Studies of adsorption and reaction on the stepped Pt\{211\} surface

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Thesis for the degree of Doctor of Philosophy

University College London
University of London

Ph.D.
2003
Abstract

The aim of the experiments presented in this thesis is to study the interaction of molecules on well defined stepped metal surfaces at various temperatures. To perform these experiments, an ultra high vacuum (UHV) system with an operating base pressure of below $2 \times 10^{-10}$ mbar has been constructed. The UHV system is equipped with infrared optics to perform reflection absorption infrared spectroscopy (RAIRS), a quadrupole mass spectrometer for temperature programmed desorption (TPD), and electron optics for low energy electron diffraction (LEED) experiments. To allow experiments to be performed at various temperatures, a liquid helium cooled cryostat and a resistive heating mechanism were also incorporated into the system. This apparatus has been used to undertake an extensive study of the adsorption and reactions of various molecules on the Pt\{211\} surface.

The initial system that was studied was the adsorption of CO on the Pt\{211\} surface over a range of temperatures. This adsorption system has been investigated previously and the results obtained here are in good agreement with earlier studies. However, the experiments described in this thesis also reveal additional experimental detail, not previously observed. Experiments were also performed to investigate NO adsorption on Pt\{211\} at 120 K and 300 K using both RAIRS and TPD. This adsorption system was found to be strongly temperature dependent and several different species were observed on the surface as a function of both temperature and exposure. A combination of experimental results and theoretical calculations, performed by Z-P Liu and P Hu of Queen’s University Belfast, has allowed this complicated adsorption system to be understood for the first time. The final system that was studied was the co-adsorption of O and NO on the Pt\{211\} surface. The results show that only a moderate exposure of O has a large effect on the adsorption of NO on Pt\{211\}, inhibiting the formation of N$_2$ and N$_2$O as revealed in TPD experiments.
Acknowledgements
I would like to express my thanks to the following people:

Dr. Wendy Brown for providing excellent supervision and support throughout my doctorate, having faith in me as her first Ph.D. student, and not least her infinite patience while I was writing this thesis.

My Family for giving me the peace and quiet I needed whilst writing up this thesis.

Zoe Baillie, Alastair Grant, Ronit Grant, Abigail Jones, Ashvin Mathoora and Karine Rousseau, my closest friends.

The members of the chemical physics group, both past and present, especially Amandeep Bolina, Gavin Boakes, Susan Creighan, Sarah Dixon, Kate Gawler, Dr. Jon Gingell, Sarah Harper, Dominic Kearney, Natalie Lambert, Natalie Love, Emma O'Grady, Dr. James Perry and Dr. Nurun Tafadar.

The MAPS faculty workshops especially Roy Northeast, the man who could make the impossible and decipher my drawings without the aid of the Rosetta stone, and John Dumper, the man who can fix anything.

The staff and my fellow wardens of the Ifor Evans halls: Dr. Dorothy Einon, Damien Forrest, Rupert Green, Priya Kalia, Dr. Li Li, Ian Moran, Kathryn Piquette, Dr. Ruth Siddall, Hugh Taylor, Joe Warner and Darren Watts.
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Chapter 1: Introduction

Steps, kinks and defects at surfaces play an important role in the kinetics of surface processes such as adsorption, desorption and the reaction of molecules \(^{[1-4]}\). As a result, a fundamental knowledge of the behaviour of molecules in the proximity of these surface structures is crucial in understanding chemisorption processes on catalytically active materials. Platinum is one such active material, as it is an important ingredient in automotive catalysts, especially for the catalytic oxidation of CO and the reduction of NO\(_x\). This realisation has stimulated a great deal of interest in the surface science of the interaction of these molecules with Pt surfaces. These systems are also interesting from a fundamental point of view, as to understand the nature of the chemical bond between a molecule and a surface, and the adsorption process itself, a detailed knowledge of the interaction of molecules with solid surfaces is needed.

The aim of the experiments presented in this thesis is to study the interaction of molecules on a well-defined stepped Pt surface at various temperatures to try to elucidate the role of steps in adsorption and reaction processes. RAIRS and TPD experiments to investigate the adsorption of CO, NO and NO and O on Pt\{211\} were performed during the course of the work presented in this thesis.

Experiments investigating the adsorption of CO on Pt\{211\} were performed initially to help to test and commission the apparatus that was built during the course of this doctorate. The adsorption of CO on Pt\{211\} had been previously investigated \(^{[5]}\) and hence this system was a good one to use as a test for the equipment. The experiments showed that the apparatus worked well and also allowed a higher level of detail than had previously been observed to be obtained with RAIRS.

Further experiments were performed on the NO on Pt\{211\} system. There is a wealth of information present in the literature for the study of NO on flat Pt surfaces \(^{[6]}\). This system is interesting to study from both a fundamental point of view, as well as from the industrial perspective, due to its importance in the automotive industry. However there
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still remains a large gap in the literature for the study of NO on higher index surfaces. Therefore, experiments were performed to investigate NO adsorption on Pt\{211\} at 120 K and 300 K using both RAIRS and TPD techniques. These experiments revealed novel observations that have not previously been documented in the literature, and the existence of both molecular and dissociated NO species on the surface.

To further the study of the interaction of NO on Pt\{211\}, and due to observations that were made during the NO/Pt\{211\} study, further experiments were performed to investigate the co-adsorption of O and NO on the Pt\{211\} surface. These experiments revealed interesting observations, supporting the previous assignments made in the clean surface experiments as well as revealing the sensitivity of NO adsorption on Pt\{211\} to the presence of pre-dosed O atoms.

A detailed description of the observations made for these three systems, and a discussion of the results, is presented in Chapters 4, 5 and 6. A detailed description of the ultra high vacuum (UHV) system that was constructed during the course of this thesis is given in Chapter 2.

1.1 Why study adsorption of molecules on surfaces?

The study of the adsorption of molecules on solid surfaces has greatly increased since the early 1960's. This is mainly due to the realisation of the importance of the understanding of surface properties and the fact that the information acquired about surfaces has an impact on the understanding of a wide variety of applications. This ranges from nano-fabrication of atoms at surfaces [7-13], tribology, lithography and chemical vapour deposition to the study of astronomical events and the formation of molecules in the interstellar medium [14-28]. Also, at the fundamental level, surfaces are important as they represent a special kind of defect in the solid state. Much of the understanding of solids is based on the fact that they are, essentially, perfectly periodic in three dimensions. The electronic and vibrational properties of a solid can be described in great detail using methods that rely on this periodicity. Surfaces are composed of atoms which do not have a full complement of neighbours. Hence, the
introduction of a surface breaks this special periodicity in one direction. As a result, this leads to structural changes as well as to the introduction of localised electronic and vibrational states. As the bonding of the surface is unbalanced, surface atoms will always want to react in some way to minimise the surface free energy. This can be achieved by the movement of other surface atoms to minimise the surface free energy or by the adsorption of atoms and molecules. The binding, or adsorption, of gases is strongly favoured at the surface. Adsorption at a surface can result either from the formation of a chemical bond, resulting in the transfer or sharing of electrons between the surface and the adsorbate (chemisorption), or from a weak, van der Waals type, interaction (physisorption). The different types of bonding are usually easily differentiated from each other by the enthalpy of adsorption, with that for chemisorption being much greater than that for physisorption. Once the molecule is adsorbed, the surface may enable the adsorbate to undergo reaction.

1.2 Stepped and vicinal surfaces
The chemical and physical properties of a surface depend upon its electronic structure. This in turn relies on the nature and distribution of the atoms that form the surface. The nature of the atoms arises due to the individual element(s) that make up the surface and the distribution of the atoms is due to the surface structure.

Surfaces consist of flat regions known as terraces and so-called defects such as steps, kinks and point defects. This can be seen in Figure 1.1. Flat surfaces consist of a single terrace, for example the \{001\} surface (\{001\} represents \{hkl\} in Miller index notation). Examples of point defects are adatoms or terrace vacancies, but surfaces can also be intentionally stepped or have kinks in them. This can easily be achieved by cleaving a crystal along the appropriate crystallographic plane. Figure 1.2 shows the stereographic triangle for the various crystal orientations of an fcc crystal. The \{111\}, \{100\} and \{110\} planes are the high symmetry, high density, planes of an fcc metal, while the \{210\} and \{211\} surfaces have a more open surface structure and possess geometric sites of two of the high symmetry planes.
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Figure 1.1: Model of a solid surface depicting different surface sites

Figure 1.2: Stereographic triangle for the various crystal orientations of an fcc crystal

The study of adsorption on stepped single crystals provides information about the role of site character on the adsorbate bonding. It also introduces a regular, known, defect onto the surface of the crystal, away from the flat terraces, which have been extensively studied. The introduction of steps onto a flat surface may be described as the simplest form of surface nanostructuring. The stepped surface allows deviation away from the perfect flat crystal, and ultimately allows us to understand the effects of defect sites within a real surface, which is composed of many of the surface defects described in Figure 1.1. However, care must be taken when looking at stepped surfaces as being composed of the component low index surfaces, as they may show unique adsorption characteristics. This can be seen clearly for the studies of the adsorption of NO and NO and O on the Pt{211} surface as described in Chapters 5 and 6. These results show that
the most stable adsorption site for NO on the Pt\{211\} surface is a step-bridged site. No NO adsorption species are seen at room temperature on the terrace. This is due to the presence of N atoms, from dissociated NO, on the terrace. However, when NO is adsorbed on Pt\{111\}, no dissociation occurs and the most stable adsorption site is a bridged species on the flat \{111\} terrace\[31\]. From these observations it is clear that adsorption on stepped surfaces is more complicated than that on flat surfaces and stepped surfaces should not just be considered as a composition of the low index surfaces from which they are composed.

There are two important effects that occur due to the introduction of steps on a surface. These are:

- Adsorbates exhibit a higher binding energy at step sites.
- There is a change in the electronic properties of the surface due to the step sites.

Since the concept of localized adsorption to particular sites on a surface, developed by Langmuir\[32\], the study of adsorption on these sites has been the subject of many investigations. It was originally proposed by Taylor\[33\], that metal atoms which have a low coordination number to other metal atoms on the surface significantly enhance the activity of a site. The observation of higher binding energy at stepped surfaces compared to flat surfaces can easily be seen for the adsorption of small molecules on a stepped Pt surface. For example, it has been shown using single-crystal adsorption calorimetry (SCAC) that the binding energy for CO on Pt\{211\} is larger at step sites than terrace sites\[34\].

When small adsorbates, such as CO, interact with the stepped Pt\{211\} surface, the binding energy at the step sites is always higher than at the terrace sites because the centre of the d-band at the step sites is closer to the Fermi level, thus inducing a stronger interaction with the 2\pi* molecular orbital of CO. This can be seen in Figure 1.3, which shows that the projected density of d-states at the step sites on a \{211\} surface is closer to the Fermi level than that for the \{111\} surface. This is also seen for the adsorption of oxygen on Pt\{211\}\[35\]. However, the charge transfer between the metal and the
adsorbate is more pronounced in the case of oxygen adsorption. This leads to a stronger Pt-O bond than O-O bond, and therefore O adsorbs atomically at step sites on a Pt surface \cite{36}.

The observations made for the adsorption of CO and O\textsubscript{2} on the stepped Pt\{211\} surface, and the lack of coordination at step sites, implies that the step sites are more reactive than the terrace sites. As a result of this fact, adsorption on stepped surfaces is usually assumed to occur via a sequential process whereby the more reactive step sites are occupied initially and the terrace sites only become occupied once the step sites have been saturated. However, recent theoretical investigations by Hammer and Nørskov \cite{37} have shown that, for the sequential adsorption of NO on Pd\{211\}, adsorption first occurs at the terrace and then at the step. This makes the NO/Pd\{211\} system an exception to the general rule that adsorption at steps is stronger than that at terraces \cite{38-41}. However, it was found that when adsorbate-adsorbate interactions are taken into account this anomaly disappears.

![Figure 1.3: Projected density of states for the Pt\{100\}, Pt\{111\} and Pt\{211\} surfaces]({#image1})

In addition to the stronger adsorption energy of step sites compared with terrace sites, stepped surfaces also have different electronic structures compared to flat surfaces. It was shown by Smoluchowski \cite{43}, that stepped surfaces have an additional type of
heterogeneity compared with flat surfaces, which has a direct result on their properties. The step structure is obviously different from the structure of the terraces. As a result, this causes a disruption in the local electronic structure at the steps, as shown in Figure 1.4. The electrons of the solid react to the presence of the step, by acting to minimise the energy of the defect. This has the effect of causing the electrons to spread out to make the defect less abrupt. This alters the chemical reactivity, thus making the step sites attractive for the adsorption of molecules. The reduction in the work function at the step edge that results from this change in electronic structure is seen to affect the adsorption of CO on Pt{211} (as seen in Chapter 4 and other studies).

![Figure 1.4: A diagram to show the Smoluchowski smoothing that occurs at a step site. The electrons at the step attempt to smooth out the discontinuity between the step and terrace sites of the surface.](image)

### 1.3 The Pt{211} surface

Due to the complex nature of the adsorption of atoms and molecules at surfaces, most previous studies have focused on well-defined flat surfaces such as the {111} and {100} facets. However, real surfaces are composed of many different facets and surface defects such as steps, kinks, vacancies and adatoms. As a first step towards a real surface, such as that used in heterogeneous catalysis, the study of well-defined stepped or vicinal surfaces is a significant movement forward to bridge the knowledge gap. Hence this thesis presents work for the adsorption of NO, CO and O on the stepped Pt{211} surface. A diagram of the Pt{211} surface is shown in Figure 1.5.
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The Pt\{211\} surface is composed of a combination of the lower index facets of the \{111\} and \{100\} surfaces. The surface consists of three atom wide \{111\} terraces, separated by a monoatomic \{100\} step. The surface can also be written as [3\{111\} \times 1\{100\}].

1.4 Adsorption of CO and NO on metal surfaces
The adsorption of CO, NO and NO and O has been studied in this thesis, and the results of these experiments are presented in Chapters 4, 5, and 6 respectively.

1.4.1 Adsorption of CO
Systems involving the study of the adsorption of CO on metal surfaces are among the most widely investigated \[45\]. This is mainly due to its industrial applications and impact on the environment, but it is also useful to study from a fundamental perspective as it bonds to many surfaces, making it a useful tool for studying adsorption processes. This is mainly due to the fact that the bonding of CO on metal surfaces is easily described by the Blyholder model \[46, 47\]. The wealth of information available concerning the adsorption of CO on surfaces makes it a useful subject to be studied here, as the equipment used in the experiments presented in this thesis was used for the
first time. Hence, the initial results obtained for CO adsorption on Pt{211} could be compared with those seen in the literature \cite{5} during the equipment commissioning.

### 1.4.2 Adsorption of NO

The study of the adsorption of NO on metal surfaces is an important topic from an industrial perspective, due to the catalytic reduction of NO\textsubscript{x} to N\textsubscript{2} and O\textsubscript{2} and because NO is a significant product of ammonia oxidation. It is also important from a fundamental scientific viewpoint due to the low NO bond energy \cite{48} (630 kJ mol\textsuperscript{-1}) compared to other similar molecules such as CO \cite{48} (1076 kJ mol\textsuperscript{-1}). This is due to the fact that NO has an unpaired electron in the 2\pi* orbital, hence it can either accept an electron, to fill the partially filled 2\pi* orbital, or donate an electron from this orbital. Therefore there is a high probability of finding both molecular and dissociated NO species on the surface. As a result NO shows a tendency to undergo reactions at the surface, forming species such as N\textsubscript{2}, N\textsubscript{2}O, NO\textsubscript{2} and (NO)\textsubscript{2}. The rate and probability of these reactions also relies on the surface temperature, as some species such as (NO)\textsubscript{2} \cite{49} are only observed at very low temperatures.

The possibility of NO reacting also relies on the nature of the surface. It was proposed by Rhodin \textit{et al} \cite{50} that the susceptibility of NO to dissociation varies across the periodic table. This is shown in Figure 1.6. From this Figure it can be seen that NO should not dissociate on a Pt surface. However, the probability of NO dissociating on a surface also relies on the structure of the surface. As previously stated, experiments presented in this thesis describe the adsorption of NO on a Pt{211} surface. There is currently a disagreement in the literature for this system, as previous studies on this surface and similar surfaces show that NO does not dissociate at room temperature, and dissociation only occurs on heating \cite{51}. However, Banholzer \textit{et al} \cite{52} have predicted that, due to the open structure of the Pt{211} surface, and the presence of the steps, there is a break in the symmetry of the surface allowing it to interact strongly with NO causing dissociation at room temperature. From this interpretation, and observations that were made and presented in Chapter 5, experiments to investigate the adsorption of
NO on an O pre-dosed Pt\{211\} surface were also performed, to elucidate the role of O atoms in NO adsorption, and to observe the effects of NO adsorption on this system.

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
</tr>
</tbody>
</table>

Dissociative adsorption

Non-dissociative adsorption

Figure 1.6: A diagram showing the tendency of different metal surfaces to dissociate NO, depending on the position of the substrate in the periodic table. Adapted from ref. 50.

1.5 Surface analysis techniques

To probe the adsorption process there are a multitude of different surface sensitive techniques available, all providing information about the various aspects of the interaction of the adsorbate species with the surface. Surface analysis techniques consist of firing photons, electrons, ions or neutral species at the surface, and applying heat to the surface, and then detecting any photons, electrons, ions or neutrals that are emitted or reflected from the surface. This is summarised in Figure 1.7.

The chosen techniques used to study the systems presented in this thesis are reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). The RAIRS technique \[^{53}\] has played an ever increasing role in the identification and characterisation of adsorbates and reactive intermediates and in the study of surface reactions. The advantage of RAIRS over many other surface science techniques is that data are relatively easily interpreted in terms of the chemical species present, since a simple observation of vibrational bands in the spectrum allows the identification of both the nature of the adsorbate species and also its adsorption site. RAIRS can also be used at various temperatures. This allows many interesting observations such as the study of surface diffusion processes, the observation of reaction intermediates, precursors to chemisorption and metastable species to be made and, as a result, sometimes results in the observation of completely new phenomena. In
addition, due to the high spectral resolution and sensitivity of RAIRS, the half-widths and line shape of the absorption bands can be used as a measure of inhomogeneous broadening within the adsorption system. This is as a result of inhomogeneity in the distribution of the oscillator frequencies being measured. This is commonly due to a lack of order in the adsorbate overlayer or can be due to the occupation of non-equivalent adsorption sites. Also, like the line shape and half-widths, a measure of the integrated intensity of the band can also lead to information about the interaction between adsorbate species and may be used as a measure of the relative amount of the particular species present on the surface.

In addition to the RAIRS experiments, TPD studies were also performed. This is the most elegantly simple of all surface science techniques, however it is also regarded as one of the most complex to interpret. Experiments are performed by adsorbing atoms or molecules on the surface, and then monitoring the desorption products with a mass spectrometer as a function of temperature. Experiments are usually performed by heating the sample at a constant rate. The most useful aspect of this technique is that it...
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gives an instantaneous result, showing the desorption of the adsorbate or any reaction products. However, the observed lack of a desorption product can also lead to significant interpretation. In addition, using information from the Polanyi-Wigner equation \[^{[54]}\] or the Redhead equation \[^{[55]}\], information about the strength of the bond between the adsorbate and the surface can be found. Also, information about the pre-exponential factor and order of reaction can be obtained. This allows information about the desorption process, i.e. whether the adsorbate desorbs directly from the surface, or whether associative desorption or desorption from multilayers occurs. In addition, from the fact that different species have different binding energies on the surface, multiple peaks can also be observed in the desorption spectra. This allows the identification of different species present on the surface. TPD spectra can be compared to changes in the RAIR spectra, as different species disappearing from the absorption spectrum correspond to desorption peaks in the TPD spectrum. In addition, in the TPD experiments, the area under each peak is proportional to the surface coverage and hence an indication of the amount of the desorbing species present on the surface can be obtained. Thus TPD provides complementary information to RAIRS, when studying the adsorption of molecules on surfaces.

1.5.1 Reflection absorption infrared spectroscopy (RAIRS)

RAIRS is a powerful vibrational spectroscopic technique for the study of adsorbates on metal surfaces. It allows the identification of the surface species, but also gives information concerning molecular geometry and chemical environment. The application of RAIRS to measurements on single crystal metal surfaces has been the subject of a number of reviews \[^{[4, 56-58]}\].

There are two main groupings of surface vibrations for adsorbate-surface-interactions: those between the surface and the adsorbate, and those within the adsorbate molecule. Vibrations between the surface and the adsorbate cannot be seen with the RAIRS set-up used in the experiments presented in this thesis. This is because the frequency of vibration is too low to be observed with the detector used here. The lower cut-off frequency of a typical RAIRS system using a mercury cadmium telluride (MCT)
detector is approximately 700 cm\(^{-1}\). The metal-adsorbate stretch frequency is of the order of a few hundred wavenumbers, and thus below the cut-off frequency of this type of detector. The system could be modified to see lower frequency vibrations if required, by using an alternative source and detector and an appropriate alkali halide material for the beam splitter and infrared windows.

In RAIRS, infrared light is used to probe vibrational modes of adsorbate molecules on the surface of the substrate. It can be considered as a fingerprinting technique, which can be used for identifying particular adsorbed species \(^{[53]}\). The acquisition of the infrared spectra is done by monitoring the absorption of infrared light reflected from the substrate. The absorption of infrared radiation occurs due to the excitation of vibrations within the adsorbates at the surface. The vibrational excitation of molecules by the infrared light is based upon the interaction of the electric field of the incident infrared light with the dipole moment of the molecule. The absorption of infrared light by molecules adsorbed on a metal substrate is dominated by the dielectric behaviour of the metal, since the electric field of the light, and the dipole moment of the vibrating molecule, interacts with the electrons in the metal \(^{[57]}\).

Figure 1.8: Diagram to show the reflection of infrared light at a metal surface.

Figure 1.8 shows the various components of the electric field vectors of the incident infrared light interacting with a metal surface. At all angles of incidence, the s-polarised
component of the light is reversed in phase upon reflection and hence the resultant of the incident and reflected vectors is close to zero at the surface. This is because the reflection co-efficient is near unity at a metal surface. However, the p-polarised light suffers a phase change that varies strongly as a function of angle of incidence. At grazing angles of incidence ($3^\circ < \theta < 8^\circ$), the p-component of the light is enhanced to yield a resultant amplitude nearly double the original amplitude of the incoming light. This can be more clearly seen in Figure 1.9.

\[ n = 3, \ k = 30 \]

\[ E_{p\perp} \]

\[ E_{s} \]

\[ E_{p\parallel} \]

Figure 1.9: Graph to show the variation of amplitude of the electric dipole as a function of incident angle $^{[88]}$. 

- 29 -
As a result, the s-polarised light cannot interact significantly with the intermolecular dipoles of the adsorbed molecules. However, since the p-polarised component of the light has a phase change and is enhanced, it can interact strongly with vibrational modes of adsorbed species perpendicular to the surface. Hence RAIRS is ideal for studying the adsorption of small molecules that are adsorbed perpendicular to the surface, such as CO and NO, which are of interest in the studies presented in this thesis. This effect is more clearly illustrated in Figure 1.10. This diagram depicts the dipoles of an adsorbed diatomic molecule oriented perpendicular and parallel to the surface. The resultant image charges that are formed in the substrate allow the observed dipole moment of the molecule that is perpendicular to the surface to be doubled. However, the dipole moment of the molecule that is parallel to the surface is cancelled out.

![Figure 1.10: A diagram to show the formation of image charges within the surface as a diatomic molecule is adsorbed perpendicularly and parallel on a metal surface.](image)

Not all molecules are adsorbed perpendicular to the surface and some may instead be adsorbed at an angle ($\phi$) to the surface. These molecules may also be observed using RAIRS, as long as they have a component of the intermolecular vibration that is perpendicular to the surface. Figure 1.11 shows a molecule adsorbed at an angle $\phi$ to the surface. The vertical component of the molecular vibration may be seen in a RAIR spectrum. The intensity of the absorption due to this vibration is a function of $\cos\phi$, as
the RAIRS technique only detects the component of the vibration perpendicular to the surface.

Figure 1.11: A diagram to show an adsorbed molecule that is leaning over at an angle $\phi$ to the surface.

Figures 1.9 and 1.12 show the angular dependence of the resultant amplitude of the electric field components generated at a clean metal surface relative to the amplitude of the initial incident light ($E_0$). The Figures 1.9 and 1.12 demonstrate that, to produce the greatest intensity of absorption, a near grazing incidence angle is required for the reflection of IR light.

For a given beam width, the area of the metal surface over which the enhanced field is effective increases as a function of $\sqrt{1/\cos \theta}$ and the intensity of the absorption by the surface layer experiencing this field can be expected to depend on $\theta$. This intensity function can be seen in Figure 1.12.
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From Figures 1.9 and 1.12, it can clearly be seen that there are two important considerations in a RAIRS experiment:

1. The metallic surface imposes a dipole selection rule. This rule states that the incident light should have a component which is p-polarised, and that only vibrations with a component of the dipole moment perpendicular to the surface will be excited.

2. The infrared light should be incident on the metal surface at grazing angles.

These factors were taken into account when designing the apparatus used for the experiments described in this thesis, as described in Chapter 2.

Figure 1.12: Graph to show the surface intensity function as a function of incident angle[^59].
1.5.2 Temperature programmed desorption (TPD)

Desorption of adsorbed atoms and molecules is one of the most fundamental surface kinetic processes and can provide information concerning the strength of the interaction between the surface and the adsorbed species. The monitoring of the desorption process as a function of temperature is one of the most simple techniques used for studying surface phenomena. This technique is known as temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS).

As already stated, TPD can be used to estimate the strength of the interaction between the adsorbate and the surface. As the system is heated, enough energy is acquired to allow the adsorbate-surface bond to break and the molecules to desorb from the surface. However, as molecules are often adsorbed in different sites, this can lead to multiple desorption peaks. The strength of the bond to the surface can be described by the Polanyi-Wigner equation \[ E_{\text{des}} = -\exp \left( \frac{-E_{\text{des}}}{RT_s} \right) \] (Equation 1.1):

\[
 r_{\text{des}} = -\frac{\partial \theta}{\partial t} = v_n \theta^n \exp \left( -\frac{E_{\text{des}}}{RT_s} \right) \quad \text{Equation 1.1}
\]

This equation relates the rate of desorption \( r_{\text{des}} \) to the surface coverage \( \theta \), pre-exponential factor \( v \), order of desorption \( n \), the temperature of the surface \( T_s \) and the energy of desorption \( E_{\text{des}} \). The order \( n \) of the equation relates to the path the molecule takes as it leaves the surface. In first order desorption, as the molecule is heated it leaves the surface in a one-step process. However, desorption is rarely this simple with desorption occurring via other surface processes, such as diffusion, recombination of atoms at the surface or surface mediated reactions. These desorption processes are second order or higher in nature. Equation 1.1 can be re-written for first order desorption, as in Equation 1.2, where \( T_p \) is the temperature at which maximum desorption occurs, and \( \beta \) is the applied heating rate.

\[
 \frac{E_{\text{des}}}{RT_p^2} = \frac{v}{\beta} \exp \left( -\frac{E_{\text{des}}}{RT_p} \right) \quad \text{Equation 1.2}^{[54]}
\]
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Equation 1.3 shows the same equation, rewritten for second order desorption:

\[ \frac{E_{\text{des}}}{RT_p^2} = \frac{2v^2}{\beta} \theta \exp \left( \frac{-E_{\text{des}}}{RT_p} \right) \]

Equation 1.3 \[^{[54]}\]

These results may be applied to theoretical calculations and the desorption of different species can be compared to the disappearance of vibrational bands in RAIRS experiments to identify desorption species. These equations require the knowledge of the desorption temperature, the heating rate of the experiment, the surface coverage and the pre-exponential factor. In the studies presented in this thesis, the pre-exponential factor and the surface coverage for each experiment are not known. Hence, as a first approximation, the Redhead equation \[^{[55]}\] has been used to obtain approximate values for the desorption energies as shown in Equation 1.4. In this equation the pre-exponential factor is represented by \( A \), and for a first approximation is assumed to be \( 10^{13} \) s\(^{-1}\).

\[ E_{\text{des}} = RT_p \left[ \ln \left( \frac{AT_p}{\beta} \right) - 3.46 \right] \]

Equation 1.4

It must be noted that this equation is only valid for first order desorption, as lateral interactions between adsorbate molecules and diffusion of molecules on the surface are not taken into account in this model.

1.6 Summary

The two main surface sensitive techniques that are used for the experiments described in this thesis are RAIRS and TPD. Collectively, the two experimental techniques can be used to determine surface structure and the adsorption sites of the molecules being studied. This information can be used to build up a picture of how the particular adsorbate interacts with the chosen surface, and as a result allows us to build up an image of the potential energy surface of the system. RAIRS is particularly useful as it is able to identify molecules at particular adsorption sites at very low surface coverage.
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The band shape and intensity can give information about the ordering of the molecules on the surface, dipole coupling between molecules and the molecular orientation. Coupling this technique to TPD allows information about the bond energies at the particular sites to be found. If all of these techniques are performed at various temperatures, further information on adsorption sites and chemical processes that occur at the surface as a function of temperature may be found.

This thesis describes experiments that use these techniques to study the adsorption of molecules on a stepped metal surface. These results provide information on the role of the step sites in the adsorption of molecules on high index surfaces and also provide a stepping-stone towards understanding adsorption on more complex surfaces, and the role of defects in the adsorption processes. This thesis presents a comprehensive description of the UHV chamber and associated components needed to perform RAIRS and TPD investigations on the Pt{211} surface. Studies of the adsorption of CO, NO and NO and O on the Pt{211} surface are also described in this thesis.
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1.7 References


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[48] Handbook of Chemistry and Physics, CRC Press, (1973)


Chapter 2: The design of the ultra high vacuum apparatus

2.1 Introduction
This chapter describes the design of the ultra high vacuum (UHV) apparatus that was assembled and commissioned during the course of the research described in this thesis. The UHV apparatus itself was not designed during the course of this work, however the sample mount, which allows efficient sample heating and cooling, and the infrared optics system were designed as part of this research. Hence the designs of both of these features are described in detail in this chapter. The apparatus described here was used to perform all of the experiments detailed in Chapters 4, 5 and 6.

2.2 Overview of the experimental system
The apparatus consists of a UHV chamber equipped with a liquid helium cooled manipulator, Fourier transform infrared spectrometer, infrared optics for RAIRS, and a resistive heating system. The system is also fitted with a quadrupole mass spectrometer, electron optics for LEED experiments, an argon ion gun, and a fine control leak valve. The chamber comprises two experimental levels: an upper level for sample preparation, TPD and LEED experiments, and a lower level for RAIRS experiments. The chamber has a typical base pressure of $1.2 \times 10^{-10}$ mbar.

The experiments presented in this thesis are centred on RAIRS and TPD spectroscopic measurements. The RAIRS optical system consists of a set of infrared mirrors, which are used to focus infrared light from the FTIR spectrometer onto the sample. The light that is reflected from the sample is then collected and refocused into the infrared detector. A photograph of the experimental system used for the experiments described in this thesis is shown in Figure 2.1.
Chapter 2: The design of the ultra high vacuum apparatus

(a) Manipulator
(b) Ar ion gun
(c) FTIR
(d) Infrared optics
(e) Gas manifold
(f) Feed through for cold-finger
(g) Vacuum chamber
(h) QMS
(d) Infrared optics
(i) Ion gauge
(j) Combined ion pump & TSP

Figure 2.1: Photograph showing the equipment used for the experiments that are presented in this thesis. To the left of the UHV chamber is the source of the infrared light used, the FTIR, with the infrared optics mounted on either side of the chamber.

2.3 The vacuum system

As already described, the vacuum system consists of two experimental levels: the upper level for surface preparation and the lower level for RAIRS experiments (see Figure 2.2). The sample is moved between the two experimental levels by a high precision manipulator (Omniax Translator, MX series, Vacuum Generators, UK). The manipulator can move the sample in all three directions $x$, $y$, and $z$, with micrometer precision. It is also fitted with a differentially pumped rotary feedthrough, allowing the sample to be rotated through $360^\circ$. This allows the sample to be accurately positioned for the RAIRS experiments and for the other surface analysis techniques employed here.
Chapter 2: The design of the ultra high vacuum apparatus

The upper experimental level is equipped with an argon ion gun (Physical Electronics Inc.) for sample preparation, a quadrupole mass spectrometer (HAL 201, Hiden Analytical Ltd.) for TPD experiments and residual gas analysis (RGA), and LEED electron optics (ErLEED-1000A, Specs GmbH) for surface electron diffraction experiments.

Figure 2.2 [11]: A schematic diagram of the experimental vacuum chamber used to perform the surface science experiments. It can be seen that there are two experimental levels: an upper level, which has an Ar⁺ gun, mass spectrometer and LEED optics (on reverse of chamber), and a lower level with infrared optics for RAIRS experiments.

The chamber is also fitted with an ion gauge to allow pressure measurement down to UHV and with multiple view ports to allow observation of the sample whilst positioning it in the experimental chamber. The chamber is also fitted with a fine control leak valve (LVM Series Leak Valve, Vacuum Generators) for leaking cleaning or sample gas into the chamber.
Chapter 2: The design of the ultra high vacuum apparatus

The main experimental chamber is mounted on a large stainless steel "T-section", to which the vacuum pumps used to attain UHV are fitted. The vacuum pumps used are a 145 l s\(^{-1}\) turbo-molecular pump (TMP) (Turbovac 151, Leybold Ltd.), which is backed by a 5 m\(^3\)hr\(^{-1}\) rotary pump (Trivac D5E, Leybold). The TMP is used to pump the chamber from atmospheric pressure to high vacuum (approximately 10\(^{-7}\) mbar). To attain UHV the chamber is baked and a second vacuum pump is used. This is a combined ion and titanium sublimation pump (Captorr ion pump & Boostivac TSP, Physical electronics).

For experimentation or sample cleaning to be performed, gas must be leaked into the chamber in a controlled manner. The gases used are usually extremely pure and may sometimes be corrosive. Therefore, a stainless steel gas manifold was constructed to allow efficient gas handling. This is shown in Figure 2.3.

![Figure 2.3: A diagram showing the layout of the gas handling manifold used for cleaning or dosing sample gases into the vacuum chamber.](image-url)
The gas manifold is evacuated using a 55 l s$^{-1}$ air-cooled turbo-molecular pump (Leybold, Turbvac 50), which is backed by a 2.5 m$^3$ hr$^{-1}$ rotary pump (Leybold, Trivac D2.5E). Gas is leaked into the vacuum chamber using the fine control, high precision, leak valve. This allows the entry of gas to the vacuum chamber to be carefully controlled.

2.4 Sample mount design

An integral part of the experiment is the capability to take the sample from its annealing temperature down to the temperature required for experimentation. This should be done in as short a period as possible to prevent residual gases in the chamber adsorbing onto the clean sample surface. The sample manipulator was designed to operate at liquid helium temperatures, although only liquid nitrogen temperature experiments are described in this thesis. Hence designing the sample heating and cooling system was a non-trivial process.

There are many criteria that are of importance for a very low temperature sample mount. The most important factor is the ability to take the sample between the base temperature of the system and the annealing temperature of the sample in the shortest possible time, so that it can be cleaned whilst maintaining UHV. Another aspect of the sample set up is the ability to maintain a well controlled and constant heating rate, so that TPD studies may be performed. The heating system used here employs a resistive heating mechanism. Resistive heating consists of passing a large current through filaments that are directly attached to the sample. The large current causes joule heating within the filaments, resulting in the filaments getting very hot in a short period of time. With this heating method, the filaments heat only the sample so that gas that evolves from the surface may be analysed in TPD experiments.

To allow the achievement of low temperatures, a continuous flow liquid helium cryostat (A.S Scientific products Ltd.) is used. This is shown in Figure 2.4.
Chapter 2: The design of the ultra high vacuum apparatus

Figure 2.4: Diagram of the liquid helium cryostat. Liquid gas flows through the central duct of the cryostat towards the heat exchanger. At the heat exchanger, the liquid gas is returned back up the cryostat via the outer duct, to waste. The helium returning up the cryostat is now very cold gas, (between 50 and 70 K). This acts to insulate the liquid gas in the inner duct.

The cryostat is mounted on a CF63 flange, and passed down the manipulator into the main experimental chamber. The cryostat consists of a 1 m long double-walled duct, where liquid gas is passed down the central channel to the heat exchanger at the end of the cryostat. As the gas passes through the heat exchanger, the boil-off gas is returned to waste via the outer channel. This enables a temperature of 4.2 K to be attained at the end of the heat exchanger. The boil-off gas also shields the liquid gas in the inner channel from external heat sources. The CF63 flange on which the cryostat is mounted also has four CF16 ports. These allow the mounting of two power feed-throughs, an N-type thermocouple and a standard electrical feed-through. These are used to power the resistive heating mechanism, to monitor the sample temperature and to provide an earth for the sample during sputtering and during LEED experiments. The N-type thermocouple comprises a nickel, chromium and silicon alloy, also known as Nicrosil.
for the positive wire, and a nickel, silicon and magnesium alloy, known as Nisil, for the negative wire. This type of thermocouple has a working temperature range of between 3 and 1500 K, and it was for this reason that this thermocouple was chosen. The heating wires and thermocouple are all heat sunk to the cold-finger so that they do not provide a direct path from room temperature to the very cold sample. The thermocouple heat sinking is achieved by winding the wires tightly around the cold finger. This serves two purposes: by winding the wires round the cold-finger the path from room temperature to low temperature is increased and the wires are brought into contact with the cool surface of the cold finger, hence decreasing their temperature. If the wires were not heat sunk, they would prevent the cryostat from reaching its base temperature. To aid the heat sinking of the copper heating wires, two copper heat sinking blocks were also designed and attached at equal intervals along the cryostat, as shown in Figure 2.5.

![Diagram](image)

**Figure 2.5 a & b: A diagram to show the copper heat-sink blocks used to heat sink the heating wires. Without this heat sinking it would not be possible to achieve liquid helium cooling. (a) Shows a top view and (b) shows a side view.**
Figure 2.5 shows the arrangement of the copper blocks used to heat sink the power cables to the cold finger. The heat sink blocks consist of four OFHC blocks. Two of the blocks are directly attached to the cold finger to provide the basis for thermal contact. To each of these is attached a second copper block. The positive copper heating cable is attached to one of the copper blocks, and the negative cable to the other. The cables are firmly attached to the blocks to provide maximum thermal contact. The copper heating cables are then fed out through the lower half of these blocks to the sample. The copper blocks to which the cables are attached are insulated from the cold finger, and each other, via Sapphire washers and top hat ceramics. The Sapphire washers are used as they allow heat transfer, but are electrical insulators.

To allow achievement of the minimum base temperature, the liquid helium supply is as close as possible to the sample mount which is mounted on the end of the heat exchanger. This is because thermal transport is best in the liquid. However, the set-up also has to tolerate exposure to sudden massive heat loads that may have to be maintained for prolonged periods, for example during the annealing of the sample.

At the end of the heat exchanger, a temperature of approximately 4.2 K is expected. However, this depends on the flow rate of the liquid used. The head of the heat exchanger is coupled to the sample via the sample mount. As mentioned above in the design of the sample mount, a conflict between good and poor thermal conductivity exists. Good thermal conductivity is needed to achieve good sample cooling, but at the same time poor thermal conductivity is necessary to prevent the heat from the sample transferring to the end of the cold finger. Most significantly, low temperatures and fast cooling are required as well as ease of sample heating without causing strong heating within the cryostat. In addition, the necessary electrical insulation of the sample has to be combined with good thermal contact. Another important consideration is the easy accessibility of the sample to the other components within the vacuum chamber. It is usual in a liquid helium cooled system to use a radiation shield to help the achievement of very low temperatures. However, using a radiation shield would restrict, or even prevent, the ease of sample manipulation and for this reason it was decided not to use a radiation shield, at least for initial experimentation. This lack of radiation shield leads
Chapter 2: The design of the ultra high vacuum apparatus

to the sample experiencing room temperature radiation, which makes it necessary to use a larger cooling power to attain and maintain the base temperature of the sample. Using a radiation shield can also lead to longer sample cooling times (up to 90 minutes) and can be detrimental to the stability of the UHV environment, as the large area of the radiation shield acts as a cryopump and any temperature fluctuation can lead to strong fluctuations in the UHV base pressure.

The sample mount used here is based on an original design by Schlichting and Menzel [2], with further modifications by F. Scholes[3]. A diagram of the sample mount used in the experiments described here is shown in Figures 2.6 a & b. The sample mount is made of a 28 mm diameter OFHC block. The block is composed of two halves separated by a thin ceramic plate. This allows 2.5 mm diameter copper wires to be attached to each of the blocks to allow current to be passed through the sample for the resistive heating. The copper block is bolted to the heat exchanger via three molybdenum screws and insulated from the sample mount with top-hat ceramics.

Many of the components used are compressed together, and spot welding is kept to a minimum, as it can lead to deformation of the metals and reduce the thermal conductivity of the welded components [2]. Between the heat exchanger and the sample mount is a 1 mm thick Sapphire disc. At very low temperatures, the thermal conductivity of Sapphire increases to a maximum of ~50 W cm\(^{-1}\) K\(^{-1}\) at 25 K. This can be seen in the graph, Figure 2.7. However, as the temperature of the Sapphire increases the thermal conductivity decreases to approximately 0.1 W cm\(^{-1}\) K\(^{-1}\) at 1800 K. These properties are ideal for protecting the heat exchanger and the liquid helium when the sample is heated, whilst allowing the sample to be cooled to the cryogenic temperatures that are required. 0.05 mm thick silver foil is sandwiched on either side of the Sapphire, to improve the thermal contact between the sample mount and the heat exchanger.
Figure 2.6 a & b: Diagram showing the layout of the sample mount at the head of the cryostat. The sample mount consists of an OFHC copper block in two sections. The copper sections are insulated from each other using a ceramic plate, and from the cryostat by a Sapphire disc. The sample is spot welded to heating filaments that are attached to the copper blocks via tungsten rods. (a) Shows a view of the back of the sample mount and (b) shows a side view.
Figure 2.7: Graph showing the variation in thermal conductivity of artificial Sapphire \cite{4}.
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A tungsten rod of 3 mm diameter and 30 mm length is attached to each of the copper blocks. These rods provide support for the heating filaments that are attached to the sample, as well as providing thermal contact with the sample. Each tungsten rod has two small tantalum studs of diameter 1 mm attached to them. The studs are spot welded to the heating wires, which are flattened to improve the surface area in contact with the sample and thus improve the thermal conductivity. The studs are used to reduce the contact of the heating filaments with the tungsten rods to prevent heat transfer back into the cold finger. In addition, as they are made of tantalum, they are easily welded to the heating filaments. The sample is spot welded to the heating wires via a 0.05 mm thick piece of tantalum foil which helps to further improve thermal conductivity, as shown in Figure 2.6a.

Table 2.1: A table of common materials used for making heating filaments. The table compares the thermal conductivity, melting point and electrical resistance of various materials.\(^5\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity / W m(^{-1})K(^{-1})</th>
<th>Melting point / K</th>
<th>Electrical resistance / (\mu) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>16.7</td>
<td>1708</td>
<td>85</td>
</tr>
<tr>
<td>Copper</td>
<td>401</td>
<td>1356</td>
<td>1.69</td>
</tr>
<tr>
<td>Tantalum</td>
<td>57.5</td>
<td>3269</td>
<td>13.5</td>
</tr>
<tr>
<td>Tungsten</td>
<td>173</td>
<td>5933</td>
<td>5.4</td>
</tr>
<tr>
<td>W/ Re (75%/25%)</td>
<td>39</td>
<td>3373</td>
<td>29</td>
</tr>
<tr>
<td>Inconel(^\text{TM})</td>
<td>11.2</td>
<td>1533</td>
<td>125</td>
</tr>
<tr>
<td>(Ni 72%/Cr 16%/ Fe %/ Nb/Mo/Ti)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constantan(^\text{TM})</td>
<td>19.5</td>
<td>1498</td>
<td>52.2</td>
</tr>
<tr>
<td>(Cu 60%/Ni 40%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sizes, dimensions and materials from which the heating wires and the various components of the sample mount are made, are governed by the thermal and electrical properties of the materials used. Table 2.1 shows a list of pure metals and alloys that are often used as heating filaments. Alloy materials are often avoided in UHV systems as they outgas.
Tantalum was chosen for the heating wires, as it has a high melting point and low vapour pressure. It is also very malleable, making it easy to flatten to improve the thermal contact with the sample. It also has a relatively high thermal conductivity and electrical resistance in comparison with other materials seen in Table 2.1. The wires therefore require a smaller current to attain the required temperature during the joule heating. Tungsten and a tungsten/rhenium alloy (W75/Re25) were also tested as heating filaments. However these materials proved unsuccessful. The tungsten was too brittle, and as a result could not be spot-welded easily, and thus good thermal contact was not achieved. In the case of the tungsten/rhenium alloy, although the electrical resistance was high and it could be spot welded easily, it has poor thermal conductivity compared to the pure metals, and thus prevented the sample from cooling in an acceptable time.

A large diameter tantalum wire (1 mm) is used to support the sample, as it was found that wires of thinner diameter were unable to cool the sample sufficiently. As a result, the resistance of the heating filaments is quite low. It is therefore necessary to use high currents to achieve the required annealing temperature and it is for this reason that the copper cables which provide the current to the heating system are 2.5 mm in diameter. The large currents would cause too much heating in thinner wires. Calculations were performed to estimate the current required to heat the sample and the resistive losses that were incurred whilst heating the sample. Figure 2.8 shows the circuit diagram for the various components of the sample heating system.

To calculate the significance of the different sections of the heating circuit, the resistance of the circuit was calculated. The calculations were based on the dimensions and the physical properties of the materials used to make the heating circuit, as shown in Figure 2.8.
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Figure 2.8: Circuit diagram for the heating system. The major sections of the circuit are the copper heating wires \( (R_1) \) that allow current to pass directly to the sample mount, the tungsten support rods \( (R_2) \), the tantalum heating filaments \( (R_3) \) and the sample \( (R_4) \).

The resistance \( (R) \) of the individual parts of the circuit was calculated using Equation 2.1.

\[
R = \frac{\rho L}{A} \quad \text{Equation 2.1}
\]

\( A \) is the cross-sectional area \( (m^2) \) of the wires, calculated from the diameter \( (\phi) \) of the wire. \( L \) is the length \( (m) \) of the wires and \( \rho \) is the resistivity \( (\Omega \cdot m) \) of the material used. Table 2.2 shows the dimensions of the wires used and their calculated resistances.

From the calculated values of the resistance of the major parts of the heating circuit shown in Table 2.2, it can be seen that the resistance of the tantalum heating filaments \( (R_3) \) is approximately 1.58 times that of the copper heat wires \( (R_1) \). As a result, the amount of joule heating that is produced in the copper wires is of comparable size to that in the tantalum wires.
Chapter 2: The design of the ultra high vacuum apparatus

Table 2.2: Dimensions of the wires used in the heating circuit described here and the calculated resistances.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi$ / mm</th>
<th>$A$ / m$^2$</th>
<th>$L$ / m</th>
<th>$\rho$ / $\Omega$ m</th>
<th>$R$ / $\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper heating wires</td>
<td>$R_1$</td>
<td>2.5</td>
<td>$4.9 \times 10^{-6}$</td>
<td>1</td>
<td>$3.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Tungsten rods</td>
<td>$R_2$</td>
<td>3.0</td>
<td>$7.01 \times 10^{-6}$</td>
<td>$30 \times 10^{-3}$</td>
<td>$5.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>Tantalum filaments</td>
<td>$R_3$</td>
<td>1.0</td>
<td>$7.85 \times 10^{-7}$</td>
<td>$30 \times 10^{-3}$</td>
<td>$5.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Single crystal sample (e.g. Pt)</td>
<td>$R_4$</td>
<td>$(12 \times 1)$</td>
<td>$1.20 \times 10^{-5}$</td>
<td>$20 \times 10^{-3}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

§ - The sample is a rectangle of dimensions 12 mm $\times$ 1 mm

The energy ($E$) required to raise the temperature of the sample through a certain temperature range is related to the dimensions of the sample and the specific heat capacity of the sample:

$$E = \text{specific heat capacity} \times \Delta T \times \text{mass of sample}$$

Equation 2.2

For the platinum sample:

Specific heat capacity of platinum = $133$ J K$^{-1}$ kg$^{-1}$

Density of platinum = $2.1 \times 10^4$ kg m$^3$

$\therefore$ The mass of the sample = $5.04 \times 10^{-3}$ kg = 5 g

Hence, the energy ($E$) required is

$$E = 133 \times 1000 \times 5.04 \times 10^{-3} = 670 \text{ J}$$

If the sample is to be heated in a 60 second period then

The power required ($P$) = $\frac{670}{60} = 11$ W
Chapter 2: The design of the ultra high vacuum apparatus

This 11 W of power needs to be generated by the two tantalum filaments. Therefore, approximately 5.5 W is required from each. The power generated in the filament can be calculated from Equation 2.3

\[ P = I^2 R \]  

Equation 2.3

where \( I \) is the current in the circuit, and \( R \) is the resistance of each of the tantalum heating filaments. Hence the current required, \( I \), is given by

\[ I = \sqrt{\frac{5.5}{5.2 \times 10^{-3}}} = 32.5 \text{ A} \]

The voltage across this circuit required to drive the current to heat the sample is directly related to the total resistance of the circuit \( R \).

\[ R = (2R_1) + (2R_2) + (2R_3) + (R_d) = 2.8 \times 10^{-2} \Omega \]

Thus the voltage across the entire circuit is

\[ V = IR = 32.5 \times 2.8 \times 10^{-2} = 0.9 \text{ V} \]  

Equation 2.4

Hence, to raise the sample from very low temperatures (approximately 10 K), through to the annealing temperature of the metal (1050 K for platinum), a current of approximately 32 A at 1 V is required. All of the above calculations assume perfect heat transfer, without any heat loss from the system.

Figure 2.9 shows test data for the sample heating and cooling. The graph (Figure 2.9) shows that if a current of 33 A is passed through the heating circuit, it is possible to heat the sample from 100 K to 1050 K in 1 minute and 20 s. Figure 2.9 also shows that it is possible to cool the sample back to 100 K in approximately 18 minutes. These time constraints are within practical limits. Figure 2.9 also shows the heating and cooling times for the sample flashed from room temperature to 1050 K. The Figure shows that the
heating and cooling, at least to liquid nitrogen temperatures, works as expected. Liquid helium cooling was not tested during the course of the work done in this thesis.

To control the sample heating during sample cleaning and experimentation, a Eurotherm temperature control module (2408, Eurotherm Ltd.) and Itools™ (Eurotherm Ltd.) software was used. The Itools software is capable of programming the 2408 module, to control a power supply (Xantrex 30-70, Thurlby Thandar Ltd.) to ramp the sample temperature at a constant rate or to heat to, and then maintain, a constant temperature. The sample temperature is measured via an N-type thermocouple, which is spot-welded to the crystal.

![Graph](image.png)

**Figure 2.9**: A graph to show the time taken to heat the sample from 100 K to 1050 K when 33 A is passed through the heating circuit, and the time to cool to room temperature and 105 K.

The power supply used is controlled in a voltage limiting mode via a 0 to 30 V external voltage, i.e. 0 V is 0 % output power and 30 V is 100 % output from the power supply. However, the 2408 Eurotherm module is only capable of controlling an external power supply for a 0 to 10 V output range. Consequently an attenuation circuit, shown
Figure 2.10, was constructed to enable the output from the Eurotherm to suitably control the power supply unit. Resistors $x$ (22 kΩ) and $y$ (1.2 kΩ) were incorporated into the circuit to improve the sensitivity of the power supply for the Eurotherm.

Figure 2.11 shows a typical temperature profile which is produced when the heating is controlled by the Eurotherm and power supply heating system. Initially, the sample is heated at a constant rate of 4 K s$^{-1}$. The sample temperature is then maintained at 900 K for 20 minutes, before cooling back down to room temperature.

![Circuit diagram](image)

**Figure 2.10:** Circuit diagram to show the Eurotherm temperature control mechanism. The Eurotherm control unit can be programmed via a PC to ramp the sample temperature at a constant rate, or to maintain a constant temperature.
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Figure 2.11: Graph showing the variation of sample temperature with time, as it is heated from room temperature to 900 K at a rate of 4 K s\(^{-1}\). The sample temperature was then maintained at 900 K for 20 minutes, before cooling to room temperature.

This type of heating control system is ideal for TPD experiments, where a constant, known, heating rate is required. In RAIRS experiments, this heating system can also be used to elevate the sample temperature and hold it at that temperature for a desired period of time, while studying the effects of temperature on the system. The heating system can also be used to control the sample temperature during the cleaning process. Even though accurate temperature control is not as crucial during cleaning as during experimentation, the heating system can be used to maintain a constant temperature while annealing the crystal.

2.5 RAIRS optical set-up
For RAIRS experiments, infrared light from the FTIR spectrometer is focused onto a metal crystal at a grazing angle, as described in Chapter 1. The reflected light is then refocused onto the infrared detector via a series of customised infrared mirrors and differentially pumped infrared windows. The infrared optics are housed in a pair of custom designed sealed aluminium boxes. The atmosphere in the boxes is purged with
dry, carbon dioxide free, air. This is necessary as both water and carbon dioxide are strong absorbers of infrared light in the frequency range studied, and their large signature absorptions would swamp any signal observed from surface species.

For RAIRS experiments on metal surfaces, a grazing angle of between 3-8° is required. Hence, a grazing angle of 5° was incorporated into the design of the vacuum chamber. This was done by angling the ports through which the infrared light passes in and out of the vacuum chamber. Differentially pumped infrared windows, shown in Figure 2.12, were used to transmit the infrared light in and out of the vacuum chamber. Table 2.3 shows a list of common materials used for windows in infrared spectroscopy. The chosen material in this case was KBr, as its optical transmission frequency range is in the absorption region of adsorbed molecules on the surface. In addition, KBr is inexpensive and easily polished to a smooth finish. The beam splitter in the FTIR is also made of KBr, and thus using a material with a larger frequency range would not be of any extra advantage.

Figure 2.12: Diagram to show the differentially pumped infrared window assembly. The KBr window is clamped between two concentric viton o-rings, and the inter-space is differentially pumped with a rotary pump.
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Table 2.3: List of common materials used for infrared windows.

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency range / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>400-4,000</td>
</tr>
<tr>
<td>KRS-5 (Thallous bromide / thallous iodide)</td>
<td>250-40,000</td>
</tr>
<tr>
<td>CsI</td>
<td>200-40,000</td>
</tr>
<tr>
<td>ZnSe</td>
<td>720-17,000</td>
</tr>
</tbody>
</table>

To allow light from the infrared spectrometer (Research series, Mattson Instruments) to
be incident on the sample, it is initially focused via a polished flat aluminium mirror
(Aero Research Ltd.), a 90°off-axis parabolic mirror (Aero Research Ltd.), and finally
through the KBr window assembly onto the sample. The reflected light from the sample
then passes through a similar KBr window assembly and is then refocused using another
similar 90°off-axis parabolic mirror and a 75°off-axis parabolic mirror onto the infrared
detector. The optical path of the infrared light is shown in Figure 2.13.

The intermolecular vibrations of adsorbed molecules generally have vibrational
frequencies of above 800 cm\(^{-1}\). Therefore a detector with this frequency response was
required. Table 2.4 shows a list of detectors commonly used in infrared spectroscopy.
The detector chosen was a liquid nitrogen cooled narrow band MCT (EG&G, Optoelectronics) detector. It was chosen for both its high sensitivity and frequency
response between 700 – 4000 cm\(^{-1}\).

Table 2.4: List of infrared detectors commonly used in infrared spectroscopy.

<table>
<thead>
<tr>
<th>Detector type</th>
<th>Frequency range / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narrow band MCT</td>
<td>700-4000</td>
</tr>
<tr>
<td>Wide band MCT</td>
<td>500-4000</td>
</tr>
<tr>
<td>Bolometer</td>
<td>Below 1000</td>
</tr>
</tbody>
</table>

Once the infrared signal from the sample is detected by the MCT detector it is passed
back to the FTIR spectrometer. Using the Win-First™ software (Mattson), an infrared
absorption spectrum can be produced.
Figure 2.13: A diagram to show the optical path of the infrared light in the RAIRS experiment. Infrared light is focused onto the sample using a parabolic mirror. The reflected light is then refocused into the detector.

2.6 Summary

The experimental system used to perform the surface science experiments presented in this thesis has been described in this Chapter. The equipment consists of a standard UHV chamber equipped with a liquid helium cooled manipulator. The vacuum system is pumped by a TMP and a combined ion and TSP, enabling a base pressure of $1.2 \times 10^{-10}$ mbar to be achieved.

It has been shown that the heating and cooling system designed here is capable of taking a sample to 1050 K, the annealing temperature of Pt, and then cooling it back down to the desired experimental temperature. Special attention has been paid to the various aspects of this heating and cooling system, especially with respect to the efficiency of the system and the heat losses to the cold-finger. Further modifications were made to
Chapter 2: The design of the ultra high vacuum apparatus

the heating and cooling system by heat sinking the copper heating cables to the cold-finger. This was done to prevent these cables from being a direct heat source to room temperature, which would ultimately reduce the efficiency of the cooling system. With these adaptations, the metal sample can be cleaned and TPD experiments can be performed successfully.

The vacuum system has been designed in such a way as to allow a grazing angle of 5° for RAIRS experiments to be achieved. The optics required to perform these experiments are housed in custom designed sealed aluminium boxes. These aluminium sealed boxes allow the optical path of the infrared light to be purged with dry, CO\textsubscript{2} free, air and prevent contamination of the infrared spectra by water and CO\textsubscript{2}. As a result a suitable infrared signal was obtained which allows the performance of RAIRS experiments of adsorbed molecules on metal surfaces.
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2.7 References

Chapter 3: Experimental methods

3.1 Introduction
As described in Chapter 1, all of the experiments presented in this thesis were performed on the single crystal Pt\{211\} surface. This sample was mounted in the UHV system described in Chapter 2. The UHV environment was necessary in order to maintain atomic cleanliness, as atoms and molecules from the atmosphere would contaminate the surface of the crystal if it were placed in a higher pressure environment. Sample cleanliness in a UHV environment is usually achieved using argon ion sputtering to knock off impurities, followed by treating in an oxygen rich environment at elevated temperatures to remove any impurities from the surface. These treatments often lead to the formation of surface defects, thus in addition to these techniques the sample is usually annealed to reform the desired structure. This Chapter presents an overview of the methods used to prepare the Pt\{211\} sample prior to experimentation and the experimental methods used to study the adsorption systems presented in Chapters 4, 5 and 6.

3.2 Sample preparation
All of the studies that are presented in this thesis were performed using the equipment described in Chapter 2. The UHV chamber has a base pressure of better than $2.0 \times 10^{-10}$ mbar.

The Pt\{211\} crystal was cleaned by repeated cycles of argon ion sputtering, oxygen treatment and annealing. The crystal was argon ion sputtered at room temperature, at an Ar pressure of approximately $1.6 \times 10^{-5}$ mbar and an emission current of 25 mA, such that a drain current of approximately 2.2 $\mu$A was obtained from the crystal. The crystal was moved every 10 minutes so that the Ar ions could be incident on as much of the sample face as possible. The crystal was moved six times, to give a total sputtering time of one hour. Following sputtering, the sample was heated to 900 K and exposed to
Chapter 3: Experimental methods

O₂ (Purity 99.97%, BOC Ltd.) at a pressure of approximately $5.0 \times 10^{-8}$ mbar for 20 minutes. The oxygen was then evacuated and, before the crystal was allowed to cool significantly, the crystal was heated to an annealing temperature of 1050 K, held there for 15 minutes, before being allowed to cool. Sample cleaning was repeated until the expected LEED pattern for a clean {211} surface was achieved. An example of a LEED pattern recorded for Pt{211} is shown in Figure 3.1.

Figure 3.1: Figure showing the LEED pattern for the Pt{211} surface at a electron energy of 184 eV, used in the experiments presented in Chapters 4, 5 and 6. Marked on the LEED pattern is the unit cell of a {211} surface, with lattice vectors $a$ and $b$ in the ratio of $2.5 \pm 0.1$:1.

Figure 3.1 shows the LEED pattern for the Pt{211} surface used for the experiments presented in this thesis. Marked on the LEED pattern are the two unit cell vectors $a$ and $b$. These two vectors are in the ratio of $2.5 \pm 0.1$:1. It has been shown previously that the ratio of the unit cell vectors for a {211} surface is $2.4:1$ [1], thus confirming the clean surface structure. The unit cell has dimensions of $6.74 \times 2.77$ Å [1].
It was found that CO TPD measurements were also a sensitive indicator of the cleanliness of the Pt\{211\} surface. Hence, in addition to the observation of the clean surface LEED pattern, and to further confirm the cleanliness of the surface, 20 L of CO was dosed onto the Pt\{211\} surface at room temperature. TPD experiments were then performed until a good desorption spectrum, similar to that observed by Xu and Yates\,[2], was obtained. Figure 3.2 shows a CO TPD spectrum that results from a 20 L dose of CO onto a clean Pt\{211\} surface.

![CO TPD Spectrum](image)

**Figure 3.2**: A temperature programmed desorption spectrum, recorded with a heating rate of 4 K s\(^{-1}\), for a 20 L exposure of CO on Pt\{211\}. The CO was dosed at 330 K.

Once the sample cleanliness was established, RAIRS and TPD experiments were performed to investigate the adsorption of CO (99.97% purity, BOC Ltd.), NO (99.5% purity, BOC Ltd.) and NO and O\(_2\) (99.97% purity, BOC Ltd.) on Pt\{211\} as described in Chapters 4, 5 and 6.
3.3 RAIRS experiments

RAIR spectra were taken with a Mattson RS1 Research Series FTIR spectrometer coupled to a liquid nitrogen cooled narrow band MCT detector. As already described in Chapter 2, the infrared optical path outside of the vacuum chamber was purged with dry air. The purge was broken to allow the MCT detector to be cooled with liquid nitrogen. The purge system was allowed to settle for at least half an hour before any experimentation, to re-establish a suitably purged optical path. During this period, the sample was approximately positioned in the infrared optical path to gain a signal at the detector. The sample position was then adjusted to gain a maximum peak-to-peak signal. A typical peak-to-peak voltage of approximately 5 V was obtained at room temperature, with the signal increasing to 5.5 V for liquid nitrogen temperature experiments.

In the RAIRS experiments, an initial clean surface spectrum was taken (a background spectrum). The sample gas was then admitted to the vacuum chamber in a controlled manner, via a high precision leak valve, and a RAIR spectrum was taken at 4 cm\(^{-1}\) resolution over 256 scans, taking approximately 3 minutes (a sample spectrum). As the intensity of the absorption bands studied in RAIRS is often only of the order of a fraction of a percent, RAIR spectra are generated by taking the difference between the sample spectrum and the background spectrum, and then ratioing the result to the background spectrum. This results in a plot of \(\Delta R/R\) vs Wavenumber. RAIR spectra were taken for different exposures by admitting further doses of gas to the sample until the RAIR spectra stopped changing and a saturation dose had been achieved.

After a saturation dose of the sample gas, the surface was heated in a controlled manner to determine the effect of annealing on the spectra. The sample was heated to a predetermined temperature, held at this temperature for 40 seconds, and then allowed to cool back down to the original temperature, at which a RAIR spectrum was taken. This was repeated until no absorption peaks were observed in the spectrum.
3.4 TPD experiments

TPD experiments were performed by cleaning the sample as described in Section 3.2. The sample was then moved so that it was directly in front of the quadrupole mass spectrometer (HAL 201, Hiden Analytical Ltd.). Care was taken to ensure the sample was positioned in the same place for each experiment, so that spectral intensities could be easily compared. Spectra were acquired by heating the sample at a constant rate, while recording the mass spectra for the appropriate gases that were evolved from the surface as a function of time. In addition, the temperature rise of the sample was also recorded as a function of time. The two sets of intensity (at a given mass) vs time and temperature vs time data were then combined to give a TPD spectrum of intensity vs temperature. In some experiments, the integrated intensities of the desorption peaks were used to estimate the relative amounts of the desorption products evolved from the surface. The integrated areas were found by subtracting the background intensity from the spectrum and then using the trapezium rule to find the area below the TPD peak.

As in the RAIRS experiments, TPD spectra were taken for successive doses of the sample gases studied. The surface was cleaned between each experiment to ensure that any dissociation or reaction products did not contaminate the sample and affect subsequent experiments. This was especially true for the adsorption of NO and O, as O is believed to remain at the surface, even following heating to 1000 K, as described in Chapters 5 and 6.
3.5 References


Chapter 4: The adsorption of CO on Pt\{211\}

4.1 Overview

The adsorption of CO on Pt\{211\} has been studied, and the results of these experiments are described here. As the apparatus in the experiments described in this thesis is new, the purpose of this study was to look at a system that is reasonably well understood, in order to enable the equipment to be commissioned. In addition, the study of CO adsorption allows insight into the interaction of molecules with stepped metal surfaces to be obtained. The results presented in this chapter are for RAIRS and TPD investigations of CO adsorption on Pt\{211\}. Both experimental measurements were performed at 330 K and 106 K.

RAIR spectra at 106 K show four different vibrational bands for CO on the Pt\{211\} surface. Initial adsorption gives a band at 2070 cm\(^{-1}\). On further exposure a second absorption peak at 1880 cm\(^{-1}\) appears in the spectrum. These two absorption features are assigned to CO adsorbed in step-top and bridge sites respectively. On further exposure of CO, two additional absorption features are observed at 2094 cm\(^{-1}\) and 1893 cm\(^{-1}\). These are assigned to CO adsorption in top and bridge sites on the terrace. In the RAIRS experiments at 330 K only three absorption features at 2094, 2070 and 1880 cm\(^{-1}\) are observed. TPD experiments conducted at both 106 K and 330 K show sequential adsorption of CO on the Pt\{211\} surface and yield two desorption peaks at 500 K and 400 K. These are attributed to the desorption of CO from step and terrace sites respectively. The apparent discrepancy between the number of species observed in the RAIRS and TPD experiments is attributed to the negligible difference in the binding energy of the top and bridge sites in comparison to that between the step and terrace sites.
4.2 Introduction

One of the primary pollutants found in the atmosphere is carbon monoxide emitted by car exhausts and many industrial processes. As a result, there has been significant investigation into the catalytic removal of CO. Hence, the interaction of CO with various metal surfaces has been studied for many years in an effort to reduce its emission \[^1\]. In addition, CO has a relatively high bond energy (1076 kJ mol\(^{-1}\)) compared to other similar diatomic molecules such as NO (630 kJ mol\(^{-1}\)) and O\(_2\) (498 kJ mol\(^{-1}\)), making it interesting from a fundamental scientific point of view. As a result, CO has been used as a model system to study many different aspects of the interaction of molecules with surfaces including thermodynamic processes, adsorbed states, adsorption/desorption kinetics and dynamics at the surface-molecule interface.

Most UHV surface science experiments are performed on well-defined single crystal surfaces, however, real catalytic surfaces are much more complicated and contain large quantities of defect sites. However, due to their complexity it is very difficult to directly study these systems. Therefore, the study of well-defined stepped and kinked surfaces is an important first step towards understanding the role of defect sites in the adsorption and reaction of molecules on metal surfaces.

In this chapter, the results of a study of the interaction of CO with Pt\{211\} are presented. The Pt\{211\} surface is composed of 3-atom wide terraces with \{111\} orientation. These terraces are separated by an atomic high step, which has \{100\} orientation. A more detailed description of this surface is given in Chapter 1.

The adsorption of CO on Pt\{211\} has previously been studied by Yates \textit{et al} \[^2-10\]. These studies employed several different techniques to investigate this system including TPD \[^2-4,9,10\], RAIRS \[^3,9\], ESDIAD \[^2-6\] and LEED \[^2,4\]. In RAIRS and TPD studies of the adsorption of CO on Pt\{211\} and Pt\{533\}, it was shown that CO adsorbed preferentially at the step sites \[^9\]. On initial exposure of CO to the Pt\{533\} surface, preferential adsorption into top sites at the step edge was seen. As the CO exposure was increased, bridge sites at the step edge were populated, resulting in an absorption band at \(\sim 1880 \text{ cm}^{-1}\). On further exposure of CO, corresponding top and bridge sites at the
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terrace were then populated. Similar results were seen for CO adsorption on the Pt{211} surface. However, unlike the CO/Pt{533} system, it was not possible to differentiate between CO in top sites at the step and terrace. This was attributed to the smaller terrace width of the Pt{211} surface compared to Pt{533} \[9\]. TPD experiments for the CO/Pt{211} system showed two desorption features at ~ 400 K and ~ 500 K. When these results were compared to the CO/Pt{111} system, where only one TPD desorption feature is observed \[11\], it was shown that the lower temperature desorption feature seen in the Pt{211} TPD \[9\] corresponded to the desorption of CO from the {111} terrace.

The adsorption of CO on Pt{211} has also been studied using ESDIAD and LEED techniques \[4, 6\]. These studies showed that the structure of the adsorbed CO is strongly coverage dependent. At low coverage, it was observed that CO adsorbs on every other top site at the step edge, with a 20° tilt down the step. On further exposure, CO was observed to fill the empty sites at the step, before populating terrace sites. This structure was attributed to steric repulsion between the adsorbate molecules.

In addition to TPD spectroscopy, microcalorimetry experiments have been performed on the CO/Pt{211} system by Kose \[12\]. These experiments gave the heat of adsorption and the sticking probability of CO on the Pt{211} surface at 300 K. Measurements showed that at zero coverage, the sticking probability and heat of adsorption were 0.76 and 185 kJ mol\(^{-1}\) respectively. When numerical models were applied to the data, adsorption energies of 190 kJ mol\(^{-1}\) and 165 kJ mol\(^{-1}\) were calculated for initial adsorption in step and terrace sites respectively.

There have been very few theoretical studies of the adsorption of CO on Pt{211} \[13, 14\]. These calculations show similar results to each other, with CO in a bridge site at the step edge found to be the most stable species on the surface. The next most stable species was top bound CO, also at the step. The next most stable sites were top and bridge bound species at the terrace. However, these sites had significantly lower adsorption energies than those at the step edge. These results are in disagreement with previous experimental results \[2-10\] which showed that the atop site at the step edge is the
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most stable site on the surface. Various reasons for the disagreement between experiment and theory have been presented\textsuperscript{[13,14].}

The adsorption of CO on Pt\{321\}\textsuperscript{[15, 16]}, a stepped kinked surface, and Pt\textsubscript{6}111\times111\textsuperscript{[11]} and Pt\{533\}\textsuperscript{[17-24]} has also been investigated. In these studies, it was also shown that CO initially adsorbed in step-kink sites and then in terrace sites.

In this Chapter, the results for RAIRS and TPD investigations of the adsorption of CO on Pt\{211\} at various temperatures are described. The way in which these experiments were performed has been described in Chapter 3.

**4.3 Results and discussion**

**4.3.1 Adsorption of CO on Pt\{211\} at 106 K**

RAIRS data for CO adsorption on Pt\{211\} at 106 K are shown in Figure 4.1. There are two distinct absorption features in the infrared spectra. These occur between 2070 - 2100 cm\(^{-1}\) and 1880 - 1915 cm\(^{-1}\). The region showing the lower frequency band can be more clearly seen in Figure 4.2.

On initial exposure of the surface to 0.05 L of CO (Figure 4.1a), a small absorption band at 2071 cm\(^{-1}\) is observed. This band increases in frequency and intensity with increasing CO exposure. Following exposure of the sample to 1 L of CO (Figure 4.1e), a second absorption band, approximately 10 cm\(^{-1}\) higher in frequency, appears and grows to dominate the spectrum at saturation.

Figure 4.2 shows a close up of the lower frequency absorption band seen in Figure 4.1. It is clear that this band does not start to appear in the spectrum until the surface has been exposed to 0.2 L of CO. The band initially appears with an absorption frequency of 1880 cm\(^{-1}\).
Figure 4.1: RAIR spectra following successive exposure of CO to Pt{211} at 106 K. The sample was exposed to (a) 0.05 L, (b) 0.1 L, (c) 0.2 L, (d) 0.5 L, (e) 1 L, (f) 2 L and (g) 5 L of CO.
Figure 4.2: RAIR spectra following successive exposure of CO to Pt\{211\} at 106 K. The spectra shown are an enlarged view of those shown in Figure 4.1, showing the lower intensity, low frequency, absorption bands between 1800 and 2000 cm\(^{-1}\). Here spectra resulting from CO exposures of (a) 0.2 L, (b) 0.5 L, (c) 1 L, (d) 2 L and (e) 5 L are shown.
As with the higher frequency absorption band (Figure 4.1) a second band, approximately 10 cm\(^{-1}\) higher, starts to appear at higher exposure (Figure 4.2). In the saturation absorption spectrum following exposure of the surface to 5 L of CO, this band has shifted to a frequency of 1918 cm\(^{-1}\).

On initial observation of the RAIR spectra, there are two different CO species that are present on the Pt\{211\} surface with vibrational frequencies of 2070-2090 cm\(^{-1}\) and 1880-1915 cm\(^{-1}\). These can be assigned to top and bridged CO species respectively. Unlike the previous results in the literature \cite{9}, it has also been possible in these experiments to resolve these two absorption bands further into peaks at 2094, 2080, 1918 and 1888 cm\(^{-1}\).

The absorption band observed initially at 2071 cm\(^{-1}\) is assigned to the adsorption of CO to a top-step site. This assignment is in agreement with both Yates et al \cite{9} and with theoretical calculations \cite{14}. The band observed at 2094 cm\(^{-1}\), which grows to dominate the spectrum at saturation, is assigned to top-terrace bound CO. It has been shown that there is a positive outward dipole present at the step \cite{9}. This has the effect of lowering the work function at the step edge. The net result of this is that the molecular orbitals of the adsorbed CO are split, causing a lowering of the 2\(\pi^*\) orbital energy. This increases the amount of back donation possible from the metal to the CO in the region of the step. As a result, it is expected that CO at the step edge will have a lower vibrational frequency than CO at the terrace. This is in good agreement with the assignment of the vibrational bands made here. The lower frequency bands observed at 1880 and 1918 cm\(^{-1}\) are assigned to bridge bound CO at the step and terrace, respectively.

These results may be compared to studies of CO adsorption on Pt\{111\}, where two absorption bands at 2093 cm\(^{-1}\) and 1869 cm\(^{-1}\), corresponding to top and bridge bound CO \cite{25}, were observed. These results support the assignment here of the band at 2094 cm\(^{-1}\) to top bound CO at the terrace. However, the band assigned to the bridge bonded CO at the terrace has a significantly higher frequency than that observed for CO on Pt\{111\}. This can be accounted for by the different bridge sites that are available for the CO to bond to on the stepped surface. CO can either bond to two Pt atoms on the
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terrace or to one on the terrace and one at the step. It would be expected that these different species would have different vibrational frequencies. Although it is not possible to differentiate between these species in the present study, it is postulated that the terrace bridge species observed here is a species where CO is bonded between a step and a terrace atom. This species has been shown theoretically to be the most stable bridge species on the terrace\textsuperscript{14}. This bridged species will not have the same frequency as bridged CO bonded to Pt\{111\}.

Whilst these results are in general agreement with those of Yates \textit{et al}\textsuperscript{9}, it has also been possible to observe additional experimental detail. The observed difference can be attributed to the different temperatures at which the two experiments were conducted. In those conducted by Yates \textit{et al}\textsuperscript{9}, adsorption occurred at 90 K and the sample was annealed to 290 K before cooling back to 90 K to take the RAIR spectra. In the results presented here, adsorption and the acquisition of the RAIR spectra occurred at 106 K. In fact, the observations made by Yates are very similar to those obtained here for experiments where the Pt sample was dosed at 330 K.

Figure 4.3 shows the variation in peak height as a function of exposure for the top-step (2070 cm\textsuperscript{-1}) and top-terrace (2094 cm\textsuperscript{-1}) bound species. Peak height was used as opposed to measuring the area under the peaks, as it was difficult to deconvolute the two peaks observed. This measurement is a good approximation of the amount of different species present, as the full width half maximum (FWHM) of the different peaks does not vary significantly as a function of coverage. It can be seen that, as the substrate is exposed to CO, the initial absorption peak (labelled top-step in the graph) increases in intensity. As it reaches a maximum and then levels out, the second species at 2094 cm\textsuperscript{-1} (labelled in the graph as top-terrace) starts to grow in. As the exposure of the CO is increased, the top-terrace species also starts to plateau.
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![Graph showing the variation in peak height of the infrared absorption peaks at 2071 cm\(^{-1}\), labelled top-step, and 2094 cm\(^{-1}\), labelled top-terrace, as a function of increasing exposure of CO at 106 K.]

Figure 4.3 shows that the peak height of the RAIRS band due to the top-terrace species is three times that of the top-step species. This may be due to there being more adsorption sites available at the terrace. The observed drop in intensity of the top-step band when the top-terrace species grows into the spectrum may be due to intensity stealing by the higher frequency top bound species. The drop in peak height may also be caused by the tilting of the adsorbed step edge molecules caused by steric repulsion effects.

It is clear from Figure 4.1 that the frequency of the two peaks at 2080 and 2094 cm\(^{-1}\), which are labelled top-step and top-terrace respectively in Figure 4.3, shifts as a function of exposure. This can be more clearly seen in Figure 4.4. This graph shows a plot of the variation in frequency of the two top bound species at 2071 cm\(^{-1}\) (top-step) and 2094 cm\(^{-1}\) (top-terrace) as a function of exposure. The observed increase in frequency as a function of increasing exposure is due to dipole – dipole coupling between the CO molecules adsorbed on the surface.
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Figure 4.4: Graph to show the variation in wavenumber of the infrared absorption peaks at 2071 cm$^{-1}$, labelled top-step, and 2094 cm$^{-1}$, labelled top-terrace.

The absorption spectra in Figure 4.2 show that, like the top species, the bridge bound species also increases in intensity as a function of exposure, and a further species of slightly higher frequency grows in as the CO exposure is increased. However, in contrast to the top bound species seen in Figure 4.1, the maximum intensity of the bridge bands in Figure 4.2 is much smaller than that observed for the top bound CO bands. This is in agreement with observations made by Yates et al.$^9$

One possible reason for the lower peak height of the bridge bound species compared to the top species is that there are fewer molecules adsorbed in this state. This may be due to this species requiring two Pt atoms for bonding, hence there are less sites available at the surface. It may also be that the bridge species is less stable than the top species, and hence the bridge sites are less likely to be occupied. An alternative is that the bridge bound CO species are bent. Theoretical studies$^{14}$ have shown that step-bridge bound species are adsorbed on the surface with a 20° tilt angle, with the molecules shown to be pointing in a “downstairs” direction, as shown in Figure 4.5. ESDIAD studies$^4$ have
also shown that CO molecules are tilted at 20° to the surface, however, they do not specify whether these are bridge or top bound species.

If the bridged CO molecules were inclined at an angle of 20°, this would affect the intensity of this species in the infrared absorption spectrum. Figure 1.11 (Chapter 1) shows that, compared to a molecule that is perpendicular to the macroscopic surface, the expected band intensity would be reduced to 93%, \(\cos(20°)\), of the intensity of the band for an upright species. If it is assumed that bridge bonded CO is attenuated at an angle of 20° (as indicated by the theoretical calculations \(^{[14]}\)), this may explain why this species does not appear until the surface has been exposed to 0.2 L of CO, as the bridge species would have a significantly lower intensity than the top species and would not be observable until a larger coverage of CO. Another reason why the intensity of the bands due to bridged CO may be lower than those due to top CO is that the extinction co-efficient for the bridge species is smaller than for the top bound species. This is due to the smaller dynamic dipole of the bridged species compared to the top species. This leads to less infrared absorption, and therefore a smaller band intensity is expected. The observed lower intensity of the bridged species compared to the top species is in agreement with previous observations made by Yates et al. \(^{[9]}\).

Figure 4.6 shows a series of infrared absorption spectra taken following heating of the sample to various temperatures following CO adsorption at 106 K. Again, due to the
low absorption intensity of the bridge bound species, Figure 4.7 shows this region of the infrared spectrum in more detail.

![RAIR spectra following successive heating of the Pt{211} surface following exposure to 5 L of CO. The sample temperature at adsorption was 106 K and (a) shows the spectrum that results from this adsorption. The sample was then heated to (b) 202 K, (c) 302 K, (d) 352 K, (e) 408 K, (f) 452 K, (g) 500 K and (h) 598 K, and subsequently cooled back to 106 K and the spectrum taken.](image-url)
Figure 4.7: RAIR spectra following successive heating of Pt(211) following exposure to 5 L of CO. The data shown here is an enlarged view of the spectra in Figure 4.6, showing the low frequency absorption peaks between 1700 and 2000 cm\(^{-1}\). (a) The sample temperature at adsorption was 106 K. The sample was heated to (b) 150 K, (c) 202 K, (d) 252 K, (e) 302 K, (f) 352 K, (g) 408 K, (h) 452 K, and (i) 500 K, and subsequently cooled back to 106 K and the spectrum taken.
As for the adsorption sequence for CO on Pt\{211\}, the top bound species, with absorption bands between 2067-2095 cm\(^{-1}\), dominate the spectra. The band at 2067 cm\(^{-1}\) is the last species to be observed before desorption. All species have desorbed by \(\sim 600\) K. The species at 2095 cm\(^{-1}\) has the largest intensity and the frequency of this species remains relatively constant throughout the heating sequence, until it disappears at 352 K. At this temperature, the absorption peak at 2084 cm\(^{-1}\) increases dramatically in intensity. Previously it was observed only as a shoulder on the 2094 cm\(^{-1}\) peak.

Figure 4.8 shows the variation in intensity of the two absorption peaks at 2095 cm\(^{-1}\) (top-terrace CO) and 2083 cm\(^{-1}\) (top-step CO) as a function of annealing temperature. These two curves are labelled top-terrace and top-step respectively. Again the peak height has been used to give an approximation of the peak intensity as it is difficult to deconvolute the bands due to step and terrace CO. It is obvious from this data that the relative intensity of the top-terrace species slowly increases as a function of increasing temperature.
This increase may be attributed to temperature induced ordering or to an alignment effect which reduces the inhomogenous broadening observed. It may also be due to the adsorbed molecules changing orientation with respect to the surface. If the molecules start to become more normal to the surface, the relative intensity of the signal should increase. The relative intensity of the CO at the top-step sites remains constant until the top-terrace species disappears.

The top-terrace species disappears at 352 K and, as it does so, the intensity of the top-step species dramatically grows, increasing in intensity almost six times. This again may be due to some form of ordering effect of the adsorbate layer, due to the increased mobility at the elevated temperature. However, it may also be due to migration from the terrace to the step as previously observed by Yates et al. In their study, exchange between terrace and step bonded CO molecules during the TPD experiments was observed. As the step sites have a larger affinity for adsorbing molecules, it may be energetically favourable for these molecules to move to the step sites at this temperature. In addition, as the top-terrace species leaves the surface, there may be a reduction or loss of intensity stealing between the different species present, which could result in an increase in intensity of the band due to the top-step species.

On further heating, the intensity of the step species peaks at a temperature of approximately 400 K. By ~600 K the band has disappeared, implying that the CO has completely desorbed from the surface by this temperature. As this is the last species to be observed, it also implies that it is the most stable species on the surface. This further confirms the assignment of this peak to the top-step species since this species is the first to be observed in the RAIR spectrum.

Figure 4.9 shows the variation in frequency of the absorption peaks at 2095 cm⁻¹ and 2080 cm⁻¹ as a function of annealing temperature. These curves are labelled in a similar manner to those in Figure 4.8, with the two curves labelled as top-terrace and top-step respectively. For the adsorption sequence, it was noticed that, as the exposure of CO was increased, the frequency of the absorption bands increased, before levelling out. This was attributed to dipole–dipole coupling between the CO molecules. In Figure 4.9,
a similar mechanism acting in reverse may explain the drop in frequency of the step species. As it is also postulated that the CO molecules migrate from the terrace sites to the step sites, this might explain why the frequency of the terrace species does not change significantly before this species disappears at about 400 K.

![Figure 4.9: Graph to show the variation in frequency of the top bound adsorption species at the step and terrace as a function of temperature. The starting temperature was 106 K. The curves labelled Top-Terrace and Top-Step are for the absorption peaks observed at 2095 cm$^{-1}$ and 2080 cm$^{-1}$ respectively.](image)

As with the top bound step and terrace species, the bridge bound species also show an intensity change as a function of temperature. This can be seen in Figure 4.10. At 350 K, the bridge-terrace species disappears, and the bridge-step species dramatically increases in peak height. This is not as large a change as observed for the top-step species. However, this may be due to less bridge species being present on the surface. The increase in peak height of the step-bridge species may also be due to the migration of molecules from the terrace to the step, as proposed for the top bound species, or due to an ordering effect of the adsorbate. As before, peak height has been used to estimate
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the amount of adsorbate present at the surface, as it is difficult to separate the two absorption peaks and measure their integrated area.

![Graph showing the variation in intensity of the two bridged CO species adsorbed on Pt\{211\}](image)

Figure 4.10: Graph to show the variation in intensity of the two bridged CO species adsorbed on Pt\{211\}. The absorption feature at 1893 cm\(^{-1}\) is labelled as Bridge-Terrace in the graph, and the absorption feature at 1880 cm\(^{-1}\) is labelled as Bridge-Step in the graph above.

To complement the RAIRS studies, TPD experiments were also performed for the CO/Pt\{211\} system. Figure 4.11 shows TPD spectra for successively increasing exposures of CO to the platinum surface at 106 K. On initial exposure of the sample to CO, a peak starts to form at approximately 550 K, labelled \(\beta\) in Figure 4.11. This peak steadily grows with increasing CO exposure. At CO exposures of greater than 0.5 L, a second, lower temperature, peak starts to grow into the spectrum, with an initial peak temperature of 466 K, labelled \(\alpha\). On further exposure, the \(\alpha\) peak grows to dominate the spectrum, such that by an exposure of 5 L, it is the largest peak in the spectrum. In addition, the peak temperature of the \(\alpha\) peak decreases by \(~20\) K, until it reaches 446 K at saturation exposure. These results are consistent with previous TPD studies of the CO/ Pt\{211\} system by Yates et al.\(^9\).
When the TPD results are compared with the RAIRS data presented here, it is noted that there are four species present in the RAIR spectra, but only two species are observed in the TPD spectra. This can be explained by grouping the four identified infrared active species into two obvious sets: either step and terrace species, or bridge and top bound species.

Figure 4.11: TPD spectra for successively increasing exposure of CO to Pt{211} at 106 K. The spectra are for exposures of (a) 0.2 L, (b) 0.5 L, (c) 1 L, (d) 2 L, (e) 5 L and (f) 20 L CO.
Previous studies of CO adsorbed on Pt\{111\} observed that there was only one peak in the TPD spectra\textsuperscript{[11, 26, 27]}. This study showed a single desorption peak at 460 K, which shifted down in temperature on increasing exposure of CO\textsuperscript{[11]}. Top and bridge species were observed in the RAIRS experiments, however it was concluded that the difference in binding energy between these species was too small to be observed in the TPD. A small hump was also observed in the TPD spectra for Pt\{111\} at about 550 K. This was attributed to defect sites on the surface, most likely to be steps\textsuperscript{[11]}. Using this information about Pt\{111\}\textsuperscript{[11]}, and previous Pt\{211\} surface studies, the two peaks that are observed in the TPD spectra in Figure 4.11 are assigned to the desorption of step and terrace bound CO species. The low temperature $\alpha$ peak can be attributed to the terrace bound species, and the higher temperature $\beta$ peak is attributed to the desorption of CO from the step sites. Evidence to support these assignments comes from theoretical calculations\textsuperscript{[13, 14, 25]} which have shown that the difference in the binding energy of a top and bridge (step) site is approximately 12 kJ mol\textsuperscript{-1}, whereas the difference in binding energy between a step and terrace (top) site is approximately 34 kJ mol\textsuperscript{-1}. Hence it is not expected to be able to differentiate between top and bridge species on the step in the TPD, and similarly for the terrace species.

4.3.2 Adsorption of CO on Pt\{211\} at 330 K
A study of the adsorption of CO on Pt\{211\} was also performed at 330 K using infrared and TPD spectroscopic techniques. Figure 4.12 shows the infrared absorption sequence for successively increasing exposures of CO to the Pt\{211\} surface. The surface was initially dosed with 0.05 L of CO at a starting temperature of 330 K. At an exposure of 5 L of CO the absorption spectra stopped changing. It was therefore assumed that this was a saturation dose for this system. As Figure 4.12 shows, these spectra are broadly similar to those observed for adsorption at 106 K. The first feature observed in the RAIR spectra is an absorption peak at 2067 cm\textsuperscript{-1}, at an exposure of 0.05 L. On further exposure of CO, this peak increases in intensity and shifts up in frequency to 2075 cm\textsuperscript{-1}.
Figure 4.12: RAIR spectra following successive exposures of CO on Pt{211} at 330 K. The figure shows spectra for exposures of (a) 0.05 L, (b) 0.2 L, (c) 0.5 L, (d) 1 L, (e) 1.5 L and (f) 5 L and (g) 10 L of CO.
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At an exposure of 1.5 L, a second peak 10 cm\(^{-1}\) higher in frequency is also observed in the spectra. This peak grows to dominate the spectrum. Figure 4.13 shows an enlarged view of the region between 1750 cm\(^{-1}\) and 1950 cm\(^{-1}\) in Figure 4.12. As with the experiments at 106 K, the absorption feature observed in this region is much lower in intensity than those observed in the 2050 – 2100 cm\(^{-1}\) region. However, unlike the experiments at 106 K where two absorption features are seen, there is only one band observed in this region of the spectrum following adsorption at 330 K.

As the adsorption sequence for CO on Pt\{211\} at room temperature is very similar to that observed at liquid nitrogen temperature, it is reasonable to assign the first absorption peak observed to the adsorption of CO in a top site on the step-edge. The high frequency peak at 2092 cm\(^{-1}\), which ultimately dominates the spectra, can be assigned to CO bound in a top site on the terrace. However, unlike the results obtained at liquid nitrogen temperatures, there is only one peak observed in the infrared spectra in the low frequency region, even following a saturation CO dose. This peak has the same frequency as the first observed low frequency peak in the 106 K spectrum. It is therefore assigned to the bridge-step species. These observations and assignments are in broad agreement with those seen in the literature\(^9\), where absorption spectra were taken at 90 K after annealing the adsorbate-covered surface to 290 K. This experiment is similar to the experiments performed at 330 K, as the sample was annealed to 290 K. The absence of a bridge-terrace species in the 330 K experiments compared to the 106 K experiments may be due to it being the least stable of the four different species observed. It is the last species to be observed in the experiments at 106 K, implying that it is the least stable of the four species observed at this temperature. In addition, as the experiments are performed at a higher temperature, the CO sticking probability is expected to be lower and thus the surface coverage is much lower. As a result, this site may not be occupied at 330 K.

Figure 4.14 shows the variation in peak height as a function of exposure for the top-step and top-terrace species in the infrared spectra shown in Figure 4.12. Peak height has again been used as a measure of the relative intensity of the bands as it is difficult to deconvolute the two top species. The graph shows a similar shape, and has comparable
Figure 4.13: RAIR spectra following successive exposure of CO to Pt(211) at 330 K. The spectra shown result from exposures of (a) 1 L, (b) 1.5 L, (c) 2 L and (d) 5 L of CO respectively. The spectra show the low frequency absorption peaks from Figure 4.12.
features, to that for 106 K adsorption shown in Figure 4.3. However, there are some noticeable differences between the two sets of results at the different temperatures.

The most noticeable difference between the results at the two temperatures is the exposure at which the intensity of the top-step species reaches a maximum, and that at which the top-terrace species starts to be observed. In the experiments at 106 K, the first observation of the top-terrace species occurs at an exposure of 0.5 L. In the 330 K experiments this occurs closer to 1.5 L exposure. Both of these effects can be attributed to a higher sticking probability at the lower temperature than at 330 K.

Figure 4.14: Graph to show the variation in intensity of the infrared absorption peaks for the two atop species observed during the adsorption of CO at room temperature. The peak labelled top-step is the species at 2067 cm⁻¹. The species at 2092 cm⁻¹ is labelled top-terrace.
Figures 4.15-4.17 show RAIR spectra for the desorption of CO from the Pt\{211\} surface as the sample is heated following CO exposure at 330 K. As with the liquid nitrogen temperature desorption experiments, the sample was heated to the appropriate temperature, held there for 40 seconds, before being allowed to cool back down and an infrared spectrum taken. Like the adsorption sequence for the room and liquid nitrogen temperature RAIRS experiments, the desorption sequences are also very similar to those observed at the lower temperature, with the peak at 2079 cm\(^{-1}\) being the last observed band in the spectra.

Figure 4.17 shows infrared spectra for the region of the spectrum between 1700 to 2000 cm\(^{-1}\) for the desorption of CO from Pt\{211\}. Again, as with the adsorption sequence at room temperature, only one peak is observed in this region. The intensity of this band is significantly lower than that observed for the top bound species at the step and terrace. As already suggested for the 106 K experiments, this may be due to the molecular orientation with respect to the surface or due to there being less of this species present at the surface.

Figure 4.18 shows the variation in peak height of the three CO species observed in the room temperature infrared desorption spectra (Figures 4.15-4.17) as a function of temperature. This graph shows similar features for the top-terrace and top-step bound CO to those seen for the 106 K experiments (Figure 4.8). The first species to disappear is the top-terrace CO species at 390 K. In addition, at this temperature, the intensity of the top-step species drastically increases as the top-terrace species disappears from the spectrum. A possible explanation for this is that the CO is migrating from the terrace to step sites. Other possible reasons for the increase in peak height of the top-step species include a loss of intensity stealing due to the absence of the top-terrace species, or a change in the orientation of the adsorbate with respect to the surface, or an ordering of the adsorbate due to the elevated temperature and higher mobility of the molecules.
Figure 4.15: RAIR spectra following successive heating of the Pt[211] sample, following a CO dose of 5 L. The initial spectrum (Figure 4.15a) was taken at 330 K. Subsequent spectra, Figures 4.15b-d, were taken following heating to 362, 390 and 410 K.
Figure 4.16: RAIR spectra following successive heating of the Pt\{211\} sample, after being dosed at an exposure of 5 L. The spectra shown here are a continuation of those in Figure 4.15. Figures 4.16a – d are for a sample heated to 425, 450, 475 and 510 K, respectively.
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Figure 4.17: RAIR spectra following successive heating of the Pt\{211\} sample, following an exposure of 5 L. Spectra a-g show the absorption region between 1700 cm\(^{-1}\) and 2000 cm\(^{-1}\) and are the result of heating the sample to 330, 390, 410, 425, 450, 475 and 510 K respectively.
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Figure 4.18: Graph to show the variation in intensity of the three CO species adsorbed on Pt{211} at 330 K as the sample is heated. The absorption peak at 2092 cm⁻¹ is labelled as top-terrace in the graph, and the absorption peak at 2076 cm⁻¹ is labelled as top-step. The peak at 1860 cm⁻¹ is labelled bridge-step in the graph above.

As at 106 K, TPD spectra were also recorded following adsorption at 330 K. Figure 4.19 shows TPD spectra for the adsorption of CO on Pt{211} at 330 K. These spectra again show similar features to those in the literature [9]. As the sample is exposed to a larger dose of gas, the peak temperature of the α peak decreases from 420 K to 402 K. This is a similar decrease to that observed in the experiments starting at 106 K. This observation would imply that the desorption temperature is coverage dependant, and that this species is less strongly bound to the surface with increasing amounts of CO to the surface or that it is second order desorption.
Figure 4.19: TPD spectra for successively increasing exposures of CO to Pt(211) at an initial starting temperature of 330 K. Here the spectra are for CO exposures of (a) 1.5 L, (b) 3 L, (c) 4 L, (d) 5 L and (e) 10 L.
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The ratio between the height of the peak due to terrace and step adsorption is much higher in the experiments at 330 K than at 106 K, with a ratio of 1.4:1. This is in agreement with the greater intensity of the terrace bound atop infrared band seen at 330 K compared to 106 K. This also reflects the ability of the CO molecule to diffuse across the surface in the experiments at 330 K compared to those performed at 106 K.

As with the experiments conducted at 106 K, two desorption features are seen. It is believed that these are again due to step and terrace bound CO species (with the low temperature peak representing the terrace species). As before, theoretical calculations \cite{13, 14, 25} showed the difference in binding energy between terrace and bridge sites to be much more significant than that between top and bridge sites.

It is clear from the TPD spectra shown for adsorption at 106 K (Figure 4.11), that there is a shift of ~ 50 K between the desorption temperatures observed following adsorption at 330 K (Figure 4.19) and at 106 K. This is surprising, as it has already been proposed that these peaks are due to the same desorption species and hence it would be expected that they have the same desorption temperature. One possibility for this observation is an artefact in the experiment. An alternative explanation is that the desorption energy of the step and terrace species is dosing temperature dependant. It is clear from the RAIRS experiments recorded at 106 K that there are four infrared species. However, RAIR spectra recorded at 330 K show only three bands. This suggests that the two sets of experiments do not result in exactly the same adsorption coverage and environment. Hence, it is possible that these different conditions at the two adsorption temperatures could cause the desorption energy of the adsorbed CO to be dosing temperature dependant, leading to the different desorption temperatures seen in the TPD experiments recorded following adsorption at 106 K and 330 K.

4.4 Conclusions

RAIRS and TPD studies have been performed at 106 K and 330 K for the CO on Pt{211} system. From these studies, it has been possible to observe several different features concerning the adsorption of CO on this surface.
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(1) At 106 K it was possible to observe four different species on the surface with RAIRS. These were assigned to the formation of top and bridge bound CO at the step and terrace.

(2) The most stable adsorption species is the top-step species, as it is the first band observed in the RAIR spectra at very low exposures of CO at both 106 and 330 K. It is also the last species observed in the infrared spectra when the sample is heated.

(3) These observations are in broad agreement with previous studies. However, unlike previous studies, it has been possible to resolve the absorption bands for top and bridge bound CO at the step and terrace when adsorption occurred at 106 K. The study at 330 K also yielded similar results to those in the literature.

(4) TPD results show two desorption peaks. These are assigned to the desorption of CO from step and terrace sites of the \{211\} surface. It was not possible to distinguish between the top and bridge bound CO.

In addition, the data in this chapter has shown that the equipment that has been constructed for these experiments is capable of acquiring results comparable to, or better than, those found in the literature for similar systems. This demonstrates that the equipment is fully operational.
4.5 References


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Chapter 5: The adsorption of NO on Pt{211}

5.1 Overview
This chapter presents the results of RAIRS and TPD studies of the interaction of NO with a Pt{211} surface at 120, 300 and 330 K. Also presented are the results of theoretical calculations performed by Zhi-Pan Liu and P. Hu of Queen's University, Belfast, for the NO/Pt{211} system. The calculations have been used to help interpret the experimental results. It is proposed that at 307 K, NO initially adsorbs in a bridge site at the step edge with a vibrational frequency of 1590 cm\(^{-1}\). On further exposure, a NO—O complex, with a vibrational frequency of 1803 cm\(^{-1}\), is formed by a reaction of NO with O atoms formed by the dissociation of NO at the surface. At 120 K the dissociation of NO is suppressed, allowing the population of a top bound NO species at the terrace (1689 cm\(^{-1}\)) and the same step-bridge species that is observed in the experiments at 307 K. On heating the NO overlayer formed by adsorption at 120 K, the NO—O complex observed at 307 K is formed. TPD experiments following adsorption at 120 K show three NO, one N\(_2\) and one N\(_2\)O species in desorption. TPD experiments performed following adsorption at 300 K show similar desorption features, when a heating rate of 1 K s\(^{-1}\) is used. However, TPD experiments following adsorption at 330 K with a heating rate of 8 K s\(^{-1}\) show only two NO species, along with one N\(_2\) and one N\(_2\)O species. Using the information from the RAIRS studies and the theoretical calculations, the three NO species observed in the TPD are attributed to the desorption of the NO—O complex, the recombination of N and O at the surface, and the desorption of the step-bridge NO species respectively. The observation of peaks in the TPD due to N\(_2\) and N\(_2\)O is attributed to the reaction of N atoms with NO at the surface forming N\(_2\)O and the subsequent decomposition into N\(_2\). The absence of O\(_2\) in the desorption spectra is attributed to the diffusion of O atoms into sub-surface sites, in agreement with previous observations on the Pt{211} surface.
5.2 Introduction
The chemistry of NO on surfaces is of great scientific and technological value. One example of this is the reaction of NO over a Pt surface, since Pt has significant activity in the removal of NO in the three-way car exhaust catalyst. In addition to its obvious practical applications, NO is also interesting to study from a basic chemical point of view, due to its significantly lower dissociation energy (630 kJ mol\(^{-1}\)) compared to other similar simple molecules like CO (1076 kJ mol\(^{-1}\)), and also due to its amphoteric nature. Because of the low dissociation energy, there is a considerable probability of finding both molecular and dissociated NO species adsorbed on metal surfaces.

One of the most important substrates for the study of NO adsorption is Pt, due to its aforementioned catalytic reduction of NO. Studying the adsorption of NO on a stepped Pt surface is attractive, as the step sites are regions of high energy and, as a result, increase the probability of finding both molecular and dissociated NO species at the surface. By using a stepped surface as a substrate, it is also possible to learn about the effects of structural defects on surfaces, and their resulting implications.

There have been a limited number of previous studies of the adsorption of NO on Pt\{211\}. These studies have centred around vibrational \(^{[1,2]}\) and desorption based spectroscopic \(^{[3-7]}\) experiments performed at room temperature. No previous theoretical calculations have been performed on this system. In the previous experimental studies, assignments have been made based mainly upon comparison with the low index surfaces that the \{211\} surface is composed of, such as the \{111\} and \{100\} surfaces. This can be a useful and valid method, however it may lead to misassignments of the observed species as the \{211\} surface has a very small terrace width of only three atoms wide, and therefore should be considered as a new surface.

Table 5.1 shows a summary of the previous vibrational studies that have been performed for the adsorption of NO on Pt\{211\} and other related surfaces. The two studies of the NO/Pt\{211\} system by Yates et al\(^{[1,2]}\), performed at 350 K, reported the observation of two vibrational bands at 1593 and 1794 cm\(^{-1}\). At low coverage, only the absorption peak at 1593 cm\(^{-1}\) was observed, with the higher frequency band (1794 cm\(^{-1}\))
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growing into the spectrum with increasing exposure. The band at 1593 cm\(^{-1}\) was assigned to a bridged or bent NO species at the step edge, and the 1794 cm\(^{-1}\) band was assigned to a top bound species at the step. In other vibrational studies of the adsorption of NO on polycrystalline Pt\(^{[7]}\) and defect rich Pt\{111\}\(^{[8]}\) surfaces, similar infrared bands were observed, and similar assignments were made. In the vibrational study of NO on polycrystalline Pt\(^{[7]}\), the absorption band at 1600 cm\(^{-1}\) was resolved into two peaks at 1600-1610 and 1625-1640 cm\(^{-1}\). The peak between 1600-1610 cm\(^{-1}\) was assigned to a bridged or bent NO species at the step edge. Due to the polycrystalline nature of the surface there was ambiguity in the assignment of the band at 1625-1640 cm\(^{-1}\). It was believed that this peak was either due to NO on a terrace site, adjacent to a step site, or to NO adsorbed on a \{110\} facet.

Table 5.1: Table showing the results of previous RAIRS studies of NO on Pt\{211\} and other similar surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorption Temperature / K</th>
<th>Observed vibrational frequencies / cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt{211}(^{[1,2]})</td>
<td>350</td>
<td>1593, 1794</td>
<td>Bridged or bent NO at the step, Terminal NO at the step</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycrystalline Pt foil</td>
<td>300</td>
<td>1600-1610</td>
<td>Bridged or bent NO at the step</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1625-1640</td>
<td>NO on a terrace site, adjacent to a step site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~1800</td>
<td>Linear terminal NO at a step-like defect</td>
</tr>
<tr>
<td>Defect covered Pt{111}</td>
<td>81</td>
<td>1367, 1493-1497, 1591, 1616-1634, 1702, 1813-1820</td>
<td>3-fold hollow site NO, (111) terrace bridged NO, NO at stepped kinked sites, NO in a perturbed top-step site, (111) terrace top NO, Top bound NO at defect sites</td>
</tr>
</tbody>
</table>

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In a study by Agrawal and Trenary of the adsorption of NO on a defect rich Pt{111} surface [8], further absorption bands were observed in addition to those for the Pt{211} system[1, 2]. These bands were at 1367 cm\(^{-1}\), 1493-1497 cm\(^{-1}\) and 1702 cm\(^{-1}\) and were assigned to NO adsorbed in a 3-fold hollow site, a bridge site and a top site at the terrace, respectively. The three other vibrational peaks that were previously assigned to bridge and top bound species by other groups [1, 2, 7] were assigned to different species by Agrawal and Trenary [8]. The 1591 cm\(^{-1}\) band was assigned to NO at a stepped-kinked site, the 1616-1634 cm\(^{-1}\) band was assigned to NO in a step-top site, influenced by other NO molecules, and the 1813-1820 cm\(^{-1}\) band was assigned to NO in a top bound site at a defect.

In light of the information presented above, caution has to be applied when assigning vibrational bands to NO. The various different studies of NO adsorption on Pt{211} [1, 2, 4, 5] and other polycrystalline [6, 7] and defect covered surfaces [8] have all assigned similar vibrational bands to different species. Studies of gas-surface interactions have been done for many years, and vibrational assignments have generally been made by comparison of vibrational frequencies with those measured for organometallic and co-ordination compounds [9, 10]. For the study of NO adsorption on metal surfaces, site assignments are based around the comparison of the vibrational data with NO group stretching frequencies in nitrosyl compounds [11]. However, it has been shown that this comparison may yield misleading conclusions. Several examples of this have been reported for studies of the adsorption of NO on both Ni and Pt surfaces [12-17]. One such illustration of an incorrect assignment was for NO adsorption on a Ni{111} surface [18, 19]. Vibrational studies assigned the observed bands to NO adsorbed in a bridge site, with bent and upright species populated as a function of coverage. However, DFT calculations [20, 21] and diffraction based studies [13, 16, 17] showed that NO was, in fact, adsorbed in a three-fold hollow site over the whole range of exposures.

The adsorption of NO on Pt{211} has also been studied using TPD, UPS and XPS by Sugisawa et al. [5] A summary of these results can be seen in Tables 5.2 & 5.3. The TPD experiments showed three NO desorption peaks at 303, 378 and 488 K, and a N\(_2\) desorption peak at 483 K.
Table 5.2: Table showing the results of previous TPD studies of NO adsorption on Pt\{211\} and other similar surfaces. Shown are the temperatures at which the samples were dosed, the observed atomic mass units (amu) and their desorption temperatures.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorption Temperature / K</th>
<th>Desorption temperature / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stepped Pt{111} [3]</td>
<td>300</td>
<td>Mass 28: 525, 610</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 30: 370, 470</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 44: 450, 480</td>
</tr>
<tr>
<td>Pt{211} [4]</td>
<td>300</td>
<td>Mass 28: 450-500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 30: 370, 483, 500</td>
</tr>
<tr>
<td>Pt{211} [5]</td>
<td>95</td>
<td>Mass 28: 303, 378, 483, 488</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 30: 483, 378, 488</td>
</tr>
<tr>
<td>Polycrystalline Pt [6]</td>
<td>300</td>
<td>Mass 28: 485-460</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 30: 373, 473-503</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 32: 700, 373, 473</td>
</tr>
<tr>
<td>Polycrystalline Pt [7]</td>
<td>300</td>
<td>Mass 28: 490, 400, 480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass 32: 850</td>
</tr>
</tbody>
</table>
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Table 5.3: Table showing a summary of the results of XPS and UPS experiments used to study the adsorption of NO on Pt{211} and related surfaces. Shown are the temperatures at which the experiments were performed, the observed peaks and the assignments of the peaks.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Technique</th>
<th>Temperature / K</th>
<th>Observed peak energy/eV</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt{211} [5]</td>
<td>UPS</td>
<td>95</td>
<td>10.2</td>
<td>$1\pi$ and $5\sigma$ of molecular NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.2</td>
<td>$2\pi$ of molecular NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15.5</td>
<td>$4\sigma$ of molecular NO</td>
</tr>
<tr>
<td>Pt{211} [5]</td>
<td>XPS</td>
<td>95</td>
<td>400.5</td>
<td>N (1s) peak of molecular NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$$</td>
<td>O (1s) peak of molecular NO</td>
</tr>
<tr>
<td>Polycrystalline Pt foil [6]</td>
<td>XPS</td>
<td>330</td>
<td>530.2</td>
<td>O (1s) peak of molecular NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>413</td>
<td>O (1s) peak of atomic oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>483</td>
<td>O (1s) peak of atomic oxygen</td>
</tr>
</tbody>
</table>

$\$- Published as 538.6 eV in Ref. 5. Apparently incorrect.

The NO peaks were attributed to three different types of molecular NO desorbing from the surface. The peaks at 303 and 378 K were assigned to top and bridge bound NO species at the {111} terrace, as the spectra were similar to those for NO on Pt{111} [22]. The highest temperature peak at 488 K was assigned to NO desorbing from the {100} step edge. The N$_2$ peak was attributed to the recombination of N atoms at step sites on the surface. Another significant observation from the TPD experiments was that no O$_2$ desorption (mass 32) was observed. Only after repeated NO exposure and TPD experiments could an O$_2$ desorption peak be observed at 860 K. This observation was attributed to oxygen dissolving into the sub-surface region, and only upon saturation of these sites was oxygen evolved in the desorption spectrum. Similar observations were made by Gohndrone and Masel [4]. In the TPD study by Lee et al [3] of a stepped Pt{111} surface, two desorption features were seen in each of the mass 28, 30 and 44
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spectra. These species were all attributed to the desorption of N\textsubscript{2}, NO and N\textsubscript{2}O from terrace and step sites respectively.

The desorption features observed for the adsorption of NO at 300 K on polycrystalline Pt surfaces \cite{6, 7} are similar to those seen for the NO/Pt\{211\} system, with masses 28 and 30 being observed. However, a noticeable difference was the presence of mass 32 and 44 desorption peaks. This may be due to the number and type of surface defects present, especially the number of step-like defects. The presence of both of these species may also be due to the very high heating rates used in both of these studies.

In the UPS studies \cite{5}, spectra were taken for a saturation exposure of NO. In this study, peaks at 10.2, 15.5 and 2.2 eV below the Fermi edge were observed. These observations were attributed to molecular NO, which was observed to be stable between 100 and 470 K. No peaks were observed for dissociated species such as N and O. XPS studies \cite{5, 6} confirmed the presence of molecular NO by the observation of N (1s) and O (1s) peaks at 400.5 and 538.6 eV, respectively. No peaks representing atomic N (399.5 eV) \cite{23} or O (531.5 eV) \cite{23} were observed. The sample was then heated, and peaks at 399.5 eV and 531.5 eV were observed at temperatures above 483 K. It was thus concluded that NO does not decompose until 483 K on a Pt\{211\} surface.

This Chapter describes a full investigation of the adsorption of NO on Pt\{211\} which has been performed using RAIRS and TPD. The way in which these experiments were performed has been described in Chapter 3. To help with the assignment of NO vibrational bands observed in the RAIR spectra, the vibrational spectra presented here have been compared with previous experiments \cite{1-8} and with the results of theoretical calculations performed by Zhi-Pan Liu and P. Hu of Queen’s University, Belfast.
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5.3 Results

5.3.1 Adsorption of NO on Pt{211} at 307 K

Figure 5.1 shows RAIRS data for the sequential adsorption of NO on Pt{211} at 307 K. An initial absorption peak at 1590 cm\(^{-1}\) is observed at an exposure of 0.05 L. On further exposure of NO, this peak grows in intensity, and shifts up in frequency to 1613 cm\(^{-1}\). At 1 L exposure, this peak shifts back down in frequency to 1601 cm\(^{-1}\) and falls in intensity, and a second absorption peak develops at 1584 cm\(^{-1}\). At this exposure a third absorption feature at 1803 cm\(^{-1}\) is also observed. This peak increases in intensity up to a saturation exposure of 5 L, where the infrared spectra stop changing with increasing exposure of NO. The absorption peak at 1601 cm\(^{-1}\) continues to fall in intensity with increasing NO exposure and the peak at 1580 cm\(^{-1}\) increases in intensity until both features have a similar intensity at saturation.

After the Pt{211} sample was exposed to a saturation dose of NO at 307 K, the sample was annealed to 315 K for 40 seconds before being cooled back down and a RAIR spectrum taken (Figure 5.2). This was repeated for increasing annealing temperatures until no bands were observed in the RAIR spectrum. The resulting infrared spectra are shown in Figure 5.2. On initial heating to 315 K, the intensity of the peaks at 1610 and 1580 cm\(^{-1}\) increases, and the peak at 1800 cm\(^{-1}\) loses intensity. By 350 K, this species has disappeared from the spectrum. On further heating, the two peaks initially seen at 1610 and 1580 cm\(^{-1}\) merge into one peak at 1597 cm\(^{-1}\). This peak grows to a maximum intensity at 375 K, before falling in intensity and disappearing by 451 K.

Figure 5.3 shows TPD spectra recorded following a saturation exposure of NO on Pt{211} at 330 K, with a heating rate of 8 K s\(^{-1}\). It can be seen from the spectra that there are two desorption features in the mass 30 spectrum, labelled \(\alpha\) and \(\beta\), at 471 and 393 K respectively. Desorption peaks for masses 28 and 44 are also observed. These desorption features are in coincidence with each other, with a desorption temperature of 482 K.
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Figure 5.1: RAIR spectra for the sequential adsorption of NO on the Pt\{211\} surface at 307 K. The NO exposures are indicated on the figure.
Figure 5.2: RAIR spectra showing the sequential heating of the Pt{211} sample after a saturation dose of NO at 307 K. The temperatures to which the sample was annealed are shown on the figure.
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Figure 5.3: TPD spectra following a 5 L exposure of NO on Pt\{211\} at 330 K, at a heating rate of 8 K s\(^{-1}\). The spectra shown are for the desorption of mass units 28, 30 and 44.

TPD experiments were also performed as a function of increasing NO exposure at 330 K. In these experiments a single desorption peak at 470 K was observed following an NO exposure of 0.05 L. On increasing the NO exposure, this peak did not shift in desorption temperature, however it increased in intensity with increasing coverage to reach a maximum intensity at an NO exposure of 0.5 L. Following an NO exposure of 0.2 L, a second desorption feature at \(\sim 390 \) K is also seen in the spectrum. Desorption sequences as a function of increasing NO exposure were also recorded for masses 28 and 44. In these spectra, desorption peaks for both masses were observed even at very low NO exposures. With increasing NO exposure the peaks due to mass 28 and 44 grew in intensity, until a saturation dose of 5 L when the spectrum seen in Figure 5.3 was observed.

Further TPD experiments were also recorded at a heating rate of 1 K s\(^{-1}\). Figure 5.4 shows TPD spectra for masses 28, 30 and 44 for a saturation dose of NO (20 L) at 300 K. These spectra show similar features to those seen in Figure 5.3, where the heating rate was 8 K s\(^{-1}\). However, in the spectra shown in Figure 5.4 it is possible to
resolve the first peak in the mass 30 spectrum into two peaks, at 321 K and 353 K. The mass 28 and 44 peaks are still in coincidence, with a peak at 440 K.

![TPD spectra of a Pt{211} sample following a 20 L exposure of NO at 300 K, at a heating rate of 1 K s\(^{-1}\). The spectra shown are for the desorption of mass units 28, 30 and 44.]

In all of the TPD experiments, mass 32 was also monitored to check for the desorption of O\(_2\). However, no signal was observed for this species over all exposures of NO, and up to a desorption temperature of 1000 K.

### 5.3.2 Adsorption of NO on Pt{211} at 120 K

Figure 5.5 shows RAIRS data for the sequential adsorption of NO on Pt{211} at 120 K. There is an initial absorption feature seen at 1612 cm\(^{-1}\). On further exposure of NO, this peak increases in intensity to reach a maximum at 0.5 L exposure. Further increasing the exposure of NO causes this peak to decrease in intensity and shift down in frequency to reach 1620 cm\(^{-1}\) at saturation. At 1 L exposure, a second absorption feature is seen in the infrared spectrum, at 1689 cm\(^{-1}\).
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Figure 5.5: RAIR spectra for the sequential adsorption of NO on the Pt{211} surface at 120 K. The NO exposures are marked on the figure.
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This peak grows in intensity until it reaches a maximum at 20 L NO exposure. No other absorption features are seen in the infrared spectra at this temperature.

After the Pt\{211\} sample was exposed to 20 L of NO at 120 K, it was annealed to 153 K for 40 seconds before being cooled back down to 120 K and a RAIR spectrum taken. This was repeated for increasing annealing temperatures until no bands were observed in the RAIR spectra. The resulting infrared absorption spectra are shown in Figure 5.6. On initial heating, the absorption peak at 1620 cm\(^{-1}\) increases in intensity to reach a maximum at 260 K and shifts up in frequency to 1634 cm\(^{-1}\). The peak at 1688 cm\(^{-1}\) slowly decreases in intensity and disappears from the spectrum by 260 K. On further heating to 330 K, absorption features at 1615 and 1594 cm\(^{-1}\) appear in the spectrum. With further heating, these peaks merge to form one peak at 1606 cm\(^{-1}\). This peak falls in intensity on further heating and disappears from the spectrum by 450 K. Also seen in these spectra is the formation of an absorption peak at 1802 cm\(^{-1}\), which appears at 230 K. On further heating, this peak increases in intensity to a maximum at 300 K, after which the peak falls in intensity, and disappears from the spectrum by 360 K.

As with the data at 307 K, TPD experiments were also performed following NO exposure at 120 K, with a heating rate of 8 K s\(^{-1}\). Figure 5.7 shows the TPD spectra which result from a saturation dose of NO at 120 K. Masses 28, 30 and 44 were monitored. As can be seen from the spectra, there are three desorption peaks in the mass 30 spectrum (labelled \(\alpha\), \(\beta\) and \(\gamma\)) at 503, 416 and 338 K. Also seen in the spectra are desorption peaks at 515 and 510 K for masses 28 and 44 respectively.
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Figure 5.6: RAIR spectra showing the sequential heating of the Pt\{211\} sample after a saturation dose of NO at 120 K. The temperatures to which the sample was annealed are marked on the figure.
Figure 5.7: TPD spectra following a 5 L exposure of NO to Pt{211} at 120 K, at a heating rate of 8 K s\(^{-1}\). The spectra shown are for the desorption of mass units 28, 30 and 44.

Figure 5.8 shows a desorption sequence for NO as a function of increasing NO exposure at 120 K. This shows similar features to the desorption spectra in the 330 K experiments. There is an initial desorption peak (\(\alpha\)) seen at 500 K at an NO exposure of 0.05 L. On increasing the NO exposure to 0.5 L, a second lower temperature peak (\(\beta\)) appears in the desorption spectrum at 413 K. This peak increases in intensity with increasing NO exposure. Further to the desorption of the \(\alpha\) and \(\beta\) peaks, a lower temperature peak, labelled \(\gamma\), is seen at 334 K. This peak also grows in intensity with increasing NO exposure. By 5 L exposure a similar saturation spectrum to that seen in Figure 5.7 is obtained.

As with the experiments conducted at 307 K and 330 K, the sample was taken to 1000 K in the effort to observe a mass 32 signal. However, no such signal was observed.
Figure 5.8: NO TPD spectra at a heating rate of 8 K s$^{-1}$ following exposure of a Pt{211} surface held at 120 K to various exposures of NO.
5.3.3 Theoretical studies of the adsorption of NO on Pt{211}

To help understand the observations of the RAIRS and TPD experiments, theoretical calculations were performed for the NO on Pt{211} system by Zhi-Pan Liu and P.Hu of Queen's University Belfast. Calculations were performed using density functional theory (DFT) with the generalized gradient approximation (GGA) \(^{[24]}\). The program used to perform these calculations was CASTEP \(^{[25]}\). Calculations were performed with the electronic wave functions expanded in a plane wave basis set and the ion cores were described by ultrasoft pseudopotentials \(^{[26]}\). The vacuum region between slabs was 10 Å, and a cut-off energy of 340 eV was used. Monkhorst-Pack k-point sampling with 0.07 Å\(^{-1}\) spacing was utilized for all of the calculations. The Pt{211} surface was modelled by (1x2) (1/6 ML) or (1x3) (1/9 ML) unit cells with three effective layers, as shown in Figure 5.9. In all of the calculations, the top layer of the slab was relaxed and the other layers were fixed at the bulk-truncated structure.

![Illustration of the geometrical structures of the modelled Pt{211} surface: a top view (left) and a side view (right). The dotted line shows the (1x2) unit cell of Pt{211}. The step-edge Pt atoms are white balls \(^{[27]}\).](image)

To assist the characterization of the infrared spectra observed in the experiments, the stretching frequencies of NO in various configurations on Pt{211} were calculated. In order to evaluate the systematic error in the calculated NO stretching frequencies in a Pt surface-NO bonding environment, NO adsorption on flat Pt{111} was first calculated. For this system, the experimental value for the NO stretching frequency on the
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fcc hollow site is available (1476-1498 cm\(^{-1}\) [22, 28]). The calculated value was 1608 cm\(^{-1}\), which is 121 cm\(^{-1}\) larger than the experimental value. In light of this, 121 cm\(^{-1}\) was subtracted from each calculated NO stretching frequency on Pt{211} and the result was taken as the predicted value hereafter. Previous work [26, 29-33] has demonstrated that the above set-up for the DFT total energy calculation [31, 33] and the vibrational frequency calculation [32] affords good accuracy. Figure 5.10 shows a schematic diagram of the \{211\} surface, showing the five different NO adsorption sites for which calculations were performed. These sites were the step-bridge (SB), step-hollow (SH), step-top (ST), terrace-bridge (TB) and terrace-top (TT) sites.

![Figure 5.10: A schematic diagram of the Pt{211} surface, showing the sites on which NO adsorption was investigated theoretically. Labelled are adsorption sites for NO on the Pt{211} surface: SB (step-bridge), terrace (terrace-hcp-hollow), ST (step-top), TB (terrace-bridge) and TT (terrace-top).](image)

Tables 5.4 and 5.5 show the results of these calculations for each of the sites shown in Figure 5.10. It was found that the most stable molecularly adsorbed NO species on the Pt{211} surface is a bridge species at the step edge, with a calculated adsorption energy of 227 kJ mol\(^{-1}\), and a predicted vibrational frequency of 1586 cm\(^{-1}\). The next most stable species calculated was a hollow species, also at the step edge. This species has an adsorption energy of 186 kJ mol\(^{-1}\) and vibrational frequency of 1558 cm\(^{-1}\). The N—O bond length for this species is 1.203 Å, and the N-Pt bond lengths are 2.027, 2.026 and 2.333 Å, with the longer length of 2.333 Å being that made to the Pt atom at the step.
Other adsorption sites calculated were atop species at the step and terrace. These species had adsorption energies of 177 and 137 kJ mol\(^{-1}\), and vibrational frequencies of 1664 and 1670 cm\(^{-1}\) respectively.

Table 5.4: Table showing the theoretically calculated adsorption energies and the predicted NO vibrational frequencies for NO adsorbed in different sites on Pt\{211\}. These species correspond to the sites shown in Figure 5.10.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption energy / kJ mol(^{-1})</th>
<th>Predicted N—O vibrational frequency / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step-bridge (SB)</td>
<td>227</td>
<td>1586</td>
</tr>
<tr>
<td>Step-hcp-hollow (SH)</td>
<td>186</td>
<td>1558</td>
</tr>
<tr>
<td>Step-top (ST)</td>
<td>177</td>
<td>1664</td>
</tr>
<tr>
<td>Terrace-bridge (TB)(^\S)</td>
<td>166</td>
<td>1586</td>
</tr>
<tr>
<td>Terrace-top (TT)(^\S)</td>
<td>137</td>
<td>1670</td>
</tr>
</tbody>
</table>

\(^\S\) - NO adsorption on terrace-top and terrace-bridge sites was calculated with the step-bridge sites already occupied by NO molecules.

Table 5.5: Table showing the bond geometries for NO adsorbed at various sites on Pt\{211\}.

<table>
<thead>
<tr>
<th>Species</th>
<th>N—O bond length / Å</th>
<th>N—Pt bond length / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO (SB)</td>
<td>1.199</td>
<td>1.970</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.968</td>
</tr>
<tr>
<td>NO (SH)</td>
<td>1.203</td>
<td>2.027</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.333</td>
</tr>
<tr>
<td>NO (ST)</td>
<td>1.181</td>
<td>1.887</td>
</tr>
<tr>
<td>NO (TB)(^\S)</td>
<td>1.198</td>
<td>2.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.012</td>
</tr>
<tr>
<td>NO (TT)(^\S)</td>
<td>1.179</td>
<td>1.949</td>
</tr>
</tbody>
</table>

\(^\S\) - NO adsorption on terrace-top and terrace-bridge sites was calculated with the step-bridge sites already occupied by NO molecules.

### 5.4 Discussion

#### 5.4.1 RAIRS

The theoretical calculations show that the most stable adsorption site for NO on Pt\{211\} is a step-bridge site (see Table 5.4), with a predicted vibrational frequency of 1586 cm\(^{-1}\).
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It can be seen in Figure 5.1 that in the experiments conducted at 307 K, an absorption band with a frequency of 1590 cm\(^{-1}\) is observed at low coverage. This band is the first to appear in the spectrum, and hence corresponds to the most stable NO species on the surface. It is therefore proposed that this band is due to NO adsorbed in a step-bridge site. This assignment is consistent with the previous assignment made by Yates et al.\(^{[1,2]}\) in their study of the NO/Pt\{211\} system. As the surface is further exposed to NO, this band increases in intensity and shifts up in frequency to 1613 cm\(^{-1}\). This frequency shift is most likely due to dipole-dipole coupling between the adsorbed molecules.

As the surface is further exposed, up to 1 L of NO, two other absorption features appear in the spectrum, at 1803 cm\(^{-1}\) and 1584 cm\(^{-1}\). As in the literature\(^{[1,2]}\), one possible assignment of the peak at 1803 cm\(^{-1}\) is to a top bound NO species at the step-edge. However, as seen in Table 5.4, the predicted vibrational frequency for this species, 1664 cm\(^{-1}\), is much lower than the experimentally observed frequency. In addition, the calculated binding energy of the step-top species is lower than that of the step-bridge species. As the top bound species would have to displace the bridge species to form, this is energetically unfavourable. It is therefore suggested that this absorption peak is not due to NO in a top site at the step edge as previously indicated\(^{[1,2]}\), but due to another NO infrared active species. Possible sources of the absorption peak at 1803 cm\(^{-1}\) are:

- An (NO)\(_2\) dimer species.
- An N\(_2\)O molecule.
- An N—O vibrational stretch of a complex formed between N or O atoms and NO.

The formation of (NO)\(_2\) has been observed on metal surfaces such as Ag, Pd, Pt and Cu\(^{[34-39]}\), and vibrational frequencies of between 1688 cm\(^{-1}\) and 1850 cm\(^{-1}\) have been observed for this species. However, in most of these experiments (NO)\(_2\) was only observed at temperatures lower than 120 K, typically at temperatures below 60 K. Calculations were performed to determine the vibrational frequencies of (NO)\(_2\) adsorbed...
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on the Pt\{211\} surface. Theory showed that the (NO)_2 species gives rise to predicted vibrational bands at 1607 and 1680 cm\(^{-1}\). Hence, it is not thought that the band at 1800 cm\(^{-1}\) is due to the formation of (NO)_2.

The formation of N\(_2\)O, following the interaction of NO with the surface, has been observed on several metals including Ag and Cu\(^{[34, 35, 40, 41]}\). In addition, N\(_2\)O is seen to form in the TPD spectra following adsorption of NO on Pt\{211\} as seen in Figures 5.3, 5.4 and 5.7. The vibrational frequencies that have been previously observed for N\(_2\)O are between 1250-1275 cm\(^{-1}\) and 2229-2242 cm\(^{-1}\)\(^{[34, 35, 41]}\). Calculations were also performed for N\(_2\)O adsorbed on Pt\{211\} and the predicted vibrational frequency of this species was 2250 cm\(^{-1}\). This is consistent with observations made for other systems. However, it is not consistent with the bands observed for the adsorption of NO on Pt\{211\}, as seen in Figure 5.1. Therefore, it is not believed that the absorption band at 1803 cm\(^{-1}\) is due to the formation of N\(_2\)O at the surface.

The theoretical calculations by Liu and Hu found that an NO molecule adsorbed on an O atom in a step-bridge site has a predicted vibrational frequency of 1813 cm\(^{-1}\). This vibrational frequency is much closer to that observed in the experimental studies. Hence the band observed at 1803 cm\(^{-1}\) is tentatively assigned to the formation of a complex between NO and O atoms adsorbed on a step-bridge site. The source of the O atoms is most likely dissociated NO molecules. This idea is in direct contradiction to previous studies that have suggested that NO does not dissociate on Pt\{211\} until 483 K\(^{[5]}\). Results of XPS experiments for the adsorption of NO on polycrystalline Pt show similar observations\(^{[6]}\). In this study, a single peak was observed at 530.2 eV, at 343 K\(^{[6]}\), with a width of 2 eV. This peak represented the 1s peak for O in NO. On heating to 453 K, this peak underwent a chemical shift of 1.4 eV, to 528.8 eV, representing the formation of the 1s peak of atomic O. This implied that, on heating, the majority of the adsorbed NO dissociated. However, due to the width of the initial peak seen at 343 K, it cannot be conclusively stated that dissociation had not occurred. It is possible that the 1s peak of the atomic O species was masked by the molecular species at this temperature. In particular, this could occur if only a small amount of atomic O was present on the surface at 343 K. As the sample was heated, more of the
atomic O was formed and the NO species was lost from the surface, resulting in the peak due to atomic O dominating the spectrum.

In contradiction to the XPS work, a study by Banholzer et al.\textsuperscript{[42]} showed that the variation in the rate of decomposition of NO on a Pt surface changed as a function of surface structure. In this study they noted that, when going from Pt\{111\} to Pt\{411\}, there is a large change in the symmetry of the orbitals available to interact with NO and thus in the ability of the surface to dissociate NO. It was noted for the Pt\{111\} surface that the orbitals available to interact with NO have a symmetry which is unfavourable for NO dissociation. However this symmetry is reduced as the surface is altered to the \{411\} surface, where almost 98\% NO dissociation is predicted\textsuperscript{[42]}. One of the largest effects that lowers the symmetry of the surface, and causes the resulting dissociation of NO, is the presence of steps on the surface. Hence, in agreement with the observations made here, a Pt\{111\} surface with \{100\} steps should show activity for NO dissociation, as the step is similar to the Pt\{411\} surface that shows high NO dissociation\textsuperscript{[42]}.

Further evidence that dissociation may be occurring on the Pt\{211\} surface comes from the temperature dependence of the 1803 cm\(^{-1}\) band. In the RAIRS experiments for the adsorption of NO at 120 K (Figure 5.5) the peak at 1803 cm\(^{-1}\) is not observed in the adsorption sequence. This implies that the dissociation of NO at 120 K is suppressed, preventing the formation of the 1803 cm\(^{-1}\) peak. However, when this surface is heated to 230 K (Figure 5.6) a peak at 1802 cm\(^{-1}\) grows into the spectrum. It is likely that this peak appears in the spectrum at 230 K due to the onset of NO dissociation.

Even though the proposed NO—O species is formed from the adsorption of NO onto an O atom, it must be noted that this species is not an NO\(_2\) molecule. The adsorption of NO\(_2\) on various metal surfaces has been investigated\textsuperscript{[43-49]}. In all of these studies, multiple absorption peaks have been observed, representing the ONO bend and the ONO symmetric and anti-symmetric stretch modes. The highest absorption frequency observed is the ONO anti-symmetric stretch on Pt\{111\}\textsuperscript{[48, 49]}, which occurs at 1560 cm\(^{-1}\). This is a significantly lower frequency than the observed peak at 1803 cm\(^{-1}\).
Here only one absorption peak is attributed to the NO—O species, whereas multiple absorption peaks would be expected to be observed for an NO$_2$ molecule on Pt$\{211\}$. In addition, the binding energy of the NO molecule to the adsorbed O atom in the NO—O complex is calculated to be 68 kJ mol$^{-1}$, compared to 305 kJ mol$^{-1}$\textsuperscript{50} for the N—O bond in NO$_2$. Also, the calculated bond length between the step-bridged O and the NO is 1.776 Å, compared to 1.188 Å for the NO bond in NO$_2$\textsuperscript{50}. Thus, the NO—O complex shows a very different bond structure compared to that observed in gas phase NO$_2$.

As already stated, a third species, which has a vibrational frequency of 1584 cm$^{-1}$, is observed in the spectrum at the same time as the NO—O complex. This band shifts down to 1576 cm$^{-1}$ with increasing NO exposure. A possible assignment for this species is that of a 3-fold hollow species at the step. From the theoretical calculations (see Table 5.4) it was found that this is the second most stable species at the surface. However, it is not clear why this species should be formed in preference to the step-bridge species, as they occupy similar regions of the surface. In addition, at the point where this band appears in the spectrum, it is likely that the steps are already saturated with bridged NO, and hence there would be no room for the NO to adsorb into a 3-fold site at the step. It is therefore proposed that the two peaks observed between 1576 cm$^{-1}$ and 1609 cm$^{-1}$ are due to NO adsorbed in a step-bridge site in two different environments. It has already been proposed that the frequency of the band due to the step-bridged species increases due to dipole-dipole coupling between the adsorbed molecules. However, this frequency shift may also be due to the influence of adsorbed O atoms from dissociated NO. When NO is adsorbed in the presence of pre-dosed O atoms (see Chapter 6) the frequency of the N-O vibration is observed to increase with increasing O$_2$ pre-dose. As the NO—O complex is formed, O atoms are no longer available to directly influence the step-bridged NO species. This gives rise to a mixture of perturbed and unperturbed step-bridged NO species on the surface, and thus the observation of the double peak between 1576 and 1609 cm$^{-1}$. The higher frequency peak, at 1609 cm$^{-1}$, is assigned to NO influenced by O atoms and the lower frequency peak, at 1576 cm$^{-1}$, is assigned to NO which is not influenced by O atoms. The observed frequency of the unperturbed step-bridged NO species, 1584 cm$^{-1}$, is very
close to the predicted vibrational frequency found for step-bridged NO in the theoretical calculations, further confirming this band assignment.

In the RAIRS study of the desorption of NO from Pt\{211\}, shown in Figure 5.2, it can be seen that, on heating, the peak at 1800 cm\(^{-1}\) starts to fall in intensity and has disappeared from the spectrum by 350 K. This observation is consistent with the proposed assignment of this band to the NO—O complex, since the binding energy of NO to the O atom was found to be only 68 kJ mol\(^{-1}\). Therefore, it would be expected that this would be the first NO species to desorb from the surface.

Another observation on heating is the fact that the double peak at 1610 cm\(^{-1}\) and 1580 cm\(^{-1}\) grows in intensity and merges into one peak, at 1597 cm\(^{-1}\), by 350 K. These two bands have already been assigned to step-bridged NO in different environments: either influenced by nearby O atoms (the 1610 cm\(^{-1}\) peak) or not influenced by nearby O atoms (the 1580 cm\(^{-1}\) peak). It is believed that heating a Pt\{211\} surface causes the adsorbed O atoms to dissolve into the sub-surface region \[^{51}\]. This suggestion is supported by the fact that no O\(_2\) is observed in the TPD spectra from NO dosed Pt\{211\}, as seen by Sugisawa et al \[^5\] and the present study. If the O atoms go sub-surface, they are no longer available to influence the step-bridged NO species when the surface is heated. As a result, this causes all of the step-bridged NO to revert to one type, and the doublet peak merges to form one peak. The frequency of the resulting peak (Figure 5.6) is very close to the lower frequency absorption peak, agreeing with the previous assignment of this peak to the step-bridged NO species uninfluenced by O atoms. This absorption peak is the last one to disappear from the RAIR spectrum, supporting the evidence that the step-bridged NO is the most stable species at the surface.

In the adsorption experiments conducted at 120 K (Figure 5.5), it can be seen that the NO/Pt\{211\} system is strongly temperature dependent, as a different adsorption sequence is observed compared to the experiments conducted at 307 K (Figure 5.1). An initial absorption peak is observed at 1612 cm\(^{-1}\), which increases in intensity with increasing NO exposure. This peak is similar to the initial band observed in the
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experiments at 307 K (Figure 5.1). Therefore, this peak is also assigned to NO adsorbed in a step-bridge site. The fact that this species is also the first to be observed on adsorption at 120 K further confirms the assignment of this band to the step-bridge site, since calculations suggest that this is always the most stable surface species. The observed frequency of the band, 1612 cm\(^{-1}\), is 22 cm\(^{-1}\) higher than that observed at 307 K. This may be due to a higher sticking probability at the lower adsorption temperature, which means that more NO is adsorbed, thus increasing the dipole-dipole coupling between the molecules at the surface.

On further exposure of NO to the surface, a second absorption peak at 1689 cm\(^{-1}\) is observed (Figure 5.5). This peak grows to dominate the spectrum at saturation. This band has a frequency higher than that of the bridge bound species and hence it is suggested that it is due to the presence of a top bonded NO species on the Pt{211} surface. Indeed, theoretical calculations show that, after the step bridge and step-hollow species, the next most stable species are top bound NO at the step (177 kJmol\(^{-1}\)) and at the terrace (137 kJmol\(^{-1}\)). These species both have a higher calculated vibrational frequency than the bridge bonded NO species. It is therefore suggested that the band at 1689 cm\(^{-1}\) is due to a top bound NO species. Since the step edge is already decorated with NO molecules in bridge sites, it is proposed that this species is in fact due to NO in top sites on the \{111\} terraces. This top species was not seen at 307 K. In experiments investigating the dissociative adsorption of NO on Ru\(^{[52]}\), dissociation was observed to occur at the step. The resulting O atoms remained at the step, and the N atoms migrated to terrace sites. Assuming that this also occurs for the NO/Pt{211} system, this explains why top bound NO is only seen at low temperatures, as at 307 K all of the terrace sites are filled with atomic N, preventing the adsorption of NO at the terrace.

In contrast to the RAIR spectra recorded at 307 K (Figure 5.6), no absorption peak at 1803 cm\(^{-1}\) was observed in the experiments at 120 K. Since this band has been already assigned to the presence of an NO—O complex this implies that dissociation is suppressed at 120 K, preventing the formation of the complex.
In the heating sequence, starting at 120 K, there is no significant change in the absorption spectrum until 230 K. At this temperature, the band at 1688 cm$^{-1}$ disappears from the spectrum and, at the same time, a peak at 1802 cm$^{-1}$ is observed. It is not thought that the species observed at 1688 cm$^{-1}$ desorbs from the surface, as no NO desorption peak is seen in the TPD experiments until 300 K (see section 5.4.2). Therefore, the NO must remain at the surface, but become adsorbed in a different site. One way that this could occur would be if the NO migrates across the surface to form a new adsorption species. Since the band at 1802 cm$^{-1}$ is formed at the same time as the 1688 cm$^{-1}$ peak is lost, it is possible that the terrace-top NO migrates across the surface to form a new species which gives rise to the 1802 cm$^{-1}$ band.

As for the RAIRS spectra recorded following NO adsorption at 307 K, the band at 1802 cm$^{-1}$ is assigned to the formation of the NO—O complex at the step edge. Hence the loss of the 1688 cm$^{-1}$ band, and the appearance of the band at 1802 cm$^{-1}$, at 230 K is assigned to the migration of the terrace top NO species to the step edge, where it forms the NO—O complex.

The observation of the 1802 cm$^{-1}$ band following heating to 230 K also suggests that at temperatures above 230 K, dissociation of NO on Pt{211} can occur. It is likely that the N atoms formed from the dissociated NO diffuse to the terrace, thus displacing the terrace-top NO species. This results in the terrace-top NO migrating to the steps to form the NO—O complex. It is expected that dissociation of NO will occur at the step-edge due to the unsaturated nature of the stepped surface. Thus, it is believed that it is the step-bridged NO that dissociates to give the N and O atoms at the surface. This is supported by the observed fall in intensity, and almost disappearance, of the peak at 1634 cm$^{-1}$ (representing the step-bridge species) following heating to 300 K, as seen in Figure 5.6. However, it is not clear why the band at 1606 cm$^{-1}$ reappears at 360 K (Figure 5.6), although re-adsorption of NO from the dissociation of the NO—O complex, may occur on heating.
5.4.2 TPD
TPD experiments following dosing at 120 K, with a heating rate of 8 K s\(^{-1}\), showed three mass 30 species, one mass 28 and one mass 44 species (Figure 5.7). Figure 5.8 shows sequential desorption spectra for NO from the surface with increasing exposure. At low coverage there is only one NO desorption feature at 500 K (labelled \(\alpha\) in Figures 5.7 & 5.8). With increasing exposure, a lower temperature desorption peak grows in at 413 K (labelled \(\beta\), and ultimately the lowest temperature desorption peak grows in at 334 K (labelled \(\gamma\)). A similar desorption sequence was observed by Sugisawa \textit{et al} \cite{Sugisawa1995} for the desorption of NO from Pt\{211\} dosed at 95 K. The theoretical calculations (Table 5.4) show that the step-bridge species is the most stable NO species on the surface. In addition, the RAIRS experiments indicate that the only NO species observed at low exposures is the step-bridge species. It is also the last species that is observed in the RAIRS experiments as the sample is heated. Therefore the NO\(_\alpha\) desorption peak is attributed to the desorption of step-bridged NO from the surface. The least strongly bound NO species predicted from the calculations is NO adsorbed on an O atom in a step-bridge site. Hence, the lowest temperature NO desorption peak (NO\(_\gamma\)) at 334 K is attributed to NO desorption from the NO—O complex. This assignment is different to that made in the literature \cite{Sugisawa1995} as it was previously believed that NO does not dissociate on Pt\{211\} until 483 K.

The only remaining peak in the mass 30 TPD spectrum is that labelled \(\beta\) in Figures 5.7 & 5.8. This peak is attributed to the recombination of N and O at the surface. It has already been established that the NO\(_\alpha\) and NO\(_\gamma\) species are formed from the desorption of step-bridged NO and the decomposition of the NO—O complex respectively. To identify the NO\(_\beta\) peak, the formation of the NO—O complex has to be considered. Figure 5.11 shows a flow diagram to demonstrate the formation of the NO—O complex at the surface. It has been established from the RAIRS experiments that, at 120 K, only step-bridged and terrace-top NO species are formed. However, on heating, some of the NO at the step dissociates to form atomic N and O, with the O atoms remaining at the step and the N atoms migrating to the terrace \cite{Sugisawa1995}. As the N migrates to the terrace, this displaces the top bound terrace NO, and the band due to the terrace-top NO completely
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Adsorption of NO on Pt\{211\} at 120 K

Heat

Dissociation of NO at the step

Displacement of terrace-top NO by adsorbed N atoms

1. Formation of NO-O complex
2. Adsorbed step-bridged NO
3. Adsorbed atomic N at the terrace

Figure 5.11: Flow diagram to show the dissociation of NO at the Pt\{211\} surface and the subsequent formation of the NO—O complex.
disappears from the RAIR spectrum by 260 K. Instead of desorbing from the surface, it is suggested that this NO moves to the step edge to form the NO—O complex. Since the step-bridged NO is seen to desorb above 400 K in the RAIRS, and the NO from the NO—O complex desorbs from the surface by 360 K, the only remaining surface species are atomic N and O. It is therefore suggested that the NO$_\beta$ peak, seen at 413 K, arises as a result of recombinative desorption of these N and O atoms.

An alternative explanation for the assignment of the $\alpha$ and $\beta$ desorption peaks is to the desorption of NO from N and O recombination, and to the desorption of NO from step-bridge sites, respectively. This is the reverse of the assignments previously made. This interpretation arises from the fact that the band seen in the RAIRS experiments (Figure 5.6) at 1606 cm$^{-1}$, representing the step-bridged species, disappears from the spectrum between 400 K and 450 K. This temperature corresponds to the temperature of the $\beta$ peak seen in the TPD spectrum (Figure 5.7). The remaining $\alpha$ peak would then be assigned to N and O recombination. However, it is noted that the heating rate used in the RAIRS experiments (0.5 – 2 K s$^{-1}$) is different to that used in the TPD spectra shown in Figure 5.7 (8 K s$^{-1}$). As a result, one would expect a higher desorption temperature for the increased heating rate used in the TPD experiments, compared to the RAIRS experiments. When the RAIR spectra are compared with the TPD spectra presented in Figure 5.4, where a 1 K s$^{-1}$ heating rate was used, it is quite clear that the highest temperature desorption peak occurs between 400 and 450 K. This is exactly the same temperature at which the RAIRS band assigned to the step-bridge species is observed to disappear from the spectrum seen in Figure 5.6. This therefore supports the original assignment of the $\alpha$ TPD peak to step-bridged NO and not to N and O recombination.

Also observed in the TPD experiments following dosing of NO at 120 K (Figure 5.7) and at 330 K (Figure 5.3) are peaks due to N$_2$O and N$_2$ desorption. These peaks are in coincidence, with a desorption temperature of 515 K, implying they are from the same source. One possible explanation for the coincidence of these peaks is that N$_2$O is formed on the surface and subsequent cracking of the N$_2$O occurs in the mass spectrometer, also producing the N$_2$ peak, as shown in Equation 5.1.
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\[ N_2O(g) \rightarrow N_2(g) + O_2(g) \] \hspace{1cm} \text{Equation 5.1}

Figure 5.12 shows a cracking pattern for N\textsubscript{2}O recorded using the same mass spectrometer used for the TPD experiments. It can be seen that N\textsubscript{2}O cracks into masses 44, 28 and 30, in the ratio of 5:4:1 for the three different gases. Figure 5.7 shows that there is a much larger quantity of N\textsubscript{2} formed in the TPD experiments than that which arises due to N\textsubscript{2}O cracking alone. Hence, there must be another source of N\textsubscript{2} in addition to any N\textsubscript{2} produced from the cracking of N\textsubscript{2}O in the mass spectrometer.

![Mass spectrum](image)

**Figure 5.12:** Mass spectrum resulting from an N\textsubscript{2}O dose of $1 \times 10^{-7}$ mbar in the UHV chamber. The graph shows the relative intensities for masses 28, 30 and 44.

It has already been suggested from the RAIRS experiments that NO dissociates on the Pt\{211\} surface above room temperature. Therefore, another possible explanation for the formation of both the N\textsubscript{2} and N\textsubscript{2}O is by the recombination of N atoms or N atoms...
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with NO at the surface. As already stated, N\textsubscript{2} and N\textsubscript{2}O are observed in coincidence in the TPD spectrum. For this to occur, either the activation energy for the formation of both of these molecules at the surface is the same, or the formation of both of these species is dictated by a common factor. Since both of these species involve the reaction of adsorbed N atoms, it is possible that the formation of N\textsubscript{2} and N\textsubscript{2}O may be mediated by the diffusion of N atoms on the surface. Equation 5.2 shows a possible mechanism for the formation of N\textsubscript{2} at the surface.

\[ N_{\text{(ad)}} + N_{\text{(ad)}} \rightarrow N_2(g) \quad \text{Equation 5.2} \]

Unlike the formation of N\textsubscript{2}, there are various possible reaction mechanisms for the formation of N\textsubscript{2}O at the surface\textsuperscript{[53]}. These are shown in Equations 5.3 & 5.4.

\[ NO_{\text{(ad)}}^{\text{step}} + N_{\text{(ad)}}^{\text{terrace}} \rightarrow N_2O(g) \quad \text{Equation 5.3} \]
\[ NO_{\text{(ad)}} + NO_{\text{(ad)}} \rightarrow (NO)_{2\text{(ad)}} \]
\[ (NO)_{2\text{(ad)}} \rightarrow N_2O(g) + O_{\text{(ad)}} \quad \text{Equation 5.4} \]

The first equation shows the reaction of adsorbed NO and N at the surface, forming N\textsubscript{2}O. NO is present at the step and the N atoms are at the terrace. Therefore, the reaction mechanism for the formation of the N\textsubscript{2}O is via the diffusion of the N atoms to the step edges. The N atoms then react with the NO at the step sites to form N\textsubscript{2}O, which subsequently desorbs.

The second possible reaction mechanism for N\textsubscript{2}O formation is via the formation of NO dimers at the surface, as shown in Equation 5.4. However, from the theoretical calculations and the RAIRS experiments, it was found that NO dimers do not form on the Pt\{211\} surface at temperatures above 120 K. Hence, the mechanism described in Equation 5.3 is the preferable method for N\textsubscript{2}O formation on Pt\{211\}. 

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If the formation of N\(_2\) and N\(_2\)O on Pt{211} occurs via the reaction of an N atom either with another N atom or with NO, then the only way for N\(_2\) and N\(_2\)O desorption to occur in coincidence is if the same process mediated the formation of both of these species. This would be the case if the diffusion of N atoms initiated the formation of N\(_2\) and N\(_2\)O on Pt{211}. However, if this was the proposed mechanism, this would also imply that the formation of NO\(_β\), by the association of adsorbed N and O, would occur at the same temperature. However, the desorption temperature of NO\(_β\) is 413 K. This is approximately 100 K lower than the desorption temperature of the N\(_2\) and N\(_2\)O. Therefore, it is unlikely that the diffusion of N atoms on the surface dictates the formation, and subsequent desorption, of N\(_2\) and N\(_2\)O on the Pt{211} surface.

Another possible explanation for the observation of the coincident desorption of N\(_2\) and N\(_2\)O in the TPD spectrum is if N\(_2\)O was formed at the surface and subsequently decomposed to give gaseous N\(_2\) and O\(_{(ad)}\), as shown in Equation 5.5.

\[
\begin{align*}
N_{(ad)} + NO_{(ad)} &\rightarrow N_2O_{(ad)} \\
N_2O_{(ad)} &\rightarrow N_2(g) + O_{(ad)}
\end{align*}
\]

In this reaction mechanism adsorbed N atoms react with adsorbed NO, forming N\(_2\)O. The N\(_2\)O either desorbs from the surface, or dissociates immediately into N\(_2\) and adsorbed O atoms. This would account for the observation of the coincident desorption of N\(_2\) and N\(_2\)O. A similar reaction mechanism has been observed previously for the formation of N\(_2\)O on Cu\(^{36}\) and Ru\(^{54}\) surfaces. It is known from RAIRS and TPD experiments that N\(_2\)O does not stick on the Pt{211} surface at temperatures above 120 K. This suggests that, as N\(_2\)O is formed, it desorbs from the surface immediately. This also implies that N\(_2\) and N\(_2\)O are formed as a result of heating during the TPD experiments.

Previous TPD studies have reported the observation of two peaks in the mass 28 spectrum following the adsorption of NO on Pt{211}\(^{3}\). These peaks were assigned to N\(_2\) desorbing from step and terrace sites. However, in the results presented here only
one mass 28 peak is observed in the spectra. To discern the difference between the two observations, TPD experiments were repeated, also monitoring mass 14. Experiments were performed by leaving the sample for 15 minutes before dosing the surface with NO. In these experiments, two mass 28 peaks were observed at ~ 480 and ~ 525 K in correlation with literature results \[3\]. However, only one mass 14 peak was observed at ~ 480 K. This was in coincidence with the lower temperature mass 28 desorption peak. This observation suggests that the lower temperature mass 28 peak is due to \( \text{N}_2 \), as the source of the mass 14 peak is the cracking of \( \text{N}_2 \) in the mass spectrometer. However, these observations show that the higher temperature mass 28 peak is due to CO contamination on the surface. Desorption of CO would also be observed as a mass 28 signal in the TPD spectrum, but mass 14 would not be observed in coincidence with CO desorption.

In all of the TPD spectra recorded for the adsorption of NO on \( \text{Pt}\{211\} \), there was no observation of a mass 32 signal, implying no \( \text{O}_2 \) desorption from the surface. This observation has also been made by Sugisawa \textit{et al} \[5\]. Similar results have also been observed in the study of the adsorption of NO on an oxygen pre-dosed \( \text{Pt}\{211\} \) surface, as described in Chapter 6. In the experiments conducted by Sugisawa \textit{et al} \[5\], a mass 32 peak was only observed after repeated NO TPD experiments without cleaning the surface between experiments. This observation was attributed to the O atoms dissolving into the sub-surface region. \( \text{O}_2 \) is only observed after these sub-surface sites have been saturated. It is therefore assumed that the inability to observe mass 32 in the TPD shown here is also due to the formation of sub-surface O.

In the TPD experiments for the NO/\( \text{Pt}\{211\} \) system following adsorption at 330 K, with a heating rate of 8 K s\(^{-1}\) (Figure 5.3), one peak is observed in the mass 28 (\( \text{N}_2 \)) and mass 44 (\( \text{N}_2\text{O} \)) spectra. Two peaks are observed in the mass 30 (NO) spectrum, labelled \( \alpha \) (471 K) and \( \beta \) (393 K) in Figure 5.3. These results are similar to those seen in the literature for the adsorption of NO on Pt\{211\} \[4\], stepped Pt\{111\} \[3\] and polycrystalline Pt\[6, 7\] surfaces at 300 K. At low exposures of NO only the \( \alpha \) peak is observed. Hence, the high temperature desorption peak can be attributed to the step-bridged species, as before. However, unlike the experiments when NO was dosed at
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120 K, only one low temperature NO desorption peak grows into the spectrum with increasing exposure of NO. To establish the nature of this desorption peak, the desorption energies for the different species observed were calculated and compared to the results at 120 K. The results of these calculations are shown in Table 5.6. The Redhead equation with a pre-exponential factor of $10^{15}$ s$^{-1}$, was used to calculate the desorption energies of the different species observed in the TPD. It must be noted that the values calculated for the binding energies are only approximations as the calculations assume that the activation energy for desorption, and the pre-exponential factor, are coverage independent. To use the Redhead equation, it is also assumed that the desorption processes are first order in nature and molecules leave the surface in a single step. Values of the pre-exponential factor for the adsorption of NO on Pt range between $10^{11}$ s$^{-1}$ to $10^{18}$ s$^{-1}$ \cite{56, 57}. Thus, for a first approximation, a pre-exponential factor of $10^{15}$ s$^{-1}$ is used. Using values of the pre-exponential factor between $10^{11}$ to $10^{18}$ s$^{-1}$ gives rise to a range of values between $\pm 34$ kJmol$^{-1}$ of those quoted.

| Table 5.6: Calculated desorption energies for the species observed in the TPD experiments at the various temperatures at various heating rates. The desorption energies were calculated using the Redhead equation with a pre-exponential factor of $10^{15}$ s$^{-1}$. |
|---|---|---|---|
| NO$\gamma$ | T = 120 K, $\beta = 8$ K s$^{-1}$ | T = 330 K, $\beta = 8$ K s$^{-1}$ | T = 300 K, $\beta = 1$ K s$^{-1}$ |
| Desorption temperature / K | $E_d$ / kJ mol$^{-1}$ | Desorption temperature / K | $E_d$ / kJ mol$^{-1}$ | Desorption temperature / K | $E_d$ / kJ mol$^{-1}$ |
| 334 | 97 $\pm$ 22 | 393 | 114 $\pm$ 23 | 326 | 100 $\pm$ 22 |
| NO$\beta$ | 413 | 120 $\pm$ 28 | 355 | 109 $\pm$ 24 |
| NO$\alpha$ | 500 | 146 $\pm$ 34 | 430 | 133 $\pm$ 28 |

$T =$ Adsorption temperature

It is noted that the binding energy of the lower temperature desorption peak in the experiments performed at 330 K falls between the value of the binding energies of the NO $\beta$ and $\gamma$ peaks which result from the experiments at 120 K. It was therefore postulated that this low temperature peak may be a combination of the $\beta$ and $\gamma$ peaks.
To confirm this observation, the experiments at 330 K were repeated with a lower adsorption temperature of 300 K, and a heating rate of 1 K s\(^{-1}\) (Figure 5.4). Redhead calculations for these results are also shown in Table 5.6. From these results it can be seen that the low temperature desorption peak from the 330 K experiments could be resolved into two separate peaks, with desorption energies similar to those observed for the experiments where the NO was dosed at 120 K. Hence these peaks (NO\(_y\) and NO\(_p\)) are attributed to the desorption of NO from the decomposition of the NO—O complex and the recombination of N and O at the surface, just as at 120 K. In addition, the low temperature peak in the 330 K experiments is attributed to a combination of both of these peaks.

It is also noted that there is a difference of 29 kJ mol\(^{-1}\) between the calculated value of the binding energy of the NO—O complex (68 kJ mol\(^{-1}\)) and the experimentally determined desorption energy of the NO\(_y\) TPD peak (97 kJ mol\(^{-1}\)). A possible explanation for this difference is that the calculations were performed at zero coverage and hence the influence of other adsorbed species such as NO, N and O atoms were not taken into account. An alternative explanation is that the experimentally determined value makes use of the Redhead equation\(^{[55]}\). This equation has many approximations and in particular it assumes a value for the pre-exponential factor. As this NO species is adsorbed on an O atom and not on the surface the value of the pre-exponential factor may vary considerably from that expected for a typical molecule adsorbed directly on a surface. In addition, it should be noted that these calculations have been used simply to determine whether the peaks observed in the TPD, following adsorption at different temperatures, are due to the desorption of the same NO species.

**5.5 Conclusions**

RAIRS and TPD studies have been performed at 120 K, 300 K and 330 K and theoretical calculations have been performed for the adsorption of NO on Pt\{211\}. From these studies, it has been possible to observe several different features for the adsorption of NO on this surface. A summary of the observed vibrational frequencies and the assignments made is shown in Table 5.7.
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Table 5.7: The assignments of the N—O vibrational bands which are observed as a result of NO adsorption on Pt{211}.

<table>
<thead>
<tr>
<th>Frequency range / cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1580-1620</td>
<td>Step-bridged NO</td>
</tr>
<tr>
<td>1688</td>
<td>Terrace-top NO</td>
</tr>
<tr>
<td>1803</td>
<td>NO—O complex at step</td>
</tr>
</tbody>
</table>

Several conclusions can be drawn from these observations:

(1) Very different adsorption behaviour occurs at 120 K and 300 K. At all temperatures above 120 K, the most stable adsorption site is that of the step-bridge species.

(2) At 300 K, dissociation of NO occurs at the surface. This allows the formation of atomic N and O species at the surface. On further adsorption of NO on the surface at 300 K, an NO—O complex is formed between molecular NO and the adsorbed O. This complex is adsorbed at the step edge. The N species are adsorbed at terrace sites, thus preventing the adsorption of NO on the terrace at 300 K.

(3) In the experiments at 120 K, dissociation of NO is suppressed and this allows the uptake of NO into terrace sites. However, this also prevents the formation of the NO—O complex, as there are no atomic O species present at the surface.

(4) The onset of NO dissociation occurs at ~ 230 K. This allows the formation of the NO—O complex at the step edge. However, because of the formation of atomic N species, this also causes a loss of the terrace top NO species.

(5) In the TPD experiments three NO, one N$_2$ and one N$_2$O species are observed. The three NO species are attributed to the decomposition of the NO—O complex, the recombination of N and O atoms at the surface and to the desorption of the step-bridge species.

(6) Also noticeable in the TPD experiments is the lack of a mass 32 peak, due to O$_2$. It has been previously proposed that as the Pt sample is heated, adsorbed O at
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the surface dissolves into a sub-surface region, and can only be observed in the desorption spectra when these sites are all filled. The results presented here support these findings.
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5.6 References


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Chapter 6: The adsorption of NO on an O pre-dosed Pt\{211\} surface

6.1 Overview
This Chapter presents a study of the adsorption of NO on an O pre-dosed Pt\{211\} surface. In Chapter 5, it was shown that NO adsorbs both molecularly and dissociatively at 300 K on a Pt\{211\} surface. Therefore, in an attempt to elucidate the role of O atoms in the adsorption of NO on this surface, experiments have been performed to investigate the adsorption of NO on an O pre-dosed Pt\{211\} surface. This Chapter presents the results of TPD experiments for the O/Pt\{211\} system, and RAIRS and TPD results for the adsorption of NO on an O pre-dosed Pt\{211\} surface at 300 K.

It was shown in Chapter 5 that at 300 K, NO initially adsorbs into a step-bridged site. This species has a vibrational frequency of 1590 cm\(^{-1}\) and, on further exposure, the peak shifts up in frequency to 1613 cm\(^{-1}\). The shift in frequency was assigned both to dipole coupling between adsorbate molecules and to electron withdrawal by adsorbed O atoms, which resulted from NO dissociation. At a saturation exposure of NO, two further absorption peaks were observed, at 1801 and 1576 cm\(^{-1}\). These peaks were attributed to the formation of an NO—O complex at the step edge and to a step-bridged NO species unperturbed by the presence of O atoms. The lack of influence of O atoms on the second step-bridged species was attributed to the O being used to form the NO—O complex. In the present study, pre-dosing the surface with O atoms is observed to have an effect on the frequency and intensity of the infrared bands due to these adsorbate species. However, for the O pre-doses given, none of the absorption peaks are suppressed, nor are any new species formed. In contrast to the RAIRS experiments, TPD experiments show that the formation of N\(_2\) and N\(_2\)O, seen in the clean surface experiments, is completely suppressed by pre-dosed O atoms. In addition, the development of a fourth NO desorption peak is observed in the TPD spectra. The suppression of N\(_2\) and N\(_2\)O formation is attributed to a reduction in the ability of NO to adsorb on the surface and subsequently dissociate into N and O atoms. This reduces the
number of N atoms on the surface available to form N₂ and N₂O. The new NO desorption peak is tentatively assigned to the desorption of step-bridged NO, influenced by the presence of adsorbed O.

6.2 Introduction
To study the adsorption of NO on an O pre-dosed Pt{211} surface, knowledge of the adsorption of NO, O and NO and O on the Pt{211} surface is required. The NO/Pt{211} system was described in detail in Chapter 5, and a review of the previous work for the NO/Pt{211} system has already been given. A summary of the relevant results is given below. A review of the adsorption of O and NO and O on Pt{211} and other related surfaces is given in sections 6.2.2 and 6.2.3 respectively.

6.2.1 Adsorption of NO on Pt{211}
The results in Chapter 5 showed that, initially, NO adsorbs in a step-bridge site on the Pt{211} surface at room temperature. With increasing NO exposure, some of the NO dissociates to give N and O species, as well as NO, at the surface. Further exposure of NO also allows an NO – O complex to form. Table 6.1 shows a summary of the observed vibrational bands and the assignments made for the NO/Pt{211} system as described in Chapter 5. The terrace-top species can only be populated at low temperatures, as at room temperature dissociation of NO occurs, filling the terrace sites with N atoms and thus preventing NO adsorbing at the terrace.

Table 6.1: Assignment of the vibrational NO stretch bands observed when NO is adsorbed on the Pt{211} surface.

<table>
<thead>
<tr>
<th>Wavenumber / cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1580-1620</td>
<td>NO stretch of step-bridge NO</td>
</tr>
<tr>
<td>1688</td>
<td>NO stretch of terrace-top NO‡</td>
</tr>
<tr>
<td>1803</td>
<td>NO stretch of NO – O complex at step</td>
</tr>
</tbody>
</table>

‡-This species is only observed at low temperatures.
Chapter 6: The adsorption of NO on an O pre-dosed Pt{211} surface

The initial absorption frequency of the step-bridged NO is 1580 cm$^{-1}$. As the surface is further exposed to NO, this band shifts up in frequency by 30 cm$^{-1}$. This shift has been assigned to both dipole-dipole coupling between adsorbate molecules and to the presence of the O atoms at the step formed from the dissociated NO molecules.

With increasing NO exposure, the band assigned to step-bridged NO splits into two peaks at 1601 cm$^{-1}$ and 1584 cm$^{-1}$. The higher frequency band is assigned to NO influenced by O atoms and the lower frequency band is assigned to NO that is unaffected by O atoms. At the same time as the step-bridged NO band is observed to split into two peaks a band at 1800 cm$^{-1}$, assigned to the formation of an NO—O complex, appears in the spectrum. The complex is formed by the reaction of O atoms at the step edge with NO. This reduces the effect of the O atoms on the neighbouring step-bridged NO, and allows the step-bridged species to appear as a doublet peak. In addition to the assignments already described, Table 6.1 shows the assignment of a terrace-top bound NO species observed at 1688 cm$^{-1}$ when adsorption occurs at 120 K. This species is not observed at 300 K, as it is believed that the N atoms from dissociated NO migrate to the terraces upon dissociation. These atoms fill the terrace sites, preventing the adsorption of NO.

On heating the NO/Pt{211} system, ordering occurs causing an increase in the intensity of the bands due to the different surface species. As the system is heated to 330 K, the intensity of the band at 1800 cm$^{-1}$ falls. This is due to the decomposition of the NO—O complex. This species was found, from theoretical calculations, to be the least stable NO species at the surface. As this band disappears, the two peaks due to the step-bridged NO species start to merge into one peak. At 350 K, this peak is seen at 1597 cm$^{-1}$. As the NO—O complex decomposes it would be expected that the step-bridged NO species would be affected more by the remaining O atoms at the surface. However it is believed that, as the sample is heated, O atoms dissolve into the subsurface region and hence are no longer available to perturb the step-bridge species. As a result, the doublet peak merges to form a single peak with an absorption frequency close to that of the unperturbed step-bridged species.
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In addition to the RAIRS experiments presented in Chapter 5, TPD experiments were also performed for the NO/Pt\{211\} system. In these experiments desorption peaks were observed for NO, N\textsubscript{2}O and N\textsubscript{2}. It was found that, at low NO exposures, a single NO desorption peak was observed. With increasing NO exposures, two other lower temperature peaks were observed. At all exposures, a single N\textsubscript{2}O peak and a N\textsubscript{2} peak were observed to occur in coincidence. These desorption peaks grew in intensity with increasing exposure, up to a saturation exposure of NO.

With the aid of the RAIRS experiments and the theoretical calculations, it was possible to assign the three NO TPD peaks. These were assigned to the desorption of NO from the decomposition of the NO—O complex, the recombination of N and O atoms at the surface, and the desorption of step-bridged NO. The desorption of the N\textsubscript{2} and N\textsubscript{2}O peaks was attributed to the reaction of adsorbed N atoms with NO, to form N\textsubscript{2}O which subsequently desorbed or dissociated into N\textsubscript{2} and adsorbed O atoms. In all of the TPD experiments, no O\textsubscript{2} desorption peak was observed at any exposure of NO. This supports the suggestion that heating causes adsorbed O atoms to dissolve into a subsurface region on Pt\{211\} as proposed by Winkler *et al* [1].

6.2.2 Adsorption of O\textsubscript{2} on Pt\{211\}

It is clear that knowledge of the adsorption of O\textsubscript{2} on the Pt\{211\} surface is important in the study of the adsorption of NO on an O pre-dosed Pt\{211\} surface. O\textsubscript{2} adsorption on stepped Pt surfaces has been studied using STM [2, 3], LDA [3], TPD [1, 4] AES [1, 4], LEED [1, 4], XPS [5] and DFT [2] techniques. In these studies, it has been established that, at temperatures below 150 K, oxygen adsorbs molecularly on a stepped Pt surface. At higher temperatures, or on heating, dissociation occurs and the oxygen adsorbs atomically on the surface. Figure 6.1 shows the results of a TPD experiment for the desorption of adsorbed O from Pt\{211\}. The oxygen was adsorbed at 300 K [1]. The Figure shows the desorption of O\textsubscript{2}, mass 32. At low coverage one desorption feature, labelled \(\beta_2\), is observed at a temperature similar to that observed on the Pt\{111\} surface [1]. As the exposure is increased, there is a pronounced downwards shift in the desorption temperature. Also observed, at higher oxygen exposures, is a very sharp
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desorption feature, labelled $\beta_1$, which exhibits a slight shift to higher temperatures with increasing coverage.

![Graph showing desorption features $\beta_1$ and $\beta_2$.]

Figure 6.1: Thermal desorption spectra of oxygen on Pt\{211\} following various exposures of O$_2$ ($\times 10^{14}$ molecules cm$^{-2}$) at 300 K, with a heating rate of 2 K s$^{-1}$: (a) 1.8, (b) 2.7, (c) 9.2, (d) 62.3, (e) 133, (f) 222, (g) 309, (h) 1075.

From this study it was proposed that the two desorption features, $\beta_1$ and $\beta_2$, were due to very different states of O on the surface. The $\beta_2$ state was attributed to the associative desorption of adsorbed O atoms at the surface. This peak was attributed to desorption from the step sites as it is known that they bind oxygen more strongly than terrace sites \cite{1, 3-5}. The step sites also show higher activity to oxygen dissociation compared to terrace sites. This O species bonded to the steps has been identified as an O atom adsorbed in a step-bridge site and has also been observed on the Pt\{533\} surface, with an absorption frequency of 560 cm$^{-1}$ \cite{6}. The source of the $\beta_1$ TPD peak was attributed to a very different type of O on the Pt\{211\} surface. It was speculated that the $\beta_1$ peak was formed from O atoms desorbing from a sub-surface region. The observation of sub-surface oxygen has been reported previously on the Pt\{111\} surface by Gland \textit{et al} \cite{7}. It has been shown that sub-surface O may be, in reality, a sub-surface

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silicon oxide or oxide formed from other bulk impurities beneath the surface \[^8, 9\]. However, there is no general consensus on either the nature of sub-surface oxygen or its influence on subsequent adsorption.

Also observed during the adsorption of O\(_2\) onto Pt surfaces, but very often unnoticed, is the so-called “clean-off” effect \[^1\]. This is where O\(_2\) is adsorbed on the surface and reacts with other adsorbed impurities, such as carbon and hydrogen, to form CO and H\(_2\)O \[^10\]. This observation has been attributed to the measurement of a low sticking probability for O\(_2\) on Pt surfaces \[^1\], and as a result a low intensity is observed for the \(\beta_2\) peak in the TPD experiments shown in Figure 6.1. \[^1\].

**6.2.3 Adsorption of NO on O pre-dosed Pt surfaces**

Whilst there are no previous investigations of NO adsorbed on an O pre-dosed Pt\{211\} surface, the adsorption of NO has been studied on an O pre-dosed polycrystalline Pt surface \[^11\]. In these experiments, absorption bands similar to those observed in Chapter 5 were seen. At 300 K, two peaks were seen at 1800 cm\(^{-1}\) and 1638 cm\(^{-1}\). The peak at 1638 cm\(^{-1}\) was also observed to have a shoulder at about 1600 cm\(^{-1}\). The band at 1800 cm\(^{-1}\) was assigned to the adsorption of NO in a top site at a step-like defect on the polycrystalline surface. The band at 1638 cm\(^{-1}\) was assigned to NO adsorbed on a step-like defect or on a Pt\{110\} facet.

In this study it was seen that an O\(_2\) exposure of 1 L caused the band at 1800 cm\(^{-1}\) to be severely attenuated and a 6 L O\(_2\) pre-dose caused the peak to almost disappear from the spectrum. O pre-dosing the surface also had the effect of increasing the absorption frequency of the 1638 cm\(^{-1}\) band to 1640 cm\(^{-1}\), although its intensity remained relatively unchanged. The shoulder at 1600 cm\(^{-1}\) did not form in the O pre-dosed experiments. In addition to the bands seen in the clean surface experiments, a third absorption band at 1710 cm\(^{-1}\), with a very low intensity, was also observed in the O pre-dosed experiments. When the surface was annealed to 400 K, this band disappeared from the spectrum.

In these experiments the disappearance of the peak at 1800 cm\(^{-1}\), and the band that appeared at \(~1600\) cm\(^{-1}\), were attributed to site blocking by adsorbed O atoms. In
addition, because the two bands observed between 1600 and 1640 cm$^{-1}$ showed significantly different responses in the O pre-dosed experiments, it was believed that these species were due to NO in slightly different environments. As a result, the assignment of the latter NO species was modified to either be NO adsorbed on \{100\} or \{110\} surface sites, as both of these species exhibit absorptions in this spectral range\cite{11,12}. The peak that was seen to form in the O pre-dosed experiments, at 1710 cm$^{-1}$, was believed to be due to the adsorption of NO in a top site on a \{111\} terrace, by comparison with the low index surface\cite{13-15}. It is believed that this site could only be populated in the O pre-dosed experiments due to site blocking of other species. The low intensity of the species was attributed to the low density of \{111\} sites on the polycrystalline surface.

A similar study was performed by Agrawal and Trenary\cite{13} on a defect rich Pt\{111\} surface. In this study\cite{13}, similar features were seen in the infrared spectra at 1611 cm$^{-1}$ and 1813 cm$^{-1}$ for adsorption at 300 K. These bands were assigned to bent NO and linear NO at the step edge. However, unlike Levoguer and Nix\cite{11}, increasing pre-exposures of O to the surface had the effect of enhancing the intensity of the absorption peak seen at 1813 cm$^{-1}$, and attenuating the species seen at 1611 cm$^{-1}$. This effect was attributed to O blocking the adsorption sites for the lower frequency species, making the adsorption site giving rise to the band at 1813 cm$^{-1}$ more favourable. It was also concluded that the species seen at 1813 cm$^{-1}$ was assigned to molecules at a site that was not directly blocked by adsorbed atomic O. The discrepancy between these two studies was attributed to the size of the O$_2$ pre-dose. In the experiments performed by Agrawal and Trenary\cite{13}, the O$_2$ exposure was much lower that that used by Levoguer and Nix\cite{11} and therefore, in the latter experiments, the O$_2$ dose was sufficient to block many more sites.

In this Chapter, the results for RAIRS and TPD investigations of the adsorption of NO on an O pre-dosed Pt\{211\} surface at room temperature are presented. These experiments have been performed in an effort to elucidate the role of O atoms in the adsorption of NO on the Pt\{211\} surface. Chapter 3 presents the experimental details of the RAIRS and TPD experiments presented in this thesis.
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6.3 Preliminary experiments - O/Pt\{211\}

Preliminary TPD experiments for the adsorption of oxygen on the Pt\{211\} surface were performed, to estimate the coverage of O atoms on the surface, prior to the O pre-dosed experiments. Comparison was made with previous TPD results obtained by Winkler et al.\[^{1}\] for the O/Pt\{211\} system, shown in Figure 6.1. Figure 6.2 shows the results of experiments performed for the desorption of mass 32 from the Pt\{211\} surface, following O\(_2\) adsorption at 300 K. It can clearly be seen that there is a single peak that appears at an exposure of 5 L, with a desorption temperature of 787 K. This peak increases in intensity with increasing exposure of O\(_2\) to the surface, and shifts down in temperature to 747 K. This desorption sequence is similar to that shown in Figure 6.1, for low O\(_2\) exposures.

Comparing these results (Figure 6.2) with the results from the literature (Figure 6.1), it is clear that the results presented here are for low coverages of O atoms, as only a single peak, equivalent to \(\beta_2\), is observed. Thus the desorption peak observed can be attributed to the associative desorption of O atoms adsorbed on step-bridge sites on the Pt\{211\} surface. The different desorption temperatures in the two experiments may be assigned to the different heating rates used. It is clear from the comparison between Figures 6.1 and 6.2 that the surface is not saturated with O atoms at the exposures used in these experiments, and in the subsequent experiments investigating the effect of O pre-dose on NO adsorption on Pt\{211\}. Note that no O\(_2\) desorption is observed in the TPD spectrum for O\(_2\) exposures below 5 L. It is assumed, in this case, that the O atoms adsorbed on the surface dissolve into the sub-surface region on heating and are therefore not available for desorption. This effect has previously been observed on Pt\{111\}\[^{1}\] and has also been suggested to account for the absence of O\(_2\) desorption following NO adsorption on Pt\{211\} in Chapter 5. Only once the sub-surface sites have become fully saturated is O\(_2\) desorption seen in the TPD spectrum.
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Figure 6.2: TPD spectra recorded at a heating rate of 1 K s\(^{-1}\) following various exposures of O\(_2\) to the Pt\{211\} surface at 300 K. Note that the spectra recorded were rather noisy and hence they have been fitted with a simple smoothing spline to allow the features of the spectrum to be observed more clearly.

6.4 Adsorption of NO on the O pre-dosed Pt\{211\} surface

6.4.1 RAIRS
The adsorption of NO on an O pre-dosed Pt\{211\} surface has been studied as a function of O\(_2\) pre-dose, NO exposure and annealing temperature. RAIR spectra for increasing NO exposure at room temperature were recorded following O\(_2\) pre-doses of 0, 1, 5, 10, and 20 L. As already shown in Section 6.3, these O\(_2\) exposures do not correspond to the saturation of the surface with O atoms. Figure 6.3B shows a representative set of RAIR spectra, showing the sequential adsorption of NO on a Pt\{211\} surface that has previously been exposed to 20 L of oxygen. For comparison, Figure 6.3A shows RAIR spectra for the sequential adsorption of NO on a clean Pt\{211\} surface at room temperature.
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Figure 6.3: RAIR spectra for the sequential adsorption of NO on (A) a clean Pt\{211\} surface and (B) a Pt\{211\} surface with a 20 L oxygen pre-dose at 304 K. The NO exposures are indicated on the figures.
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It can clearly be seen from these two sets of data that there are no new species formed and no species are lost from the infrared spectra, due to the presence of the O atoms at the surface. This is also true for all intermediate exposures of O₂.

Just as for the clean Pt{211} surface, on initial adsorption of NO an absorption band at ~1600 cm⁻¹ is observed. With further exposure, this peak develops into two bands at 1623 and 1583 cm⁻¹. Also observed is a peak at ~1800 cm⁻¹. This peak is observed at 1801 cm⁻¹ in the clean surface experiments, but shifts up in frequency to reach 1811 cm⁻¹ at saturation NO coverage following a 20 L O₂ pre-dose.

Whilst no new species are formed and no species are lost when NO is exposed to an O pre-dosed surface, there are changes in the observed frequencies and intensities of some of the NO infrared bands. In the experiments on the clean surface, the initial absorption peak observed at an exposure of 0.05 L NO has a frequency of 1590 cm⁻¹. As the surface is further exposed to NO, this peak shifts up in frequency to 1613 cm⁻¹. In the experiments where the sample is pre-exposed to 20 L O₂, this initial peak is observed at 1611 cm⁻¹, and it does not shift in frequency as the sample is further exposed to NO.

Figure 6.4 shows the variation in frequency of the initial absorption peak seen for the NO/Pt{211} RAIRS experiments as a function of O₂ pre-dose, up to an exposure of 0.5 L NO. It can clearly be seen from Figure 6.4 that, with increasing O₂ pre-dose, there is a systematic increase in the frequency of the initial absorption peak. In addition, there is a smaller overall change in absorption frequency between 0.05 and 0.5 L NO, with increasing O₂ pre-dose.

For a saturation exposure of NO on all of the oxygen pre-dosed surfaces (O₂ pre-doses between 0 and 20 L of oxygen), three NO vibrational bands are observed. For 0 L O₂ exposure, these peaks are seen at 1584, 1601 and 1803 cm⁻¹. Increasing the O₂ pre-dose causes the frequency of these three bands to change. Figure 6.5 shows the variation in peak frequency of the bands observed at saturation NO dose with increasing O₂ pre-dose. It can be seen that, with increasing amounts of O₂ at the surface, the two absorption peaks at 1576 and 1609 cm⁻¹ steadily increase in frequency. The peak
observed at 1801 cm$^{-1}$ increases in frequency up to 1810 cm$^{-1}$, at a 5 L pre-exposure of oxygen, where the absorption frequency remains constant.

As well as frequency changes, the band intensities are also observed to change as a function of O pre-dose. Figure 6.6 shows the variation in maximum band intensity, measured as the integrated area of the peak, for the band at $\sim$ 1600 cm$^{-1}$ (A) and at $\sim$ 1800 cm$^{-1}$ (B), as a function increasing oxygen pre-dose. The area of the 1600 cm$^{-1}$ peak was measured at 0.5 L NO exposure, as this is when this peak shows maximum intensity. The area of the 1800 cm$^{-1}$ band was measured at a saturation coverage of NO.
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Figure 6.5: Figure to show the variation in peak frequency of the three NO absorption peaks observed at a saturation NO exposure on Pt\{211\}, with increasing oxygen pre-dose at 300 K. The NO peaks are observed at (A) 1576 cm\(^{-1}\), (B) 1609 cm\(^{-1}\) and (C) 1801 cm\(^{-1}\) on a clean Pt\{211\} surface.
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![Graph showing variation in maximum intensity as a function of oxygen pre-dose](image)

Figure 6.6: Figure to show the variation in maximum intensity as a function of oxygen pre-dose for (A) the peak at 1600 cm\(^{-1}\) and (B) the peak at 1800 cm\(^{-1}\) observed when NO is exposed to an O pre-dosed Pt\{211\} surface at 300 K.

In both cases it was assumed that the geometry of the NO was unchanged as a function of O\(_2\) pre-dose. It can be seen that at low O\(_2\) exposures the peak at 1600 cm\(^{-1}\) initially falls in intensity slightly, before levelling out. However, the peak observed at 1800 cm\(^{-1}\) initially doubles in intensity following an O\(_2\) exposure of 5 L. After this point, the intensity steadily falls, to reach 0.7 of the maximum intensity following a 20 L exposure of O\(_2\).

One further difference between spectra recorded for the clean surface and those recorded following NO adsorption onto an O pre-dosed surface, concerns the NO exposure at which the ~1800 cm\(^{-1}\) band is first observed. In the experiments where the Pt\{211\} surface has been exposed to 20 L of O\(_2\), the absorption peak at 1800 cm\(^{-1}\) appears at an NO exposure of 0.5 L, compared to 1 L in the clean surface experiments.

After the O pre-dosed Pt\{211\} sample had been exposed to 20 L of NO at 307 K, it was annealed to 315 K for 40 seconds before being cooled back down to 307 K and a
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RAIR spectrum taken. This was repeated for increasing annealing temperatures until no bands were observed in the spectrum. The resulting infrared spectra for a 0 L O pre-dosed surface is shown in Figure 6.7A. The experiment was repeated for increasing oxygen pre-doses of 1, 5, 10 and 20 L. Figure 6.7B shows a representative set of data, for the 20 L oxygen pre-dose.

As for the adsorption experiments, no new species are observed and no species are lost from the RAIR spectra when the sample is heated, when compared to the clean surface experiments. Following adsorption at 307 K, three absorption species are observed at 1583, 1626, and 1806 cm\(^{-1}\). As the sample is heated, the intensity of all of the peaks initially increases, before falling, until ultimately the peaks disappear from the spectrum. Figure 6.7B shows that the resolution of the two absorption peaks at \(\sim 1600\) cm\(^{-1}\) is much more distinct than in the spectra in Figure 6.7A where the surface has not been pre-dosed with O atoms.

A marked change in the intensity of the 1800 cm\(^{-1}\) peak during the annealing process is also seen with increased O\(_2\) pre-dose. The intensity of the peak at 1800 cm\(^{-1}\), measured as a function of oxygen pre-dose and temperature, is shown in Figure 6.8. It can be seen from these results that, with increasing oxygen pre-dose, there is an initial increase in the intensity of the 1800 cm\(^{-1}\) peak. Also observed is the fact that the absorption peak disappears from the spectrum at a higher temperature with increased oxygen pre-dose.
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Figure 6.7: RAIR spectra showing the sequential heating of (A) an NO saturated Pt{211} sample, and (B) an NO saturated Pt{211} sample, which had been pre-dosed with 20 L of oxygen. The temperatures to which the sample was annealed are shown on the figures.
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Figure 6.8: Figure to show the variation in integrated intensity of the absorption peak at 1800 cm\(^{-1}\), seen for the adsorption of NO on an O pre-dosed Pt\{211\} surface, as a function of temperature and for various oxygen pre-doses. The system is heated to the desired temperature, before cooling to room temperature and acquisition of the RAIR spectrum.

6.4.2 TPD

TPD experiments were also performed to investigate the effect of O pre-dose on the NO/Pt\{211\} system at room temperature. Figure 6.9 shows the TPD spectra for masses 28, 30 and 44 following a 20 L NO exposure to a clean Pt\{211\} surface at 300 K. Figure 6.10 shows the same spectra following a 20 L NO exposure to a Pt\{211\} surface which was pre-dosed with 20 L of O\(_2\) at room temperature.

It can clearly be seen from the spectra shown in Figures 6.9 and 6.10 that pre-dosing O atoms has a marked effect on the desorption spectra that result from the adsorption of NO on Pt\{211\}. The most noticeable difference is the absence of mass 28 (N\(_2\)) and mass 44 (N\(_2\)O) desorption peaks, when the surface is exposed to 20 L of O\(_2\). Also observed is a fourth mass 30 (NO) desorption peak at 400 K, that does not occur in the clean surface experiments (Figure 6.9).
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Figure 6.9: TPD spectra of a Pt{211} surface following a 20 L exposure of NO at 300 K, at a heating rate of 1 K s$^{-1}$. The spectra shown are for the desorption of masses 28, 30 and 44.

Figure 6.10: TPD spectra of a Pt{211} surface following a 20 L exposure of O$_2$ and a 20 L exposure of NO at 300 K, at a heating rate of 1 K s$^{-1}$. The spectra shown are for the desorption of masses 28, 30 and 44.
Figures 6.11, 6.12 and 6.13 show sequential desorption spectra for N$_2$O, N$_2$, and NO, respectively, for increasing O$_2$ pre-doses on the Pt{211} surface. In all cases the NO dose was 20 L. It can clearly be seen that, with increasing oxygen pre-dose, the intensities of the N$_2$ and N$_2$O TPD peaks are drastically reduced. Figure 6.14 shows the variation in integrated intensity of the N$_2$ and N$_2$O peaks labelled (A) and (B) respectively, as a function of O$_2$ pre-dose. At a 1 L exposure of O$_2$ the intensity of the N$_2$ peak is relatively stable, however, by 5 L O$_2$ pre-dose the intensity falls to less than 20 % of its original intensity. The intensity of the N$_2$O TPD peak falls to 17 % of its original intensity at 1 L O$_2$ exposure. As well as drastically reducing the amount of N$_2$ formed at the surface, the oxygen pre-dose also has the effect of increasing the desorption temperature of the N$_2$ species from 442 to 460 K.

Figure 6.13 shows the desorption spectra for NO from the Pt{211} surface with increasing O$_2$ pre-dose. It can be seen that there are initially three desorption peaks at 325, 354 and 430 K for the clean surface experiments, labelled $\alpha$, $\beta$, and $\gamma$ (Figure 6.13). Following a 1 L O$_2$ pre-dose, three desorption peaks are still seen in the spectrum, however the $\gamma$ peak appears as a very broad desorption feature, with a peak width of $\sim$80 K, and shifts up in desorption temperature to 460 K. On further increasing the O$_2$ pre-dose the intensity of the $\alpha$ peak increases and a fourth desorption peak, labelled $\nu$ appears as a high temperature shoulder on the $\beta$ desorption peak, at 388 K. Following a 20 L pre-dose of O$_2$, it can quite clearly be seen that there are four desorption peaks labelled $\alpha$, $\beta$, $\nu$ and $\gamma$ with desorption temperatures of 325, 358, 395 and 461 K respectively. The $\alpha$ desorption peak dominates the spectrum following a 20 L O$_2$ pre-dose. In addition, the width of the $\gamma$ peak is still approximately 80 K.
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Figure 6.11: N\textsubscript{2}O multiplot recorded at a heating rate of 1 K s\textsuperscript{-1} following NO adsorption on an O\textsubscript{2} pre-dosed Pt\{211\} surface at 300 K. The spectra shown are for an NO dose of 20 L and O\textsubscript{2} pre-doses between 0 and 20 L.
Figure 6.12: $N_2$ multiplot recorded at a heating rate of $1 \text{ K s}^{-1}$ following NO adsorption on an O$_2$ pre-dosed Pt[211] surface at 300 K. The spectra shown are for an NO dose of 20 L and O$_2$ pre-doses between 0 and 20 L.
Figure 6.13: NO multiplet recorded at a heating rate of 1 K s\(^{-1}\) following NO adsorption on an O\(_2\) pre-dosed Pt\{211\} surface at 300 K. The spectra shown are for an NO dose of 20 L and O\(_2\) pre-doses between 0 and 20 L.
Figure 6.14: Figure to show the variation in intensity (measured as the integrated area under the peak) of the N$_2$ (A) and N$_2$O (B) desorption peaks which result when 20 L of NO is dosed onto an oxygen pre-dosed Pt{211} surface at room temperature.

6.5 Discussion
In the RAIRS study of the adsorption of NO on a clean Pt{211} surface presented in Chapter 5, three absorption species were seen. These were assigned to NO in a step-bridge site (1576 cm$^{-1}$), NO in a step-bridge site perturbed by the presence of adsorbed O (1609 cm$^{-1}$), and the formation of an NO—O complex between the adsorbed step-bridged O and adsorbed NO (1801 cm$^{-1}$). In the RAIRS experiments presented in this Chapter for the adsorption of NO on an O pre-dosed Pt{211} surface, the same three species were also observed. In addition, no new species are seen in the RAIRS experiments. It is therefore clear that pre-dosing the surface with O, at least at the doses used here, does not prevent any of the species forming that were seen in the clean surface experiments, nor does it promote the formation of any new species.

These initial observations imply that similar NO species are formed on Pt{211} in both sets of experiments. For the adsorption of oxygen on Pt{211} it is believed that the most stable site for the O atom is a step-bridge site. This is also the most stable adsorption site for NO. As a result, it is expected that there should be a fall in the
amount of step-bridged NO adsorbed on the surface, hence the intensity of the step-bridged NO bands seen in the RAIR spectrum should decrease with increasing O pre-dose. Figure 6.6 shows the variation in intensity of the band due to the step-bridged NO species seen at ~1600 cm\(^{-1}\) and, indeed, with a 1 L pre-dose of O\(_2\) the integrated intensity of this peak falls by approximately 15%. Note that it is assumed that there is no change in the geometry of the NO species with the O\(_2\) pre-dose. This observation is in agreement with that seen by Agrawal and Trenary for the adsorption of NO on an O pre-dosed defect covered Pt\{111\} surface\(^{[13]}\). However, in a similar study by Levoguer and Nix on a polycrystalline Pt surface\(^{[11]}\), the main absorption band seen at ~1638 cm\(^{-1}\) was unaffected by the O pre-dose. The difference in these observations may be attributed to the composition of the surface. The polycrystalline surface is composed of many crystal facets, and contains many different defect sites. It is therefore expected that there are many more sites available for both NO and O atoms to adsorb on the polycrystalline surface and hence it is less likely that pre-dosed O atoms would block NO adsorption.

Also observed in the study by Agrawal and Trenary\(^{[13]}\) was an enhancement of the intensity of the species seen at 1800 cm\(^{-1}\), with increasing O\(_2\) pre-dose. This was also observed in the present study (Figure 6.6). The integrated intensity of the peak observed in the RAIR spectra at ~1800 cm\(^{-1}\) increased to approximately 2.5 times that observed on the clean surface following an O\(_2\) pre-dose of 5 L. This observation may be explained by the quantity of adsorbed O on the surface. It was previously proposed in Chapter 5 that the peak at 1800 cm\(^{-1}\) is due to an NO—O complex. As there are more adsorbed O atoms on the surface in the O pre-dosed experiments, this allows more of the complex to be formed as NO is dosed onto the surface. However, after a 5 L O\(_2\) pre-dose the intensity of this absorption peak starts to fall (Figure 6.6), and by a 20 L O\(_2\) pre-dose, the intensity of the peak due to the NO—O complex has fallen to 50% of the maximum intensity. However, even following a 20 L O\(_2\) pre-dose, the intensity of this peak in the RAIR spectrum is still larger than that observed for NO adsorbed on clean Pt\{211\}. The observation that O\(_2\) pre-doses greater than 5 L cause the intensity of the peak due to the NO—O complex to decrease may be explained by the fact that increasing O\(_2\) doses are sufficient to inhibit the uptake of NO, and cause less of the
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NO—O complex to be formed. If the O₂ dose were increased further, it is expected that this would completely prevent the formation of all the NO absorption peaks, as the surface would be saturated with adsorbed O atoms.

The proposal that the O pre-doses used in the present study are not sufficient to saturate the surface is supported by the preliminary O/Pt{211} TPD experiments in Section 6.3. These experiments showed that the O exposures used here are only sufficient to partially cover the surface. Similar experiments were performed by Levoguer and Nix [11], where NO was dosed onto an O-pre-dosed polycrystalline Pt surface. In these experiments, a peak was seen at 1800 cm⁻¹ in the clean surface experiments. However, this peak could be completely suppressed by pre-dosing the surface with O₂. It is believed that the difference in these observations is due to the size of the oxygen pre-dose, and supports the assumption that larger O₂ pre-doses on Pt{211} would lead to loss of the NO—O complex. A difference in the O₂ pre-dose was also assumed to be the cause of the different behaviour of the ≈1800 cm⁻¹ peak in the experiments of Levoguer and Nix [11] and Agrawal and Trenary [13].

In the literature [13], and as described in Chapter 5, it has been suggested that the frequency of the step-bridged NO species, initially seen at 1590 cm⁻¹ on the clean Pt{211} surface, is perturbed by the presence of adsorbed O at the surface. This, in combination with dipole coupling between the adsorbed molecules, results in the observed frequency shift in the clean surface experiments (Chapter 5). Therefore, with increasing O pre-doses, it is expected that the frequency of the step-bridged NO species that gives rise to the RAIRS band at ≈1600 cm⁻¹ should increase. Figure 6.4 shows the variation in frequency of the step-bridged NO species as a function of O pre-dose and NO exposure. It can be quite clearly seen from this data that there is indeed an increase in the initial frequency of the band with increasing O pre-dose. In addition, with increasing exposure of NO, there is a continuing positive trend in the observed absorption frequency, however the overall frequency increase for all O pre-doses is much less than that observed for NO on a clean Pt{211} surface. One possible explanation for this is that, even though there are larger quantities of adsorbed O at the surface leading to an increased frequency, the adsorbed O also prevents further NO
adsorption on the step-bridge site. This results in less dipole coupling between the adsorbed NO molecules and, as a result, there is a smaller overall frequency increase as the NO coverage increases. An alternative explanation is that the main frequency increase of this band is due to the presence of co-adsorbed O atoms and hence increasing the coverage of NO on the surface only has a small effect on the vibrational frequency. It is believed that the frequency increase is dominated by the O$_2$ pre-dose and not by the quantity of NO adsorbed at the surface. It can be seen that the intensity of the NO band at -1600 cm$^{-1}$ is only very slightly reduced by the pre-dosing of O atoms as seen in Figure 6.6, and therefore there are similar quantities of NO adsorbed in the clean surface experiments and the O$_2$ pre-dosed experiments. In addition, there is a larger total frequency increase in the clean surface room temperature experiments compared to the low temperature NO adsorption experiments where no adsorbed O atoms are able to form (see Chapter 5), implying that the observed frequency shift is mainly due to the presence of O atoms on the surface.

Pre-dosing O onto the Pt{211} surface also causes frequency shifts for the other NO species observed following a saturation dose of NO. This can be seen in Figure 6.5. The frequency of both the band at 1576 cm$^{-1}$ (step-bridge species) and the band at 1801 cm$^{-1}$ (NO—O complex) increases with increasing O pre-dose. The frequency shift for the 1576 cm$^{-1}$ band may be attributed to the adsorbed O at the surface which perturbs this species. In the case of the NO—O complex, seen at 1801 cm$^{-1}$ for a saturation coverage on the clean surface, there is an initial increase in frequency of -10 cm$^{-1}$, following a 5 L O$_2$ pre-dose. For increasing O$_2$ pre-doses the frequency of this species remains relatively constant (Figure 6.5C). Since increasing the O$_2$ pre-dose causes more of this species to be formed, it is likely that increased dipole coupling occurs and, as a result, an increase in the observed frequency occurs.

The affect of annealing on NO adsorption on various O pre-dosed Pt{211} surfaces was also investigated. Figure 6.7A shows the heating sequence for a clean Pt{211} surface that has been saturated with NO. Figure 6.7B shows the same thing for a surface pre-dosed with 20 L of O$_2$. As with the adsorption experiments performed as a function of O pre-dose, no new species were observed to be formed and no additional species were
observed or lost due to the O\textsubscript{2} pre-dose. However, the pre-adsorption of O atoms on the Pt\{211\} surface does have an effect on the intensity of the infrared bands observed in the annealing experiments. This is most clearly seen in Figure 6.8. Figure 6.8 shows the variation in integrated intensity of the 1800 cm\textsuperscript{-1} peak as a function of temperature and oxygen pre-dose. It can be seen that there is an initial increase in the intensity of this peak with increasing O\textsubscript{2} pre-dose, however, on further O\textsubscript{2} pre-dose, the intensity then falls. In addition, it can also be seen that the desorption temperature of this species increases from 350 K to 420 K with increasing O\textsubscript{2} pre-dose. It has already been established that this infrared band is due to the NO—O complex, therefore the increasing number of O atoms at the surface, due to the larger O\textsubscript{2} pre-dose, must allow more of the NO—O complex to form, leading to a larger observed intensity in the spectrum. The increased desorption temperature must be due to the NO in the NO—O complex being more strongly bound to the adsorbed O atom at the surface.

A similar analysis of the absorption bands seen at \textasciitilde 1600 cm\textsuperscript{-1} is difficult, as the two bands seen in this region of the spectrum appear as a doublet peak in the annealing experiments. As a result it is difficult to deconvolute these two peaks and measure the relative contributions to the integrated intensity of the individual species. However, from inspection of the spectra, it is clear that the resolution of these two peaks improves with increasing O pre-dose. As already stated, the two species that give rise to these bands are believed to be step-bridged NO (1576 cm\textsuperscript{-1}) and step-bridged NO perturbed by adsorbed O (1609 cm\textsuperscript{-1}). Thus, it is plausible that, as more O atoms are adsorbed on the surface, the sub-surface sites become saturated, allowing adsorbed O atoms to remain at the surface, as the system is heated. As a result, these atoms continue to perturb the step-bridge species, allowing it to be more clearly observed in the RAIR spectrum.

Unlike the RAIR spectra, where no new species were observed or lost, more drastic changes were observed in the TPD experiments following NO exposure to an O\textsubscript{2} pre-dosed Pt\{211\} surface. In these studies it was seen that, with increasing O pre-dose, the amount of N\textsubscript{2}O and N\textsubscript{2} formed during the TPD experiments was drastically reduced, and ultimately both of these species were eliminated from the desorption spectra (Figures
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6.11 & 6.12). In addition, an extra NO desorption peak (labelled \(v\)) is seen at 388 K in the TPD. This peak grows in intensity with increasing O pre-dose (Figure 6.13). The highest temperature desorption peak, seen at 430 K in the clean surface experiments, was also seen to shift up to 460 K following a 1 L O\(_2\) dose. This peak remained at this desorption temperature for all other O\(_2\) pre-doses studied. In addition, the lowest temperature desorption peak (\(a\)) at 325 K is seen to increase in intensity with increased O\(_2\) pre-dose.

It has already been proposed in Chapter 5 that N\(_2\)O is formed from the reaction of NO with N atoms at the surface. The N\(_2\)O can either desorb forming N\(_2\)O\(_g\) (Equation 6.1a) or decompose into N\(_2\) (Equation 6.1b). This then can desorb from the surface:

\[
N_2O_{(ad)} \rightarrow N_2O_{(g)} \quad \text{Equation 6.1a}
\]

\[
N_2O_{(ad)} \rightarrow N_2(g) + O_{(ad)} \quad \text{Equation 6.1b}
\]

This leads to the observed coincident peaks in the TPD spectrum for N\(_2\) and N\(_2\)O in the desorption spectra seen in Chapter 5. From initial observations, it is likely that a similar desorption process occurs for NO on an O pre-dosed Pt\{211\} surface. From Equation 6.1 it can be seen that the quantity of N\(_2\)O and N\(_2\) observed in the TPD spectrum reflects the ability of N\(_2\)O to form at the surface. Hence, the most likely reason for the observed decrease in the desorption of N\(_2\) and N\(_2\)O in the O pre-dosed experiments is that there are less N atoms available at the surface for the N\(_2\)O to form. This is caused by the presence of the pre-adsorbed O atoms which block the sites for NO dissociation. In addition, the most favourable adsorption site for O on a Pt\{211\} surface is a step-bridge site\(^{[1]}\). The most stable site for NO adsorbed on Pt\{211\} is also the step-bridge site. Hence, as well as blocking NO dissociation, pre-dosing O\(_2\) on the surface also blocks the adsorption of NO and reduces the amount of NO that is available to decompose to form N and O species.
Another explanation for the reduction in the formation of N₂ is the presence of adsorbed O atoms at the surface, which inhibit N₂O dissociation into N₂(g) and O(ad). It can be seen from Figures 6.9 and 6.14 that the intensity of the N₂ desorption peak is always greater than that of the N₂O desorption peak. This implies that dissociation of N₂O at the surface is preferable to the desorption of N₂O. Hence, since O atoms should prevent the dissociation of N₂O, it would be reasonable to assume that there should be an increase in the amount of desorbing N₂O, and a fall in the desorption of N₂, with increasing O₂ pre-doses. However, it can quite clearly be seen in Figures 6.11 and 6.12 that, with a 1 L O₂ pre-dose, the desorption of N₂O is almost eliminated, whereas the desorption of N₂ is still seen following a 5 L O₂ pre-dose. This suggests that the O₂ pre-dose does not, in fact, prevent the formation of N₂. Instead, it must be inhibition of NO dissociation by pre-dosed O atoms, leading to a smaller concentration of N atoms on the surface, that leads to the fall in the intensity of both the N₂ and the N₂O peaks in the TPD spectrum.

Another observation from the TPD experiments is the increase in intensity of the NOₓ TPD peak (Figure 6.13) with increasing O₂ pre-dose. It has been shown in Chapter 5 that the most weakly bound NO species on the Pt{211} surface is NO bonded in an NO—O complex at the surface. This species is expected to be the first NO species to desorb from the surface, and thus the NOₓ TPD peak has been attributed to the decomposition of the NO—O complex. With increasing O₂ pre-doses, more O atoms are present on the surface, and hence more of the NO—O complex is formed. This leads to the observed increase in the intensity of the NOₓ peak with increasing O₂ pre-dose. In line with the observations from the RAIRS experiments (Figure 6.6), O₂ pre-doses greater than 5 L leads to a decrease in the intensity of the NOₓ TPD peak.

An extra desorption peak (v) at 388 K was also seen in the TPD spectra (Figure 6.13), in addition to the three desorption peaks seen in the clean surface experiments presented in Chapter 5. No new species were observed in the RAIRS experiments for the same O₂ pre-doses that can easily account for this desorption peak. However, in the RAIRS desorption spectra (Figure 6.7), the absorption peak seen at 1609 cm⁻¹ (perturbed step-bridged NO) is seen to become more resolved from the peak at 1576 cm⁻¹ (step-bridged...
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NO) with increasing O$_2$ pre-dose. The perturbed step-bridged NO species is also seen to desorb between 377 K and 422 K in these results. Since the $\nu$ species is observed to desorb at 388 K, the perturbed step-bridged NO species could account for the observation of the $\nu$ desorption peak.

Further evidence for the assignment of the $\nu$ TPD peak to the perturbed step-bridged NO species comes from the observation that it is not seen at low O$_2$ pre-doses. At low O$_2$ pre-doses, it is expected that the adsorbed O atoms dissolve into a sub-surface region as the sample is heated. As a result, the adsorbed O atoms are no longer available to affect the step-bridged NO species, and only one step-bridged NO band is seen in the RAIRS. In this case the two peaks due to the step-bridged NO observed in RAIRS merge into one peak on heating, as seen for the clean surface experiments in Chapter 5. However, at higher O$_2$ pre-doses, the sub-surface O sites become saturated and hence not all of the adsorbed O atoms dissolve into the sub-surface region on heating. In this case, two types of step-bridged NO are observed on the surface: the unperturbed step-bridged species and the step-bridged species that is perturbed by the O atoms. It has previously been reported by Sugisawa et al.\cite{16}, that sub-surface oxygen does not affect the desorption of NO. It is therefore proposed that by a 20 L O$_2$ pre-dose, the sub-surface O sites are saturated allowing O atoms to remain at the surface when heating occurs. It is these O atoms that remain on the surface that perturb the step-bridged NO species, and thus result in the observation of the $\nu$ desorption peak at higher O$_2$ pre-doses.

6.6 Conclusions

Pre-dosing the Pt{211} surface with O$_2$ prior to NO adsorption does not yield any new infrared active species that are observed in the RAIR spectra. In addition, no species are lost from the infrared spectra. On first observation this would imply that O$_2$ pre-dosing has no effect on NO adsorption on a Pt{211} surface. However, further inspection of the RAIRS data shows subtle trends in the spectra showing that O$_2$ does have an effect on the NO/Pt{211} system. Conversely, TPD studies of this system show drastic effects on all of the desorption spectra for NO, N$_2$O and N$_2$. With
increasing O\textsubscript{2} pre-dose an extra desorption peak is seen in the NO TPD spectrum, while the N\textsubscript{2}O and N\textsubscript{2} peaks are eliminated.

From the RAIRS studies, it can be seen that the same species are seen in the O\textsubscript{2} pre-dosed NO experiments as in the clean surface experiments. In addition, the O\textsubscript{2} pre-doses given here are not sufficient to saturate the surface and prevent the adsorption of NO. However, with larger O\textsubscript{2} pre-doses it can be seen that adsorbed O atoms do reduce the ability of NO to adsorb in step-bridge sites. This is demonstrated by a slight reduction in the intensity of this species in the RAIR spectra. Also observed in the RAIRS experiments is the observed enhancement of the absorption peak seen at ~1800 cm\textsuperscript{-1}. This peak was assigned to the formation of an NO—O complex in the clean surface experiments. As there are more O atoms available on the O\textsubscript{2} pre-dosed surface, it is expected that more of this complex is able to form. This supports the previous assignment of the 1800 cm\textsuperscript{-1} RAIRS band to the formation of the NO—O complex (Chapter 5). The RAIRS experiments also show that there is an increase in frequency of the band due to the step-bridged NO species due to the presence of O atoms at the surface.

Pre-dosing O\textsubscript{2} onto the Pt\{211\} surface was also observed to have an effect on the behaviour of the NO overlayer during annealing. When an O\textsubscript{2} pre-dosed NO saturated sample was annealed following adsorption at room temperature, it was possible to further resolve the two absorption peaks observed at ~1600 cm\textsuperscript{-1} in the RAIR spectrum compared to those observed on the clean surface. In addition, the two peaks were observable on the surface to a higher temperature than on the clean surface. As already discussed, it is known that O atoms dissolve into a sub-surface region on Pt\{211\} when heated. However, at large O\textsubscript{2} pre-doses, these sites become saturated allowing O atoms to remain at the surface following heating. These O atoms therefore continue to perturb the step-bridged NO species to higher temperatures. This is in contrast to the clean surface experiments, where the adsorbed O atoms from dissociated NO all dissolve into the sub-surface region on heating. Thus they are no longer available to affect the step-bridged NO, and this allows these two absorption peaks to merge into one peak. The presence of the adsorbed O atoms at the surface at higher temperatures also has an
Chapter 6: The adsorption of NO on an O pre-dosed Pt\{211\} surface

affect on the desorption temperature of both the NO—O complex and the step-bridged NO species, causing them to desorb at a higher temperature.

Further information about the affect of pre-dosed O on NO adsorbed on Pt\{211\} was obtained from the TPD studies. Experiments show that, with increasing O\textsubscript{2} pre-doses, the desorption of N\textsubscript{2} and N\textsubscript{2}O are eliminated from the spectrum. This has been attributed to a reduction in the ability of NO to dissociate on the surface, therefore there are less N atoms at the surface available to form these molecules. This occurs due to the adsorbed O atoms which block the dissociation of NO. Also observed in the TPD experiments is the desorption of an additional species in the NO spectrum at high O\textsubscript{2} pre-doses. This peak has been attributed to the desorption of the perturbed step-bridged NO species. This assignment supports those made in the RAIRS experiments, where it is believed that O atoms remain at the surface on heating following the larger O\textsubscript{2} pre-doses, as all of the sub-surface sites for the O atoms are saturated. One further observation from the TPD experiments is an increase in the intensity of the desorption peak attributed to the desorption of NO from the NO—O complex. The observed increase in intensity of this species, with increasing O\textsubscript{2} pre-dose, supports the assignment of this peak to the NO—O complex.
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6.7 References

Appendix A: Abbreviations

AES  Auger Electron Spectroscopy
amu  Atomic Mass Unit
cm$^{-1}$ Wavenumber
DFT  Density Functional Theory
EELS  Energy Electron Loss Spectroscopy
ESD  Electron Stimulated Desorption
ESDIAD  Electron Stimulated Desorption Ion Angle Distributions
eV  Electronvolt
FTIR  Fourier Transform Infrared
FWHM  Full Width at Half Maximum
GGA  Generalised Gradient Approximation
HREELS  High Resolution Electron Energy Loss Spectroscopy
IRAS  Infra-Red Absorption Spectroscopy
k  Reciprocal lattice space vector
L  Langmuir
LDA  Local Density Approximation
LEED  Low Energy Electron Diffraction
MCT  Mercury Cadmium Telluride
ML  Monolayer
OFHC  Oxygen Free High Conductivity copper
PES  Potential Energy Surface
QMS  Quadrupole Mass Spectrometer
RAIRS  Reflection Absorption Infrared Spectroscopy
RHEED  Reflection High Energy Electron Diffraction
SCAC  Single Crystal Adsorption Calorimetry
SEXAFS  Surface Extended X-ray Absorption Spectroscopy
SIMS  Secondary Ion Mass Spectrometry
STM  Scanning Tunnelling Microscopy
## Appendix A: Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TDS</td>
<td>Thermal Desorption Spectroscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Appendix B: Publications

   “The adsorption of CO on the stepped Pt\{211\} surface: a comparison of
   theory and experiment”.

2. R. J. Mukerji, A. S. Bolina and W. A. Brown
   “A RAIRS and TPD investigation of the adsorption of CO on Pt\{211\}”

   “The temperature dependence of the adsorption of NO on Pt\{211\}: A RAIRS
   and DFT investigation”.

4. R. J. Mukerji, A. S. Bolina and W. A. Brown
   “The influence of steps on the dissociation of NO on Pt surfaces: TPD studies
   of NO adsorption on Pt\{211\}”.

5. R. J. Mukerji, A. S. Bolina and W. A. Brown
   “An investigation of the affect of pre-dosed O on the adsorption of NO on
   Pt\{211\}”.