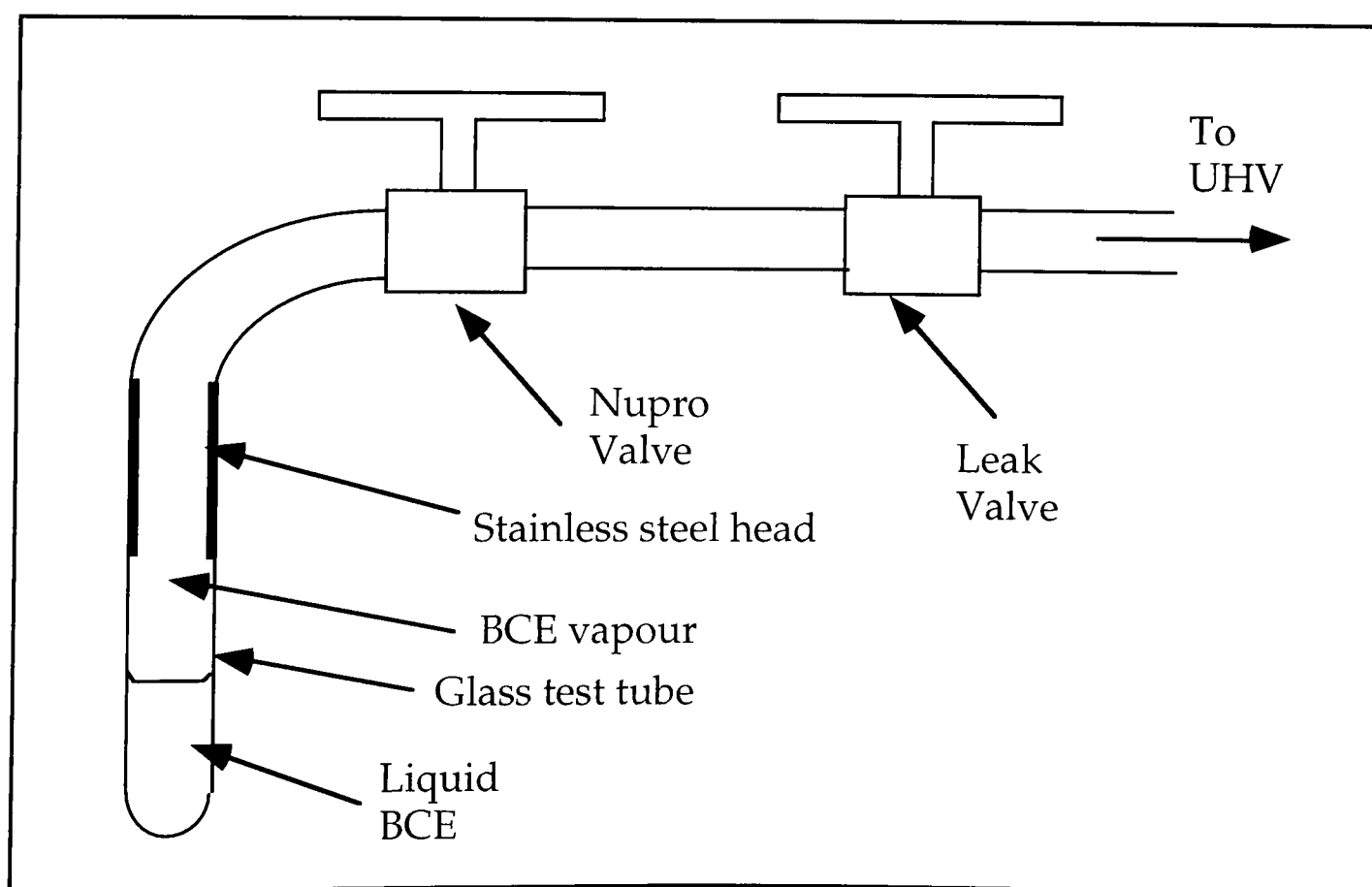


Figure 7.1: A schematic diagram showing the principal features of a Young's tap and its connections to the Ultra High Vacuum system.

Prior to each dosing experiment, the Young's tap was immersed in a bath of liquid nitrogen. This froze the BCE and allowed the vapour above it to be pumped out of the gas line without the vapour being replaced from the liquid reservoir. The idea behind this process was to extract any impurities in the gas line and is the vacuum analogy of rinsing a beaker. The BCE was then removed from the liquid nitrogen bath and "fresh" BCE vapour used in dosing experiments. All dosing experiments were performed with the sample and the vapour at room temperature; typical dosing pressures were $\sim 1 \times 10^{-8}$ mBar.

7.3.2 Mass Spectroscopy and Auger Electron Spectroscopy:

During the dosing experiments, the chemical species present in the vacuum were analysed by taking a mass-spectrum. **Figure 7.2** below shows the results of one such experiment. A reference cracking pattern [7.7] is included for comparison.

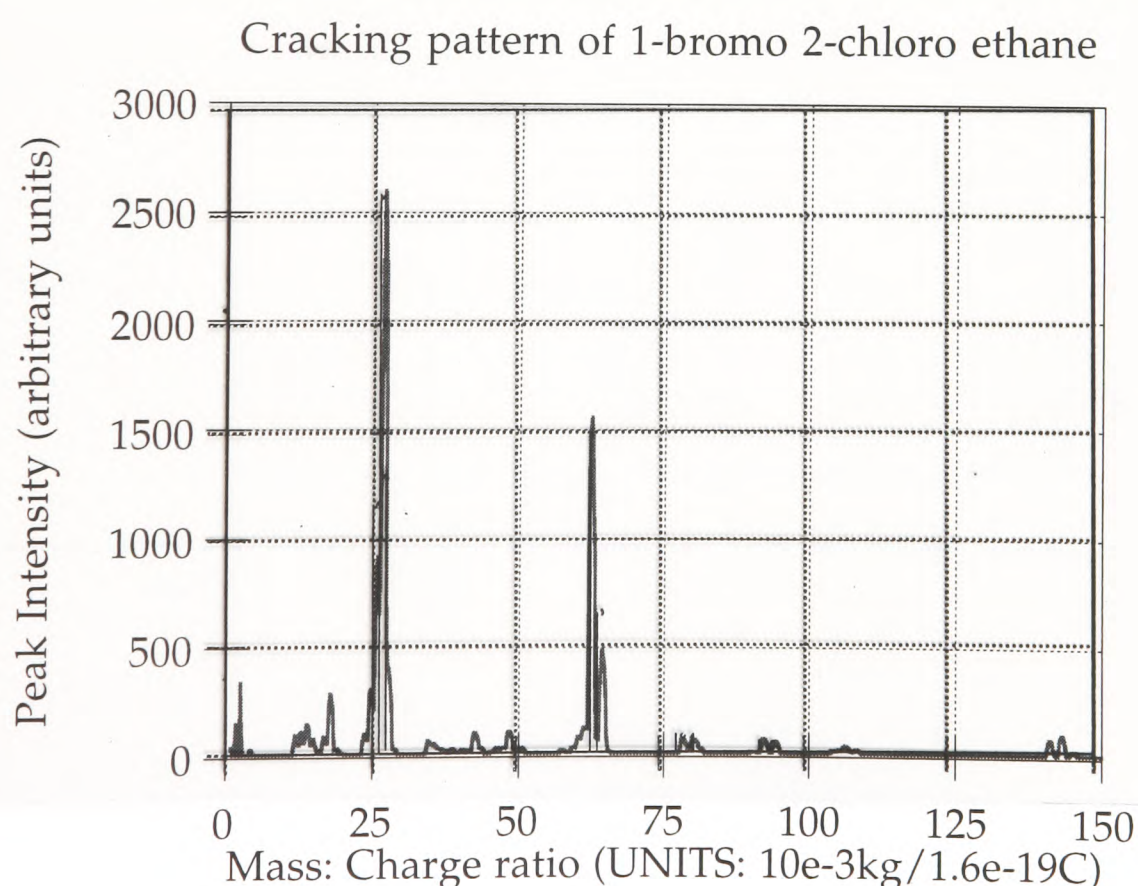


Figure 7.2: A pair of mass-spectrographs showing the cracking pattern of 1-bromo 2-chloro ethane. The printed page shows the reference pattern, while the overlayer shows a cracking pattern obtained in this work.

Auger analysis was performed both prior to gas dosing and immediately afterwards to check the chemical composition of the surface. **Figure 7.3** overleaf shows an Auger-electron spectrum for the Cu(100) surface, after it had been exposed to 5 Langmuir of BCE (1 Langmuir exposure of any gas is equal to 1.32×10^{-6} mBar-seconds). In this spectrum, the chlorine peak at 181eV is clear enough. However, the main bromine peaks occur at 102eV and 108eV and cannot be so easily discerned because the clean copper surface has an Auger peak at 105eV. The presence of bromine on the surface is deduced from the observation of the broadening of the Auger spectrum at ~ 105 eV. This region of the spectrum has a different shape from the equivalent energy range of the clean copper Auger spectrum (compare with **figure 3.11**).

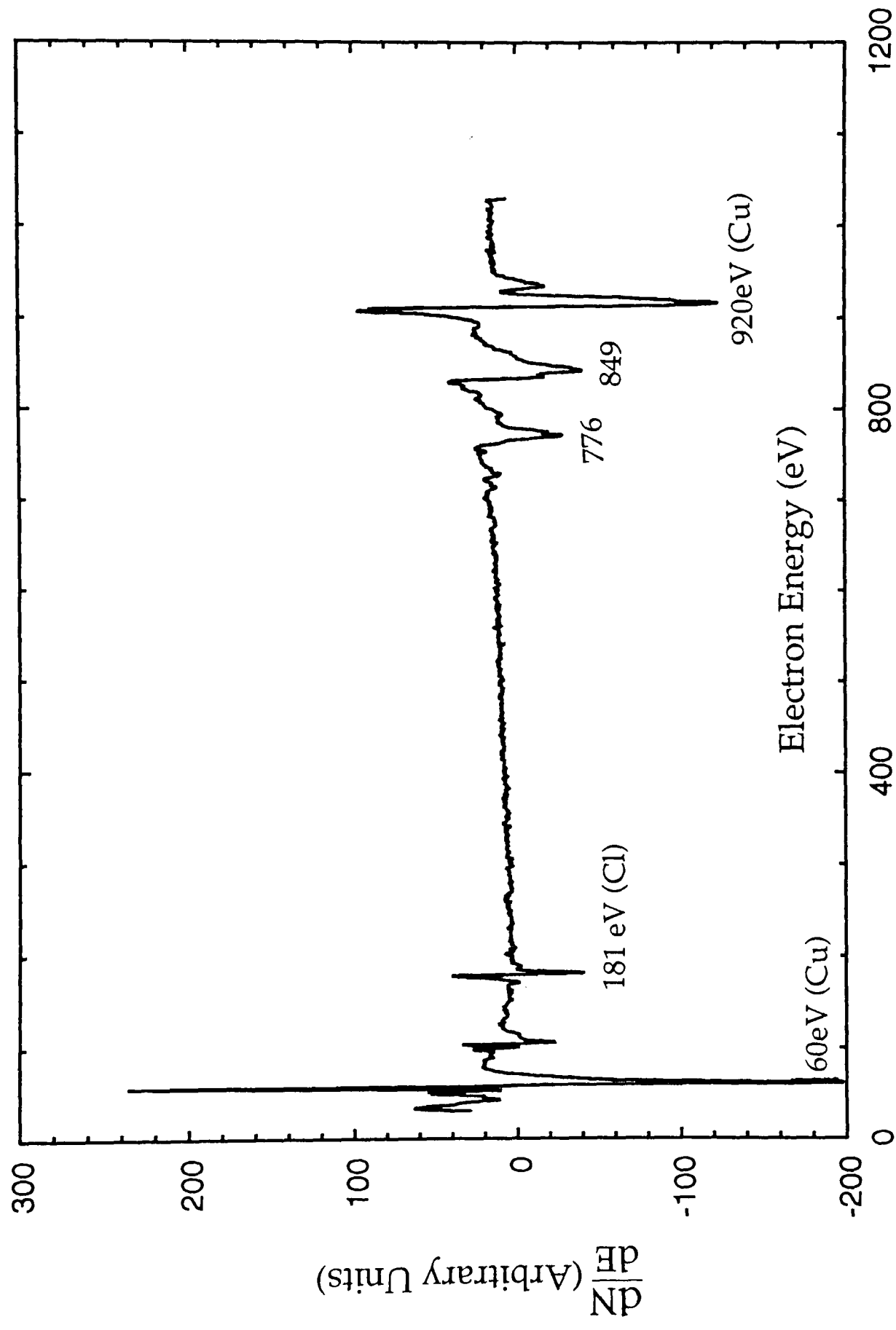


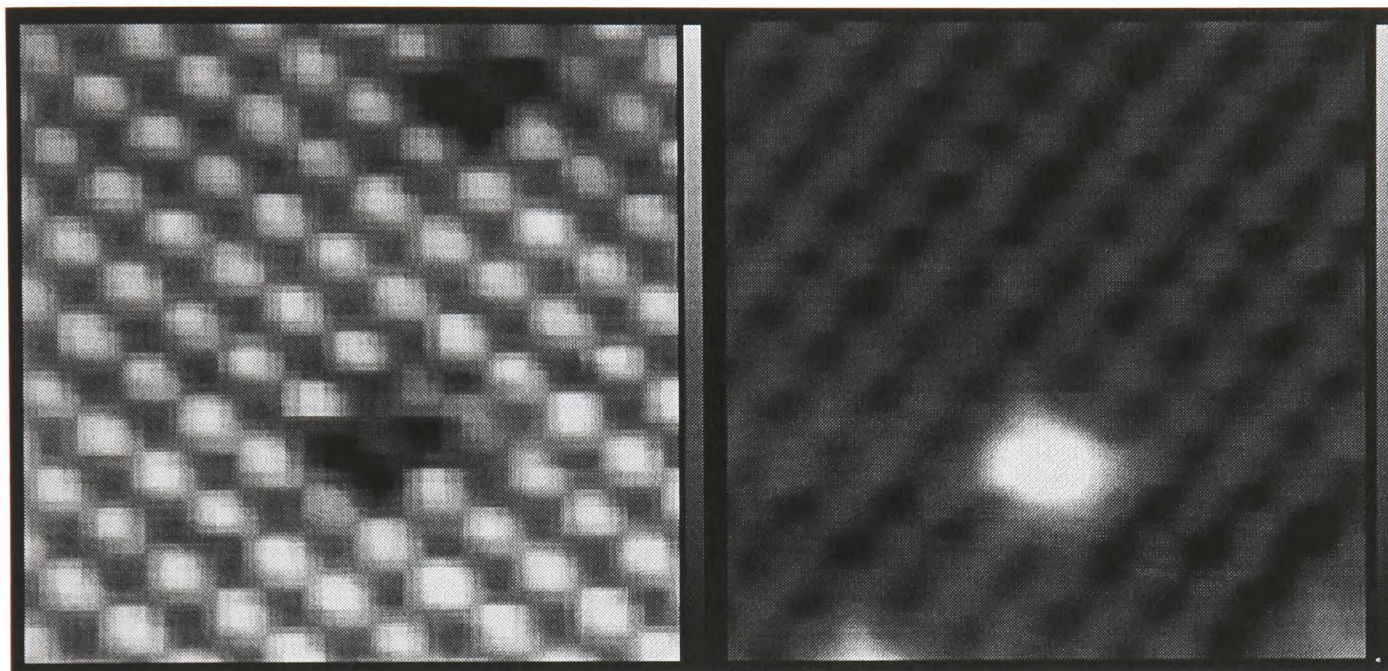
Figure 7.3: An Auger-electron spectrum taken from a Cu(100) surface modified by the adsorption of 5Langmuir of 1-bromo 2-chloro ethane.

7.4 Imaging Single-Atom Halogen Adsorbates on Cu(100):

7.4.1 Corrugation Height Measurements:

At low coverages of BCE (exposure ~ 0.15 Langmuir), single halogen atoms are randomly arranged over the surface and do not exhibit any preference to form dimer pairs or larger formula units on the surface. Two different types of adsorbate were observed in this study, their appearance being independent of the sign of the imaging bias voltage used. The most commonly observed features were “single-atom” depressions of approximate depth $0.5\text{\AA}$ below the mean level of the corrugated metal surface, see **figure 7.4** overleaf. On a minority of occasions, “single-atom” positive protrusions of approximate height $0.6\text{\AA}$ above the mean corrugation of the metal surface were also observed, see **figure 7.5** overleaf. By inspection of high resolution images, the binding site for both species was revealed as directly above a surface atom. This result is in contrast to physical intuition as well as previous surface science experimental studies [7.8, 7.9, 7.10] which established the four-fold hollow site of Cu(100) as the binding site for halogen atoms. One possible interpretation of these findings is that the STM images of **figures 7.4** and **7.5** are exhibiting a contrast reversal with minima in these images corresponding to atomic sites and vice versa. However, one piece of evidence which does not support this view is shown in **figure 7.6** overleaf. In this figure, a halogen-like depression is seen to be located on a four-fold hollow site. The image also shows a carbon atom easily identifiable from its characteristic cross-shape [7.11]. This carbon atom is bound above an atomic site which does not agree with the four-fold hollow binding site proposed by Klink et al. [7.11]. This dilemma is reconciled by assigning **figure 7.6** as a reverse contrast image, which is consistent with the view that a carbon atom is bound to a four-fold hollow site and that halogen atoms are bound to on-top sites.

It is worth pointing out here that STM data taken by the author for BCE + Cu(111) shows similar protrusion and depression-like features. However, in this latter case these species are located on the expected three-fold hollow sites of the substrate [7.5].



Figures 7.4: (left hand image) and **Figure 7.5:** (right hand image): STM images showing the two types of halogen species observed in this study. Both images are $30 \times 30 \text{ \AA}$ in size (vertical scales $0.7 \text{ \AA}$ and $0.5 \text{ \AA}$ respectively). The tunnelling parameters used to take **figure 7.4** were $I=4.4 \text{ nA}$, $V = -14 \text{ mV}$. The tunnelling parameters used to **figure 7.5** were $I=5.6 \text{ nA}$, $V = -8 \text{ mV}$.

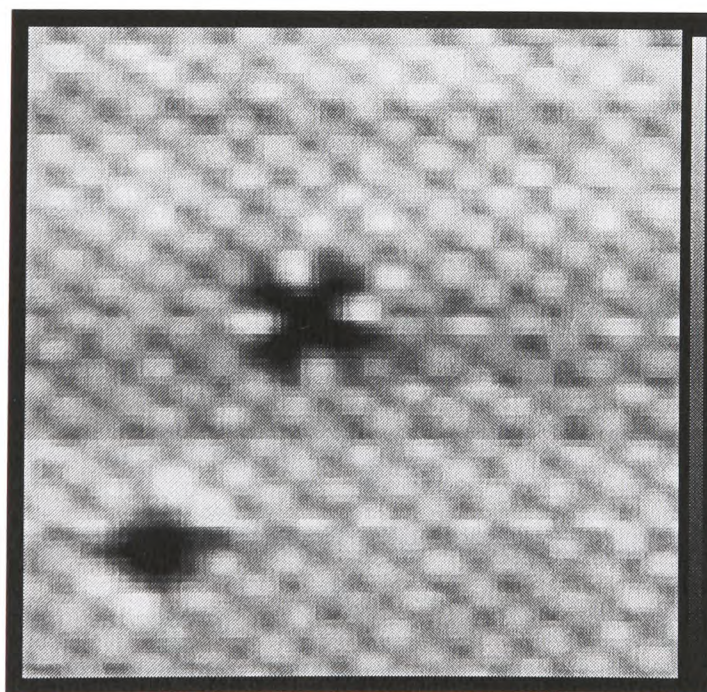


Figure 7.6: An $30 \times 30 \text{ \AA}$ (vertical scale $0.25 \text{ \AA}$) STM image showing a halogen atom (bottom left hand corner) and a carbon atom (centre). Both adsorbates are found to be bound on unexpected sites and so this image is interpreted as a reverse contrast image. The tunnelling parameters used to take this image were $I=5.6 \text{ nA}$, $V = -8 \text{ mV}$.

The two halogen species were never imaged simultaneously and so they cannot be interpreted as a means of distinguishing the two different elements present on the surface. Rather, these two species are regarded as an indication of the chemistry at the tip-apex. At low coverages, the adsorbates were usually, although not always, seen as depressions, while at higher dosing levels in the vacuum chamber (exposures ~ 5 Langmuir), the adsorbates were always seen as positive protrusions. It is thus speculated that a positive protrusion in the image should be associated with a halogen atom at the tip-apex, while a metallic tip gives rise to a depression shaped halogen-adsorbate in the image.

Additional support for this interpretation comes from the LDOS calculations of Lang [7.12, 7.13] for single adatoms adsorbed on a jellium electrode. In this work, small electronegative atoms such as oxygen are predicted to polarise metallic states away from the Fermi-level, thereby causing the tip to approach the surface in order to maintain a constant tunnel current. Atoms like chlorine and bromine would be expected to behave similarly in STM giving rise to depression-shaped features in the STM image when using a metallic (i.e. s-wave) tip.

7.4.2 Tunnel Barrier Height Measurements:

It was possible to take a small number of $\text{Ln}(\Delta):\text{Ln}(\sigma)$ data sets from images which exhibited isolated adsorbates. **Figures 7.7 and 7.8** overleaf show results of corrugation analysis for an adsorbate imaged as a depression and as a protrusion respectively.

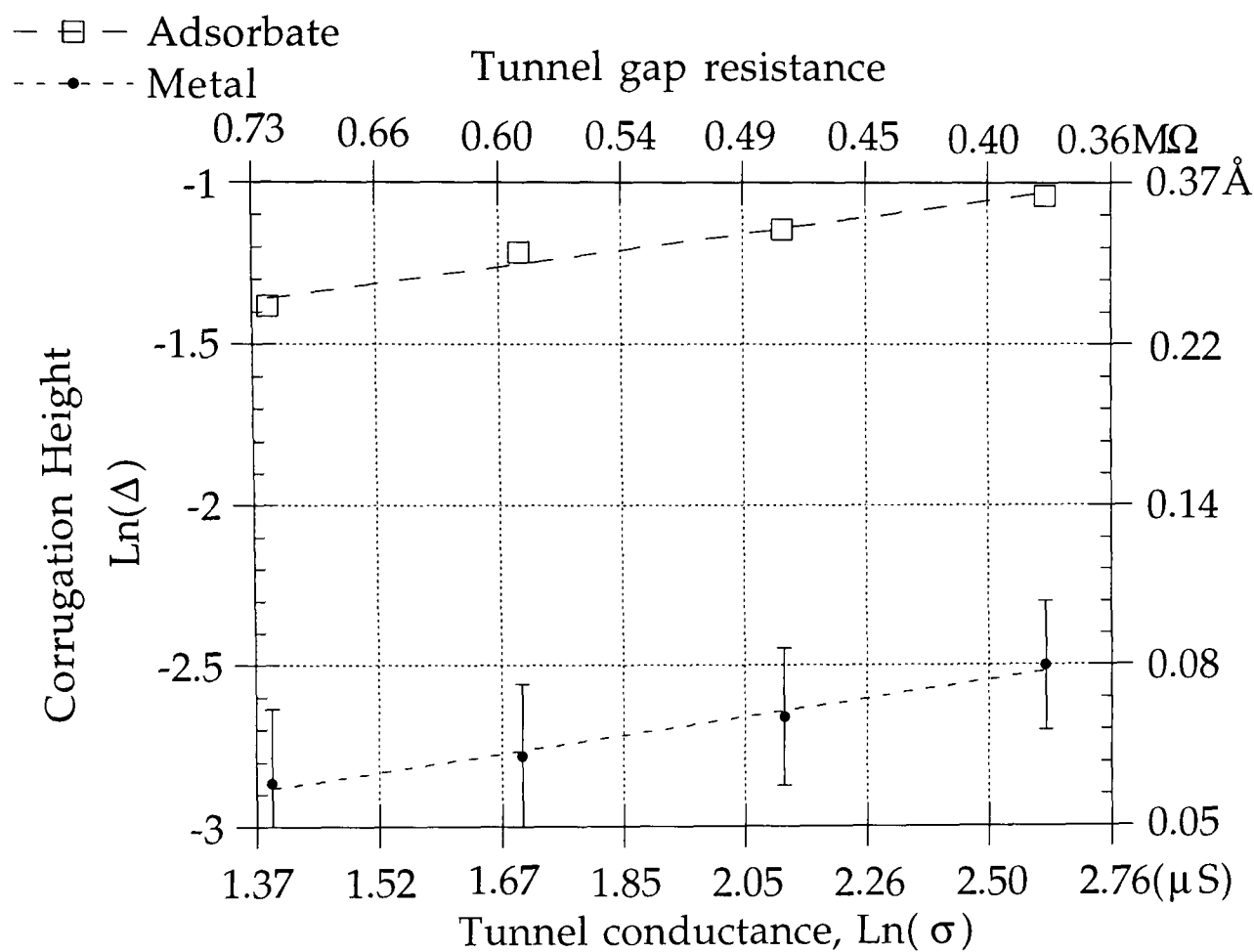


Figure 7.7: A $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot showing the decay of corrugations measured above the clean metal surface along $\langle 001 \rangle$ and also above a halogen adsorbate which was seen in these images as a depression. Adsorbate corrugations are measured as the *depth* below the mean level of the metal corrugation.

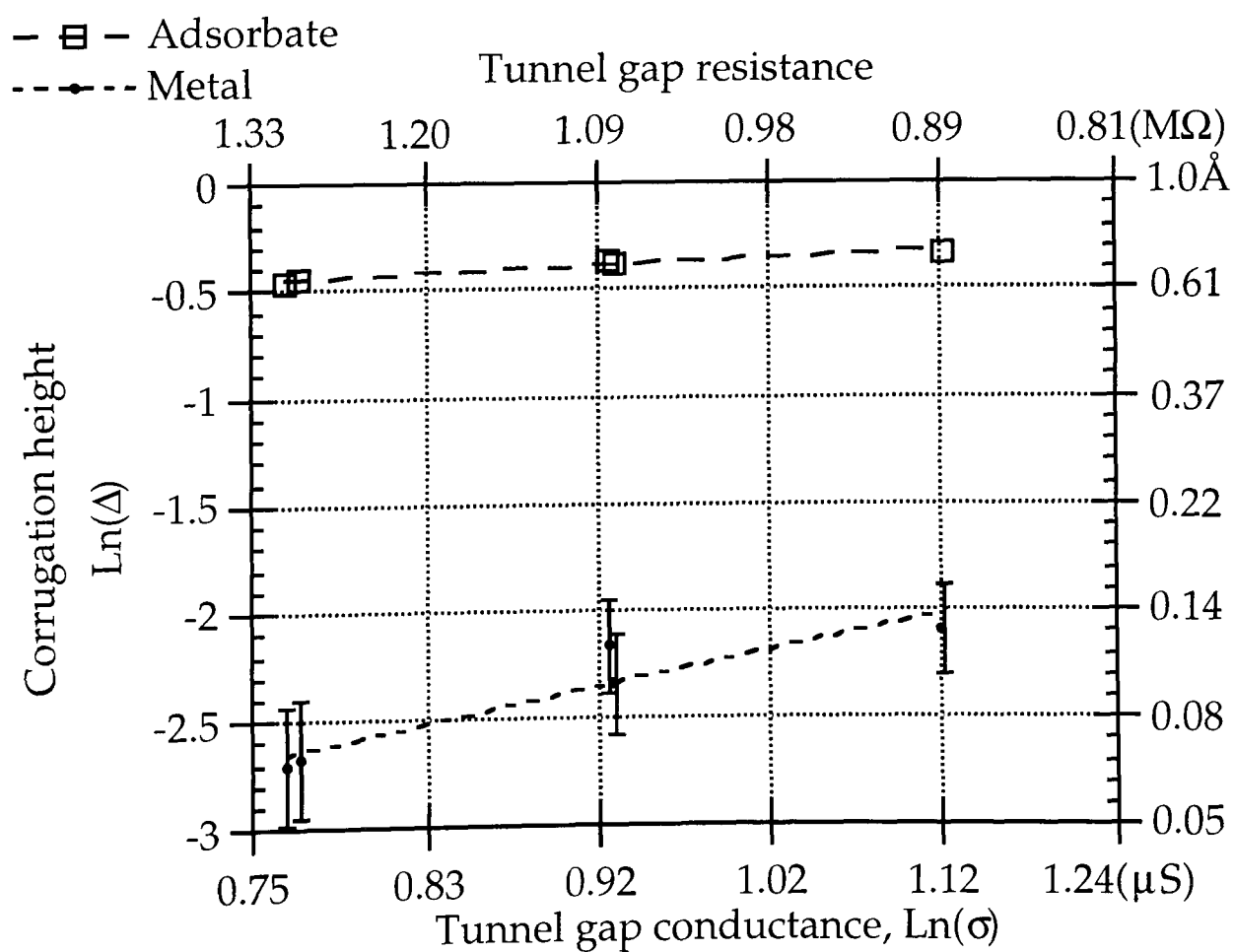


Figure 7.8: as figure 7.7 but the adsorbate was imaged as a positive protrusion. Adsorbate corrugations are measured as the height above the mean level of the metal corrugation.

In the $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots of **figures 7.7 and 7.8**, the adsorbate atom data exhibits a shallower slope than the metal data which qualitatively corresponds to a larger tunnel barrier height over the adsorbate compared with the clean metal.

The increase in the local tunnel barrier height over the adsorbate sites is interpreted as the result of the formation of an electrical-dipole layer at the surface. The electric-potential due to a dipole is well known quantity [7.14]. and it is straightforward to calculate the increase in mean tunnel barrier height due to such a surface-dipole, $\Delta\phi_{\text{Dipole}}$, see equation (7.1). The dipole has its negative end extending out into the vacuum and is assumed to be oriented perpendicular to the metal surface.

$$\Delta\phi_{\text{Dipole}} = \frac{ne^2a}{4\pi\epsilon_0s_1(s - s_1)} \quad (7.1)$$

where ne is the charge associated with each pole in the dipole, e is the unit of electric charge, a is the spacing of the charges in the dipole, s_1 is the classical turning point distance above the surface, and s is the tip-sample separation.

Using the value of $\left(\frac{\partial\text{Ln}(\Delta)}{\partial\text{Ln}(\sigma)}\right)$ measured from the metal corrugations, a value for the tunnel barrier height can be deduced as discussed in Section 5.3 of Chapter Five. The effect on the local tunnel barrier height of the adsorbate is deduced by adding the dipole term of equation (7.1) in to the expression for the tunnel barrier height of equation (5.3) and deducing a modified value for $\left(\frac{\partial\text{Ln}(\Delta)}{\partial\text{Ln}(\sigma)}\right)$. It is assumed that there is no adsorbate induced change in tunnel gap width and so modifications to the tunnel barrier height are due to the dipole moment which is given by the product, nea . The numerical value of this term is adjusted until agreement with experiment is obtained.

The table in **figure 7.9** below summarises the tunnel barrier heights calculated from this data.

	Tunnel Barrier Height above metal (eV)	Tunnel Barrier Height above adsorbate (eV)	Dipole moment: (Cm)
Figure 7.7	0.72±0.13	0.92±0.23	2.10x10 ⁻³⁰
Figure 7.8	0.26±0.10	2.23±0.51	1.52x10 ⁻²⁹

Figure 7.9: A table showing the values deduced for the tunnel barrier height over a Cu(100) surface and above a single halogen atom.

The dipole moments calculated here can be used to estimate the charge transfer between the metal surface and the adsorbate. Using Surface Extended X-Ray Absorption Fine Structure (SEXAFS) Citrin et al. [7.8] have determined the length of the Cu-Cl bond for the case of chlorine adsorbed on a four-fold hollow site of Cu(100) as 2.37±0.02Å. This is in close agreement with the value deduced by Jona et al. [7.9] using LEED of 2.41±0.02Å. It is unfortunate that the halogens were seen here over "atomic" sites. However some estimate is required for the Cu-Cl dipole length and so these bond lengths were used to calculate a vertical distance of the chlorine atom above the copper surface. The dipole moments obtained here lead to calculated charge transfer values of 0.04 electrons in the case of the depression shaped adsorbate (**figures 7.4 and 7.7**) and 0.3 electrons in the case of the protrusion (**figures 7.5 and 7.8**). Slightly reduced values are obtained if it is assumed that the adsorbates are in fact bromine species because of the ~ 10% larger radius of bromine.

Simple calculations based on angular-resolved photoemission data by Kleinherbers et al. [7.10] deduced charge transfer values of 0.10±0.01 and 0.07±0.01 electrons for chlorine and bromine respectively adsorbed on Cu(100).

The charge transfer measured for the depression-shaped adsorbate is in fair agreement with these values and is consistent with the idea that a metal atom terminated tip was used to take the data of **figure 7.7**.

However, the large value of charge transfer deduced for the protrusion shaped adsorbate indicates that some extra interaction needs to be considered. Earlier in section 7.4, it was postulated that observation of a protrusion in the image corresponds to the presence of a halogen atom at the tip apex. Similar to the case of a halogen adsorbate on the surface, a dipole layer may also be induced at the tip electrode. This would halve the necessary charge transfer for both dipoles in order to generate the same tunnel barrier height. However, it is also necessary to account for the mutual potential energy of these two dipoles in the expression for the tunnel barrier height.

The potential energy, W , of two anti-parallel dipoles, facing one another along a mutual length axis and separated by a distance, x , is given by equation (7.2):

$$W = \frac{2p_1p_2}{4\pi\epsilon_0x^3} \tag{7.2}$$

where p_1 and p_2 are the dipole moments (equal to the product, n.e.a.)

The contribution of the doublet mutual-energy to the mean tunnel barrier height is given by equation (7.3):

$$\Delta\phi_{\text{Doublet}} = \frac{P_1P_2}{8\pi\epsilon_0(s_2 + s_1)(s_2 - s_1)^2} \tag{7.3}$$

For simplicity, it is assumed that both dipoles are the result of a chlorine atom adsorbed on a copper surface. Proceeding as before but this time adding both the dipole terms of equations (7.1) and (7.3) into the expression for the mean tunnel barrier height, agreement between the theory and the experimental data of **figure 7.8** is obtained with a charge transfer 0.14 electrons to the chlorine atom which is in close agreement with the value calculated by Kleinherbers et al. [7.10].

7.4.3 Effects of Topography on the Local Barrier Height:

Thus far, this work has only considered the effects of the adsorbate-induced dipole upon the tunnel barrier height. However, an important additional factor is the influence of geometric topography. Species which are revealed as protrusions in conventional constant current topographic images show up as local maxima in barrier height images. This result has been confirmed for sulphur atoms on Mo(001) [7.15]. Similarly, depressions in a constant current STM image are expected to show up as local minima in barrier height images.

The implications of these effects for the data in **figures 7.7** and **7.8** are that in the case of a halogen-protrusion, the local increase in the tunnel barrier height is due to the additive effects of both the dipole and topography. However when a halogen-depression is seen in the image, the effects of the induced dipole and topography act in opposition. This means that the change in local barrier height due to a protrusion should be much larger than that due to a depression which was exactly what was measured experimentally, see data in **figure 7.9**. The relatively small increase ($\sim 0.2\text{eV}$) in the tunnel barrier height seen over the depression shaped adsorbates indicates that although the dipole component to the local barrier height is larger than the decrease in barrier height due to the depression in the local topography, these factors are almost equal in magnitude.

If the increase in the local tunnel barrier height is now regarded as being due to the combined influences of topography and induced dipoles, then the approximate contributions of each term to the overall increase in the tunnel barrier height can be estimated. When the adsorbate is seen as a depression, the increase in the tunnel barrier height is equal to the difference in the induced-dipole and topographic contributions. For the case of the adsorbate imaged as a protrusion, following the arguments of section 7.4.2., the increase in the tunnel barrier height is taken as the sum of *two* dipoles and the effect of topography. For simplicity, the interaction between the two dipoles is omitted, as it contributes a relatively small amount to the total increase in barrier height anyway. Because both types of adsorbate are approximately of the same height/depth relative to the surface, the topographic contribution to the barrier height of the protrusion and the depression are taken as being equal and opposite. Two equations emerge which can be solved simultaneously producing the result that the topographic contribution to the change in local tunnel barrier height is $\sim 0.5\text{eV}$ and the dipole contribution is $\sim 0.7\text{eV}$.

The estimation of these quantities allows for a revised calculation of the charge transfer to the halogens adsorbates. By adding the topographic contribution to the barrier height to the increase in barrier height due to the depression shaped adsorbate (0.2eV) and proceeding in the manner described in section 7.4.2. a charge transfer to the adsorbate of 0.14 electrons was calculated. Similarly by subtracting the topographic barrier height contribution from the increase in barrier height due to the protrusion shaped adsorbate (2eV) a charge transfer of 0.11 electrons was calculated. Note that both of these charge transfer values are close to the values evaluated using other surface science techniques for halogen atoms on Cu(100). It is speculated that the difference in these values may be used as a means of discriminating between chlorine and bromine.

7.5 Adatom Manipulation Using the Sliding Mechanism:

In Chapter Six, it was shown that significant forces are present between the tip and sample in the normal mode of STM imaging. In many imaging situations, the interactions between the tip and sample are comparatively unimportant in determining the surface morphology. However, occasionally these influences do become important. The extrema of such phenomena are two-fold: (i) unwanted interactions such as has been proposed for the non-observation of carbon monoxide at low coverages [7.16] and (ii) deliberate interactions such as the manipulation of Xenon atoms over Ni(110) at 4K [7.17]. In this section the latter type of phenomenon is demonstrated, the basic idea is illustrated in **figure 7.10** below.

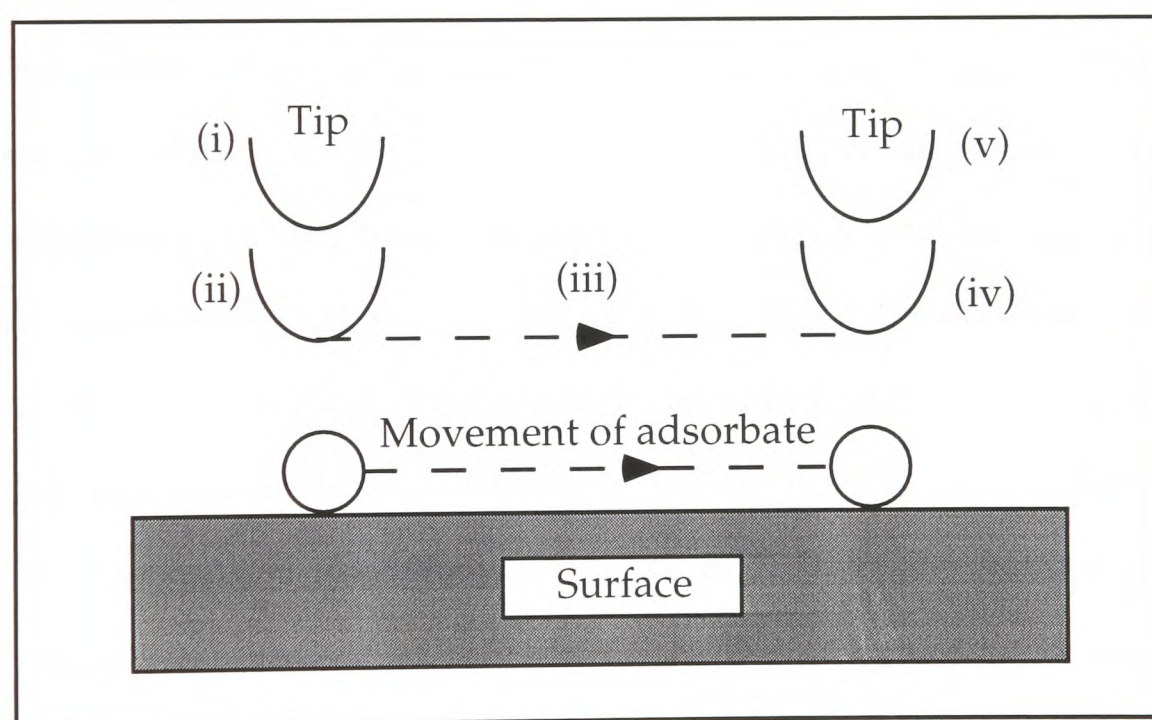


Figure 7.10: A schematic diagram showing the key elements in the atomic manipulation sliding process developed by Eigler et al. [7.17].

The sequence of events in the manipulation process is as follows: (i) The tip is located over the desired adsorbate; (ii) the tip is lowered to a position where the adsorbate experiences a considerable interaction due to the proximity of the tip; (iii) the tip is then moved across the substrate bringing the adsorbate along with it; (iv) the tip is withdrawn; (v) the adsorbate is left in a new location. In

the sliding process, the motion of the adsorbate is parallel to the plane of the macroscopic surface. It should be noted that there is a second class of atomic manipulation processes in which adsorbates are positioned at new locations on the surface by applying medium-sized bias pulses ($\sim 3\text{-}5\text{V}$) between the tip and the sample [7.18]. The adsorbates usually move towards the positively biased electrode and so the basic strategy comprises applying a large positive bias pulse to a tip which is directly over an adsorbate, moving the tip to a new location over the surface and then applying a reversed bias pulse to the tunnel junction in order to place the adsorbate back on the surface. Manipulations of this latter type were not attempted in this work.

Figure 7.11 overleaf below shows a single-atom adsorbate on the Cu(100) surface. This image was taken at a tunnel conductance of $0.49\mu\text{S}$ (resistance $\sim 2\text{M}\Omega$). The surface was immediately re-imaged using a larger value for the tunnel current and hence also using a larger value of tunnel conductance of $0.72\mu\text{S}$ (resistance $\sim 1.4\text{M}\Omega$), see **figure 7.12** overleaf. The tip and the surface were then interacting sufficiently strongly that the tip was able to move the adsorbate over the surface. The image was taken as a series of line-scans moving left to right and from bottom to top. The atom was re-imaged on a number of occasions, so that the path of the adsorbate can be seen as moving along a $\langle 001 \rangle$ direction. After two jumps up the image, the adsorbate jumps one atomic row to the right.

Prior to this manipulation, it had been possible to image the adsorbate at a number of different sets of tunnelling parameters. The results of corrugation analysis of this data are shown in **figure 7.13** overleaf.

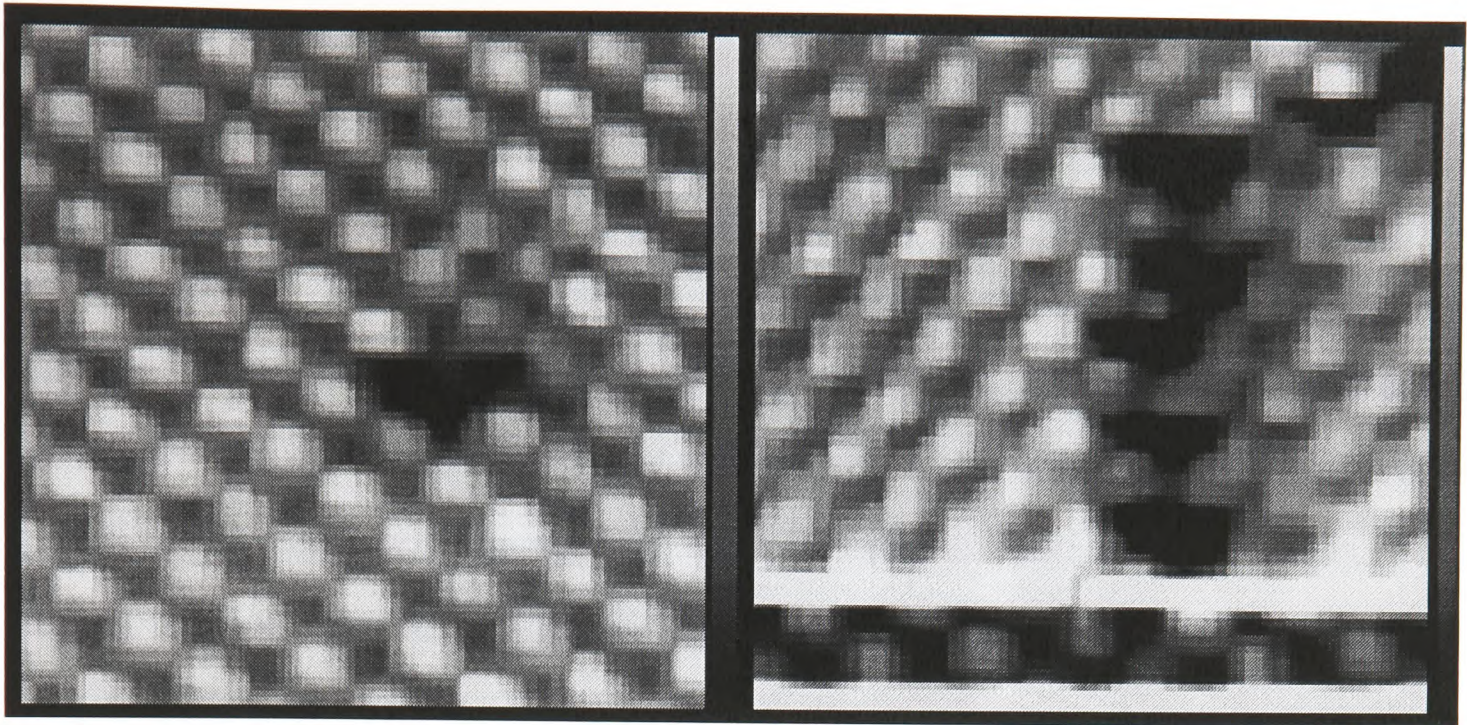


Figure 7.11 and 7.12: These two images were taken sequentially and illustrate tip-induced adatom manipulation. The former image was taken using a tunnel current of $I = 7.4\text{ nA}$, $V = -16\text{ mV}$, while the latter was taken at $I = 10.6\text{ nA}$, $V = -16\text{ mV}$. Each image is $30 \times 30\text{ \AA}$ in size (vertical scales 0.5 and $0.9\text{ \AA}$ respectively), but the right hand image had as its origin a point displaced $6\text{--}7\text{ \AA}$ up the "y-axis" of the left hand image.

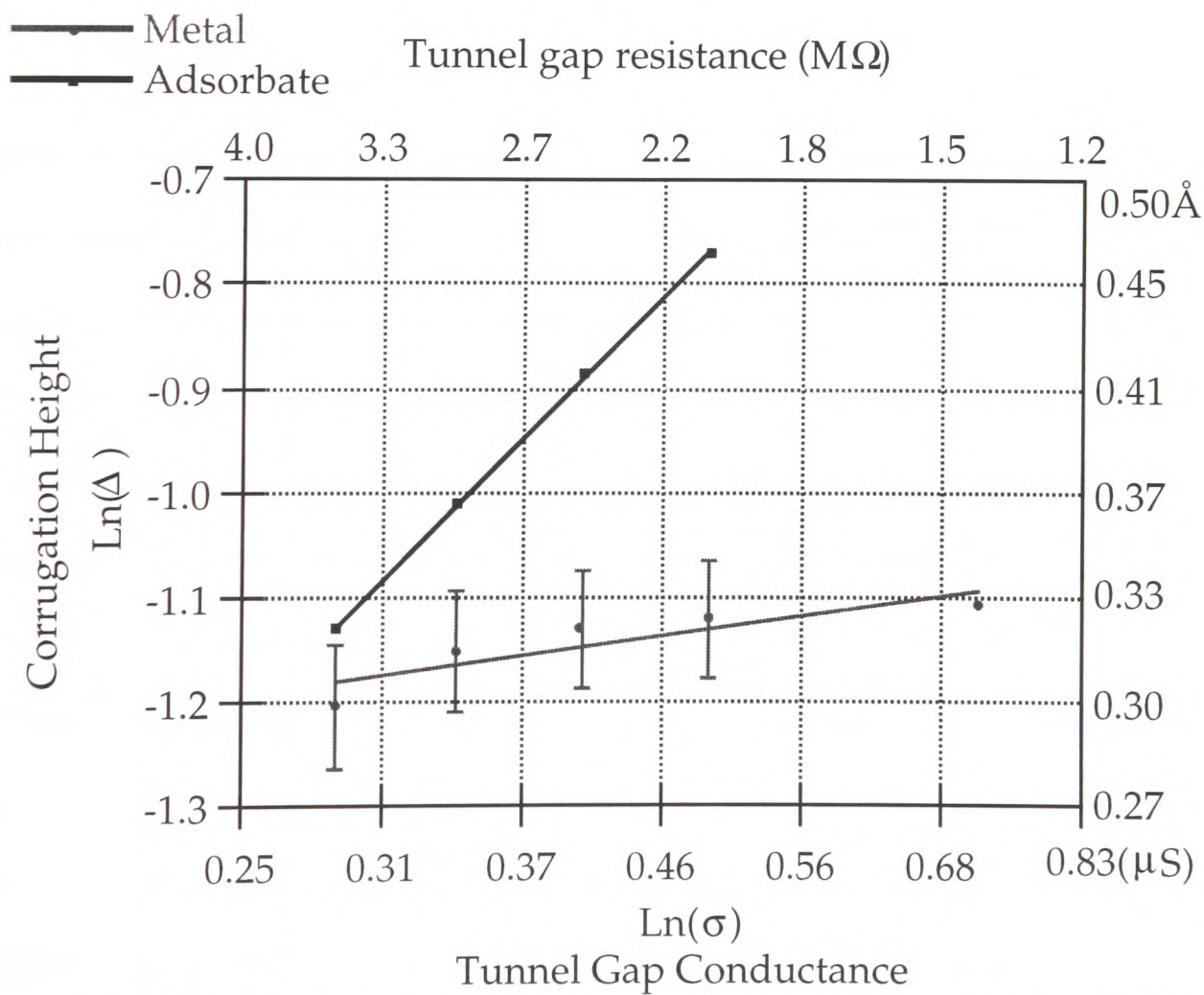


Figure 7.13: A $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plot for the halogen adsorbate of **figure 7.11** which was eventually moved over the surface by the tip, see **figure 7.12**. Adsorbate corrugations are measured as the *depth* below the mean level of the metal corrugation.

This data shows that the tip-induced adsorbate manipulation process commences prior to any significant surface corrugation roll-off. This result is consistent with the data presented in Chapter Four where the corrugation height roll-off did not commence until a tunnel conductance of $\sim 1\mu\text{S}$ was reached. However, from inspection of **figure 7.12**, it appears that the tip-adsorbate forces are sufficiently strongly attractive for the adsorbate to be pulled off the surface, causing a tip-apex reconfiguration. At the bottom of the image, the corrugation height for one $\langle 001 \rangle$ line can be measured ($\sim 0.33\text{\AA}$) and it is in accord with the trend of the other experimental data points (see the single data point on the right-hand side of **figure 7.13**). However, once the adsorbate starts to move over the surface, the metal corrugation is reduced ($\sim 0.25\text{\AA}$ along $\langle 001 \rangle$) as a result of the rearrangement of the tip apex after it collided with the adsorbate.

Eigler et al. [7.17] found that in order to manipulate surface atoms it was necessary to place the tip at a threshold height above the surface. This height did not significantly depend upon the characteristics of tip or the imaging voltage and implies that the dominant force between the tip and sample was the Van der Waals interaction. However it seems unlikely that Van der Waals forces are responsible for the manipulation event observed here unless they act very close to the point at which the tip touches the adsorbate.

Adsorbates such as the one in **figure 7.14** overleaf were often manipulated by the tip along the ready made channels provided by the surface crystallographic directions. It is interesting to note that despite the scanning process in which the left to right motion of the tip favours the adsorbate moving along a diagonal oriented towards the top right hand corner of the image, the atom still had enough thermal energy to make single jumps towards the top left hand corner of the image every $20\text{\AA}$ or so.

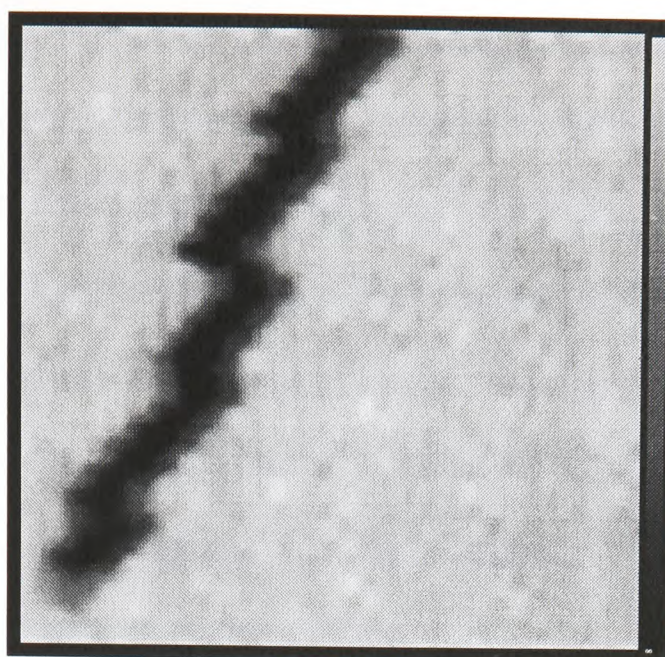


Figure 7.14: A $70 \times 70 \text{ \AA}$ (vertical scale $0.6 \text{ \AA}$) STM image showing a depression shaped adsorbate being manipulated by the tip along a $\langle 0\bar{1}1 \rangle$ direction of the Cu(100) surface. The tunnel parameters used to take this image were $I = 6.2 \text{ nA}$, $V = -16 \text{ mV}$.

It was also possible to manipulate protrusion-shaped adsorbates over the surface, see **figure 7.15** below.

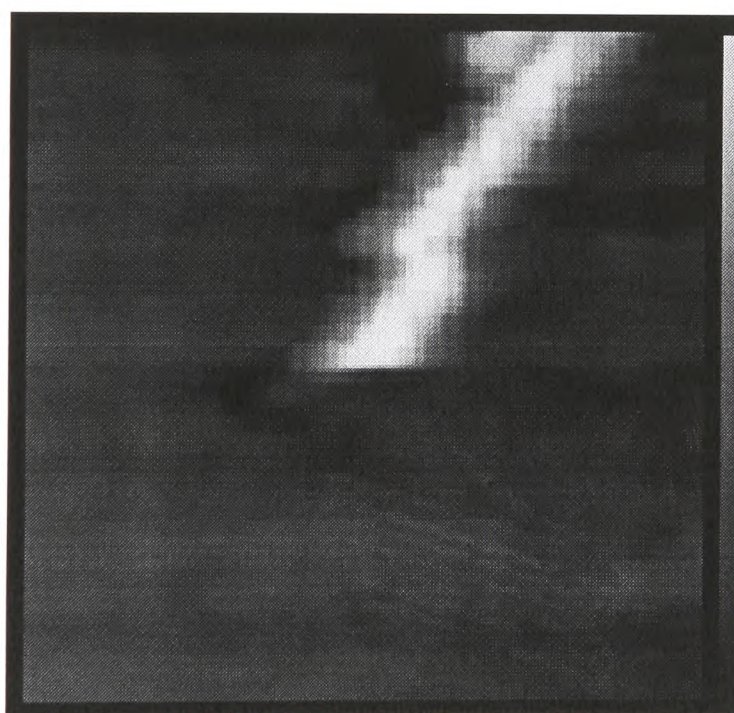


Figure 7.15: A $70 \times 70 \text{ \AA}$ (vertical scale $0.5 \text{ \AA}$) STM image showing the tip-induced manipulation of a protrusion shaped adsorbate. The tunnelling parameters used were $I = 7.32 \text{ nA}$, $V = -14 \text{ mV}$.

In this case, the threshold value of the tunnel conductance was somewhat lower than for the depression taking a value of $0.56 \mu\text{S}$. Unfortunately in this

case, the data obtained is not of sufficient quality to undertake a corrugation height analysis. However, if the earlier assertion about the nature of the tip species is correct then this result is consistent with the observation in Chapter Four that tip-surface interactions produce measurable effects at larger tip-sample separations when a non-metal atom is present at the tip apex. By making use of the Molecular Dynamics data of Chapter Six, a very rough estimate of $\sim 0.1\text{nN}$ is obtained for the normal tip-surface force at this threshold value for the tunnel conductance.

7.6 Summary:

The tunnel barrier height above a Cu(100) surface modified by adsorption of small numbers of halogen atoms has been investigated in this Chapter. In co-adsorption experiments, involving chlorine and bromine two main types of adsorbate species were observed. Single-atom depression shaped species produced a small change in the local tunnel barrier height of $\sim 0.2\text{eV}$, while larger changes ($\sim 2\text{eV}$) in the tunnel barrier height were seen from a single-atom protrusion-shaped species. These observations have been accounted for in terms of differences in surface topography and the need to include the effects of a surface dipole layer in the expression for the tunnel barrier height. It has been shown that the halogen-adsorbate topography contributes about $\pm 0.5\text{eV}$ to the local change in tunnel barrier height, while the dipole contribution is slightly larger ($\sim 0.7\text{eV}$). Values for the charge transfer (~ 0.11 - 0.14 electrons) between the substrate and the halogen adsorbates have shown to be in accord with values deduced using other surface science techniques. It has also been shown that by imaging the surface at sufficiently large values of the tunnel conductance ($> 0.5\mu\text{S}$), the tip can be used to manipulate halogen atoms over the surface. This halogen work is only a preliminary study and further experiments are needed to consolidate the findings of this Chapter.

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Chapter 8

Conclusions and Suggestions for Further Work

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8.1 Closing Remarks:

At the beginning of this Thesis, it was shown that many bizarre imaging phenomena have been reported in Scanning Tunnelling Microscopy (STM). It is important to understand such features, not only because they are of interest in their own right, but also because it is important for data interpretation to recognise when they occur in every day STM studies. The collection of interesting STM artefacts is now rather large and it was with the aim of understanding such features, that the experiments and calculations presented in this Thesis were undertaken.

As I write the conclusions of this Thesis, it is clear that most of the effort in the STM community is directed towards studies involving the determination of lateral atomic geometries of adsorbates on metal or semiconductor substrates. Undoubtedly many workers have shied away from the difficult problem of obtaining quantitative understanding of STM because of the uncharacterised nature of certain aspects of this microscope. This means that one can only perform partially controlled experiments which is in contradiction to the well established scientific method of investigation. Nevertheless, I hope that this

This Thesis demonstrates the importance of a quantitative understanding of STM and also makes some small positive contribution towards solving this problem. Perhaps more work will be performed in this area in the future.

8.2 Tip-Stability:

The cause of many problems in STM is the tip-needle. Some workers [8.1, 8.2, 8.3] have combined STM with Field-Ion Microscopy with the aim of producing single-atom terminated tips of known chemistry. Unfortunately, experience has shown that once a tip is inserted into the microscope, uncontrollable and spontaneous "tip-changes" are all too common an occurrence. The nature of the tip then becomes uncertain making it impossible to perform a well-controlled experiment.

Ironically, however, the first conclusion of this Thesis involves the deliberate, uncontrolled modification of the tip. In experiments on metallic surfaces, it has been observed that in the early stages of imaging, a tip can sometimes be "stabilised" (i.e. the frequency of unwanted tip-changes substantially reduced) by performing a series of indentations into the surface. Molecular Dynamics simulations by Landman et al. [8.4] suggest that this process results in the transfer of material from the surface to the tip. Experimental studies of the formation of a tip-surface point contact by Olesen [8.5] indicate that the source of the transferred atoms is in fact the flux of atoms diffusing over the surface. A requirement for stabilising the tip in order to take atomic-scale resolution data seems to be that the tip has a cluster of surface material at its apex. Demuth et al. [8.6] have similarly observed that a high level of surface resolution can sometimes be induced by gently crashing the tip into the surface. They cite an example of the indentation of a tip into a silicon surface. This action is thought to provide a silicon-derived p_z orbital at the tip-apex in a favourable orientation for imaging the surface.

It would be most interesting to see whether the stability of STM could be improved by using a tip made entirely from the same material as the underlying substrate. I am only aware of two studies where this was the case [8.7, 8.8]. These investigations used conventional tip materials, iridium and tungsten and so perhaps further studies in this area could be devoted to metals such as copper and nickel as well as semiconductors such as doped silicon.

8.3 The Tunnel Barrier Height:

One aspect of STM where a substantial body of work has been performed with the aim of quantitative understanding is in the measurement of the tunnel barrier height. In the simple LDOS model of Tersoff and Hamann [8.9, 8.10], a spatially-uniform tunnel barrier was assumed. However, evidence from "barrier-height" images [8.11, 8.12] indicates that this parameter is strongly site-dependent and contributes significantly to the STM image.

Previous attempts to deduce the tunnel barrier height have been based upon the measurement of $\left(\frac{\partial \text{Ln}(I)}{\partial s}\right)$. However, these methods have suffered from difficulties in accurately calibrating the movement of the tip apex. In this Thesis, a new method for deducing the tunnel barrier height has been developed. This technique uses the normal mode of constant-current STM imaging which by design is most accurate. The only necessary calibration is that obtained from step-heights.

The tunnel barrier height is calculated by measuring the rate of decay of the corrugation height, Δ , of topographic images as the tip-sample separation is increased. A sequence of images is taken using the same tip, each image taken at a different value of tunnel conductance, σ . Corrugation heights are then systematically measured along all the principal directions in the image and a

$\ln(\Delta):\ln(\sigma)$ plot made for each data set. The tunnel barrier height, ϕ , is obtained from the slope of the linear region of such a plot, which is observed at small values of the tunnel conductance ($< 1\mu\text{S}$).

Experiments on Cu(100) have shown $\left(\frac{\partial \ln(\Delta)}{\partial \ln(\sigma)}\right)$ to be independent of the crystallographic direction along which the corrugation heights are measured. Initially a simple model was used to calculate the tunnel barrier height which was based upon only the exponential decay terms of one-dimensional models for the corrugation height [8.9, 8.10] and tunnel current [8.13, 8.14]. This model includes the effect of surface reciprocal-lattice vectors and leads to the unfortunate result that values calculated for the tunnel barrier height from different corrugation height data sets differ by a factor equal to ratio of the squares of the different G-vector directions along which the corrugations were measured. Typical values for the tunnel barrier height obtained from measurements made along the $\langle 01\bar{1} \rangle$ direction of Cu(100) are in the range 1-2.5eV and are a factor of two larger than the values deduced from $\langle 001 \rangle$ data. These values are somewhat lower than theoretical predictions which suggest the tunnel barrier height should be equal to the surface workfunction [8.15]. This theory strictly applies to larger tip-sample separations ($> 6\text{\AA}$) than have been estimated for this data ($\sim 4\text{-}5\text{\AA}$) using Molecular Dynamics simulations. However, the values deduced here are in good agreement with those obtained from atomically-resolved barrier height data obtained for both metallic [8.12] and semiconductor surfaces [8.11]. A requirement for such high resolution data is a small tip-sample separation and in this region the mean tunnel barrier height is substantially reduced by the exchange and correlation potentials in the tunnel gap.

By using a more complete expression for $\left(\frac{\partial \ln(\Delta)}{\partial \ln(\sigma)}\right)$, which took account of the separation dependent pre-exponential terms in the equations for the

corrugation height and tunnel current, even lower values were deduced for the tunnel barrier height (~ 0.5 -1eV). However, it was still not possible to eliminate the influence of G-vectors when calculating tunnel barrier heights.

Despite this difficulty it has been possible to explain the variation in measured values of $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ as a function tunnel gap conductance using a model adapted from the apparent barrier height theory of Lang [8.16]. There are two main contributions to this tunnel barrier: an electrostatic-dipole layer which is due to the spill-over of the "electron-fluid" a small distance into the tunnel gap and the exchange-correlation potential. The reason for the success of this tunnel barrier model in explaining the experimental findings is that it does not vary so rapidly with increasing tip-sample separation at small tunnel gap widths ($\Delta s < 5\text{\AA}$) compared with the more well known Multiple Image-Potential reduced tunnel barrier.

Clearly the major problem of using $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ to deduce the tunnel barrier height is its *theoretical* dependence upon the surface G-vector. By making a series of approximations, it has been possible to derive a simple approximate relationship between $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ and the tunnel barrier height. This relationship gives a good estimate of the tunnel barrier height when imaging metal surfaces with large inter-atomic spacings ($> 10\text{\AA}$) at moderate tip-surface separations (~ 6 -7 $\text{\AA}$).

From this work, it has been shown that $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ can in principal be used to calculate the tunnel barrier height. However, the models used here to deduce this parameter are rather simplistic and only valid in certain limiting cases. More sophisticated calculations are needed to evaluate both tunnel current and the corrugation height in order to extend the range for which $\left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)}\right)$ can be used to deduce the tunnel barrier height. Calculations of corrugation heights

may be a difficult task as it is necessary to make assumptions about the nature of the tip. However some progress in this direction has already been made by Sautet et al. [8.17] who have calculated the size and shape of adsorbates in STM images as a function of different idealised tip structures. The technique used in these calculations is the Electron Scattering Quantum Chemical (ESQC) method. In such a calculation, the tunnel current is regarded the result of a electron wavefunction scattering phenomenon induced by a defect comprising the surface adsorbate layer, the tunnel gap and the tip apex in an otherwise periodically repeating uniform atomic structure. Thus far only a limited class of systems in which the tip is made of the same material as the substrate have been investigated using ESQC. Although as noted in section 8.2 this may in fact be a realistic description of the experiment! Nevertheless it would be interesting to see the effect of different tip materials in calculations of STM images using this method. One of the attractions of the ESQC method is that it retains a high degree of physical transparency in the results it produces which is unusual in highly sophisticated calculations.

Experimentally, it is very time consuming to deduce values for the tunnel barrier height using this corrugation based method. It would be most useful to develop data analysis software which calculates the mean corrugation height of a topographic image. Because of the problems of tip stability, it is also suggested that the data acquisition software be modified to take a number of images simultaneously. This could be achieved by adopting a "spectroscopic" approach by taking a number of data points using different tunnelling parameters at every pixel in the image. However, the amount of data that can be obtained using such a technique is likely to be limited by thermal drift.

8.4 Corrugation Heights:

Another problem when making quantitative STM measurements has been the inability to take images using the same tunnelling parameters with reproducible values for the corrugation height. This difficulty reflects the uncertain nature of the tip apex. Corrugation heights measured just prior to the on-set of roll-off were investigated in this study. The distribution of these heights is most likely to be the result of an independent variation in both the tip apex chemistry and geometry. This view is in accord with the findings of Berndt et al. [8.18] who were unable to find a reproducible relationship between the corrugation height and the tunnelling resistance when imaging the Cu(111) and Ag(111) surfaces.

From the data obtained in this study, it has been hard to discern a definite relationship between the measured corrugations and the calculated tunnel barrier heights. This is because the large corrugation height data was also taken at smaller values of the tunnel conductance. It is thus difficult to distinguish changes in the tunnel barrier height which are the result of chemical differences and those which are simply caused by imaging the surface at larger tip-sample separations. In preliminary studies of surfaces modified by single halogen-atom adsorbates, where it is thought that a metal atom was present at the tip, small changes in the tunnel barrier height ($\sim 0.2\text{eV}$) have been observed. The variation in the tunnel barrier heights calculated in the clean metal work are larger than such “chemically” induced effects and further work is necessary to determine the different contributions to the tunnel barrier height.

Additional studies are required to clarify the relationship between the tip-chemistry and STM parameters such as corrugation and tunnel barrier heights. More substantial conclusions may be obtained by exploiting some of the

suggestions made in section 8.2. By making in-situ measurements of the corrugation height, it may be possible to make reproducible corrugation height measurements.

A good starting point for investigations of the tip-apex chemistry comes from the observation of Ruan et al. [8.19] that the different species in the (2x1) oxygen-Cu(110) reconstruction are “highlighted” in STM images according to the nature of the tip atom. By introducing very small exposures ($\sim 0.05L$) of oxygen into the vacuum system, a non-metallic terminated tip could be deliberately created. After taking some data with this tip, it could then be “cleaned” by field-desorption i.e. ramping the tip up to 5-10V for 1 milli-second and a second data set taken using a metal tip.

8.5 Tip-Surface Interactions:

At large values of the tunnel conductance, $\sim 1\mu S$, a typical $\ln(\Delta):\ln(\sigma)$ plot no longer exhibits linear behaviour and shows a roll-off. In other words, the corrugation heights do not increase by as much as would be expected based upon a linear extrapolation of the data taken at smaller values of the tunnel conductance. This is taken as a signature of significant tip-sample interaction. In this Thesis, the roll-off phenomenon has been modelled using a Molecular Dynamics (MD) simulation of a pyramid-shaped Cu(100) oriented tip approaching a Cu(100) surface. It has been argued that at small tip-sample separations, the tip apex is subject to short-range interactions which cause the tip to strain towards the surface. The change in length of the z-piezo element is no longer equal to the true change in tip-sample separation. The surface site-dependence of this effect leads to an apparently reduced value for the corrugation height.

Additional tip-displacements towards the surface have been found to be upto $0.5\text{\AA}$, however, corrugation height reductions are somewhat smaller than this ($\sim <0.2\text{\AA}$) because corrugation is a site-difference measurement. The MD simulations have been used to obtain a good estimate of the tip-sample separation. This is an important result and represents a major contribution to the STM community; the tip-sample separation is a parameter that has not been successfully measured before. The data obtained here indicates that the corrugation roll-off data was taken at separations $\sim 3.5\text{-}4.5\text{\AA}$.

No account was made in the MD simulations of electronic-structure perturbations as a source of the corrugation height roll-off. The tip-sample separations for which the mechanically-induced roll-offs are predicted to begin are $\sim 1\text{\AA}$ larger than those calculated by Doyen [8.20] ($s < 3.7\text{\AA}$) for electronic-structure based corrugation reductions. It is thus conjectured that the mechanical-mechanism proposed in this Thesis is dominant in causing the corrugation height roll-off although electronic effects may be important at very small tip-sample separations.

At a separation $\sim 2.9\text{\AA}$, Doyen [8.20] predicted a corrugation reversal in the topographic image. This effect is not found by the MD simulations and the loss in resolution observed at very high values of the tunnel conductance is interpreted here as the result of a tip jump to point contact with the surface.

Numerical values for the compliance of the tip-apex atom with respect to the remainder of the bulk tip vary by about 2 Nm^{-1} between on-top and bridge sites and a further 2 Nm^{-1} between the bridge and hollow sites. Absolute values for the compliance are reduced by almost exactly one order of magnitude compared with the bulk value (213 Nm^{-1}) obtained from the Debye frequency of

copper. An important conclusion from this study, worthy of further investigation is that atomic-scale resolution non-contact Atomic Force Microscopy may be possible based upon a constant compliance measurement.

With the uncertainty of the nature of the tip-apex discussed earlier in this Chapter, additional work is required to investigate the corrugation roll-off effect. Different apex species may change significantly the point at which the roll-off begins. This will in turn alter the site-dependent compliance of the tip-apex atom and may suitably suggest systems for which to investigate atomic-scale resolution imaging using non-contact Atomic Force Microscopy.

The forces calculated in the MD simulation are quite large ($\sim 0.1\text{-}0.5\text{ nN}$) and comparable to those deduced by Dürig [8.7] in STM studies of metallic adhesion. By imaging a hexagonal close-packed metal with a large $\frac{c}{a}$ stacking ratio such as Ruthenium, it may be possible to exploit these forces and image the surface using the shearing mechanism first suggested by Pethica [8.21] in the case of graphite.

8.6 Halogen Adsorbate Studies:

Some preliminary STM investigations have been performed on a Cu(100) surface which had been modified by the co-adsorption of small numbers of halogen (bromine and chlorine) atoms. Surprisingly, the binding site of these species on the Cu(100) surface was found to be directly above a surface atom, rather than the expected four-fold hollow site. This odd behaviour appears to be a property of the Cu(100) surface as the halogens were found in the expected three-fold hollow sites of the Cu(111) surface. Unfortunately in this work it was not possible to uniquely identify the two different chemical adsorbates.

However by following the methods outlined earlier, it was possible to use the measured corrugation heights to deduce the change in local tunnel barrier height over these species.

Two different types of adsorbate were seen in these studies - depression shaped features of depth $\sim 0.5\text{\AA}$ below the mean corrugation of the metal surface and protrusion shaped adsorbates of height $\sim 0.6\text{\AA}$. These species were never seen together in the same image and so are regarded as an indication of the tip-chemistry. A protrusion shaped adsorbate is thought to indicate the presence of a halogen atom at the tip apex, while a depression in the image corresponds to a metal atom terminated tip.

Both adsorbate species caused a local increase in the tunnel barrier height. A substantially larger increase in the tunnel barrier height was found above protrusions ($\sim 2\text{eV}$) than over depressions ($\sim 0.2\text{eV}$). Adsorbate-induced modifications to the tunnel barrier have been explained by including the effects of surface dipoles and adsorbate topography in the expression for the local mean tunnel barrier height. While a surface dipole due to an electronegative adsorbate increases the local tunnel barrier height, the topographic effect may act to increase or decrease the local barrier height according to whether the adsorbate is seen as a protrusion or depression in the image. When depression shaped features were observed in the STM images, only a small increase in the tunnel barrier height was measured implying that the dipole and topographic effects are of a similar magnitude.

From a consideration of the halogen data as a whole, adsorbate topography was estimated to contribute $\sim \pm 0.5\text{eV}$ to the local tunnel barrier height, while a surface dipole was estimated to contribute $\sim +0.7\text{eV}$. Values for the charge transfer between the metal surface and the adsorbate were calculated to be $\sim$

0.11-0.14 electrons, which are close to values obtained using other surface science techniques. It is suggested that the value for the charge transfer could be used in future work as a means to distinguish between different surface adsorbates. The relative importance of effects such as topography and surface dipoles on the tunnel barrier height could be investigated further by studying the tip conditions necessary to simultaneously image these halogen atoms as both protrusions and depressions.

By imaging the surface at high values of the tunnel conductance $\sim 0.5\mu\text{S}$, it was possible to move both types of adsorbate over the surface using the tip. The mechanism for this manipulation is uncertain at present, although the initial evidence from this work is that it is due to a tip-surface mechanical interaction with the tip literally sweeping the adsorbate over the surface as it takes an image. However further study at both an experimental and theoretical level is needed to clarify this point and to see whether both types of adsorbate use the same mechanism. It is speculated that electrostatic based forces and hence the potential bias used when taking an image are likely to be important factors.

This halogen work was based upon Cu(100) which is a highly symmetric surface. In further investigations, it would be interesting to compare the imaging conditions required to move adsorbates along different directions of anisotropic surfaces such as Cu(110).

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Appendix A:

Note to the reader. Appendix A is a reprint of a paper submitted to the journal Physical Review Letters in July, 1995. Minor modifications were made to this paper in November, 1995 when it was accepted for publication. The intention of including it is to give the interesting reader a quick summary of the work undertaken in this Thesis, but in more detail than is possible in the abstract which can be found at the front of this Thesis.

Quantitative STM at Atomic Resolution: Influence of Forces and Tip Configuration.

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ABSTRACT: Atom resolved STM images are known to depend on the nature of the tip and its interaction with the surface. In this paper, we present a new method for determining barrier height and tip-surface interactions. For Cu(100) images, two distinct tip types are seen. At larger tunnel currents there is evidence for forces acting between tip and surface. We show that a molecular dynamics simulation of tip and surface is able to quantitatively explain the results, and gives a good estimate of both absolute tip-surface separation and the site dependent forces on individual atoms.

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The remarkable capabilities of STM and related techniques to image and manipulate atoms are well known [1, 2]. The understanding of individual experiments is, however, surprisingly undeveloped. The model of Tersoff and Hamann [3] gives a general picture of STM operation based on topography and local densities of states at the surface. More complex calculations [4] give some insight into the position of adsorbates, and possible tip structures. Quantitative modelling of specific images, however, relies on parameters which are not easily determined in experiment. For example, the tip radius and its actual separation from the surface are not directly known. The chemical nature of the tip significantly affects images, [5, 6] and may even reverse the contrast, yet it is in practice unidentified. Furthermore, forces between tip and surface can play a significant role in STM imaging [7, 8] as well as in their more obvious role in AFM and in deliberate movement of atoms [9, 10]. For quantitative understanding of STM and its applications there is thus considerable interest in experiments which cast light on these phenomena.

An important parameter in STM imaging is the tunnel barrier, or the decay length, κ , normal to the surface. This is experimentally accessible from the variation of tunnel current with tip-surface separation. In practice, accurate measurement of the barrier, particularly at specific atom sites, is quite difficult. Measurements which avoid the displacement compensating effects of the STM feedback loop work either at relatively low speeds, where drift can be a problem, or at high modulation rates where calibration of the actual piezo displacement can be difficult. In this paper we demonstrate a method which minimises calibration uncertainties, and uses the imaging mode, for which the STM is by design most accurately calibrated. We measure the variation of image corrugation height with tip surface separation. Our results provide evidence for two distinct types of tip behaviour, likely related to composition. A decrease in corrugation height is observed at higher tunnel currents. We show this can be quantitatively modelled by tip-surface interaction forces, and allows an estimate of true tip-surface separation.

The peak to trough height, Δ , of STM image corrugations at larger tip-surface separations s , is given [3] by the expression:

$$\Delta \propto \exp(-\beta s) \quad (\text{A.1})$$

where $\beta = 2(\kappa^2 + 0.25G^2)^{1/2} - 2\kappa$, with $\kappa = \frac{2\pi(2m_e\Phi)^{1/2}}{h}$ where Φ is the mean tunnel barrier height, and $G = \frac{2\pi}{a}$ is the surface reciprocal lattice vector along the direction of interest. Now the variation of tunnel gap conductance s with separation, is dominated by κ , [11] and is given by

$$\sigma \propto \exp(-2\kappa s) \quad (\text{A.2})$$

If the prefactors in equations (A.1) and (A.2) are treated as constants, it is easy to show that the corrugation deduced barrier height is given by:

$$\Phi_{M, \text{Corrugation}} = \frac{\hbar^2 G^2}{8m_e X} \quad (\text{A.3})$$

$$\text{where } X = \left(\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} \right) \left[\frac{\partial \text{Ln}(\Delta)}{\partial \text{Ln}(\sigma)} + 2 \right]$$

Thus the slope in a plot of $\text{Ln}(\Delta)$ vs. $\text{Ln}(\sigma)$ gives a direct measure of Φ . A full analysis allowing for the prefactors in (A.1) and (A.2) makes the expression more complex but does not significantly affect the quantitative conclusions. Note that by choosing different surface G -vectors, independent measurements of Φ are possible from the same set of images, and by comparing different G directions, insight is gained into the symmetry of tip geometry.

The experiments were performed using a UHV compatible fast scanning STM which has been described elsewhere [12]. All the STM images were recorded using the constant current mode of operation. The tip was a tungsten single crystal oriented along [100]. Despite exhibiting smaller corrugations, a metal surface was chosen for this study in preference to a semiconductor. The high density of states and its relatively weak variation with voltage minimise the effects of electronic structure on variations in corrugations in the image. Interpretation and modelling is thus more straightforward for metals. A Cu(100) crystal was prepared using sputtering cycles with neon ion bombardment (3kV, 5 μ A) followed by annealing the crystal to 530°C. Imaging conditions were in the ranges $I = 1\text{-}20\text{ nA}$ and $V = \pm 3\text{-}20\text{ mV}$. Allowance was made for the 120k Ω input resistance of the tunnel current amplifier [13]. A typical STM image is shown in **Figure A.1** overleaf.

A key ingredient in our method is that the tip must not change while a set of images is obtained. That the tip remains the same is, however, easily checked, by returning to the current used in the first image and ensuring both corrugation height and image features remain same. Only data sets are accepted where this lack of tip change within the set was carefully confirmed. An interesting general observation is that the corrugation heights were repeatable and reliable within a given data set, but the actual corrugation heights between different data sets varied considerably. For example, typical experimental values for corrugations measured along $\langle 0\bar{1}1 \rangle$ were in the range 0.05-0.2Å. This variability due to differing tips between data sets does not invalidate our analysis, because only the relative variation of the corrugation heights within a single data set is important. A histogram of corrugation heights across different data sets showed two peaks. This suggests that in our experiments there are two generally stable types of tip.

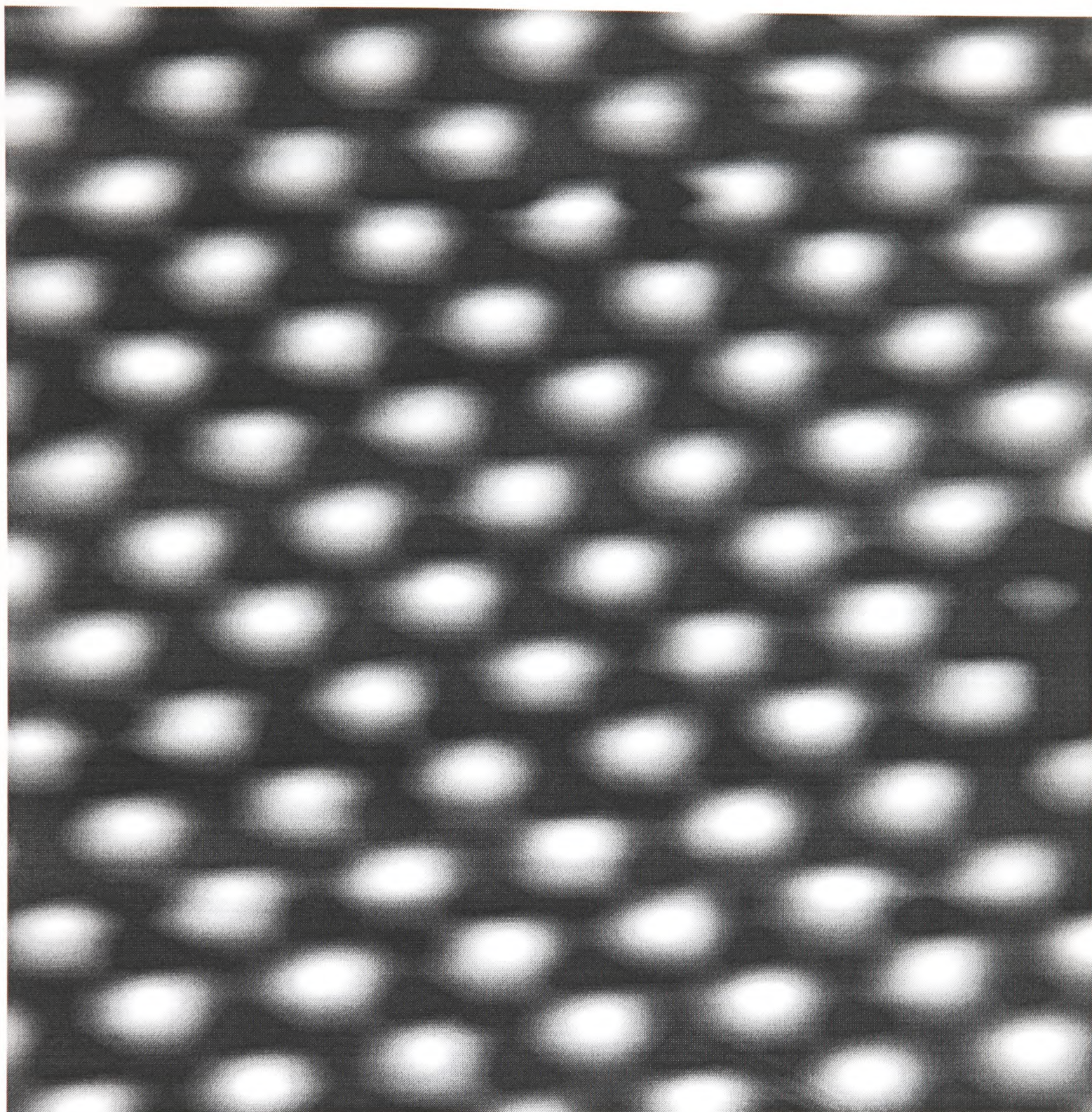


Figure A.1: A $23\text{\AA} \times 23\text{\AA}$ image of Cu(100), taken at 12.5nA and 28mV. The defect shows the tip is sharp.

Eighteen data sets, taken over a period of several weeks, were analysed in detail. Within each data set the voltage was fixed and the current varied. The individual data points had small standard deviations (<10% of their measured mean value). **Figure A.2** overleaf shows the results from two sets for corrugations measured along $\langle 0\bar{1}1 \rangle$. First there is a linear region at lower values of tunnel current. This can be used to deduce the barrier height in the tunnel gap from the model described above. There is also a "roll off" region at

high tunnel conductance (i.e. at smaller tip sample separations), typically characterised by a tunnel gap resistance of 0.5-3M Ω , where the corrugation height does not increase so much with current, and eventually actually falls with increasing current. This is a clear departure from the Tersoff and Hamman model and a signature of tip-surface interaction. Doyen et al. [14] have observed a similar corrugation roll off in experiments on the clean Au(110) missing row structure. By drawing a best fit line through the linear regime of the data sets in **figure A.2** and substituting the gradient in equation (A.3), the value of the apparent barrier height is found to be 2.05 $\pm$ 0.1eV in the case of the upper data set and 1.9 $\pm$ 0.2eV for the lower set. These values are typical of the data as a whole, which exhibited a range between 1.6 and 2.6eV with a preponderance of values around 2eV. The barriers are thus comparable with those obtained by other methods where the STM is giving atomic resolution [15].

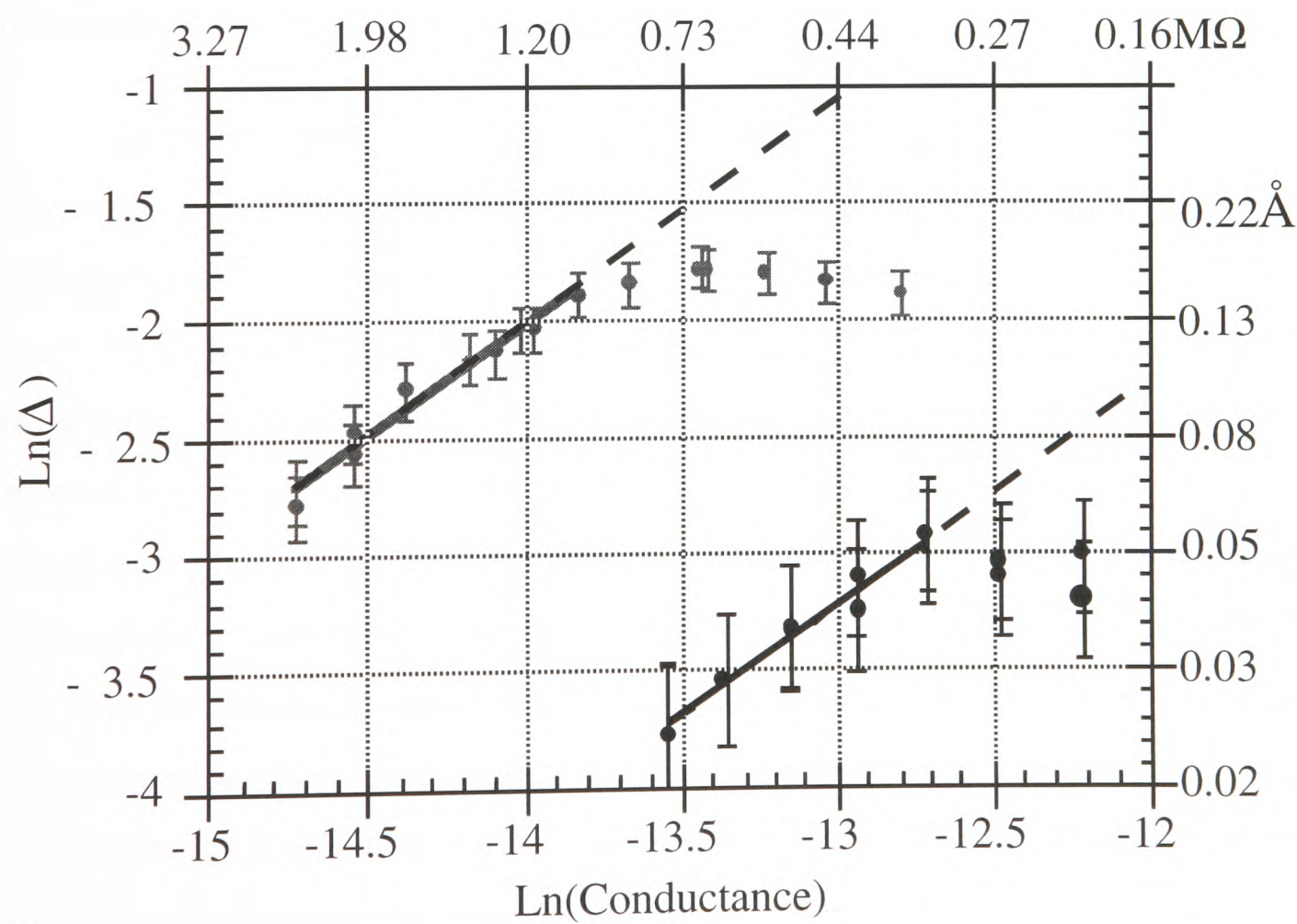


Figure A.2: $\text{Ln}(\Delta):\text{Ln}(\sigma)$ plots illustrating the two general types of tip obtained in this work. Tunnel Voltage 3mV for upper plot and 4mV for lower.

The first implication of these results is that we have two types of tip capable of taking high resolution images. McIntyre et al. [16] have noted that the corrugation measured for the sulphur ($\sqrt{3} \times \sqrt{3}$)R30° overlayer on Pt(111) dramatically increases upon indenting the tip into the surface and (probably) transferring a sulphur atom onto the tip apex. Our higher corrugation data might thus be associated with a non-metal atom adsorbed at the tip apex, while the lower corrugation height data might be due to a metallic atom adsorbed at the tip. Ruan et al. [6] have also shown that by varying the chemical species between a metallic and a non-metallic atom at the apex the image contrast is strongly affected. Surprisingly, however, there was no obvious correlation between the variation of barrier between different data sets and the variation of corrugation heights. If there is a different chemical species at the tip for the two broadly different groups as suggested above, then it does not obviously affect the tunnel barrier. We conclude therefore that difference of tip geometry, (that is, of effective tip radius) rather than chemical composition is more likely to be the cause of the two groups of corrugation height.

From the "roll-off" region of the data in **figure A.2** at higher tunnel currents, it is clear that additional interactions have a role to play in the formation of STM images. The key to understanding their effect is that when forces start to act, the relative movement of the tip apex and surface atoms is no longer the same as that of more distant parts of tip and sample where the displacements are measured experimentally [7]. Ciraci et al. [17], showed how forces can give rise to reduced image corrugation. To evaluate these concepts in modelling experiment we have made a molecular dynamics calculation of the relative displacements for a Cu tip and surface. Full details of the method are given elsewhere [18]. In this simulation, there are 676 atoms in the tip, and 768 in the surface. The surface normal is (100) and the tip has the same alignment. Sutton-Chen potentials [19] are used for the interatomic forces. **Figure A.3** overleaf shows the actual displacement of tip apex atom above the plane of the surface topmost atoms, versus relative displacement of points far

from the tunnel zone. Curves are shown for two lateral positions of the apex atom, one over the 4-fold hollow site, the other 'on top' of a surface atom.

At large separations, the forces are small, so the two displacements are virtually the same, as expected. At smaller separations, the far field displacement becomes less than the actual tip atom motion, since the tip atom is attracted towards the surface. The measured image corrugation will therefore fall below the true corrugation motion of the tip atom, which is the roll-off which we observe in the experiments. The fall-off in corrugation may be calculated from the MD data. A given tip atom corrugation in the $\langle 010 \rangle$ direction, for example, is converted to measured corrugation by finding the far field displacement for the hollow site at corrugation minima (closest approach to surface), and for the on-top site at maxima. See the graphical construction on **figure A.3**. Similarly, the bridge site and on-top site results are used for the $\langle 0\bar{1}1 \rangle$ direction data.

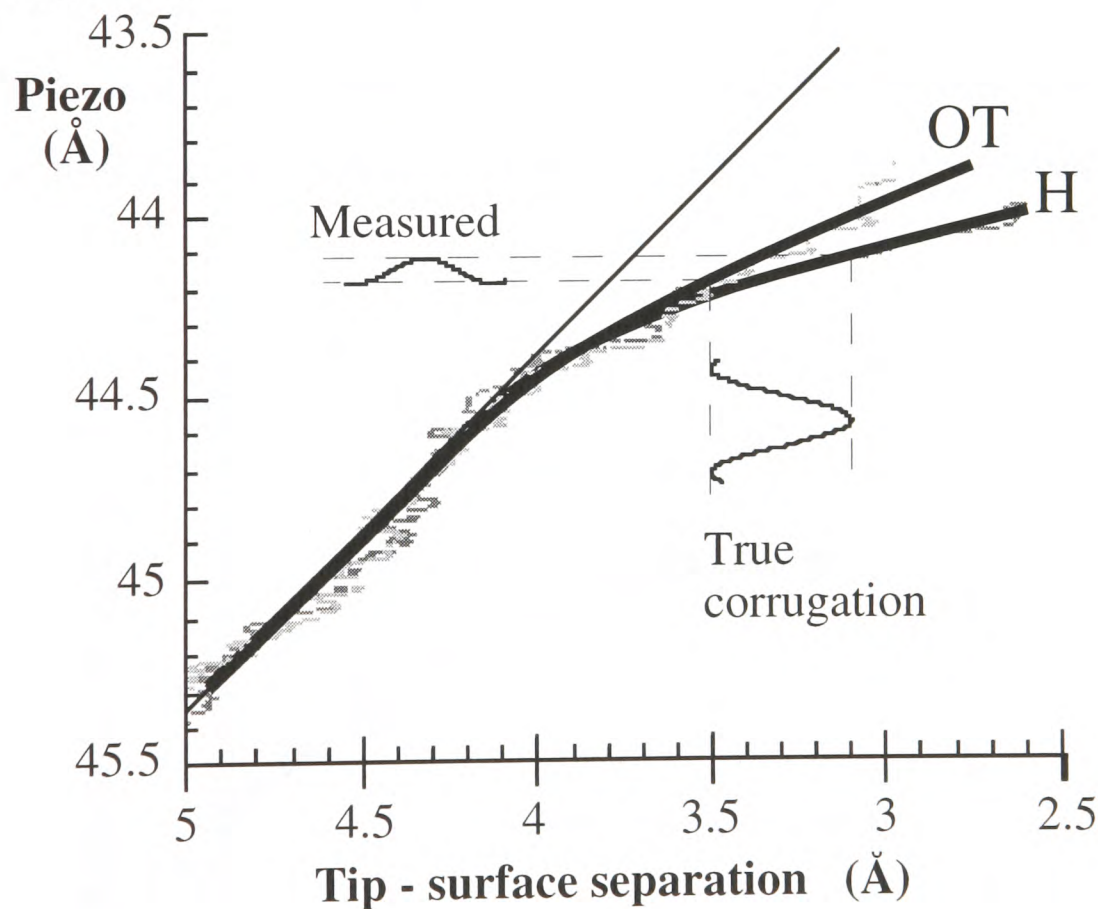


Figure A.3: Molecular dynamics calculation of displacement of tip atom above surface atom plane relative to that of points further away from tip. OT is tip above a surface atom (on top) and H is above a 4-fold hollow in the Cu(100) surface. Bridge sites show an intermediate behaviour.

To make the comparison with experiment, it is necessary to relate current changes to displacements. *Changes* in displacements are easily calculated from equation (A.2) using the experimental value of the barrier height. Thus the true (tip atom) corrugations are obtained from the straight line section of **figure A.2** and its extrapolation to smaller separations. However, use of equation (A.2) to determine *absolute* separation is far too dubious a procedure. Even if the tip geometry and composition were known, calculation of actual tunnel currents is problematic. Therefore we reverse the argument – absolute separation is set by a simple shift of the separation to give a best fit between the MD prediction of roll-off and experiment. In other words, we determine the absolute separation of tip and surface atom avoiding use of the absolute value of the tunnel current. Note this does not mean there is any arbitrariness in the separation axis scale. The agreement of model and experiment is seen to be good, (see **figure A.4** below) and gives a remarkably sensitive determination of separation which avoids the serious uncertainties involved in making full physical tip contact (crash) to determine zero of separation.

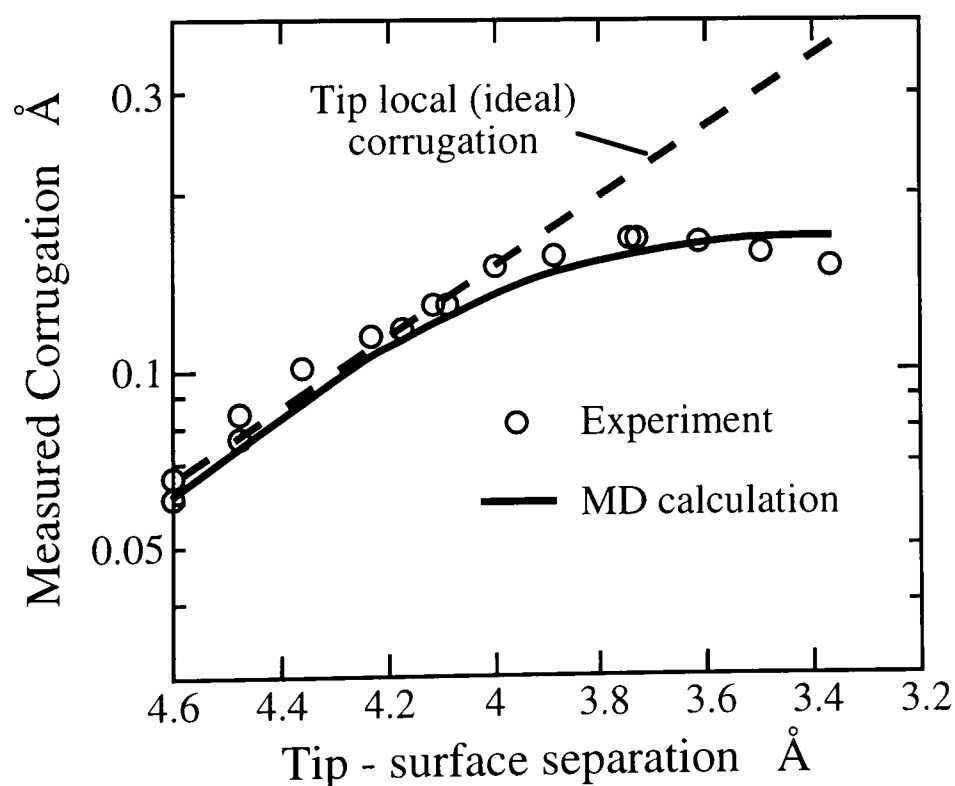


Figure A.4: Comparison of experimental roll-off in corrugation (top data of **Figure A.2**) with that deduced from the Molecular Dynamics calculations.

The calculations show that the force between the tip and the sample is around 1 nN at a separation of $3.5\text{\AA}$, in good agreement with the measurements of Dürig et al. [20]. It varies by roughly 6% between hollow and on-top sites. Also at this separation the measurable stiffness varies by roughly 1N/m between the sites, which suggests that atomic resolution AFM based on compliance measurement is possible. However, the absolute separations are very small, and rather close to instability. Finally we note that use in the simulation of different chemical species at the tip apex will give other force constants, and may provide a means of characterising the bond and surface interaction; the technique presented here is in a sense a combination of STM and AFM.

We have, of course, ignored the possibility of significant change in density of states (DOS) near to the Fermi level, as the tip and surface start to interact. Doyen et al. [14] suggested this was the cause of the roll-off in corrugations they observed. However, we note that the force mechanism we propose acts at almost $1\text{\AA}$ greater separation than the DOS changes found by Doyen et al, and so should be a dominant effect. It is also a universal mechanism which occurs for all tip species. Furthermore, the required substantial changes in DOS due to the proximity of the tip might not easily occur for many metal crystal faces.

In summary, we have shown that a straightforward measurement of corrugation height variation with tunnel current can give significant insight into imaging mechanisms. For our experiments on Cu(100) we observe two types of tip, most likely due to different tip atom geometric arrangement. We also show that image corrugations fall off at small tunnel resistances, and that this may be quantitatively explained by forces acting between tip and surface. In particular we can estimate true tip surface separation, and the force

variation between sites. The new measurement technique provides a method of assessing forces before they induce actual motion of atoms at surfaces, and could therefore provide insight into the critical early stages of atomic manipulation.

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Appendix B:

To Show That the Barrier Height Should be Independent of k parallel:

A large part of this thesis has been concerned with the fact that the measured value for the barrier height appears to depend upon the crystallographic direction in the STM image that is selected to measure the corrugation heights. This cannot be correct as the following analysis shows. I have enclosed this proof because I cannot find it in any standard physics text book.

Consider an electron at the Fermi level, E_F of a free-electron metal whose wavefunction is incident upon a potential barrier, height, Φ , at some general angle, θ (**figure B.1**).

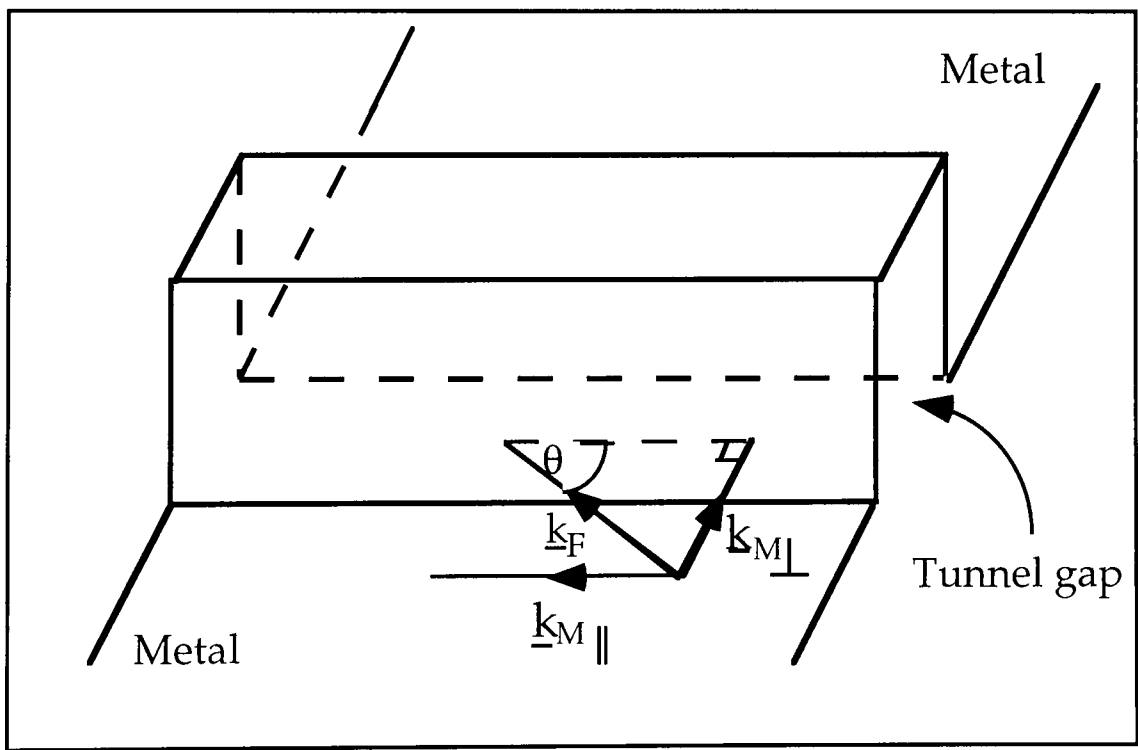


Figure B.1: A schematic diagram showing an electron wavefunction incident upon a tunnel barrier at an angle, θ .

Using the principal of Conservation of Energy, we have:

$$E = T + V \tag{B.1}$$

where E is the total energy, T is the Kinetic Energy and V is the potential energy.

Inside the metal $V = 0$ and so at the Fermi level:

$$E = T_{\text{METAL}} = E_F \quad (\text{B.2})$$

In the elastic tunnel process, the total energy and the momentum parallel to the tunnel barrier are conserved and using the principle of conservation of energy again in the tunnel barrier leads to:

$$E_F = T + (E_F + \Phi) \quad (\text{B.3})$$

$$T_{\text{BARRIER}} = -\Phi \quad (\text{B.4})$$

Equation (B.2) can be written in term of the electron's momentum parallel, $k_{||}$, and perpendicular, $k_{\perp}$, to the tunnel barrier:

$$T_{\text{METAL}} = \frac{\hbar^2}{2m_e} (k_{M\perp}^2 + k_{||}^2) = E_F \quad (\text{B.5})$$

Similarly equation (B.4) can be formulated in terms of parallel and perpendicular momentum components:

$$T_{\text{BARRIER}} = \frac{\hbar^2}{2m_e} (k_{B\perp}^2 + k_{||}^2) = -\Phi \quad (\text{B.6})$$

By equating the parallel momentum terms of (B.5) and (B.6):

$$k_F^2 - k_{M\perp}^2 = -k_{B\perp}^2 \quad (\text{B.7})$$

$$\text{and hence } \Phi = \frac{\hbar^2}{2m_e} (k_{M\perp}^2 - k_{B\perp}^2 - k_F^2) \quad (\text{B.8})$$

Equation (B.8) shows that the barrier height, Φ , only depends upon momentum components which are *perpendicular* to the surface.

