

Molecular Oxygen Adsorbates at a Au/Ni(111) Surface Alloy
and Their Role in Catalytic CO Oxidation at 70 - 250 K

by

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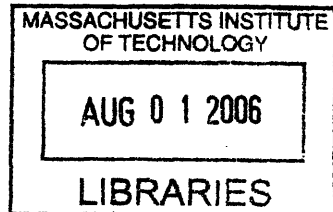
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ABSTRACT

Oxygen is observed to adsorb molecularly on 0.13 – 0.27 ML Au/Ni(111) surface alloys at 77 K, in stark contrast to dissociative adsorption on Ni and no adsorption on Au surfaces. Molecular O₂ adsorbates on the Au/Ni(111) surface alloy are identified by their O=O vibrational modes at 790, 850 and 950 cm⁻¹, measured by electron energy loss spectroscopy. Possible Ni adsorption sites for the three types of molecularly adsorbed O₂ are proposed. The dramatic change in Ni reactivity occurs within a narrow Au coverage range around 0.13 ML Au and arises from poorer overlap between the Ni d-band and the O₂ LUMO as the Ni d-band shifts to lower energy with increasing Au content of the Au/Ni surface alloy. The amount of molecular adsorption as a function of Au coverage cannot be described by an analytical or simulated model based on Au atom proximity to Ni sites, suggesting the role of cooperative effects in O₂ stabilization. Adsorbed molecular O₂ dissociates between 110 to 150 K. No oxygen desorbs. At Au coverages greater than 0.27 ML, the energy of the Ni d-band is shifted sufficiently low to destabilize oxygen adsorption.

Carbon monoxide is catalytically oxidized on the Au/Ni(111) surface alloy at 70 and 77 K via a Langmuir-Hinshelwood mechanism. Molecularly adsorbed O₂ is identified as the reactant with adsorbed CO. The reaction probability at 77 K is 0.4. Atomically adsorbed O and CO do not react at 77 or 300 K. Between 108 and 125 K, CO reacts with either atomic O adsorbed on Au atoms or with molecularly adsorbed O₂. Between 125-150 K, CO₂ production coincides with O₂ dissociation, suggesting a "hot atom" mechanism. The reactive potential energy surfaces likely have a late transition state. This work demonstrates that the nanoscale size of Au clusters and its associated quantum size effect are not the necessary feature that enables Au-catalyzed low temperature CO oxidation. Rather, this work strongly suggests that an adsorbed O₂ species similarly stabilized at the perimeter of Au nanoparticles is the critical reactant in supported oxide systems.

Thesis Supervisor: Sylvia T. Ceyer

Title: J. C. Sheehan Professor of Chemistry

To My Parents
and
In Memory of Jae-Young Kim

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This thesis would not have been possible without the patience and financial support of my advisor, Sylvia Ceyer. For eight years she has provided advice and guidance, and most importantly, encouragement – especially during the “darkest” hours, when the machine was in a million pieces, and I had no hope of ever getting it working again. Equally important has been her financial support – all told, I have to guess she has used more than \$500,000 of her grant money to pay for my stipend, tuition and overhead. This number, of course, doesn’t include money spent on buying equipment to replace that which I accidentally damaged or destroyed. I know I wouldn’t have been provided with that kind of support in any other lab, and I doubt I could have produced this thesis without it.

I learned about the day-to-day work of science from Jae-Young Kim. Jae-Young taught me the discipline that is required in science. Control experiments aren’t “fun”, but they’re just as important, and without them you haven’t *learned* anything. That sounds like an obvious statement about science, but it is one I needed to learn, even in my fourth year of graduate school, and it is one that was taught rigorously by Jae-Young. Hand-in-hand with that lesson, he taught meticulous attention to all details, which was eminently lacking from my work prior to Jae-Young’s instruction.

All of the results presented in this thesis were obtained *after* I learned these lessons from Jae-Young. None of them would have been possible, not in a million years, without him. He displayed an inhuman amount of patience towards my accidents in lab, ranging from breaking the H atom filament for the 3rd time to venting the chamber through the diffusion pump. It was a crippling blow to lose him to cancer, but my loss is nothing in comparison to that of his family. I trudged on after he left us, and produced the results presented here, but it never would have been possible without Jae-Young.

The greatest thing that has happened to me in graduate school was meeting Jenny Yang, and going out with her for the last 3.5 years. She’s been my joy. She’s nursed me back to health after numerous trips to the hospital, and during the toughest times of writing this thesis. Looking forward to fun events she’d planned motivated me to work harder, to get up earlier and get to lab. It would be a bleak and dreary existence if not for her.

My parents were a constant source of support and encouragement. They never once wavered in their belief in me. Year after year, they never questioned the sanity of my decision, and were always willing to help in whatever way I needed. Whether I would be visiting my mom in Florida, or my Dad in Maple Springs, I could always find complete and utter refuge from everything related to graduate school – and the ability to recharge, and try again. The same has to be said for my grandmother D.P., who took me in and watched over me continuously for 2 weeks while I was recovering from my burst appendix. I’m convinced that the absolute rest I got during that time was the reason I recovered so quickly.

In a break from tradition, I’d like to thank the current members of the Ceyer lab first. Jon Fischer, Mike Blair, and Jae-Gook Lee have been fantastic to argue (and occasionally work) with. Every topic has been open to debate, and everyone has given as good as they have gotten. I wish them the best luck in all their future endeavors.

I wouldn't have been able to make it through these last years without my friends outside of lab, who provided much needed perspective. Luke Sullivan provided many a rousing discussion about both Litchenstein and Wittgenstein, while introducing me to the world of Ultimate frisbee and beer brewing. Aristos "Stos" Koyanis and Alicia Volpicelli always welcomed me into their home, and graciously invited me on many much needed vacations. Alex Paraskos introduced me to the world of mountain biking, and a whole new world of snowboarding. Greg Paraskos completed our trio of mountain bikers, beer drinkers, poker players, and of course a hockey rivalry that will never die.

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My entire graduate school experience began when I saw Mathew Tate give a presentation during prospective weekend, when I was visiting MIT for the first time. "Tate" demonstrated how straightforward and clear science could be (a hallmark of Sylvia's work in general) – which ultimately led to my decision to come to MIT and work for Sylvia. During my first year, Tate set the gold standard to which I would aspire. I hope he won't mind me writing "The circle is now complete. Once I was but the learner, now I. Am. The. Old. Man."

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CHAPTER 1 - Measurement of Absolute Au Coverage

I. INTRODUCTION

Industrial heterogeneous catalysis often has to balance two competing issues - effectiveness of the catalyst vs. cost of the catalyst.¹ Nickel is one of the cheapest catalysts, the raw metal costing \$0.38 per ounce. Its major applications are in steam reforming (converting natural gas to carbon monoxide and hydrogen) and hydrogenation (converting unsaturated fats into saturated fats, e.g. oils to solid fats). Palladium is a more effective catalyst for the hydrogenation reactions, and platinum survives longer before becoming poisoned as a steam reforming catalyst – but both are orders of magnitude more expensive than nickel.

One method of enhancing a catalyst's performance is by "promoting" its activity by doping it with another metal. In the case of Ni for steam reforming, a goal of promotion is to reduce the rate at which the catalyst becomes poisoned under steam reforming conditions. In 1996, whether by design or accident, Holmblad, Larsen and Chorkendorff discovered - using ultra-high vacuum (UHV) surface science - a promoter for Ni that did just this. By depositing increasing amounts of Au onto a Ni(111) surface, they were able to steadily reduce the reactivity of the surface with respect to methane dissociation - the first step in the methane steam reforming reaction. They also demonstrated that the saturation coverage of carbon from dissociated methane on this surface decreased linearly with increasing Au coverage.² Although both of these effects potentially detract from the value of the catalyst, subsequent experiments demonstrated that the Au greatly reduced the poisoning, or coking, of the catalyst under practical operating conditions.³ These discoveries led to the creation of a patent, by the company

Haldor-Topsoe, for the use of a Au-Ni catalyst in steam reforming.⁴ Perhaps in hindsight the use of Au as an anti-coking agent, due to the inert nature of Au, should have been obvious. But the very first work done on the system (prior to the catalytic discoveries), using scanning-tunneling microscopy (STM), revealed that the Au/Ni(111) surface alloy was structurally much more complicated than previously studied bimetallic alloys - and hence any attempt to predict the effect of Au on the reactivity would have been pure speculation.^{5,6}

Initially, deposition of Au onto the Ni(111) and Ni(110) surfaces was interpreted by STM as coinciding with the appearance of “vacancies” located randomly at the lattice sites of each surface. These “vacancies” only had a depth of 0.15 – 0.25 Å, but the coverage of the “vacancies” was equal to the amount of deposited Au. Ultimately, a more rigorous cleaning of the STM tip resulted in the correct interpretation of the “vacancies” as protrusions, which were identified as Au atoms alloyed into the surface, and located at lattice sites of the unperturbed Ni surface.^{6,7} The small height difference between Ni atoms and Au atoms, coupled with the fact that the Au atoms can be imaged as protrusions or depressions depending upon the tip conditions, is consistent with the picture that Au atoms are alloyed into the surface layer, replacing Ni atoms at lattice positions. The random alloying of Au into the Ni surfaces is the only feature observed for Au coverages up to 0.3 ML. Furthermore, the random alloying creates a range of new adsorption sites, with differing numbers of Au atoms as nearest and next nearest neighbors.

Above 0.3 ML, Au atoms are observed to accrete at the step edges of the Ni surface. The Au atoms are observed to be slightly lower in height than the adjacent Ni

step ($0.4 \text{ \AA}$). As the Au coverage is increased, increasingly large dendritic Au islands form. The Au-Au distance in these islands is $2.80 \pm 0.10 \text{ \AA}$, slightly less than the spacing for the unreconstructed Au(111) surface ($2.88 \text{ \AA}$). This distance is about 16% larger than the Ni-Ni spacing on a pure Ni(111) surface. There are three possibilities in an epitaxial situation where a lattice mismatch is observed. In some cases, there is no registry between the substrate and the overlayer, leading to weak bonding, as observed for noble gases on transition metals and other systems where the dominant attraction between substrate and overlayer is via van der Waals forces. Another is that the lattice of the overlayer can be rotated with respect to the lattice of the substrate, the angle of rotation being that which provides the most energetically favorable match between the different lattices. Lastly, registry can be achieved by periodic formation of defect sites. The defect sites are generally a higher energy structure than would be found on the surface of either pure material. However, they are lower in energy than having either atoms of the overlayer out of registry with the substrate, or a change in the lattice constant of the overlayer and/or surface of the substrate to allow for registration at the interface.⁸

In the case of Au islands on the Ni(111) surface at coverages greater than 0.3 ML, it is the formation of defect sites that has been observed to lead to registry between the Au islands and the Ni substrate.⁵ Somewhat surprisingly, the defects form in the Ni substrate, and not in the Au islands. They take the form of triangular misfit dislocation loops, in which Ni atoms have been removed from the substrate. The location of these removed Ni atoms correspond to locations at which, if the two lattices were unperturbed, a Au atom would sit directly atop a Ni atom. While STM is only able to provide images

of the triangular misfit dislocation loops, effective medium theory calculations demonstrated that the formation of the dislocation loops is lower in energy than either having a Au atom directly atop a Ni atom, or a change in lattice constant of either material.

In addition to demonstrating the new chemical behavior of a Au/Ni(111) surface alloy with respect to CH_4 dissociation, Holmblad et. al. also observed new behavior of this system towards dissociative D_2 adsorption.² The experimental technique involved measuring the thermal desorption spectra (TDS) of a series of Au/Ni(111) surface alloys, after saturating the surface with D_2 . Similar to CH_4 chemisorption, the total amount of dissociatively adsorbed D_2 decreased with increasing Au coverage. In addition to this, at 0.08 ML Au, adsorbed D atoms were observed to recombine and desorb as D_2 at low temperatures, between (180 - 220 K). Such low temperature recombination and desorption does not occur on a Ni(111) surface exposed to D_2 or H_2 . Holmblad et. al. attributed this low temperature desorption to the recombination of D atoms which are bound to Ni three-fold hollow sites that have two Au next nearest neighbors. A similar feature, however, had been observed on the Ni(111) surface that had been exposed to gas phase H atoms, and was shown to be the result of the recombination of bulk H atoms as they emerged onto the surface.⁹

The identification of bulk H absorbed in a Ni(111) surface, and its subsequent migration to the surface where it recombines and desorbs as H_2 , was demonstrated by Johnson et. al. in 1991.⁹ The initial discovery was made when a Ni(111) surface was exposed to H atoms. This surface was then heated to 600 K, while the partial pressure of H_2 in the chamber was monitored. A rapid increase in the partial pressure of H_2 gas was

observed between 180 – 220 K. This low temperature increase in the partial pressure is not observed when a Ni(111) surface is exposed to H₂ molecules. Furthermore, increasing the exposure of H atoms to the Ni(111) surface causes an increase in the partial pressure of H₂ observed between 180 – 220 K. In contrast to the partial pressure increase attributed to recombination of surface H atoms (observed at 380 K), the partial pressure increase between 180 – 220 K does not saturate with increasing H atom exposures. This observation strongly suggested that the H atoms responsible for this low temperature increase in the partial pressure of H₂ are not bound to the surface, but rather are absorbed in the bulk.

In order to identify the species of H atoms that is responsible for the partial pressure increase at low temperature, high resolution electron energy loss spectroscopy (HREELS), a vibrational spectroscopy, was employed. Spectra measured after exposure of the Ni(111) surface to H atoms revealed a new vibrational mode at 800 cm⁻¹, not present after exposure of Ni(111) to H₂ gas. The vibrational mode at 800 cm⁻¹ disappears upon heating the surface to 220 K. This disappearance coincides with the low temperature (180 – 220 K) H₂ partial pressure increase observed when a Ni(111) surface, exposed to H atoms, is heated between 77 and 600 K. Therefore, the mode at 800 cm⁻¹ was assigned as arising from the species that is responsible for the H₂ partial pressure increase observed between 180 – 220 K.

HREELS probes the vibrational modes at a surface using a monoenergetic beam of electrons. Due to the small penetration depth of these electrons, HREELS was generally considered to be limited to observation of surface species. However, the penetration depth is non-zero. Furthermore, the penetration depth can be varied by

variation of the energy of the electron beam.⁸ For the range of energies typically employed in HREELS (3 – 20 eV), increasing the energy of the electrons reduces the penetration depth. In fact, the penetration depth of the electrons is inversely proportional to the quadratic of the electron energy. If the intensity of the loss feature observed at 800 cm^{-1} decreased as the inverse quadratic of the impact energy of the electron beam, it would confirm the identification of this species of H atoms as being absorbed in the bulk. Johnson et. al. performed this measurement, and observed that indeed, the intensity of the 800 cm^{-1} decreased as the inverse quadratic of the energy of the electron beam, confirming the identity of the 800 cm^{-1} feature as belonging to H atoms absorbed in bulk sites of the Ni(111) crystal.

The idea that then arose was the possibility that the low temperature D_2 recombination and desorption observed on the Au/Ni(111) surface alloy was actually from bulk D recombination – implying that the deposited Au had lowered the barrier to bulk absorption sufficiently to allow D_2 molecules to dissociatively absorb into the subsurface sites. An ideal way to test this hypothesis would be to apply the HREELS technique described above for identification of bulk H in Ni(111) to the H/Au/Ni(111) system. This experiment was the initial motivation for the addition of a Au evaporation source to the experimental apparatus described in this chapter, and which led to all the subsequent experiments carried out on the Au/Ni(111) surface alloy. This chapter describes the method used to determine the absolute coverage of Au on the surface using the available experimental techniques. The measurement of the absolute Au coverage is fundamental to any study performed on the Au/Ni(111) surface alloy. Using the method to determine absolute Au coverages, subsequent chapters describe studies of the

adsorption and reaction of various gases on the Au/Ni(111) surface alloys.

Although the relative Au coverage can be determined by the relative intensities of Auger transitions measured by Auger electron spectroscopy (AES), a calibration is necessary to determine the absolute coverage. The absolute Au coverage in this work is determined by comparison to the previous work by Holmblad et. al.,² who measured the saturation coverage of D atoms at Au/Ni(111) surface alloys as a function of absolute Au coverage. Holmblad et. al. measured the absolute Au coverage by comparison of low-energy electron diffraction (LEED) patterns to previous work, in which the relationship between absolute Au coverage as determined by STM, and a LEED pattern was established.⁷

For a given Au/Ni(111) surface alloy, the saturation coverage of H atoms is measured as the H₂ partial pressure increase that occurs when a H atom saturated Au/Ni(111) surface alloy is heated from 77 to 600 K. The saturation coverage in this work, measured at some relative Au coverage as determined by the relative intensities of Auger transitions, is compared to that of Holmblad et. al. measured at some absolute Au coverage. By repeating this experiment for a range of Au coverages, and simultaneously measuring the relative Au coverage by AES, a relationship between the relative Au coverage measured by AES and the absolute Au coverage is determined. This relationship between relative Au coverage measured by AES and absolute Au coverage then serves as the calibration standard from which future AES measurements of the relative Au coverage can be converted into absolute Au coverages.

This chapter reports on the determination of this calibration. The experimental section demonstrates how AES is used to determine the relative coverage of Au with

respect to Ni at the surface. In the results section, measurements of the saturation H atom coverage on Au/Ni(111) surface alloys as a function of relative Au coverage are presented. The procedure for relating the relative Au coverages as determined by AES to the absolute Au coverages is then described. Thus, for the experiments on the adsorption and reaction of gases on the Au/Ni(111) surface presented in the subsequent chapters, the absolute Au coverage is determined by conversion of the measured relative Au coverage (by AES) into the absolute Au coverage using the relationship determined in this chapter. The discussion section describes the significance of the absolute and relative errors in the Au coverage.

II. EXPERIMENTAL

A. Description of the Experimental Apparatus

The experimental apparatus has been described extensively elsewhere.¹⁰ Briefly, it consists of an ultra-high vacuum (UHV) chamber (base pressure 8×10^{-11} torr) precisely coupled to a triply differentially pumped molecular beam source. Mounted axially with the molecular beam is a quadrupole mass spectrometer (QMS) for characterization of the molecular beam by time-of-flight spectroscopy (TOFS), residual gas analysis (RGA) of the chamber, thermal desorption spectroscopy (TDS), and monitoring of partial pressures during molecular beam exposures to the sample. A Ni(111) crystal is mounted on a manipulator, which is capable of rotation about its vertical axis, and translation in the x, y, and z directions. The crystal is spot welded to two 0.020" tungsten rods that are clamped to two vertical copper supports by two Cu-Be screws. The vertical support rods, and hence the crystal, are electrically isolated from the rest of the manipulator by a sapphire washer that is placed between the support rods and the bottom of the

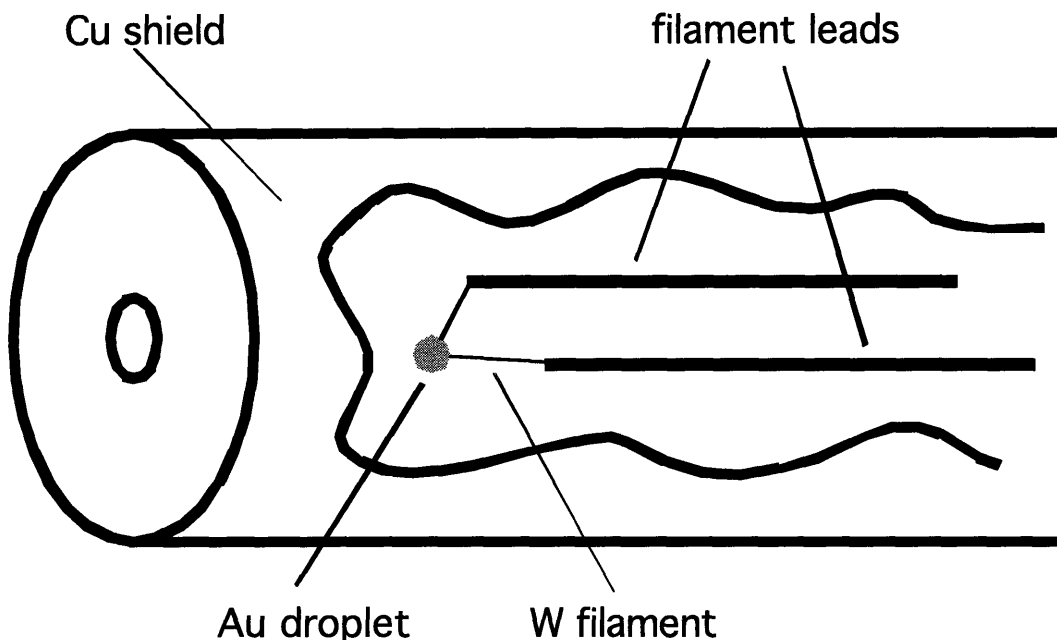


Figure 1. Schematic diagram of Au evaporation source.

manipulator cryostat. The cryostat allows the Ni(111) to be cooled to 77 K when filled with liquid nitrogen, and cooled to 8 K if liquid helium is used.

A high-resolution electron energy loss spectrometer (HREELS) is also mounted in the chamber. In HREELS, a mono-energetic beam of electrons is directed at the surface of the crystal. The intensity of scattered electrons are measured, as a function of energy and angle. Most of the electrons scatter from the surface elastically, but if the cross section for excitation of the adsorbate vibration is sufficiently large, some electrons excite the vibration and lose one quantum of energy. These electrons are detected in the energy scans at lower energy than that of the elastically scattered electrons. Measurement of the energy difference between the elastically and inelastically scattered electrons determines the energy lost to excite the adsorbate vibration, and consequently

the frequency of the vibration. This technique is thus a vibrational spectroscopy, and provides information on the amount and nature of chemical bonds present at the surface.

An Auger electron spectrometer (AES) mounted in the chamber is used to determine the Au coverage, the coverage of adsorbed molecules and atoms, and the extent of contamination of the surface.

A schematic diagram of the Au evaporation source is presented in Figure 1. The Au evaporation source consists of a Au droplet suspended from a 0.010" tungsten filament. Initially, 0.04" diameter Au wire (99.999% purity, Alfa Aesar) is wrapped around the tungsten filament. After the initial heating of the Au source to its operating conditions (as determined by observation of Au deposition at the Ni(111) surface), the Au wire is observed to have melted and formed a droplet on the tungsten filament. The Au droplet and filament are inside a Cu tube, which is open at one end (to allow the feedthroughs to connect to the filament) and capped at the other end. The capped end has a 0.25" inch hole through which Au is deposited onto the Ni(111) surface. The purpose of the Cu shield is ensure that the effusive Au beam is directed at the Ni(111) crystal, and not to other instruments in the UHV chamber. The Au exposure to the Ni(111) crystal is controlled by lowering and raising the crystal from its Au dose position using the Z-translation of the sample manipulator. This design the of Au source is the based on the description given by Holmblad et. al.²

A second 0.010" diameter tungsten filament is mounted directly below the Au source, and is used to generate H atoms. H₂ molecules dissociate on the hot filament, and the resulting H atoms travel the short distance to the crystal surface. The filament is mounted on a feedthrough that allows the distance it projects into the chamber to be

adjusted. The H-atom filament can be positioned to within 0.100" of the front face of the crystal. The filament is heated resistively by passing 3.5 - 4.2 A of DC current through it. The voltage required to generate this current is generally ~ 1.5 V. Hydrogen atoms are prepared by backfilling the chamber with H_2 gas at pressures from 1×10^{-6} to 2×10^{-5} torr, with the H atom filament on and 0.100" in front of the crystal.

The crystal manipulator is mounted on a lid on the chamber that can rotate 180° . The manipulator is mounted such that the axis of rotation of the Ni(111) crystal is 3.75" away from the center of rotation of the lid. Thus, by rotation of the lid, the Ni(111) crystal can be translated to different positions within the UHV chamber. This allows the chamber to contain different instruments that are spatially isolated from each other, but still accessible to the crystal. There are three lid positions. In one, called "TDS" position, the crystal is closest to the QMS, the Au source, and the H atom filament. In another, called "Auger", the crystal is directly in front of the cylindrical mirror analyzer of the Auger spectrometer. In the last, called "EELS", the crystal is contained within the EELS spectrometer. The TDS and EELS positions are separated by 180° rotation of the lid, and both lie along the path of the molecular beam. Thus the two crystal positions along the beam line are 7.5" apart. Because the molecular beam diverges slightly as it travels this distance, the cross sectional area of the beam interception with the Ni(111) crystal can be varied by changing the position of the crystal between the TDS and EELS positions.

B. Preparation of Au/Ni(111) Surface Alloys

Au/Ni(111) surface alloys are prepared by exposure of the Ni(111) crystal to an effusive beam of Au atoms from the Au source described in the previous section. Prior to

exposure to the effusive Au beam, the Ni(111) surface is cleaned by sputtering with 1 keV Ar^+ ions for 5 min., followed by annealing for 20 min. at 1000 K. The Ni(111) surface, held at 450 K, is then exposed to the effusive Au beam for 5 – 30 minutes to prepare a Au/Ni(111) surface alloy. The crystal was held at 450 K using the electron bombardment heating method described previously, with a crystal bias of 300 V. Holding the Ni(111) surface at 450 K during Au exposures eliminated carbon deposition that was observed to occur during Au exposures with the crystal at 77 K. The Au source was typically operated with ~ 1.3 V from a constant voltage power supply applied to the filament, generating a current of ~ 4.2 A. The voltage and current settings are determined empirically based on the previous run, so as to achieve an exposure rate of 0.02 ML Au/min.

As reported previously by Holmblad et. al.,² heating a Au/Ni(111) surface alloy above 800 K results in the Au at the surface dissolving into the bulk of the Ni(111) crystal. Sputtering with 1000 keV Ar^+ ions will not remove this Au effectively, as it is observed to re-surface when the crystal is annealed at 1000 K. It was found that the most effective way of removing any residual Au at the surface was to anneal the surface at 1200 – 1300 K (causing the face of the crystal to glow red) for 2 – 10 min. This heating procedure either causes the Au to evaporate from the surface, or drives it deeply enough into the bulk that it is no longer observable by AES.

C. Identification of Impurities Using Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a widely used technique for identifying the elemental composition of a surface. In general, AES involves directing an electron beam with energy of a few kV at the surface. In the experiments reported in this thesis, the

energy of the incident electron beam is always 2 kV. These electrons eject a core electron from a surface atom. When a valence electron relaxes to fill the core vacancy, the energy released causes a different valence electron to be ejected from the atom. This last ejected valence electron is known as the Auger electron, and its energy is characteristic of the element from which it originated. A typical AES experiment measures the number of electrons ejected from the surface as a function of their energy, typically in the range of 30-1000 eV. The energy resolution is typically ~ 2 eV, which is sufficient to resolve all Auger transitions measured in this work, which have widths of at least 10 eV.

The technique is sensitive to the surface layer because of the very small (0.5 – 1 nm) penetration depth of the incident electrons. A side effect of the incident electron beam is the production of secondary electrons. These secondary electrons show up as a large background in the AES. However, the intensity of the secondary electrons changes relatively slowly as a function of energy. In order to clearly identify Auger peaks, AES are typically collected as the first derivative of the intensity vs. energy spectra.

One problem associated with identification of contaminants is the presence of “diffraction features”¹¹ that appear at or near the energies of typical contaminants. These features are the result of secondary electrons which have energy (and therefore wavelength) such that they scatter coherently from the crystal structure of the Ni(111) surface. The ability of these electrons to superimpose results in a large electron intensity at the detector. This diffraction results in the appearance of peaks in the AES that are not the result of the Auger process, and hence not related to elements at the surface. Previous work in our group has required subtraction of the diffraction features from the spectra in

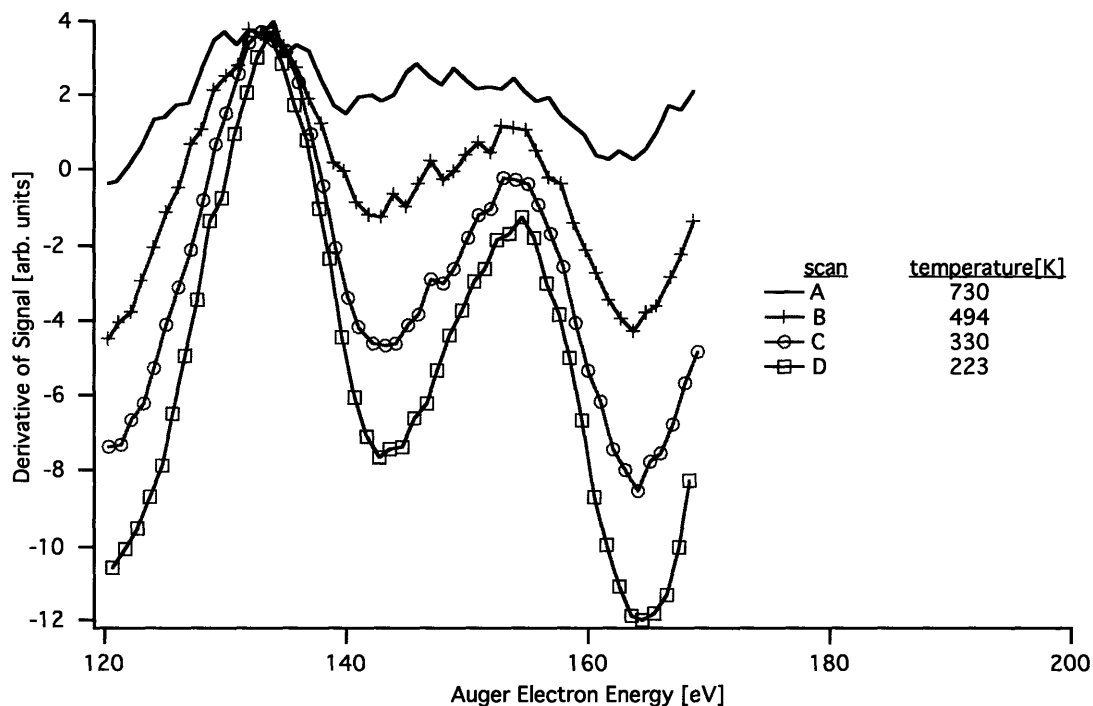


Figure 2. Auger electron spectra of Ni(111) crystal in the temperature range 730 - 223 K, measured while cooling the crystal from 1050 K. Spectra are collected with a beam current of 0.2 μA , a scan rate of 3 eV/s, a time constant of 1 s, and a lock-in amplifier sensitivity of 200x.

order to make quantitative measurements of the elemental composition of the Ni(111) surface.¹⁰ In the present work, the unambiguous identification of these background features as resulting from diffraction is presented.

The primary contaminants present at the Ni(111) surface are sulfur, carbon and oxygen, which have Auger transitions at 152, 272, and 510 eV respectively. Unfortunately, diffraction features from the Ni(111) surface also appear at these energies. However, based on the Debye-Waller factor, it is possible to distinguish between Auger transitions and diffraction peaks, by measuring Auger spectra as a function of substrate temperature. The Debye-Waller factor describes the intensity of a diffraction feature as a function of temperature. As the temperature increases, the amplitudes of the lattice

vibrations increase. This increased amplitude results in the atoms spending less time at their equilibrium lattice positions, resulting in a lower diffraction intensity.¹²

The main problem with the diffraction features at 138, 160 and 285 eV is that they obscure the presence of S and C contaminants. In contrast, the main problem associated with the feature at 503 eV is that it can be mistaken for the O AES feature (515 eV). However, its temperature dependence and lack of change as a function of time demonstrate that it is a diffraction feature, and not an O AES peak.

Figure 2 shows a set of AES measured as the Ni(111) crystal is cooled from 1050 K. There are two features present (138 and 160 eV) at 223 K, but their intensities are drastically reduced at 730 K, leading to their identification as diffraction features. Furthermore, the spectrum is flat around 150 eV, indicating there is no adsorbed S, whose transition occurs at 150 eV, on this surface *at 730 K*. However, if a background gas containing S was present in the chamber it is possible that it desorbed or was driven into the bulk when the surface was heated to 1050 K, and had not re-adsorbed until lower temperatures, at which point it was obscured by the presence of the diffraction features. To test this possibility, the AES of the crystal was measured at 77 K over a period of several hours, with the crystal held at 77 K. If S adsorption from background gas in the chamber occurs at low temperatures, then holding the crystal at low temperature in the chamber for several hours should result in accumulation of S at the surface. The accumulated S should be observable despite the diffraction feature. However, no change was observed in the spectra, indicating that no S accumulation occurred, within the detection limit of the AES.

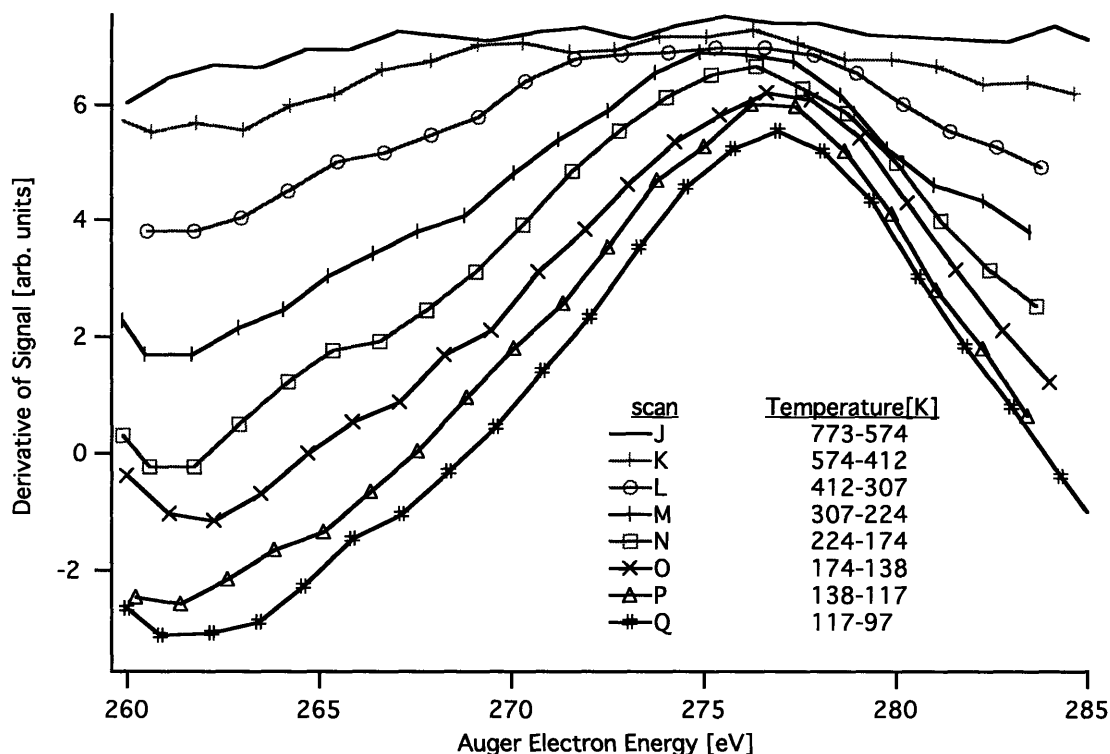


Figure 3. Auger electron spectra of Ni(111) crystal in the temperature range 773 - 97 K, measured while cooling the crystal from 1000 K. Spectra are collected with a beam current of 0.2 μ A, a scan rate of 3 eV/s, a time constant of 1 s, and a lock-in amplifier sensitivity of 200x.

Another series of AES, collected in the range 250-290 eV as the crystal was cooled from 1000 K is shown in Figure 3. For AES collected at 77 K, a feature at 285 eV is present. However, at the highest temperature range (773 – 574 K), the feature at 285 eV is absent, indicating it is a diffraction feature. It also shows that there is no C (whose transition occurs at 272 eV) present at the surface in the temperature range 773-574 K. Experiments in which AES were measured as a function of time, with the crystal held at 77 K have no appreciable change, suggesting that there is no C adsorption from the background gas.

Figure 4 shows AES (490 - 530 eV) as the crystal cools from 1000 K to temperatures between 761 – 85 K. The feature at 503 eV, observed at 85 K, is absent in

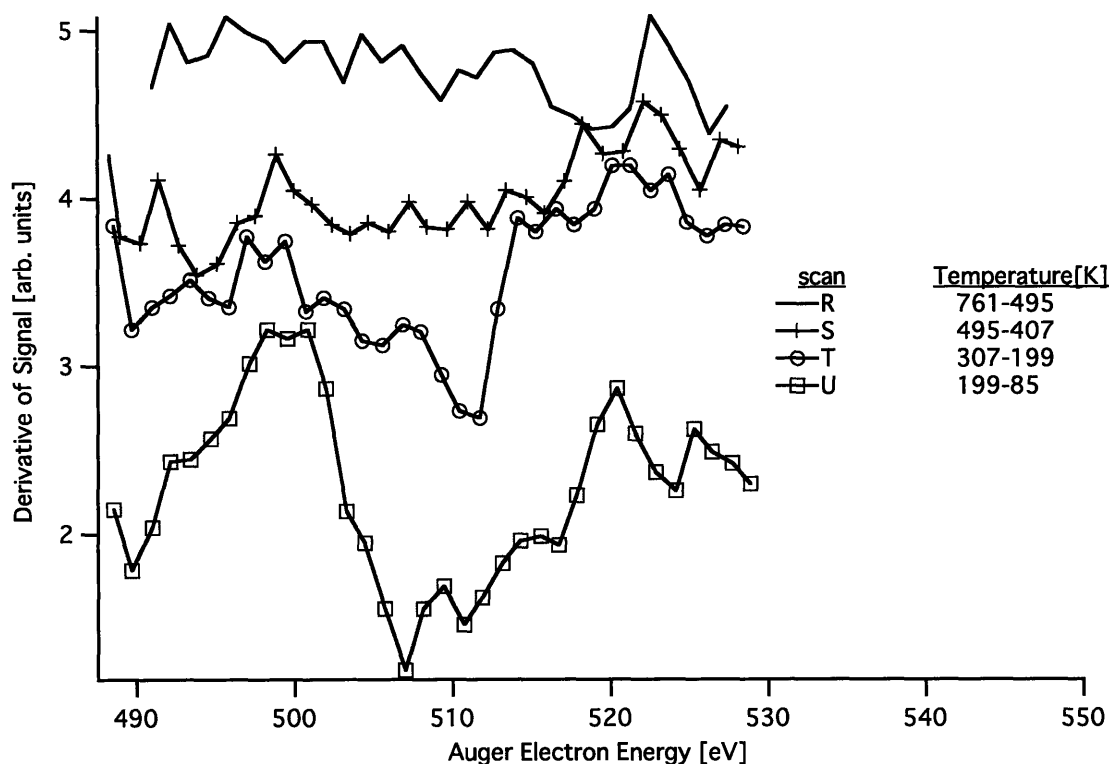


Figure 4. Auger electron spectra of Ni(111) crystal in the temperature range 773 - 97 K, measured while cooling the crystal from 1000 K. Spectra are collected with a beam current of $0.2 \mu\text{A}$, a scan rate of 3 eV/s , a time constant of 1 s , and a lock-in amplifier sensitivity of $200\times$.

the temperature range 495 - 407 K. Furthermore, experiments in which AES were measured as a function of time, with the crystal held at 77 K have no appreciable change, suggesting that there is no O (whose transition occurs at 515 eV) adsorption from the background gas.

For all three cases, further corroboration of the absence of contaminants at the surface is provided by high energy electron energy loss spectroscopy (HREELS), a vibrational spectroscopy. S, C, and O adsorbed on a Ni(111) surface have vibrational frequencies of 330, 430, and 580 cm^{-1} respectively. Although the typical HREELS resolution of 55 cm^{-1} may prevent unambiguous identification of the elemental nature of the contaminant, any broad shoulder or peak observed in the range $300\text{-}500 \text{ cm}^{-1}$ clearly

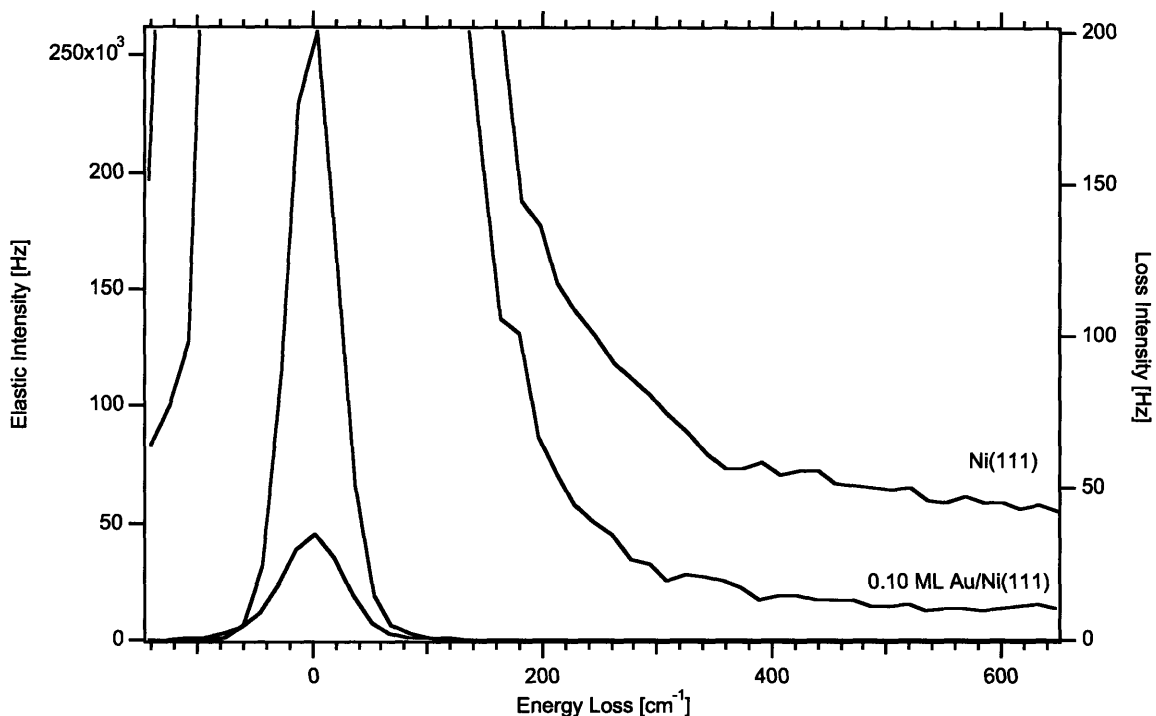


Figure 5. Typical HREELS spectrum measured after preparing a clean Ni(111) and clean Au/Ni(111) surface with 0.10 ML Au. Surfaces are sputtered and annealed prior to experiments. Au is exposed to the Ni(111) crystal at 450 K, for 10-20 min. Spectrum is measured on-specular and has resolution of 55 cm⁻¹ FWHM.

indicates the presence of contaminants. HREELS (at 77 K) was routinely measured (Figure 5) after sputtering and annealing and/or after Au exposures, before running experiments, and had no such peaks or shoulders, confirming that there was no contamination.

D. Measurement of Relative Amounts of Au and Ni Using Auger Electron Spectroscopy

The relative amount of Au on the Ni(111) surface is determined by comparing the intensities of the Au 69 eV and Ni 61 eV Auger transitions. For isolated Auger transitions, the intensity can be measured by determining the peak-to-peak intensity of

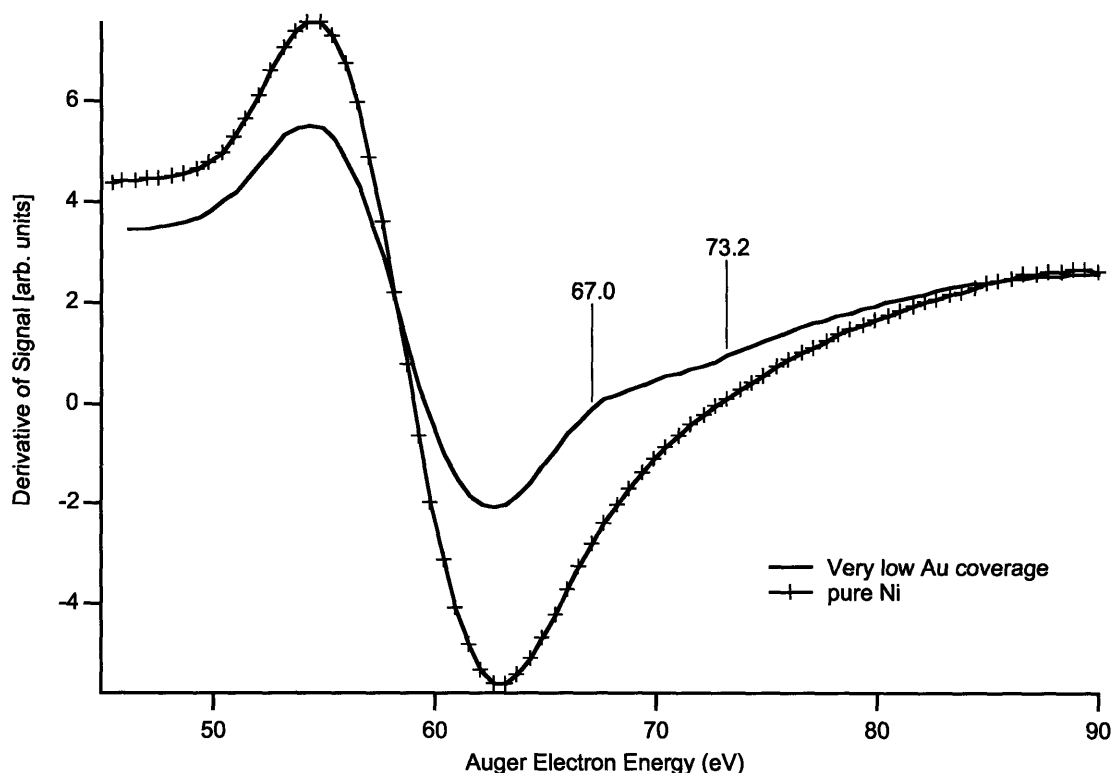


Figure 6. Auger electron spectra for Ni(111) surface, and for Au/Ni(111) surface alloy with very low (< 0.05 ML) Au coverage. The two labeled inflection points at 67.0 and 73.2 eV are characteristic of the presence of Au on the surface.

each derivative signal. However, these two transitions overlap in energy, rendering that method ineffective.

For very low Au coverages, there is no definitive two-peak, first-derivative signal observed for Au. Rather, the presence of Au is indicated by a shoulder on the Ni 61 eV transition. A typical example of an Auger spectrum of a Ni(111) surface with very low Au coverage is shown in Figure 6. For comparison, an Auger spectrum of a pure Ni(111) surface is also shown. The shoulder that results from the presence of a small amount of Au on the surface is labeled by its inflection points at 67.0 and 73.2 eV. Although the presence of Au on this surface can be detected in this Auger spectrum, there is no clear derivative signal corresponding to Au – and hence no peak-to-peak measure of the Au

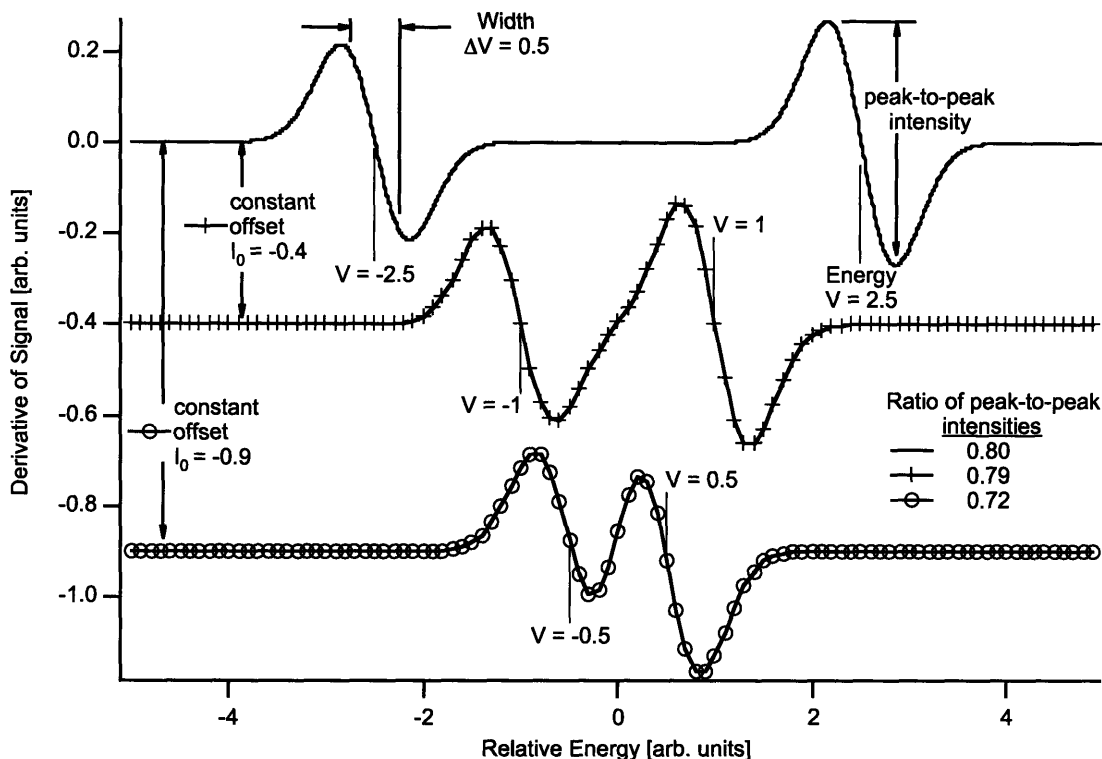


Figure 7. Plot of two Gaussian derivative functions for decreasing energy separations between the individual Gaussian derivatives. The ratio of the peak-to-peak intensities (defined on the top trace) changes even though the only parameter changed is the separation between functions. The labeled variables are defined in the text.

intensity. This suggests the use of a fitting function to determine the relative intensities of the Au 69 eV and Ni 61 eV Auger transitions.

An additional complication arises when two Gaussian derivative functions overlap in energy. This complication is illustrated in Figure 7, in which two Gaussian derivatives are plotted for decreasing values of their energy separation. The peak-to-peak intensity of the derivative of the Auger signal is defined as the difference between the highest and lowest points of the derivative signal, as illustrated in Figure 7. In the top trace of Figure 7, in which the two Gaussian derivatives are well separated in energy, the peak-to-peak intensity of the first Gaussian derivative is set at 80% the value of the second, as labeled in the legend. For the middle and bottom traces of Figure 7, the ratio

of the peak-to-peak intensity has changed, despite the fact that the functions have been replotted only with a change in the value of their energy separation. Despite the fact that no change has been made in the intensity of the underlying functions, the value of the ratio of the peak-to-peak intensities decreases for the middle and lower plot. Changing the value of the separation has drastically affected both the relative peak-to-peak intensities of the Gaussian derivatives. If the lower trace represented an Auger spectrum, then a simple measure of the ratio of the peak-to-peak intensities would not be proportional to the relative coverages of the species corresponding to the two transitions. For AES of the Au/Ni(111) surface alloy, the spectrum of the Ni (61 eV) and the Au (69 eV) is similar to the bottom trace of Figure 7. Hence the ratio of the peak-to-peak intensities of the Ni (61 eV) and the Au (69 eV) is not proportional to the relative amounts of Ni and Au at the surface.

Although the relative intensities of two Gaussian derivative functions that have a small energy separation (Figure 7, bottom trace) cannot be determined by peak-to-peak intensity measurements, they can be determined by fitting the spectrum to a representative function. Two fitting parameters are equal to the intensities of each transition, and hence the ratio of intensities can be determined. The function used to deconvolute the Au 69 eV and Ni 61 eV Auger transitions is the sum of two Gaussian derivatives:

$$I = I_0 + I_{Ni}(V - V_{Ni}) \cdot e^{-\left(\frac{V - V_{Ni}}{\Delta V_{Ni}}\right)^2} + I_{Au}(V - V_{Au}) \cdot e^{-\left(\frac{V - V_{Au}}{\Delta V_{Au}}\right)^2} \quad (1)$$

where I_0 is a constant offset term, I_{Ni} is proportional to the peak-to-peak intensity of the Ni transition, V is the scan energy, V_{Ni} is the energy of the Ni transition, ΔV_{Ni} is the energy width of the Ni transition, I_{Au} is proportional to the peak-to-peak intensity of the

Au transition, V_{Au} is the energy of the center of the Au transition, and ΔV_{Au} is the energy width of the Au transition. These terms are defined graphically for the Gaussian derivative functions presented in Figure 7.

The two Gaussian derivative function (Equation 1) is fit to each Auger spectrum in the range 52 – 73 eV using the least squares minimization routine of Levenberg-Marquadt.¹³ All parameters are allowed to vary during the fitting procedure. The results of the fitting routine indicate that the energy of the Ni transition V_{Ni} and the width of this transition ΔV_{Ni} vary only by about 1% for all the fits performed. The energy of the Au transition V_{Au} and the width of this transition ΔV_{Au} vary by up to 5%, but the variation is systematic – the largest change is observed for very low Au coverages, and is attributed to a change in the chemical environment of the Au atoms. A change in the energy V_{Au} and width ΔV_{Au} of Auger transitions is well known to occur when elements are subjected to different chemical environments.¹⁴

The relative fraction of Au on the surface is then calculated using the formula:

$$R_{Au} = \frac{I_{Au}}{I_{Ni} + I_{Au}} \quad (2)$$

where I_{Ni} is the peak-to-peak intensity of the Ni 61 eV peak from the best fit of Eqn. 1 and I_{Au} is the peak-to-peak intensity of the Au 69 eV peak from the best fit of Eqn. 1. Figure 8 shows a set of Auger spectra measured at 77 K for increasing amounts of Au deposited on the Ni(111) crystal. Also plotted are the best fit of the two-Gaussian derivative functions (Equation 1) to each of the spectra. Each spectrum is labeled in the legend with the relative fraction of Au at the surface R_{Au} , as calculated by Eqn. 2 using the fitting parameters, I_{Ni} and I_{Au} , from the best fit of Eqn. 1.

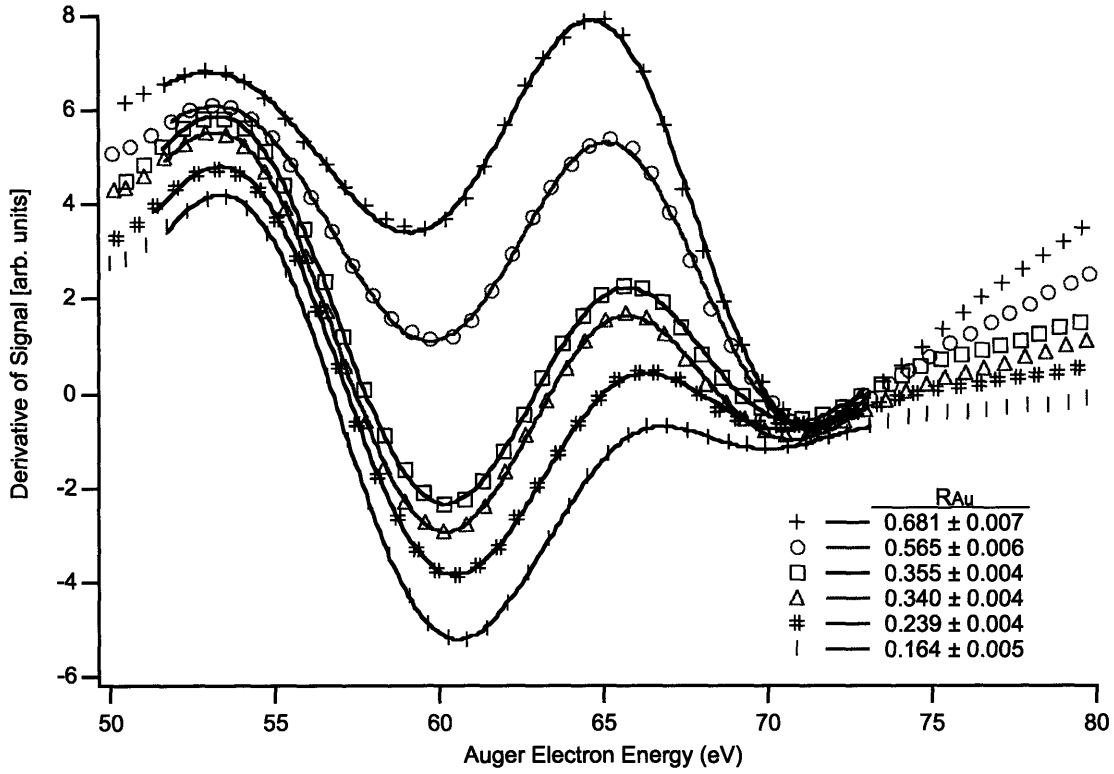


Figure 8. Auger electron spectra for increasing Au coverages of Au/Ni(111) surface alloys. The markers represent data points, the lines are best fit curves, as described in the text.

Also included in the legend of Figure 8 are the standard deviations of the relative Au coverage, determined from the standard deviation in the fitting parameters calculated by the fitting algorithm. The error in the relative fraction of Au, R_{Au} , can be calculated by applying Pythagorean error propagation to Equation 2 for the relative Au fraction:

$$\sigma_{R_{Au}}^2 = \sigma_{I_{Au}}^2 \left(\frac{\partial R_{Au}}{\partial I_{Au}} \right)^2 + \sigma_{I_{Ni}}^2 \left(\frac{\partial R_{Au}}{\partial I_{Ni}} \right)^2 \quad (3)$$

where $\sigma_{I_{Au}}$ is the standard deviation of the Au (69 eV) Auger intensity I_{Au} and $\sigma_{I_{Ni}}$ is the standard deviation of the Ni (69 eV) Auger intensity I_{Ni} . The values of $\sigma_{I_{Au}}$ and $\sigma_{I_{Ni}}$ are calculated by the fitting routine which generates the best-fit of Equation 1 to the AES

data. Taking the derivative of Equation 2 with respect to I_{Au} and I_{Ni} , and plugging the result into Equation 3 yields:

$$\begin{aligned}\sigma_{R_{Au}}^2 &= \sigma_{I_{Au}}^2 \left(\frac{I_{Ni}}{(I_{Au} + I_{Ni})^2} \right)^2 + \sigma_{I_{Ni}}^2 \left(-\frac{I_{Au}}{(I_{Au} + I_{Ni})^2} \right)^2 = \sigma_{I_{Au}}^2 \frac{I_{Ni}^2}{(I_{Au} + I_{Ni})^4} + \sigma_{I_{Ni}}^2 \frac{I_{Au}^2}{(I_{Au} + I_{Ni})^4} \\ &= \frac{\sigma_{I_{Au}}^2 I_{Ni}^2 + \sigma_{I_{Ni}}^2 I_{Au}^2}{(I_{Au} + I_{Ni})^4}\end{aligned}$$

Using typical values for I_{Ni} , I_{Au} , $\sigma_{I_{Au}}$ and $\sigma_{I_{Ni}}$ for the Au/Ni(111) surface alloys studied in this thesis, one standard deviation of the relative fraction of Au, $\sigma_{R_{Au}}$, at the surface is typically about 1% of the measured relative fraction of Au, R_{Au} .

III. RESULTS

The absolute amount of Au on the surface of the Au/Ni(111) surface alloy can be determined by comparing the saturation H atom coverage on the prepared Au/Ni(111) surface alloy to the previous work of Holmblad et. al. Specifically, Holmblad et. al. prepared D atom saturated Au/Ni(111) surface alloys with known absolute Au coverages by exposure to D_2 gas, then measured the amount of D_2 that desorbed in a TDS, and hence the saturation D atom coverage on these surfaces as a function of their absolute Au coverage. Their results are normalized to that obtained on a D atom saturated Ni(111) surface, which is known from previous work to correspond to 1 ML of D atoms. The saturated D atom coverage of the Au/Ni(111) surface alloys monotonically decreased with increasing Au coverage. Therefore, measurement of the saturated D (or H) atom coverage of a Au/Ni(111) surface alloy, can, by comparison to the work of Holmblad et. al., determine the absolute coverage of Au.

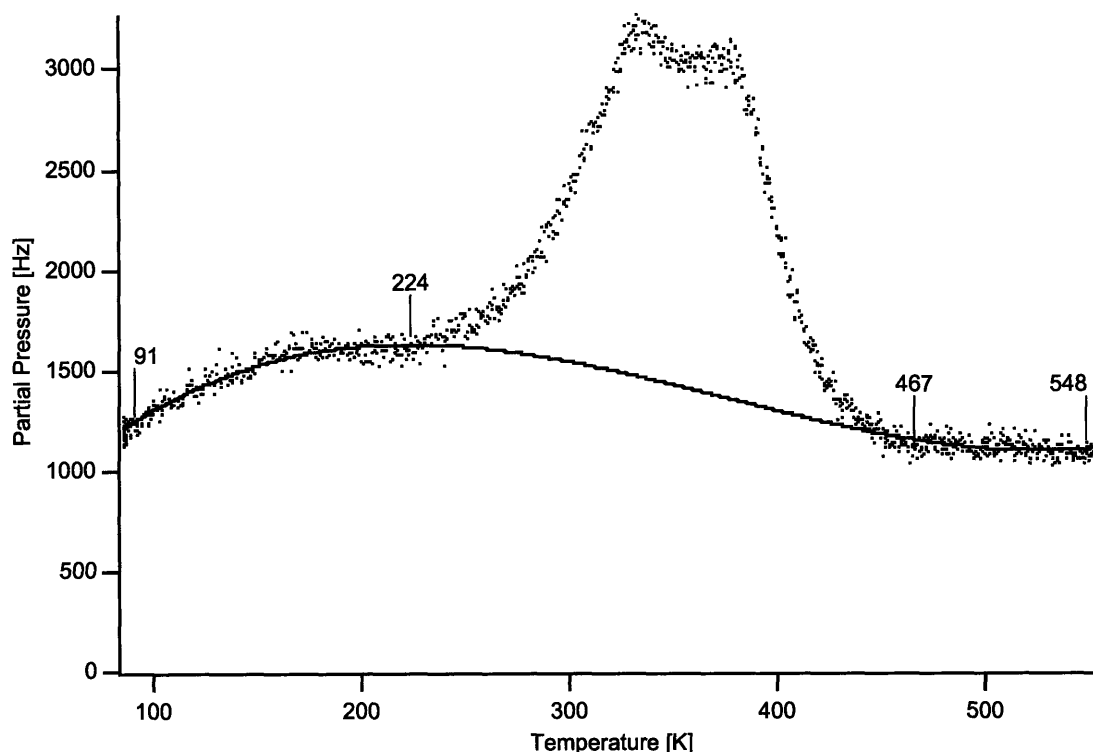


Figure 9. Partial pressure of H_2 (dots) as an H-atom saturated (1 ML H) Ni(111) surface is heated at 2 K/s from 77 to 550 K. Background desorption of H_2 occurs in the two temperature ranges indicated by the labels. The line is a 3rd order polynomial (Eqn. 4) fit to the H_2 partial pressure in the indicated temperature ranges.

For these experiments, Au/Ni(111) surface alloys are prepared, and the relative values R_{Au} are measured by AES, as described in the experimental section. The surfaces are then saturated with H atoms by exposure to H_2 gas. A saturated H layer is achieved by exposure of the Au/Ni(111) surface alloys to 2×10^{-5} torr H_2 gas while the surface alloys cool from 600 to 77 K. This procedure is analogous to that used by Holmblad et. al. in preparing D atom saturated Au/Ni(111) surface alloys.² Measurement of the H_2 partial pressure as the surface is heated from 77 to 600 K yields the total amount of H atoms adsorbed on the surface, and hence the saturation coverage of H atoms at the surface. By comparison of the saturation H atom coverage to the work of Holmblad et.

al., the absolute Au coverage can be determined. This procedure is repeated for multiple Au coverages, yielding the relationship between the relative amount of Au measured by AES, R_{Au} , and the absolute amount of Au, θ_{Au} .

The results section is divided into sections covering the determination of the absolute coverage of adsorbed H atoms, the measurement of the saturation H atom coverage for increasing Au coverages, and finally the relation between relative Au coverage, R_{Au} , and absolute Au coverage, θ_{Au} .

A. Calibration of Absolute Amount of H₂ Desorption from Ni(111) Surface

The saturation exposure of H₂ to the Ni(111) surface is achieved by exposing the surface to 2×10^{-5} torr H₂ gas while the surface cools rapidly from 600 to 77 K (typically ~5 min).² The partial pressure of H₂ in the chamber as the crystal is heated from 77 to 600 K is then measured. The results are presented in Figure 9.

One problem associated with this method for exposure of the crystal to H₂ is that the other metal surfaces of the crystal manipulator receive the same dose of H₂ gas as the Ni(111) crystal. In particular, the heating filament, the tungsten support posts and the edges and back face of the Ni(111) crystal can adsorb hydrogen when the chamber is backfilled. When the crystal is heated during an experiment, the temperature of these surfaces is also raised somewhat, resulting in the desorption of H₂ gas. This results in the background partial pressure of H₂ gas in the chamber changing during the course of the scan. To correct for this effect, the background desorption is identified for the H₂ TDS from a Ni(111) surface. The background in the data shown in Figure 9 is defined as the H₂ partial pressure between 91 and 224 K, and between 467 and 548 K, as indicated by the labels in Figure 9. A plot of these background data, and a best-fit 3rd order

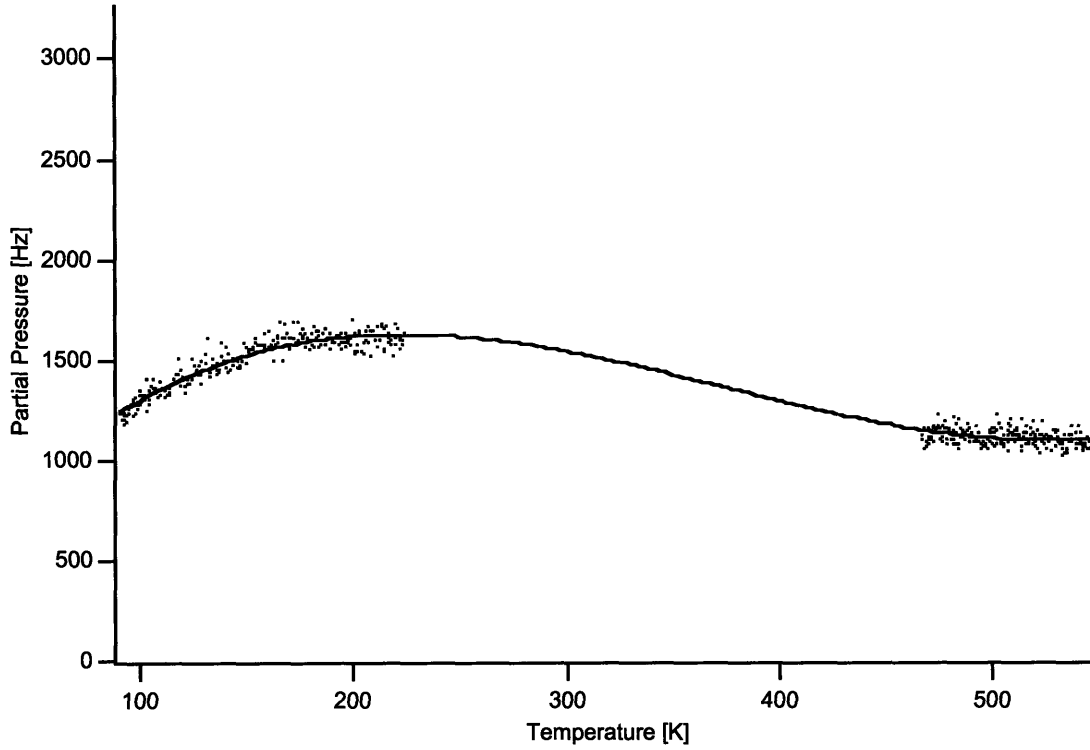


Figure 10. Background partial pressure of H_2 (dots) measured while heating a H-atom saturated (1 ML H) Ni(111) surface at 2 K/s. The line is the best fit 3rd order polynomial, Eqn. 4, as described in the text.

polynomial that models these data are shown in Figure 10. The equation for the polynomial is given by:

$$B(T) = b_0 + b_1T + b_2T^2 + b_3T^3 \quad (4)$$

where T is the temperature, and b_i are the coefficients that are determined when the polynomial is fit to background data. The coefficients that yield the best linear-least squares fit to the data in Figure 10 are given in Table 1.

The error in the background function $B(T)$ is given by the standard Pythagorean error equation:

$$\sigma_{B(T)}^2 = \sigma_T^2 \left(\frac{\partial B}{\partial T} \right)^2 + \sum_{i=0}^3 \sigma_{b_i}^2 \left(\frac{\partial B}{\partial b_i} \right)^2$$

	b_0 [Hz]	b_1 [Hz / K]	b_2 [Hz / K ²]	b_3 [Hz / K ³]
Coefficients (b_i)	351	13.3	-0.043	3.8×10^{-5}
Error in coefficients (σ_{b_i})	24	0.3	0.001	1×10^{-6}
Percent error in coefficients (σ_{b_i}/b_i)	6.8	2.1	2.3	2.7

Table 1. Coefficients, error in coefficients, and fraction error of coefficients for 3rd order polynomial (Eqn. 4) fit to background partial pressure of H₂ desorbing from a H atom saturated (1 ML H) Ni(111) crystal heated at 2 K/s from 77 to 550 K.

where σ_T is the error in the temperature T and σ_{b_i} are the errors in the fitting coefficients b_i of the polynomial in Eqn. 4. The error in the temperature σ_T is measured by holding the crystal at 77 K, and recording the temperature for several minutes. The standard deviation of the temperature measured under these conditions is 0.5% of the measured value of the temperature. This standard deviation is consistent the experimental apparatus employed. The current data acquisition (DAQ) system measures the temperature via a thermocouple. The thermocouple voltage is amplified by a factor of 100 and then measured by the digital to analog converter (DAC) of the computer. The current DAC contains 12 bits, and is set to measure over the range -10 to 10 V. A change in the lowest order bit of the DAC then corresponds to a change in voltage of:

$$\frac{20 \text{ V}}{2^{12}} = \frac{20 \text{ V}}{4096} = 0.0049 \text{ V}$$

At 77 K, the measured voltage is -0.85 V. Therefore, the error is $0.0049/0.85 = 0.0057 = 0.6\%$. This percent error is consistent with the experimentally measured error in the temperature, and indicates that the bulk of the error in the temperature measurement arises from the limitation of the 12-bit DAC.

The error in the measured temperature ($\sigma_T \sim 0.5\%$) is a factor of 7 smaller than the error in the fitting parameters (Table 1, $\sigma_{b_i} \sim 3.5\%$ on average), so the first term

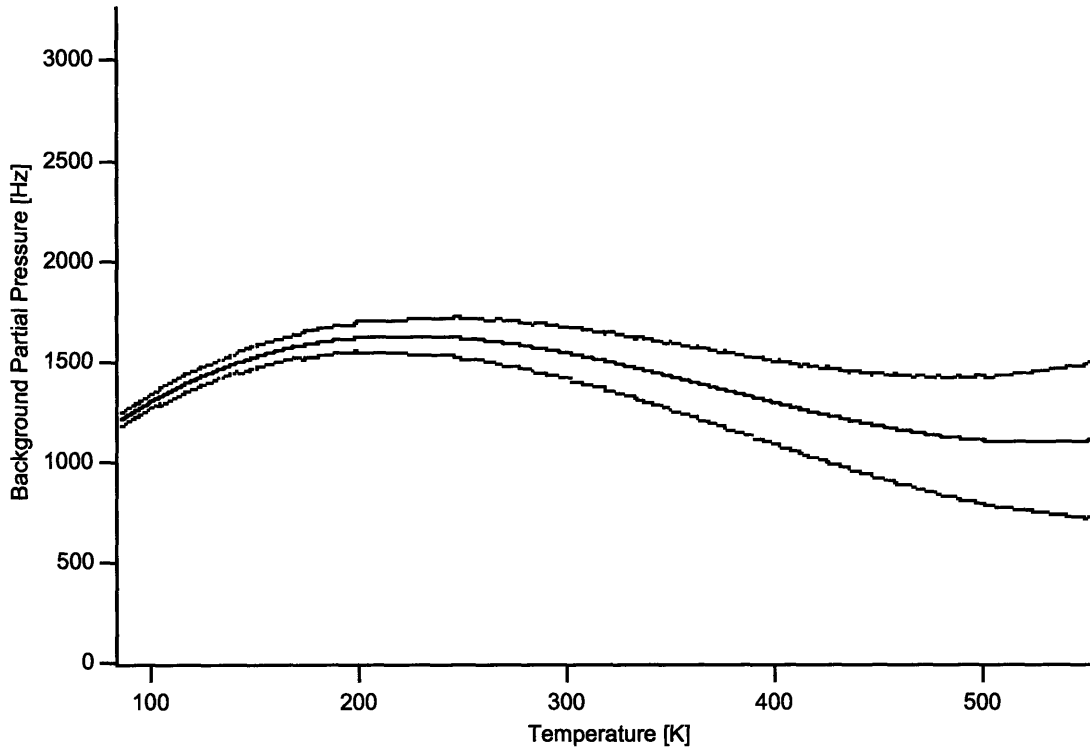


Figure 11. Best fit 3rd order polynomial (Eqn. 4) to background partial pressure of H₂ (middle trace) measured while heating a H-atom saturated (1 ML H) Ni(111) surface at 2 K/s. The uppermost and lowermost curves represent this curve recalculated using coefficients from Table 1 increased and decreased by one standard deviation.

contributes a negligible amount to the error and can be ignored. The equation then becomes:

$$\begin{aligned}\sigma_{B(T)}^2 &= \sum_{i=0}^3 \sigma_{b_i}^2 \left(\frac{\partial B}{\partial b_i} \right)^2 = \sigma_{b_0}^2 \left(\frac{\partial B}{\partial b_0} \right)^2 + \sigma_{b_1}^2 \left(\frac{\partial B}{\partial b_1} \right)^2 + \sigma_{b_2}^2 \left(\frac{\partial B}{\partial b_2} \right)^2 + \sigma_{b_3}^2 \left(\frac{\partial B}{\partial b_3} \right)^2 \\ &= \sigma_{b_0}^2 + \sigma_{b_1}^2 T^2 + \sigma_{b_2}^2 T^4 + \sigma_{b_3}^2 T^6 = \sum_{i=0}^3 \sigma_{b_i}^2 T^{2i}\end{aligned}\quad (5)$$

Using the coefficients of the best fit polynomial (Table 1), $B(T)$ is then calculated for each value of the temperature at which a partial pressure measurement is made. The result from Eqn. 4 is plotted as the line in Figure 9, and the middle trace in Figure 11.

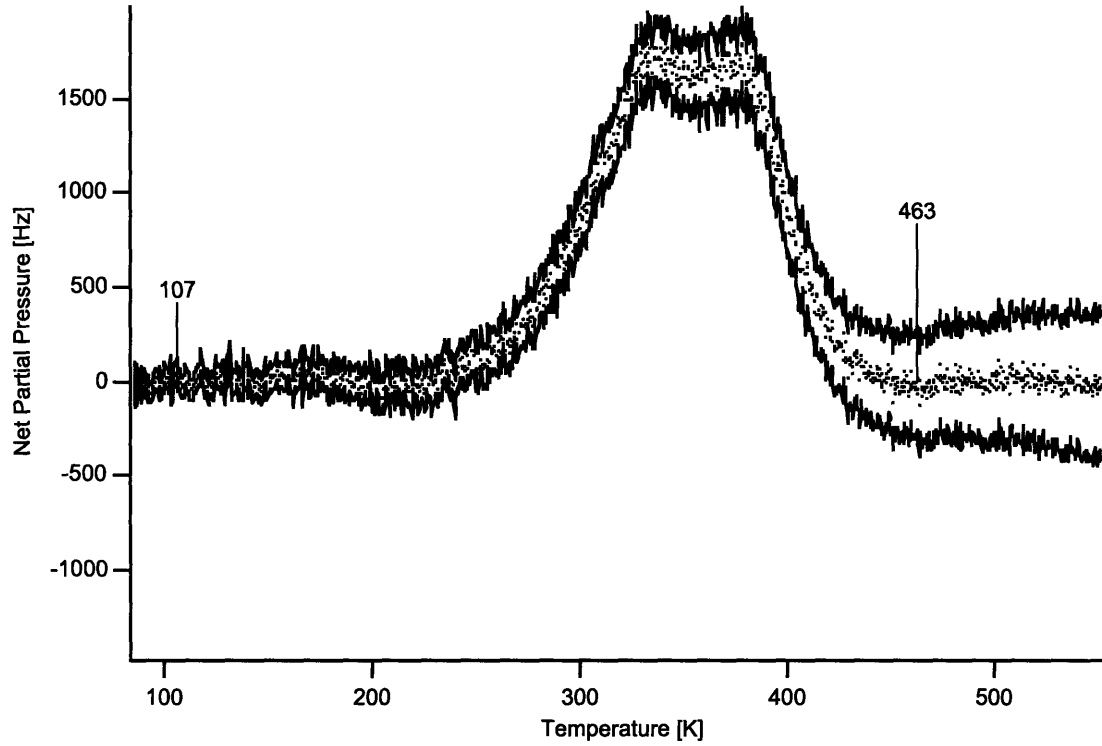


Figure 12. Net partial pressure of H_2 (dots) as an H-atom saturated (1 ML H) Ni(111) surface is heated at 2 K/s from 77 to 550 K, calculated by subtraction of background H_2 partial pressure (Figure 11, middle trace) from raw data (Figure 9). Also plotted is the net partial pressure of H_2 representing one standard deviation of error in the background H_2 partial pressure function (upper and lower traces) $\sigma_{B(T)}$ calculated from the square root of Eqn. 5.

The error in $B(T)$, calculated as the square root of Eqn. 5, $\sigma_{B(T)}$ is shown in Figure 11 as the upper- and lower-most traces. These curves represent one standard deviation.

By subtracting this calculated background from the measured H_2 partial pressure plotted in Figure 9, the net partial pressure of H_2 desorbing from the crystal is obtained, as given by:

$$N(T) = C(T) - B(T) \quad (6)$$

where $C(T)$ is the measured H_2 partial pressure at temperature T and $B(T)$ is the background fitting function (Eqn. 4), described above, at temperature T . This net signal $N(T)$ is plotted as the middle trace in Figure 12.

The error in the net signal $\sigma_{N(T)}$ is calculated using Pythagorean error propagation:

$$\sigma_{N(T)}^2 = \sigma_{C(T)}^2 \left(\frac{\partial N}{\partial C} \right)^2 + \sigma_{B(T)}^2 \left(\frac{\partial N}{\partial B} \right)^2 = \sigma_{C(T)}^2 + \sigma_{B(T)}^2 \quad (7)$$

$C(T)$ follows Poisson statistics, therefore:

$$\sigma_{C(T)} = \sqrt{C(T)} \quad (8)$$

Substituting Equation 5 and Equation 8 into Equation 7 yields:

$$\sigma_{N(T)}^2 = C(T) + \sum_{i=0}^3 \sigma_{b_i}^2 T^{2i} \quad (9)$$

The calculated error in the net H_2 partial pressure $\sigma_{N(T)}$ is plotted above and below the value of the net H_2 partial pressure $N(T)$ in Figure 12. These upper and lower traces represent one standard deviation of error.

This net signal represents hydrogen desorbing solely from the surface of the Ni(111) crystal. It is known that under the conditions of these experiments, the H_2 exposure saturates the surface with a coverage of 1 ML of H atoms.¹⁵ Therefore, the total area represented by the net signal is directly proportional to 1 ML of H atoms. Integration of the net signal yields this area. The integration is performed by summing the net signal over the discrete temperatures at which the data were sampled. The equation for this integral can then be written as:

$$I = \sum_{j=1}^m N(T_j) = N(T_1) + N(T_2) + N(T_3) + \dots + N(T_m) \quad (10)$$

where m is the number of discrete temperatures at which the partial pressure is measured, j is the index of the discrete temperatures, T_j is the discrete temperature at which data

point j was sampled and $N(T_j)$ is the net partial pressure of H_2 (Equation 6) measured at T_j . The value of this integral is 4.60×10^5 counts. This value is directly proportional to 1 ML of H atoms, therefore all future measurements of H_2 in the mass spectrometer, which use the same electron ionization energy (80 eV), ion energy (20 eV), channeltron voltage (3 keV) and emission current (2 mA), can be converted to absolute monolayers of H atoms using this value. All of the measurements of the partial pressure reported here were obtained on the same day. Therefore, no calibration due to instrumental drift is required.

The error in the value of each $N(T_j)$ contributes to the error in the value of the integral I , which is calculated as:

$$\sigma_I^2 = \sum_{j=0}^m \sigma_{N(T_j)}^2 \left(\frac{\partial I}{\partial N(T_j)} \right)^2$$

where σ_I is the error in the value of the integral and $\sigma_{N(T_j)}$ is the error in the value of the net signal at temperature T_j . This equation can be re-written as:

$$\begin{aligned} \sigma_I^2 &= \sum_{j=1}^m \sigma_{N(T_j)}^2 = \sum_{j=1}^m \left[\sigma_{C(T_j)}^2 + \sigma_{B(T_j)}^2 \right] = \sum_{j=1}^m \left[C(T_j) + \sigma_{b_0}^2 + \sigma_{b_1}^2 T_j^2 + \sigma_{b_2}^2 T_j^4 + \sigma_{b_3}^2 T_j^6 + \sigma_{b_4}^2 T_j^8 \right] \\ &= m \cdot \sigma_{b_0}^2 + \sum_{j=1}^m C(T_j) + \sigma_{b_1}^2 \sum_{j=1}^m T_j^2 + \sigma_{b_2}^2 \sum_{j=1}^m T_j^4 + \sigma_{b_3}^2 \sum_{j=1}^m T_j^6 + \sigma_{b_4}^2 \sum_{j=1}^m T_j^8 \end{aligned} \quad (11)$$

For the data in Figure 12, given a value of 4.6×10^5 counts for I , this error calculation yields a value of 5×10^3 counts for σ_I . The fractional error is 1%.

B. Absolute H atom Coverage for Non-Zero Au Coverages

Figure 13 shows the partial pressure of H_2 measured as the surface is heated from 77 to 500 K, after a saturation exposure of H_2 for a series of Au/Ni alloy surfaces with

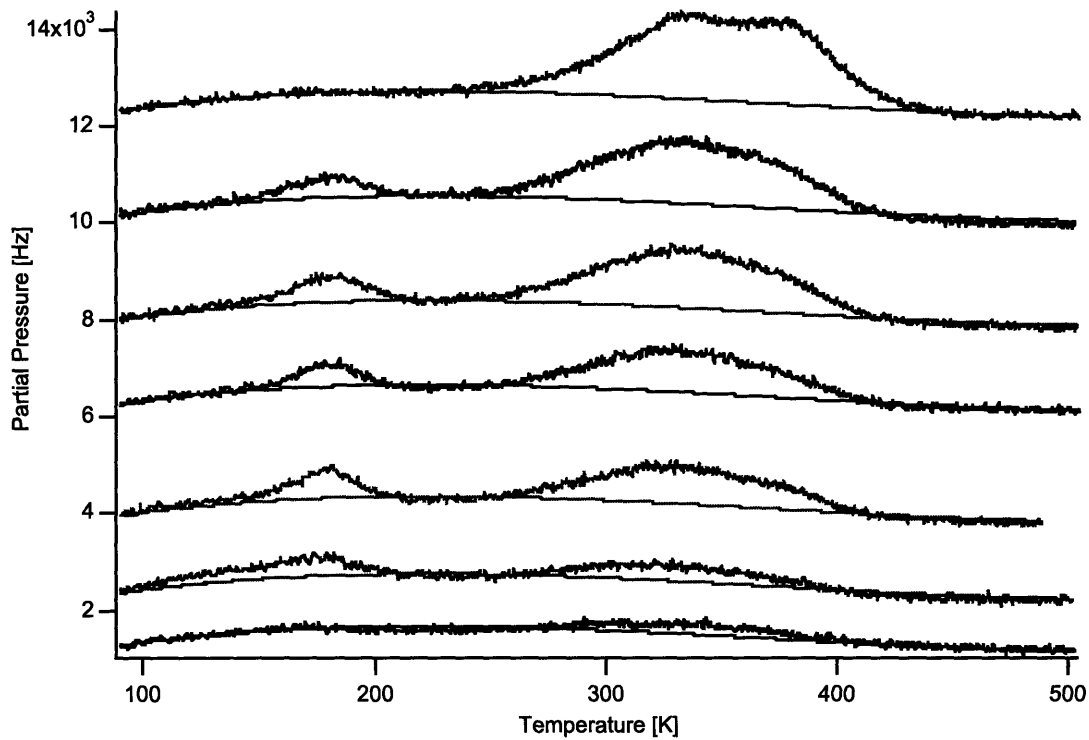


Figure 13. Partial pressure of H_2 measured as H-atom saturated Au/Ni(111) surface alloys are heated at 2 K/s from 77 to 500 K. Top trace is measured from a Ni(111) surface, Au coverage increases for subsequent traces. Also shown are the background subtraction functions for each data set, based on Figure 10, Eqn. 4, and Table 1. See text.

increasing Au coverage (from top trace to bottom trace). For reference, the top trace is the same as that in Figure 9, corresponding to 0 ML Au. Also shown in Figure 13 is the background subtraction function $B(T)$ (Equation 4) for each data set. For each trace, the values $B(T)$ are calculated using the polynomial coefficients b_1 , b_2 and b_3 from Table 1 and the discrete temperatures T_j at which the H_2 partial pressures were measured. The offset coefficient b_0 of the background trace $B(T)$ is calculated for each trace as the average background partial pressure of H_2 measured for 20 s prior to each experiment.

Figure 14 shows the net H_2 partial pressure desorbing from the front surface of the Au/Ni(111) surface alloy, which is determined by subtracting the background function $B(T)$ from the measured H_2 partial pressure. The integral of each of these traces

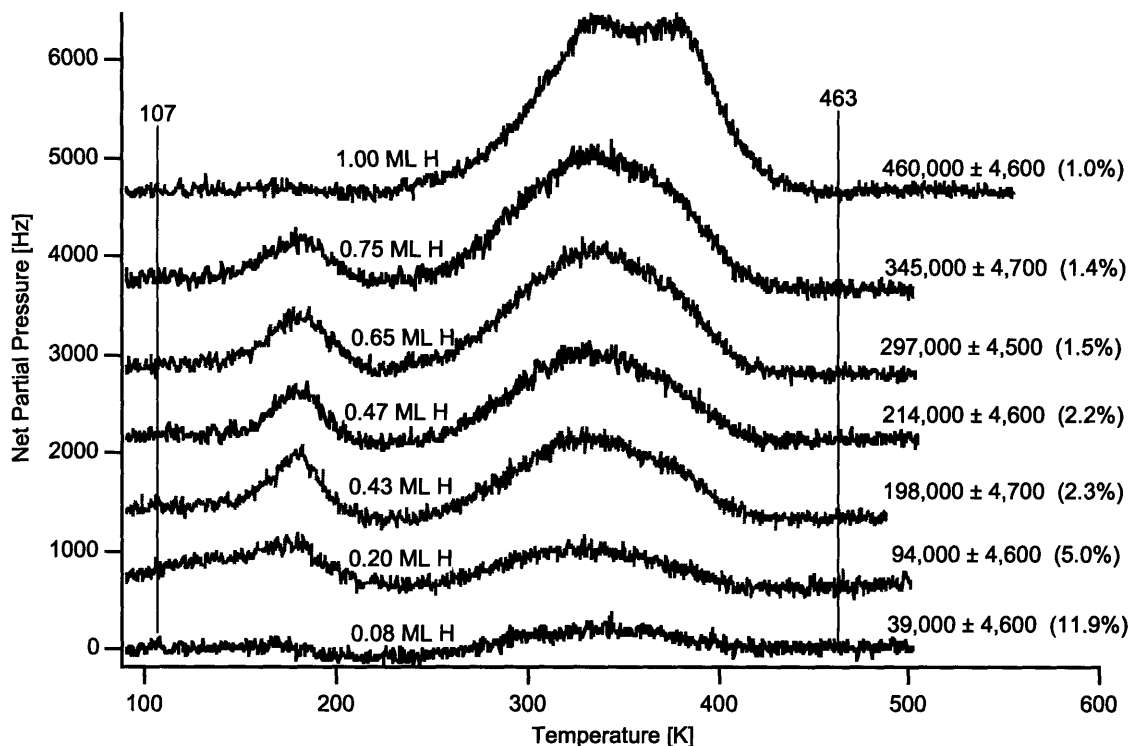


Figure 14. Net partial pressure of H_2 as H-atom saturated Au/Ni(111) surface alloys are heated at 2 K/s from 77 to 500 K. Calculated by subtraction of the background H_2 desorption (Figure 13) from the raw H_2 desorption (Figure 13). The vertical lines indicate the limits of integration, and the labels for each trace are the value of the integration (Eqn. 10), with absolute and percent error calculated from Eqn 11. The traces are also labeled with the calculated H atom coverage (Eqn 12). The error in the H atom coverage (Eqn. 12) is ± 0.01 ML.

(Equation 10) is directly proportional to the amount of H_2 desorbing from the surface. Consistent with the results of Holmblad et. al,² a low temperature feature appears (~ 180 K) with increasing Au coverage, and then disappears at the highest Au coverages. Each trace in Figure 14 is labeled with its integrated area and the error associated with the integrated area, as calculated using Equation 11. The limits of integration used are 107 to 463 K, as indicated by the labeled vertical lines in Figure 14.

The absolute error of the integral for each H_2 TDS is relatively constant. The major source of error results from the use of the background subtraction function. It contributes error equally to each experiment, regardless of the Au coverage of the

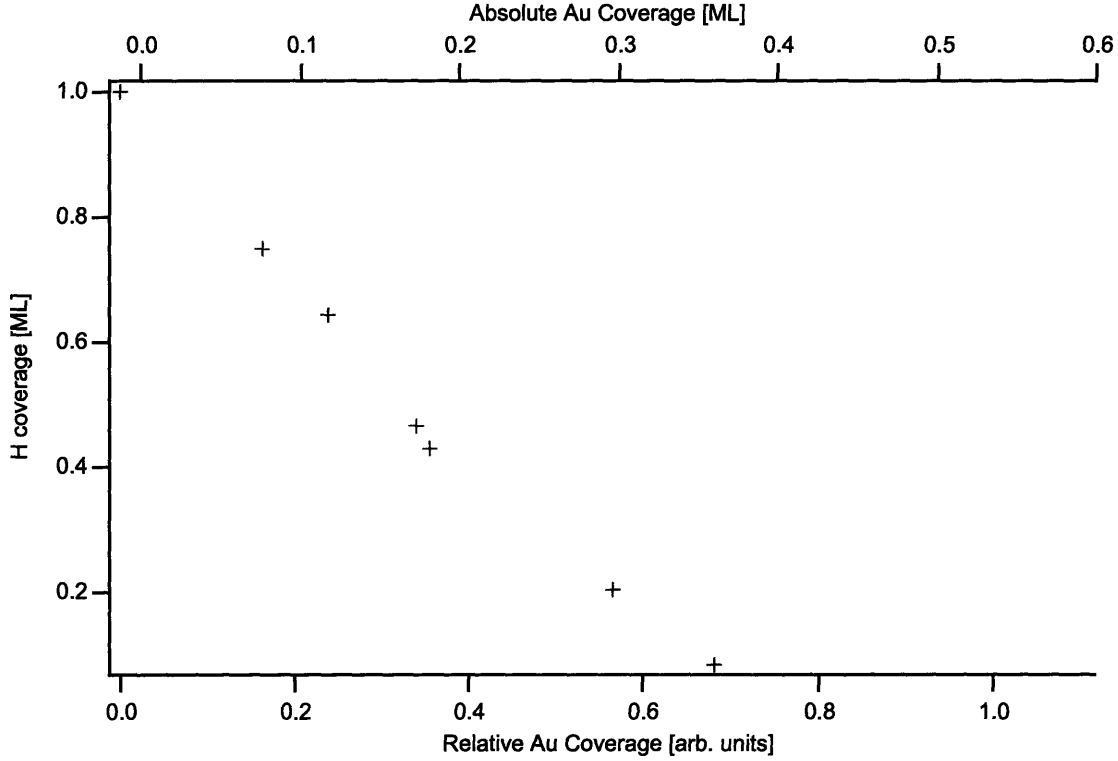


Figure 15. H atom coverage measured from Figure 14 vs. relative Au coverage measured from Figure 8 plotted against bottom axis. Also, H atom coverage vs. absolute Au coverage from best-fit line in Figure 19, plotted against upper axis.

surface. The measurement with the smallest integrated amount of desorbing H_2 (at the highest Au coverage) has the highest fractional error.

Using the integrated values of the net H_2 partial pressure, the absolute coverage of H_2 desorbing from each surface can now be calculated relative to the net H_2 which desorbs from a monolayer of adsorbed H on Ni(111):

$$\theta_H = \frac{I}{I_0} \quad (12)$$

where θ_H is the absolute amount of H atoms desorbing from the surface (in ML), I is the value of the H_2 TDS integral and I_0 is the value of the H_2 TDS integral for a Ni(111) surface with 0 ML Au. The calculated value of the absolute hydrogen coverage is labeled on each trace in Figure 14.

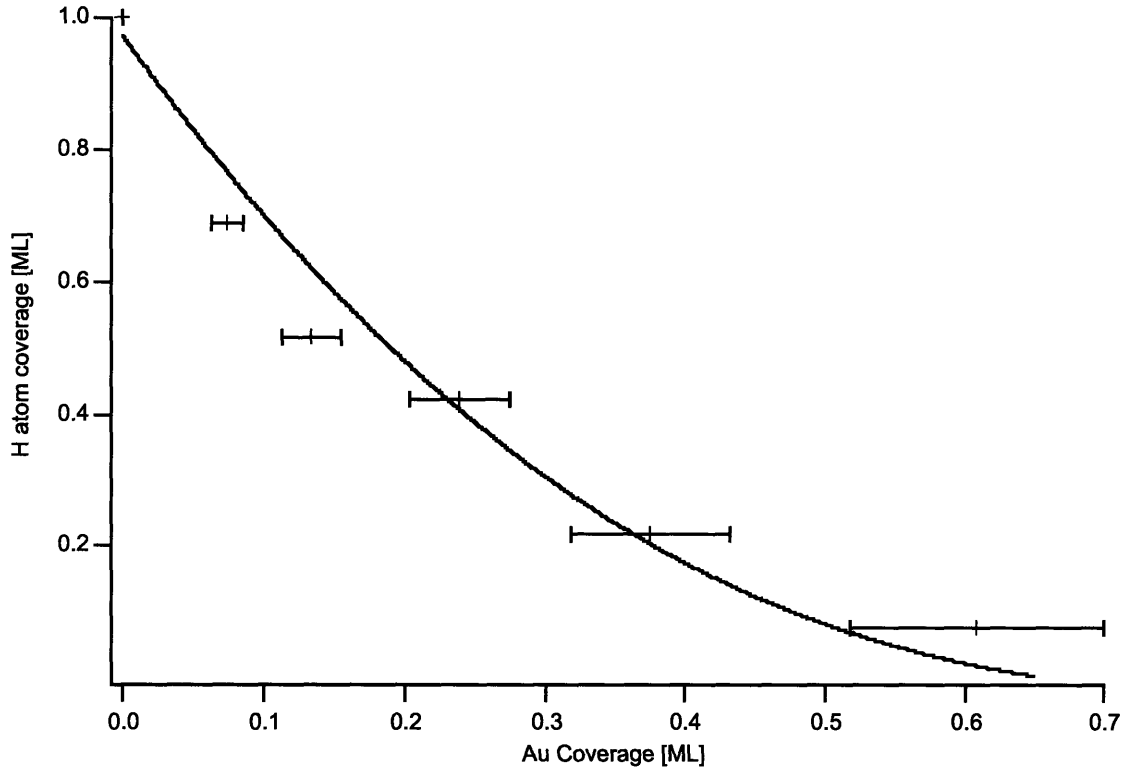


Figure 16. H atom coverage vs. Au coverage, as reported by Holmblad, Larsen and Chorkendorff.² Crosses are data, line is model proposed by the authors. Horizontal error bars on the data points are 15% upper limit on the error, as reported by the authors.

For each of these absolute H coverages, a relative Au coverage has been measured using AES (Figure 8). Figure 15 plots these absolute H coverages against the relative Au coverages. Now, by converting from absolute H coverage to absolute Au coverage, the relationship between the absolute Au coverage and the relative Au coverage will be known.

The error in θ_H is given by:

$$\sigma_{\theta_H}^2 = \sigma_I^2 \left(\frac{\partial \theta_H}{\partial I} \right)^2 + \sigma_{I_0}^2 \left(\frac{\partial \theta_H}{\partial I_0} \right)^2 = \sigma_I^2 \left(\frac{1}{I_0} \right)^2 + \sigma_{I_0}^2 \left(-\frac{1}{I_0^2} \right)^2 = \frac{\sigma_I^2}{I_0^2} + \frac{\sigma_{I_0}^2}{I_0^4} \quad (13)$$

The calculation of this error yields a value of ± 0.01 ML for all the measurements. As was shown previously, the absolute error in the value of each integral σ_I is

approximately the same for each experiment. Since the denominator of each term is the constant value of the integral for 0 ML Au which is also independent of the Au coverage, the term $\frac{\sigma_I^2}{I_0^2}$ is independent of the Au coverage.

C. Absolute Au Coverage Determined from Absolute H Atom Coverage

Figure 16 is reproduced from reference 2. The data points are the absolute H atom coverage versus absolute Au coverage. The absolute Au coverage is effectively determined from STM measurements. The solid line is a model used by the authors to simulate the H atom coverage dependence on Au coverage. These data (but not the model) relating H atom coverage to Au coverage are used to determine the absolute Au coverage based on the measured H atom coverage in Figures 14 and 15.

The model used by Holmblad et. al. proposes that 3-fold hollow sites on the Au/Ni(111) surface alloy that have no or one next-nearest neighbor Au atoms adsorb H atoms which desorb in the high-temperature desorption feature. Three-fold hollow sites that have two Au atom next-nearest neighbors adsorb H atoms which desorb in the low temperature feature in the TDS. The number of each of these types of sites is calculated based on a random distribution of Au atoms into the Ni(111) surface. This assumption, while valid for Au coverages below 0.3 ML, is incorrect for higher Au coverages. In work published prior to the work of Holmblad et. al., Jacobsen et. al. demonstrated that 0.4 ML Au deposited onto a Ni(111) surface forms “dendritic islands” at the Ni step edges.⁵ This islanding invalidates the use of a statistical model based on the random alloy structure above 0.3 ML Au.

Therefore, instead of using this model to convert the H atom coverage measurements (Figure 14 and 15) into absolute Au coverages, a cubic spline interpolation

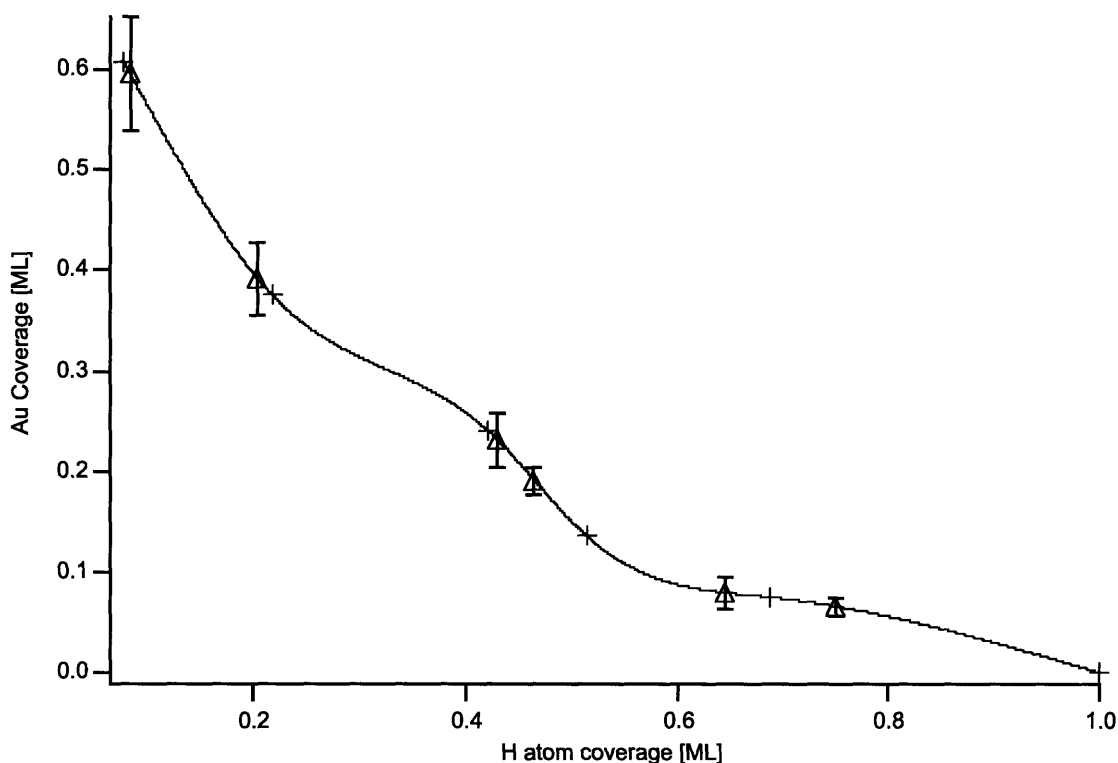


Figure 17. Data from Holmblad et. al.² (crosses, Figure 15) and cubic spline interpolation of that data (line). The cubic spline is then used to calculate θ_{Au} (triangles) from the values of θ_H calculated from Eqn. 12 and based on the integrated values of the spectra in Figure. 14. Error bars are calculated using Eqn. 14 and subsequent equations.

of the published data points is used. The data and the cubic spline interpolation from the Holmblad paper (plotted as absolute Au coverage vs. H atom coverage) are plotted in Figure 17. Also plotted in Figure 17 are the Au coverages that result when the measured H atom coverages from Figure 14 and 15 are converted to absolute Au coverages using the cubic spline interpolation.

The cubic spline interpolation fits a 3rd order polynomial to groups of 4 data points, subject to the condition that adjacent/overlapping polynomials have continuous first and second derivatives. The conditions for the first and second derivatives create a set of W linear equations, where W is the number of data points, which are then solved

numerically.¹³ Unfortunately, no analytical formula for the interpolated curve results, which poses a problem for calculating the propagated error because the Pythagorean error equation requires the first derivative of the function with respect to each of its parameters. However, the error can be calculated by evaluating the derivatives numerically. If an interpolation “function” is defined :

$$\theta_{Au}(\theta_H) = f(\theta_H; \phi_0, \phi_1, \phi_2, \dots, \nu_0, \nu_1, \nu_2, \dots) \quad (14)$$

where f is the numerical function/calculation of the cubic spline, θ_H is the measured H atom coverage measured (Figure 14), ϕ_i is the Au coverage of data point i in Holmblad et. al.,² and ν_i is the H atom coverage of data point i in Holmblad et. al.,² then the error formula is:

$$\sigma_{\theta_{Au}}^2 = \sigma_{\theta_H}^2 \left(\frac{\partial f}{\partial \theta_H} \right)^2 + \sigma_{\phi_0}^2 \left(\frac{\partial f}{\partial \phi_0} \right)^2 + \sigma_{\phi_1}^2 \left(\frac{\partial f}{\partial \phi_1} \right)^2 + \dots + \sigma_{\nu_0}^2 \left(\frac{\partial f}{\partial \nu_0} \right)^2 + \sigma_{\nu_1}^2 \left(\frac{\partial f}{\partial \nu_1} \right)^2 + \dots \quad (15)$$

where σ_{θ_H} is the error in the measured H atom coverage (Equation 13), σ_{ϕ_i} is the error in the Au coverage for data point i in Holmblad et. al.,² and σ_{ν_i} is the error in the H atom coverage for data point i in Holmblad et. al.² The error in the H atom coverage of the data points in the Holmblad paper (σ_{ϕ_i}) is not reported. However, the noise in their measurements of the H_2 partial pressure during desorption is lower than those measured in the current experiments (Figure 13), so it is assumed that σ_{ϕ_i} is at most the same as the value calculated in Equation 6 (± 0.01 ML H). The error in the Au coverage of the data points in the Holmblad paper (σ_{ν_i}) is reported by the authors to be 10-15%, so a value of 15% is used in all calculations.

The remaining terms in the error calculation are the derivatives of the cubic spline interpolation function with respect to the measured H atom coverage θ_H and the

derivatives of the cubic spline interpolation function with respect to each data point that is used to generate the cubic spline interpolation (ϕ_i, ν_i) . The calculation of $\frac{\partial f}{\partial \theta_H}$ is the least numerically intensive, as it requires calculation of the cubic-spline interpolation function only once. By calculating the cubic spline for a series of very closely spaced θ_H , the numerical derivative is determined using:

$$\frac{\partial f}{\partial \theta_H} \approx \frac{\Delta f}{\Delta \theta_H} = \frac{f(\theta_H + \delta_{\theta_H}) - f(\theta_H)}{\delta_{\theta_H}}$$

where δ_{θ_H} is the spacing between adjacent points θ_H in the interpolation routine.

The calculation of the other derivatives involves making a small change in the value of one of the data points, and then re-calculating the entire cubic spline interpolation:

$$\frac{\partial f}{\partial \phi_i} \approx \frac{\Delta f}{\Delta \phi_i} = \frac{f(\phi_i + \Delta \phi_i) - f(\phi_i)}{\phi_i + \Delta \phi_i - \phi_i} = \frac{f(\phi_i + \Delta \phi_i) - f(\phi_i)}{\Delta \phi_i} \quad (16)$$

$\Delta \phi_i$ is a small incremental change in the Au coverage ϕ_i of data point i

This equation is also used to find the derivatives of f with respect to the H atom coverage of the data point ν_i , by replacing ϕ_i with ν_i , and $\Delta \phi_i$ with $\Delta \nu_i$ (a small incremental change in the H atom coverage ϕ_i of data point i).

The numerical calculation of these derivatives is illustrated graphically in Figure 18. The data from Holmblad et. al.² is represented by the + symbols, and the cubic spline interpolation of these data is the solid line. The calculated Au coverages θ_{Au} from the measured H atom coverages θ_H (Figure 14) are represented by the triangles. The calculation begins by incrementing one of the Holmblad data points (in this case, point # 2) by a small amount $\Delta \phi_2$. The value of the increment $\Delta \phi_2$ is exaggerated in Figure 18.

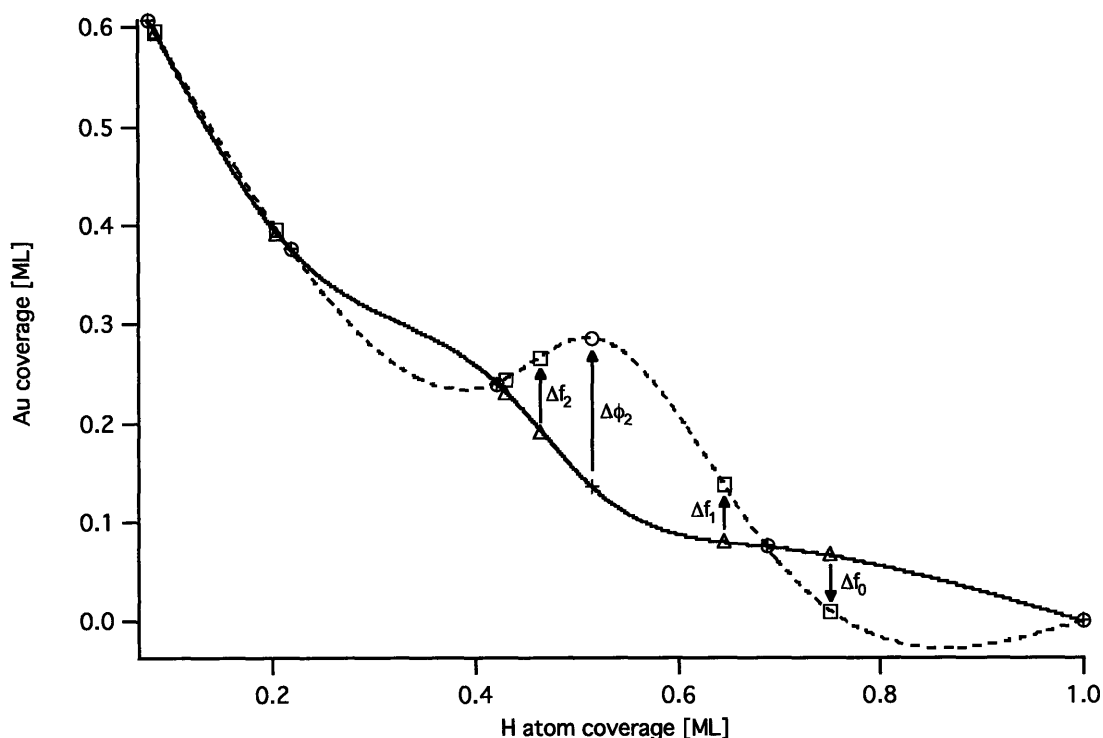


Figure 18. Graphical illustration of the numerical calculation of the derivative of the cubic spline function with respect to the data points used to calculate the cubic spline. Solid line is the original cubic spline (Figure 16) calculated from the original Holmblad data points (crosses, Figure 15). Dashed line is the new cubic spline calculated from the perturbed set of Holmblad data points (circles). Triangles are data points at H atom coverages measured in the experiments reported in Figure 14, with corresponding Au coverages calculated from original cubic spline (Eqn. 14). Squares are data points that have the same H atom coverages as the triangles, but the corresponding Au coverage calculated from the new cubic spline. See text.

The resulting new value of the data point is represented by the circle. The values of all other Holmblad data points are unchanged. This new set of Holmblad et. al.² data points (circles) are used to calculate a new cubic spline interpolation (dashed line). Using this new cubic spline interpolation, a new set of Au coverages are then calculated, for each of the experimentally measured H atom coverages θ_H . These new points are plotted as squares in Figure 18. As can be seen from the figure, the use of the new cubic spline function results in significant changes in the calculated Au coverages for data points 0, 1

and 2 (labeled in Figure 18). The amount of this change Δf_i is then used to calculate the numerical derivative, using Equation 16. Using the numerical derivatives calculated in this manner, and the known errors in each of the data points, the error in the calculated Au coverages $\sigma_{\theta_{Au}}$ is determined using Equation 14, and plotted in Figure 17.

It would be instructive to compare the values of the absolute Au coverage determined by the cubic spline interpolation of the data points of Holmblad et. al.² (Equation 13, Figure 17) to the absolute Au coverage determined by using the statistical model presented in Holmblad et. al. (Figure 16). However, there is some inconsistency in their model that precludes this comparison. Figure 16 is a reproduction of the inset of Figure 10 in Holmblad et. al.² If Holmblad's statistical model was applied without any fitting parameters, then at 0 ML Au coverage the value of both the H atom coverage from the data and from the model should be 1 ML H atoms. However, it appears from the figure in Holmblad et. al.² that these values are not the same. This mismatch indicates that Holmblad et. al. have chosen to apply a scaling factor to their model, to achieve a "best-fit" to the data. Since neither the scaling factor nor its method of calculation are reported, it is not possible to reproduce their model. Therefore, it is not possible to compare Au coverages calculated using a cubic spline interpolation of their data points to Au coverages calculated using the model of Holmblad et. al.

Using the relationship between absolute Au coverage and absolute H saturation coverage shown in Figure 17, it is now possible to calibrate the abscissa of Figure 15 for absolute Au coverage. This plot is shown as the upper trace in Figure 15.

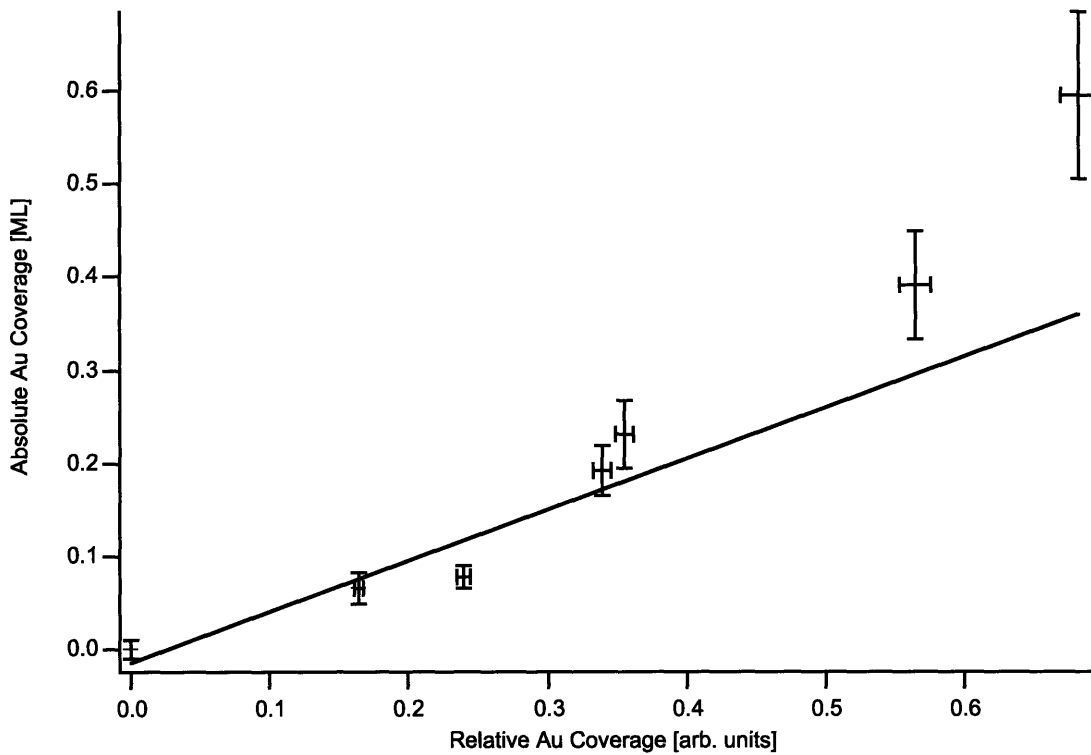


Figure 19. Absolute Au coverage (determined in section C, Figure 14 and Eqn. 13) vs. relative Au coverage measured by AES (determined in experimental section, Figure 8 and Eqn. 2). The error bars represent one standard deviation. The horizontal error bars are calculated using Eqn. 3, the vertical error bars are calculated using Eqn. 14. The best-fit line is calculated using linear least squares, using the error in the errors in the absolute Au coverage as weighting factors.

D. Relationship Between Relative Au Coverage R_{Au} from AES and Absolute Au Coverage θ_{Au} from H Atom Coverage θ_H

While the relationship shown in Figure 15 between the absolute H saturation coverage and absolute Au coverage could be used to determine the Au coverage in all future experiments, measurement of the H saturation coverage is time consuming. Measurement of the relative Au coverage by the ratio of the Auger transitions is more convenient. Therefore, Figure 19 plots the absolute Au coverage θ_{Au} (as determined in Section C) vs. the relative Au coverage R_{Au} measured by AES (as determined in the experimental section). Each value of the relative Au coverage R_{Au} was measured from the

AES spectra in Figure 8. Each these spectra were measured immediately prior to measurements of the saturation H coverage (Figures 13 and 14), which were used to calculate the absolute Au coverage. The error bars are as calculated in their respective sections. Also shown in the figure is the best-fit line to the data, using the errors in the absolute Au coverage as weighting factors. A non-linear fit has also been performed taking into account the error bars in both dimensions simultaneously. However, the resulting best-fit parameters were different by only 0.5%.

In the subsequent experiments, described in Chapters 2 and 3, the absolute Au coverage is determined by converting the relative Au coverage measured by AES into an absolute Au coverage using the relationship given by the best-fit line in Figure 19. The equation for this line is:

$$\theta_{Au} = m \cdot R_{Au} + b \quad (17)$$

where m is the slope of the best-fit line in Figure 18 ($m = 0.55 \pm 0.05$), R_{Au} is the relative fraction of Au at the surface determined by AES and given by Eqn. 2 and b is the intercept of the best-fit line in Figure 19 ($b = -0.013 \pm 0.009$).

The error in the absolute Au coverage calculated using Equation 17 is given by:

$$\begin{aligned} \sigma_{\theta_{Au}}^2 &= \sigma_m^2 \left(\frac{\partial \theta_{Au}}{\partial m} \right)^2 + \sigma_{R_{Au}}^2 \left(\frac{\partial \theta_{Au}}{\partial R_{Au}} \right)^2 + \sigma_b^2 \left(\frac{\partial \theta_{Au}}{\partial b} \right)^2 = \sigma_m^2 (R_{Au})^2 + \sigma_{R_{Au}}^2 (m)^2 + \sigma_b^2 (1)^2 \\ &= \sigma_m^2 R_{Au}^2 + \sigma_{R_{Au}}^2 m^2 + \sigma_b^2 \end{aligned}$$

Using this equation, the errors in the absolute Au coverages for the measurements made in this chapter are ~10% of each value. Therefore, a value of the error of 10% is used in all subsequent reports of the Au coverage.

IV. DISCUSSION

This chapter has reported on the determination of the absolute Au coverage at Au/Ni(111) surface alloys, by comparison of the saturation H-atom coverage of the prepared surfaces to previously published results.² In effect, the surface is titrated by exposure to H₂ to determine the amount of Au on the Ni(111) surface. Furthermore, the relationship between the relative Au coverage, as measured by AES, and the absolute Au coverage has been determined, allowing subsequent measurements of the relative Au coverage by AES to be converted to absolute Au coverages. The ability to measure the absolute Au coverage using AES is an experimental convenience. It is much quicker to measure the Auger electron spectrum of the surface, than it is to saturate the surface with H₂, then measure and integrate the partial pressure of H₂ that desorbs from the surface, and then perform a background subtraction on the data.

Holmblad et. al.² determined the absolute Au coverage at their Au/Ni(111) surface alloys by comparison of low-energy electron diffraction (LEED) patterns to previous results LEED measurements that were calibrated by STM measurements of the absolute Au coverage. As described in the introduction, the Au islands that occur above 0.3 ML Au on the Au/Ni(111) surface alloy have misfit dislocation loops, which form in regular patterns. The regular patterns of these misfit dislocation loops are observable by LEED. The periodicity of these loops depends strongly on the Au coverage. Work done by Nielsen related the LEED patterns to the absolute Au coverage as measured by STM.⁷ It would be possible in theory to measure the LEED pattern of the Au/Ni(111) surface alloys prepared in the experiments of this thesis, and use the same conversion method as

Holmblad et. al. However, the current experimental arrangement precludes simultaneous use of the Au evaporation source and the LEED diffractometer.

It is important to note that the 10% value of the error bar in the Au coverage is the uncertainty in the *absolute* Au coverage. In contrast, the uncertainty in the *relative* Au coverage is only 1%. This fact has important consequences for the experiments in subsequent chapters. Experiments that are described in subsequent chapters have absolute Au coverages that are within 10% of each other. However, these coverages are not within 1%. If the error in the relative Au coverage were 10%, then these data points would not be useful in determining trends as a function of Au coverage. However, since the relative error is 1%, the reported data points have statistically distinguishable Au coverages. In effect, the 10% error bar can be seen to apply with the same magnitude and direction to all data points simultaneously. A more accurate determination of the absolute Au coverage may indicate that all Au coverages should have higher or lower values, but the relative Au coverages will remain unaffected.

V. CONCLUSIONS

The temperature dependence of features observed in the AES of Ni(111) has been observed, and it can be concluded that these features arise from diffraction of secondary electrons,¹¹ and not contaminants on the Ni(111) surface. In addition, a method for determining the absolute Au coverage on a Ni(111) surface using AES has been developed. The method yields an absolute error of ~10% in the Au coverage, and a relative error of 1%. The coverage determination is only applicable in the coverage range 0 – 0.4 ML Au.

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CHAPTER 2 - Adsorption of Oxygen on Au/Ni(111) Surface Alloys

I. INTRODUCTION

Oxidation reactions at transition metal surfaces are some of the most prevalent reactions known to mankind and are important for many reasons. The oxidation reactions of iron, nickel and chromium (the constituents of steel) are the essence of corrosion, which is relevant to metal structures exposed to ambient environmental conditions.¹ From the perspective of the chemical industry, oxidation reactions for the manufacture of many important chemicals (e.g. ethylene oxidation to ethylene oxide) are carried out catalytically at transition metal surfaces.² Finally, catalytic oxidation reactions constitute an important class of pollution abatement reactions, such as oxidation of carbon monoxide to carbon dioxide, or the complete oxidation of organic compounds.^{3,4,5} In each of these disparate types of reactions, there is one common initial chemical step – the adsorption of oxygen at the transition metal surface.^{1,6} The energetics and mechanism of this step determines, for many of these reactions, the ideal operating conditions under which the reaction can be achieved, or in the case of corrosion, prevented.⁶

Adsorption of oxygen on transition metal surfaces has been studied extensively using ultra-high vacuum surface science techniques.⁶ These experiments directly probe the interaction of gas phase O₂ molecules with a clean, well-defined surface. In the most elementary description of O₂ adsorption, there are three possible states for the molecule at the surface: physisorbed, molecularly chemisorbed, and dissociatively (atomically) chemisorbed.^{6,7} In the physisorbed state, there is no chemical bond between the surface and the molecule. The molecule is weakly bound to the surface by van der Waals forces. In the molecularly chemisorbed state there is a chemical bond between the surface and

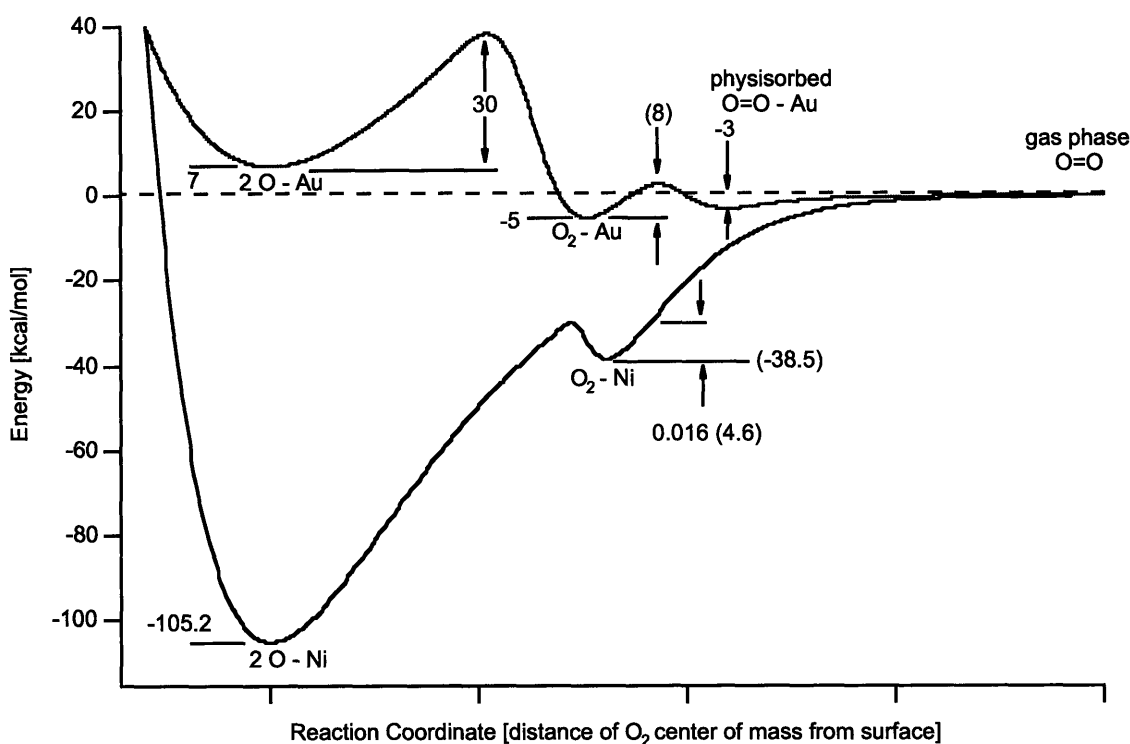


Figure 1. Schematic potential energy diagrams of O_2 interaction with Au(111) (top) and Ni(111) (bottom) surfaces. The abscissa qualitatively represents the reaction coordinate for adsorption. Experimentally determined energies^{8,9} are reported where known. Theoretical values are reported in parenthesis.

each oxygen atom and an internal bond between the oxygen atoms. However, this O-O bond is weaker than in the gas phase. For atomically adsorbed oxygen, each oxygen atom of the original molecule is chemically bonded solely to the surface.

A schematic potential energy diagram, which illustrates the interaction of oxygen with Au(111)^{8,9} and Ni(111)¹⁰ surfaces is presented in Figure 1. Numerous calculations of the interaction of molecular O_2 with other transition metal surfaces (Rh(111),¹¹ Pd(111),^{10,12} Pd(110),¹³ Pt(111),^{10,14,15} Cu(111),¹⁶ Cu(211),¹⁷ Au(100),¹⁸ Au(211),⁹ Ir(111),¹⁹ Ni(100),²⁰ and Pt₃Co(111)²¹ and Pt₃Fe(111)²¹ alloys) have yielded results that are qualitatively similar to the schematic presented in Figure 1.²² The most notable difference between the schematics for Au(111) and Ni(111) and other transition metal

surfaces is that the other surfaces have a deep potential energy minimum corresponding to molecularly chemisorbed oxygen, which is either absent or very shallow on the Au(111) and Ni(111) surfaces.

Much of the observed behavior of oxygen adsorption on Ni(111) and Au(111), and hence oxidation reactions at these surfaces, can be described using the schematic in Figure 1. For example, on Ni(111), no physisorbed or molecularly chemisorbed species is observed to form after O₂ exposures, even at surface temperatures as low as 8 K.²³ Rather, dissociative chemisorption, leading to atomically adsorbed O atoms is observed. This determination was made unambiguously by spectroscopic identification of the vibration of O atoms bound to Ni(111) occurring at 580 cm⁻¹. The signature of physisorbed (at ~1550 cm⁻¹), or molecularly chemisorbed O₂ (in the range 700-1100 cm⁻¹) was absent. This result implies that the barrier to dissociation is less than 0.016 kcal/mol, in contrast to a calculation that has shown a barrier of 4.6 kcal/mol.¹⁰

Although a surface temperature of 8 K may have been sufficiently cold to trap the physisorbed or molecularly chemisorbed species, the mechanism for dissociative adsorption may be such that the energy of the incident molecules is the most important factor in determining the final state of the adsorbed species. For example, the reaction coordinate may predominantly require approach of the molecule close to the surface, concomitant with stretching of the internal molecular bond. Molecules with higher translational energies will be able to approach closer to the surface before scattering, and thus will be more likely to undergo dissociation. In this case, the energy (and hence temperature) of the surface will play a minor role in dissociative adsorption. Instead, the energy of the incoming molecule will be the most important factor in determining

whether or not dissociative adsorption occurs. In general, the importance of the energy of incident molecules in determining whether or not a gas-surface reaction occurs has been well established,²⁴ and in order to test this possibility for oxygen adsorption, Beckerle et. al. exposed O₂ molecules with translational energy as low as 3.5 meV normal to a Ni(111) surface at 8 K. Under these conditions, the same spectroscopic signature of atomically chemisorbed oxygen with a clear lack of molecular or physisorbed species was observed, indicating that the barrier to dissociation of molecularly chemisorbed or physisorbed state of oxygen on a Ni(111) surface is very small.

Similar results regarding the existence and limits on the stabilization energy of molecular O₂ adsorbates on Ni surfaces with other structures have been observed using a variety of experimental techniques. Specifically, oxygen adsorbs solely dissociatively at the lowest temperatures investigated, 20 K of a Ni(110) surface²⁵ and 80 K of a Ni(100) surface.²⁶

These experimental and theoretical results collectively form the basis for the schematic of the O₂-Ni(111) potential energy diagram in Figure 1, in which the two minima in the potential energy surface correspond to atomically chemisorbed oxygen and to the molecular adsorbate. The abscissa represents a generalized reaction coordinate. For adsorption from the gas phase into the molecularly chemisorbed state, the reaction coordinate involves stretching of the O-O bond, concomitant with approach of the molecule towards the surface. For dissociation of the molecularly chemisorbed O₂, the reaction coordinate involves additional stretching of the O-O bond, and likely diffusion of O atoms into adjacent 3-fold hollow adsorption sites.

The diagram is drawn to scale such that the depth of the potential energy well corresponds to the calculated adsorption energy when an O_2 molecule dissociatively adsorbs to form two adsorbed oxygen atoms, a process which is exothermic by 105.2 kcal/mol.²⁷ Also shown is the potential energy minimum corresponding to molecularly chemisorbed oxygen, labeled with the theoretical values for its energy and barrier to dissociation, as well as the experimentally determined upper limit for the barrier to dissociation of 0.016 kcal/mol.

Very different behavior is observed on Au surfaces exposed to molecular O_2 . For Au(111),²⁸ Au(110),²⁹ and Au(100)³⁰ at temperatures as low as 20 K, no chemisorption of oxygen, either atomic or molecular has been observed after exposure to O_2 . Molecular O_2 has been observed to physisorb on Au(110) at 20 K. Heating a physisorbed O_2 layer results only in desorption of molecular O_2 , and no dissociation.²⁹ Atomic oxygen will chemisorb on Au(111) if the surface is exposed to either gas phase oxygen atoms³¹ or more highly reactive oxygen containing species, such as ozone.⁸ Using the latter, Saliba et. al. were able to conduct experiments on atomically adsorbed oxygen on Au(111). Using temperature programmed desorption, they determined an activation energy of 30 kcal/mol for recombinative desorption of oxygen. Based on this result, and interpretation of previous experimental work,³² they presented a potential energy diagram for the interaction of molecular oxygen with Au(111). The energetics of the physisorbed and atomically chemisorbed states of the potential energy diagram presented by Saliba et. al. are reproduced in Figure 1. In contrast to chemisorbed atomic oxygen on Ni(111), chemisorbed atomic oxygen is a more energetic species than gas phase O_2 molecules. That is, dissociative adsorption of O_2 on Au(111) is endothermic. Atomic O adsorbed on

Au(111) is stabilized by the large activation barrier for dissociation of gas phase O_2 molecules to form chemisorbed O atoms. This barrier is responsible for the lack of reactivity of Au surfaces towards gas-phase molecular O_2 , even at high temperature and pressure.³² Given the lack of reactivity of the other Au surfaces towards gas phase molecular O_2 , the barrier is probably also present for the other Au surfaces. A further difference between the Ni and Au surfaces is the presence of an experimentally observed physisorbed state of oxygen on Au, stabilized by 3 kcal/mol with respect to gas phase O_2 . As noted earlier, the physisorbed species, if present on the Ni(111) surface, is stabilized by a barrier of less than 0.016 kcal/mol.

The energetics of oxygen adsorption presented in Figure 1 are determined by the overlap of the d-band of the metal surface with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of gas phase O_2 . Good overlap between the d-band of the metal and that of the HOMO and LUMO of incident O_2 molecules facilitates charge transfer to occur. Electrons from the bonding π HOMO of the molecule are donated to the surface, while electrons from the metal are donated to the anti-bonding π^* LUMO. Both of these processes result in a reduction in the bond order of the O_2 adsorbate, and the formation of adsorbate-surface bonds. In general, the magnitude of this effect is determined by the difference in energy between the metal d-bands and the Fermi level. The molecular HOMO of O_2 is, by definition, at or below the Fermi level, while the LUMO is above it. Therefore, when the d-band of a metal is closer to the Fermi level, it has better energetic overlap with the HOMO and LUMO of the incident O_2 molecule.^{33,34}

The energetics and reactivity of Au and Ni surfaces can be explained using this theory. The d-band of Ni is located at the Fermi level.³⁵ When an O₂ molecule approaches a Ni surface, there is good energetic overlap between the Ni d-bands and the π^* LUMO of O₂, which facilitates electron transfer into the π^* LUMO of O₂, resulting in reduction of the internal bond-order of the incident O₂ molecule. This efficient charge transfer is the origin of the high adsorption energy calculated for molecular O₂ adsorbed on Ni (-38.5 kcal/mol, Figure 1). In fact, the process is so efficient that the barrier to dissociation is inconsequently small, resulting in no stabilization of the molecular O₂ adsorbate at the surface. Presumably, charge transfer from the Ni d-band to the π^* LUMO of O₂ proceeds until the LUMO is fully occupied and the bond order of the “molecule” is zero, resulting in two adsorbed oxygen *atoms*.

Of course, the actual process of adsorption is not as simple as described above. Rehybridization of the molecular orbitals occurs as the O₂ molecule approaches the surface, so the gas phase HOMO and LUMO are no longer clearly defined as the molecule approaches the surface. However, regardless of the specific nature of the orbitals that exist during the process, half will be bonding, half will be anti-bonding, and efficient charge transfer from the metal d-band into the anti-bonding orbitals will result in dissociation.

In contrast to the electronic structure of Ni, the center of the d-band of Au is ~3 eV below the Fermi level.³⁵ The energetic overlap of the Au d-band with that of the HOMO and LUMO of molecular O₂ is hence significantly less than that for the Ni d-bands. The net result is that electrons are not transferred effectively from the Au d-band into the π^* LUMO of O₂, and the molecular bond order is not reduced. Consequently,

only a weak molecular-surface bonds form. This poor orbital overlap then explains the lack of experimental observation of molecular O₂ chemisorption at Au surfaces. With respect to O₂ dissociation at Au surfaces, the energetic overlap between the Au d-bands and the HOMO and LUMO of O₂ is so poor that the required charge transfer is endothermic by 7 kcal/mol (Figure 1).

This chapter reports on the adsorption of molecular O₂ on a Au/Ni(111) surface alloy. The adsorption behavior is highly dependent on the Au coverage, but at 77 K and in the range of 0.13 to 0.27 ML Au, O₂ chemisorbs molecularly at this surface. As described in the previous paragraphs, this behavior starkly contrasts with that observed at either Au or Ni surfaces. The molecular species are identified by their internal O-O vibrational stretching modes at 790, 850 and 950 cm⁻¹, observed with high resolution electron energy loss spectroscopy (HREELS). Similar frequencies have been observed for molecularly chemisorbed oxygen on other transition metal surfaces (Cu(111),³⁶ Ag(110),³⁷ Ag(100),³⁸ Pd(111),^{39,40} Pd(100),⁴¹ Pt(111),^{42,43,44} Pt(321),⁴⁵ Rh(711),⁴⁶ Ir(111),⁴⁷ Ru(100),⁴⁸ Cr(110),⁴⁹ Mo(112),⁵⁰ W(112),⁵¹ and V(110)⁵²). For some of these metals, there are two possible molecularly chemisorbed states, a peroxo and superoxo-like species, which have a formal charge transfer of two and one electrons from the metal to the chemisorbed oxygen species respectively.⁵³ The multiple frequencies corresponding to multiple adsorbates on the Au/Ni(111) surface alloy suggests that both peroxo and superoxo-like species form on this surface as well.

The discussion section investigates the relationship between the observed reactivity of the Au/Ni(111) surface alloy towards molecular O₂ and previously observed downward shifts in energy of the Au and Ni d-bands that occur upon alloying of Au into

the Ni(111) surface.³⁵ An analytical model for the arrangement of Au atoms around a Ni site for O₂ dissociation is proposed, based on the occurrence of 8 or less Au atoms within an ensemble of 82 surface atoms. For molecular chemisorption, the results of a simulation of a similar arrangement of Au atoms around a Ni site required for molecular chemisorption is presented. The observation that molecularly chemisorbed O₂ dissociates, and does not desorb, is explained by a simple kinetic model, from which the difference in energy of gas phase O₂ and the dissociation barrier is calculated.

II. EXPERIMENTAL

The experimental apparatus has been described extensively elsewhere⁵⁴ and in the previous chapter. Au was deposited onto the Ni(111) surface, and its coverage measured as described in Chapter 1. High resolution electron-energy loss spectroscopy (HREELS) confirmed that the prepared Au/Ni(111) surface alloy was clean of all contaminants. An incident electron energy of 5.5 eV was used for all spectra reported here.

A crystal temperature of 77 K is used for most HREELS experiments, and is achieved by filling the cryostat with liquid nitrogen. For the experiments at 70 K, the cryostat was filled with liquid nitrogen, then sealed and pumped by the house vacuum system. The lower pressure created by the vacuum in the cryostat lowers the boiling point of the liquid nitrogen, and hence the crystal temperature.

In all experiments, oxygen is adsorbed on the surface by exposure to a molecular beam of pure O₂ or a mixture of 10% O₂ in argon. The dilution of O₂ in Ar was used to lengthen the times of exposure so that accurate and repeatable exposures of O₂ could be achieved. The molecular beam nozzle had a diameter of 0.001", was at room temperature for all exposures, and the stagnation pressure was 20 psia for all experiments.

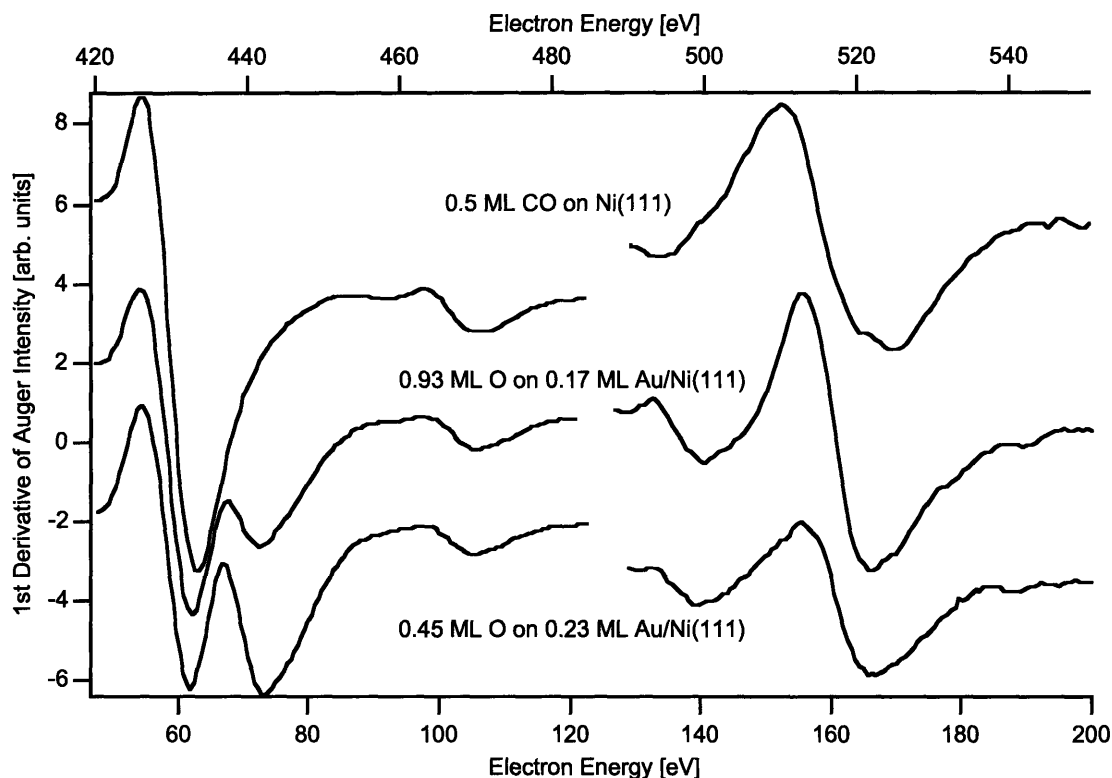


Figure 2. AES spectra used for calibration of oxygen coverage. Spectra in energy region of Ni (61 eV) and Au (69 eV) transitions are plotted against the bottom axis. O (515 eV) spectra are collected with higher instrumental sensitivity (x5), and are plotted against the top axis. The top spectra are measured after exposing 6 L of CO to a Ni(111) surface held at 77 K, creating a saturated layer of 0.5 ML CO. The middle and lower spectra are measured after exposing 4.5 s of a molecular beam of 10% O₂/Ar to Ni(111) surfaces with 0.17 and 0.23 ML of Au respectively.

The absolute amount of oxygen adsorbed at the surface was measured using Auger electron spectroscopy (AES) in the following procedure. AES does not measure the absolute coverage directly, rather it measures the relative coverage of oxygen. In order to convert the relative amount of oxygen measured by AES into the absolute coverage, a calibration standard is required. A saturated layer of carbon monoxide on Ni(111) provides this standard. It is known from previous work that 0.5 ML of CO molecules adsorb at saturation.⁵⁴ The ratio of the peak-to-peak intensities of O (515 eV) to Ni (61 eV) Auger transitions measured for this surface (Figure 2) then corresponds to

0.5 ML of O. In order to convert from measurements of the ratio of these Auger intensities to absolute coverage, a conversion factor R , is defined as:

$$R = \frac{0.5 \text{ ML O}}{(1.0 \text{ ML Ni}) \cdot \left(I_{\text{AES}}(515 \text{ eV}) / I_{\text{AES}}(61 \text{ eV}) \right)} \quad (1)$$

where $I_{\text{AES}}(x \text{ eV})$ is the peak-to-peak intensity of the AES transition with energy x . Using the above equation, and the measured Auger ratios of O (515 eV) to Ni (61 eV) for the CO saturated surface shown in Figure 2 (top spectra), the ratio R has been determined. Subsequent measurements of $I_{\text{AES}}(515 \text{ eV}) / I_{\text{AES}}(61 \text{ eV})$ for other conditions (e.g. adsorption of O_2 instead of CO) of the Ni(111) surface then yields the absolute coverage of oxygen under those conditions.

The lower and middle spectra in Figure 1 were measured after exposing each Au/Ni surface alloy to a molecular beam of 10% O_2/Ar for 4.5 s. However, for surfaces in which the top layer is not composed of pure Ni, the calculation of the absolute oxygen coverage has to be determined using:

$$\theta_{\text{O}} = R \cdot \theta_{\text{Ni}} \cdot I_{\text{AES}}(515 \text{ eV}) / I_{\text{AES}}(61 \text{ eV}) \quad (2)$$

where θ_{Ni} is the fractional coverage of Ni at the surface. For the Au/Ni(111) surface alloys with 0.17 and 0.23 ML Au shown in Figure 2, the amounts of oxygen at each surface after exposure to the 10% O_2/Ar beam for 4.5 s are 0.93 and 0.45 ML O atoms, respectively. This Auger measurement does not indicate which species of oxygen adsorbate are present, rather it just reports the coverage of O atoms present at the surface, either as chemisorbed molecular or atomic oxygen.

There are several factors that contribute error to the calculation of these coverages. The largest contribution comes from the error in the Ni coverage θ_{Ni} , which derives directly from the error in the Au coverage θ_{Au} , determined as described in Chapter 1, to be about 10%. Due to the linear dependence of Equation 2 on the Au coverage, the error in the Au coverage contributes directly to the error in the calculated value of the O coverage. Other contributions, which are not quantifiable include the effect of the electron beam of the Auger spectrometer on the sample surface. It is well established that electron beams incident on metal surfaces can induce chemistry in the adsorbed overlayers, including dissociation and desorption. Both of these processes almost certainly occur on the time scale of the Auger scans in Figure 2. These processes were minimized experimentally by measuring the intensity of O (515 eV) Auger transition before measuring the Ni (61 eV) and Au (69 eV) Auger transitions, thereby reducing the electron beam exposure to the sample prior to data acquisition. The time span of all measurements of the oxygen coverage were the same, so that the unquantifiable effects were the same for all measurements, thus facilitating comparison.

Another unquantifiable effect is the difference in Auger scattering cross sections for oxygen atoms that are part of CO molecules as opposed to chemisorbed O atoms or O atoms in molecularly chemisorbed O₂. It is well established that the chemical environment of an atom generally results in observable differences in the lineshape of its Auger transitions. For example, if a change in chemical environment induced a broadening of the O (515 eV) Auger lineshape, the peak-to-peak intensity would be reduced, although the amount of O present would not have changed. An alternative method that would alleviate the lineshape problem would be to prepare a 0.25 ML

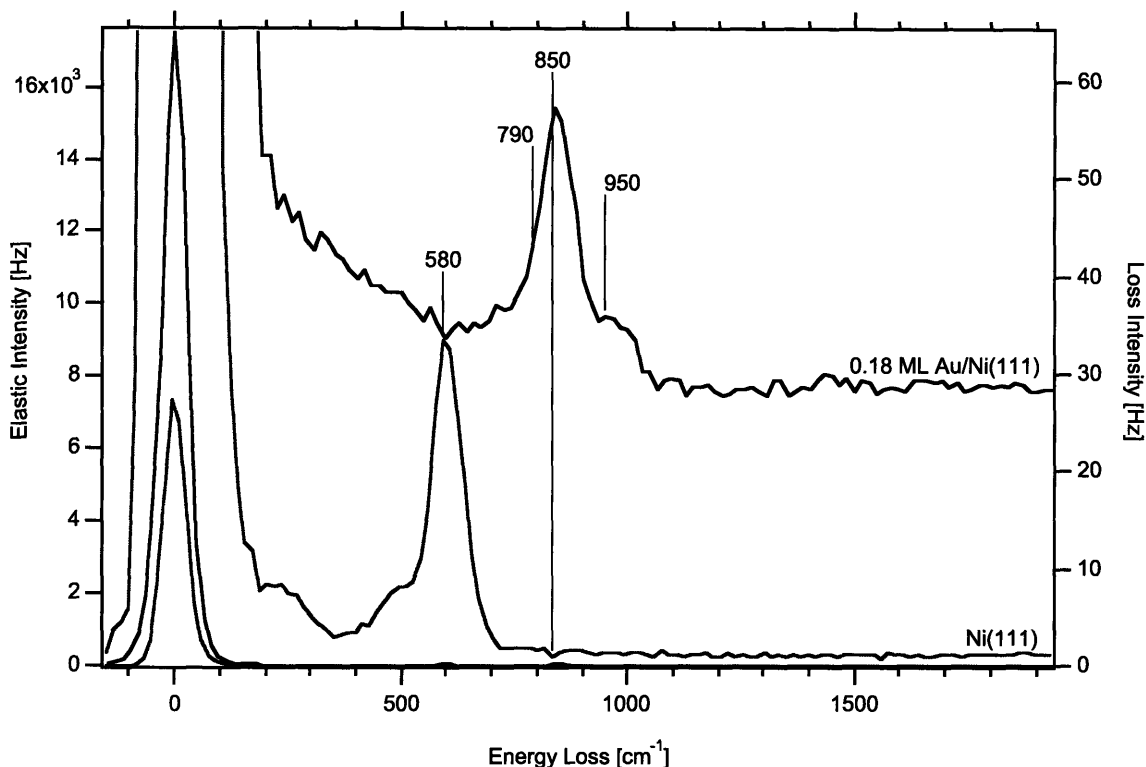


Figure 3. HREELS spectra measured after exposure of Ni(111) and 0.18 ML Au/Ni(111) (at 77 K) to 10% O₂/Ar for 5 s. Spectra are measured at the specular angle, with a FWHM of 55 cm⁻¹.

O/Ni(111) surface. The coverage of this surface can be unambiguously identified by low-energy electron diffraction (LEED), and then the ratio of Eqn. 1 could be calculated using atomic O species, as opposed to molecular CO. However, it is currently not possible to have both the Au deposition source and the LEED instrument in the chamber simultaneously. Furthermore, this method would still not take into account lineshape differences between chemisorbed O atoms and O atoms in chemisorbed molecular O₂.

The 10% error contribution from the uncertainty in the Au coverage, combined with the unquantifiable lineshape error, and possible surface damage by the electron beam described above, indicate that these O coverages should be used as an estimate, and not for any firm mechanistic conclusions. They are provided to serve as a guide to the

relative surface composition that is present during the experiments described in this and future chapters.

III. RESULTS

A. O₂ Adsorption at 77 K

Figure 3 presents HREELS spectra measured after exposure of Ni(111) and 0.18 ML Au/Ni(111) surfaces to a 10% O₂/Ar molecular beam for 5 s. The dominant loss feature observed at 850 cm⁻¹ is assigned to the O–O stretch of a molecularly adsorbed oxygen species. The assignment is based on previous assignments of the vibrational frequency of peroxy or superoxy-like species adsorbed on other transition metal surfaces, as described in the introduction.⁵⁵ Also labeled on this spectrum are two additional features at 790 and 950 cm⁻¹ which appear as shoulders on the main feature at 850 cm⁻¹. These features are assigned to the stretch modes of molecular oxygen species, which are adsorbed at different sites on the surface.

The spectrum in Figure 3 of oxygen on a 0.18 ML Au/Ni surface alloy is in stark contrast to that observed when a Ni(111) surface is exposed to a molecular beam of oxygen, also shown in Figure 3. In this case, the only loss observed occurs at 580 cm⁻¹, and has been previously assigned to the Ni–O stretch vibration of oxygen atoms adsorbed in 3-fold hollow sites. The low-energy shoulder on the 580 cm⁻¹ feature (460 cm⁻¹, not labeled) has been previously observed for high coverages of O atoms on the Ni(111) surface, and has been attributed to O atoms occupying both types of 3-fold hollow sites.⁵⁶ By comparison of the two spectra in Figure 3, it is clear that there is no species present on the 0.18 ML Au/Ni surface alloy with a frequency of 580 cm⁻¹.

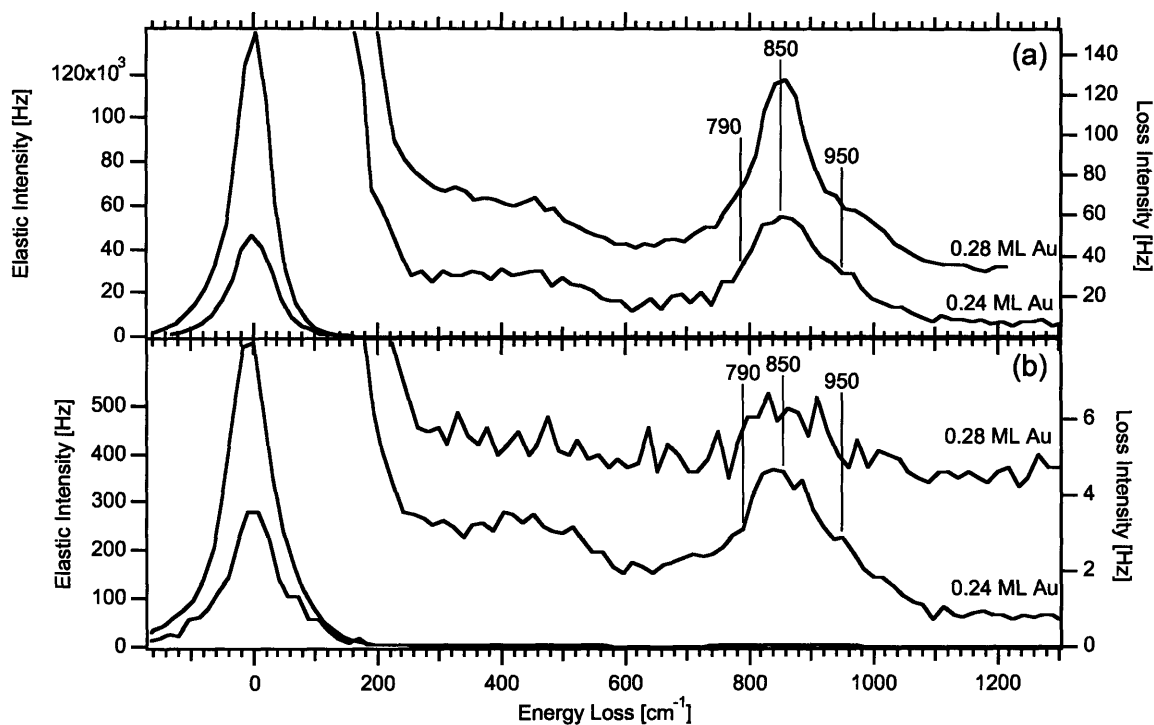


Figure 4. HREELS spectra measured after exposure of 0.24 and 0.28 ML Au/Ni(111) (at 77 K) to 1 L O₂. a) Spectra measured at the specular angle, with a FWHM of 75 cm⁻¹ b) Spectra measured at an off-specular angle, lower trace is measured 6° off-specular, upper trace is measured 10° off-specular. FWHM is 85 cm⁻¹.

HREELS spectra of the O₂/Au/Ni(111) surface have been measured at off-specular angles to determine the mechanism of excitation of the O-O stretching vibrations (at frequencies of 790, 850 and 950 cm⁻¹). The results are presented in Figure 4. For these experiments, the 0.24 ML Au/Ni(111) surface alloy was exposed to O₂ by backfilling the chamber with O₂ gas, such that the total exposure of O₂ was 1 L. Figures 4a and b present spectra measured at the specular angle and at an off-specular angle, respectively, for two different Au coverages. The off-specular angle is defined as the difference, in degrees, between the angle of incidence and the scattering angle. The intensity of the 850 cm⁻¹ feature decreases from 60 to 4.6 Hz when the angle is changed from 0° to 6°. The intensity of the 850 cm⁻¹ feature, measured on the 0.28 ML

Feature (cm^{-1})	0.24 ML Au specular	0.24 ML Au 6° off specular	0.28 ML Au on-specular	0.28 ML Au 10° off- specular
790	34	3.1	58	2.1
850	60	4.6	108	2.7

Table 1. Intensity of 790, 850 and 950 cm^{-1} features, for 0.24 and 0.28 ML Au/Ni(111) surfaces, measured on and off specular.

Au/Ni(111) surface alloy, decreases from 108 to 2.7 Hz when the angle is changed from 0° to 10°. The intensity of the features at 790, 850 and 950 cm^{-1} are presented in Table 1. All three modes are observed to have large decreases in intensity as the detection angle is increased from the specular. This decrease indicates that these modes are dipole active, and that there is a derivative of the adsorbate dipole normal to the surface associated with the O-O stretching mode.⁵⁷

B. Coverage Dependence of Vibrational Spectra

Figure 5 presents HREELS spectra measured after a 5 s exposure of Au/Ni surface alloys with various Au coverages, from 0 to 0.13 ML Au, to a molecular beam of 10% O₂/Ar. In these spectra, the features at 270, 350 – 500, and 580 cm^{-1} , are assigned to the S₂ phonon,⁵⁶ unresolved atomic O-Ni stretch modes for O atoms adsorbed on Ni atoms near Au atoms, and an O-Ni stretch mode, respectively.⁵⁸ The unresolved atomic O-Ni stretch modes are proposed to arise from O atoms adsorbed in 3-fold hollow sites with three Ni nearest neighbors, but with Au atoms as next-nearest and/or next-next-nearest neighbors. Due to the random nature of the Au/Ni(111) surface alloy, there is a wide distribution of these 3-fold hollow sites. For example, O atoms are adsorbed on three-fold hollow sites with one next-nearest neighbor Au atom, some with two next-nearest neighbor Au atoms, some with all Ni next-nearest neighbors but one Au atom next-nearest neighbor. These possible adsorption sites are explained in more detail in the

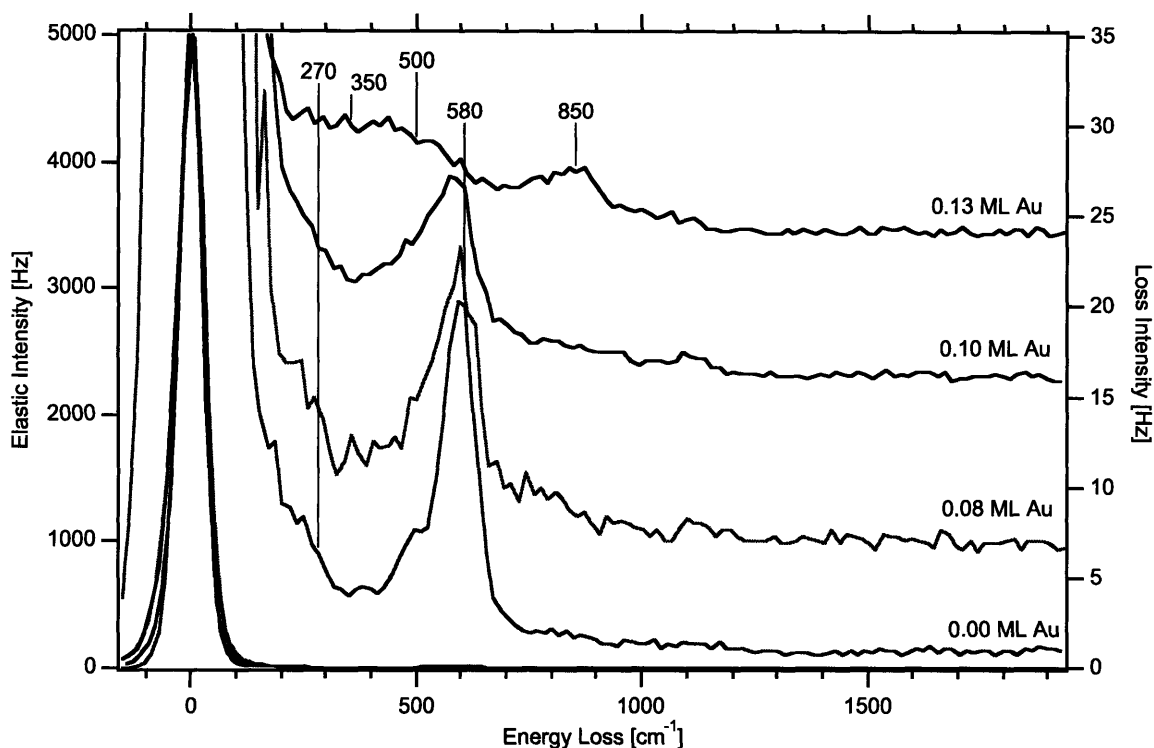


Figure 5. HREELS spectra measured after exposure of Ni(111) 0.08, 0.10 and 0.13 ML Au/Ni(111) (at 77 K) to 10% O₂/Ar for 5 s. Spectra are measured at the specular angle, with a FWHM of 55 cm⁻¹, and are normalized to an elastic peak intensity of 5 kHz for comparison of relative loss intensities.

discussion section, in addition to the assumption that O atoms do not adsorb in 3-fold hollow sites with one or more Au atom nearest neighbors.

The 580 cm⁻¹ feature has been assigned previously to oxygen atoms adsorbed on a Ni(111) surface,⁵⁶ and is assigned to O atoms adsorbed in mostly Au free regions of the Au/Ni(111) surface. At 0.13 ML Au, the first appearance of the 850 cm⁻¹ stretching mode corresponding to molecularly adsorbed oxygen occurs.

In Figure 6, HREELS spectra are shown for Au/Ni(111) surface alloys with between 0.15 to 0.25 ML Au after exposure to a molecular beam of 10% O₂/Ar for 5 s. At 0.18 ML Au, the intensity of the 850 cm⁻¹ feature is a maximum, implying the maximum coverage of peroxo/superoxo-like species. At 0.15 ML Au, there is still some

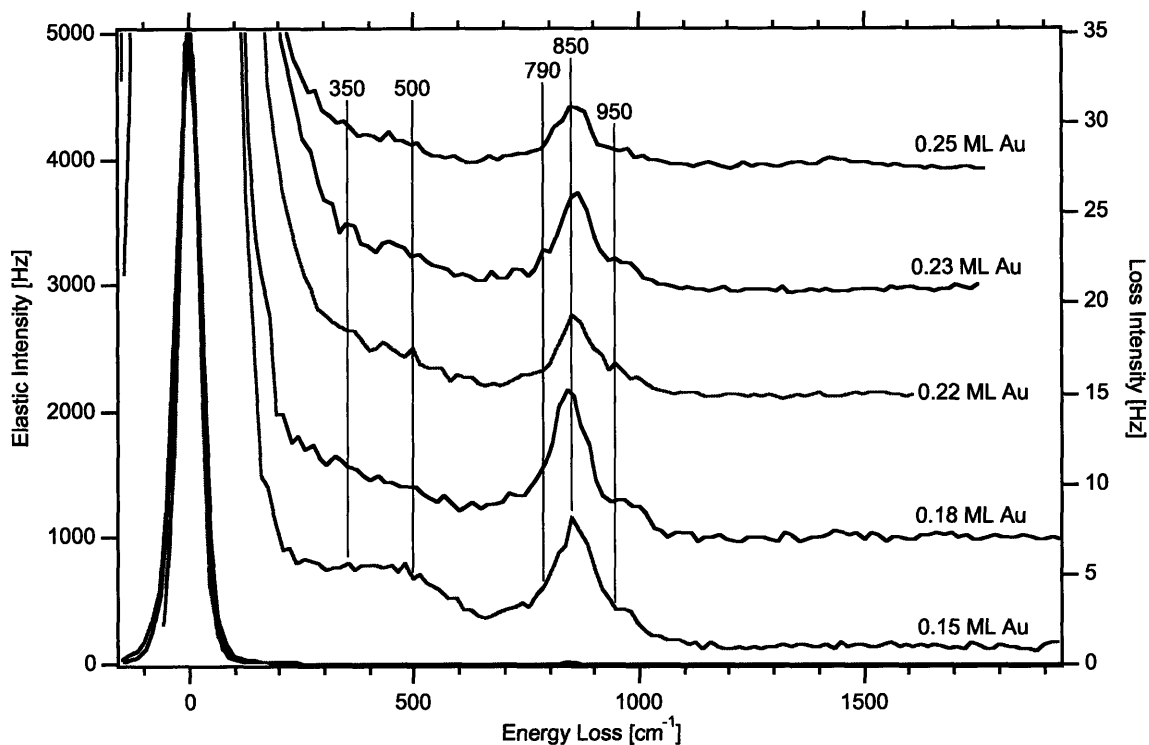


Figure 6. HREELS spectra measured after exposure of Ni(111) 0.15, 0.18, 0.22, 0.23 and 0.25 ML Au/Ni(111) (at 77 K) to 10% O₂/Ar for 5 s. Spectra are measured at the specular angle, with a FWHM of 55 cm⁻¹, and are normalized to an elastic peak intensity of 5 kHz for comparison of relative loss intensities.

intensity in the 350-500 cm⁻¹ region, but in contrast to the spectrum in Figure 5 at 0.13 ML Au, the 850 cm⁻¹ feature is more intense than the unresolved features at 350 - 500 cm⁻¹. The unresolved intensity at 350-500 cm⁻¹ decreases further as the Au coverage is increased, and is barely discernible at 0.25 ML Au, in contrast with the features at 790, 850 and 950 cm⁻¹ which have significant intensity.

The unresolved intensity at 350-500 cm⁻¹ has been assigned above to the vibration of O atoms adsorbed in 3-fold hollow sites with Au atoms as next-nearest and/or next-next-nearest neighbors. Another possibility is that this feature corresponds to the molecule-surface vibration of the molecularly chemisorbed oxygen species. However, the observation that the unresolved intensity between 350-500 cm⁻¹ decreases as the Au

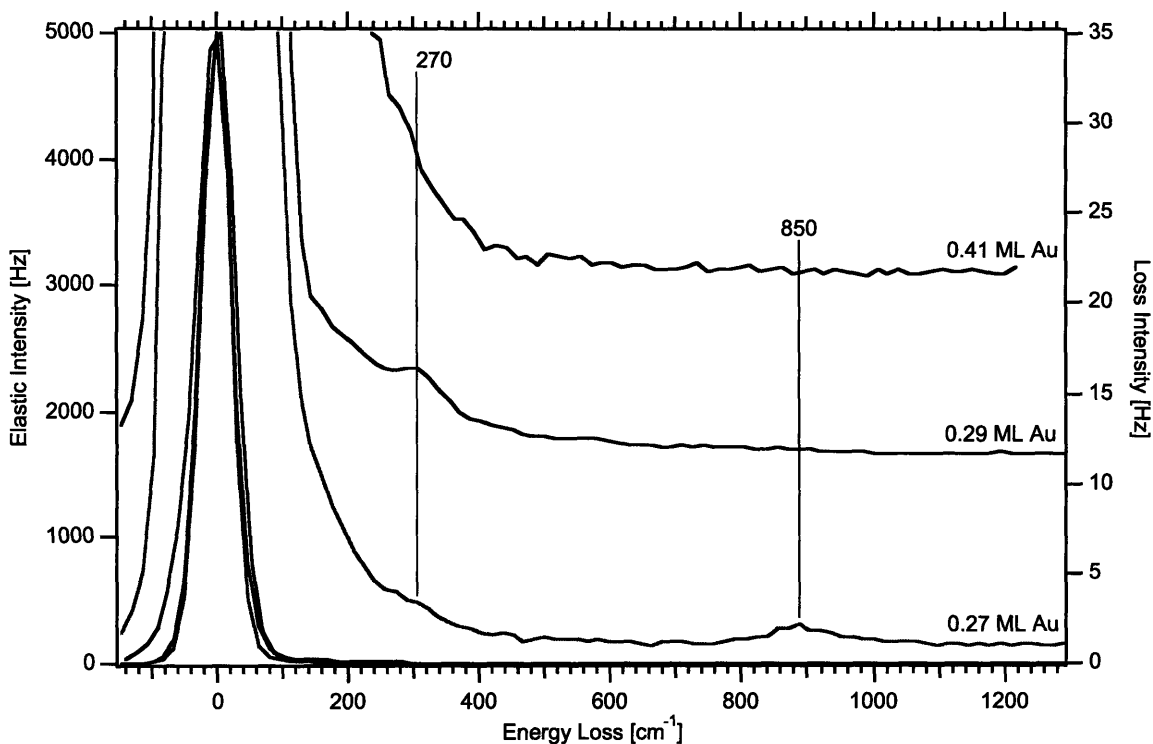


Figure 7. HREELS spectra measured after exposure of Ni(111) 0.27, 0.29, and 0.41 ML Au/Ni(111) (at 77 K) to 10% O₂/Ar for 5 s. Spectra are measured at the specular angle, with a FWHM of 55 cm⁻¹, and are normalized to an elastic peak intensity of 5 kHz for comparison of relative loss intensities.

coverage increases from 0.13 to 0.18 ML, while the intensity of the 790, 850 and 950 cm⁻¹ features increase in this range of Au coverages, suggests that the unresolved features between 350-500 cm⁻¹ are not solely associated with the species that have vibrational modes at 790, 850 and 950 cm⁻¹.

The HREELS spectra measured after exposing Au/Ni surface alloys with Au coverages in the range 0.27 – 0.41 ML Au are shown in Figure 7. The intensity of the 850 cm⁻¹ feature is weak at 0.27 ML Au, and zero at 0.29 ML Au. For these spectra, the only other observed feature occurs at 290 cm⁻¹, and is assigned to the S₂ surface phonon. There is no intensity in the region of 350 – 500 cm⁻¹ or at 580 cm⁻¹, and hence no atomic oxygen present at these Au coverages.

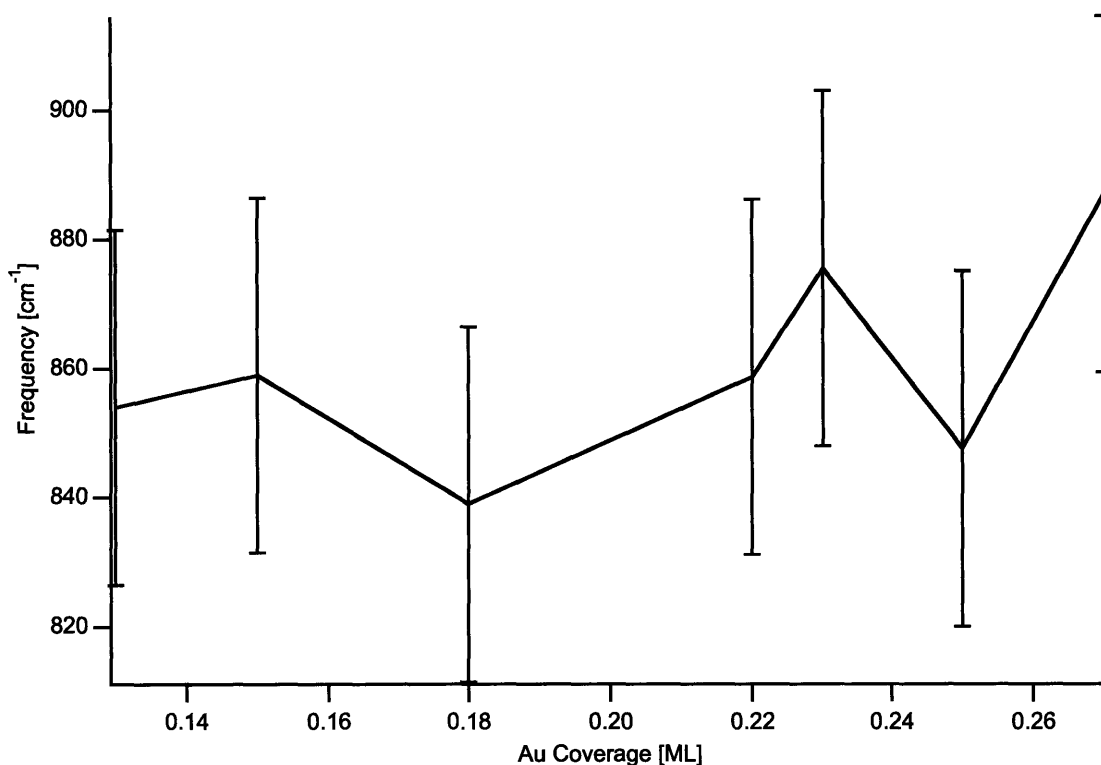


Figure 8. Average frequency of O-O vibrational mode in Figures 5 - 7 as a function of Au coverage. The error bars are ± 27.5 cm⁻¹, the half-width at half max of the elastic peaks of the spectra in Figures 5 - 7.

For the spectra in Figures 5 - 7 in which the 850 cm⁻¹ feature is observed (Au coverages of 0.13 - 0.27 ML), the average frequency of the 850 cm⁻¹ feature has been calculated for each spectra. The calculation was performed by taking a 3-point intensity weighted averaged centered around the most intense data point. The results are plotted in Figure 8. The error bars in the figure represent the half-width at half max of the elastic peaks of the spectra in Figures 5 - 7 (27.5 cm⁻¹). Within the statistical error of the measurement, the frequency does not change as a function of Au coverage. The average of these frequencies is 855 cm⁻¹, with a standard deviation of 14 cm⁻¹. In addition, the average value of the frequency was calculated for 6 spectra at approximately the same Au coverage (0.19 - 0.22 ML Au). The average frequency was 860, with a 95% confidence interval of 20 cm⁻¹.

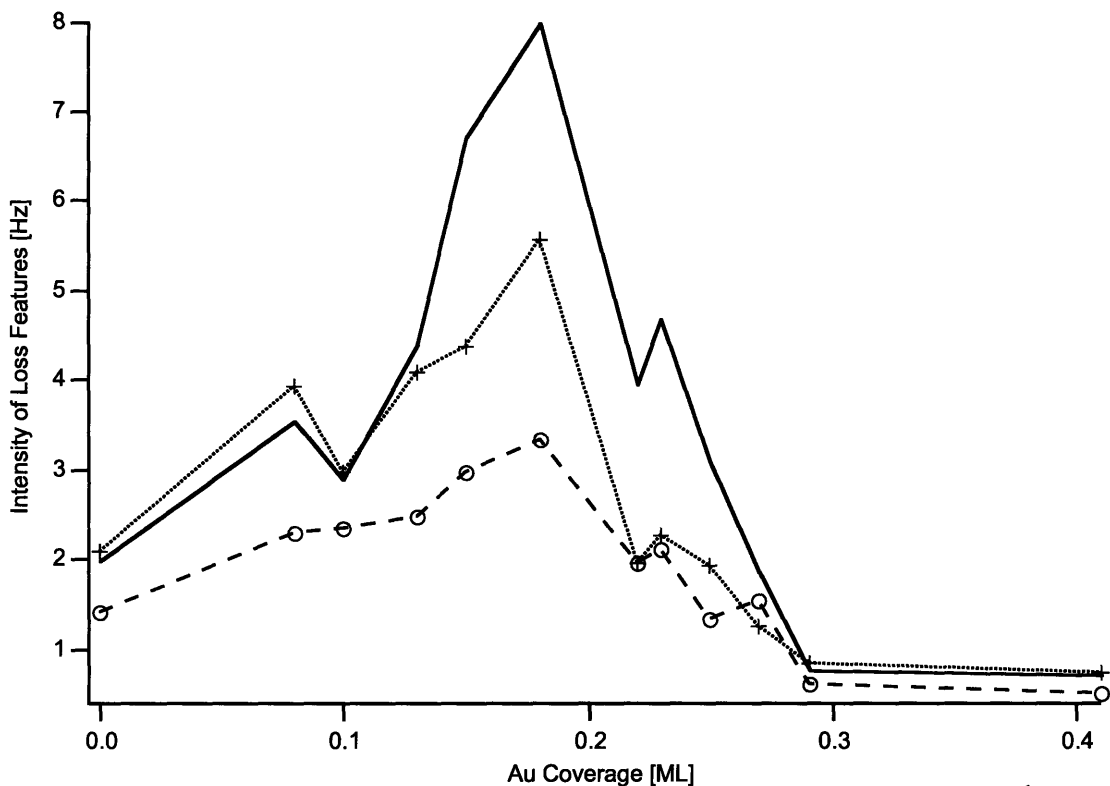


Figure 9. Intensities of the 790 (+ with dotted line), 850 (line) and 950 cm^{-1} (circles with dashed line) features as a function of Au coverage, measured from the spectra shown in Figures 5 – 7.

C. Relationships Between Intensities of Oxygen Features and Au Coverage

Figure 9 demonstrates that the intensities of the features at 790, 850 and 950 cm^{-1} have the same dependence on Au coverage. The intensity of all three modes increases as the Au coverage is increased to 0.18 ML Au. Further increase in the Au coverage causes the intensity of these modes to decrease. At 0.29 ML Au, the lowest intensity (within experimental error) is observed. A notable difference in behavior between the shoulder feature at 790 cm^{-1} and the main feature at 850 cm^{-1} occurs at lower Au coverages (0 – 0.13 ML). At these coverages, the intensity of the 790 cm^{-1} feature is slightly higher than that of the 850 cm^{-1} feature. A possible explanation for this behavior is the background contributions resulting from the tail of the 580 cm^{-1} has larger contribution to the 790 cm^{-1} feature than it does to the 850 cm^{-1} feature.

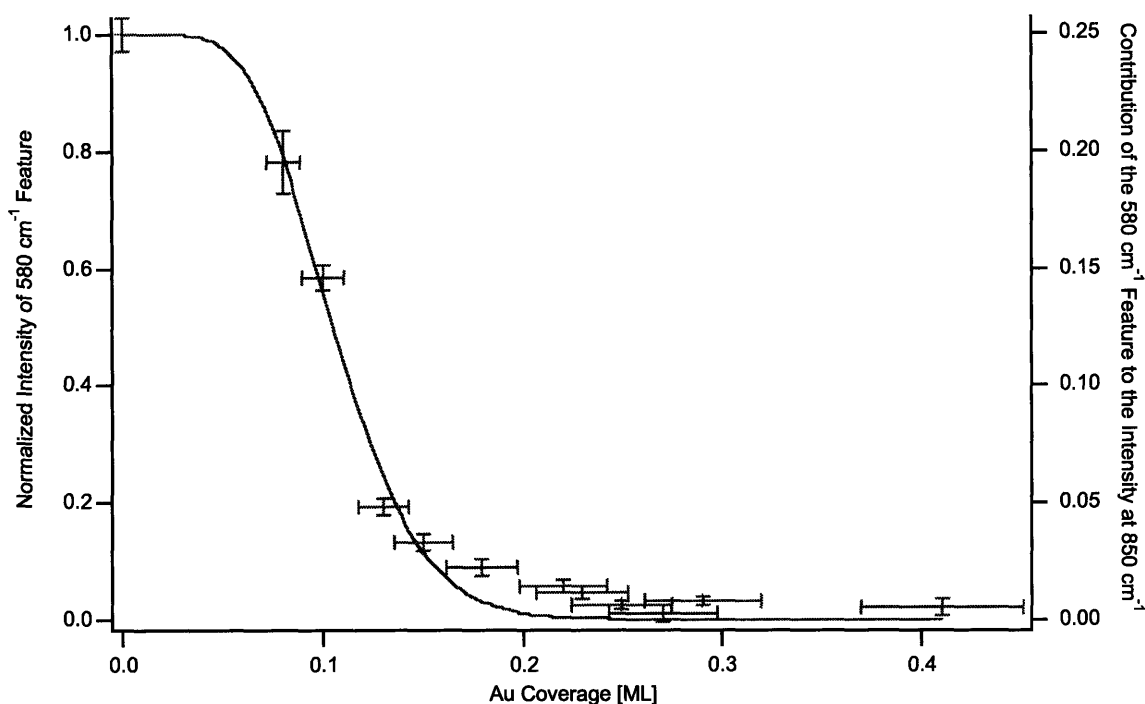


Figure 10. Intensity of 580 cm^{-1} feature (corresponding to O atom coverage) vs. Au coverage with error bars (crosses), and statistical model (line) described in the text. Plotted against the right axis is the contribution that the tail of the 580 cm^{-1} feature gives to the intensity at 850 cm^{-1} .

The intensity of the 580 cm^{-1} feature in the HREELS spectra in Figs. 5 – 7 is plotted as a function of Au coverage in Figure 10. The intensity of the feature is calculated as a 3 point average centered around 580 cm^{-1} in each spectrum, in order to reduce the noise in the data. The HREELS spectra are collected with a channel width of 16 cm^{-1} . Therefore, the 3 point average is the average of the intensities measured at 564 , 580 , and 596 cm^{-1} . Also shown is a statistical model, to be described in the discussion section. The horizontal error bars are $\pm 10\%$ of the value of the Au coverage, as calculated in Chapter 1. As stated in Chapter 1, the majority of this error is in the determination of the absolute Au coverage – the error in the relative Au coverage is 1-

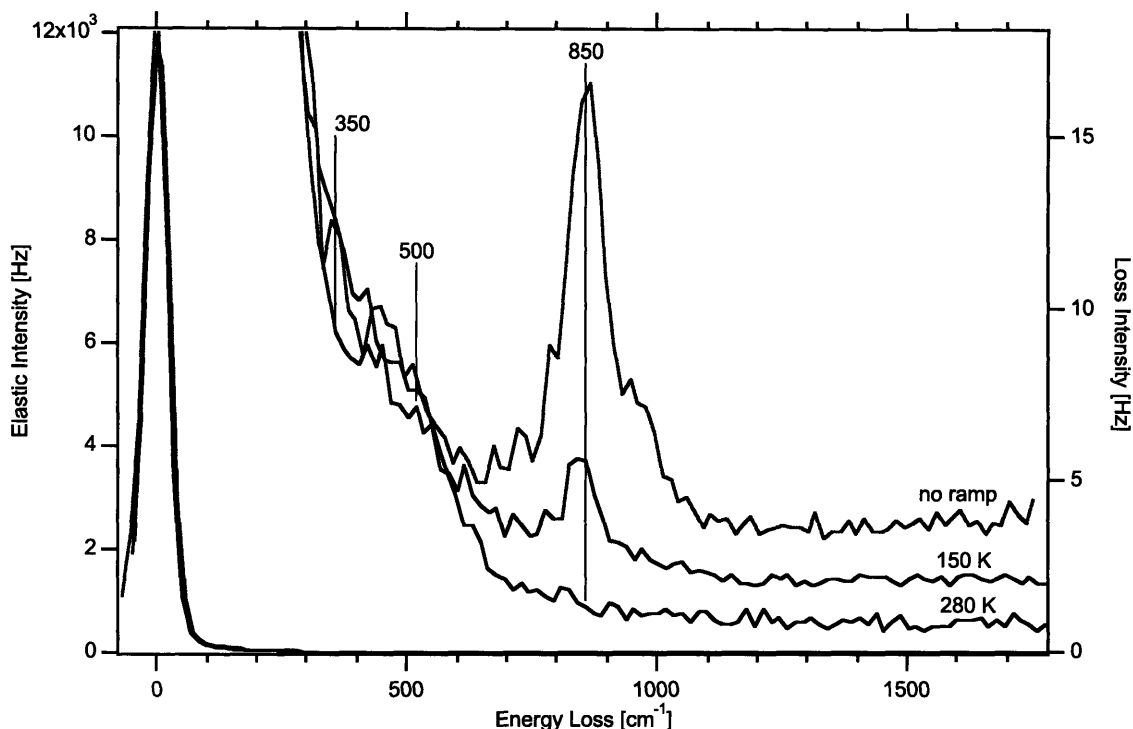


Figure 11. HREELS spectra measured after exposure of a 0.24 ML Au/Ni(111) surface to a 10% O₂/Ar molecular beam for 5 s. The crystal is heated at 2 K/s to the indicated temperature, and then cooled rapidly to 77 K, the temperature at which the spectra are recorded. Spectra are measured at the specular angle with a resolution of 55 cm⁻¹ FWHM.

2%. Therefore, although the horizontal error bars of individual points overlap those of adjacent points in Figure 10, the error bars for the relative coverages do not overlap.

D. Effect of Temperature on Molecular O₂ Adsorbates

The behavior of the peroxo-like species as the temperature of the crystal is raised is investigated by HREELS. Au/Ni(111) surface alloys with 0.24 and 0.23 ML Au (Figures 11 and 12 respectively), saturated with molecular O₂, are heated at 2 K/s to the indicated temperature, then cooled rapidly to 77 K, at which point the spectra are recorded. Spectra measured at 77 K and after heating to 150 and 280 K are shown in Figures 11 and 12. After heating to 150 K, the intensity of the 850 cm⁻¹ species is reduced by ~75%, and unresolved features between 350 - 500 cm⁻¹ appear as a shoulder

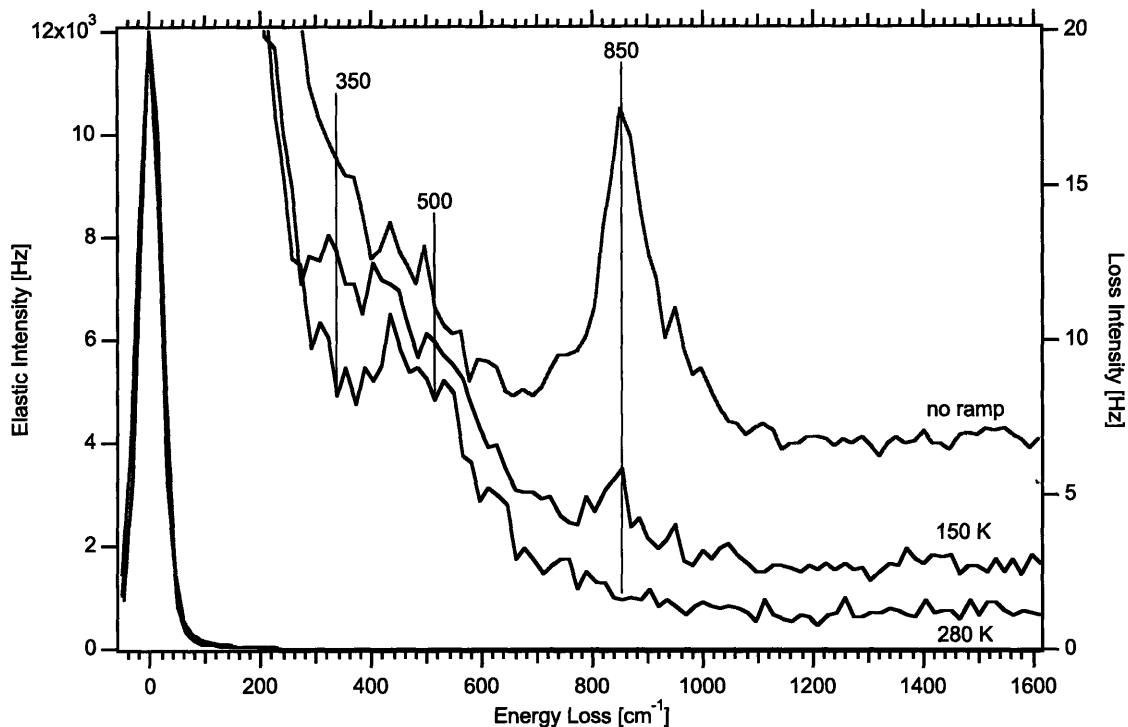


Figure 12. HREELS spectra measured after exposure of a 0.23 ML Au/Ni(111) surface to a 10% O₂/Ar molecular beam for 5 s. The crystal is heated at 2 K/s to the indicated temperature, and then cooled rapidly to 77 K, the temperature at which the spectra are recorded. Spectra are measured at the specular angle with a resolution of 55 cm⁻¹ FWHM.

on the elastic peak. The unresolved features are tentatively identified as the same unresolved intensity observed in Figures 5 – 6, assigned in Section B to atomic oxygen adsorbed in 3-fold hollow sites with Au atoms as next-nearest and/or next-next-nearest neighbors. After heating to 280 K, the 850 cm⁻¹ feature is absent.

To determine more accurately the temperature at which dissociation occurs, a Au/Ni(111) surface alloy with 0.22 ML Au, saturated with molecular O₂, is heated at 2 K/s to 120 K, then cooled rapidly to 77 K, the temperature at which HREELS is measured. The crystal is then heated at 2 K/s to 120 K a second time, and cooled rapidly to 77 K, the temperature at which HREELS is measured again. The results are presented in Figure 13, along with HREELS measured at 77 K prior to heating the surface. The first time the

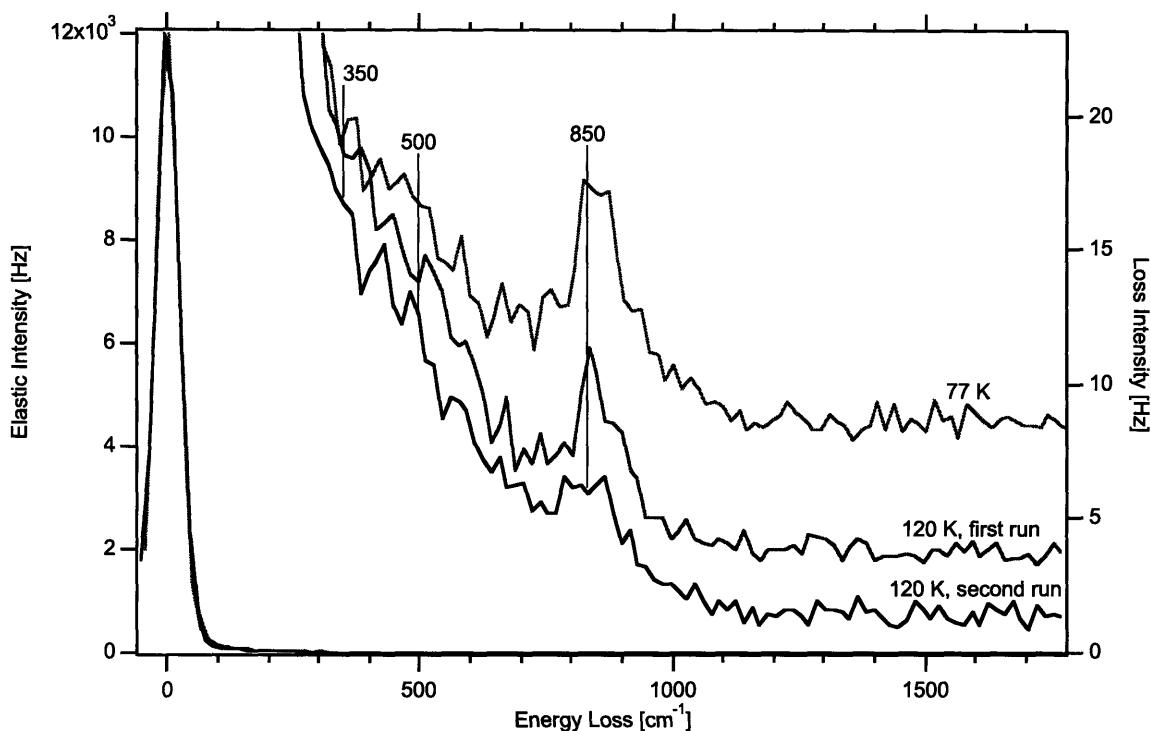


Figure 13. HREELS spectra measured after exposure of a 0.22 ML Au/Ni(111) surface to a 10% O₂/Ar molecular beam for 5 s. The crystal is heated at 2 K/s to the indicated temperature, and then cooled rapidly to 77 K, the temperature at which the spectra are recorded. Spectra are measured at the specular angle with a resolution of 55 cm⁻¹ FWHM.

crystal is heated to 120 K reduces the intensity of the 850 cm⁻¹ feature by ~16%. The second heating to 120 K reduces the intensity of the 850 cm⁻¹ feature by an additional ~40%. Although this decrease in intensity is not as large as observed when the crystal is heated to 150 K (~75%, Figures 11 – 12), it is a significant and observable reduction.

In another experiment, a Au/Ni(111) surface alloy with 0.24 ML Au, saturated with molecular O₂, is heated at 2 K/s from 77 to 300 K, while the partial pressure of O₂ is monitored (Figure 14). No desorption of O₂ is observed. The disappearance of the 850 cm⁻¹ feature concomitant with the appearance of the unresolved features in the range 350 – 500 cm⁻¹, coupled with the absence molecular O₂ desorption indicates that the

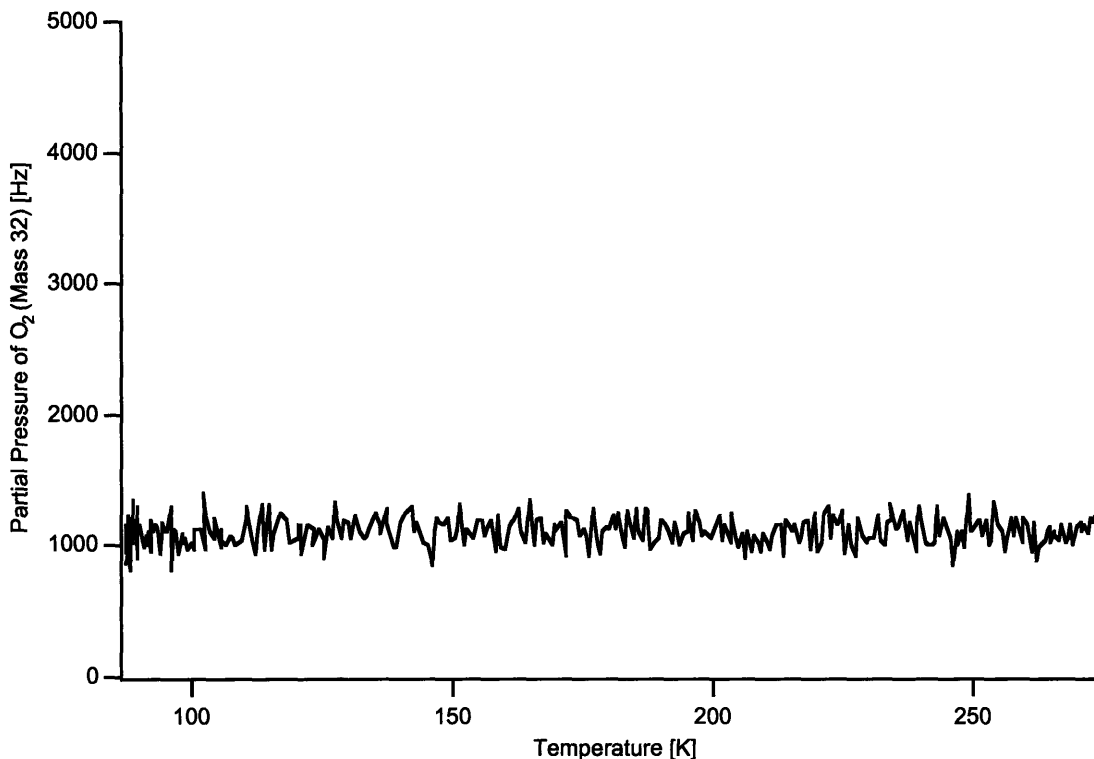


Figure 14. Partial pressure of O_2 (mass 32) monitored as a molecular O_2 saturated Au/Ni(111) surface alloy with 0.24 ML Au is heated from 77 to 300 K at 2 K/s.

molecularly chemisorbed species dissociate when the temperature of the surface is raised to 120 K.

IV. DISCUSSION

A. Molecular Chemisorption

1. Assignment of 790, 850 and 950 cm^{-1} Features

As discussed in the introduction, the chemisorption of molecular O_2 involves charge transfer from the metal surface to the adsorbate. The degree of this charge transfer results in two general sub-classes of molecular oxygen adsorbate: peroxo- and superoxo-like species. Peroxo-like species have a formal charge of -2 , while superoxo-like species have a formal charge of -1 . Since the charge is transferred into the π^* LUMO of the O_2 adsorbate, the amount of transferred charge directly correlates with the

internal bond order of the adsorbate. Therefore, the peroxo-like adsorbates, having accepted about two electrons from the metal d-band, have a bond order of about one. In contrast, the superoxo-like adsorbates, having accepted approximately one electron, have a bond order of about 1.5.

The bond order difference between peroxo- and superoxo-like species manifests itself in the observed vibrational frequencies of these species. For example, both peroxo and superoxo-like species have been observed on Ag(110),³⁷ Pd(111)^{39,40} and Pt(111),^{42,43,44} and have been characterized by the frequencies of their internal O-O stretching mode. Generally, the peroxo-like species have a lower frequency for this mode than the superoxo-like species. On Pd(111), frequencies of 650 and 850 cm⁻¹ were assigned to peroxo-like species, while a frequency of 1035 cm⁻¹ was assigned to a superoxo-like species. On Pt(111), the two observed molecular oxygen adsorbates, with frequencies of 700 and 875 cm⁻¹ have been assigned to peroxo-like species. A frequency of 630 cm⁻¹ has been assigned to a peroxo-like species which forms at Ag(110) surfaces. Further work, using UPS, identified the π^* orbital of this peroxo-like species, confirming that transfer of charge into the π^* LUMO of the O₂ adsorbate and reduction of the bond order occur.⁵⁹ These examples demonstrate that a lower bond frequency of the peroxo-like species with respect to the superoxo-like species results from the weaker internal bond of the peroxo.

Based on these previous observations and assignments, the 790, 850 and 950 cm⁻¹ vibrational modes observed on the Au/Ni(111) surface alloy are assigned to peroxo and superoxo-like species. The 950 cm⁻¹ feature is identified as a superoxo-like species,

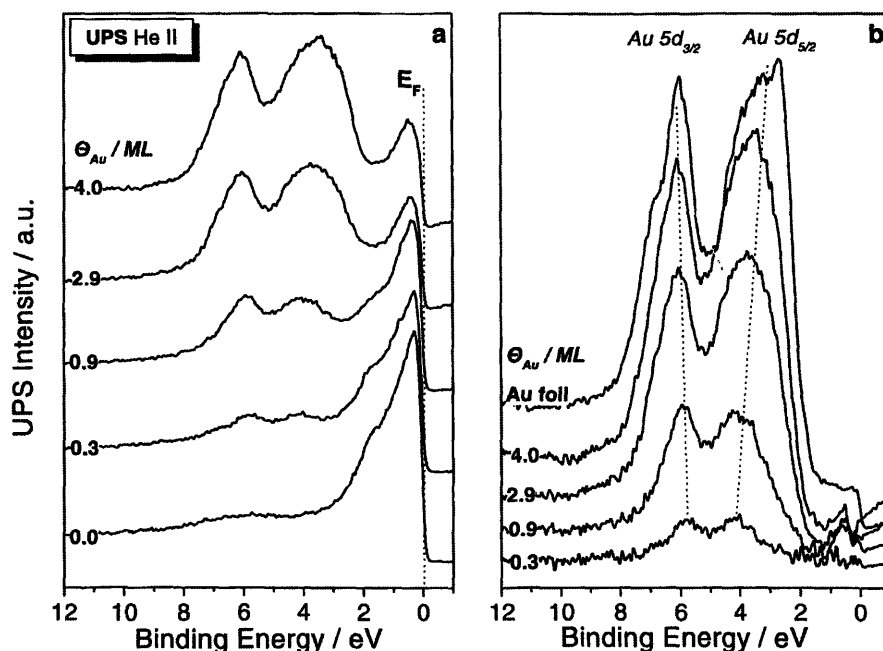


Figure 15.⁷² From reference 34. He II UPS spectra of Au/Ni(111) surface alloys. a) Measured spectra b) is the difference spectrum after subtracting the spectrum for the Ni(111) surface from (a), yielding the UPS of the Au atoms in the surface alloy.

while the 790 and 850 cm^{-1} features have frequencies generally associated with peroxo-like species.

2. Adsorption Sites of Species Corresponding to 790, 850 and 950 cm^{-1} Features

The observation that O_2 chemisorbs molecularly at the Au/Ni(111) surface alloy is explained by the observation that the Ni d-band shifts down in energy upon formation of the Au/Ni(111) surface alloy, resulting in reduced reactivity towards O_2 . The shift of the d-band has been measured by Zafeiratos and Kennou using photoelectron spectra of Au/Ni(111) surface alloys. Their results (Figure 15) indicate that upon alloying, the Ni d-band is still present and close to the Fermi level.³⁵ In contrast, they observe that the Au d-band, already 3 eV below the Fermi level for the pure metal, shifts down to 4 eV upon formation of the Au/Ni(111) surface alloy. The larger the energy difference between the

d-band of a metal and the Fermi level, the less reactive in general that metal will be. The observation that the Au d-band, unreactive in the pure metal, shifts down in energy indicate that it is unlikely that Au atoms participate directly in the reactivity of the Au/Ni(111) surface alloy. Therefore, the Ni d-band, and hence Ni atoms, are proposed as being primarily responsible for the reactivity of the Au/Ni(111) surface alloy.

Since the Ni d-band is responsible for the reactivity of the Au/Ni(111) surface towards O₂, the adsorption of the peroxo and superoxo-like species corresponding to the 790, 850 and 950 cm⁻¹ features occurs at sites primarily involving Ni atoms. It is proposed that one or more Au atoms, possibly as next-nearest neighbors, induces the downward shift of the Ni d-band that is responsible for the stabilization of the molecular O₂ adsorbate. It is proposed that the proximity and/or number of nearby Au atoms is responsible for the degree of charge transfer between the metal d-band and the π^* LUMO of the molecularly chemisorbed O₂ species. The superoxo-like species, characterized by a stretching frequency of 950 cm⁻¹, has a higher bond order than the peroxo-like species (characterized by frequencies of 790 and 850 cm⁻¹). The higher bond order is the result of less charge transfer to the π^* LUMO of the superoxo than the π^* LUMO of the peroxo-like species. Since proximity to Au atoms is proposed as causing the downward shift in the metal d-band, the superoxo-like species, which has less charge transfer, should therefore be closer to Au atoms than the peroxo-like species. Figure 16 presents three hypothetical bonding arrangements of the peroxo- and superoxo-like species at the Au/Ni(111) surface alloy, based on the above arguments.

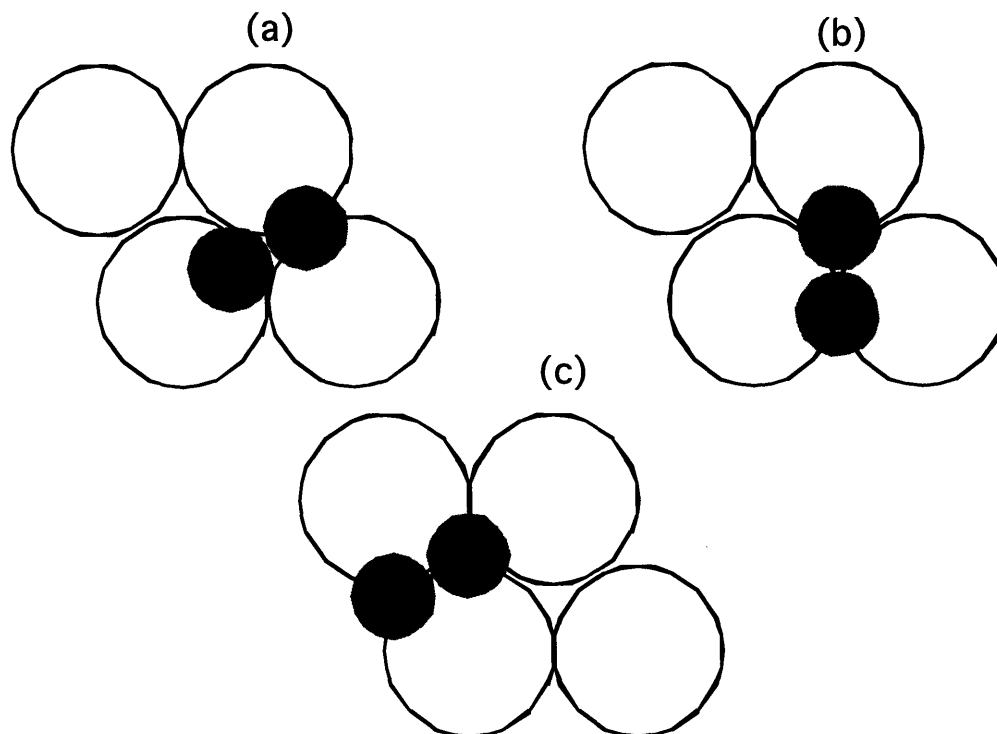


Figure 16. Possible adsorption sites for peroxo- and superoxo-like species on Au/Ni(111) surface alloy. Au atoms are large gray-filled circles, Ni atoms are large open circles, O atoms are small dark-filled circles. The sites represents the following species and their frequencies: a) peroxo, 790 cm^{-1} b) peroxo, 850 cm^{-1} c) superoxo, 950 cm^{-1}

3. Geometry of Molecular Oxygen Adsorbates

Using Near-Edge X-Ray Adsorption Fine Structure (NEXAFS), the geometry of molecular oxygen adsorbates at Pt(111)⁶⁰ and Ag(110)⁶¹ surfaces has been determined. In this technique, the Auger electrons produced by X-rays incident on the surface are measured as a function of energy. For the experiments on Ag(110), a transition is observed corresponding to electrons with energy of 532.6 eV. This transition is identified as resulting from the initial ejection of a core electron from oxygen atoms comprising molecularly chemisorbed oxygen at Ag(110). The specific transition is attributed to a resonance between the O(1s) core level and the unfilled σ^* anti-bonding orbital of the O-O bond.

Spectra were recorded as a function of incident angle of the incident X-ray radiation. The observed transition at 532.6 eV is a maximum when the radiation is incident at 90° to the surface. In this situation, the electric field of the radiation is in the plane of the surface. Since the excitation of the O(1s) to σ^* transition is maximized when the radiation field is parallel to the O-O bond, the O-O bond is in the plane of the surface.⁶²

Similar results were obtained for molecularly chemisorbed O₂ on a Pt(111) surface. In this case, two transitions were observed: the O(1s) to O-O π^* (533.1 eV), and the O(1s) to O-O σ^* (538.0 eV). The observation of the additional transition indicates that for the O₂/Pt(111) system, the π^* orbital is not completely occupied. Analogous to the case of O₂ adsorbed on Ag(110), the O(1s) to O-O σ^* transition was maximized when the angle of incidence of the exciting X-ray radiation was at 90° to the surface, indicating that the O-O bond was in the plane of the surface.

The O(1s) to O-O π^* transition displayed the opposite behavior. Its intensity was maximized when the angle of incidence of the X-rays was at a grazing angle (10°). The O(1s) to O-O π^* is maximized when the electric field of the radiation is co-planar with the π^* molecular orbital, hence the observation that the π^* orbital is perpendicular to the surface,⁶² confirming that the O-O bond is in the plane of the surface.

In addition to determining the geometry of the adsorbed peroxo-like species, these experiments confirm the relationship between bond order and vibrational frequency. As described in Section IV.A.1, the peroxo-like species observed on the Ag(110) has a frequency of 630 cm⁻¹, while the species observed on Pt(111) have frequencies of 700 and 875 cm⁻¹. In the NEXAFS experiment, the existence of the O(1s) to O-O π^*

resonance in the $\text{O}_2/\text{Pt}(111)$ system indicated that the π^* anti-bonding orbital of the peroxo-like species are only partially filled. In contrast, this resonance was not observed for the $\text{O}_2/\text{Ag}(110)$ system, indicating that for this molecular O_2 adsorbate, the π^* orbital is completely filled. Therefore, the bond order of the O_2 adsorbates on $\text{Pt}(111)$ are higher than the species on $\text{Ag}(110)$. This is consistent with the observation that the O-O bond frequency on $\text{Ag}(110)$ (630 cm^{-1}) is lower than those observed on $\text{Pt}(111)$ (700 and 875 cm^{-1}).

The geometry of a molecular oxygen adsorbate with its bond in the plane of the surface is *prima facie* in contrast to the observation, in Figure 4 of this chapter, that the O-O bond is dipole active. The dipole excitation mechanism of molecular vibrations requires that there is a derivative in the dipole of the adsorbate that occurs as a result of the motion associated with the normal mode of the vibration. For adsorbates at metal surfaces, any charge, dipole or dipole derivative in the adsorbate creates a corresponding image charge in the metal binding site of the adsorbate. For a normal mode in which the dipole derivative is in the plane of the surface, the corresponding image charge directly cancels out the dipole derivative associated with the adsorbate's normal mode – eliminating the dipole excitation mechanism for the mode. Since the vibrational motion of the O-O bond of chemisorbed molecular oxygen on transition metal surfaces is generally in the plane of the surface, it would seem that the dipole derivative created as a result of this motion would also be in the plane of the surface, and hence would be canceled by the image charge in the metal atoms below the O_2 adsorbate. Based on this reasoning, the O-O bond of molecular O_2 adsorbates on the $\text{Au}/\text{Ni}(111)$ surface alloy

should be perpendicular to the surface, due to the observation in Figure 4 that the O-O stretching mode is dipole active.⁵⁷

The above reasoning neglects the possibility that normal mode motion in the plane of the surface can create a dipole derivative perpendicular to the surface. An example of a mechanism by which a dipole derivative normal to the surface can be created by a normal mode motion in the plane of the surface is the following. It is well established that for many adsorbates at surfaces, vibrational motion is correlated strongly with rehybridization of the internal adsorbate bonds. Rehybridization during vibrational motion can lead to periodic charge transfer from the surface to the adsorbate and back. For the case of oxygen adsorbed at transition metal surfaces, it has been previously established that changing the length of the O-O bond has profound effect on the hybridization.^{61,63} As the bond stretches, charge is more efficiently transferred from the metal to π^* anti-bonding orbitals, while compression of the bond results in the reverse process. The result of this charge transfer to and from the O₂ adsorbate and the surface during a vibrational period of the O-O bond stretch is an oscillating dipole normal to the surface. Therefore, the observation that the O-O stretching modes observed at the Au/Ni(111) surface alloy are dipole active does not determine whether or not the O-O bond is parallel to the surface.

Based on the NEXAFS results that demonstrate the O-O bond of O₂ adsorbates on Ag(110) and Pt(111) surfaces is parallel to the surface, and the observation that these species also display dipole active modes for the O-O bond vibration, it is proposed that the molecular axes of the peroxo and superoxo-like species on the Au/Ni(111) surface alloy also are parallel to the surface.

B. Energetics of Oxygen Species at the Au/Ni(111) Surface Alloy

In order to understand why molecular oxygen adsorbates are stable on the Au/Ni(111) surface alloy, it is instructive to consider the theoretically proposed energetics of atomic and molecular oxygen on transition metal and alloy surfaces. The following sections discuss previous theoretical work on oxygen adsorption at surfaces, and its relevance to the present work.

1. Atomic Oxygen

Recent theoretical work by Greeley and Norskov determined the effect of alloying and overlayers on the adsorption energy of atomic oxygen on transition metal surfaces.³⁴ Consistent with previous work done for CO adsorption on transition metal alloy surfaces,³³ changes in the adsorption energy were found to correlate directly with the shifts in the energy of the center of the d-band of the surface. As described in the introduction, metal surfaces with d-bands located closer in energy to the Fermi level are generally more reactive than those with d-bands whose energy is much lower than the Fermi level. Since one of the major electronic effects of forming a metal alloy or overlayer is a shift in the position of the d-band, it is therefore expected that there will be a correlated shift in the reactivity of the metal surface. Greeley and Norskov have calculated a quantitative correlation between the shift in the metal d-band center and the adsorption energy of atomic oxygen. This correlation can be represented by:

$$\Delta E_{ads} = C \cdot \Delta \epsilon_d$$

where ΔE_{ads} is the change in adsorption energy, C is the constant of proportionality and $\Delta \epsilon_d$ is the shift in the center of the d-band. ΔE_{ads} is defined by the equation:

$$\Delta E_{ads} = E_{ads,alloy} - E_{ads,pure}$$

where $E_{ads,alloy}$ is the adsorption energy of O atoms on the alloy surface, and $E_{ads,pure}$ is the adsorption energy of O atoms on the pure surface. $\Delta\epsilon_d$ is defined by the equation:

$$\Delta\epsilon_d = \epsilon_{d,alloy} - \epsilon_{d,pure}$$

where $\epsilon_{d,alloy}$ is the energy of the center of the d-band of the alloy surface, and $\epsilon_{d,pure}$ is the energy of the center of the d-band of the pure surface.

For oxygen adsorption on the Au/Ni system, two relevant correlations have been calculated. One is the change in adsorption energy of atomic oxygen when the Au d-band shifts upon alloying. Another is the change in adsorption energy when the Ni d-band shifts upon alloying. As described previously, Zafeiratos and Kennou have measured photoelectron spectra of Au/Ni(111) surface alloys (reproduced in Figure 15), and their results indicate that upon alloying, the Ni d-band is still present and close to the Fermi level.³⁵ In contrast, the Au d-band, already 3 eV below the Fermi level, shifts down to 4 eV upon formation of the Au/Ni(111) surface alloy. These observations indicate it is unlikely that Au atoms participate directly in the reactivity of the Au/Ni(111) surface alloy. Therefore, the Ni d-band is proposed as being primarily responsible for the reactivity of the Au/Ni(111) surface alloy.

The shift of the Ni d-band that occurs upon alloying, and the correlation factor between Ni d-band shifts and adsorption energy (calculated by Greeley and Norskov) can be used to calculate the expected change in adsorption energy of atomic oxygen for the Au/Ni(111) surface alloy. The correlation factor between the change in adsorption energy and d-band shift C for the Ni band has been calculated to be -2.12.³⁴ The photoelectron spectra taken by Zafeiratos and Kennou indicate that alloying of 0.4 ML Au onto the Ni(111) surface causes a Ni d-band shift of $\Delta\epsilon_d = -0.025$ eV. Multiplying C

(-2.12) by $\Delta\epsilon_d$ (-0.025) yields a value of the change in adsorption energy of $\Delta E_{ads} = 0.053$ eV (1.2 kcal/mol) for atomic oxygen. Since the adsorption energy of O atoms on Ni(111) is negative, this positive change in adsorption energy causes the adsorption energy to be less negative. Hence O atoms on the Au/Ni(111) surface alloy are less strongly bound than they are on the Ni(111) surface. However, this prediction is a change of less than 2% in the adsorption energy of atomic oxygen on Ni(111), measured to be 57.6 kcal/mol (Figure 1).

A 2% decrease in the adsorption energy of atomic oxygen is not a reasonable explanation for the absence of oxygen atom adsorption (Figure 7) on a 0.4 ML Au/Ni(111) surface alloy. Rather, the surface alloy at high Au coverages must significantly destabilize the molecular O₂ adsorbate, which serves as a precursor to adsorbed atomic O. More importantly, at moderate Au coverages, there is a barrier to dissociation of molecularly adsorbed O₂. Unfortunately, no theoretical work analogous to that of Greeley and Norskov calculates the change in the barrier to dissociation and/or the adsorption energy of molecular O₂ species upon formation of transition metal alloy surfaces.

2. Molecular Oxygen

A calculation carried out by Eichler et. al. describes a possible molecular precursor state of adsorbed O₂ (bound by 38.5 kcal/mol), with a barrier to dissociation of kcal/mol.¹⁰ The molecular precursor adsorbs in a three-fold hollow site, with one O atom close to the center of the site, and the other atom closer to an adjacent bridge site. The transition state for dissociation involves movement of both O atoms over adjacent bridging sites to their 3-fold hollow sites, which are their final adsorption sites. Similar

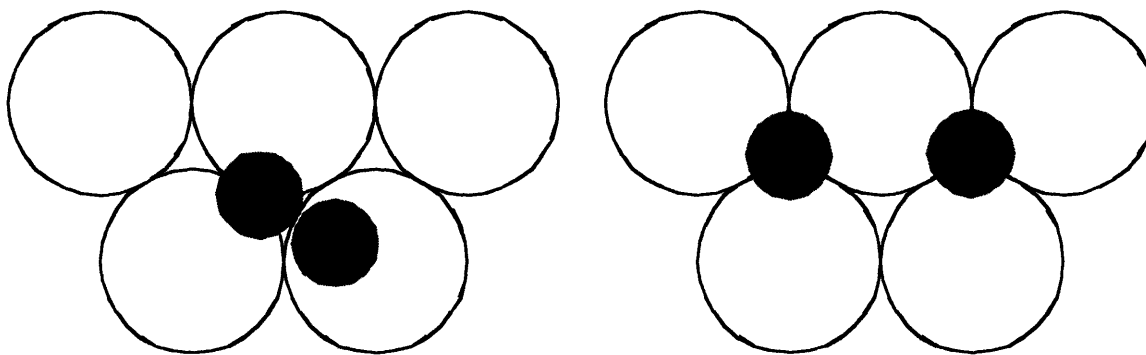


Figure 17. Schematic diagram of dissociation of chemisorbed molecular oxygen, derived by modifying model proposed by Eichler et. al. Open circles are Ni atoms, filled, small circles are oxygen atoms, filled, large, gray circle is a Au atom. Left side is prior to dissociation, right side is during/after dissociation.

calculations for O_2 adsorption on Ni(100) indicate the presence of a molecular adsorbate with a 6 – 8 kcal/mol barrier to dissociation.²⁰ Regarding chemisorption of molecular O_2 on Au/Ni(111), a possible hypothesis is that modification of the local molecular adsorbate's binding site by replacement of a next-nearest neighbor Ni atom with a Au atom decreases the adsorption energy and raises the barrier to dissociation, such that the molecular precursor is stable at 77 K. A diagram of this mechanism is presented in Figure 17, and the associated energetics are presented in Figure 18.

C. Dissociation of Molecularly Adsorbed O_2

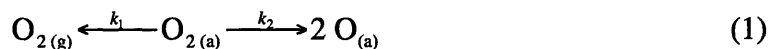
1. Previous Theoretical Work

The dissociation of the molecular O_2 species on the Au/Ni(111) surface alloy as the temperature is raised, without any desorption, is strikingly different from the behavior of O_2 on pure transition metal surfaces which chemisorb O_2 molecularly.^{37,46,64} According to the calculations of Eichler et. al., the dissociation barriers on Pt(111) and Pd(111) are 4

and 2 kcal/mol higher in energy than the potential energy gas phase O_2 , respectively, explaining why desorption of O_2 is observed on these surfaces. In contrast to Pt and Pd, the barrier to dissociation on the Au/Ni(111) surface alloy must be lower than that for desorption. For Ni, the top of the barrier to dissociation is ~ 1.5 eV lower in energy than the potential energy of gas phase O_2 . Since no molecular O_2 is stabilized on Ni(111), a substantial increase in the barrier to dissociation must occur as a result of the presence of Au atoms. However, the increase must be less than 1.5 eV in order to favor dissociation of molecularly chemisorbed O_2 over desorption. Figure 18 presents the potential energy pathway of an O_2 molecule as it chemisorbs molecularly, then dissociates on Ni(111), as calculated by Eichler et. al. The small barrier to dissociation (9 kcal/mol) is consistent qualitatively, but not quantitatively, with the lack of observed chemisorbed O_2 on Ni(111). Also included are our proposed changes in the pathway that results when a Au atom replaces one of the five surface metal atoms that are directly involved in the chemisorption event.

2. Kinetic Model of Dissociation and Desorption Pathways

A simple kinetic model can be used to determine a rough estimate of the change in the barrier to dissociation of molecularly chemisorbed oxygen that occurs when Au is alloyed into the Ni(111) surface. In the simplest kinetic model, molecularly chemisorbed O_2 can either dissociate or desorb:



where k_1 is the rate of desorption, and k_2 is the rate of dissociation.

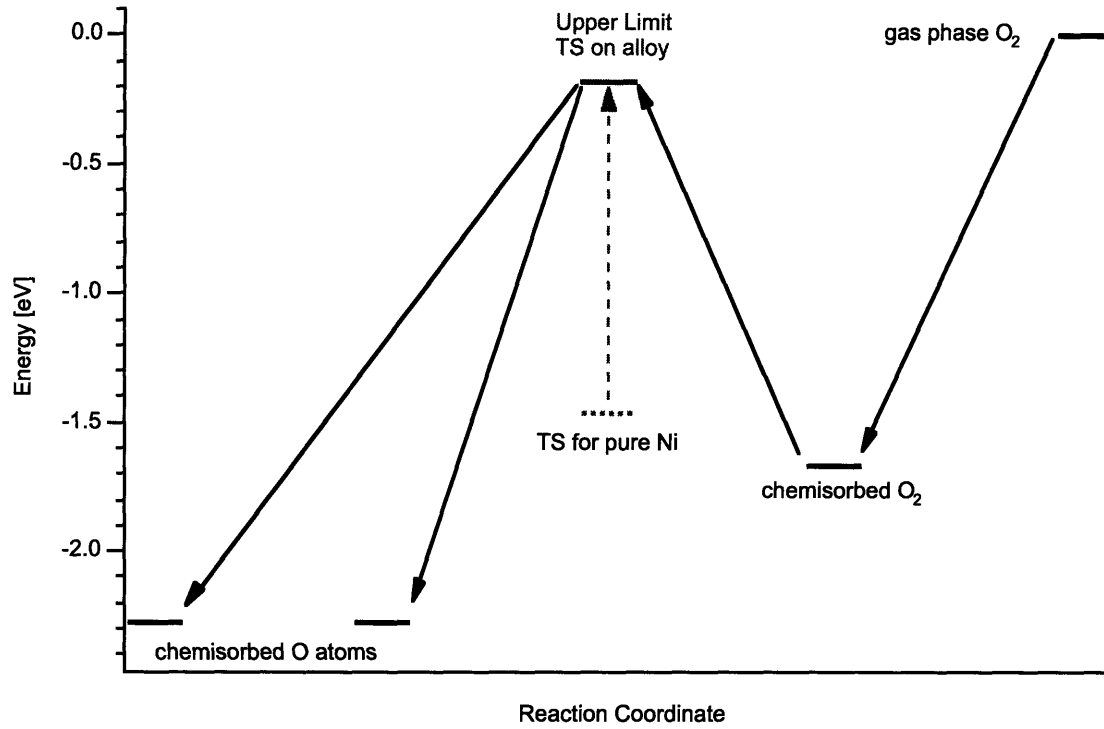


Figure 18. Reaction coordinate for adsorption and dissociation of O_2 on Au/Ni(111) surface alloy, based on modification of model by Eichler et. al. Energy of chemisorbed O_2 and O atoms, and energy of TS for pure Ni are from the calculation. Upper limit of the energy of the TS on the alloy is hypothesized based on experimental results.

In this model, the ratio of the rate of dissociation to the rate of desorption is given by:

$$R = \frac{k_2}{k_1} \quad (2)$$

If the rate constant is modeled as a first order Arrhenius expression, the ratio can be expressed as:

$$R = \frac{A_2}{A_1} \cdot e^{\frac{E_1 - E_2}{k_B T}} \quad (3)$$

The pre-exponential factor A can be calculated using transition state theory:⁶⁵

$$A = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} \quad (4)$$

where k_B is Boltzmann's constant, T is the temperature, h is Planck's constant, Q_R is the partition function of the reactants, $Q^\ddagger$ is the partition function of the transition state, excluding the degree(s) of freedom along the reaction coordinate. The ratio of pre-exponential factors is then given by:

$$\frac{A_2}{A_1} = \frac{Q_2^\ddagger}{Q_1^\ddagger} \quad (5)$$

Generally, for desorption and dissociation reactions at surfaces, the value of this ratio is 1×10^{-5} .⁶⁶

3. Application of the Model

Based on a 1% detection limit of our QMS, we assume a ratio of rate constants (R) of 99:1. Using a value of the temperature of 150 K and a value of 10^{-5} for the ratio of pre-exponential factors, the calculated difference in barrier heights ($E_1 - E_2$) is calculated from Eqn. 3 to be 4.2 kcal/mol (0.18 eV). Since the barrier to desorption is the difference in energy between the bottom of the molecular chemisorption well and the energy of a gas phase O_2 molecule, this calculation indicates that the transition state for dissociation is 4.2 kcal/mol or lower in energy than a gas phase O_2 molecule.

The transition state energy is described as an upper limit because the sensitivity of the QMS limits the detectable level of gas phase O_2 desorption that may occur during heating of the crystal. For higher values of the QMS sensitivity, assuming that no desorption of O_2 is still observed, a greater difference in the activation barriers between desorption and dissociation is calculated – resulting in a lower energy of the transition state for dissociation depicted in Figure 18.

D. Dissociative Adsorption at 77 K as a Function of Au Coverage

Regarding the dissociative adsorption of O₂ on the Au/Ni(111) surface alloy between 0 and 0.13 ML Au coverage (Figures 3 and 8), the most striking feature is the sudden disappearance of the 580 cm⁻¹ feature between 0.10 and 0.13 ML Au concomitant with the appearance of unresolved intensity in the range 350 – 500 cm⁻¹. The model presented here is an attempt to understand this sudden disappearance in terms of the number of clustered Ni atoms required for the appearance of the 580 cm⁻¹ feature.

For an ensemble size m , the probability of there being only Ni atoms in this ensemble is given by:

$$P_0 = (1 - \theta_{Au})^m \quad (6)$$

where P_0 is the probability of zero Au atoms being located within the ensemble, θ_{Au} is the Au coverage and m is the ensemble size.

For ensembles that have one Au atom, the probability is given by:

$$P_1 = {}_m C_1 \cdot \theta_{Au} (1 - \theta_{Au})^{m-1} = m \cdot \theta_{Au} (1 - \theta_{Au})^{m-1} \quad (7)$$

where ${}_m C_1$ is defined as the binomial coefficient m-choose-1:

$${}_m C_n = \frac{m!}{(m-n)!n!} \quad (8)$$

The binomial coefficient represents the number of distinct ways in which n objects can be distributed among m sites. In this case, it determines the number of unique configurations in which n Au atoms may be distributed among m surface lattice sites.

The probability of n Au atoms in an ensemble of m sites is then given by:

$$P_n = {}_m C_n \cdot \theta_{Au}^n (1 - \theta_{Au})^{m-n} = \frac{m!}{(m-n)!n!} \cdot \theta_{Au}^n (1 - \theta_{Au})^{m-n} \quad (9)$$

The statistical model of the occurrence of the O atoms species corresponding to the 580 cm^{-1} feature, presented in Figure 10, is a sum of the probabilities of ensembles P_n with increasing numbers of allowed Au atoms :

$$\begin{aligned}
 P_T &= P_0 + P_1 + P_2 + \dots + P_{n_{\max}} \\
 &= \theta_{\text{Au}}^0 (1 - \theta_{\text{Au}})^{m-0} + \frac{m!}{(m-1)!1!} \cdot \theta_{\text{Au}}^1 (1 - \theta_{\text{Au}})^{m-1} + \frac{m!}{(m-2)!2!} \cdot \theta_{\text{Au}}^2 (1 - \theta_{\text{Au}})^{m-2} + \\
 &\dots + \frac{m!}{(m - n_{\max})! n_{\max}!} \cdot \theta_{\text{Au}}^{n_{\max}} (1 - \theta_{\text{Au}})^{m - n_{\max}} \quad (10) \\
 &= (1 - \theta_{\text{Au}})^m + m \cdot \theta_{\text{Au}} (1 - \theta_{\text{Au}})^{m-1} + \frac{1}{2} m(m-1) \cdot \theta_{\text{Au}}^2 (1 - \theta_{\text{Au}})^{m-2} \\
 &\dots + \frac{m!}{(m - n_{\max})! n_{\max}!} \cdot \theta_{\text{Au}}^{n_{\max}} (1 - \theta_{\text{Au}})^{m - n_{\max}}
 \end{aligned}$$

where $n_{\max}$ is defined as the maximum number of Au atoms which can occupy an ensemble which is associated with the 580 cm^{-1} feature.

The best-fit model is determined by varying the values of the maximum number of allowed Au atoms $n_{\max}$ and the size of the ensemble m , and choosing the set of these parameters which has the lowest chi-squared (Figure 10). The procedure is as follows. First, the intensity of the 580 cm^{-1} feature as a function of Au coverage is normalized such that the intensity at 0 ML Au coverage has a value of 1. This normalization is used on the physical basis that only the 580 cm^{-1} feature represents O atoms adsorbed in 3-fold hollow sites with no nearest neighbor Au atoms. Then, a fixed value of the maximum number of allowed Au atoms $n_{\max}$ is chosen (initially $n_{\max} = 1$), and the value of the ensemble size m is varied from 5 to 100. For each value of m , the chi-squared value of the fit of the model to the data is calculated. The value of $n_{\max}$ is then incremented, and the process repeated. For each value of $n_{\max}$ used in this procedure (up to 12), the value of m that produced the lowest chi-squared was approximately 10 times the value of $n_{\max}$. By comparison of the chi-squared values using the best value of m as a function of $n_{\max}$,

the optimal model that has the lowest chi-squared value as a function of both n_{max} and m is determined to be for values of $m = 82$, and $n_{max} = 8$.

This value of 82 for the ensemble size m is significantly larger than has been observed previously for adsorption at surfaces. Holmblad et. al. measured the dissociative adsorption of CH_4 and H_2 on Au/Ni(111) surface alloys, and were able to statistically model the dependence of the dissociative adsorption on the Au coverage using ensemble sizes of 7 and 6, respectively.⁶⁷ Paffett et. al. studied CO adsorption for the Bi/Pt(111) system, and observed blocking of CO adsorption on Pt by Bi could be modeled using an ensemble size of $m = 2$.⁶⁸

Mathematically, the high value of the ensemble size is the result of the low Au coverage (0.13 ML) at which the intensity of the 580 cm^{-1} feature is zero. In contrast, for CH_4 and H_2 dissociation on the Au/Ni(111) surface alloy, significant dissociation is still observed at Au coverages of 0.37 and 0.26 ML, respectively.

The physical interpretation of the ensemble size is the number of surface atoms that participate in the adsorption event. Based on the previous results described above, it seems unlikely that 82 surface metal atoms are involved in the dissociative adsorption of one O_2 molecule, as is suggested by the model. Another possibility is that a phase transition at the surface occurs as the Au coverage is raised from 0.10 to 0.13 ML, resulting in the observed disappearance of the 580 cm^{-1} feature. One possible phase transition is a structural change in the Au/Ni(111) surface alloy that occurs (when the surface is saturated with oxygen) as the Au coverage is increased from 0.10 to 0.13 ML Au. However, STM experiments have revealed that after exposures of 20 L O_2 to Au/Ni(111) surface alloy with > 0.10 ML Au, the Au atoms are still randomly alloyed

into the Ni(111) surface at lattice positions.⁶⁹ This result suggests that if there is a phase transition occurring between 0.10 and 0.13 for the oxygen saturated Au/Ni(111) surface alloy, it occurs in the adsorbed oxygen layer, and is not a structural change in the arrangement of the Au and Ni atoms.

Evidence in support of a phase change in the state of the adsorbed oxygen comes from a measurement of Stuckless et. al., who determined that O atoms chemisorbed at the Ni(111) surface have an attractive lateral interaction of 1.6 kcal/mol.²⁷ This value is comparable to the calculated decrease in adsorption energy (1.2 kcal/mol, Section IV.B.1) that results from alloying of Au into the Ni(111) surface. It is possible that for Au coverages at 0.10 ML or less, O atoms adsorb at Au modified 3-fold hollow sites, as a result of the stabilization provided by adjacent adsorbed O atoms, but that at 0.13 ML Au, there is a collective failure of the mutual stabilization, resulting in the observed sharp decrease in the intensity of the 580 cm⁻¹ feature. Future work will attempt to apply a model based on this premise to understanding the intensity of the 580 cm⁻¹ feature as a function of Au coverage.

E. Probability of Dissociation of O₂: Measurement and Simulation

In the previous section, an attempt was made to apply an analytical model to the amount of atomic O at the surface as a function of Au coverage. The result was that the model requires an un-physically large ensemble of surface metal atoms to reproduce the data. In another attempt to gain insight into this system, this section presents attempts to understand a phenomena intimately related to the coverage of atomic O, the probability of dissociation. Instead of using an analytical model as was used in the previous section, a simulation is used to reproduce the experimental results. The use of a simulation

instead of an analytical model was attempted based on previous results⁷⁰ that demonstrated inherent problems that arise when an analytical statistical model is applied to systems with large ensemble sizes. Analytical models inherently undercount the number of sites available because they assume each site exists independently of all other sites. In other words, analytical models assume that sites do not overlap. For small ensemble sizes, this assumption is valid, however Campbell et. al. demonstrated that for ensemble sizes of 7 the assumption causes analytical models to produce erroneous results.⁷⁰ Therefore, in an attempt to more accurately model the dissociation process of O₂ on Au/Ni(111) surface alloys, a simulation was used to calculate the probability of dissociation as a function of Au coverage. The simulation is performed by generating a random Au/Ni(111) surface alloy, and then counting the number of dissociation sites that are present. The probability of dissociation is then calculated as the number of dissociation sites divided by the total number of sites at the surface.

The experimentally measured values for the probability of dissociation are calculated in the following manner. It has been demonstrated that as the Au coverage of the Au/Ni(111) surface alloy increases, the adsorption of oxygen switches from dissociative (0.0 to 0.10 ML Au) to molecular (0.18 to 0.27 ML Au). Based on the HREELS presented in Figure 7 – 9, adsorption is solely dissociative at 0 ML Au coverage, and adsorption is solely molecular at 0.18 ML Au. Therefore, the probability of dissociation is set as unity for a Au coverage of 0 ML, and zero for a Au coverage of 0.18 ML. The probability of dissociation between 0 and 0.18 ML Au coverage is then determined based on the linear relationship between the number of dissociation sites and the coverage of molecular O₂, which is measured by the intensity of 850 cm⁻¹ feature in

the vibrational spectra (HREELS) in Figures 7 – 9. In Section 1, the probability of dissociation is calculated using this method, and in Section 2, the simulation of the probability of dissociation as a function of Au coverage is presented.

1. Calculation of the Probability of Dissociation

The probability of dissociation is directly related to the probability of molecular chemisorption by the following relationship:

$$P_{dissoc} = 1 - P_{chem-O_2} \quad (11)$$

where P_{dissoc} is the probability of dissociation, and P_{chem-O_2} is the probability of molecular O_2 chemisorption. Therefore, determination of the probability of molecular O_2 chemisorption P_{chem-O_2} directly yields the probability of dissociation P_{dissoc} .

The probability of molecular O_2 chemisorption P_{chem-O_2} is directly proportional to the amount of chemisorbed O_2 at the Au/Ni(111) surface alloy, as measured by the intensity of the 850 cm^{-1} feature, $I_{850}(\theta_{Au})$. It is assumed that at 0.18 ML Au coverage, when the amount of chemisorbed O_2 at the surface is at its maximum value, the probability of molecular O_2 chemisorption P_{chem-O_2} is 1. Conversely, for a Ni(111) surface (0 ML Au coverage), there is no molecular O_2 chemisorption and the probability of molecular O_2 chemisorption P_{chem-O_2} is 0. Between the Au coverages of 0 and 0.18 ML Au, the functional form of the probability of molecular O_2 chemisorption P_{chem-O_2} is determined by the intensity of the 850 cm^{-1} feature in this range of Au coverages.

A problem that arises is that at 0 ML Au coverage, the intensity of the 850 cm^{-1} feature is non-zero, and hence the apparent amount of adsorbed O_2 at the surface is non-zero, implying that the probability of molecular O_2 chemisorption P_{chem-O_2} is greater than

0 (Figure 9). The non-zero intensity at 850 cm^{-1} for 0 ML Au coverage arises from the tail of the adjacent 580 cm^{-1} feature. In order to correctly measure the probability of molecular O_2 chemisorption $P_{chem-\text{O}_2}$, the contribution of the tail of the 580 cm^{-1} feature to the intensity at 850 cm^{-1} must be removed.

The contribution of the tail of the 580 cm^{-1} feature to the intensity at 850 cm^{-1} is removed by the following procedure. It is known that for a Ni(111) surface, there is no molecularly chemisorbed O_2 . Therefore, any intensity at 850 cm^{-1} for this surface is due solely to the tail of the 580 cm^{-1} feature. The intensity of the tail of the 580 cm^{-1} feature at 850 cm^{-1} is directly proportional to the intensity of the 580 cm^{-1} feature. Therefore, the contribution of the tail of the 580 cm^{-1} feature to the intensity at 850 cm^{-1} can be written as:

$$B_{580} = D \cdot I_{580}(\theta_{Au}) \quad (12)$$

where B_{580} is the background contribution of the tail of the 580 cm^{-1} feature to the intensity at 850 cm^{-1} , $I_{580}(\theta_{Au})$ is the intensity of the 580 cm^{-1} feature as a function of Au coverage, normalized to a value of 1 at 0 ML Au coverage, and D is the constant of proportionality, namely the intensity at 850 cm^{-1} at 0 ML Au coverage. The value of the intensity at 850 cm^{-1} for 0 ML Au coverage D is read directly off Figure 9 to be 0.25. The function $I_{580}(\theta_{Au})$ is plotted against the left axis of Figure 10. The function B_{580} is plotted in Figure 10 against the right axis.

The probability of molecular O_2 chemisorption $P_{chem-\text{O}_2}$ is then given by:

$$P_{chem-\text{O}_2} = I_{850}(\theta_{Au}) - B_{580} \quad (13)$$

where $I_{850}(\theta_{Au})$ is the intensity of the 850 cm^{-1} feature as a function of Au coverage, normalized such that at 0.18 ML Au it has a value of 1. The probability of molecular

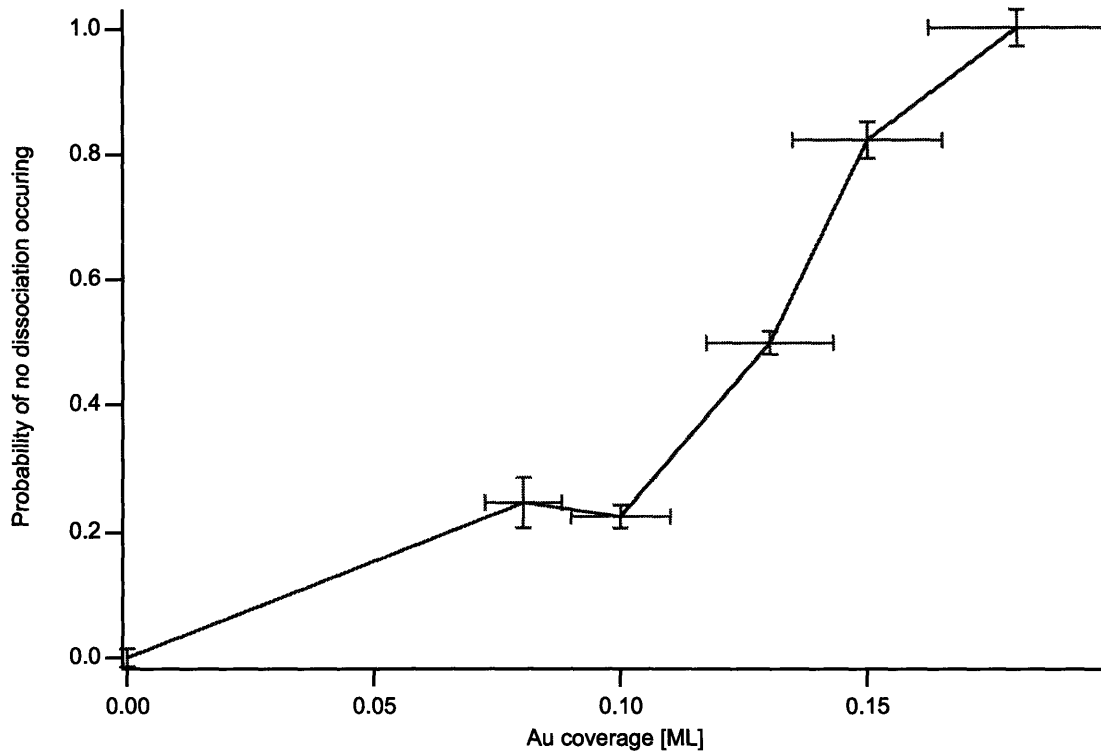


Figure 19. Probability of molecular chemisorption as a function of Au coverage. See text.

chemisorption P_{chem-O_2} , calculated using Eqn. 13, is plotted in Figure 19. The corresponding probability of dissociation P_{dissoc} has been calculated using Eqn. 11, and is plotted in Figure 20 (crosses).

2. Simulation of the Probability of Dissociation

A simulation has been used to reproduce the probability of dissociation of O_2 at the Au/Ni(111) surface alloy. The dissociation probability, in the low-O atom coverage limit, is equal to the number of sites at the surface that are active for dissociation. The number of sites available are determined by simulation a random Au/Ni(111) surface alloy, and the counting how many sites are present. This result of the simulation is then compared to the data for the probability of dissociation, as the configuration of Au atoms at the dissociation site changed. The simulation which most closely reproduces the

measured probability of dissociation indicates the configuration of Au atoms at the dissociation site. The result is that a site is active for dissociation if it has one or less nearest neighbor Au atoms, two or less next-nearest neighbor Au atoms, two or less next-next-nearest Au atoms, and 10 or less Au atoms in the next closest 76 atoms. The following sections explain how the values for the probability of dissociation that arise from this model are calculated, and describe the systematic variation in the allowed configuration of the dissociation site which produced the result presented above.

a. Method of Calculation of the Simulation

The number of sites at the Au/Ni(111) surface that meet the requirements for dissociation of O₂ has been calculated using a numerical method (in contrast to the analytical method employed in the Section IV.D for the coverage of O atoms with a frequency of 580 cm⁻¹). A random number generator, described originally by L'Ecuyer,⁷¹ is used to place Au atoms randomly at lattice locations of an ideal hexagonal Ni(111) surface lattice. For each lattice position of the 1000 x 1000 atom surface, a random number between 0.0 and 1.0 is generated. If the generated number is less than the Au coverage θ_{Au} being investigated in the calculation, then a Au atom is placed at the lattice site. Otherwise, a Ni atom is placed at the lattice site. Once the surface is generated, the calculation proceeds as follows. Starting at a lattice position in a corner of the surface (inset from edge by six atoms), the surrounding surface atoms are checked to see if they fulfill the requirements described above for a dissociation site – one or less Au nearest neighbors, two or less Au next-nearest neighbors, two or less Au next-next-nearest neighbors, and 10 or less Au atoms within the 76 next closest atoms. If the site meets these requirements for dissociation, the numbers of Au atoms that are nearest, next-

nearest, next-next-nearest, and within the outer 76 positions are recorded. Then, the lattice position is incremented, and the new lattice position is checked to see if it meets the dissociation requirement. After the procedure has been performed on every lattice site, the probability of dissociation is calculated as the number of dissociation sites found divided by the total number of sites. Increasing the lattice size, and repeating the calculation for multiple randomly generated surfaces resulted in changes in the calculated dissociation probabilities of less than 0.1%, indicating that the error in the calculated values is no more than 0.2%.

The numerical method described above was employed so as to eliminate undercounting of the number of available sites for dissociation (and hence underestimation of the dissociation probability) that occurs when an analytical statistical model is employed. The attempt was suggested by previous work by Campbell et. al., who demonstrated that analytical models undercount the number of available adsorption sites when applied to systems in which the ensemble size m of surface atoms required for adsorption is large.⁷⁰ They specifically observed a failure of the analytical model for a value of the ensemble size $m = 7$. Based on the results of Section IV.D, in which an ensemble size $m = 82$ was required for the analytical model of atomic O at the Au/Ni(111) surface alloy, the use of a simulation instead of an analytical model is justified.

b. Comparison of the Simulation Results to the Measured Probability of Dissociation

Figure 20 presents the measured probability of dissociation and the results of the calculation of the probability of the dissociation of O₂ at the Au/Ni(111) surface alloy as

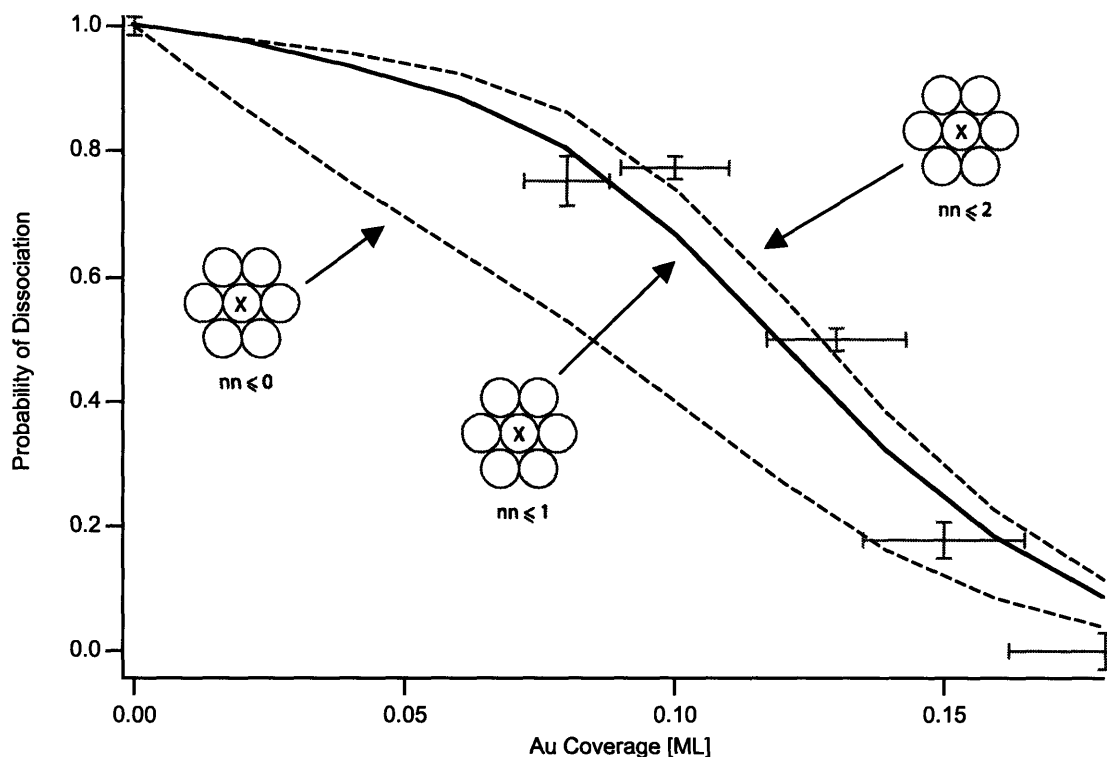


Figure 20. Probability of dissociation of O_2 at the Au/Ni(111) surface alloy as a function of Au coverage (crosses), showing variation of Au allowed as nearest neighbors nn . The horizontal error bars are 10% of the value, the vertical error bars are as calculated for Figure 9. The solid line represents the best reproduction of the data by the simulation. The dashed lines represent variations of the number of allowed Au atom nearest neighbors nn , in the model. The inset schematics of an adsorption site that does allow O_2 dissociation is shown for each calculation. See text.

a function of Au coverage. Also shown in Figure 20 are the results of a calculation of the dissociation probability when the requirement for the dissociation site has been changed such that dissociation occurs at sites with zero Au nearest neighbors and two or less Au nearest neighbors. Inset in Figure 20 are schematic lattice diagrams representing the maximum Au occupancy of the nearest neighbor lattice positions used in these models. Comparison of the measured probability of dissociation to the three models in Figure 20 demonstrates that the model, in which one or less Au atom is allowed as a nearest neighbor, reproduces the measured values the most closely.

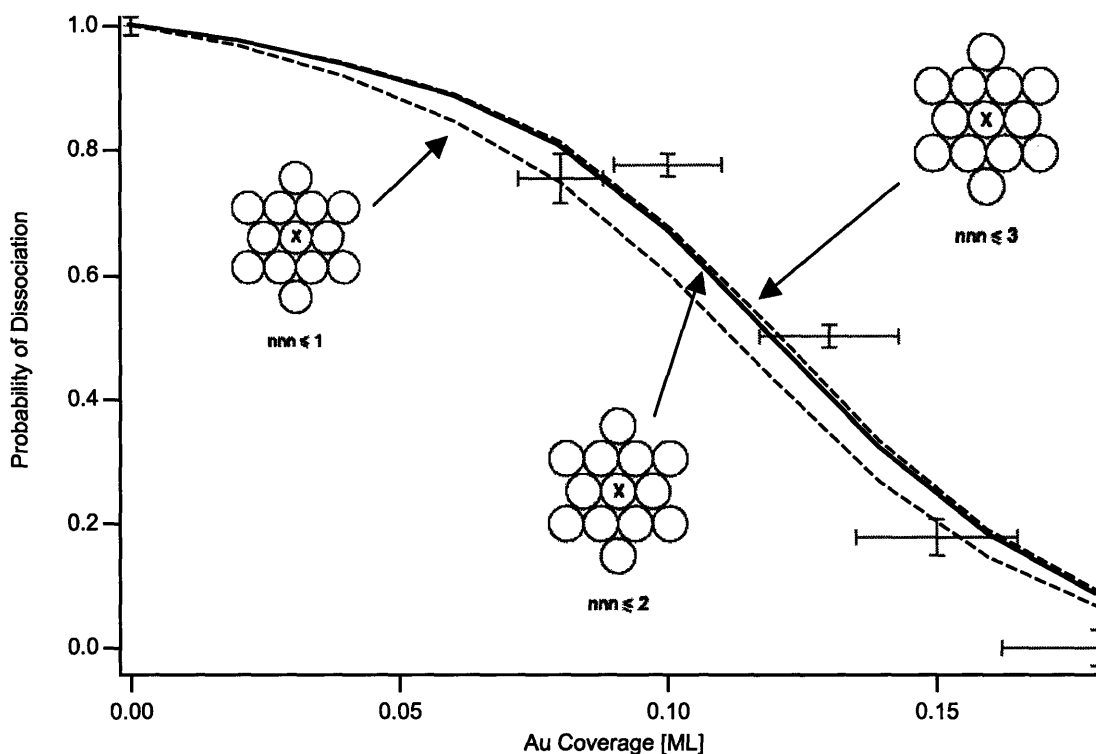


Figure 21. Probability of dissociation of O_2 at the Au/Ni(111) surface alloy as a function of Au coverage (crosses), showing variation of Au allowed as next-nearest neighbors nnn . The horizontal error bars are 10% of the value, the vertical error bars are as calculated for Figure 9. The solid line represents the best reproduction of the data by the simulation, with $nnn = 2$. The dashed lines represent variations of the number of allowed Au atom next-nearest neighbors nnn , in the model. The inset schematics of an adsorption site that does allow O_2 dissociation is shown for each calculation. See text.

A comparison of the measured dissociation probability to three models, in which the maximum number of allowed Au next-nearest neighbors has been varied is presented in Figure 21. The solid line represents the model, described in the beginning of this section, in which a dissociation site is defined as having one or less Au nearest neighbors, two or less Au next-nearest neighbors, two or less Au next-next-nearest neighbors, and 10 or less Au atoms among the 76 next closest atoms. The dashed lines to the left and right of the solid line represent models in which the dissociation site is allowed to have a maximum of one and three Au next-nearest neighbors, respectively. Also shown are

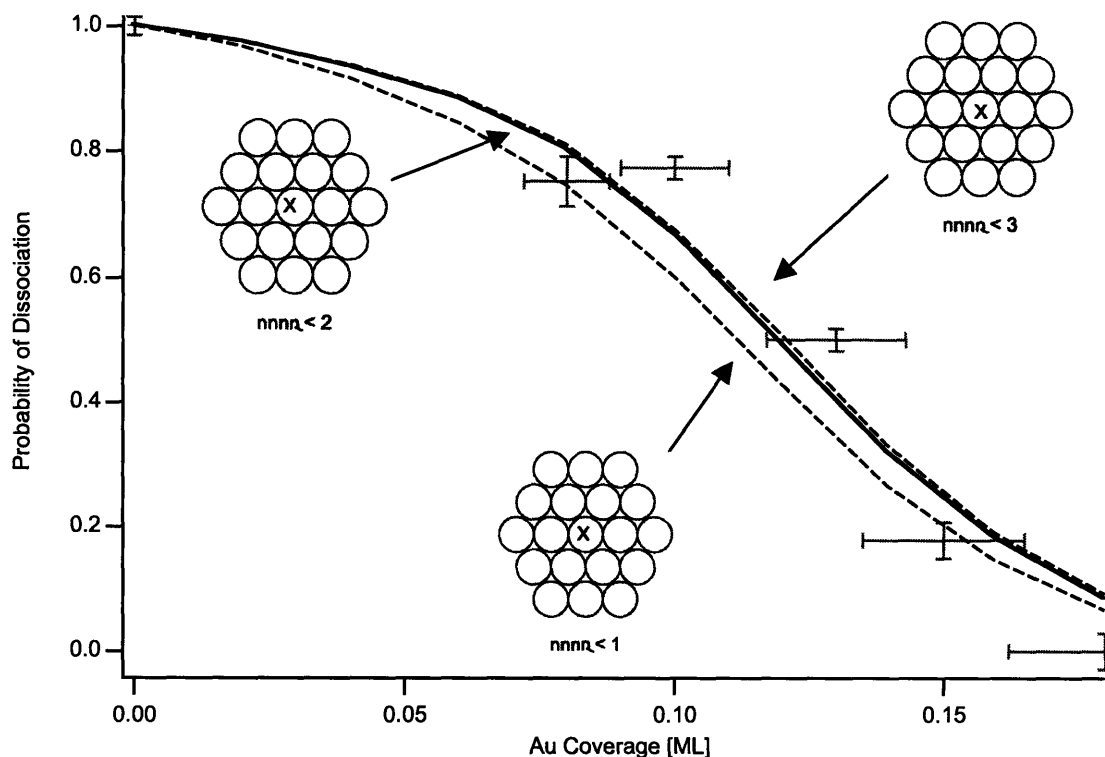


Figure 22. Probability of dissociation of O_2 at the Au/Ni(111) surface alloy as a function of Au coverage (crosses), showing variation of Au allowed as next-next-nearest neighbors $nnnn$. The horizontal error bars are 10% of the value, the vertical error bars are as calculated for Figure 9. The solid line represents the best reproduction of the data by the simulation, with $nnnn \leq 2$ and total ensemble size of 95 atoms. The dashed lines represent variations of the number of allowed Au atom next-next-nearest neighbors $nnnn$ in the simulation. The inset schematics of an adsorption site correspond that allows O_2 dissociation is shown for each calculation. See text.

lattice schematics representing the maximum Au occupancy of the next-nearest neighbor lattice positions used in these models. The model in which up to one Au atom is allowed as a next-nearest neighbor is significantly different from the ideal models in which up to either two or three Au atoms are allowed as next-nearest neighbors. Therefore, allowing up to two Au atoms as next-nearest neighbors is a minimum value for a model that accurately recreates the probability of dissociation data.

The effect on the model of varying the number of allowed Au atom next-next-nearest neighbors is presented in Figure 22. The solid line is the same model as

described in the previous paragraphs. The dashed lines to the left and right of the solid line are calculated using models in which up to one and three Au atoms are allowed as next-next-nearest neighbors, respectively. Lattice schematics representing the maximum Au occupancy of the next-next-nearest neighbor lattice positions used in these models are inset into Figure 22. Increasing the maximum number of allowed Au atom next-next-nearest neighbors from one to two improves the relation of the model to the probability of dissociation data. However, a further increase in the maximum number of allowed Au atom next-next-nearest neighbors from two to three does not significantly alter the model. As in the case of next-nearest neighbors above, allowing up to two Au atoms as next-next-nearest neighbors is a minimum value for a model that accurately recreates the probability of dissociation data.

Figure 23 presents the effects of varying the number of allowed Au atoms in the outermost 76 surface atoms. The dashed curves to the left and right of the solid curve represent calculated models in which up to 9 and 11 Au atoms were allowed in the outermost 76 atoms of the adsorption site, respectively. Varying the number of allowed Au atoms in the outermost 76 surface atoms significantly alters the calculated probability of dissociation as a function of Au coverage. The model that best recreates the data is the one in which up to 10 Au atoms are allowed in the outermost 76 surface atoms. The significantly worse modeling of the probability of dissociation that occurs when up to 9 or 11 Au atoms are allowed in the outermost 76 surface atoms indicates that allowing up to 10 Au atoms in the outermost 76 atoms is important for accurately modeling the probability of dissociation.

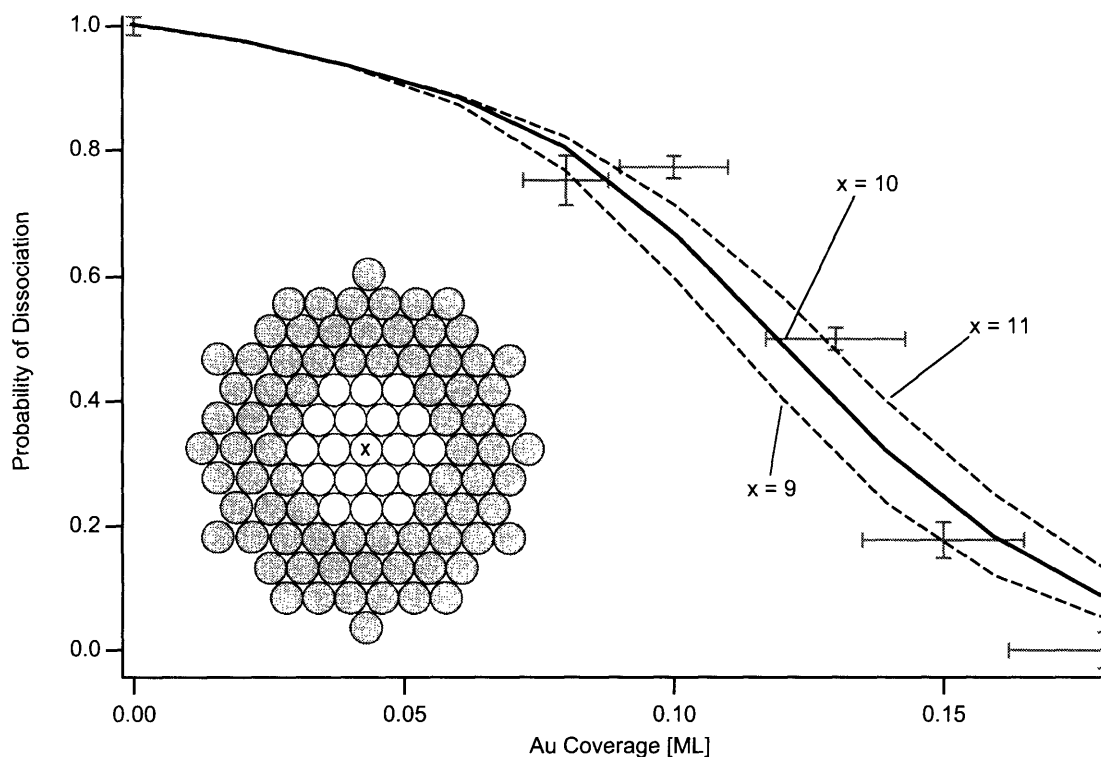


Figure 23. Probability of dissociation of O_2 at the Au/Ni(111) surface alloy as a function of Au coverage (crosses). The horizontal error bars are 10% of the value, the vertical error bars are as calculated for Figure 9. The solid line represents the best reproduction of the data by the simulation, with $x = 10$. The dashed lines represent variations of the maximum number of allowed Au atoms within the outermost 76 surface atoms x of the adsorption site in the model. The inset shows the total surface site for dissociation, based on the model. The filled circles represent the 76 outermost surface atoms. See text.

In Figures 20 – 23, the data for the dissociation probability is compared with models generated by systematic, independent variation of the parameters of the model, namely, the maximum number of allowed Au atoms as nearest, next-nearest, next-next-nearest, and next closest 76 neighbors. The results indicate that closest reproduction of the data occurs when a model is used that allows up to one Au nearest neighbor, up to two Au next-nearest neighbors, up to two Au next-next-nearest neighbors, and up to 10 Au atoms as the next closest 76 neighbors. Based on this definition of the dissociation site, a site that adsorbs oxygen molecularly would violate one of these conditions for

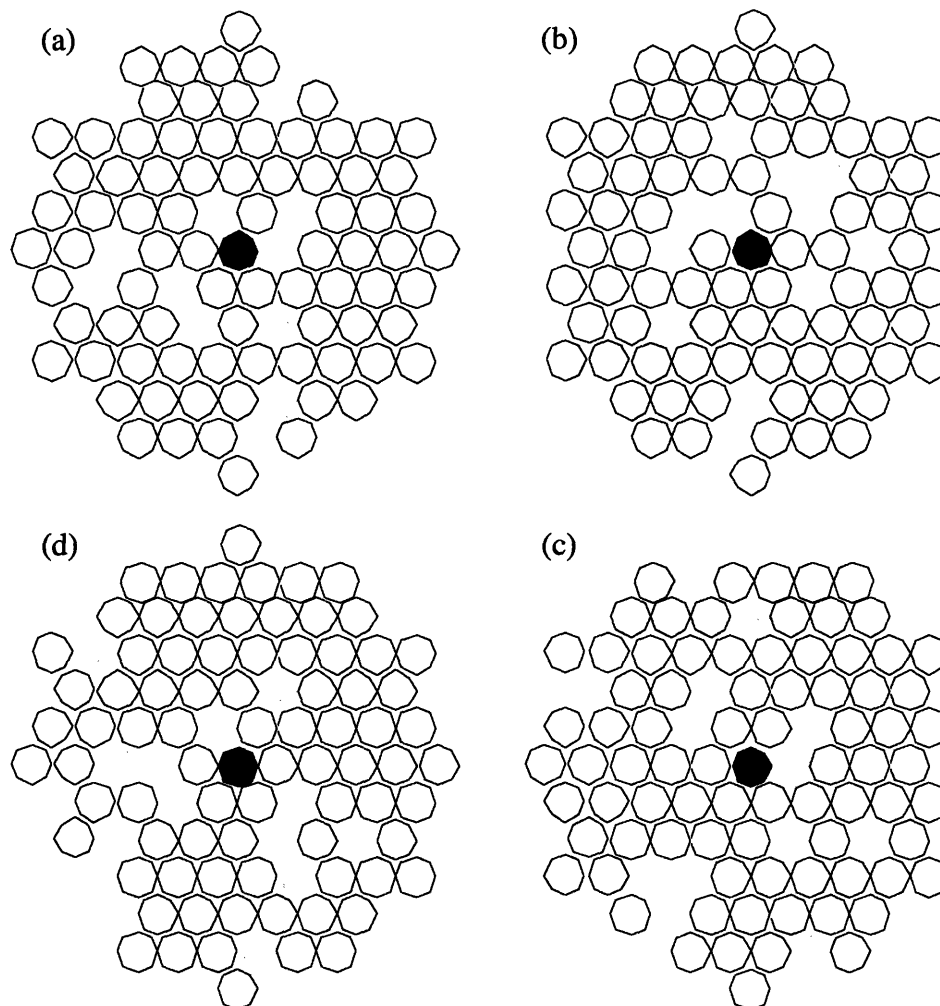


Figure 24. Possible adsorption sites for molecular O_2 chemisorption at the Au/Ni(111) surface alloy. Ni atoms are open circles, Au atoms are gray circles. The central Ni atom of each adsorption site is a dark filled circle. Each site has the following values for the number Au nearest neighbors, next-nearest neighbors, next-next-nearest neighbors, and outermost 76 surface atoms: a) $nn = 2$, $nnn = 2$, $nnnn = 2$, $x = 10$ b) $nn = 1$, $nnn = 3$, $nnnn = 2$, $x = 10$ c) $nn = 1$, $nnn = 2$, $nnnn = 3$, $x = 10$ d) $nn = 1$, $nnn = 2$, $nnnn = 2$, $x = 11$

dissociation. For example, a site that had two Au nearest neighbors, or three Au next-nearest neighbors, or three Au next-next-nearest neighbors, or 11 Au atoms within the 76 next closest neighbors adsorbs oxygen molecularly. Examples of each of these sites for molecular chemisorption are presented in Figure 24.

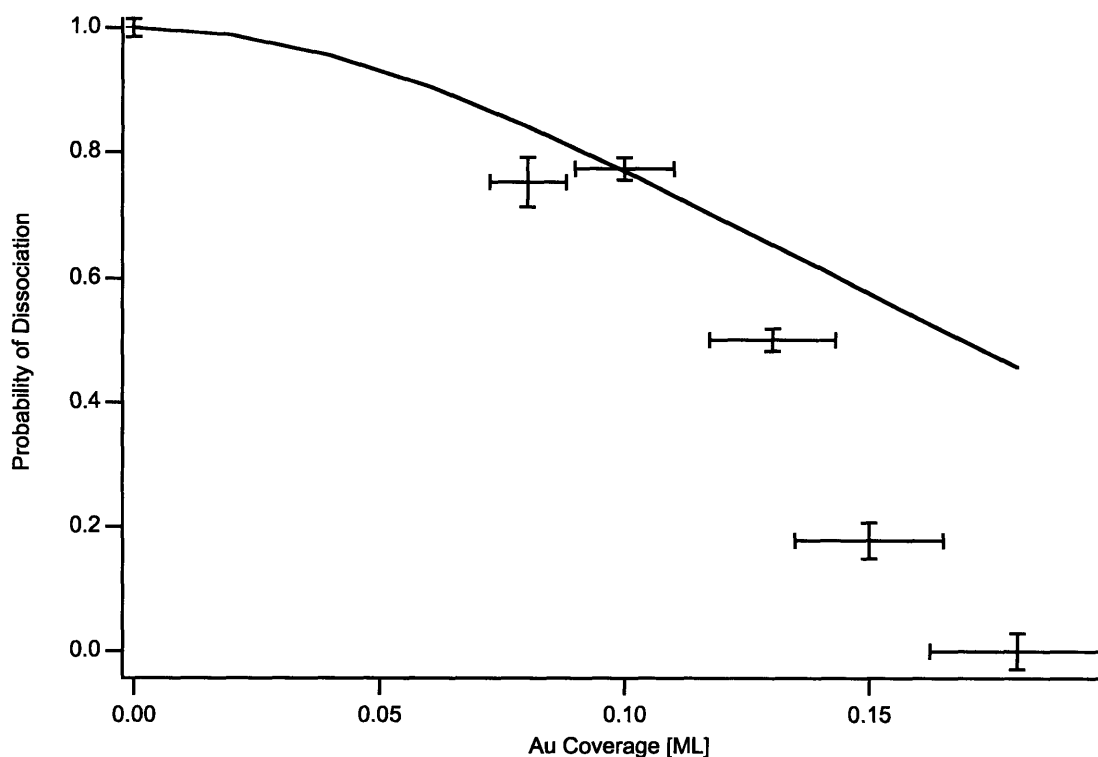


Figure 25. Probability of dissociation of O_2 at the Au/Ni(111) surface alloy as a function of Au coverage (crosses). The horizontal error bars are 10% of the value, the vertical error bars are as calculated for Figure 9. The solid line represents the best reproduction of the data by a simulation with $nn \leq 1$, $nnn \leq 1$, and $nnnn \leq 2$. Total ensemble size is 19 atoms.

For the sites presented in Figure 24, there are a total of 95 atoms involved in the dissociation site. As described in Section IV.B for the statistical model of the amount of adsorbed O atoms characterized by an O-Ni stretch with a frequency of 580 cm^{-1} , an ensemble size of 95 atoms that play a role in the dissociation process is physically unreasonable. A sharp cut off in the dissociation probability more likely arises from cooperative effects among adsorbates, rather than a direct physical interaction between 95 surface metal atoms and an incident O_2 molecule.

To illustrate the requirement of the large ensemble size, the results of a model calculation involving only nearest, next-nearest and next-next-nearest neighbors with a

total ensemble size of 19 atoms is compared to the dissociation probability data in Figure 25. For this calculation, the requirements for a dissociation site are one or less Au atom nearest neighbors, one or less Au atom next-nearest neighbors and two or less Au atom next-next-nearest neighbors. These numbers were chosen using the same systematic variation as described above. This model fails to accurately reproduce the sharp decrease in the dissociation probability that occurs between Au coverages of 0.10 and 0.15 ML. Further reduction of the ensemble size used by the model for dissociation results in a worse match to the data.

Another variation in the model that was attempted involved taking into account the blocking effect that O atoms have on dissociative adsorption. For this model calculation, instead of systematically checking the lattice for dissociation sites, lattice sites are chosen at random, and then checked for their ability to dissociate O₂. For sites that meet the dissociation requirement, two O atoms are placed at the lattice positions of their 3-fold hollow sites. The process is repeated, until no further adsorption is observed.⁶⁹ The dissociation probabilities that result from this calculation suffer from the same problems as the model presented in Figure 25, namely that there is no sharp decrease in the dissociation probability between 0.10 and 0.15 ML Au. The sharp decrease is likely the result of cooperative effects in the oxygen atom overlayer, a phenomenon that is not explored here.

V. CONCLUSIONS

Adsorption of oxygen onto Au/Ni(111) surface alloys falls into three general regions. At 0.10 ML Au and below, O₂ adsorbs solely dissociatively. O atoms adsorbed in 3-fold hollow sites in mostly Au free regions are identified by the frequency of the O-

Ni stretch at 580 cm^{-1} . O atoms adsorbed with Au atoms as next-nearest neighbors are identified by the unresolved features with frequency between $350\text{-}500\text{ cm}^{-1}$. At 0.13 ML Au, a feature corresponding to molecular O_2 adsorbates is observed for the first time, with frequency at 850 cm^{-1} . Between 0.13 and 0.18 ML Au, the amount of dissociative chemisorption is decreasing, while the amount of molecular adsorption increases to its maximum value. The feature at 850 cm^{-1} is observed to have two shoulders at 790 and 950 cm^{-1} , both of which have the same intensity as a function of Au coverage as the 850 cm^{-1} feature. These shoulders are assigned to additional molecular O_2 adsorbates, bound to sites with different orientation and proximity to nearby Au atoms.

It is hypothesized that the appearance of molecularly chemisorbed O_2 results from a downward shift in energy of the Ni d-bands as a result of alloying Au into the surface. At 0.18 ML Au, the shift of the Ni d-band is such that only molecular chemisorption of oxygen occurs. It is proposed that the presence of a Au atom, within a group of five surface atoms required for dissociation of O_2 on a Ni(111) surface, stabilizes the molecular O_2 adsorbate by raising the barrier to dissociation.

From 0.22 to 0.27 ML Au, dissociative chemisorption is absent, and molecular adsorption is steadily decreasing. At 0.29 ML Au, there is no oxygen chemisorption on the surface. The presence of Au atoms has caused the d-band to shift to the extent that the surface no longer is able to stabilize even the molecularly chemisorbed species.

When a Au/Ni(111) surface saturated with molecular O_2 is heated from 77 to 300 K , the molecular species dissociates into chemisorbed O atoms. Dissociation begins to occur at 115 K , is rapid at 150 K , and is complete at 300 K . No desorption of O_2 is observed. A kinetic model is used to obtain an estimate of the difference in barrier

heights to dissociation and desorption, based on the observation that thermally excited chemisorbed O₂ molecules exclusively dissociate, and do not desorb. The difference is calculated to be 4 kcal/mol.

The intensity of the 580 cm⁻¹ feature, and by extension the coverage of O atoms adsorbed in 3-fold hollow sites in mostly Au free regions, has been reproduced using a statistical model. The model which best reproduces the data requires an ensemble size of 82 atoms to interact with each adsorbed O atom. This number is physically unreasonable and arises from the sharp decrease in the intensity of the 580 cm⁻¹ feature that is observed as the Au coverage is increased from 0.10 to 0.13 ML. This sharp cutoff in intensity and large ensemble size are suggestive that a phase transition in the oxygen overlayer occurs as the Au coverage is increased from 0.10 to 0.13 ML.

The probability of dissociation of O₂ at the Au/Ni(111) surface alloy, as a function of Au coverage, has been measured. The results of a simulation are presented which reproduce the probability of dissociation, by assuming that the site required for dissociation has one or less nearest neighbor Au atoms, two or less next-nearest neighbor Au atoms, two or less next-next nearest neighbor Au atoms, and 10 or less Au atoms in the surrounding 76 atoms. Based on these requirements for the dissociation site, several possible sites that do not allow dissociation, and hence adsorb O₂ molecularly, have been proposed.

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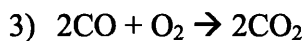
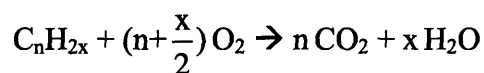
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- ⁷² Reprinted from *Applied Surface Science* Volume number 173, S. Zafeiratos and S. Kennou, Photoelectron spectroscopy study of surface alloying in the Au/Ni(s): 5(0 0 1) x (1 1 1) system, Page 69, Copyright (2001) with permission from Elsevier

CHAPTER 3 - CO Oxidation Catalyzed by Au/Ni(111) Surface Alloys**I. INTRODUCTION**

One indication of the importance of automotive pollution abatement is given by the size of the world market for the heterogeneous catalysts for this process. In the year 2000, this market was about \$1.5 billion, almost half of the total market for all heterogeneous catalysts. The catalysts employed for this process are known as three-way catalysts (TWC) because of the three major reactions that they catalyze:



2) Combustion of residual hydrocarbons (from unburned fuel) e.g.



The transition metals Pt, Rh and Pd supported on ceria and alumina are used as the catalysts, either independently or in combination with one another to affect these reactions in the exhaust streams of current automobiles.¹ These metals are collectively known as platinum-group metals. Although the discovery and implementation of their catalysis of the above reactions was a major step forward in pollution abatement, they still suffer from several problems.²

One problem is the high cost and limited/unstable supply of the platinum group metals. For example, on a weight for weight basis, platinum is almost twice as expensive as gold – making even the relatively expensive gold a feasible alternative. The cost of rhodium is ~50% higher than that of platinum. Although palladium is cheaper than gold (by about a factor of 3), its supply is neither as stable nor as large as that of gold.²

From the standpoint of the effectiveness of the TWC catalyst, the major problem is the requirement of a high temperature (~300°C) before the catalyst becomes active.

The activation temperature of $\sim 300^{\circ}\text{C}$ is attained during steady operation, but is not attained during engine starts and idling. During engine starts and idling, significant amounts of unprocessed exhaust gas escape due to the catalyst temperature being less than 300°C . The net result is that 90% of all hydrocarbon exhaust occurs during the cold start period.^{2,3}

The TWC will catalyze hydrocarbon combustion to CO_2 at room temperature, however it is not active towards CO oxidation. During the cold start period, unreacted CO poisons the catalyst thereby precluding hydrocarbon combustion, and leads to the observed large amount of hydrocarbon emission during engine starting.³ Therefore, a new catalyst for CO oxidation that is efficient at lower temperatures would greatly reduce the amount of total hydrocarbon exhaust.

In addition to reducing exhaust from internal combustion engines, a low-temperature CO oxidation catalyst would be of great benefit in fuel cells. Fuel cells have been proposed as an energy efficient and clean alternative to the internal combustion engine. One major problem associated with their deployment is that the currently employed platinum membranes are extremely sensitive to de-activation by CO adsorption. Because the hydrogen gas on which fuel cells rely is produced via steam reforming of methane,



the CO induced deactivation of fuel cell membranes is a significant problem. Although the amount of CO remaining in the final H_2 product is only $\sim 1\%$, it is more than enough to poison a fuel cell. A catalyst that could effectively and selectively oxidize CO at low temperatures would be useful in cleaning up H_2 streams in fuel cells – and hence would be useful in not just the present, but the next generation of automobiles.^{2,4}

It is instructive to examine the mechanism of CO oxidation on Pt and Rh, in order to understand the high temperature requirement on the molecular level. Ultra-high vacuum (UHV) surface science has provided a wealth of insight into this problem. From the standpoint of the reactants, it is well established that the reaction occurs between adsorbed oxygen atoms and co-adsorbed CO molecules. At low temperature (< 200 K), oxygen adsorbs solely molecularly on Pt surfaces. On Pt, this species of oxygen is unreactive towards CO, (unless ultra-violet light is used to dissociate the oxygen).⁵ Therefore, at temperatures below 200 K, one of the key reactants (atomic O) is not present at the surface, and hence the reaction is not possible.

It has also been established that CO oxidation on Pt occurs via the Langmuir-Hinshelwood mechanism. In this mechanism, the reactants first adsorb and equilibrate with the surface. The reaction then occurs as a result of the thermal motion of the adsorbates at the surface. This mechanism is in contrast to the Eley-Rideal mechanism, in which an incident gas phase molecule reacts with a surface adsorbate before it equilibrates with the surface and adsorbs.

Adsorption of the reactants on and their equilibration with the surface prior to reaction means that the activation energy required for the reactants to proceed over the barrier must flow from the surface in order for the reaction to proceed. The mechanistic constraint that the surface acts as the energy source for the reaction leads to the requirement that the entire structure of the catalyst – the oxide support as well as the reactive metal surface – be heated to 300°C . In effect, due to this mechanism, the bulk/non-reactive parts of the catalyst system must be heated to 300°C , even though they play no role in the reaction. However, some systems do not require heating of the entire structure of the catalyst to the activation temperature for the reaction to proceed. Some

reactions only require energy to be in the gas phase molecules, and the surface temperature is of minor importance.⁶ If a catalyst carries out CO oxidation via a mechanism that is not of the Langmuir-Hinshelwood type, this catalyst should be active at much lower temperature surface temperatures. If the catalyst in a catalytic converter in an automobile oxidized CO by a mechanism other than the Langmuir-Hinshelwood, then during engine starting, when the catalyst is cold, but the exhaust gas is hot, CO oxidation (and by extension, hydrocarbon combustion) would occur.

An example of CO oxidation that does not operate via the Langmuir-Hinshelwood mechanism occurs when chemisorbed O_2 molecules dissociate, producing non-equilibrated hot O atoms. These hot O atoms react with adsorbed CO to form CO_2 , at temperatures as low as 125 K.^{5,7,8} Another example of a non-Langmuir-Hinshelwood reaction is the first step of catalytic hydrocarbon combustion, dissociative adsorption of the hydrocarbon. The dissociative adsorption of CH_4 on a Ni(111) surface is a specific case that has been studied in detail. This reaction occurs readily at surface temperatures of 77 K, as long as the gas phase CH_4 molecules have sufficient energy to overcome the activation barrier.⁶

These mechanistic alternatives reveal a wealth of possible chemical reactions at surfaces that might solve the problems of the TWC. The potential exists for discovery of a new catalyst, which may or may not catalyze CO oxidation using the same mechanism as the TWC. One such potential new catalyst was discovered by Haruta in 1989. He demonstrated that a catalyst composed of supported Au nanoparticles was effective for CO oxidation, overturning the conventional wisdom that Au was an inert, unreactive metal.⁹ Since his discovery, research into Au as a catalyst has revealed that it catalyzes a wide range of reactions, including NO reduction and hydrocarbon combustion. Although

there has been an explosion of research into Au nanoparticle and even Au single-crystal surface catalysis,^{10,11,12} there are still many unanswered questions regarding the basic mechanisms.

Valden et. al. attempted to explain the reactivity of supported Au nanoparticles as arising from a quantum size effect.¹³ They presented evidence that the catalytic activity of supported Au nanoparticles for CO oxidation was extremely sensitive to the size of the Au nanoparticles. Further, the catalytically active Au clusters were observed to have a band structure significantly different from that of bulk Au, suggesting that the requirement of small size for catalytic activity arises from a change in band structure and/or quantum confinement.^{13,14,15}

Another possible route to investigate why supported Au nanoparticles are an effective catalyst for CO oxidation under ambient conditions is the determination of the chemical nature of the reactive oxygen adsorbate. Most studies of catalytic oxidation of CO over supported Au nanoparticles measured the production of CO₂ and/or the spectroscopic signatures of adsorbed CO, and assumed atomic oxygen was the reactive species. However, there has been evidence to indicate that molecular oxygen is important. Evidence indicating the importance of molecular O₂ species was initially provided by Stiehl et. al., who exposed Au nanoparticles at 77 K to an oxygen plasma, containing both oxygen molecules and atoms. These nanoparticles were then exposed to CO, causing efficient CO oxidation to occur. In another experiment, the nanoparticles were heated to 300 K after the oxygen plasma exposure, and then cooled to 77 K, at which point the nanoparticles were exposed to CO. Although CO oxidation still occurred, the amount was significantly reduced. The authors hypothesized that oxygen adsorbed molecularly at low temperatures, and was a reactant in the CO oxidation

reaction. Heating to 300 K caused the molecularly chemisorbed O_2 to dissociate, and thus reduced the reactivity.^{16,17}

Strong evidence for the hypothesized participation of molecularly chemisorbed O_2 species in the catalytic CO oxidation reaction has been provided very recently by the experiments of Guzman et. al.^{18,19} Using Raman spectroscopy, they were able to identify a series of molecularly chemisorbed oxygen species that formed on their gold supported catalyst at room temperature. After exposure to an O_2 gas flow at $\sim 7.5 \times 10^{-5}$ torr, they observed frequencies at 1123, 966, 870 and 831 cm^{-1} , which they assigned to a superoxo (O_2^{1-}) and three peroxo (O_2^{2-}) species, respectively. Exposure to a flow of $O_2 + CO$ gas, and subsequent Raman spectra revealed that the 966 cm^{-1} feature was absent and the 1123 cm^{-1} feature was greatly reduced in intensity, indicating that these two species take part in the observed CO oxidation reaction.^{18,19} In addition, earlier work using Electron Paramagnetic Resonance (EPR) had identified the presence of an O_2^- superoxo species at the surface of Au catalysts supported on TiO_2 ,^{20,21} Al_2O_3 ,²¹ and ZnO ,²² and the possible involvement of this species in low temperature CO oxidation. For the case of TiO_2 supported Au nanoparticles, EPR peaks with $g = 2.020$, 2.010 and 2.005 were attributed to a superoxide radical at the surface. These peaks were observed to disappear when the catalyst, at room temperature, was exposed to CO, suggesting that the superoxide species at the surface reacted with CO to form CO_2 .²⁰

In addition to the experimental evidence presented above, several theoretical papers have indicated the possible existence of a stable molecular O_2 adsorbate at the interface between the oxide support (MgO , TiO_2) and the Au nanoparticle, and that this species is reactive towards CO oxidation.^{23,24} The formation and reactivity of molecularly chemisorbed O_2 is in agreement with the original mechanism of supported Au

nanoparticle reactivity proposed by Haruta. He proposed that CO oxidation occurred at the perimeter of the Au nanoparticles, and that when Au was in nanoparticle form, the number of these perimeter sites was such that significant catalytic activity became possible. In general agreement with Haruta's original hypothesis, theory^{23,24} proposed that the perimeter sites stabilized molecularly adsorbed O₂, which was revealed to be the source of the low temperature CO oxidation reactivity of supported Au nanoparticle catalysts.

The above theoretical and experimental evidence presents a strong case for existence and reactivity of molecularly chemisorbed O₂ species at supported Au nanoparticle catalysts. The reactivity of these species towards CO oxidation is in sharp contrast to their reactivity on the platinum group metals, and may be one explanation for the large observed difference in required temperatures for catalytic CO oxidation between platinum group metals and supported Au nanoparticles.

Another important aspect of the mechanism of CO oxidation on supported Au nanoparticles is the state of the CO adsorbate present at the surface. From FTIR spectroscopy, it is observed that generally the CO species are adsorbed linearly atop metal atoms of the surface. CO species with frequencies $\sim 2100\text{ cm}^{-1}$ have been assigned to adsorption of CO on metallic Au atoms (terraces of the Au nanoparticles), while higher frequency species have been assigned to species adsorbed atop metal ions (Au³⁺, Ti⁴⁺, Zn²⁺).^{25,26} It was initially proposed by Haruta that one reason for the low-temperature reactivity is the presence of a highly mobile CO adsorbate.⁹ Recent work by Bianchi et. al. has demonstrated that for Au supported on TiO₂, CO bound to Ti⁴⁺ ions has a lower adsorption energy than CO bound to metallic Au atoms.²⁷ It has been proposed that the

lower adsorption energy directly translates to a lower required temperature for thermal activation of adsorbed CO, and hence enhanced reactivity at low temperatures.

This chapter reports on a new system for catalytic oxidation of CO: a Au/Ni(111) surface alloy. The evidence presented suggests that Au-Ni alloys may be effective CO oxidation catalysts, with improved properties over the conventional TWC system, and supported Au nanoparticle catalysts. This discovery has led to the filing, on January 19, 2006, of a patent application for the use of Au-Ni alloy catalysts for CO oxidation.²⁸ In addition, the spectroscopic identification of molecularly chemisorbed O₂ as the reactive species sheds light on the mechanistic debate regarding the low temperature CO oxidation observed for supported Au nanoparticle catalysts. Most importantly, the observation that the Au/Ni(111) surface alloy catalyzes CO oxidation at low temperatures casts doubt on the previously proposed hypothesis that the quantum nature of supported Au nanoparticles is responsible for their low temperature CO oxidation. Part A of the Results Section describes the observation that the reaction proceeds rapidly at 77 K, and appreciably as low as 70 K, when a molecular beam of CO is exposed to a Au/Ni(111) surface alloy saturated with molecularly adsorbed O₂. Co-adsorbed O₂, O atoms and CO are identified at the surface after the reaction at 77 K, using vibrational spectroscopy, as presented in Part B of the Results Section. Heating of these co-adsorbed species causes them to react to form gas phase CO₂, presented in Part C of the Results Section. Formation of chemisorbed molecular O₂ prior to reaction is identified as a critical step, as presented in Part D of the Results Section. Finally, the reactive CO species has been identified spectroscopically as having a lower binding energy, as presented in Part E of the Results Section.

II. EXPERIMENTAL

The experimental apparatus has been described extensively elsewhere²⁹ and in Chapter 1. Oxygen exposures are described in Chapter 2. Research grade CO from Matheson (99.998%) was dosed using the molecular beam system described in Chapter 2. For experiments in which the reactivity was monitored by the quadrupole mass spectrometer (QMS), the partial pressures of CO (mass 28), O₂ (mass 32) and CO₂ (mass 44) are monitored. The small beam hole was used for CO exposures. Usage of the small beam hole reduced the background pressure of CO in the chamber, and hence any reactions that might occur on the edges of the crystal or other surfaces in the chamber. For experiments in which vibrational spectra are measured by high resolution electron energy loss spectroscopy (HREELS), the large beam hole was used to ensure a uniform coverage of CO on the surface. All molecular beam exposures were performed with the crystal in the “TDS” position (described in Chapter 1), with the nozzle at room temperature and a stagnation pressure of 20 psia. The flux of CO has been estimated using the equation²⁹:

$$F = \frac{P \cdot S}{RTA} \quad (2)$$

where P is the steady state pressure of CO in the chamber when the molecular beam enters through the small beam hole (measured using the ion gauge to be 3.0×10^{-8} torr = 3.9×10^{-11} atm), S is the pumping speed (measured to be ~ 1000 L/s), R is the ideal gas constant ($0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$), T is the temperature (300 K), and A is area of the beam cross section (0.7 cm^2). Using these values yields a flux of $\sim 2.3 \times 10^{-9} \text{ mol/s} \cdot \text{cm}^2 = 1.4 \times 10^{15} \text{ molecules/s} \cdot \text{cm}^2$. For a Ni(111) surface, $1 \text{ ML} = 1.9 \times 10^{15} \text{ molecules/cm}^2$, therefore the flux of CO is estimated to be $\sim 0.7 \text{ ML/s}$.

The Au/Ni(111) surface alloy is prepared as described in Chapter 1. HREELS confirms that the prepared Au/Ni(111) surface alloy is clean of all contaminants. All HREELS spectra are measured with an impact energy of 5.5 eV. Average frequencies of loss features are calculated by averaging the frequency of the loss feature over 10 spectra. Reported error in the frequency is the 95% confidence limit.

All exposures of the crystal to the molecular beam and HREELS measurements occurred with the crystal temperature at 77 K, unless stated otherwise in the text. A temperature of 77 K is achieved by using liquid nitrogen in the cryostat. For the experiments run at 70 K, the cryostat is filled with liquid nitrogen, then sealed and pumped by the house vacuum system. The lower pressure created by applying vacuum to the cryostat lowers the boiling point of liquid nitrogen, and hence the ultimate crystal temperature.

Thermal desorption spectroscopy (TDS) is performed by heating the crystal at 2 K/s, while monitoring the background pressure of the indicated masses in the chamber using the QMS. The crystal is in the “TDS” position, and facing the QMS. All TDS experiments begin with crystal temperatures ~ 77 K, unless stated otherwise in the text.

The catalytic oxidation of CO is performed by first exposing the Au/Ni(111) surface alloy to a 10% O₂/Ar beam for 5 s, then exposing it to a CO beam for 8 s. The times of the exposures are chosen so as to maximize the observed production of CO₂. Decreasing either exposure time results in reduced production of CO₂ between 108 – 250 K, while increasing exposures of both O₂ and CO has no observable effect on the amount of CO₂ produced.

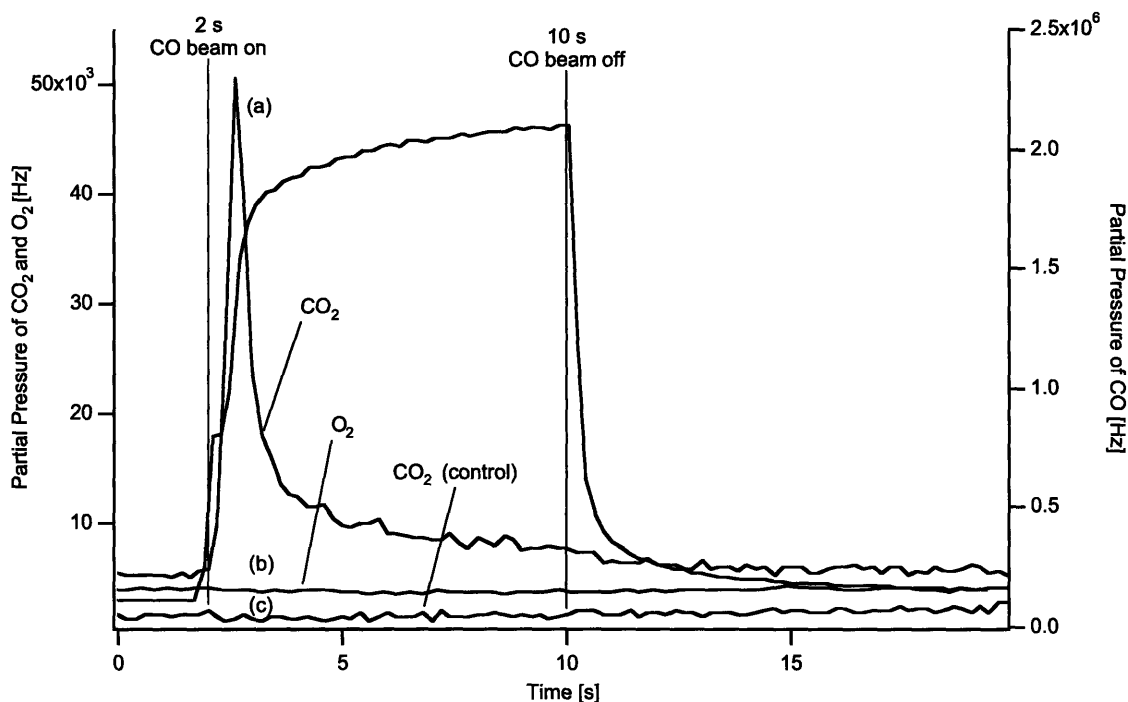


Figure 1. Partial pressure of CO₂ (a) and O₂ (b) (masses 44 and 32 respectively) during exposure of a 0.19 ML Au/Ni(111) surface alloy at 77 K saturated with molecularly chemisorbed O₂ to a CO beam. Trace (c) is CO₂ partial pressure when the experiment is repeated with the crystal rotated 180° away from the CO beam. See text.

III. RESULTS

A. CO Oxidation at 70 and 77 K

Figure 1 shows that CO₂ is produced when a CO beam is directed at a saturated layer of O₂ on a Au/Ni(111) surface alloy (0.19 ML Au) at 77 K. The experiment is carried out by exposing a 0.19 ML Au/Ni(111) surface alloy to a 10% O₂/Ar beam for 5 s. This exposure produces the saturation coverage of chemisorbed molecular O₂, which is estimated to be 0.45 ML as described in Chapter 2. The vibrational spectrum of this layer is shown in Chapter 2, Figure 3. The crystal is then exposed to a beam of CO, while the partial pressure of CO₂ (mass 44) is monitored (Figure 1a) by the QMS. The partial pressure of oxygen (mass 32) is also monitored, but no desorption of O₂ is observed (Figure 1b). The length of CO exposure is 8 s, beginning at 2 s (as indicated in

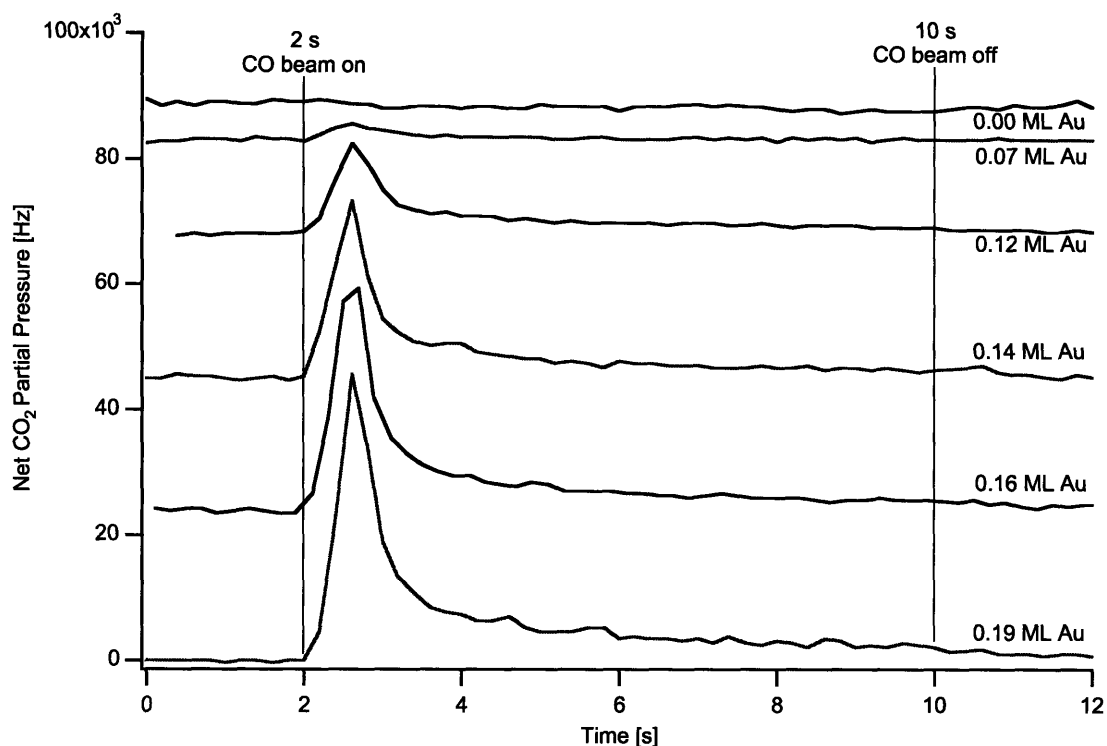


Figure 2. Net partial pressure of CO₂ (mass 44) during exposure of a CO beam to Au/Ni(111) surface alloys at 77 K saturated with molecularly chemisorbed O₂. The data for 0.0, 0.07 and 0.12 ML Au have been scaled to correct for drift in the QMS sensitivity. See text.

Figure 1) and ending at 10 s. CO₂ production coincides with the CO exposure from the beam (at 2 s as labeled in Figure 1). The partial pressures are measured in 0.2 s increments.

As a control experiment, the O₂ saturated Au/Ni(111) surface alloy, rotated 180°, is exposed to the CO beam, such that the beam impinges on the back of the crystal mount. The results, shown in Figure 1c, demonstrate that no CO₂ production occurs. To eliminate the background level of CO₂ from the signal in Figure 1a, the data from the control experiment are subtracted from the primary experiment. The background partial pressure of CO₂ prior to the primary and control experiments is sometimes different, therefore this difference in the background partial pressures of CO₂ is also subtracted from the data of the primary experiment. The net result is plotted in Figure 2 (bottom

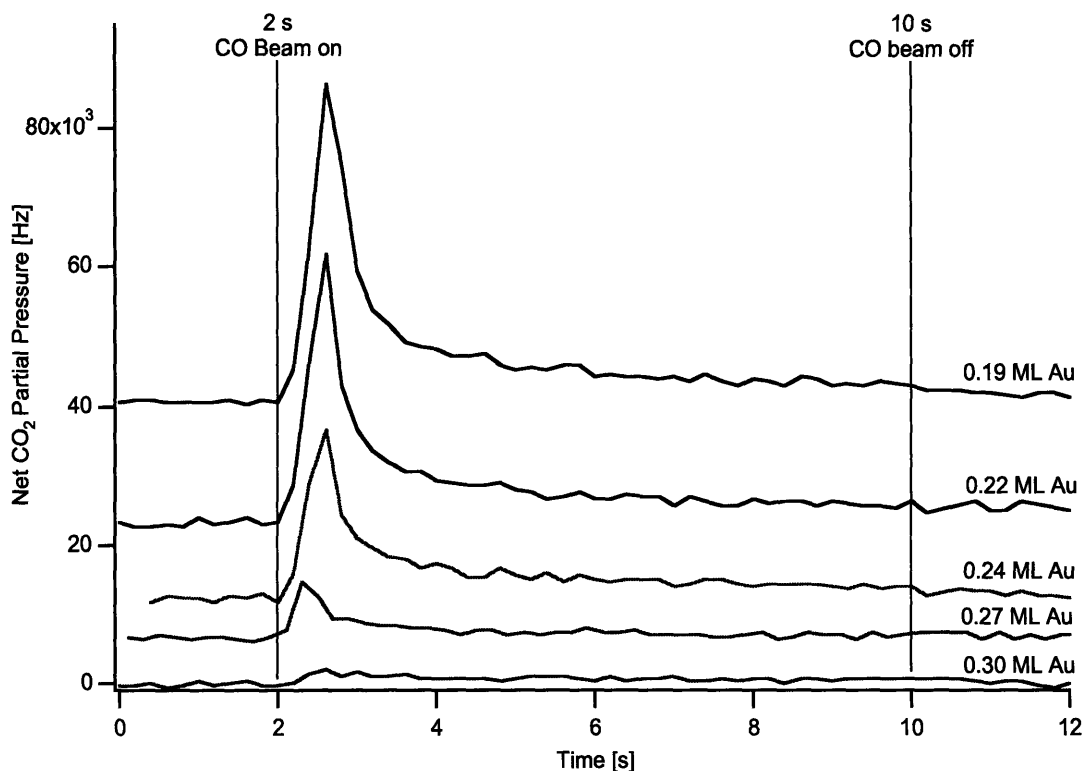


Figure 3. Net partial pressure of CO_2 (mass 44) measured during exposure of a CO beam to Au/Ni(111) surface alloys saturated with molecularly chemisorbed O_2 . See text.

trace). The same experiments and background subtraction procedure are carried out for Au coverages 0.0 to 0.30 ML, and are shown in Figures 2 and 3.

The data presented in Figure 2 for the Ni(111) surface, and for the Au/Ni(111) surface alloys with 0.07 and 0.12 ML Au have been adjusted by a scaling factor. The scaling factor is required because the sensitivity of the QMS to the partial pressure of the CO_2 changed between these experiments and the others reported in Figures 2 and 3. To correct for this, the amount of CO_2 produced during CO oxidation is measured for a Au/Ni(111) surface alloy with 0.16 ML Au. The scaling factor is then the ratio of the amount of CO_2 produced from a Au/Ni(111) surface alloy with 0.16 ML Au on the day that the data for the 0.0, 0.07 and 0.12 ML Au/Ni(111) surface alloys were collected, to the amount of CO_2 produced from a Au/Ni(111) surface alloy with 0.16 ML Au on the

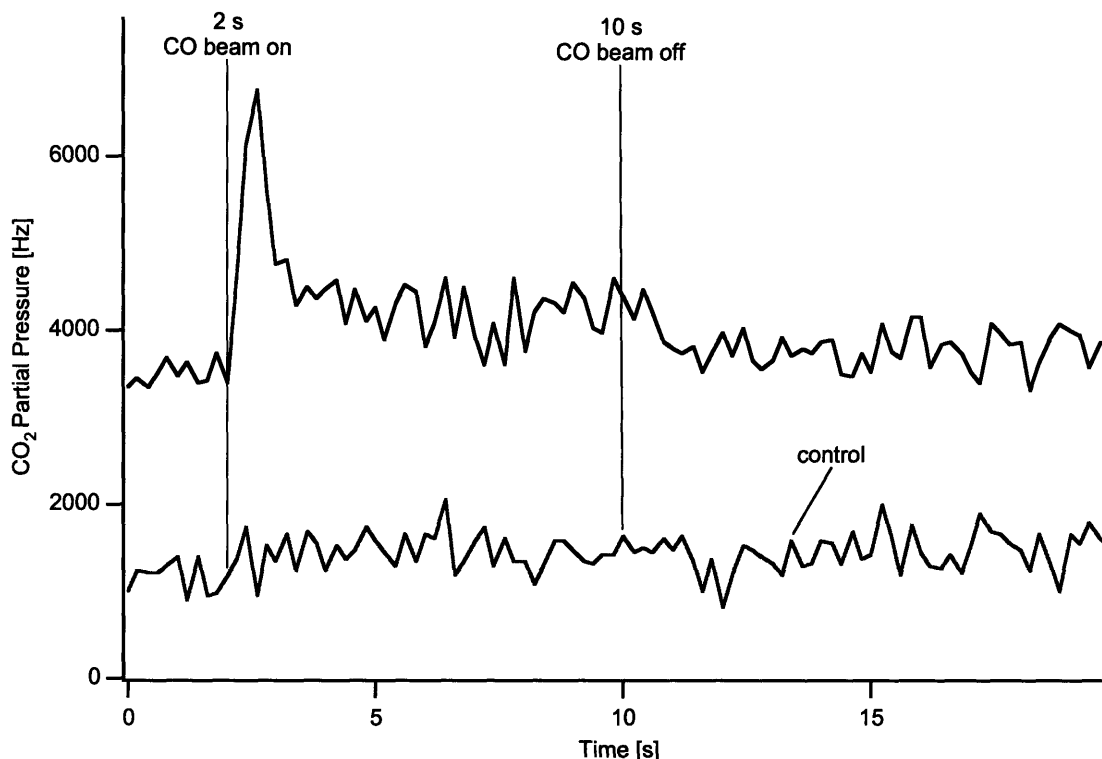


Figure 4. Partial pressure of CO_2 (mass 44) during exposure of a 0.18 ML Au/Ni(111) surface alloy at 70 K saturated with molecularly chemisorbed O_2 to a CO beam (upper trace). Lower trace is CO_2 partial pressure when the experiment is repeated with the crystal rotated 180° away from the CO beam.

day that the rest of the data in Figures 2 and 3 were collected. This scaling factor has also been applied to the data in Figure 11, for the Au/Ni(111) surface alloys with 0.0, 0.07 and 0.12 ML Au.

Reversing the order of the exposure of CO and O_2 , such that a 0.24 ML Au/Ni(111) surface alloy is exposed first to a CO beam for 8 s, then to a 10% O_2/Ar beam for 5 s, produces no CO_2 . No CO_2 production is observed when the CO exposure is reduced to times as short as 0.25 s.

The reaction has also been tested at 70 K. In this experiment, a saturated layer of molecular O_2 is prepared on a 0.18 ML Au/Ni(111) surface alloy by a 5 s exposure to the 10% O_2/Ar beam, with the crystal held at 70 K. Then, the partial pressure of CO_2 in the chamber is monitored while the crystal held at 70 K is exposed to the CO beam. The

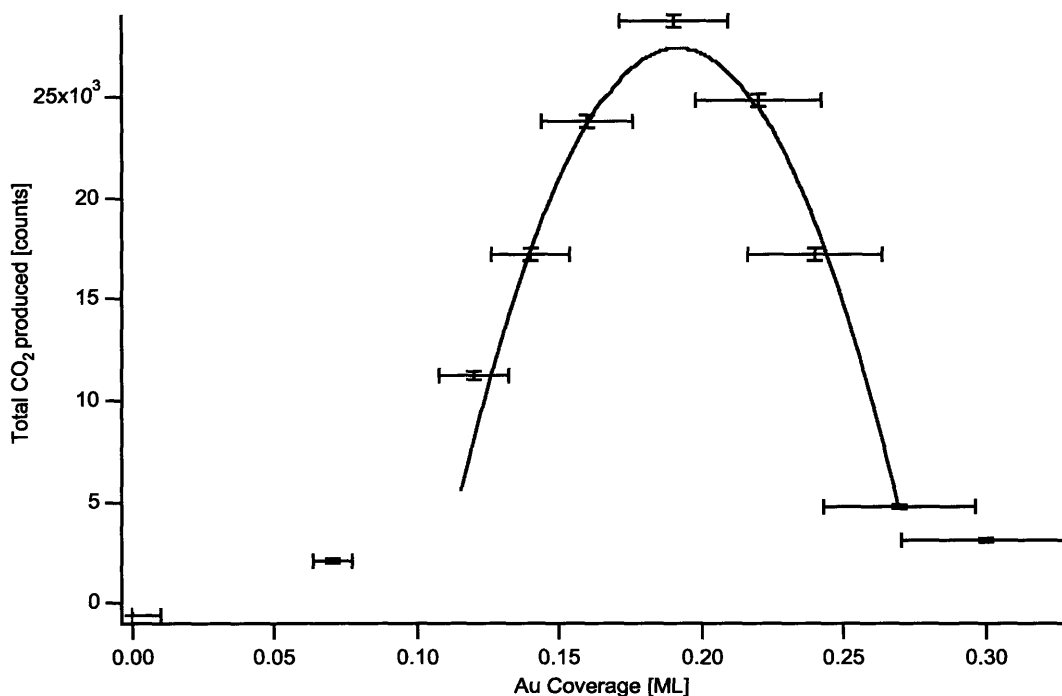


Figure 5. Total CO₂ produced during exposure of a saturated O₂ layer on Au/Ni(111) surface alloys to a CO beam. Total CO₂ is calculated by integrating the traces in Figures 2 & 3 over the length of time of CO exposure (2 to 10 s). Vertical error bars represent 95% confidence limits of Poisson counting statistics. Horizontal error bars are 10% value, see Chapter 1.

results are presented in Figure 4. The CO₂ production shown in Figure 4 is qualitatively similar to that shown in Figure 1.

To quantify the relative amount of CO₂ produced, the integrated area of each of the partial pressure traces in Figures 2 and 3 is calculated by summing the intensity of each trace over the beam exposure time, from 2 to 10 s. The results are plotted as a function of Au coverage in Figure 5. Comparison of the integrated values calculated for each trace confirms that the maximum CO₂ production occurs at 0.19 ML Au, while almost no reaction is observed at Au coverages of 0.07 and 0.30 ML Au. Integration of the trace in Figure 4, representing the reaction carried out at 70 K for a 0.18 ML Au/Ni(111) surface alloy, yields a value which is 15% that of the CO₂ production that occurs when the reaction is carried out at 77 K on a 0.19 ML Au/Ni(111) surface alloy.

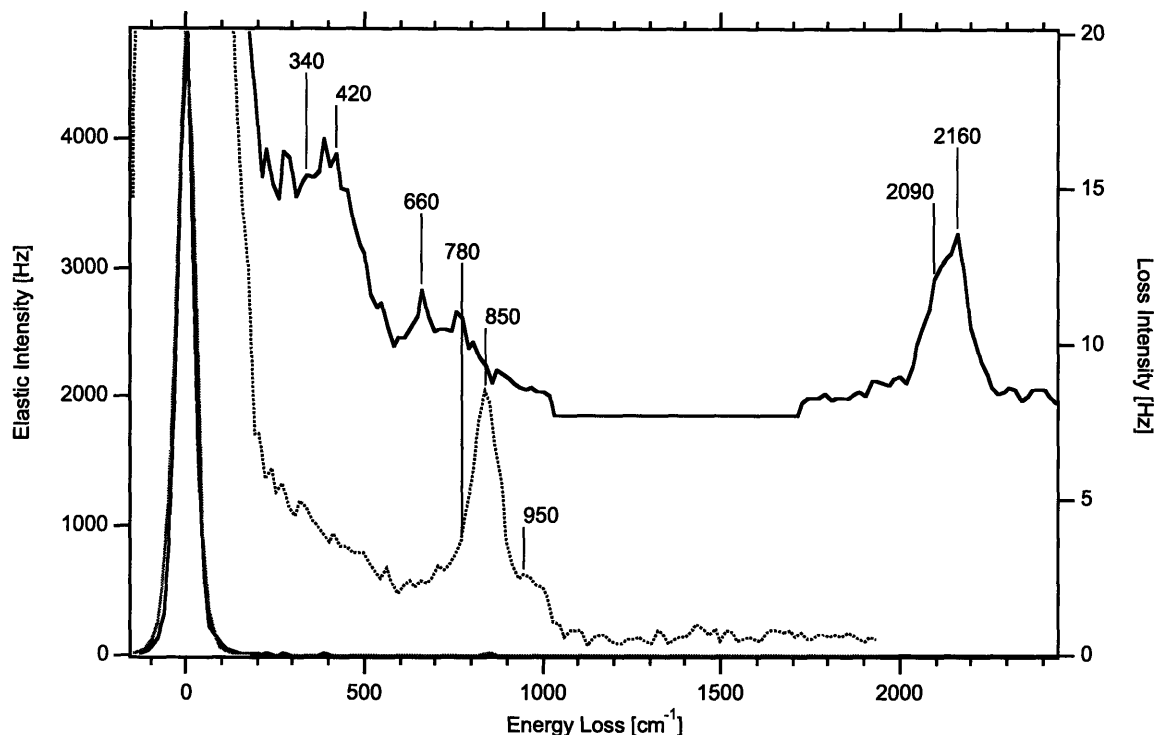


Figure 6. HREELS spectra of 0.19 ML Au/Ni(111) surface alloy saturated with molecularly chemisorbed oxygen (lower, red, dots), and the same after exposure to CO beam for 8 s (upper, blue, solid). Both spectra are measured on-specular and have 55 cm^{-1} FWHM resolution.

B. Spectroscopic Characterization of the Surface after CO Oxidation at 77 K

The surface after the initial exposure to and reaction with the CO beam is characterized spectroscopically using HREELS. Figure 6 presents spectra measured after exposure of an O_2 saturated 0.18 ML Au/Ni(111) surface alloy (bottom trace) to a beam of CO (upper trace). The dominant features of the O_2 saturated surface occur at 790, 850 and 950 cm^{-1} and have been previously assigned to the internal stretching vibrations of three chemisorbed molecular oxygen species.³⁰ The 850 and 950 cm^{-1} features are absent after exposure to the CO beam. The species with an internal stretching frequency of 790 cm^{-1} remains after exposure to CO. Calculation of the average frequency of this species yields a value of $780 \pm 54 \text{ cm}^{-1}$ (error of two standard deviations). Features at 420 and 2090 cm^{-1} are assigned to the Ni-CO and C=O stretching modes of CO adsorbed atop Ni

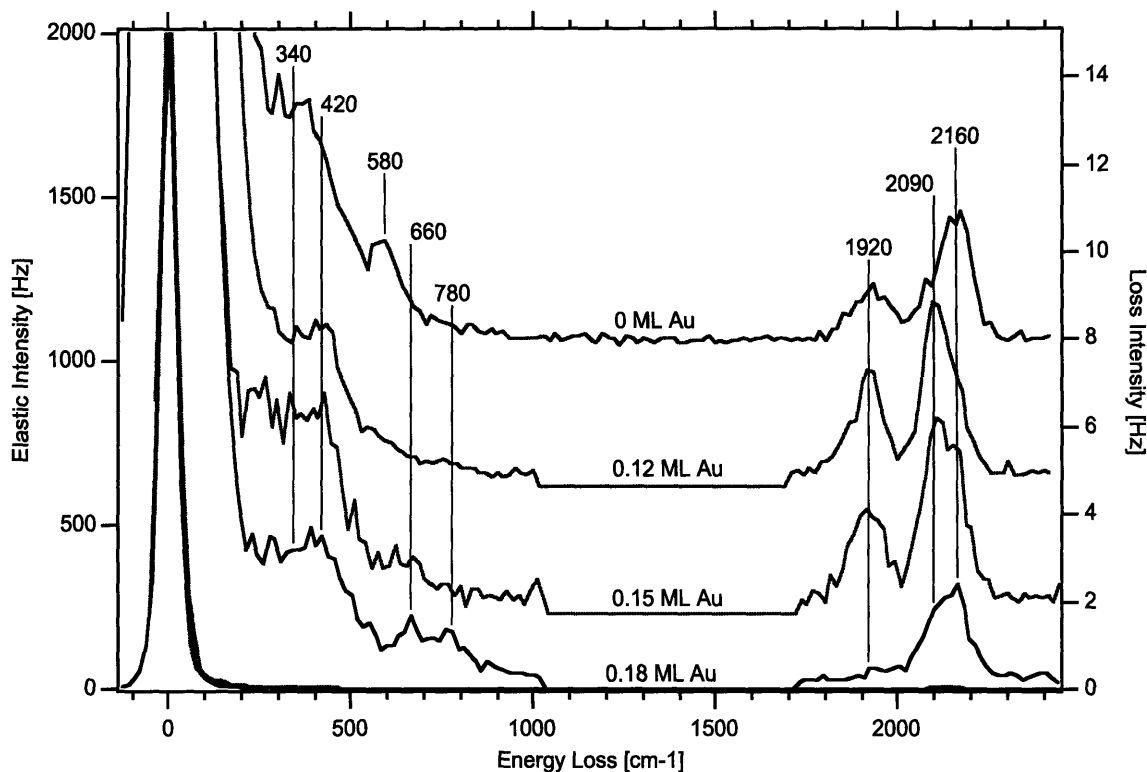


Figure 7. HREELS spectra measured on-specular after exposing Au/Ni(111) surface alloys with saturation coverages of molecularly chemisorbed oxygen to a CO beam for 8 s. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

atoms. The average value of the frequency of this C=O stretching mode is $2090 \pm 28 \text{ cm}^{-1}$. Features at 340 and 2160 cm^{-1} are assigned to the surface-CO and C=O stretching modes of a different species of CO adsorbed at the surface. The average value of this C=O stretching mode is $2160 \pm 34 \text{ cm}^{-1}$. A new feature, with an average frequency of $660 \pm 22 \text{ cm}^{-1}$, is identified as either an O atom remaining after a molecularly chemisorbed species reacts with CO in the beam, or a molecular O_2 species that is complexed with a co-adsorbed CO molecule, resulting in a change in its vibrational frequency. These two possible assignments for the 660 cm^{-1} feature are described in the Discussion Section.

The same spectroscopic characterization experiments are performed for Au coverages in the range 0 to 0.31 ML Au, and are presented in Figures 7 - 9. In contrast to

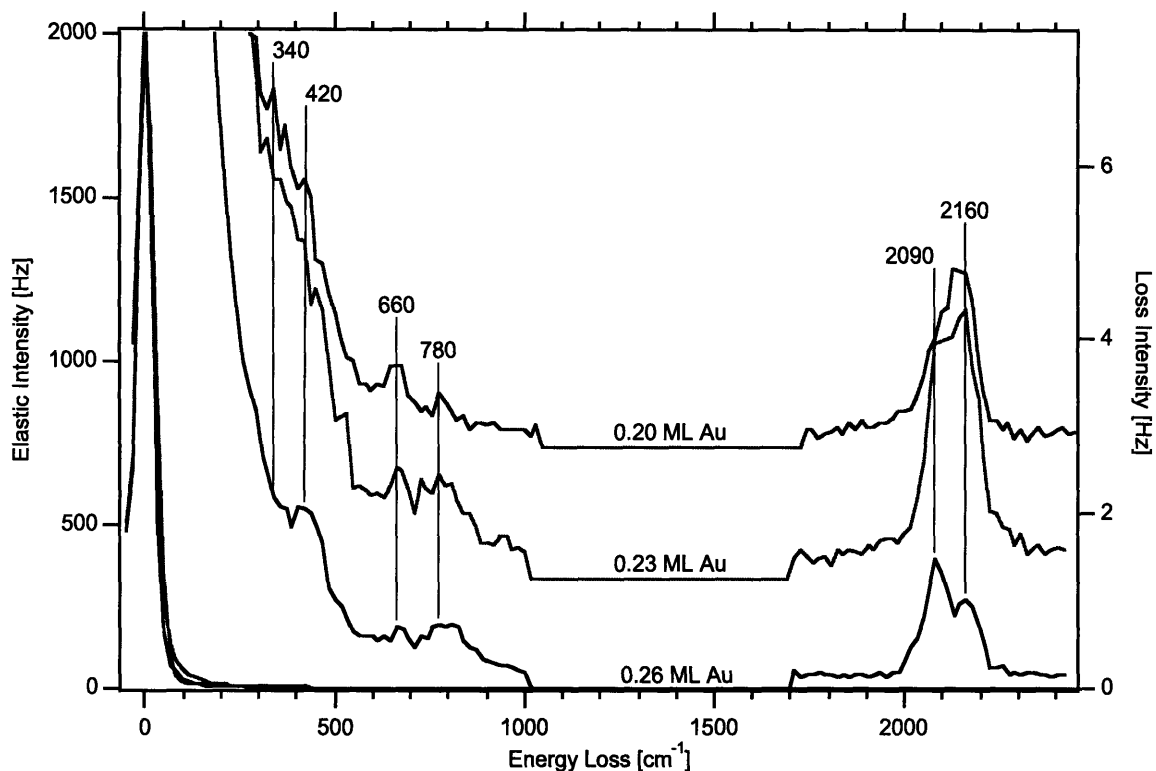


Figure 8. HREELS spectra measured on-specular after exposing Au/Ni(111) surface alloys with saturation coverages of molecularly chemisorbed oxygen to a CO beam for 8 s. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

Figure 6, the spectrum in Figure 7 measured for a surface with 0 ML Au does not exhibit features at 660, 780 and 2090 cm^{-1} , while it does have modes at 580 and 1920 cm^{-1} . The mode at 580 cm^{-1} has been previously assigned to the vibration of atomic oxygen adsorbed in a 3-fold hollow site on the Ni(111) surface.³¹ The feature at 1920 cm^{-1} has been previously assigned to the C=O stretch of a CO molecule adsorbed at bridging sites on a Ni(111) surface.²⁹ The features at 340, 420 and 2160 cm^{-1} and the weak shoulder at 2090 cm^{-1} are assigned as described in the previous paragraph. Most importantly, there is no feature at 780 cm^{-1} attributed to molecularly adsorbed O_2 nor is there any feature at 660 cm^{-1} .

As the Au coverage is increased to 0.12 ML Au, the 580 cm^{-1} feature disappears. As the Au coverage is increased to 0.18 ML, the 660 and 780 cm^{-1} modes appear. Also,

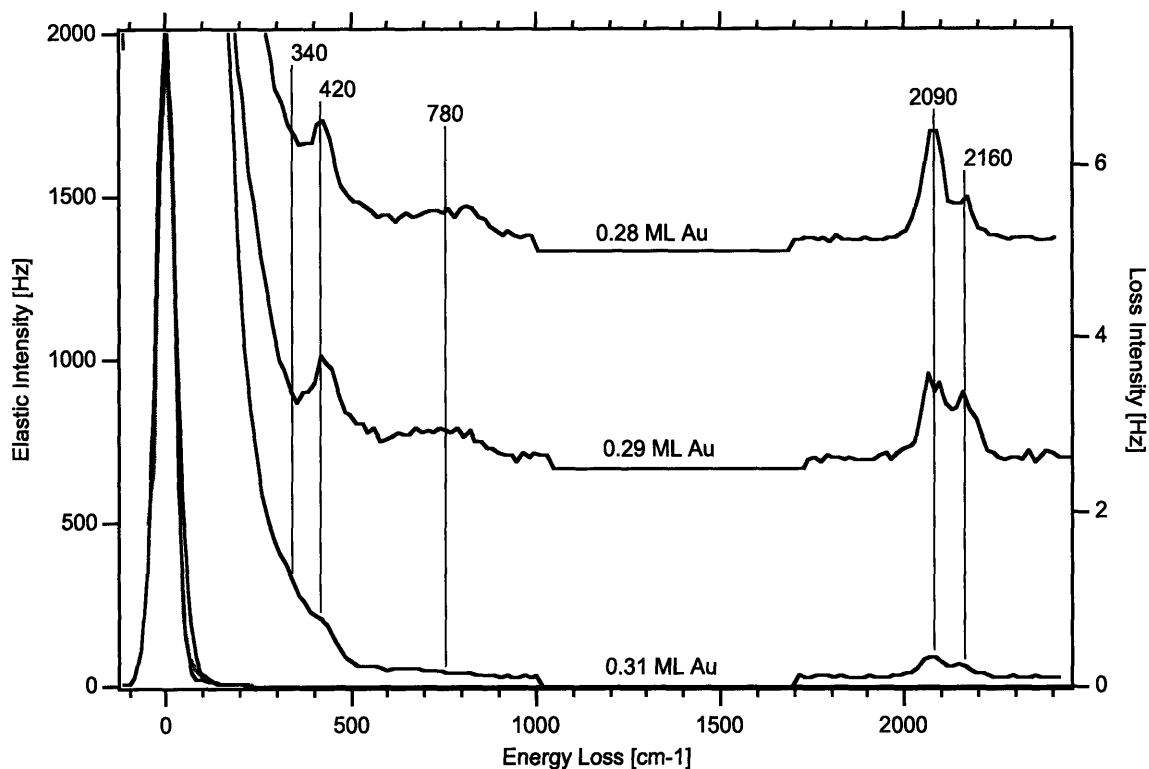


Figure 9. HREELS spectra measured on-specular after exposing Au/Ni(111) surface alloys with saturation coverages of molecularly chemisorbed oxygen to a CO beam for 8 s. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

the 2090 cm^{-1} feature changes from being a weakly intense shoulder on the 2160 cm^{-1} feature to having comparable intensity.

As the Au coverage increases from 0.20 to 0.26 (Figure 8), the intensity of the modes of the oxygen species (660 and 780 cm^{-1}) and the CO species (2090 and 2160 cm^{-1}) decrease. Beginning at 0.28 ML Au (Figure 9), there is no mode at 660 cm^{-1} , and the intensities of the CO stretch modes have decreased to values less than 20% of their maximum values. At 0.31 ML Au , there is no observable intensity at 780 cm^{-1} , and the CO intensities are another factor of 5 smaller than at 0.28 ML Au .

C. CO Oxidation Between 108 and 250 K

Following the observed CO oxidation reaction that occurs between a CO beam and an O_2 saturated layer on the Au/Ni(111) surface alloy at 77 K (Section A), CO is

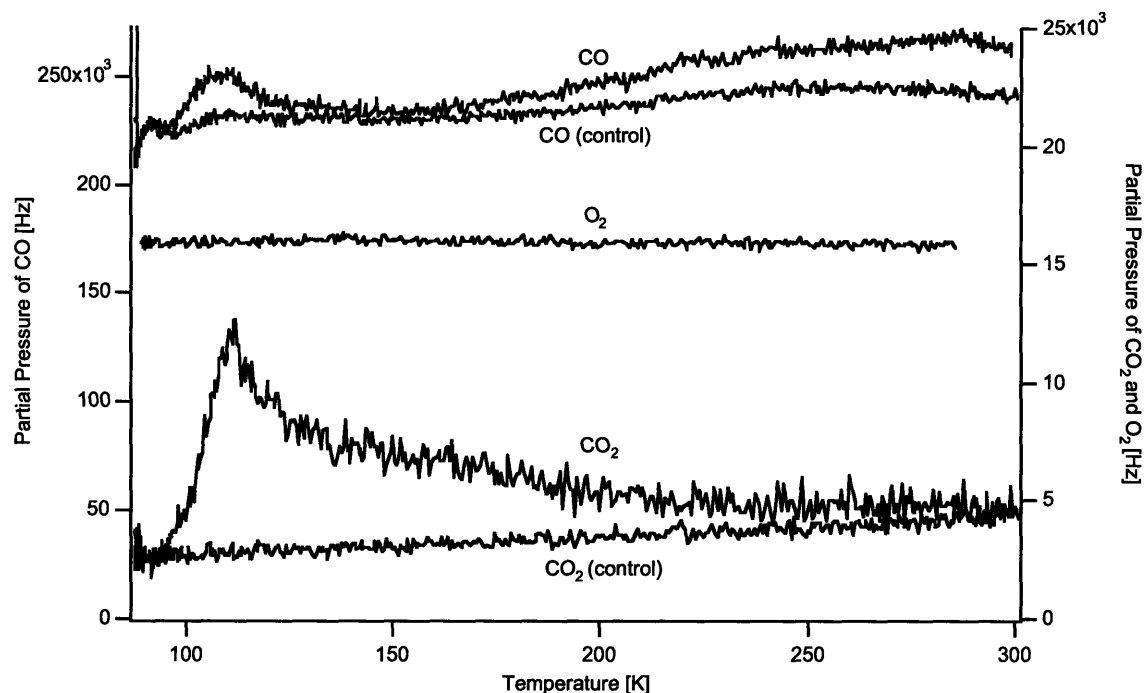


Figure 10. Partial pressure of CO_2 , CO and O_2 vs. temperature during reaction of CO co-adsorbed with molecularly and atomically chemisorbed oxygen on 0.22 ML Au/Ni(111) surface alloy monitored by QMS masses 44, 28 and 32 respectively, while heating at 2 K/s. For O_2 , and upper traces of CO_2 and CO, the surface was prepared by exposure to a 10% O_2/Ar beam for 5 s, followed by exposure to a CO beam for 8 s. In the control experiments (lower traces for CO_2 and CO) the surface preparation was identical to that for upper traces, except that before exposure to the CO beam, the crystal was rotated 180° , causing the beam to strike the sample manipulator and not the crystal surface. See text.

observed by HREELS to be co-adsorbed on the surface with the remaining oxygen (Section B). The reaction of these co-adsorbed CO and oxygen species (atoms and molecules) is investigated by heating the surfaces represented in Figures 7 - 9 at 2 K/s, while monitoring the partial pressures of CO (mass 28), O_2 (mass 32) and CO_2 (mass 44). The results for a 0.22 ML Au/Ni(111) surface alloy are shown in Figure 10. CO_2 production is observed as a sharp peak at 120 K, followed by a broad peak centered at ~ 150 K. No O_2 desorption is observed at any temperature. CO desorption is observed at 120 K and above ~ 220 K.

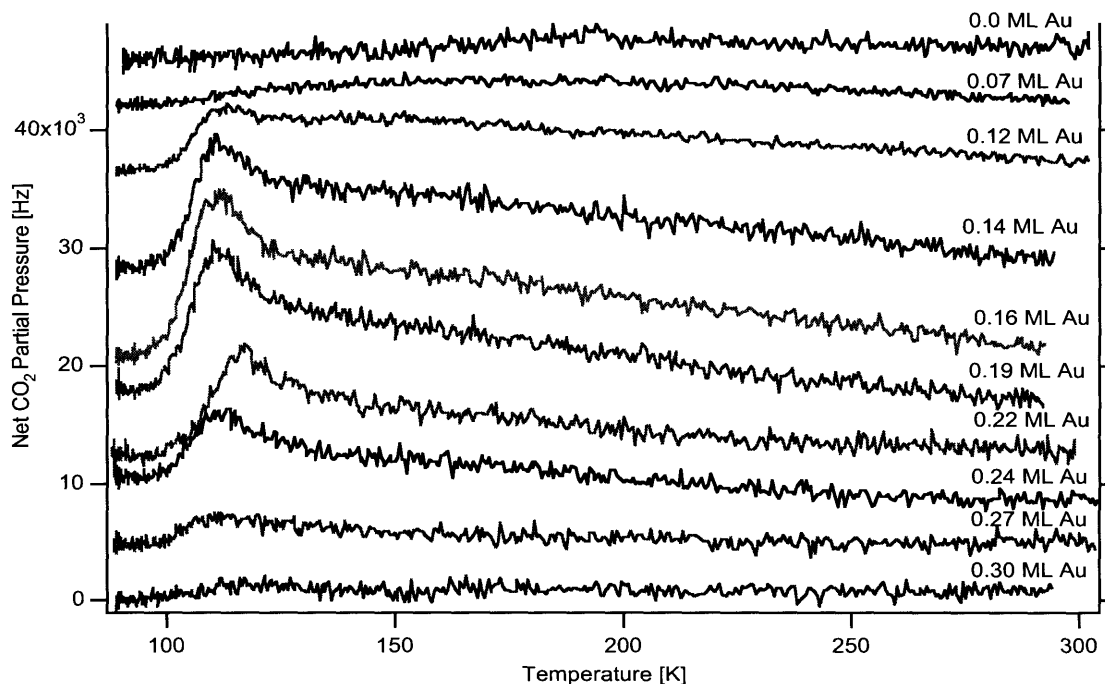


Figure 11. Net partial pressure of CO_2 vs. temperature during reaction of co-adsorbed CO and molecularly and atomically chemisorbed oxygen monitored by QMS (mass 44). The Au/Ni(111) surface alloys are heated at 2 K/s. Each surface was prepared by exposure to a 10% O_2/Ar beam for 5 s, followed by exposure to a CO beam for 8 s. Net partial pressure is obtained by subtracting the signal from a control experiment. The data for 0.0, 0.07 and 0.12 ML Au have been scaled to correct for drift in the QMS sensitivity. See text.

A control experiment is carried out on O_2 saturated Au/Ni(111) surface alloys exposed to CO beams after being rotated 180° , such that the beam impinges on the back of the crystal mount (Figure 10). A small amount of CO desorption is observed at 105 and 250 K, with a similar trend in temperature to that observed in the primary experiment. This desorption results from adsorption of background CO on the crystal holder and crystal face, respectively, that occurs when the beam impinges on the back of the crystal mount. The background pressure during the CO beam exposure is 3×10^{-8} torr, and the exposure duration is 8 s, indicating that an exposure of 0.24 L of background CO occurs. A 0.24 L exposure of CO is sufficient to account for the observed desorption of CO during the control experiment. No CO_2 production is observed in the control

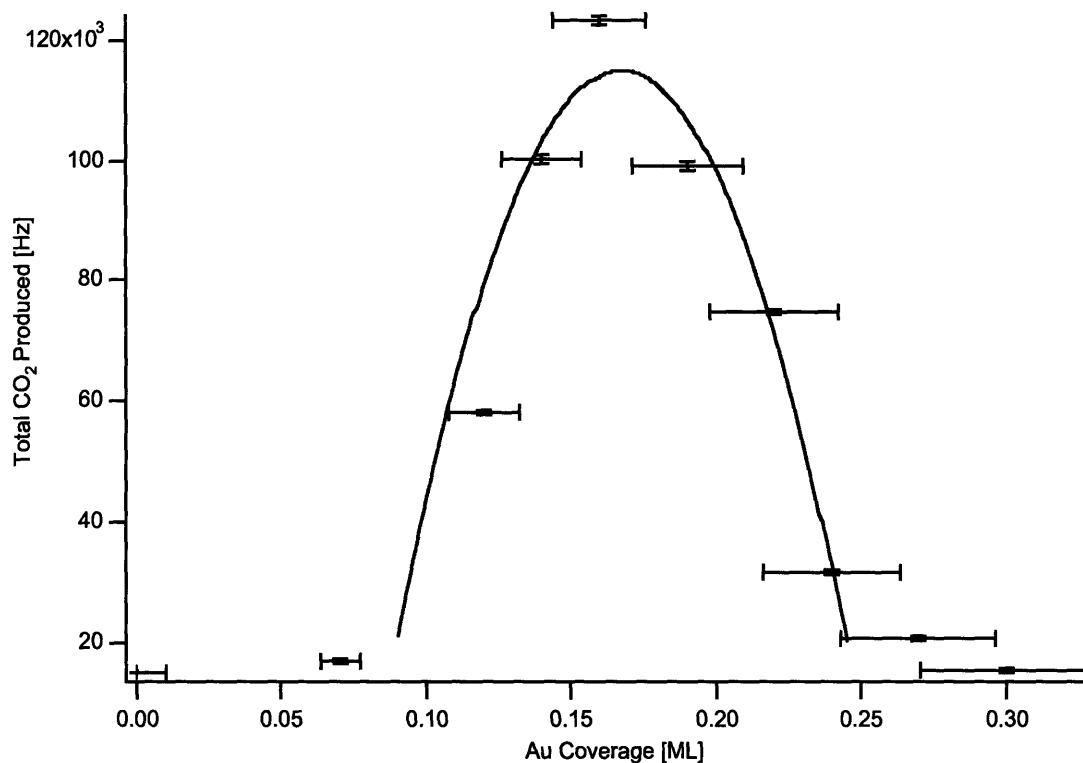


Figure 12. Total CO₂ produced between 108 and 200 K during reaction of co-adsorbed CO and molecularly (possibly some atomically) chemisorbed oxygen. Calculated by integrating the traces in Figure 11.

experiment, although the background level of CO₂ is observed to slope upwards. The increase in the background CO₂ probably results from the reaction of CO and O₂ co-adsorbed on the face and edges of the crystal imaged by the 10% O₂/Ar beam.

The control experiment is subtracted from the primary experiment using a point-by-point subtraction. The subtraction of the control experiment from the primary removes the CO₂ contribution from the presence of background CO₂ and background reactions in the chamber. The results for CO₂ are reported in Figure 11. The same procedure of performing a control experiment, and then subtracting the control experiment from the primary experiment, is carried out for each of the spectra in Figure 11. Furthermore, as described above for the reaction at 77 K, the data collected for surfaces with 0.0, 0.07 and 0.12 ML Au have been scaled, based on the ratio of the

amount of CO₂ produced for a surface with 0.16 ML Au on the different days on which the experiments were conducted. Rapid production of CO₂ is observed at 120 K, followed by slower production at higher temperatures, centered at ~150 K. For all Au coverages, the reaction is complete by 300 K.

Figure 12 presents the total amount of CO₂ produced as a function of Au coverage, calculated by integrating the CO₂ signal in Figure 11 from 105 to 200 K. The maximum total production occurs at 0.16 ± 0.02 ML Au. Increasing the Au coverage above this value results in a decrease in CO₂ production. No CO₂ is produced at 0.30 ML Au coverage. The production of CO₂ that occurs during these experiments follows a trend similar to that shown in Figure 5 for the production of CO₂ during exposure of the surface alloy at 77 K covered with a saturated layer of molecularly adsorbed O₂ to the CO beam.

It is possible that during the reaction of co-adsorbed CO and oxygen, some of the CO desorbs instead of reacting. To investigate this possibility, the net partial pressure of CO in the chamber during the reaction was measured. However, unlike experiments performed for O₂ (mass 32) and CO₂ (mass 44), the CO partial pressure is not directly observable. The QMS signal at mass 28 is not solely the result of CO in the chamber. The electron impact ionizer of the QMS causes CO₂ molecules to “crack” into an oxygen atom and a CO molecule. The ratio of CO produced from cracking, to CO₂ (mass 44) observed by the QMS is known as the cracking ratio of CO₂. The cracking ratio for CO₂ during electron impact ionization under the conditions employed is 0.066.³² In other words, part of the QMS signal at mass 28 is directly attributable to 6.6% of the measured partial pressure of CO₂ (mass 44). In order to determine the partial pressure of CO in the

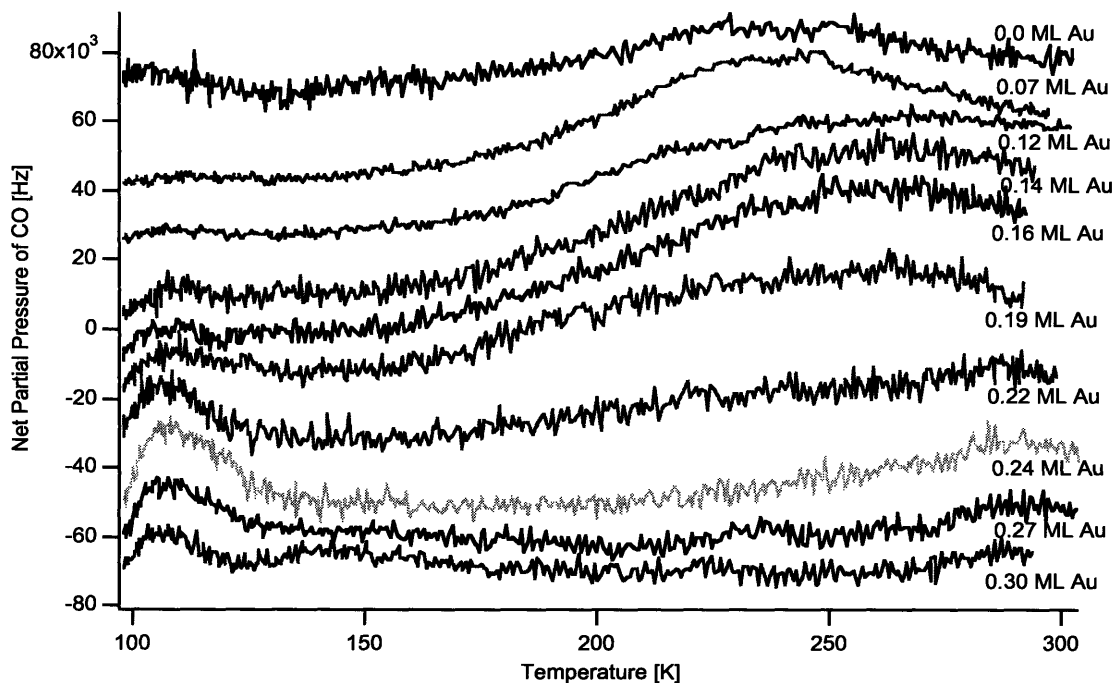


Figure 13. Net partial pressure of CO vs. temperature during reaction of co-adsorbed CO and molecularly and atomically chemisorbed oxygen monitored by QMS (mass 44). The Au/Ni(111) surface alloys are heated at 2 K/s. Each surface was prepared by exposure to a 10% O₂/Ar beam for 5 s, followed by exposure to a CO beam for 8 s. Net partial pressure is obtained by subtracting the signal from a control experiment. See text.

chamber, the contribution to the QMS mass 28 signal from the cracking of CO₂ must be subtracted.

The cracking contribution from CO₂ to the mass 28 signal is subtracted using the following procedure. The signal at mass 44 collected by the QMS, which represents the CO₂ in the chamber during the experiments, is multiplied by the cracking ratio of CO₂ (0.066). This result is then subtracted from the signal at mass 28, to yield the net signal that results solely from the presence of CO in the chamber. Subtraction of the cracking contribution of CO₂ to the mass 28 signal is applied to both the primary and control experiments. Then the same procedure for background subtraction of the control experiment from the primary experiment (used for CO₂ production between 108 and 250 K in Figure 11) is applied to the data for CO. The results are plotted in Figure 13. Rapid

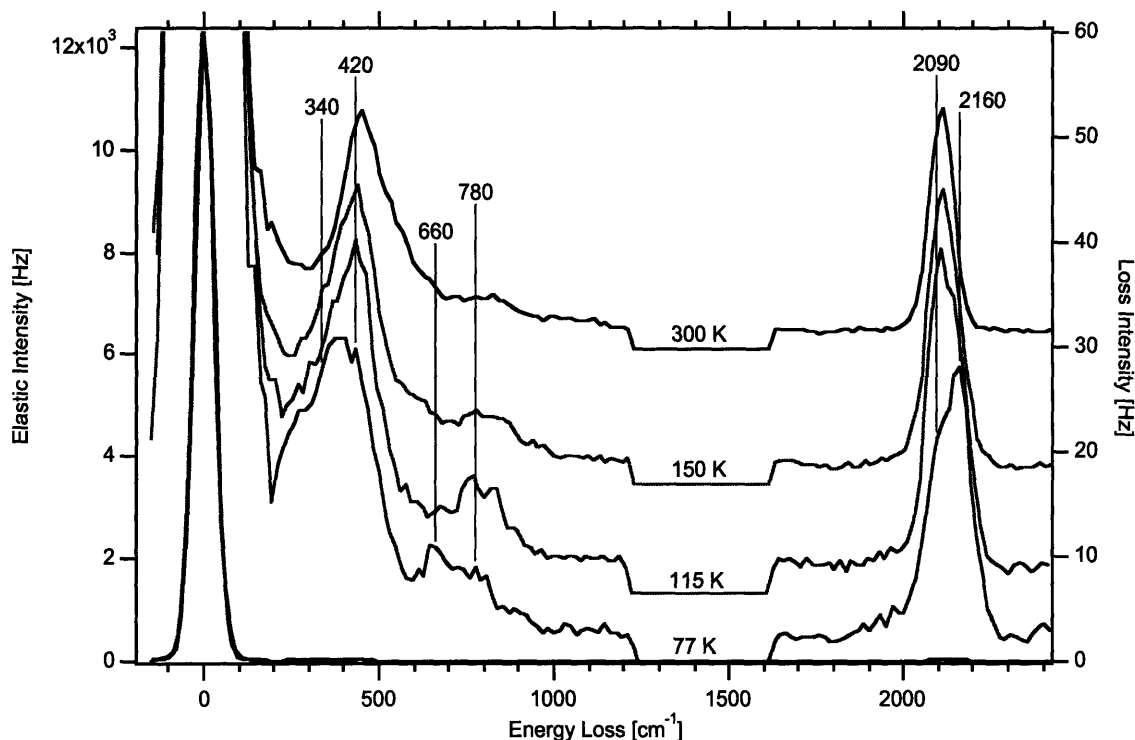


Figure 14. HREELS of 0.20 ML Au/Ni(111) surface alloy with saturated chemisorbed molecular oxygen after exposure to CO beam for 8 s, and ramped to increasingly higher temperatures. All spectra measured on-specular at 77 K. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

desorption of CO occurs at 120 and 260 K. The amount of CO desorption at 120 K is maximized for a Au coverage of 0.24 ML, while the desorption at 260 K is maximized at low Au coverages ($< 0.16 \text{ ML Au}$).

Although the production of CO_2 and desorption of CO that occurs during the reaction of co-adsorbed CO and oxygen species at the Au/Ni(111) surface alloy is measured by these experiments, no information is provided regarding the reactants at the surface. In order to probe the state and nature of the reactants, the vibrational spectrum of the surface was measured at several intermediate temperatures during the reaction of co-adsorbed CO and oxygen species between 77 and 300 K. Specifically, the procedure is as follows. An O_2 saturated surface is prepared by exposing Au/Ni(111) surface alloys at 77 K to a beam of 10% O_2/Ar for 5 s. The surface is then exposed to a beam of CO for

8 s, heated at 2 K/s to the temperature indicated in Figures 14 – 17, then rapidly cooled to 77 K, the temperature at which the spectra in Figures 14 – 17 are recorded. The Au coverages in Figures 14 – 17 are 0.20, 0.23, 0.26 and 0.16 ML Au respectively. For all four figures, the most striking feature is the disappearance of the two features corresponding to adsorbed CO at 340 and 2160 cm^{-1} as the surface is heated to higher temperatures.

For the surface with 0.20 ML Au (Figure 14), the spectrum at 77 K has higher intensity of the 2160 cm^{-1} feature than the 2090 cm^{-1} feature. At 115 K, the intensity of the 2090 cm^{-1} feature is higher than that of the 2160 cm^{-1} feature. By 150 K, the 2160 cm^{-1} feature appears as a shoulder on the 2090 cm^{-1} feature. After heating to 300 K, the 660 and 780 and 2160 cm^{-1} features disappear, but the intensity of the 2090 cm^{-1} feature is the same as at 77 K. The features at 340 and 420 cm^{-1} are not as well resolved at 77 K, but it is clear that only the 420 cm^{-1} feature remains after heating to 300 K. The CO species with a surface-CO stretching mode at 340 cm^{-1} and a C=O stretching mode at 2160 cm^{-1} is therefore identified as the reactive partner for the production of CO_2 between 108 and 250 K, observed in Figure 11 during the reaction of co-adsorbed CO and oxygen.

The feature at 660 cm^{-1} , observed at 77 K in Figure 14, has reduced intensity after heating to 115 K, and is absent after heating to 150 K. In contrast, the feature at 780 cm^{-1} has the same intensity at 77 K and after heating to 115 K. Heating to 150 K reduces the intensity of the 780 cm^{-1} feature, but it is still present. The 780 cm^{-1} feature is absent after the surface is heated to 300 K. These observations suggest that the oxygen species associated with the 660 and 780 cm^{-1} features are the reactive species during CO oxidation between 108 and 250 K. Furthermore, the species associated with the 660 cm^{-1}

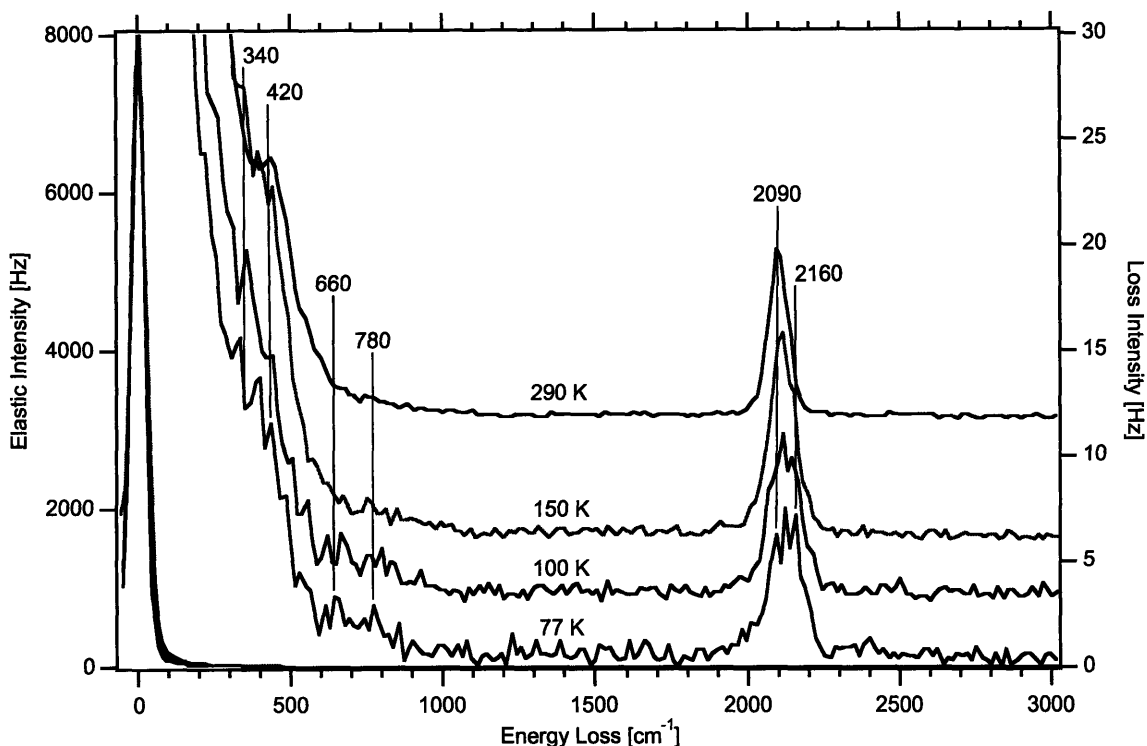


Figure 15. HREELS of 0.23 ML Au/Ni(111) surface alloy with saturated chemisorbed molecular oxygen after exposure to CO beam for 8 s, and ramped to increasingly higher temperatures. All spectra measured on-specular at 77 K. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

vibration undergoes reaction at 115 K, implying that the rapid production of CO_2 observed at 120 K in Figure 11 results from the reaction of this oxygen species with co-adsorbed CO. The slower production of CO_2 , observed in Figure 11 to occur at 150 K, is probably due to reaction of co-adsorbed CO with the peroxo-like species with vibrational frequency of 780 cm^{-1} .

The spectra in Figure 15, for a Au/Ni(111) surface alloy with 0.23 ML Au, exhibit trends similar to those in Figure 14. For these spectra, the 340 and 420 cm^{-1} features appear as shoulders on the elastic peak. However, the changes in the 660, 780, 2090, and 2160 cm^{-1} are observable. Heating the surface from 77 to 100 K does not affect the intensities of these modes. The effects of heating from 100 K to 150 and 290 K are analogous to those observed in Figure 14, namely, the 660, 780 and 2160 cm^{-1} are

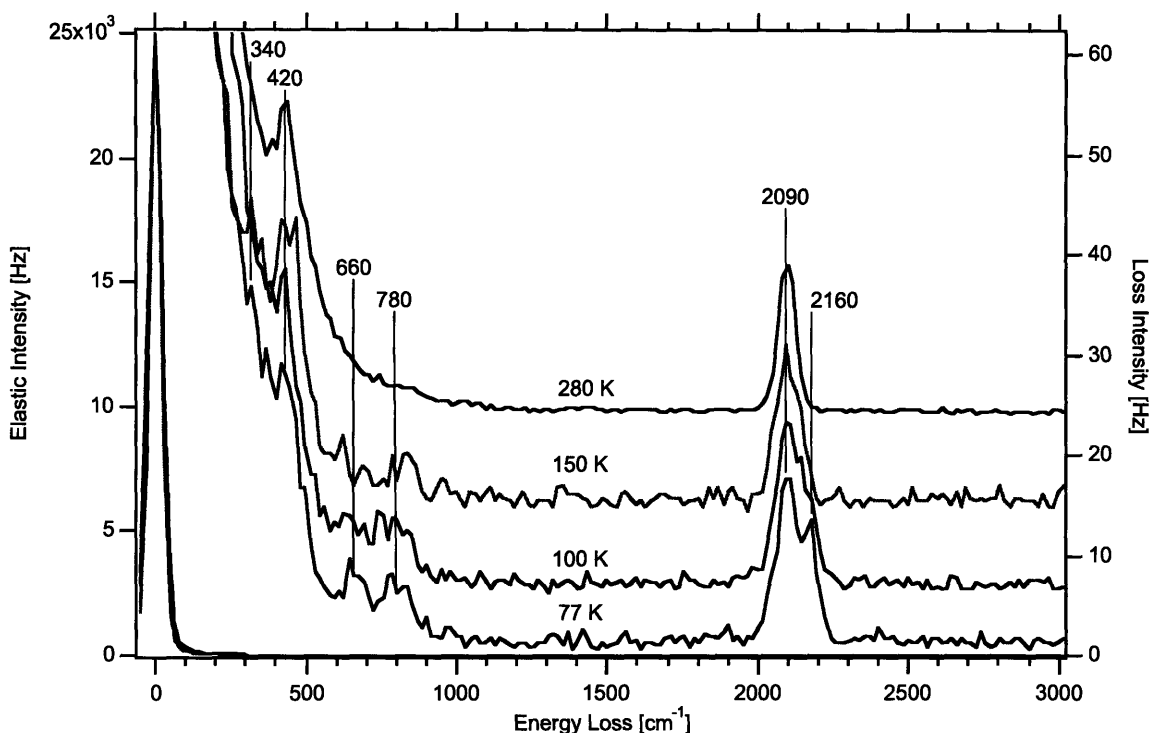


Figure 16. HREELS of 0.26 ML Au/Ni(111) surface alloy with saturated chemisorbed molecular oxygen after exposure to CO beam for 8 s, and ramped to increasingly higher temperatures. All spectra measured on-specular at 77 K. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

removed as the result of the reaction of the oxygen species (660 and 780 cm^{-1}) with co-adsorbed CO (2160 cm^{-1}).

Figure 16 presents spectra for a AuNi(111) surface alloy with 0.26 ML Au. These spectra exhibit trends similar to those in Figure 14. For these spectra, the 340 cm^{-1} feature appears as a shoulder on the elastic peak. However, the changes in the 420 , 660 , 780 , 2090 , and 2160 cm^{-1} features are observable. Heating the surface from 77 to 100 K does not affect the intensities of these modes. The effects of heating from 100 K to 150 and 290 K are analogous to those observed in Figure 14, namely, the 660 , 780 and 2160 cm^{-1} features are removed as the result of the reaction of the oxygen species (660 and 780 cm^{-1}) with co-adsorbed CO (2160 cm^{-1}). In contrast, the unreactive CO with modes at 420 and 2090 cm^{-1} is unaffected by heating to 290 K .

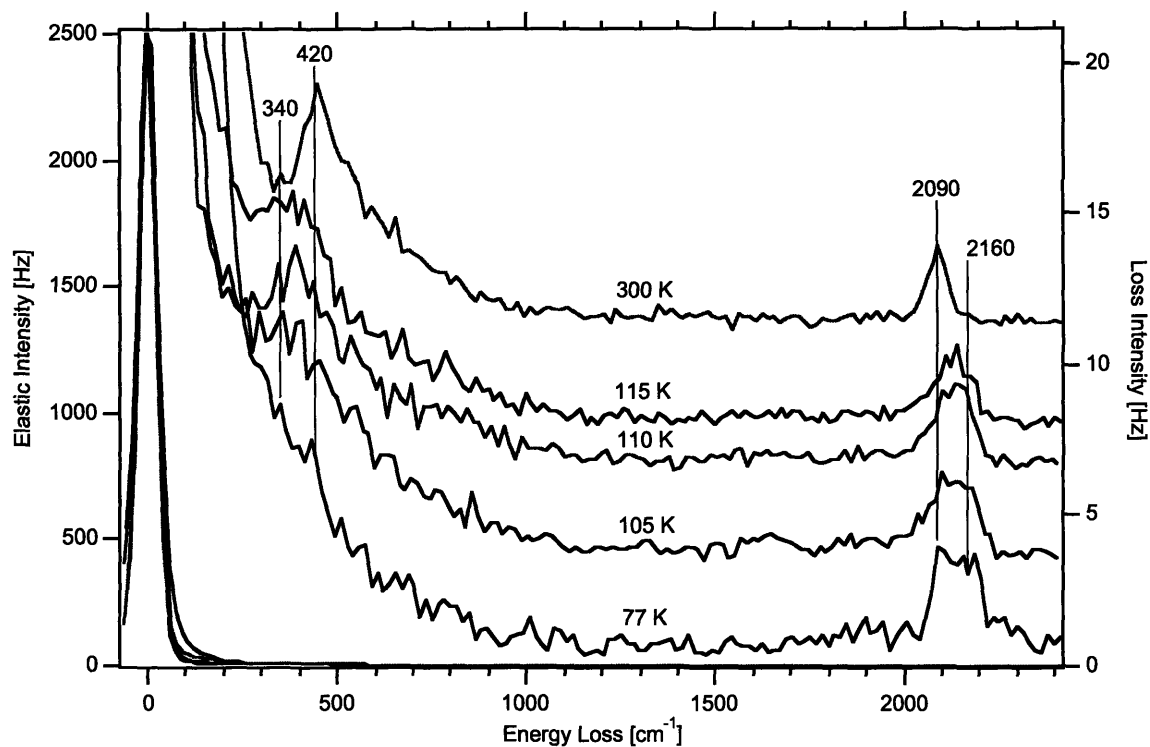


Figure 17. HREELS of 0.16 ML Au/Ni(111) surface alloy with saturated chemisorbed molecular oxygen after exposure to CO beam for 8 s, and ramped to increasingly higher temperatures. All spectra measured on-specular at 77 K. Resolution is $\sim 55 \text{ cm}^{-1}$ FWHM.

The spectra in Figure 17, for a Au/Ni(111) surface alloy with 0.16 ML Au, exhibit trends similar to those in Figure 14. For these spectra, the 660 and 780 cm^{-1} features appear as unresolved intensity between $600 - 850 \text{ cm}^{-1}$. However, the changes in the 340 , 420 , 2090 , and 2160 cm^{-1} are observable. Heating the surface to 105 and 110 K do not affect the intensities of these modes. Although the 340 cm^{-1} mode is resolved from the elastic peak after these heatings, this change results from a decreased elastic tail, and not a physical change at the surface. The effects of heating to 150 and 290 K are analogous to those observed in Figure 14, namely, the 340 and 2160 cm^{-1} corresponding to a species of adsorbed CO are removed as a result of reaction of this CO species to form CO_2 .

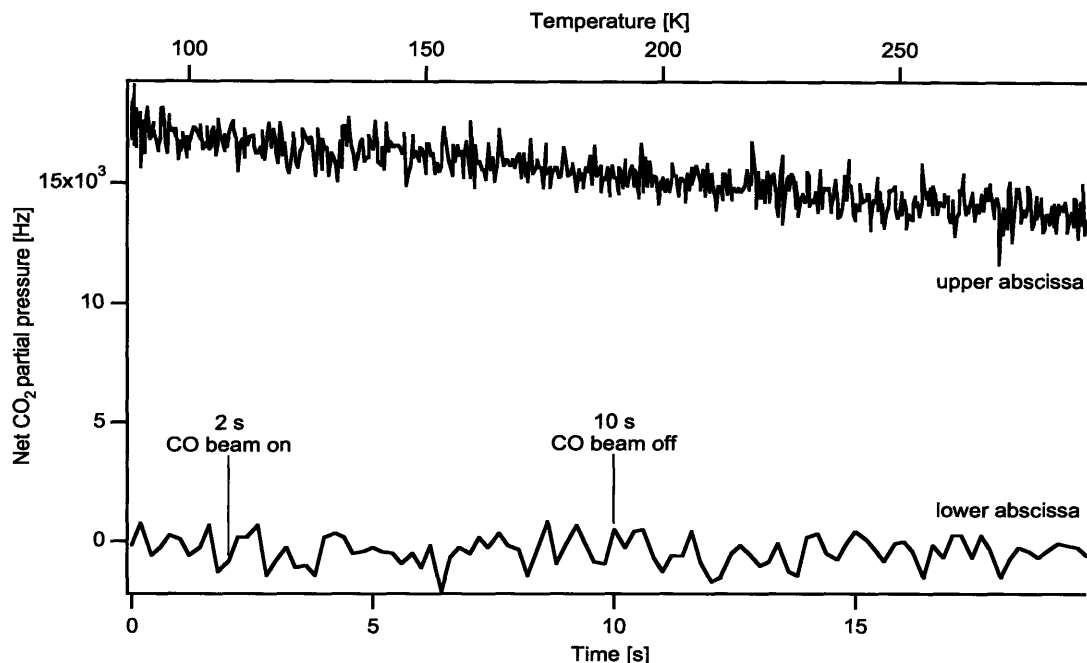


Figure 18. Partial pressure of CO_2 during attempted reaction of CO with atomic oxygen characterized by unresolved Ni-O stretches between $350 - 500 \text{ cm}^{-1}$ on a 0.18 ML Au/Ni(111) surface alloy. Lower trace: CO_2 partial pressure during exposure of surface at 77 K to CO beam. Upper trace: CO_2 partial pressure during subsequent heating of the surface at 2 K/s. Atomic oxygen is prepared prior to CO exposure by heating a saturated layer of molecular O_2 at 2 K/s to 300 K.

D. Absence of CO Oxidation with Adsorbed O Atoms

To test whether O atoms adsorbed on the Au/Ni(111) surface alloy react with CO, the following experiment was performed. A 0.18 ML Au/Ni(111) surface saturated with molecular O_2 is heated to 300 K at 2 K/s, then cooled to rapidly to 77 K. Previous work has demonstrated that heating causes all of the molecularly chemisorbed O_2 to dissociate. The atomically adsorbed O is characterized by unresolved intensity in the vibrational spectrum, in the frequency range $350 - 500 \text{ cm}^{-1}$. The O atom coverage is $\sim 0.9 \text{ ML}$.³⁰ Exposure of this surface at 77 K to the beam of CO results in no gas phase CO_2 production (Figure 18, lower trace). The lack of reaction supports the hypothesis that the 850 and 950 cm^{-1} molecular oxygen adsorbates are the reactive partners in CO oxidation at 77 K. During subsequent heating of this surface (Figure 18, upper trace), no CO_2

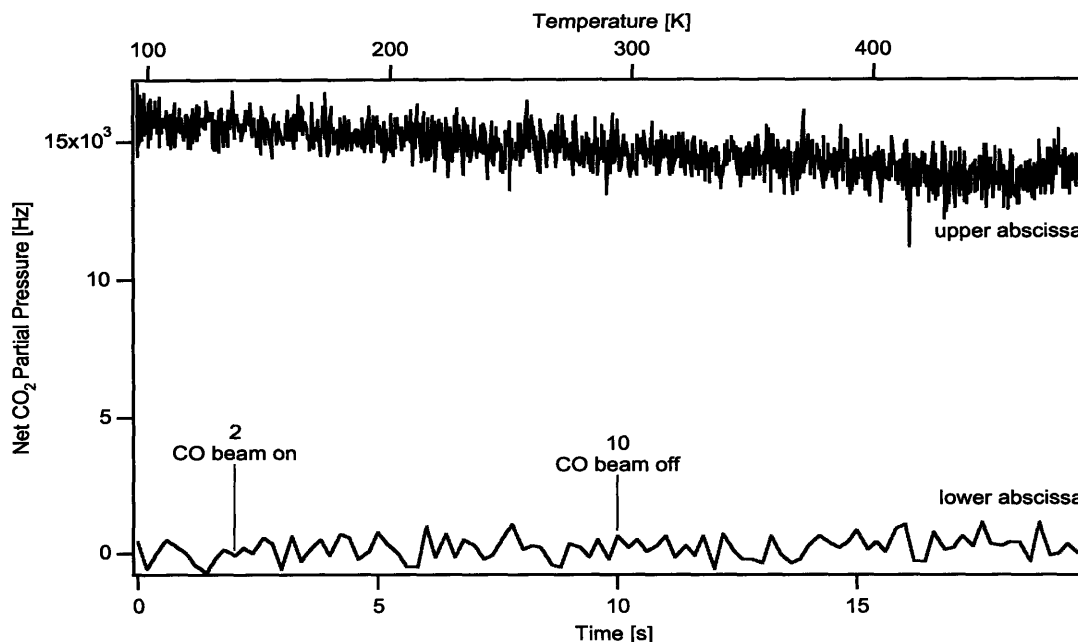


Figure 19. Partial pressure of CO_2 during attempted reaction of CO with atomic oxygen characterized by unresolved Ni-O stretches between $350 - 500 \text{ cm}^{-1}$ on a 0.18 ML Au/Ni(111) surface alloy. Lower trace: partial pressure during exposure of surface at 300 K to CO beam. After exposure to CO beam, surface is rapidly cooled to 77 K. Upper trace: partial pressure during subsequent heating of the surface at 2 K/s. Atomic oxygen is prepared prior to CO exposure by heating a saturated layer of molecular O_2 at 2 K/s to 300 K.

production occurs, demonstrating that the atomically adsorbed O is unreactive between 77 and 300 K.

To test whether the reaction between adsorbed O atoms and CO occurs at elevated temperatures (as is the case for the surfaces of the platinum group metals, described in the Introduction), the reaction is carried out at 300 K. A 0.16 ML Au/Ni(111) surface alloy is prepared with a saturated layer of molecularly chemisorbed O_2 . The surface is then heated at 2 K/s to 300 K, and held at 300 K, causing the O_2 to dissociate into ~ 0.9 ML of O atoms, characterized by unresolved vibrational modes between $350 - 500 \text{ cm}^{-1}$. Then, the surface held at 300 K is exposed to a beam of CO for 8 s. The results are shown in Figure 19 (lower trace). No CO_2 production is observed during the exposure, after which the crystal is rapidly cooled to 77 K. The partial pressure of CO_2 is then monitored while

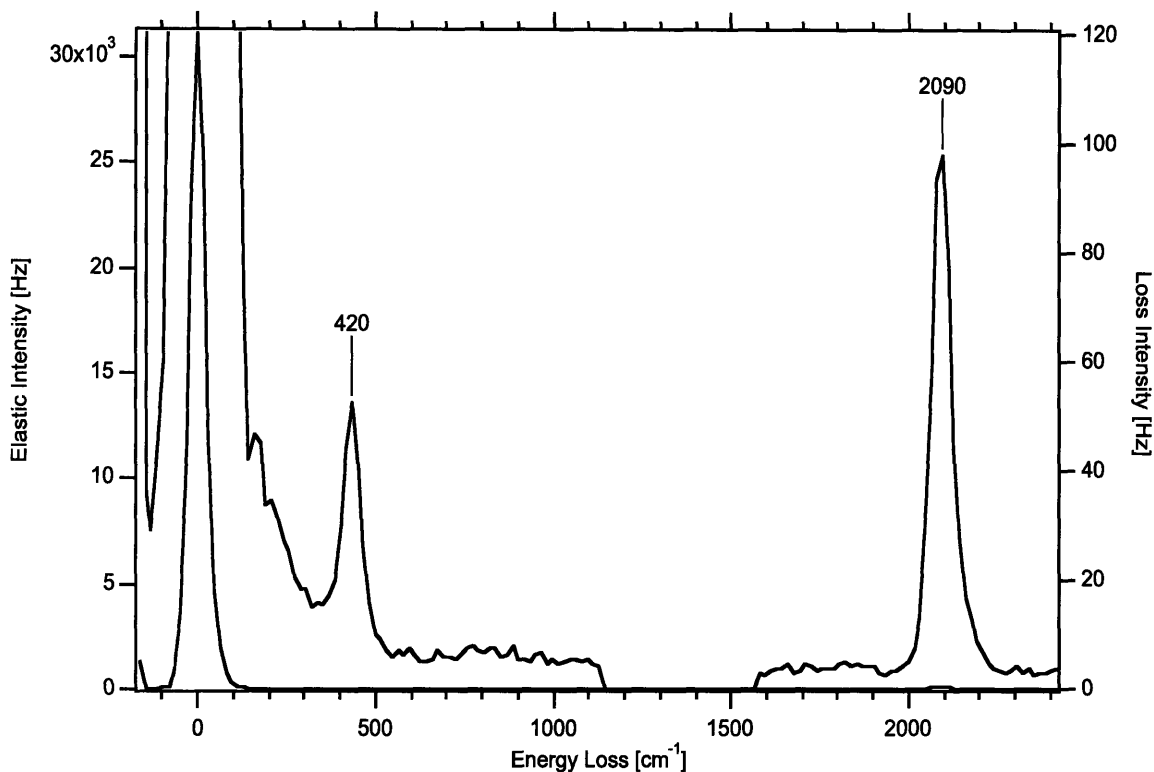


Figure 20. HREELS spectrum measured on-specular after exposing a 0.22 ML Au/Ni(111) surface alloy at 77 K to a CO beam for 8 s. Resolution is 55 cm⁻¹ FWHM.

the surface is heated at 2 K/s. No CO₂ production is observed, as demonstrated by the results presented in the upper trace of Figure 19.

E. Identification of Reactive Species of Adsorbed CO

To determine which (if any) of the species of CO that adsorb on the surface during the reaction at 77 K (characterized by HREELS in Figures 7 –9) adsorbs on a clean Au/Ni(111) surface alloy, HREELS is measured after exposing a 0.22 ML Au/Ni(111) surface alloy to a CO beam. The resulting spectrum is shown in Figure 20. The only modes present in this spectrum are at 420 and 2090 cm⁻¹, indicating that in the absence of oxygen, there is no species present with modes at 340 and 2160 cm⁻¹.

Based on the HREELS measured during the CO oxidation reaction that occurs between 108 and 250 K, a species of CO with vibrational mode frequencies of 340 and

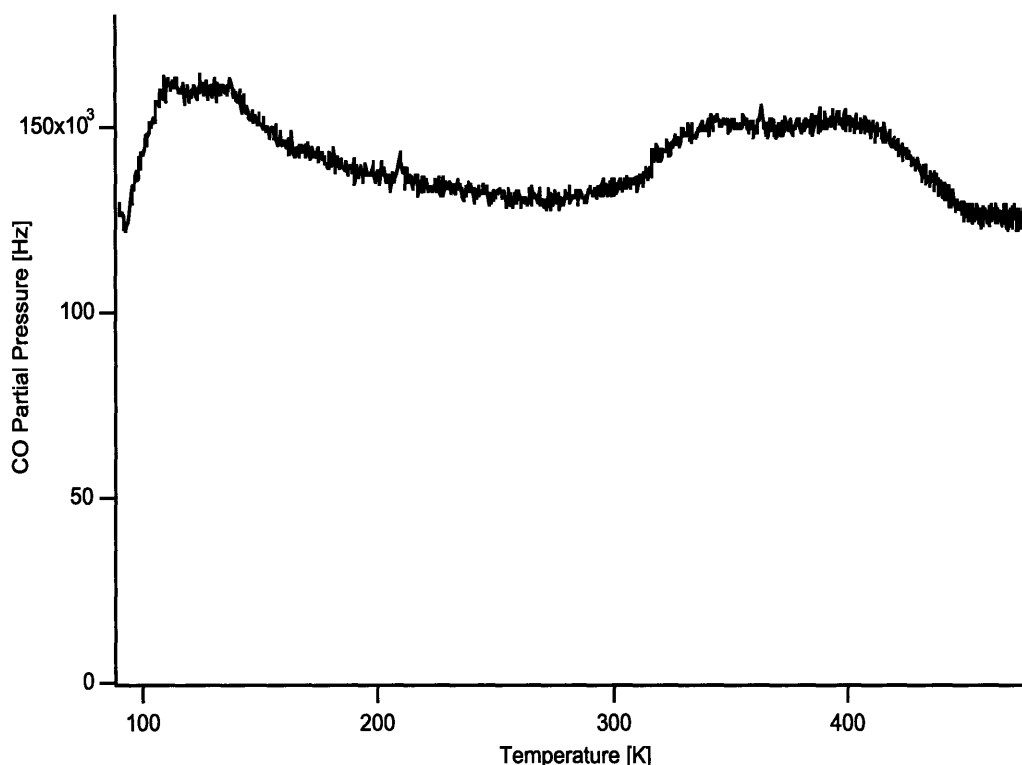


Figure 21. Partial pressure of CO (mass 28) after 8 s exposure of CO beam to a 0.19 ML Au/Ni(111) covered with 0.9 ML atomic oxygen – see text. Surface is heated at 2 K/s.

2160 cm^{-1} has been proposed as the reactant with oxygen during the CO oxidation reaction. HREELS in Figures 14 – 17 have demonstrated that after the reaction is complete at 300 K, this species is no longer present at the surface, suggesting that this species reacts and/or desorbs below 300 K. In order to identify this species of CO, a Au/Ni(111) surface alloy with 0.19 ML Au at 77 K is exposed to a 10% O_2/Ar beam for 5 s, preparing a saturated layer of chemisorbed O_2 at the surface. The surface is then heated at 2 K/s to 300 K, and cooled rapidly to 77 K, causing all of the molecularly chemisorbed O_2 to dissociate. About 0.9 ML of O atoms are adsorbed at the surface as a result of the dissociation of the molecular oxygen adsorbate. The surface is then exposed to a CO beam for 8 s, after which it is heated at 2 K/s to 300 K, while the partial pressure of CO in the chamber is monitored (Figure 21). In contrast with previous results for CO

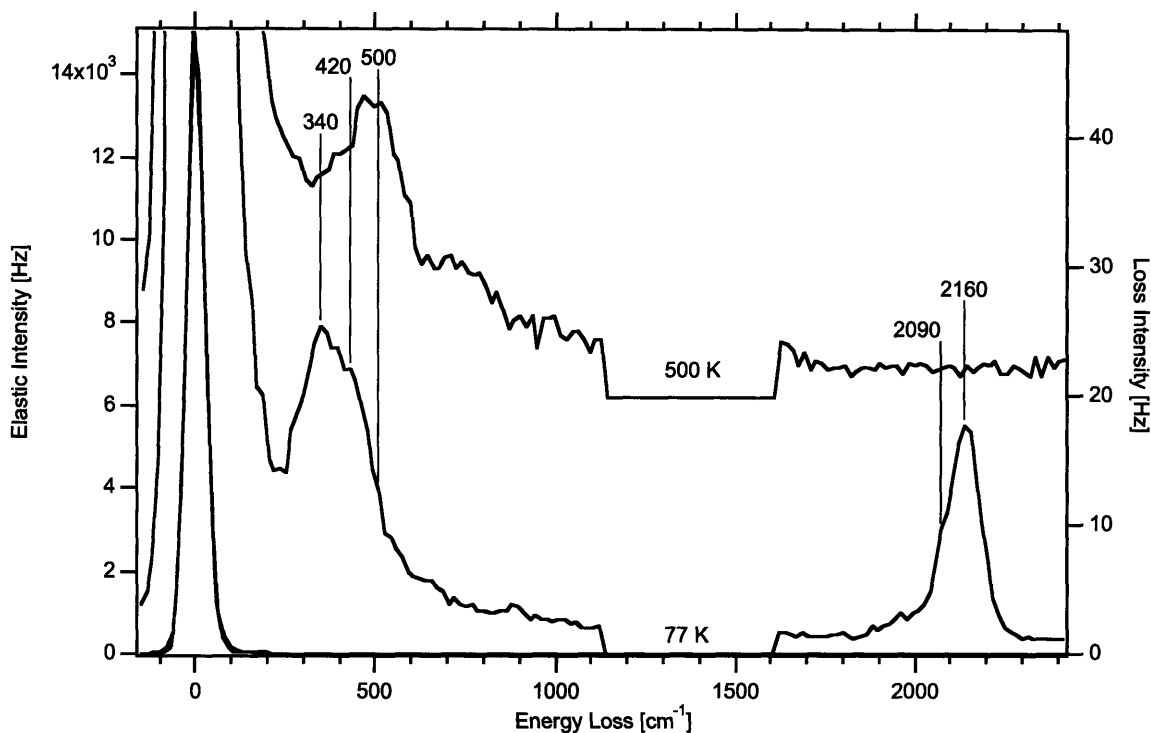


Figure 22. HREELS measured on-specular after exposing a 0.19 ML Au/Ni(111) surface alloy at 77 K prepared with atomic oxygen (bottom) to a CO beam for 8 s. Surface is subsequently heated to 500 K at 2 K/s, then rapidly cooled to 77 K, the temperature at which the upper trace is recorded. Resolution is 55 cm^{-1} FWHM.

on Au/Ni(111) surface alloys,³³ there is low temperature CO desorption between 108 and 140 K. The desorption of the CO species corresponding to this feature is complete by 225 K. The higher temperature desorption (beginning around 300 K) has been observed previously by Holmblad et. al.³³ The low temperature desorption between 108 – 225 K is similar to that observed to occur during the CO oxidation reaction. This similarity suggests that the CO, characterized by the HREELS in Figures 14 – 17, is the same species as is observed to undergo reaction with molecular O_2 adsorbates between 108 and 250 K (Figure 11).

Vibrational spectra, measured before and after the experiment presented in Figure 21, are presented in Figure 22. At 77 K, features at 340, 420, 2090 and 2160 are assigned to CO observed previously on the surface after the CO oxidation reaction at 77 K

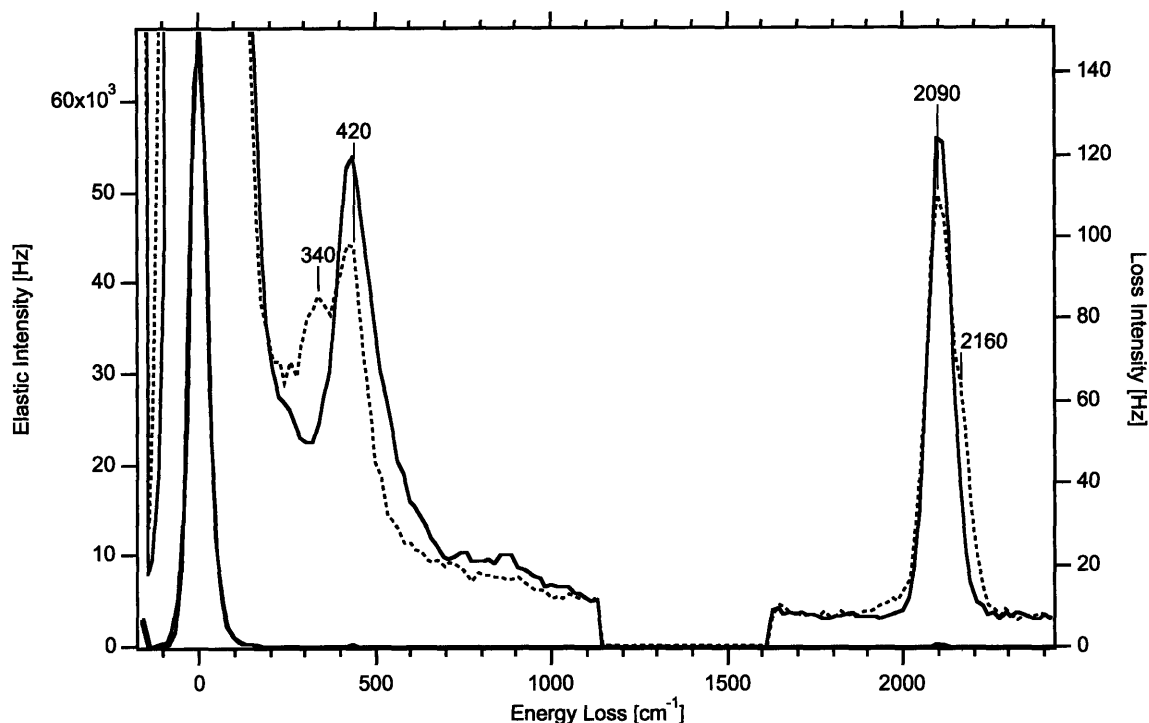


Figure 23. HREELS measured on-specular after exposing a 0.22 ML Au/Ni(111) surface alloy at 77 K prepared with atomic oxygen (dashed, red) to a CO beam for 8 s. Surface is subsequently heated to 225 K at 2 K/s, then rapidly cooled to 77 K, the temperature at which the solid trace is recorded. Resolution is 55 cm^{-1} FWHM.

(Figures 6 – 9). A shoulder at 500 cm^{-1} is also observed, and is assigned to O atoms adsorbed in 3-fold hollows sites. This species has been previously observed on the Au/Ni(111) surface alloy at low Au coverages and after heating the molecular O_2 saturated Au/Ni(111) surface alloy to 300 K (Chapter 2). After heating to 500 K, the features at 340, 420, 2090 and 2160 cm^{-1} are gone, and only the unresolved features at $350 - 500 \text{ cm}^{-1}$, attributed to atomic oxygen, remains. This result demonstrates that both species of CO, previously observed on the Au/Ni(111) surface alloy after the reaction at 77 K, are also present on the Au/Ni(111) surface alloy prepared with atomic O.

Final identification of the reactive species of CO during the CO oxidation between 108 and 250 K is obtained with HREELS. A Au/Ni(111) surface alloy with 0.22 ML Au is prepared with a saturated layer of chemisorbed molecular O_2 , heated at 2 K/s to

300 K then rapidly cooled to 77 K, in order to prepare a surface with ~ 0.9 ML chemisorbed oxygen atoms. The surface is then exposed to the beam of CO for 8 s. HREELS of this surface is presented in Figure 23 (dashed trace). There are 4 modes in this spectrum (340, 2160 and 420, 2090 cm^{-1}), previously assigned to two different species of CO adsorbed at the surface. In contrast to this result, the spectrum in Figure 20, measured in the absence of O, has only two features at 420 and 2090 cm^{-1} . Therefore, the reactive CO species characterized by vibrational frequencies at 340 and 2160 cm^{-1} is identified as only forming on an O atom pre-covered Au/Ni(111) surface alloy.

This surface, represented by the spectrum at 77 K in Figure 23, is then heated at 2 K/s to 225 K, cooled rapidly to 77 K, and HREELS is collected. The results, also shown in Figure 23 (solid trace), indicate that heating the surface to 225 K has removed the CO species corresponding to the 340 and 2160 cm^{-1} modes, and indicates that the desorption of CO observed during CO oxidation between 108 – 250 K is the desorption of this CO species.

IV. DISCUSSION

The catalytic oxidation of CO by molecularly chemisorbed oxygen at the Au/Ni(111) surface alloy occurs in two different temperature regimes. One temperature regime in which the reaction occurs is at 77 K (and less efficiently at 70 K) when Au/Ni(111) surface alloys, saturated with molecularly chemisorbed oxygen, are exposed to a CO beam. The resulting CO_2 production, monitored as partial pressure at $m/e = 44$, is shown in Figures 1 – 4.

The second temperature regime is between 108 – 250 K. After the initial production of CO_2 during exposure to a CO beam at 77 K, subsequent heating of the

surface at 2 K/s causes CO₂ production to occur with a rapid rate at 120 K and a slower rate at 150 K, as shown in Figures 10 and 11.

The discussion section is divided into two sections, one for the 77 K temperature regime and the other for temperatures above 108 K.

A. CO Oxidation at 70 and 77 K

As described in the first paragraph of the discussion, the initial production of CO₂ is observed at 70 and 77 K when the Au/Ni(111) surface alloy with a saturated layer of molecular O₂ is exposed to the CO beam. Control experiments, in which the saturated layer of O₂ is prepared, and the crystal is rotated 180° such that the CO beam strikes the back of the sample manipulator, demonstrate that the reaction occurs between CO in the molecular beam and oxygen at the surface. Vibrational spectra measured after the reaction indicate features with frequencies of 850 and 950 cm⁻¹ have been removed by the reaction with CO (Figures 6 – 9). These frequencies correspond to molecularly chemisorbed oxygen, indicating that these species are the reactive species of oxygen. The feature previously observed with frequency 790 cm⁻¹ is preserved, but is observed to have an average frequency of 780 ± 56 cm⁻¹.

Atomic oxygen is present on the Au/Ni(111) surface alloy at 77 K for Au coverages less than ~0.15 ML (c.f. Chapter 2), however it is unreactive for CO oxidation. When a CO beam is exposed to ~0.9 ML atomic O adsorbed on a Au/Ni(111) surface alloy at 77 K, there is no CO₂ production (Figure 18). The same result is obtained when the surface is at 300 K (Figure 19), confirming that during the CO beam exposure, molecular oxygen is the sole reactant for CO oxidation.

When catalytic CO oxidation is carried out on a Au/Ni(111) surface at 70 K (Figure 4), the resulting CO₂ production is 15% of the amount produced at 77 K. This

indicates that the surface temperature has a significant effect on the rate of reaction, suggesting that the mechanism of this reaction is the Langmuir-Hinshelwood. This mechanism, in which the reactants adsorb and equilibrate with the surface prior to reaction, is observed for CO oxidation on platinum group metals. However, the observation that the reaction on the Au/Ni(111) surface alloy proceeds rapidly at 77 K is in stark contrast to the reaction on the platinum group metals, which becomes appreciable at 400 K.

The shapes of the individual curves for the initial production of CO₂ (Figures 1 – 4) as a function of beam exposure time are monotonically decreasing, and are suggestive of a first- or pseudo-first order reaction mechanism. However, they are not well fit by exponential decays. The non-exponential decay is indicative that the mechanism of the reaction is more complicated than a simple first- or pseudo-first order system.

The maximum value of CO₂ produced (Figure 5) occurs at 0.19 ± 0.02 ML Au, which is the same (within experimental error) as the maximum in O₂ coverage on Au/Ni(111) surface alloys, which occurs at 0.18 ± 0.02 ML, as determined by the maximum intensity of the 850 cm⁻¹ O₂ vibration.³⁰ Additionally, the two curves have roughly the same functional form, specifically that both O₂ coverage and the CO₂ production decrease approximately quadratically away from their shared maximum value, with both decreasing to zero at 0.07 and 0.30 ML Au. This correlation supports the evidence from spectroscopic and control experiments that indicate molecularly chemisorbed oxygen species are responsible for CO oxidation at 70 and 77 K.

The adsorbates that are present at the Au/Ni(111) surface alloy immediately after the reaction between a saturated layer of molecular O₂ at 77 K and a CO beam

have been characterized using vibrational spectroscopy. Vibrational frequencies of 340, 420, 2090 and 2160 cm^{-1} have been assigned to two different species of adsorbed CO. One species, with modes at 420 and 2090 cm^{-1} (corresponding to the molecule-surface and C=O stretching modes respectively) has been assigned previously to CO adsorbed atop Ni atoms.^{29,34,35} However, CO adsorbed on oxide-supported metallic Au nanoparticles has been observed to have a frequency of 2100 cm^{-1} .³⁶ Based on the 55 cm^{-1} resolution of our spectrometer, it is not possible to unambiguously determine, based on the frequency, which type of metal atom these CO molecules are adsorbed atop. However, if the species of CO with a C=O stretch frequency of 2090 cm^{-1} is bound to Au atoms, then the frequency is lower than has been previously observed for CO bound atop metallic Au atoms of supported Au nanoparticles, implying that the CO bound atop Au atoms in the Au/Ni(111) surface alloy has a stronger interaction, and hence better energetic overlap between the Au d-band and CO LUMO. This observation is directly contradicted by the observation that Au atoms in the Au/Ni(111) surface alloy have a d-band that is lower in energy than metallic Au, and hence should have worse energetic overlap with the LUMO of CO. In contrast, if the CO molecule with C=O stretching frequency 2090 cm^{-1} is bound atop Ni atoms, then the interaction of this species has been weakened with respect to the Ni(111) surface. This hypothesis is consistent with the observation that the Ni d-band of the Au/Ni(111) surface alloy is lower in energy than the Ni d-band of Ni(111). Therefore, it is proposed that the CO species with C=O stretching frequency of 2090 cm^{-1} is bound atop Ni atoms of the Au/Ni(111) surface alloy.

The other CO species is observed to have modes with frequencies of 340 and 2160 cm^{-1} corresponding to the surface-CO and C=O stretches, respectively. In

contrast to the first species of CO, this species has an internal bond stretching frequency that is higher than that of gas phase CO (2145 cm^{-1}). Adsorbed CO molecules with frequencies higher than the gas phase value have been observed previously for CO adsorbed atop metal ions, typically at oxide surfaces. For the case of CO adsorbed atop Ni^{2+} ions at NiO(111), a frequency of 2165 cm^{-1} has been observed,³⁷ and for CO adsorption atop a Au ion a frequency of 2176 cm^{-1} has been measured.³⁶ Since the Au/Ni(111) surface alloy is not an oxide surface, it is proposed that the CO species with an internal bond frequency of 2160 cm^{-1} is bound atop a metal atom with reduced local electron density. In the language of formal charges, reduced local electron density corresponds to a partial positive charge at the metal atom. It is not clear whether the CO is bound to a Ni atom or a Au atom, but since the Ni d-band in the Au/Ni(111) surface alloy is closer to the Fermi level than the Au d-bands, Ni atoms are more reactive than Au atoms, and this CO species is probably bound to a Ni atom.

The frequency of 2160 cm^{-1} for the C=O stretch is interesting because it is higher in frequency the C=O stretch observed for gas phase CO molecules. The formation of the molecule-surface bond that occurs during CO adsorption occurs concomitantly with weakening of the internal bond, resulting in a lower frequency of the C=O stretch. However, a blue shift of the internal CO bond has been observed previously and extensively for CO adsorbed on oxide surfaces. This blue shift can be explained most simply by positing that CO adsorption occurs when electronic charge on the carbon end of the molecule is donated to a positively charged metal atom at the surface. In the language of molecular orbital (MO) theory, the 5σ orbital of CO (an anti-bonding orbital localized on the C end of the molecule) hybridizes with a band

from the surface. This hybridization reduces the electron occupancy of the 5σ anti-bonding orbital, increasing the bond order of the CO adsorbate.³⁸ In addition, the partial transfer of charge from the C atom to the metal ion increases the slightly positive charge of the C end of the molecule, and hence increases the coulombic attraction to the negatively charged oxygen atom of the molecule, hence increasing the force constant for the bond and the observed frequency.³⁸ In contrast to adsorption at a metal ion, when adsorption occurs at a neutral metal atom additional charge transfer from the metal d-band into the π^* LUMO counters the bond order increase from the 5σ – metal d-band interaction described above, with the net result being an overall weakening of the bond and a lower C=O stretch frequency.

Although there has been no direct observation of partially charged metal ions at the Au/Ni(111) surface alloys used in these experiments, their presence can be inferred by the requirement that the surface be exposed to oxygen for the formation of the 2160 cm^{-1} species of CO. This is demonstrated by the vibrational spectra presented in Figures 20 and 22, that show that the 2160 cm^{-1} species of CO forms on a Au/Ni(111) alloy surface with atomic oxygen, and not in the absence of oxygen.

An important mechanistic question that remains is the origin of the 660 cm^{-1} feature that appears after exposure of the O_2 saturated Au/Ni(111) surface alloy to the CO beam (Figures 5-8). Although this frequency could be attributed to a bending mode of adsorbed CO_2 , the lack of modes at 1390 and 2350 cm^{-1} , corresponding to the symmetric and asymmetric stretching modes, rules out this assignment. Another possible species that could be present at the surface is a carbonate anion, CO_3^{2-} . However, this species has been spectroscopically characterized on a NiO(111) surface, and observed to have modes at 906 and 1260 cm^{-1} (bending and symmetric stretch

modes, respectively),³⁹ neither of which are observed in the current work. The lack of adsorbed CO₂ at the surface suggests that either its rate of desorption is significant at 77 K, or that its mechanism of formation is such that the energy of the product molecules is greater than the barrier to desorption. The lack of adsorbed CO₃²⁻ species indicates that this species is not a stable intermediate in the reaction at 77 K.

One possible assignment of the 660 cm⁻¹ feature is the stretch vibration of O atoms against the surface. These O atoms would be the product of the initial reaction of molecular O₂ species with CO in the beam. A frequency of 660 cm⁻¹ is relatively high for an atomic oxygen-metal surface vibration. However, a vibrational frequency of 660 cm⁻¹ has been observed for O atoms adsorbed on a Au(111) surface.⁴⁰ Assuming that the cross section for vibrational excitation is the same for O-metal and O-O stretch modes, then the intensities are directly proportional to the coverage of each species. Applying this assumption to the vibrational spectrum measured on a 0.18 ML Au/Ni(111) surface alloy, the intensity of the 660 cm⁻¹ feature is only 19% of the intensity of the 790, 850 and 950 cm⁻¹ features that are removed by the reaction, indicating that if the 660 cm⁻¹ arises from reaction, it is not produced in 100% efficiency. If the 660 cm⁻¹ feature is from a new atomic oxygen species formed during the initial reaction, then some of the initially created oxygen atoms are formed from the reaction of molecularly chemisorbed oxygen must become another species of unreactive oxygen atoms at the surface. It is possible that these O atoms exist, and correspond to the 580 cm⁻¹ feature (below 0.13 ML Au) and the unresolved intensity between 350-500 cm⁻¹ (at or above 0.13 ML Au).

In the limit that all of the oxygen atoms produced from the initial reaction are the unreactive species characterized by O-Ni vibrations below 580 cm⁻¹, then the 660

cm^{-1} feature has to be assigned to another species. In this case the 660 cm^{-1} feature may arise from another type of molecularly chemisorbed oxygen. Given the absence of a feature or shoulder at 660 cm^{-1} in spectra of an O_2 layer adsorbed on Au/Ni(111) ,³⁰ this feature would have to be attributed to a previously chemisorbed molecular O_2 that did not undergo the initial reaction, but when co-adsorbed with a high coverage of CO undergoes a frequency shift to 660 cm^{-1} .

It is not possible given the resolution of our spectrometer (55 cm^{-1}) to distinguish between the atomic or molecular nature of the oxygen species characterized by the 660 cm^{-1} feature by use of the O^{18} isotope. A prediction of the isotope effect on the frequency of the 660 cm^{-1} mode demonstrates this. For the motion of O-O stretch mode, it is assumed that the motion only involves the O-O bond (e.g. no surface metal atoms are involved in the mode). For the atomic O species, it is assumed that they are adsorbed in a 3-fold hollow site with 3 Ni neighbors (no Au atoms), and that the 3 Ni atoms move in unison. The latter assumption allows the reduced mass equation, which is derived for two-particle systems, to be applied to the four-particle system of an O atom adsorbed in a 3-fold hollow site. The reduced masses for a set of possible species that could be created at the surface using isotopic substitution are:

Species	$\text{O}^{16}\text{-O}^{16}$	$\text{O}^{18}\text{-O}^{18}$	$\text{O}^{16}\text{-O}^{18}$	$\text{O}^{16}\text{-3Ni}$	$\text{O}^{18}\text{-3Ni}$	$\text{O}^{16}\text{-Ni}$	$\text{O}^{18}\text{-Ni}$
Reduced mass:	$\frac{16 \cdot 16}{16 + 16}$	$\frac{18 \cdot 18}{18 + 18}$	$\frac{16 \cdot 18}{16 + 18}$	$\frac{16 \cdot (3 \cdot 59)}{16 + (3 \cdot 59)}$	$\frac{18 \cdot (3 \cdot 59)}{18 + (3 \cdot 59)}$	$\frac{16 \cdot 59}{16 + 59}$	$\frac{18 \cdot 59}{18 + 59}$
	8.0	9.0	8.5	14.7	16.3	12.6	13.8

The fractional values for the frequency shifts and the predicted final frequency of the 660 cm^{-1} mode of the above species are:

Species:	O ¹⁶ -O ¹⁶	O ¹⁸ -O ¹⁸	O ¹⁶ -O ¹⁸	O ¹⁶ -Ni	O ¹⁸ -3Ni	O ¹⁸ -Ni
Fractional Frequency	$\sqrt{\frac{8.0}{8.0}}$	$\sqrt{\frac{8.0}{9.0}}$	$\sqrt{\frac{8.0}{8.5}}$	$\sqrt{\frac{14.7}{14.7}}$	$\sqrt{\frac{14.7}{16.3}}$	$\sqrt{\frac{12.6}{13.8}}$
	1.0	0.94	0.97	1	0.95	0.96
Frequency	660	620	640	660	627	631

The difference in frequency between a molecular species, O₂¹⁸ (620 cm⁻¹), and Ni-O¹⁸ (627 cm⁻¹) is only 7 cm⁻¹, which is not large enough to be resolved with our current resolution of 55 cm⁻¹. The molecularly adsorbed species O¹⁶-O¹⁸ would present a larger frequency difference of 13 cm⁻¹ between it (640 cm⁻¹) and the atomically adsorbed O¹⁶ and O¹⁸ species (mixture of 660 and 627 cm⁻¹ features). Although this frequency difference is too small to be resolved, it may be possible to distinguish between a molecularly and atomically adsorbed species in the following way. If the 660 cm⁻¹ mode of O¹⁶-O¹⁶ corresponds to a molecular species, then there should only be a single vibrational mode of O¹⁶-O¹⁸ at 640 cm⁻¹. If it corresponds to an atomic species, there should be two modes, at 660 and 627 cm⁻¹. The maxima of two features separated by 33 cm⁻¹ should be resolvable using the current spectrometer resolution.

B. Estimation of the Reaction Probability at 77 K

The probability of reaction at 77 K between a CO beam and a saturated O₂ layer on a 0.18 ML Au/Ni(111) surface alloy can be estimated using the known CO flux (0.7 ML/s) and the O₂ coverage before and after the reaction. Figure 1 shows that the reaction is almost entirely complete after a 1 s exposure of the CO beam, therefore the CO exposure, and hence the number of CO – O₂ collisions during the reaction is estimated to be 0.7 ML, assuming that every CO – surface collision results in a CO – O₂ collision.

The O₂ coverage prior to reaction has been estimated using AES in the experimental section of Chapter 2. The AES measurement indicated that ~0.9 ML of O

atoms are present at a saturated O₂ layer on a Au/Ni(111) surface alloy with 0.17 ML Au coverage. As reported in Chapter 2, there is no atomic O adsorbed on a 0.18 ML Au/Ni(111) surface alloy. Therefore, a coverage of 0.9 ML of O atoms observed by AES for a 0.18 ML Au/Ni(111) surface alloy corresponds to the presence of 0.45 ML of chemisorbed molecular O₂.

The amount of O₂ which reacts at 77 K, and hence the amount of CO₂ that is produced, can be estimated using the HREELS presented in Figures 7 – 9. The amount of O₂ that reacts is calculated by measuring the ratio of the intensity at 790, 850 and 950 cm⁻¹ in HREELS before the reaction (Figures 5- 7, Chapter 2) to the intensity at 790, 850 and 950 cm⁻¹ after the reaction (Figures 7 – 9, this chapter). The ratio of the 790, 850 and 950 cm⁻¹ features before and after the reaction indicates that for a 0.18 ML Au/Ni(111) surface alloy, 68% of the molecular O₂ adsorbate undergoes reaction at 77 K with the CO beam. Therefore, the amount of CO₂ produced is estimated to be $0.68 \times 0.45 \text{ ML} = 0.31 \text{ ML}$. The reaction probability is then calculated to be $(0.68 \times 0.45 \text{ ML CO}_2 \text{ produced}) / (0.7 \text{ ML CO collision required to remove } 0.31 \text{ ML O}_2) = 0.4$.

C. CO Oxidation Between 108 and 250 K

The trend in CO₂ production between 108 – 200 K as a function of Au coverage, as shown in Figures 11 and 12, is similar to that of the CO₂ production at 77 K as a function of Au coverage, and hence similar to the trends observed for O₂ coverage, as described in the first section of the discussion. The peak production of CO₂ between 108 and 250 K occurs for a Au coverage of $0.16 \pm 0.02 \text{ ML Au}$, which is within experimental error of the peak coverage of O₂ observed spectroscopically by HREELS³⁰ and only slightly less than the coverage at which maximum CO₂ production occurs at 77 K ($0.19 \pm 0.02 \text{ ML Au}$). As stated in the results section, there

is rapid production at 120 K, and slower production centered at 150 K. Although it is unclear as to the nature of the oxygen species on the surface corresponding to the 660 cm^{-1} feature that is observed after reaction with the CO beam at 77 K, it is clear that this feature is derived from the initial molecular oxygen adsorbate. As indicated by the upper traces in Figures 14 - 16, after heating the surface to 300 K, the oxygen species corresponding to the 660 and 780 cm^{-1} modes are consumed, and hence these species are the reactive partners during CO oxidation between 108 – 250 K. Hence, the initial adsorption of molecular oxygen adsorbates and their coverage are critical for CO_2 production between 108 - 250 K.

It is hypothesized that the initial step in the production of CO_2 between 108 and 250 K is the formation of hot O atoms. This hypothesis is predicated on the observation that the chemisorbed molecular O_2 on the Au/Ni(111) surface alloy is observed to undergo dissociation between 110 and 150 K (Chapter 2), the same temperature at which CO_2 is produced. Hot O atoms are generated when a thermally activated molecular O_2 adsorbate undergoes dissociation:



In this mechanism, the exothermicity released when O_2 dissociates is not lost to surface modes rapidly enough to stabilize the O atom at its dissociation site. Rather, the exothermicity is channeled into energy of the O atoms parallel to the surface, allowing them to move across the surface in an almost ballistic manner. The O may collide with an adsorbed CO:



This mechanism has been suggested previously for CO oxidation reactions at 125 K on Pt(111).^{5,7,8} For the Au/Ni(111) surface alloy, the hot O atoms react exclusively with

the CO species characterized by its vibrational frequencies of 340 and 2160 cm^{-1} and low desorption temperature (~ 120 K).

An alternative to the hot atom mechanism, or perhaps in addition to the hot atom mechanism, is that the less strongly bound CO species diffuses rapidly at temperatures between 108 – 250 K. During diffusion, the CO species is able to react with co-adsorbed O species. The CO species, characterized by its vibrational frequencies of 340 and 2160 cm^{-1} , is observed to desorb from an O atom covered Au/Ni(111) surface alloy between 108 – 225 K, suggesting that for CO oxidation between 108 – 250 K, this species of CO is rapidly diffusing. This mechanism for CO oxidation has been proposed for thermally induced CO oxidation on the platinum group metals^{41,42,43} and supported Au nanoparticles.^{11,12}

Within the temperature range 108 – 250 K, maximum production of CO_2 is observed to occur at two temperatures. There is rapid production of CO_2 at 120 K, followed by slower production at 150 K (Figure 10). This observation suggests that there are two different reactions for the production of CO_2 . Vibrational spectra (Figures 14 – 17), measured for increasing surface temperatures, indicates that the oxygen species characterized by a vibrational frequency of 660 cm^{-1} oxidizes CO at 115 K, while the molecular oxygen adsorbate characterized by a vibrational frequency of 780 cm^{-1} oxidizes CO between 115 and 150 K. In addition, in Chapter 2 it was shown that dissociation of molecular O_2 occurred between 110 – 150 K. These observations suggest that the production of CO_2 observed at 120 K is the result of a reaction between a diffusing CO molecule and the molecular oxygen species characterized by its vibrational mode with frequency 660 cm^{-1} . If this oxygen species is a molecular one, then the reaction also involves the hot O atom mechanism. The

production of CO₂ that occurs at 150 K, for which the reactive species of oxygen is known to be molecular, occurs between a hot O atom produced by thermal dissociation of adsorbed O₂ (characterized by its vibrational frequency of 780 cm⁻¹) and a co-adsorbed CO molecule.

As mentioned in the introduction, a species of CO with reduced adsorption energy has been shown to be important for low temperature CO oxidation over supported Au nanoparticles. Derrouiche et. al. has shown that CO adsorbed at Ti⁴⁺ ions of a Au/TiO₂ catalyst has a lower adsorption energy than the species bound at metallic sites (e.g. Au atoms).²⁷ This result is in good agreement with the experimental results presented here, in which CO weakly bound atop a metal atom with reduced charge density is observed to be the critical reactant for low temperature oxidation of CO.

A final mechanistic consideration is the fact that for all HREELS spectra, measured at any Au coverage and under any condition, there are never any modes observed corresponding to adsorbed CO₂ molecules or CO₃²⁻ ions. All CO₂ that forms desorbs immediately. In addition, carbonate ions are not an intermediate in this reaction. The lack of observation of CO₂ adsorbed at the surface suggests that there is a late barrier for the reaction between the oxygen species and adsorbed CO. A characteristic of reactions with late barriers is that the exothermicity is channeled into translation of the product, propelling CO₂ away from the surface. Measurements of the vibrational,⁴⁴⁻⁴⁹ rotational,^{44,45} and translational⁷ energy of CO₂ produced during CO oxidation on Pt, Pd, and Rh indicate that the temperature of CO₂ is significantly above that of the surface, leading to the conclusion that CO oxidation on these surfaces

has a late transition state. It is therefore plausible that CO oxidation on the Au/Ni(111) surface alloy displays a late barrier.

The work presented in this chapter is not the first reported CO oxidation on a modified Ni(111) surface under UHV conditions. CO oxidation at 160 K on a K promoted Ni(111) surface was recently reported by Cupolillo et. al.⁵⁰ In their experiments, first oxygen, then CO were adsorbed at a Ni(111) surface. Vibrational spectroscopy (HREELS) revealed that oxygen adsorbed dissociatively, characterized by a frequency of 580 cm^{-1} . Two species of CO were observed with frequencies 1860 and 2080 cm^{-1} . The surface was then exposed to K. When the K coverage reached 0.20 ML , a vibrational feature at 2360 cm^{-1} appeared and was attributed to CO_2 . Cupollilo et. al. stated that the order of exposure of the O, CO and K didn't affect the result, and interpreted this observation as indicating that K promotes the reaction of CO and O at the Ni(111) surface.⁵⁰ However, later work performed by the same group demonstrated that disproportionation of CO to adsorbed C atoms and CO_2 molecules occurred readily when CO and alkali metal atoms (Na or K) were co-adsorbed at the Ni(111) surface.^{51,52} This results casts significant doubt on the original work. For the original work of Cupollilo et. al., there is no experimental result that can distinguish between CO disproportionation and CO oxidation. Therefore, it is not possible to make any useful comparisons between the work of Cupollilo et. al. and the current work, until experiments that distinguishes between CO oxidation and CO disproportionation for CO and O co-adsorbed on K promoted Ni(111) are available.

D. Practical Applications of the Low-Temperature Catalytic Oxidation of CO by the Au/Ni(111) Surface Alloy

The discovery that the Au/Ni(111) surface alloy catalyzes CO oxidation at low temperatures suggest two main practical applications. As described in the introduction, the current TWC system for automobile pollution abatement is inactive below temperatures of 300° C, allowing exhaust gas to go unprocessed during engine starting and idling. A supported Au-Ni alloy catalyst, used in conjunction with the TWC system, could catalyze CO oxidation during conditions when the TWC is inactive.

In addition to processing exhaust gases from automobiles, a Au-Ni alloy catalyst could be used to remove CO from H₂ streams in fuel cells. As described in the introduction, H₂ is produced industrially by steam reforming, which, despite optimization, still contains 1% CO. The Pt membranes of fuel cells are easily deactivated by CO concentrations of 1%, therefore, a successful fuel cell system must have a means for removing this CO prior to contact of the H₂ stream with the Pt membrane. The Au-Ni alloy catalyst, which oxidizes CO effectively at low temperatures, could potentially be used in H₂ streams to remove the CO, and allow operation of fuel cells.

As described in Chapter 1, a Au-Ni catalyst has been demonstrated to be effective for steam reforming of methane – indicating that at least for this reaction, the properties of the Au/Ni(111) surface alloy observed under UHV are relevant to the catalytic activity of a practically applied system. Furthermore, work by Molenbroek et. al.⁵³ has demonstrated that the a Au-Ni nanoparticle catalyst, a form useful for practical catalytic activity, has a structure similar to the Au/Ni(111) surface alloy.

That is, for Au-Ni nanoparticles, Au atoms are observed to be alloyed into the surface layer. A benefit of the segregation of Au into the surface layer is that the amount of Au required is reduced.

One possible complication for the practical application of the Au-Ni catalyst for CO oxidation is raised by the results of Vestergaard et. al.⁵⁴ They observed by STM that a Au/Ni(111) surface alloy, when exposed to 1 atm CO, undergoes a drastic morphological change. The exposure causes Au atoms to segregate into islands at the surface. This change in morphology is observed for pressures as low as 5 torr CO. This structural change could be fatal for the reactivity of the Au/Ni(111) surface alloy, as previous work by Nielsen has indicated that oxygen and CO adsorption at the Au/Ni(111) surface alloy under UHV conditions does not perturb the structure, and hence randomly alloyed Au is a structural requirement for low temperature CO oxidation. However, there is no work to date that elucidates the structure of the Au/Ni(111) surface alloy in the presence of high pressure O₂, and it is entirely possible that under potential operating conditions, any CO which might cause a morphological change of the Au/Ni(111) surface alloy would undergo oxidation to CO₂ before the high pressure/surface coverages required to induce islanding could occur.

V. CONCLUSION

A Au/Ni(111) surface alloy catalytically oxidizes CO at a temperature as low as 70 K. At this temperature, the reaction occurs between molecularly chemisorbed O₂ on the surface (identified spectroscopically by HREELS) and a beam of CO. Two of the previously identified species of molecularly chemisorbed oxygen are consumed in the reaction at 77 K. The consumed O₂ species have frequencies of 850 and 950 cm⁻¹. One of the molecular oxygen adsorbates present prior to exposure to the CO beam,

characterized by its 790 cm^{-1} feature, does not react at 77 K. A new species of oxygen, with a vibrational frequency of 660 cm^{-1} , forms after this initial reaction. This species is tentatively identified as being one of the original species of molecular oxygen, which undergoes a frequency shift when co-adsorbed with CO, or an O atom bound to a Au atom. Control experiments indicate that the reaction does not proceed when atomic oxygen is adsorbed at the surface, and hence the formation of molecular oxygen adsorbates at the Au/Ni(111) surface alloy is critical for the reaction. The reaction probability at 77 K has been estimated to be 0.4.

Exposure to the CO beam also causes the adsorption of CO on the surface. Two species of CO are adsorbed on the surface as identified spectroscopically by HREELS. Subsequent heating of the surface causes reaction of the co-adsorbed CO species bound at a metal atom with reduced charge density (with modes of 340 and 2160 cm^{-1}) with the oxygen identified by the 660 and 780 cm^{-1} modes. The reaction has a high rate at 120 K and 150 K, as demonstrated by heating at 2 K/s. The low temperature activation of this CO species is proposed as being a critical requirement for the low temperature reactivity.

The amount of CO_2 produced in the initial reaction, and during subsequent heating is maximized for Au/Ni(111) surface alloys with 0.19 ± 0.02 and 0.16 ± 0.02 ML Au, respectively. These Au coverages are both within the experimental error of the observed maximum in the O_2 coverage (0.18 ± 0.02 ML Au) observed previously by HREELS.³⁰ No CO_2 is produced below 0.07 ML Au or above 0.30 ML Au. This confirms that the chemisorbed molecular oxygen species is critical for the catalytic oxidation of CO at the Au/Ni(111) surface alloy.

The work presented here suggests the use of a Au-Ni catalysts for low temperature oxidation in pollution abatement of automobile exhaust, and removal of CO from H₂ streams. Towards this end, a patent application for the use of a Au-Ni catalyst for CO oxidation has been filed.

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CHAPTER 4 - Attempted Reaction Between CO and NO on Au/Ni(111)

Surface Alloys

I. INTRODUCTION

As described in Chapter 3, the reaction between CO and NO to produce N₂ and CO₂ is important for pollution abatement from automobile exhaust. The reactants (CO and NO) are poisonous gases, while the products (N₂ and CO₂) are inert constituents of our atmosphere. This reaction is usually carried out by a three-way catalyst (TWC) in the catalytic converter of automobiles, which consists of a combination of Pt/Rh, Pt/Pd/Rh, Pd and Pd/Rh metals, supported on ceria and alumina. These metals and metal alloys, known as platinum group metals (PGM),¹ suffer from the linked problems of high cost and scarce, unreliable supply. A catalyst composed Au and Ni would alleviate these problems, because although the cost of Au is high, it is cheaper than either Pt or Rh, and its supply is much more stable.²

Supported Au nanoparticle catalysts have been observed to catalyze the reaction of NO and CO to form N₂ and CO₂. However, these catalysts suffer from sintering problems and have not been deployed as commercial systems yet.³ Based on the observed similarity in the catalytic ability of supported Au nanoparticles and the Au/Ni(111) surface alloy for low temperature CO oxidation (Chapter 3), the catalytic reaction of CO and NO over a Au/Ni(111) surface alloy was attempted. This chapter reports on the results of these attempts.

II. EXPERIMENTAL

The experimental apparatus has been described extensively elsewhere⁴ and in Chapter 1. Au was deposited onto the Ni(111) surface, and its coverage measured as

described in Chapter 1. High resolution electron-energy loss spectroscopy (HREELS) confirmed that the prepared Au/Ni(111) surface alloy was clean of all contaminants. An impact energy of 5.5 eV was used for all reported spectra.

The crystal was exposed to research grade NO (99.5% purity) from Matheson using the molecular beam system as described in Chapter 2. For the experiment in which the reactivity of NO and CO is monitored by the quadrupole mass spectrometer (QMS), the small beam hole was used for the CO exposure, thereby minimizing the background pressure of CO in the chamber, and hence any reactions that might occur on the back face of the crystal or other surfaces in the chamber. For the experiment in which HREELS are measured, the large beam hole is used, to ensure a uniform coverage of NO on the surface. All neat NO and CO beam exposures are performed with the crystal in the “TDS” position (described in Chapter 1), with the nozzle at room temperature and a stagnation pressure of 20 psia.

III. RESULTS AND DISCUSSION

A. Vibrational Spectrum of Adsorbed NO

In order to probe the species adsorbed on the surface after exposure to the NO beam, HREELS is measured of a Au/Ni(111) surface alloy at 77 K with 0.24 ML Au exposed to a NO beam for increasing amounts of time (Figure 1). For the lowest exposure, features at 740 and 1600 cm^{-1} are observed. A similar pair of loss features has been observed for NO adsorbed on Ni(100) at 560 and 1600 cm^{-1} ,⁵ and Ni(110) at 500 and 1675 cm^{-1} ,^{1,6} and was assigned to the bending and stretching modes of NO adsorbed in bridging sites on these surfaces. Based on these previous observations, the features at

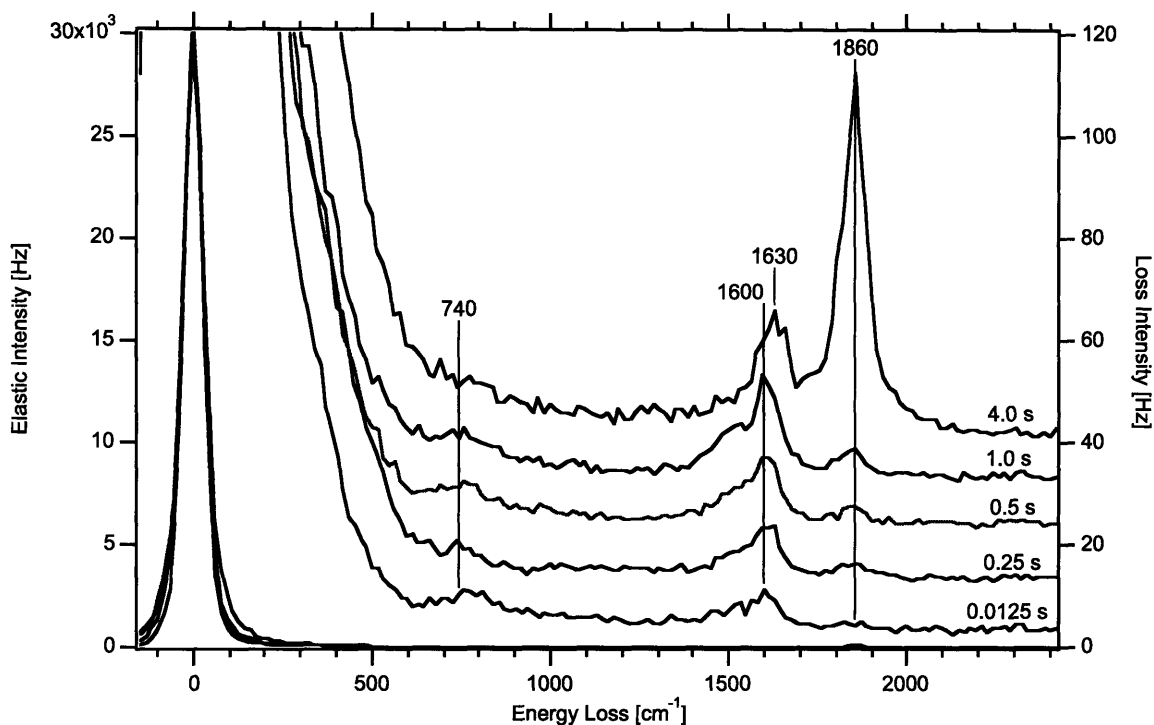


Figure 1. HREELS spectrum measured on-specular after exposing a 0.24 ML Au/Ni(111) surface alloy at 77 K to a NO beam for increasing time. Resolution is 70 cm^{-1} FWHM.

740 and 1600 cm^{-1} are assigned to the bending and N=O stretching modes, respectively, of NO molecules adsorbed in bridging sites on the Au/Ni(111) surface alloy.

As the exposure time of the NO beam to the 0.24 ML Au/Ni(111) surface alloy is increased from 0.0125 to 1 s, the intensity of the features at 740 and 1600 cm^{-1} increase. The spectrum collected after a 0.25 s NO exposure reveals the first appearance of the 1860 cm^{-1} feature as a peak distinct from the 1600 cm^{-1} feature. The 1860 cm^{-1} feature is tentatively assigned as the N=O stretch of another species of NO adsorbed at the surface. A pair of N=O stretch modes have been observed previously on Ni(111) at 1507 and 1568 cm^{-1} , assigned to bridge and atop bonded NO. On Ni(110), a pair of loss features at 1670 and 1870 cm^{-1} were assigned to the N=O stretch of bridge and atop bonded NO. The same assignment was made for a pair of loss features observed at 1600 and 1840 cm^{-1} .

¹ on Ni(100). These observations are the basis of the assignment of the 1860 cm⁻¹ feature in Figure 1 to a species of NO bound atop a metal atom at the Au/Ni(111) surface alloy.

When the exposure of the NO beam to the 0.24 ML Au/Ni(111) surface alloy is increased from 1 to 4 s, a drastic increase in the intensity of the 1860 cm⁻¹ feature is observed. In addition, the 1600 cm⁻¹ feature shifts up to 1630 cm⁻¹, and the mode with frequency 740 cm⁻¹ has disappeared. It is proposed that the NO species observed to have a N=O stretching frequency of 1600 cm⁻¹ is adsorbed with a bent geometry, such that the N=O bond is not perpendicular to the surface. This geometry is the source of the relatively high frequency of 740 cm⁻¹ observed for the bending mode of this species. When the NO coverage is increased, by exposing the Au/Ni(111) surface alloy to the NO beam for 4 s, the bent geometry is no longer energetically favorable. Rather, this species of NO bonds in a bridging site with the N=O bond perpendicular to the surface. The change in geometry results in a downward shift of the 740 cm⁻¹ feature such that it is obscured by the tail of the elastic, and an upward shift of the N=O bond from 1600 to 1630 cm⁻¹. This change in geometry is concomitant with a change in the preferential adsorption site, as observed by the change in the relative intensities of the 1600 and 1860 cm⁻¹ features as the exposure to the NO beam is increased from 1 to 4 s.

The frequencies of the N=O bond for each of the NO species observed on the 0.24 ML Au/Ni(111) surface alloy are higher than those observed on the Ni(111) surface. This observation is consistent with the observed interaction of the Au/Ni(111) surface alloy with O₂ and CO presented in Chapters 2 and 3. The presence of Au alloyed into the Ni(111) surface lowers the Ni d-band, reducing the energetic overlap between the d-band and adsorbates such as O₂, CO or NO. The reduced overlap results in reduced charge

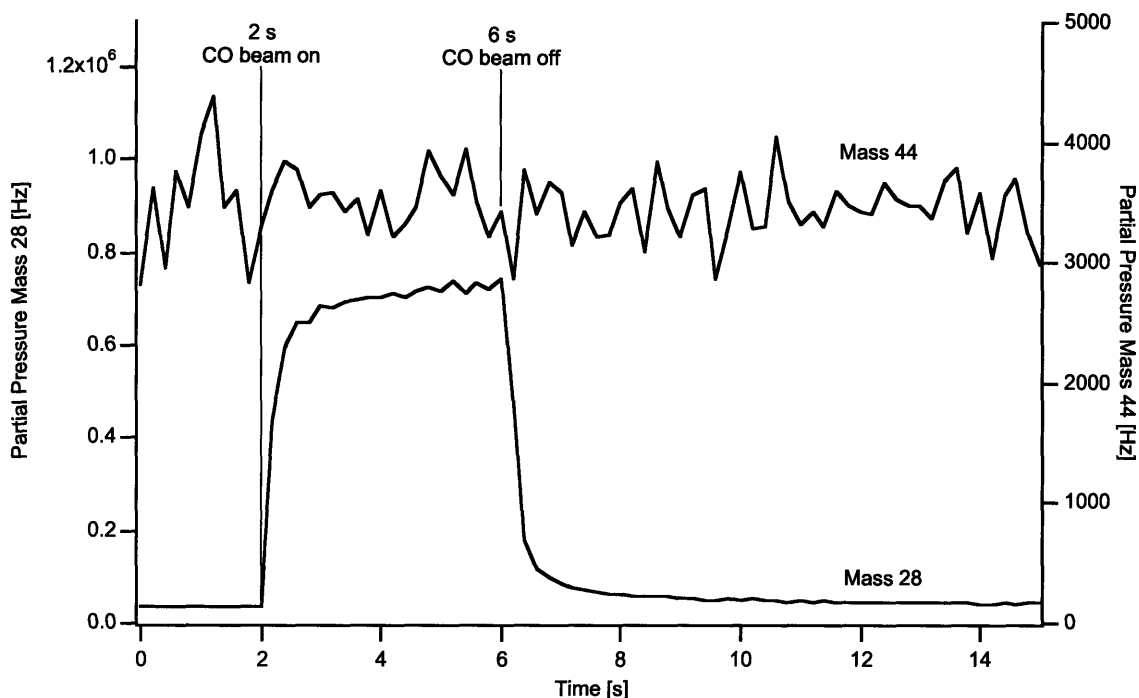


Figure 2. Partial pressure of mass 28 and mass 44 during exposure of a 0.23 ML Au/Ni(111) surface alloy at 77 K to a CO beam. Prior to CO beam exposure, the surface is exposed to a NO beam for 4 s.

transfer from the metal d-band into the antibonding LUMO of the adsorbate, causing the internal molecular bond of the adsorbate to have a higher bond order, and hence a higher observed frequency for the bond stretching mode. For the case of O_2 , this effect is the most drastic, as the reduction in charge transfer from the metal d-band to the LUMO of O_2 prevents dissociation. Although dissociation of O_2 occurs readily on Ni(111), it does not occur on 0.18 ML Au/Ni(111) surface alloys. The results for CO and NO are less drastic. The reduced charge transfer from the metal d-band to the LUMO of either CO or NO results in a higher bond order for these adsorbates, as observed by an increase in the stretching frequencies of the C=O and N=O bonds.

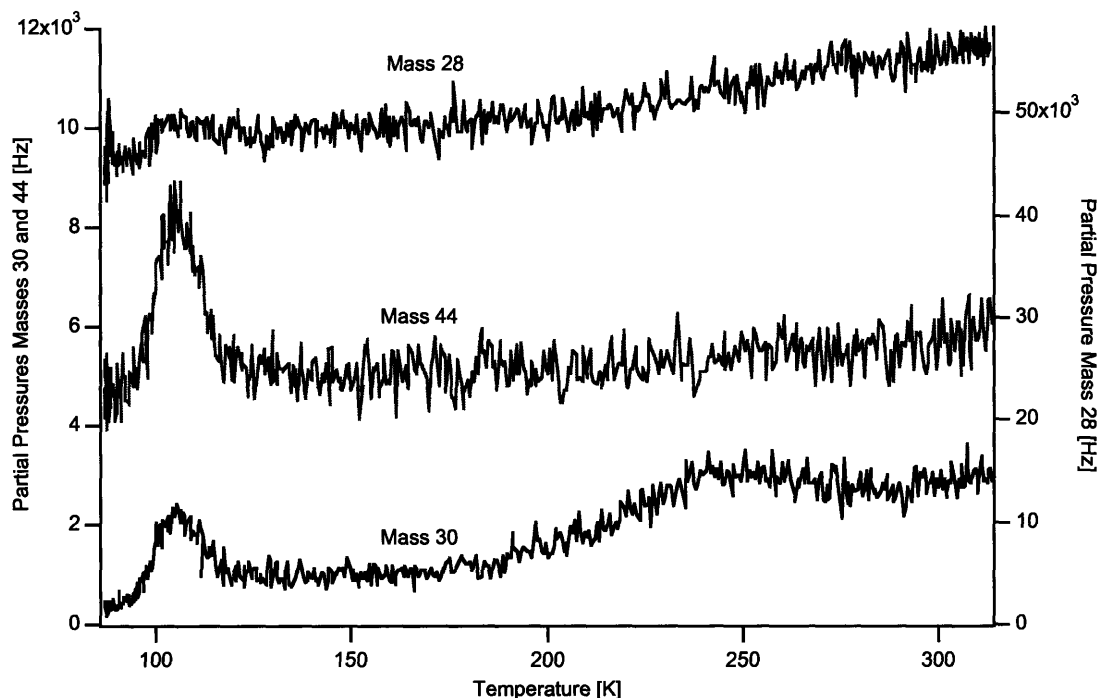


Figure 3. Partial pressure of masses 28, 30 and 44 vs. temperature as a 0.23 ML Au/Ni(111) surface alloy is heated at 2 K/s from 77 to 330 K, monitored by QMS. The surface at 77 K is exposed to a NO beam for 4 s, then a CO beam for 4 s prior to heating.

B. Attempted Reaction Between NO and CO

A Au/Ni(111) surface alloy at 77 K with 0.23 ML Au is exposed to a NO beam for 4 s. The surface is then exposed to a CO beam for 4 s, while the partial pressures of masses 28 and 44 are monitored. The results are presented in Figure 2. During the CO beam exposure, no change in the mass 44 partial pressure is observed, indicating that no CO_2 production occurs. This surface is then heated at 2 K/s from 77 to 330 K, while the partial pressures of masses 28, 30 and 44 are monitored (Figure 3). A rapid increase in the partial pressures of species with masses 30 and 44 occurs at 105 K. A slower increase in the partial pressure at higher temperatures of a mass 30 species is observed to occur,

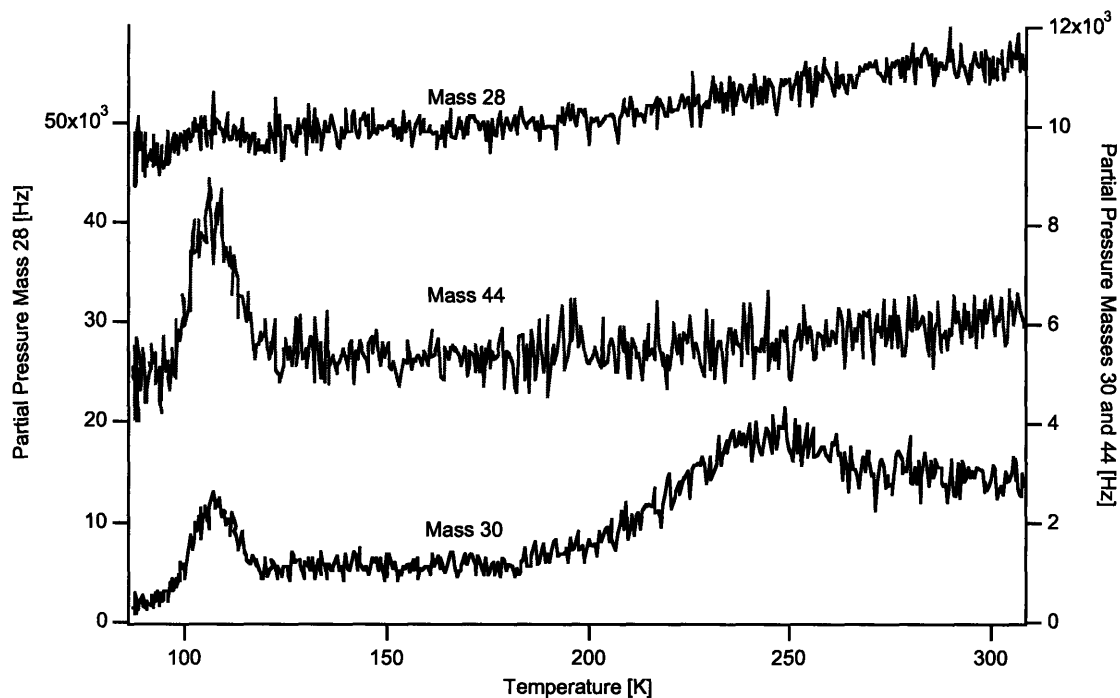


Figure 4. Partial pressure of masses 28, 30 and 44 vs. temperature as a 0.23 ML Au/Ni(111) surface alloy is heated at 2 K/s from 77 to 330 K, monitored by QMS. Prior to heating, the surface at 77 K is exposed to a NO beam for 4 s, then the crystal is rotated 180° and exposed to a CO beam for 4 s, causing the beam to impinge on the sample manipulator and not the surface.

with the maximum partial occurring at 240 K. A small change in the partial pressure measured at mass 28 is observed.

A control experiment is then performed, to determine whether CO is required for the production of the mass 44 species. A Au/Ni(111) surface alloy at 77 K with 0.23 ML Au is exposed to a NO beam for 4 s. The surface is then rotated 180°, and exposed to a CO beam for 4 s, causing the beam to impinge on the back of the crystal manipulator. This surface is then heated at 2 K/s from 77 to 330 K, while the partial pressures of masses 28, 30 and 44 are monitored (Figure 4). The same results as observed in Figure 3, namely rapid increase of the partial pressure at mass 44 and 30 at 105 K and a slower increase in the mass 30 partial pressure at 240 K, is observed. This control experiment

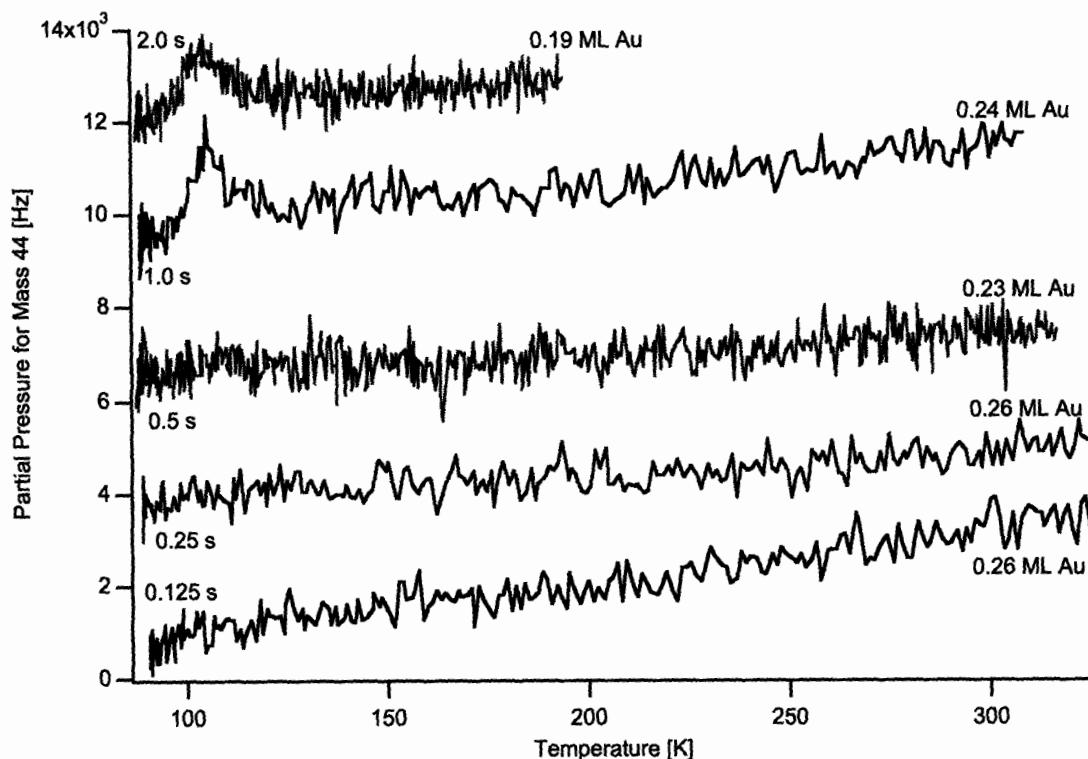


Figure 5. Partial pressure of mass 44 vs. temperature as Au/Ni(111) surface alloys are heated at 2 K/s from 77 to 330 K, monitored by QMS. The surfaces at 77 K are exposed to a NO beam for the time labeled on each trace, then a CO beam for 4 s prior to heating. The Au coverage of each surface is also labeled.

demonstrates that the species with mass 44, produced rapidly at 105 K, is the product of a reaction of adsorbed NO at the Au/Ni(111) surface alloy, and does not occur between co-adsorbed CO and NO.

In Figure 3, there is no observed desorption of CO, suggesting no CO adsorption is possible after the 0.23 ML Au/Ni(111) surface alloy is exposed to a NO beam for 4 s. In order to achieve CO adsorption, and hence attempt the reaction between co-adsorbed CO and NO, shorter exposures to a NO beam were used. The Au/Ni(111) surface alloys represented by the traces in Figure 5 are exposed to a NO beam for 0.125, 0.25, 0.5, 1 and 2 s, respectively. After each of these exposures, the surface is exposed to a CO beam for 4 s. During the exposure to the CO beam, the partial pressure of mass 44 is monitored,

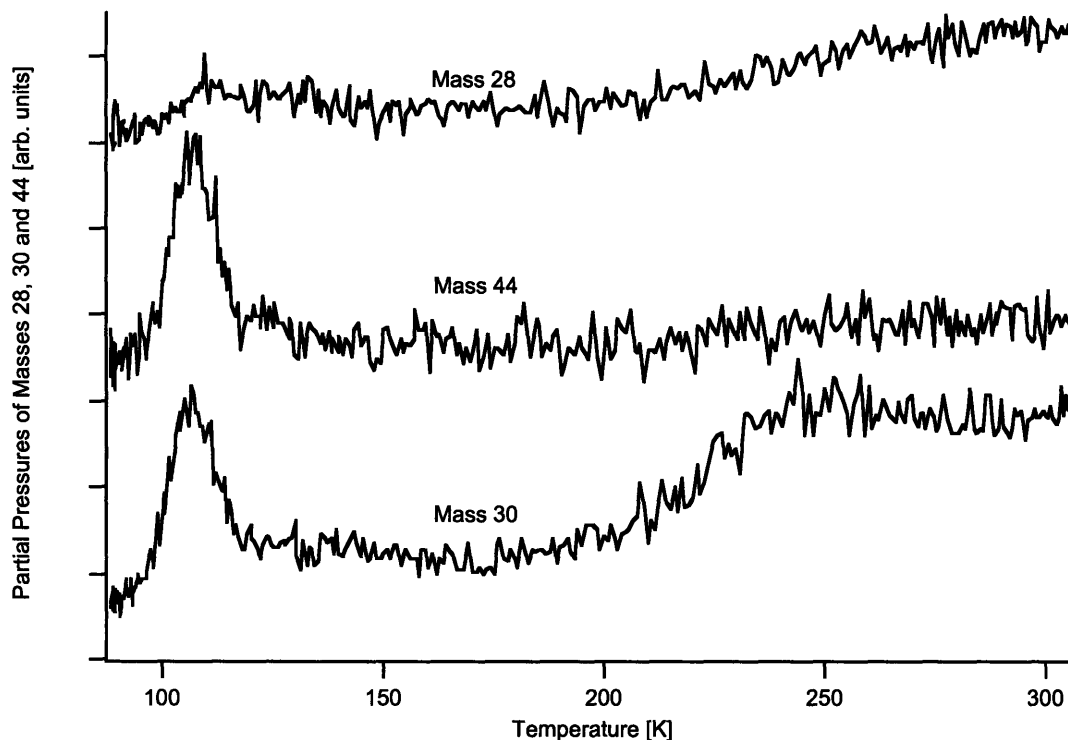


Figure 6. Partial pressure of masses 28, 30 and 44 vs. temperature as a 0.22 ML Au/Ni(111) surface alloy is heated at 2 K/s from 77 to 330 K, monitored by QMS. Prior to heating, the surface at 77 K is exposed to a NO beam for 4 s.

and no change is observed. After exposure to the CO beam for 4 s, the surface is heated at 2 K/s while the partial pressure of mass 44 is monitored. The results indicate that the rapid increase at 105 K in the partial pressure of mass 44 only occurs for NO beam exposures greater than 0.5 s, and increases with increasing NO beam exposure. If the reaction is limited by the lack of CO adsorbed at the surface, the partial pressure of mass 44 at 105 K should increase as the NO beam exposure is decreased. The observation in Figure 5 of the opposite behavior suggests that lack of CO adsorption is not the limiting factor that prevents the reaction from occurring.

As a further control, a Au/Ni(111) surface alloy at 77 K with 0.22 ML Au is exposed to a NO beam for 4 s. This surface is then heated at 2 K/s from 77 to 330 K, while the partial pressures of masses 28, 30 and 44 are monitored (Figure 6). A rapid

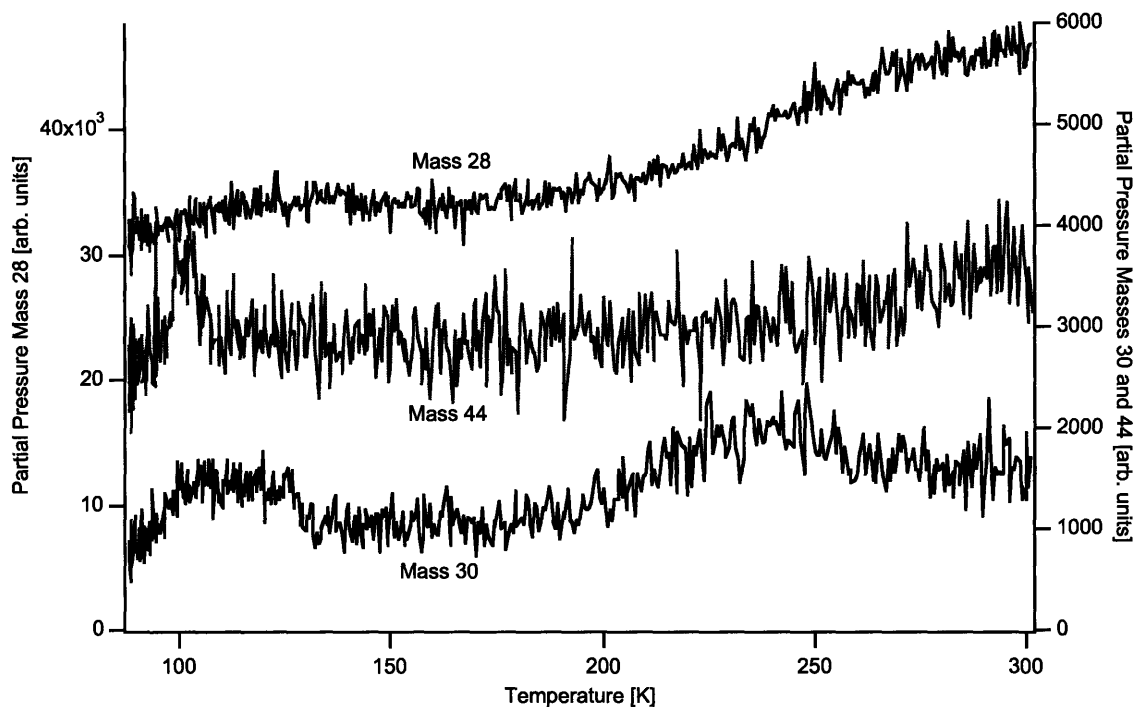
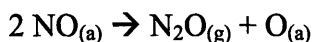


Figure 7. Partial pressure of masses 28, 30 and 44 vs. temperature as a 0.23 ML Au/Ni(111) surface alloy is heated at 2 K/s from 77 to 330 K, monitored by QMS. The surface at 77 K is exposed to a CO beam for 4 s, then a NO beam for 4 s prior to heating.

increase in the partial pressures of species with masses 30 and 44 occurs at 105 K. A slower increase in the partial pressure at higher temperatures of a mass 30 species is observed to occur, with the maximum partial pressure occurring at 240 K. This confirms that the species produced at 105 K, observed to have mass 44, does not require adsorbed CO, suggesting that the species with mass 44 is N_2O , produced by the reaction:



To test whether the order of exposing the Au/Ni(111) surface alloy to NO and CO affects the reaction, a Au/Ni(111) surface alloy at 77 K with 0.23 ML Au is exposed to a CO beam for 4 s. The surface is then exposed to a NO beam for 4 s. This surface is then heated at 2 K/s from 77 to 330 K, while the partial pressures of masses 28, 30 and 44 are

monitored (Figure 7). A rapid increase in the partial pressures of species with masses 30 and 44 occurs at 105 K. A slower increase in the partial pressure at higher temperatures of a mass 30 species is observed to occur, with the maximum partial pressure occurring at 240 K. This behavior is similar to that observed in Figure 3, in which the reaction between NO and CO was attempted by exposing first NO then CO to the surface. In contrast with Figure 3, the maximum partial pressure N₂O (mass 44) in Figure 7 is ~25% that of the maximum in partial pressure of N₂O (mass 44) in Figure 3. The reduced production of N₂O suggests that the observed reaction is that of adsorbed NO, and not a reaction between co-adsorbed NO and CO. The reduced production of N₂O results from reduced coverage of NO, caused by blocking of adsorption sites by pre-adsorbed CO.

Insight into the mechanism of N₂O formation can be gained from the vibrational spectra in Figure 1. These spectra demonstrate that at 77 K there are no vibrational frequencies corresponding to adsorbed N₂O at 2260, 1270, and 590 cm⁻¹ (asymmetric stretch, symmetric stretch, and bending mode),⁷ indicating that N₂O does not form at 77 K. Therefore the rapid increase in partial pressure of N₂O at 105 K (Figure 4) is due to reaction of NO to form N₂O, and not due to desorption of N₂O which formed during the initial NO beam exposure at 77 K.

Another possible mechanism for N₂O formation from NO is via a dimer precursor mechanism.⁸ This mechanism has been proposed for the reaction of adsorbed NO to form N₂O on other transition metal surfaces. In the spectrum in Figure 7, there is no observed weakening of the N=O bond as the NO coverage is increased, or appearance of an intermolecular NO-NO vibration, indicating that no dimer species has formed at 77 K.

IV. CONCLUSIONS

Adsorption of NO on a Au/Ni(111) surface alloy with 0.24 ML Au has been studied using vibrational spectroscopy, HREELS. Two species of NO, with N=O stretch frequencies of 1630 and 1860 cm^{-1} have been observed. These frequencies are higher than those observed for NO adsorbed on Ni(111), and this observation is rationalized by a reduced energetic overlap between the Ni d-band and the LUMO of NO that results from the presence of Au in the Au/Ni(111) surface alloy. In addition, no N_2O or $(\text{NO})_2$ dimer species is observed in the spectra, indicating that the production of N_2O observed between 95 – 120 K does not occur via the pre-formation of a $(\text{NO})_2$ dimer or N_2O at the surface at 77 K.

The reaction between NO and CO was attempted, by varying the exposures of both NO and CO, and the order in which they were exposed to the Au/Ni(111) surface alloy. The only observed reaction was the production of N_2O from adsorbed NO, as demonstrated by control experiments.

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CHAPTER 5 - Attempted Epoxidation of C₂H₄ by Molecular O₂ on Au/Ni(111) Surface Alloy

I. INTRODUCTION

The epoxidation of unsaturated hydrocarbons is a class of chemical reactions that are extremely important to industrial chemical processes and manufacturing. In 2004, 3.7 million metric tons of ethylene oxide and 1 million metric tons of propylene oxide were produced by epoxidation of ethylene (C₂H₄) and propylene (C₃H₆), respectively.¹

Ethylene epoxidation is carried out on supported Ag catalysts.² Despite heavy usage since its discovery in 1931, the mechanism by which Ag catalyzes the epoxidation remained largely unknown until very recently. It is now known that atomic oxygen, absorbed near the surface of the Ag catalyst, is responsible for the epoxidation reaction. Furthermore, the use of promoters that withdraw electronic charge from the surface (such as Cl) cause the atomic oxygen to preferentially attack the C=C bond, leading to higher selective formation of ethylene oxide, and less combustion.²

Propylene epoxidation is carried by either the chlorohydrin or Halcon (hydroperoxide) processes. Neither process uses a heterogeneous catalyst.^{3,4} Both processes suffer from serious problems; the chlorohydrin process produces large amounts of chlorinated organic waste compounds, while the Halcon process involves production of large amounts of by-products, and hence requires heavy capital investment in equipment to isolate the by-products. Recent work by Toso Co. Ltd. has yielded a supported Pd catalyst for propylene epoxidation, which eliminates both of these problems.^{3,4}

A more recently discovered heterogeneous catalyst for propylene epoxidation is supported Au nanoparticles.⁴ Au, long thought to be catalytically inert, was discovered to be an active catalyst for CO oxidation at temperatures as low as 200 K.⁵ This discovery by Haruta in 1989 sparked a flood of research into the ability of Au and supported Au nanoparticles to act as a catalyst. In 1998, Hayashi et. al. discovered that Au nanoparticles supported on TiO₂ were able to catalyze the epoxidation of propylene using H₂ and O₂. Their proposed mechanism involved reaction of an activated molecular oxygen adsorbate with co-adsorbed propylene to form propylene oxide.⁴

Since the Au/Ni(111) surface alloy has been observed to have similar catalytic behavior as supported Au nanoparticles towards catalytic CO oxidation, it was proposed that similar catalytic activity of the Au/Ni(111) surface alloy might exist for epoxidation reactions. This chapter reports on the attempted epoxidation of ethylene over a Au/Ni(111) surface alloy between 77 and 300 K.

II. EXPERIMENTAL

The experimental apparatus has been described extensively elsewhere⁶ and in Chapter 1. Au was deposited onto the Ni(111) surface, and its coverage measured as described in Chapter 1. High resolution electron-energy loss spectroscopy (HREELS) confirmed that the prepared Au/Ni(111) surface alloy was clean of all contaminants. An impact energy of 6.4 eV was used for all reported spectra.

A 2% C₂H₄/He mixture was directed at the Au/Ni(111) surface alloy using the molecular beam system as described in Chapter 2. Unless stated otherwise, the small beam hole was used for the exposures of 2% C₂H₄/He. This procedure reduced the background pressure of C₂H₄ in the chamber, and hence any reactions that might occur

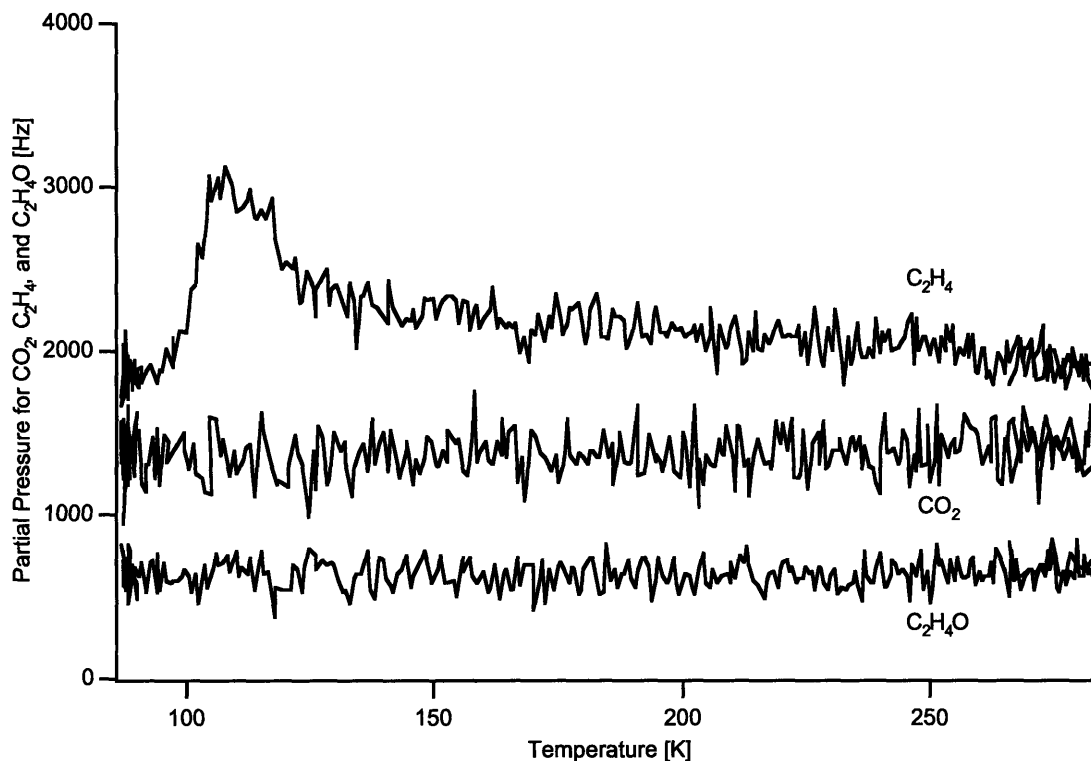


Figure 1. Partial pressures of CO_2 , $\text{C}_2\text{H}_4\text{O}$ and C_2H_4 as a 0.18 ML Au/Ni(111) surface alloy with a molecular O_2 saturated layer, exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 5 s, is heated at 2 K/s from 77 to 300 K.

on the back face of the crystal or other surfaces in the chamber. For the experiments in which HREELS was measured, the use of the large beam hole ensured a uniform coverage of C_2H_4 on the surface. All molecular beam exposures were performed with the crystal in the “TDS” position (described in Chapter 1), with the nozzle at room temperature and a stagnation pressure of 20 psia.

The partial pressures of CO_2 , $\text{C}_2\text{H}_4\text{O}$ and C_2H_4 are monitored by the QMS at masses 44, 29, and 27 respectively. For CO_2 and $\text{C}_2\text{H}_4\text{O}$, these masses correspond to the mass of the majority species observed after electron impact ionization. For C_2H_4 , the mass 27 species produced from dissociative electron impact ionization is 66% of the primary species at mass 28. However, mass 27 is chosen to eliminate the background partial pressure of CO (mass 28) from the partial pressure measurements of C_2H_4 .⁷

III. RESULTS and DISCUSSION

A Au/Ni(111) surface alloy with 0.18 ML Au is exposed to a 10% O₂/Ar beam for 5 s, producing a saturated layer of molecular O₂.⁸ The surface is then exposed to a 2% C₂H₄/He beam for 5 s. The partial pressures of C₂H₄, C₂H₄O and CO₂ are then monitored as the surface is heated at 2 K/s from 77 to 300 K. The results are presented in Figure 1. Rapid increase in the partial pressure of C₂H₄ is observed at 110 K, indicating that desorption occurs rapidly at this temperature. No change in the partial pressure of CO₂ or C₂H₄O is observed. This suggests that under these conditions, the molecular oxygen adsorbed at the Au/Ni(111) surface alloy does not react with C₂H₄ to produce either C₂H₄O or CO₂.

A possible reason that no reaction is observed under the conditions of Figure 1 is that the coverage of C₂H₄ at the surface is not high enough. To test this, a Au/Ni(111) surface alloy with 0.18 ML Au is exposed to a 10% O₂/Ar beam for 5 s, producing a saturated layer of molecular O₂. The surface is then exposed to a 2% C₂H₄/He beam for 50 s. Figure 2 presents the results when the partial pressures of C₂H₄, C₂H₄O and CO₂ are monitored as the surface is heated at 2 K/s from 77 to 300 K. A rapid increase in the partial pressure of C₂H₄ at 110 K indicates C₂H₄ desorption occurs rapidly at this temperature. Between 130 and 250 K, the partial pressure of C₂H₄ is constant, but higher than the background level, indicating that slow desorption of C₂H₄ occurs in this temperature range. There is no change in the partial pressure of CO₂ or C₂H₄O at any temperature, indicating that no reaction occurs. The partial pressure of C₂H₄ at 110 K is 50% larger than the C₂H₄ partial pressure at 110 K in Figure 1, indicating that increasing the exposure of the 2% C₂H₄/He beam from 5 to 50 s increased the coverage of C₂H₄ at

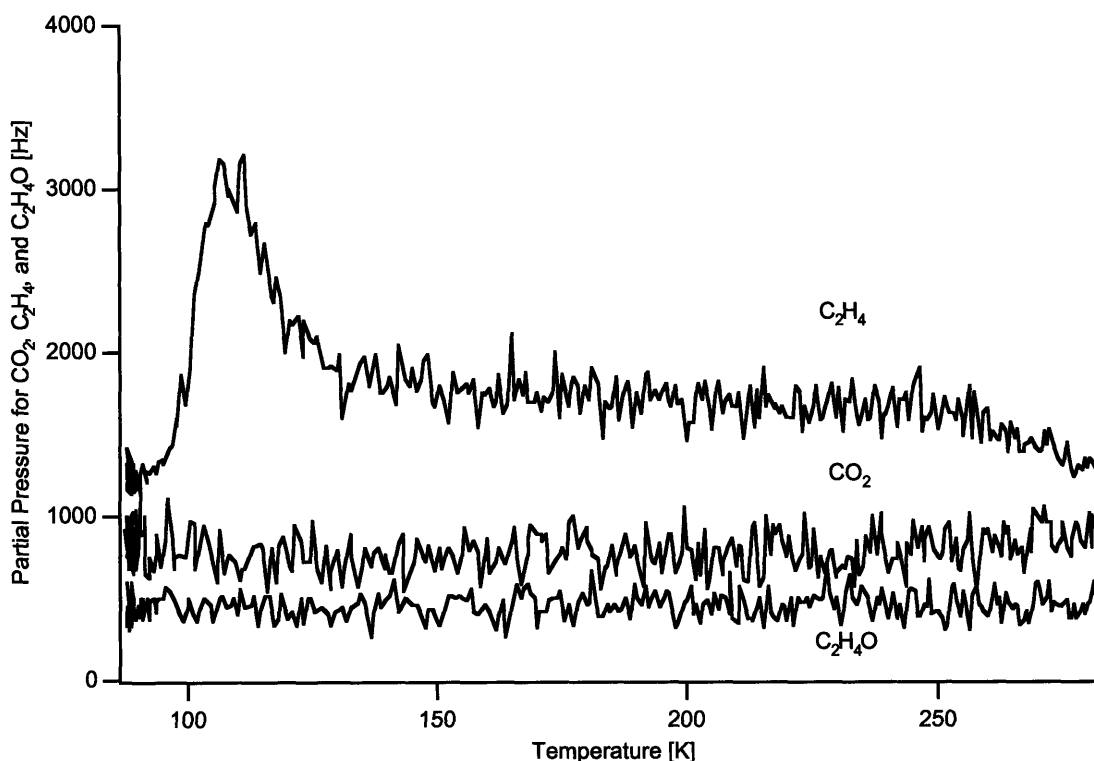


Figure 2. Partial pressures of CO_2 , $\text{C}_2\text{H}_4\text{O}$ and C_2H_4 as a 0.18 ML Au/Ni(111) surface alloy with a molecular O_2 saturated layer, exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 50 s, is heated at 2 K/s from 77 to 300 K.

the surface. However, the higher coverage of C_2H_4 did not cause any reaction to be observed.

The reaction is also attempted by increasing the exposure to the 10% O_2/Ar beam. A 0.18 ML Au/Ni(111) surface alloy is exposed to a 10% O_2/Ar beam for 10 s. This is twice the exposure required to create a saturated layer of molecularly chemisorbed O_2 . The surface is then exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 5 s. The partial pressures of C_2H_4 , $\text{C}_2\text{H}_4\text{O}$ and CO_2 as the surface is heated at 2 K/s from 77 to 300 K are reported in Figure 3. As in the previous experiments, a rapid increase in the partial pressure of C_2H_4 occurs at 110 K, indicating that C_2H_4 desorbs rapidly at this temperature. No change in the partial pressures of either CO_2 or $\text{C}_2\text{H}_4\text{O}$ is observed, indicating that no reaction has occurred.

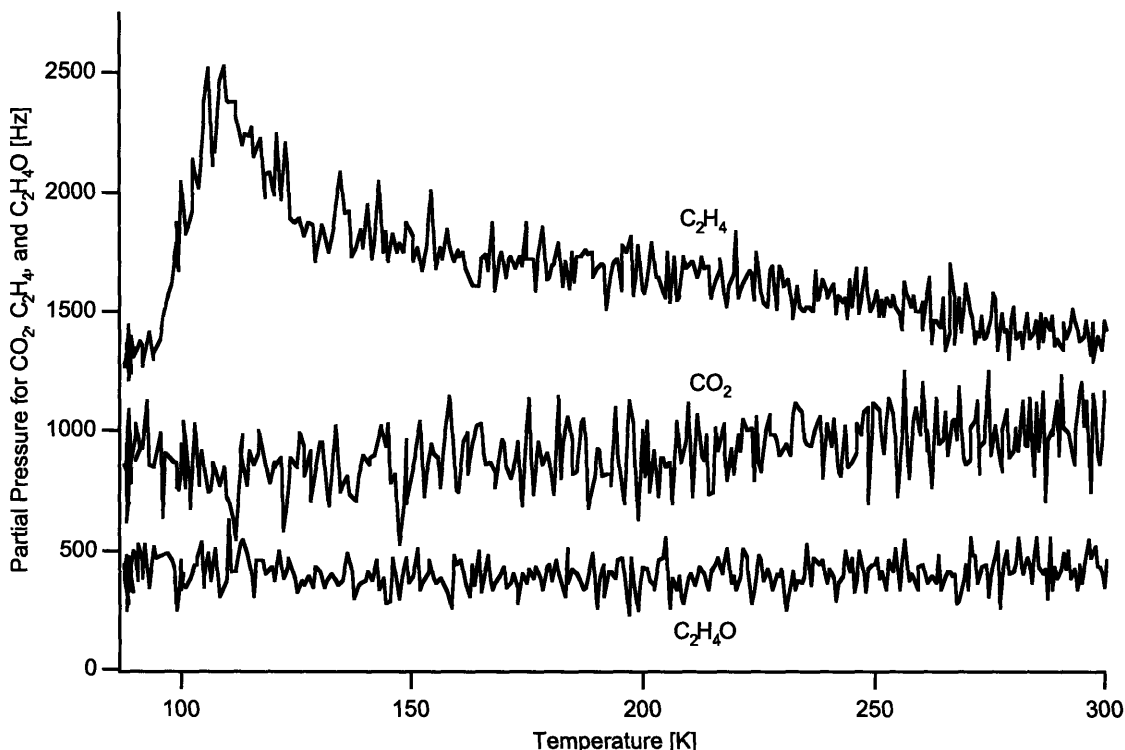


Figure 3. Partial pressures of CO_2 , $\text{C}_2\text{H}_4\text{O}$ and C_2H_4 as a 0.18 ML Au/Ni(111) surface alloy, first exposed to a 10% O_2/Ar beam for 10 s, then exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 5 s. is heated at 2 K/s from 77 to 300 K.

Another attempt of the reaction involves reducing the exposure of the surface to the 10% O_2/Ar beam. If in the above experiments molecularly chemisorbed oxygen is blocking C_2H_4 molecules from adsorbing directly to the metal surface (as opposed to atop the oxygen layer), then reduction of the exposure to the 10% O_2/Ar beam should reduce the coverage of molecular oxygen at the surface, and create metal atom sites for C_2H_4 adsorption. Adsorption of C_2H_4 onto metal atoms could be critical for the reaction, as has been shown previously for hydrogenation of C_2H_4 at Ni(111) surface. C_2H_4 undergoes rehybridization when it chemisorbs on Ni(111), forming a sigma bond between each carbon atom and the surface, concomitant with a decrease in the $\text{C}=\text{C}$ bond order from 2 to 1.^{9,10,11} C_2H_4 rehybridization has been observed to be a critical step in the hydrogenation of C_2H_4 – the reaction does not occur for C_2H_4 physisorbed on Ni(111).¹²

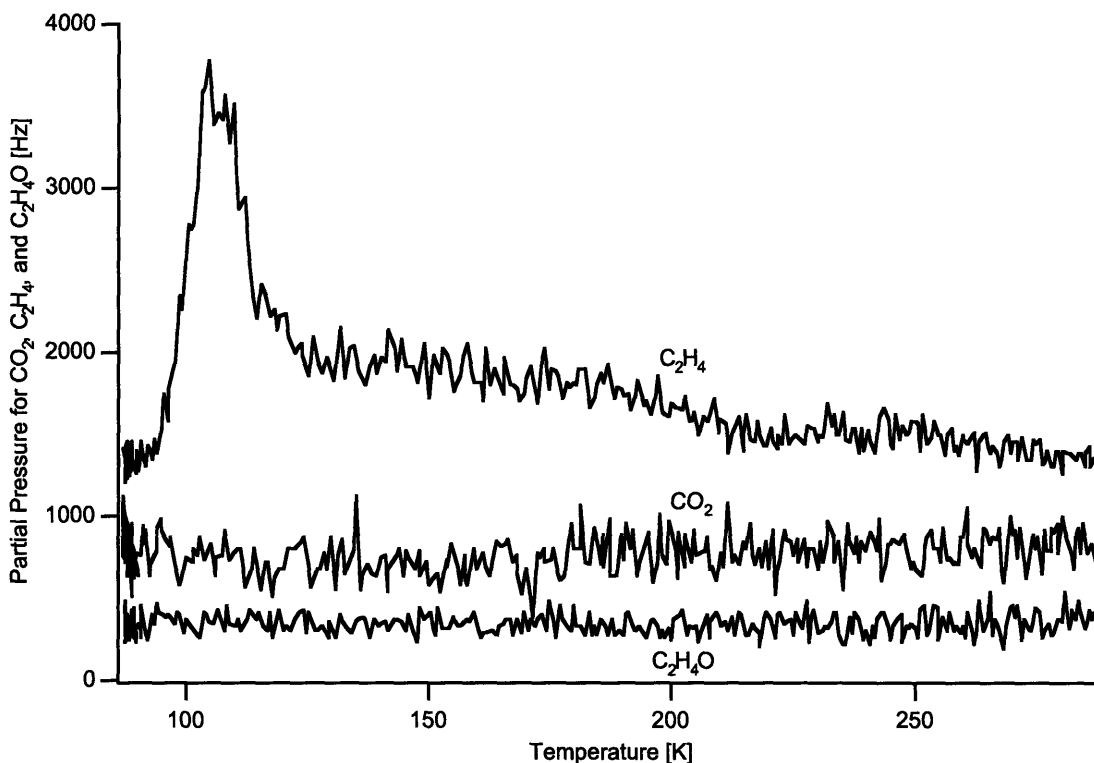


Figure 4. Partial pressures of CO₂, C₂H₄O and C₂H₄ as a 0.18 ML Au/Ni(111) surface alloy, first exposed to a 10% O₂/Ar beam for 1 s, then exposed to a 2% C₂H₄/He beam for 5 s. is heated at 2 K/s from 77 to 300 K.

Therefore, in the reaction between C₂H₄ and molecularly chemisorbed O₂, a decrease in the amount of adsorbed oxygen was attempted, in order to increase the number of metal atom sites available for C₂H₄ adsorption and rehybridization.

A decrease in the oxygen coverage is attempted by exposure of a 0.18 ML Au/Ni(111) surface alloy to a 10% O₂/Ar beam for 1 s. The surface is then exposed to a 2% C₂H₄/He beam for 5 s. The partial pressures of C₂H₄, C₂H₄O and CO₂ are then monitored as the surface is heated at 2 K/s from 77 to 300 K. The results are presented in Figure 4. No change in the partial pressures of C₂H₄O or CO₂ is observed, indicating that the reaction did not occur. The partial pressure of C₂H₄ increases rapidly at 110 K, indicating rapid desorption of C₂H₄ occurs at 110 K. The partial pressure of C₂H₄ is

above the background level between 130 and 200 K, indicating that slow desorption of C_2H_4 occurs in this temperature range.

The partial pressure scale in Figure 4 is the same as those in Figures 1 and 2. By comparison of the maximum in desorption of C_2H_4 observed at 110 K in each of these figures, the relative coverages of C_2H_4 on the surface under each set of conditions can be inferred. As stated above, the maximum desorption of C_2H_4 at 110 K in Figure 2 is 50% larger than that of Figure 1. The maximum desorption of C_2H_4 in Figure 4 is 37% larger than that in Figure 2. This observation suggests that of the conditions employed, decreasing the exposure of the 10% O_2/Ar beam to 1 s had the greatest effect in increasing the C_2H_4 coverage at the surface.

If $\text{C}_2\text{H}_4\text{O}$ or CO_2 formation occurs during exposure of the 2% $\text{C}_2\text{H}_4/\text{He}$ beam to the O_2 saturated $\text{Au}/\text{Ni}(111)$ surface alloy, it could be observed by monitoring the partial pressure of mass 44 as the 2% $\text{C}_2\text{H}_4/\text{He}$ beam is exposed to the O_2 saturated $\text{Au}/\text{Ni}(111)$ surface alloy. Additionally, if a reaction occurs between the 10% O_2/Ar beam and C_2H_4 adsorbed on a $\text{Au}/\text{Ni}(111)$ surface alloy, the product could be observed by monitoring mass 44 during the exposure to the 10% O_2/Ar beam. However, these experiments were not performed. Therefore, for the reaction conditions attempted for the data in Figures 1 – 4, it is possible that a reaction occurred at 77 K during the beam exposures.

The shape of the partial pressure of C_2H_4 as a function of temperature in Figures 1 – 4 is similar to that previously observed for desorption of C_2H_4 physisorbed atop 1 ML H atoms on a $\text{Ni}(111)$ surface.¹³ The physisorbed nature of adsorbed C_2H_4 under these latter conditions was determined spectroscopically, using HREELS. No vibrational mode corresponding to the stretch of a C-Ni bond was observed. In addition, the C-H

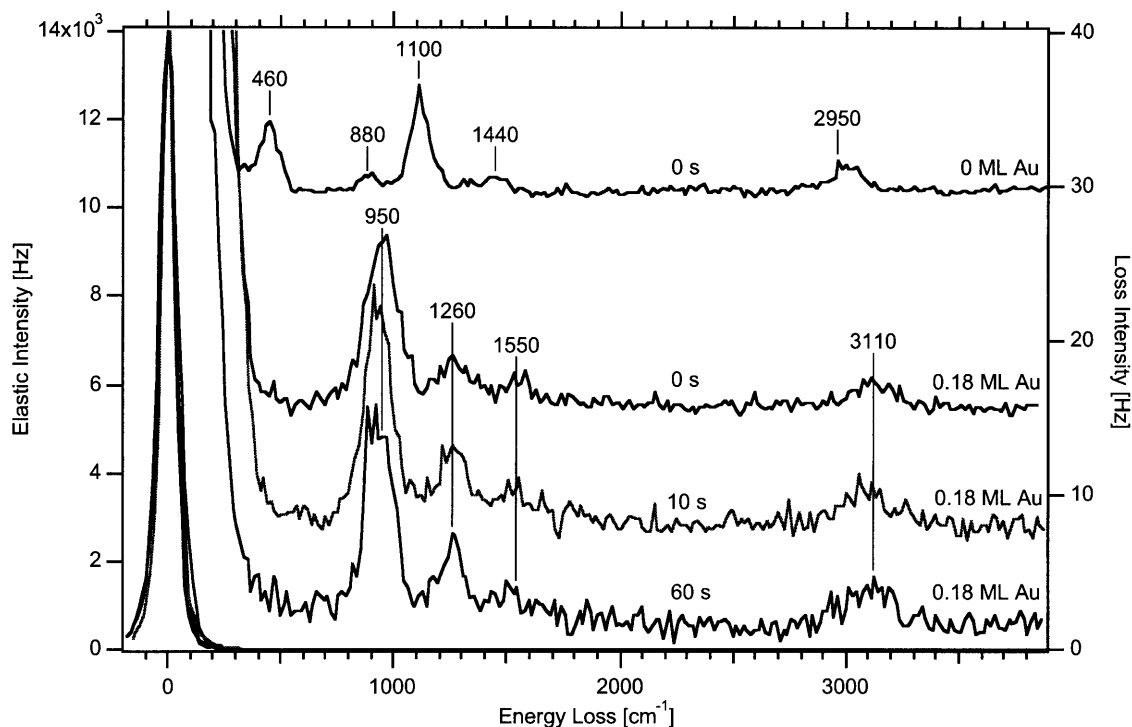


Figure 5. HREELS spectra of a Ni(111) surface and a 0.18 ML Au/Ni(111) surface alloy at 77 K, exposed to a 2% C₂H₄/He beam for 120 s. The spectra measured on the 0.18 ML Au/Ni(111) surface alloy are measured for increasing exposure to 2×10^{-8} torr O₂, and are labeled with the duration of this exposure. Spectra are measured on specular with a resolution of 70 cm⁻¹ FWHM.

stretching modes were observed to have vibrational frequencies very close to those of the gas phase value (3100 cm⁻¹). In contrast, when C₂H₄ chemisorbs at a Ni(111) surface, vibrational modes corresponding to the C-Ni stretch are observed, in addition to a lowering in frequency of the C-H stretch modes.^{9,11} Therefore, C₂H₄ was identified as physisorbing atop 1 ML of H atoms on Ni(111).¹³ The similarity in the functional form of the partial pressures of C₂H₄ desorbing from an oxygen coverage Au/Ni(111) surface alloy, and the partial pressure of physisorbed C₂H₄ desorbing from 1 ML of H atoms on Ni(111) suggests that under the conditions used in this chapter, C₂H₄ physisorbs atop molecularly chemisorbed oxygen on a Au/Ni(111) surface alloy with 0.18 ML Au.

In order to determine the nature of C_2H_4 adsorption at the Au/Ni(111) surface alloy, a HREELS vibrational spectrum of a Au/Ni(111) surface alloy with 0.18 ML Au is measured at 77 K, after exposure to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 120 s. The results are presented in Figure 5. For comparison, an HREELS vibrational spectrum of a Ni(111) surface at 77 K after exposure to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 120 s is shown in Figure 5 (top trace). The features at 460, 880, 1100, 1440 and 2950 cm^{-1} in Figure 5 observed for C_2H_4 adsorbed on Ni(111) have been previously assigned to the surface-molecule stretch, the CH_2 twist, the CH_2 wag, the CH_2 scissors and the CH_2 stretch modes respectively.^{9,11,13} For C_2H_4 adsorbed on the Au/Ni(111) surface alloy with 0.18 ML Au, the feature at 3110 cm^{-1} has been previously assigned to the unresolved CH_2 symmetric and antisymmetric stretches of physisorbed ethylene adsorbed on 1 ML H atoms on Ni(111).¹³ In addition, the lack of observed features between $400 - 600\text{ cm}^{-1}$ suggests that there are no chemical bonds between adsorbed C_2H_4 and the surface, suggesting that C_2H_4 physisorbs at a 0.18 ML Au/Ni(111) surface alloy at 77 K. The features at 1260 and 1550 cm^{-1} have been observed previously for C_2H_4 physisorbed on 1 ML H atoms on Ni(111), but no assignment was made.¹³ They are tentatively assigned as the CH_2 rock or scissors, and the $\text{C}=\text{C}$ stretch modes, respectively, based on comparison to the gas phase values.

The feature at 950 cm^{-1} in Figure 5, for C_2H_4 adsorbed on a Au/Ni(111) surface alloy with 0.18 ML Au, was observed previously when C_2H_4 was adsorbed on 1 ML H atoms on Ni(111). However, in that system, the 950 cm^{-1} feature was attributed to the H-Ni stretch of H atoms adsorbed in 3-fold hollow sites.¹³ There are no adsorbed H atoms on the Au/Ni(111) surface alloys in Figure 5, precluding the assignment of the 950 cm^{-1} feature to a H-Ni stretching mode. The 950 cm^{-1} feature is similar in frequency to the gas

phase frequencies of the two CH_2 rocking modes that have values of 949 and 943 cm^{-1} .¹⁴ Therefore, the 950 cm^{-1} feature is tentatively assigned to a CH_2 rocking mode of physisorbed C_2H_4 .

The observation that C_2H_4 has a weaker interaction with the Au/Ni(111) surface alloy than with the Ni(111) surface is the same trend as observed for O_2 , CO and NO on the Au/Ni(111) surface alloy. As in those cases, it is proposed that the Ni d-band, which is lowered in energy as a result of alloying of Au into the Ni(111) surface, has less energetic overlap with the antibonding LUMO of C_2H_4 . The reduced overlap results in less charge transfer between the Ni d-band and the LUMO of C_2H_4 , preventing the formation of chemical bonds between C_2H_4 and the surface.

In order to determine whether C_2H_4 reacts with oxygen, a 0.18 ML Au/Ni(111) surface alloy at 77 K is exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 120 s. The surface is then exposed for increasing duration to a background gas of O_2 at 2×10^{-8} torr. The lower traces of Figure 5 represent HREELS measured after exposures of O_2 for 10 and 60 s respectively. Within the constraints of the resolution of the spectra (70 cm^{-1} FWHM) and the signal-to-noise ratio, the surface is unchanged by either duration of oxygen exposure. There is no decrease in the intensity of the features assigned to physisorbed C_2H_4 , nor are there any new features. This indicates that at 77 K, a surface containing C_2H_4 physisorbed to the metal atoms of a 0.18 ML Au/Ni(111) does not react with gas phase O_2 molecules.

IV. CONCLUSION

Under the current set of conditions, C_2H_4 adsorbed on a Au/Ni(111) surface alloy with 0.18 ML Au does not react with co-adsorbed molecular oxygen in the temperature

range 77 to 300 K. The reaction has been attempted by varying the coverage of both C_2H_4 and O_2 , as well as the order in which these species are exposed to the surface.

When a Au/Ni(111) surface alloy with 0.18 ML Au at 77 K is exposed to a 2% $\text{C}_2\text{H}_4/\text{He}$ beam for 120 s, vibrational spectroscopy indicates that C_2H_4 physisorbs at the surface – neither the rehybridization of C_2H_4 bonds, or the formation of chemical bonds between the adsorbate and surface is observed. When C_2H_4 physisorbed at a Au/Ni(111) surface alloy with 0.18 ML Au is exposed to 1×10^{-8} torr O_2 for up to 60 s, there is no observed change in the vibrational spectrum, indicating that O_2 neither reacts with physisorbed C_2H_4 nor adsorbs at the surface.

Physisorption of C_2H_4 at the Au/Ni(111) surface alloy, as opposed to chemisorption on Ni(111), follows the same trend as the weakened interaction between O_2 , CO and NO with the Au/Ni(111) surface alloy as compared to the Ni(111) surface (Chapters 2 – 4). It is proposed that the weakened interaction of C_2H_4 with the Au/Ni(111) surface arises from the lowered Ni d-band that results when Au is alloyed into the Ni(111) surface.

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CHAPTER 6 - Attempted Measurements of Vibrational Modes of H adsorbed on Au/Ni(111) Surface Alloys

I. INTRODUCTION

In 1994, Holmblad et. al. observed interesting behavior of Au/Ni(111) surface alloys towards D_2 adsorption.¹ The experimental technique involved measuring the thermal desorption spectra (TDS) of a series of Au/Ni(111) surface alloys, after saturating the surface with D_2 . It was observed that as the Au coverage of the Au/Ni(111) surface alloy increased, the total amount of adsorbed D_2 decreased. In addition to this decrease, a new, low temperature D_2 desorption (180 - 220 K) feature was observed for Au/Ni(111) surface alloys with 0.08 ML or higher Au, which is not present on a Ni(111) surface exposed to D_2 or H_2 . Holmblad et. al. attributed this feature to recombination of D atoms that were bound to Ni three-fold hollow sites that have two Au atom next nearest neighbors. A similar feature, however, had been observed on the Ni(111) surface that had been exposed to gas phase H atoms, and was shown to be the result of the recombination of bulk H atoms as they emerged onto the surface.²

The identification of bulk H absorbed in a Ni(111) surface, and its subsequent migration to the surface where it recombines and desorbs as H_2 , was demonstrated by Johnson et. al. in 1991.² The initial discovery was made when a Ni(111) surface was exposed to H atoms. This surface was then heated to 600 K, while the partial pressure of H_2 in the chamber was monitored. A rapid increase in the partial pressure of H_2 gas was observed between 180 – 220 K. This low temperature increase in the partial pressure is not observed when a Ni(111) surface is exposed to H_2 molecules. Furthermore, increasing the exposure of H atoms to the Ni(111) surface causes an increase in the

partial pressure of H_2 observed between 180 – 220 K. In contrast to the partial pressure increase attributed to recombination of surface H atoms (observed at 380 K), the partial pressure increase between 180 – 220 K does not saturate with increasing H atom exposures. This observation strongly suggested that the H atoms responsible for this low temperature increase in the partial pressure of H_2 are not bound to the surface, but rather are absorbed in the bulk.

In order to identify the species of H atoms that is responsible for the partial pressure increase at low temperature, high resolution electron energy loss spectroscopy (HREELS), a vibrational spectroscopy, was employed. Spectra measured after exposure of the Ni(111) surface to H atoms revealed a new vibrational mode at 800 cm^{-1} , not present after exposure of Ni(111) to H_2 gas. The vibrational mode at 800 cm^{-1} disappears upon heating the surface to 220 K. This disappearance coincides with the low temperature (180 – 220 K) H_2 partial pressure increase observed when a Ni(111) surface, exposed to H atoms, is heated between 77 and 600 K. Therefore, the mode at 800 cm^{-1} was assigned as arising from the species that is responsible for the H_2 partial pressure increase observed between 180 – 220 K.

HREELS probes the vibrational modes at a surface using a monoenergetic beam of electrons. Due to the small penetration depth of these electrons, HREELS was generally considered to be limited to observation of surface species. However, the penetration depth is non-zero. Furthermore, the penetration depth can be varied by variation of the energy of the electron beam.³ For the range of energies typically employed in HREELS (3 – 20 eV), increasing the energy of the electrons reduces the penetration depth. In fact, the penetration depth of the electrons is inversely proportional

to the quadratic of the electron energy. If the intensity of the loss feature observed at 800 cm^{-1} decreased as the inverse quadratic of the impact energy of the electron beam, it would confirm the identification of this species of H atoms as being absorbed in the bulk. Johnson et. al. performed this measurement, and observed that indeed, the intensity of the 800 cm^{-1} decreased as the inverse quadratic of the energy of the electron beam, confirming the identity of the 800 cm^{-1} feature as belonging to H atoms absorbed in bulk sites of the Ni(111) crystal.

The idea that then arose was the possibility that the low temperature D_2 recombination and desorption observed on the Au/Ni(111) surface alloy was actually from bulk D recombination – implying that the deposited Au had lowered the barrier to bulk absorption sufficiently to allow D_2 molecules to dissociatively absorb into the subsurface sites. An ideal way to test this hypothesis would be to apply the HREELS technique described above for identification of bulk H in Ni(111) to the H/Au/Ni(111) system.

This chapter presents the experimental attempts to observe the vibrational modes of H atoms adsorbed on Au/Ni(111) surface alloys. The goal was to determine whether the low temperature H_2 TDS feature observed on the Au/Ni(111) surface alloy arose from bulk H recombination or surface H atom recombination. The former would imply that the deposited Au had lowered the barrier to bulk absorption sufficiently to allow H_2 molecules to absorb into the subsurface sites. Once the vibrational modes of H atoms adsorbed at the Au/Ni(111) surface alloy are identified, it is then possible to measure their intensity as a function of impact energy, which would provide strong evidence for discrimination between bulk absorption and surface adsorption.

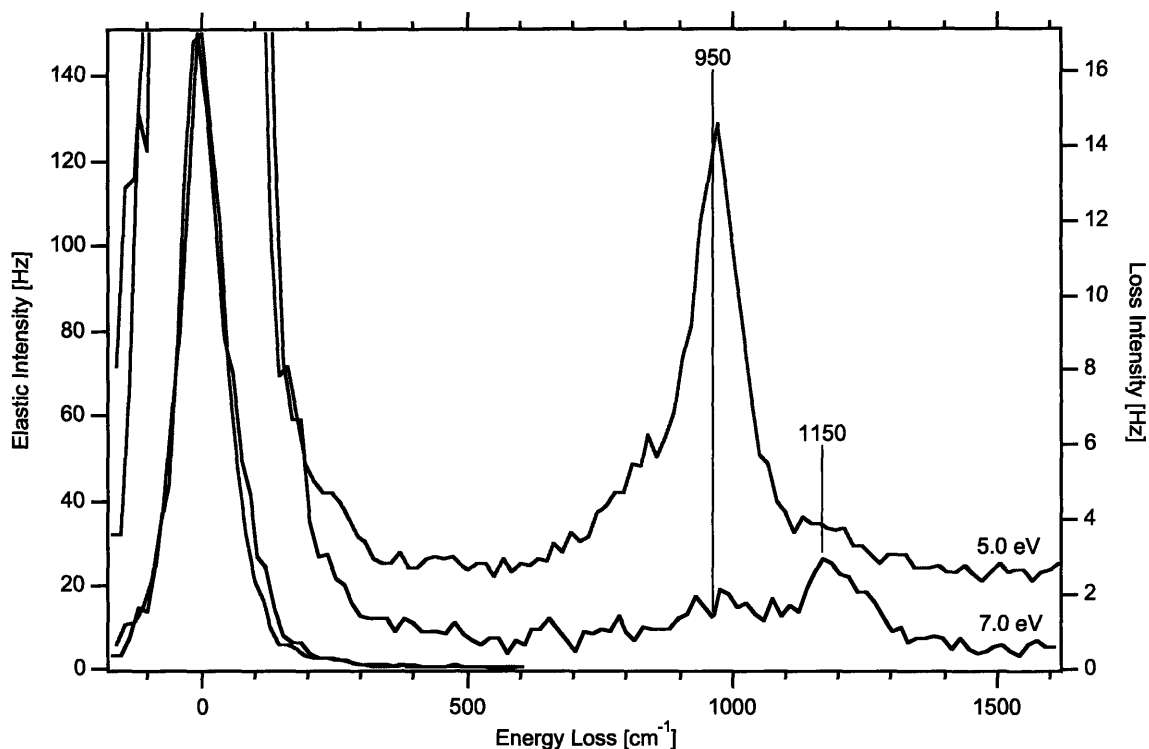


Figure 1. HREELS spectra of 1 ML H atoms on a Ni(111) surface. Each spectra is labeled with the impact energy used in its measurement. Both spectra are normalized to an elastic intensity of 150 Hz, are collected 10° off the specular angle, with a resolution of 91 cm^{-1} FWHM.

II. EXPERIMENTAL

The experimental apparatus has been described extensively elsewhere⁴ and in Chapter 1. Au was deposited onto the Ni(111) surface, and its coverage measured as described in Chapter 1. High resolution electron-energy loss spectroscopy (HREELS) confirmed that the prepared Au/Ni(111) surface alloy was clean of all contaminants. All spectra are recorded at 77 K. H_2 was exposed to the surface by backfilling the chamber with 2×10^{-6} torr H_2 gas as the crystal cooled from 600 to 77 K.

III. RESULTS and DISCUSSION

Figure 1 presents the vibrational spectra (HREELS) of the Ni(111) surface saturated with H atoms (1 ML H). Both spectra are measured 10° off the specular angle,

with impact energies of 5.0 and 7.0 eV, respectively. The spectrum measured with an impact energy of 5.0 eV has an intense loss feature at 950 cm^{-1} , with a shoulder at 1150 cm^{-1} . In contrast, the spectrum measured with an impact energy of 7.0 eV has a loss feature at 1150 cm^{-1} with weak intensity, and a shoulder at 950 cm^{-1} .

The spectra in Figure 1 demonstrate an important principle of HREELS. The impact energy of the incident electrons can have a profound impact on the intensities of the observed loss features.⁵ For the spectra in Figure 1, increasing the impact energy from 5.0 to 7.0 eV has changed the relative intensities of the 1150 cm^{-1} and 950 cm^{-1} features. In addition, increasing the impact energy from 5.0 to 7.0 eV reduces the total intensity of the 1150 and 950 cm^{-1} features in Figure 1. The total intensity of the 950 and 1150 cm^{-1} features in the spectrum collected with an impact energy of 7.0 eV is $\sim 35\%$ the total intensity of the 950 and 1150 cm^{-1} features in the spectrum collected with an impact energy of 5.0 eV. The practical consequence of the reduction in intensity as a function of impact energy is that when HREELS is used to search for new species at a surface, it is necessary to vary the impact energy to maximize the intensity.

For HREELS measured of saturated H atom layers on the Au/Ni(111) surface alloy, the impact energy is varied in an attempt to maximize the loss features corresponding to the H-surface stretch. Figure 2 presents HREELS measured on Au/Ni(111) surface alloys saturated with H atoms (1 ML H), in which the impact energy is increased from 3.5 to 10.0 eV. The saturation coverage of H atoms is prepared by exposing each surface to 2×10^{-6} torr H_2 gas while the surface cools from 600 to 77 K. No loss feature is observed in any of the spectra.

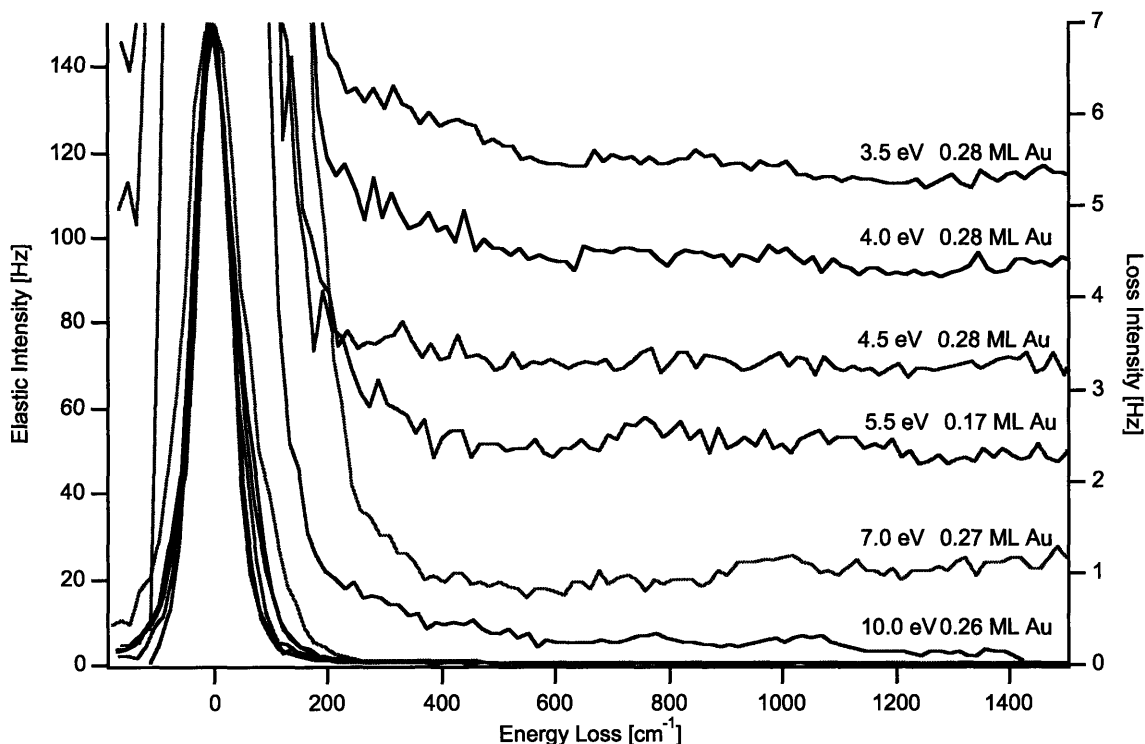


Figure 2. HREELS spectra of Au/Ni(111) surface alloys saturated with H. Each spectra is labeled with the impact energy used in its measurement. All spectra are normalized to an elastic intensity of 150 Hz, are collected 10° off the specular angle. The spectra collected with an impact energy of 7.0 eV has resolution of 121 cm^{-1} FWHM, all other spectra have resolution 84 cm^{-1} FWHM.

In Chapter 1 of this thesis, the partial pressure of H_2 was monitored as H atom saturated Au/Ni(111) surface alloys were heated from 77 to 500 K. These experiments demonstrated that for the Au coverages of the Au/Ni(111) surface alloys represented in Figure 2 of this chapter, the H atom coverage is between 0.3 to 0.5 ML. This amount of H atoms at the surface is well above the detection limit for H atoms adsorbed on a Ni(111) surface. Since the coverage of H atoms at the Au/Ni(111) surface alloy is above the typical detection limit of HREELS, the lack of detection must arise from another reason.

One possible rationalization for the lack of observed H-surface loss features in the spectra in Figure 2 is that the cross section for excitation of the H-surface loss is greatly

reduced when Au is alloyed into the Ni(111) surface. The spectra in Figure 2 are collected 10° off the specular angle. In this scattering geometry, the mechanism of excitation of vibrations is primarily impact scattering. An important factor in determining the efficacy of this mechanism is the electron-phonon coupling term at the surface.⁵ It is well established that the electron-phonon coupling term is strong in Ni, and weak in Au. If the electron-phonon coupling of the Au/Ni(111) surface alloy is significantly reduced as compared to the Ni(111) surface, a reduction of the cross section for excitation of the H-surface stretch via the impact mechanism should be observed.⁵ The spectra in Figure 2, in which no loss feature is observed, would suggest that the cross section for excitation of the H-surface stretch is low, and by extension, the electron-phonon coupling of the Au/Ni(111) surface alloy is weak.

Another possible explanation for the lack of observed loss features in Figure 2 is that the H-surface stretch may be excited by the dipole mechanism.⁶ The selection rule for dipole excitation of vibrational modes is discussed briefly in Chapter 2 of this thesis. Briefly, excitation of a vibrational mode at a metal surface requires a change in the adsorbate's dipole moment normal to the surface. Vibrational modes which are excited via the dipole mechanism are observed to have intensities which are strongly peaked towards the specular angle. If the H-surface stretch for H atoms adsorbed on the Au/Ni(111) surface alloy are dipole active, measurement of the HREELS at the specular angle should result in a large increase in the intensity of the loss modes.⁷ Figure 3 presents spectra of Au/Ni(111) surface alloys with saturated H atom layers collected at the specular angle. The spectra are collected with impact energies of 5.0 and 10.0 eV respectively. The only loss feature observed is at 290 cm^{-1} , previously identified as the

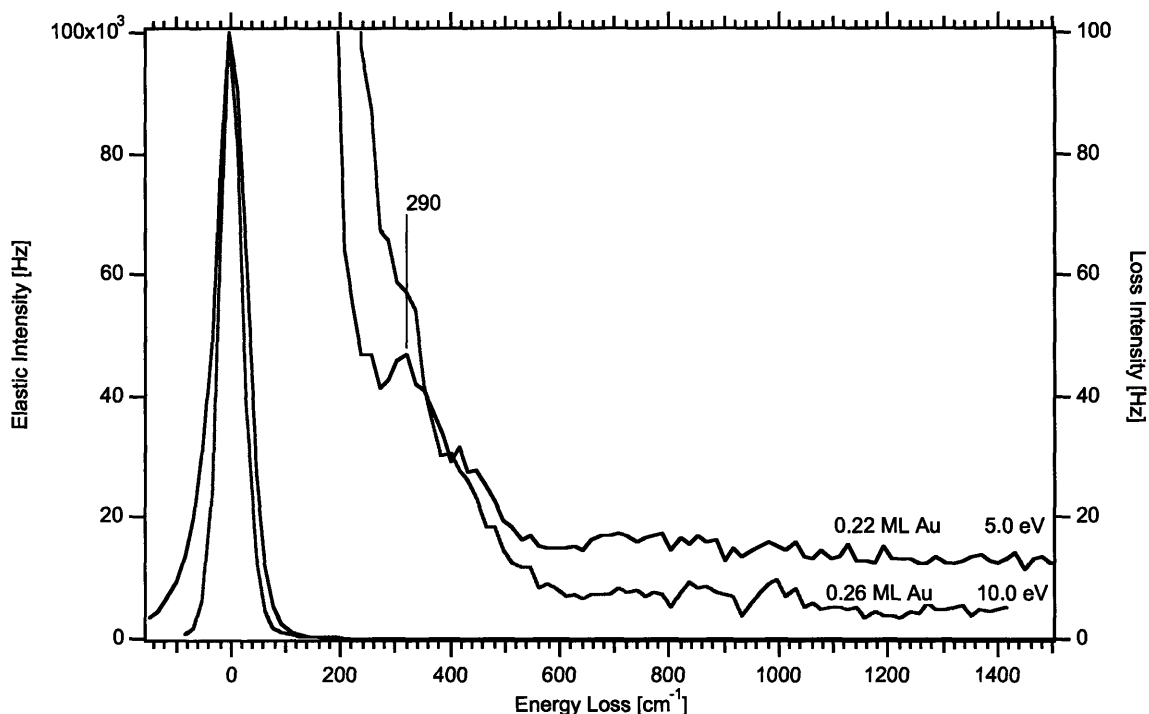


Figure 3. HREELS spectra of Au/Ni(111) surface alloys saturated with H. Each spectra is labeled with the impact energy used in its measurement. Both spectra are normalized to an elastic intensity of 1×10^5 Hz. The spectrum collected with an impact energy of 5.0 eV has resolution of 68 cm^{-1} FWHM, the spectrum with an impact energy of 10.0 eV has a resolution 51 cm^{-1} FWHM.

S_2 phonon. If the H-surface stretch is dipole active, the cross section for excitation is too low for the loss feature to be observed in these experiments.

IV. CONCLUSION

Vibrational spectra (HREELS) of saturated H atom layers on Au/Ni(111) surface alloys were collected for impact energies between 3.5 and 10.0 eV, at off-specular angles. In addition, vibrational spectra of saturated H atom layers on Au/Ni(111) surface alloys were collected at the specular angle for impact energies of 5.0 and 10.0 eV. No loss features are observed under any of the conditions employed. One possible explanation for the lack of observed loss features in spectra measured at off-specular angles is that the electron-phonon coupling on the Au/Ni(111) surface alloy is weak.

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- ³ A. Zangwill, in *Physics at Surfaces* (Cambridge University Press, New York, 1988), p. 20.
- ⁴ K. L. Haug, in *Chemistry* (Massachusetts Instituted of Technology, Cambridge, MA, 1999).
- ⁵ H. Ibach and D. L. Mills, in *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, New York, 1982), p. 102.
- ⁶ W. Ho, R. F. Willis, and E. W. Plummer, *Physical Review B* **21**, 4202 (1980).
- ⁷ H. Ibach and D. L. Mills, in *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, New York, 1982), p. 102.

APPENDIX – List of Data Files**Chapter 1**

Figure 2	Mar3100.a02
Figure 3	May1802.a01
Figure 4	May1802.a01
Figure 5	jul1105.e02, may0505.e01
Figure 6	JUN0405.a01, JUN0405.a02
Figure 8	Jul1602.a03, Jul1602.a04, Jul1602.a05, Jul1602.a06, Jul1602.a07 Jul1602.a08
Figure 9	jul1602.d03
Figure 10	jul1602.d03
Figure 12	jul1602.d03
Figure 13	jul1602.d05, jul1602.d07, jul1602.d08, jul1602.d09, jul1602.d10, jul1602.d11, jul1602.d03
Figure 14	jul1602.d05, jul1602.d07, jul1602.d08, jul1602.d09, jul1602.d10, jul1602.d11, jul1602.d03

Chapter 2

Figure 2	Feb2604.a03, Mar0204.a01, Mar0104.a02
Figure 3	may2305.e03, jul0905.e02
Figure 4	feb2403.e01, feb2703.e01, feb2403.e02, feb2703.e02, feb2703.e03, feb2703.e04, feb2703.e05, feb2703.e06, feb2703.e07
Figure 5	may2605.e03, may2605.e04, may0405.e05, may0505.e04, may1405.e03, may1405.e04, may1405.e05, may1405.e06
Figure 6	may2305.e03, apr2604.e02, apr3004.e02, apr2904.e02, may1305.e05
Figure 7	oct1605.e03, oct2105.e02, oct2105.e03, nov0104.e02
Figure 11	apr3004.e02, apr3004.e04, apr3004.e05
Figure 12	apr2604.e02, apr2604.e04, apr2604.e05
Figure 13	apr2904.e02, apr2904.e04, apr2904.e05
Figure 14	mar3004.d11

Chapter 3

Figure 1	aug0804.d24, aug0804.d21, mar3104.d02
Figure 2	aug0804.d21, aug0804.d24, aug0804.d26, aug0804.d29, aug0804.d16, aug0804.d19, jul0104.d13, jul0104.d15, jul0104.d09, jul0104.d11, jul0904.d03, jul0904.d09
Figure 3	aug0804.d36, aug0804.d39, aug0804.d31, aug0804.d34, aug0804.d11, aug0804.d14, aug0804.d02, aug0804.d08, aug0804.d21, aug0804.d24
Figure 4	oct1405.d06, oct1405.d08
Figure 6	sep2404.e05, may2305.e03
Figure 7	jul1904.e03, jul2204.e01, jul2304.e01, sep2404.e05
Figure 8	jul2904.e02, aug1904.e03, aug1404.e08
Figure 9	jul3004.e03, oct1904.e02, jul3004.e07
Figure 10	aug0804.d03, aug0804.d07, apr1404.d01
Figure 11	aug0804.d37, aug0804.d40, aug0804.d32, aug0804.d35, aug0804.d12, aug0804.d15, aug0804.d03, aug0804.d07,

Figure 13	aug0804.d22, aug0804.d25, aug0804.d27, aug0804.d30, aug0804.d17, aug0804.d20, jul0104.d10, jul0104.d12, jul0104.d14, jul0104.d16, jul0904.d04, jul0904.d10 aug0804.d37, aug0804.d40, aug0804.d32, aug0804.d35, aug0804.d12, aug0804.d15, aug0804.d03, aug0804.d07, aug0804.d22, aug0804.d25, aug0804.d27, aug0804.d30, aug0804.d17, aug0804.d20, jul0104.d10, jul0104.d12, jul0104.d14, jul0104.d16, jul0904.d04, jul0904.d10
Figure 14	dec1205.e03, dec1205.e04, dec1205.e05, dec1205.e06, dec1205.e07, dec1205.e08, dec1205.e09
Figure 15	apr1904.e02, apr1904.e03, apr1904.e04, apr1904.e05
Figure 16	apr2504.e02, apr2504.e03, apr2504.e04, apr2504.e06
Figure 17	jul1704.e01, jul1704.e09, jul1704.e10, jul1704.e11, jul1704.e14
Figure 18	oct1405.d01, oct1405.d03, oct1405.d02, oct1405.d04
Figure 19	oct2205.d01, oct2205.d03, oct2205.d02, oct2205.d04
Figure 20	nov0705.e02
Figure 21	oct1805.d01
Figure 22	oct1805.e01, oct1805.e02, oct1805.e03, oct1805.e04
Figure 23	oct1905.e04, oct1905.e01, oct1905.e02, oct1905.e03
Chapter 4	
Figure 1	feb0905.e04, feb0905.e05, feb0905.e06, feb0905.e07, jan1705.e05
Figure 2	jan0505.d04
Figure 3	jan0505.d05
Figure 4	jan0505.d08
Figure 5	jan0405.d02, jan0505.d02, jan1705.d08, jan1805.d02
Figure 6	jan1205.d04
Figure 7	jan0505.d11
Chapter 5	
Figure 1	jun0804.d01
Figure 2	jun0804.d02
Figure 3	jun0804.d03
Figure 4	jun0804.d04
Figure 5	mar1803.e01, mar1803.e02, mar1803.e03, mar1803.e04
Chapter 6	
Figure 1	mar1703.e01, mar1703.e02
Figure 2	apr0503.e01, apr0503.e02, apr0503.e03, apr0503.e04, apr0503.e05, mar1703.e04, DEC1002.e04, mar1503.e02, mar1503.e03, mar1503.e05, mar1503.e06
Figure 3	apr0203.e07, mar1303.e01, mar1303.e02, mar1303.e03, mar1303.e04