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VIBRATIONAL SPECTROSCOPIC STUDIES OF ADSORBATES
ON BIMETALLIC SURFACES

A Dissertation

by

WILLIAM KEVIN KUHN

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Texas A&M University
in partial fulfillment of the requirements for the degree of

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ABSTRACT

Vibrational Spectroscopic Studies of Adsorbates

on Bimetallic Surfaces. (December 1992)

William Kevin Kuhn, B. S., University of Hawaii;

M.S., University of Hawaii

Chair of Advisory Committee: Dr. D. Wayne Goodman

In this work, well-defined bimetallic surfaces have been studied using carbon monoxide adsorption in conjunction with infrared reflection absorption spectroscopy (IRAS). These studies have indicated that for CO adsorbed on Cu overlayers, the bond between the CO and the Cu adatoms is comprised of both π -backdonation and polarization interaction components. The sum of the contributions from these effects determines the observed bond strength with the observed CO stretching frequency being determined by the relative contributions of the components. In addition, it was determined that IR spectra of adsorbed CO show a remarkable sensitivity to surface structure. Three-dimensional Cu clusters, well-ordered two dimensional Cu islands and isolated Cu atoms are distinctively characterized by their CO IR peaks. In addition, both disorder-order and order-order transitions are observed for the metal overlayers on the single crystal metal substrates. It was also observed that localized segregation and ordering of mixed Co and S overlayers on a Mo(110) substrate occurs upon annealing.

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INTRODUCTION

In the late '60s and early '70s, catalytic systems consisting of a mixture of two different metals began replacing some traditional monometallic catalysts. These bimetallic catalytic systems are superior to the monometallic systems they replaced in terms of stability, selectivity, and/or activity [1]. These improvements can be explained in terms of structural and/or electronic modifications of one or both metals, which generally result in the promotion of the desired reaction or the poisoning of an undesirable side reaction. A typical industrial catalyst will consist of a few atom % of a metal (or metals) dispersed on a support such as alumina. Thus, for industrial bimetallic catalysts, the metal-metal and reactant-metal interactions are often difficult to study due to the intrinsic low metal concentrations and strong metal-support interactions. To simplify the study of bimetallic catalysts, a model system consisting of an ultra-thin metal film deposited on a single-crystal metal substrate at ultra-high vacuum (UHV) conditions is used. Previous studies have shown that these ultra-thin metal overlayers exhibit different structural, electronic, and chemisorptive properties compared to the surfaces of the corresponding bulk metals [2,3]. In this study, infrared reflection absorption spectroscopy (IRAS) was used in conjunction with traditional surface science techniques to study both the adsorbate-surface and overlayer-substrate interactions in these model bimetallic systems. The ultimate goal of studying

This dissertation follows the style of Surface Science.

metal overlayers and molecular adsorbates is to provide the information necessary to make correlations between composition and activity in bimetallic systems. These correlations would allow one to tailor a supported catalyst to optimize a specific reaction.

Model Bimetallic Systems

In recent years, there has been a considerable effort directed toward the understanding of the chemical, electronic and structural properties of bimetallic systems [2,3]. The understanding of interfacial properties such as phase transitions, adsorbate-adsorbate interactions, and surface diffusion is of both fundamental interest and practical importance. Conducting these studies under UHV conditions allows the physical and chemical properties of these bimetallic systems to be characterized with an array of surface analytical techniques [4-9] including: Auger electron spectroscopy (AES), low energy electron diffraction (LEED), x-ray and ultra-violet photoemission spectroscopy (XPS & UPS), high resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD) and IRAS. Studies of this type have shown that overlayer-substrate systems have electronic and chemisorptive properties that are markedly different than the corresponding pure metal surfaces. In addition, coupling a high pressure reactor cell to a UHV system [10,11] has allowed studies on adsorption and catalytic activity at elevated temperatures and pressures [11,12]. The results obtained from

the studies of these well defined systems have, in many cases, radically altered previous ideas on adsorbate-surface interactions.

To date, the thrust of the research in this area has been in studying the growth mechanism and thermal stability of the admetal and the chemisorption properties for these bimetallic systems. In addition to the surface techniques listed above, reflection high energy electron diffraction (RHEED) [13], ion scattering spectroscopy (ISS) [14-16], X-ray photoelectron diffraction (XPD) [17,18] and scanning tunneling microscopy (STM) [19] have been employed to examine the atomic structure of these overlayers. Comparisons of the overlayer-substrate AES ratio versus film thickness have shown that layer-by-layer growth typically occurs at 100K in Cu [20-25], Ni [24,26-29], Fe [24,27,30], Co [27,31] and Pd [32,33] overlayer systems. Deposition of the admetal at room temperature or above often results in the first monolayer (ML) being deposited in a layered fashion with additional metal forming 3-D islands. For different overlayer film thicknesses, LEED studies have shown that there can be distinct preferential orientations between the overlayer adatoms and the substrate. Often the first, and sometimes the second monolayer of the admetal will adopt the atomic spacing and configuration of the substrate lattice (pseudomorphic growth), independent of the natural crystal structure of the overlayer [20,21,26,27,30-32,35-37]. The strain induced by the mismatch between the bulk lattice constants of the overlayer and the substrate will perturb the properties of the overlayer. In addition, in some systems, this strain induces a re-ordering of the overlayer at higher coverages. This is particularly evident for Cu, Ni and Co overlayers on the $\langle 110 \rangle$ faces of

refractory metal substrates such as Mo, W and Ta. For overlayer coverages of ~ 1.5 ML in these systems, annealing induces a phase transition from a pseudomorphic to a more compressed "pseudo-close packed" overlayer structure as evidenced by multiple diffraction peaks in the observed LEED patterns [23,25,27-29,31,38-40]. For substrates such as Ru and Rh, on the other hand, annealing multilayer films will often leave the first monolayer pseudomorphic with additional layers coalescing into 3-D islands [21,26,35]. In addition, a recent study of ultra-thin Ti films on W(110) has shown that both site-coincidence growth (commensurate) and rotational epitaxial growth (incommensurate) are possible in a single bimetallic system [41].

The above discussion has implicitly assumed that the admetal forms as a discrete layer on top of the substrate and remains discrete upon annealing. More complicated situations can occur when the components of the bimetallic system are miscible and form alloys of variable composition and structure as a function of temperature. It is well known that many systems (Cu-Pt, Pd-Ta, Ag-Rh, for example) are miscible and form alloys upon annealing. Although alloy formation is observable via the changes in the AES intensity ratios and/or the LEED data, these studies are rarely conclusive since clustering or phase transitions in discrete overlayer films yield similar data. For metal overlayers, where the adatom-substrate bond energies are sufficiently different from the adatom-adatom bond energies, TPD of the overlayer can be used to verify the immiscibility of the overlayer and substrate metals. For non-alloying systems, the admetal overlayer will give rise to two distinct peaks in the TPD: one corresponding to desorption of the multilayer, and one to desorption of the first monolayer [21-27,29-36,38,41-42].

For alloys, on the other hand, only one broad peak due to the sublimation of the more volatile alloy component is observed [37,43].

In addition to obtaining information about the morphology and structure of the bimetallic surface, it is important to understand the aspects of bond formation between the overlayer and substrate atoms. The TPD spectra of metal overlayers have been used to investigate the strength of the admetal-substrate bond for Cu [24,34,43,47,48], Ni [24,26,27,29,38,49] and Pd [32,36,37,50] overlayers. For most systems studied to date, the admetal-admetal bonds are weaker than the admetal-substrate bonds, as evidenced by the multilayer and monolayer desorption peaks in the metal TPD spectra. The data from the studies of these different overlayer-substrate systems indicate a general trend in the admetal-substrate bond strength [4,50]. The strongest bonds were formed with substrates on the opposite side of the transition series in the periodic table. This trend is similar to what is observed in bulk alloys, where the most stable alloys are formed between two metals on opposite sides of the transition series with alloy stability decreasing as the metal components approach each other [51,52].

To further investigate bonding between admetal and substrate atoms in these model bimetallic systems, XPS, UPS and work function measurements have been conducted. Using XPS to study monolayer films, it has been observed that there is a shift in the binding energies of the admetal atoms relative to the surface atoms of the pure metal [47,49,50,53-58]. These XPS results agree well with similar results obtained using UPS. For example, UPS data show a depletion of Pd electron density near the Fermi level for supported Pd monolayers on W(110) [59], Ta(110)

[37] and Nb(110) [60]. This is in contrast to the spectrum of bulk Pd which is distinguishable by the large density of states near the Fermi level. The depletion observed in the UPS spectra is consistent with a transfer of electron density from the Pd overlayers to the substrate. Similar trends have been seen for Pd on W(110) [32] and Ru(0001) [61] and Cu, Ni and Pd on polycrystalline Re [62,63] using work function measurements. These studies support the direction and the magnitude of the charge transfer observed in XPS. In addition, it was always observed that the systems with the largest electronic perturbations also have the strongest admetal-substrate bonds. This indicates that charge transfer between the admetal and substrate atoms is an important component of the cohesive energy in metal-metal surface bonds.

Because of the close relationship among the electronic, structural, and chemical properties it is not surprising that the significant perturbations in the structural and electronic properties outlined above might radically alter the chemical properties of the components in a mixed-metal system. The results of many studies dealing with the chemisorption of simple molecules (CO, H₂, etc.) on well-defined bimetallic surfaces indicate that this is indeed the case [9,24,26,29,30,36,37,44-46]. The discussion in this section will focus on the adsorption properties of bimetallic systems with an emphasis on the significant differences between the chemistry of the isolated metal components and that of the bimetallic interface.

The chemisorptive properties of CO as well as its involvement as a reactant in many catalytic reactions make it an ideal molecule for chemisorption studies on

bimetallic surfaces. The adsorption of CO on single crystal metal surfaces has been extensively investigated [9,64] and the nature of the metal-CO bond [65] is perhaps better understood than that of any other simple molecule. On transition metals, CO desorbs molecularly between 300 and 600K with early and mid-transition metals also showing a recombinant desorption peak at temperatures $>700\text{K}$. For noble metals, on the other hand, CO desorption is strictly molecular and occurs at much lower temperatures: $\sim 200\text{K}$ for Cu and $<100\text{K}$ for Ag and Au.

Many studies have been conducted investigating the chemisorptive properties of CO on well-defined bimetallic surfaces [1-4,20-50,53-56]. For the vast majority of these systems, the desorption temperature of CO from a monolayer film on a dissimilar metal substrate is markedly different compared to the desorption temperature from the pure metal. These variations in the CO TPD peak maxima reflect the perturbations in the electronic and geometric properties of the overlayer due to its bonding interactions with the substrate. For example, the CO desorption spectra from Pd monolayers supported on various transition metals indicate much lower desorption temperatures than from the (111) or (100) surface of Pd. In the case of $\text{Pd}_{1,0}/\text{Ta}(100)$ the desorption temperature of CO is $\sim 235\text{K}$ below that found from Pd(100). In other overlayer systems, CO desorption moves to higher temperatures compared with the bulk overlayer metal {i.e. Cu/Rh(100), Cu/Pt(111)}.

The modification of the CO desorption temperatures from various bimetallic surfaces has been shown to correlate with the changes in the binding energies of the overlayers. Fig. 1 shows a comparison of the shift in the desorption temperatures

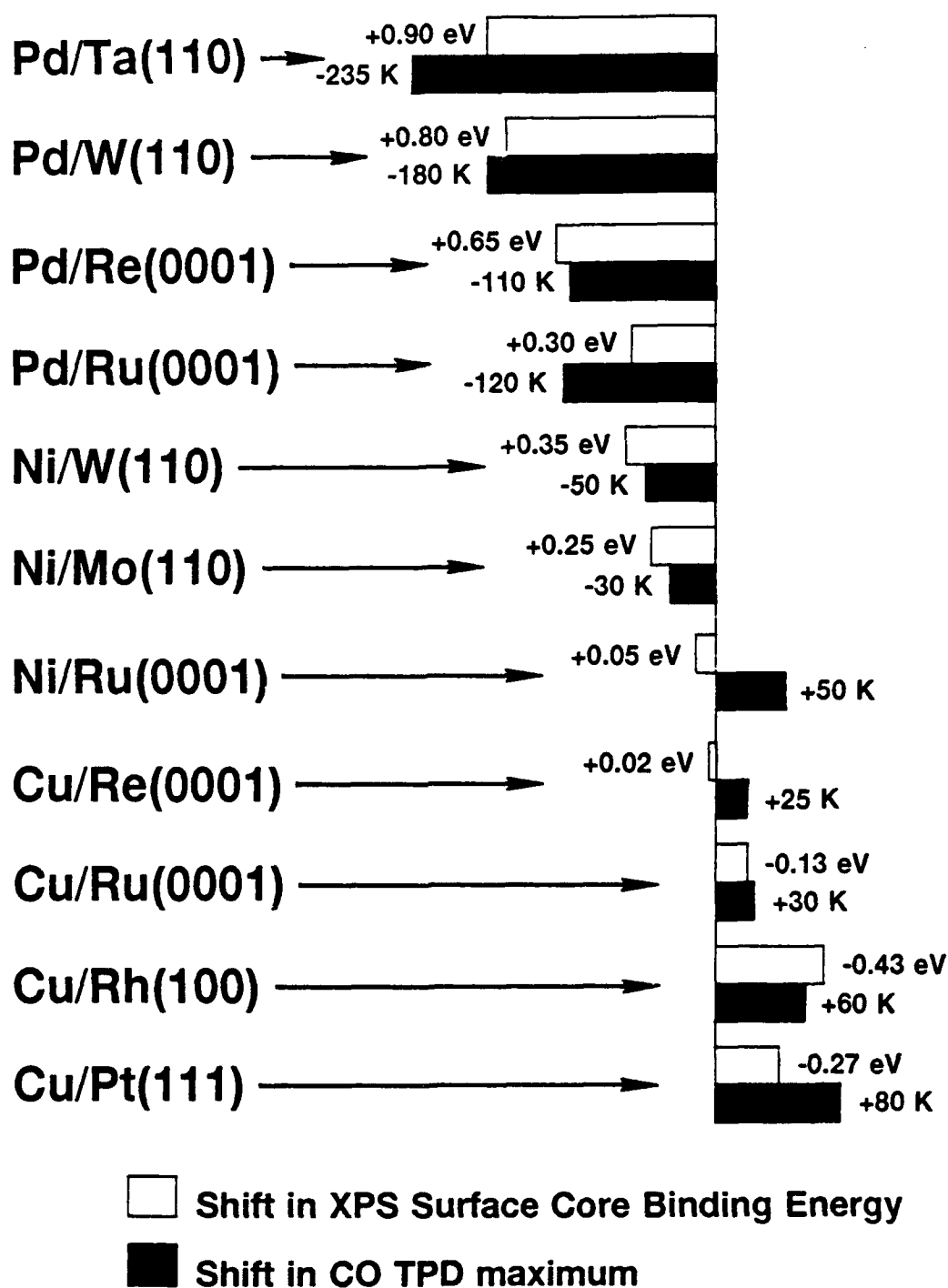


Fig. 1: Correlation between the shift in the surface core level binding energies and the shift in the CO TPD maxima.

of adsorbed CO and the shifts in the core level binding energies of the overlayer adatoms ($\text{Pd}(3d_{5/2})$, $\text{Ni}(2P_{3/2})$ and $\text{Cu}(2p_{3/2})$) for the indicated bimetallic systems. The binding energy measurements are for the clean bimetallic surfaces before CO adsorption. In general, a decrease in the CO binding energy (as evidenced by the decrease in CO desorption temperature) is accompanied by a concomitant increase in the binding energy of the monolayer film (relative to the surface atoms in a pure (100) sample) [49,50,53,54,58]. Likewise, the opposite relationship is observed for systems exhibiting an increase in the CO desorption temperature [47,55-57].

The correlation observed in fig. 1 is explainable in terms of a model based on initial-state effects [66]. The conventional description of CO chemisorption is based on the Blyholder model [67] where CO-metal bonding is described as occurring via donation of charge from the CO 5σ orbital to an unoccupied metal orbital and by backdonation from an occupied metal valence level into the unoccupied 2π orbital of the CO molecule. Additional theoretical calculations have shown that backdonation contributes more significantly to the bond strength [65,68-70]. Following CO adsorption, results for Cu(100) have shown that the surface core and valence levels are stabilized with respect to the bulk levels [71]. This shift in the surface core levels to a lower binding energy translates to a reduction in the separation between the metal valence levels and the 2π level of CO. A reduction in the metal valence band - CO 2π separation then will lead to an increase in the metal-CO overlap and to an increase in the metal-CO bond strength. This, in turn, results in a higher CO desorption temperature. A shift in the surface core levels toward higher binding energy, on the other hand, will have exactly the opposite

effect and thus will lead to a lower CO desorption temperature. This explanation is in excellent agreement with the data shown in fig. 1. A more detailed discussion of these results is given elsewhere [66,72].

Surface Vibrational Studies

The usefulness of vibrational spectroscopy to study adsorption on supported metal catalysts was demonstrated by the work of Eischens, et al. [73]. Subsequently, Baddour, et al. [74] demonstrated that catalytic activity could be correlated with the peak shapes of the adsorbed CO and therefore with the chemical state of the catalyst. These initial studies were performed using transmission IR spectroscopy, which is still the method of choice for studying adsorbates on supported metal catalysts. In subsequent studies of supported metal catalysts, CO adsorption was studied with an emphasis on understanding the chemical nature of the adsorbed species and the type of adsorption site likely to generate such a species. It was hoped that a better understanding of the nature of the adsorption site in a catalyst, when correlated with the activity of the catalyst, would shed light on specific improvements that could be used to increase the activity of the catalyst. To this end, transmission IR results for supported metal catalysts have been compared to reflection absorption IR results for single crystal metal samples [75]. For many supported metal catalysts, it was possible to identify specific peaks as arising from specific crystalline faces [75]. It was determined that, in general, CO adsorption peaks between 2200 and $\sim 2130\text{ cm}^{-1}$ are due to

adsorption on partially oxidized metal atoms; peaks between ~ 2130 and $\sim 2000\text{ cm}^{-1}$ are due to CO bonded linearly on top of a single metal atom; peaks between ~ 2000 and 1880 cm^{-1} are due to CO bonded bridging two metal atoms; and peaks between ~ 1880 and $\sim 1700\text{ cm}^{-1}$ are due to CO adsorbed in hollow sites [75].

For adsorbates on extended metal surfaces, however, transmission IR is not possible. The two most common vibrational techniques used for samples of this type are HREELS and IRAS [76]. Both of these techniques have intrinsic limitations. For HREELS, the main limitations are its low resolution (20 cm^{-1} compared to $\leq 1\text{ cm}^{-1}$ for IRAS) and the necessity of UHV conditions. For IRAS, the main limitation is its limited spectral range ($1000\text{--}4000\text{ cm}^{-1}$ compared to $100\text{--}5000\text{ cm}^{-1}$ for HREELS). Although each technique has limitations, they also have distinct advantages. Thus, if one wishes to study adsorbates on single crystal substrates with high spectral resolution and at elevated pressures, the only choice is IRAS, to which the remainder of this discussion will be limited.

To date, the vast majority of all IRAS studies have used CO as the adsorbate molecule (see for example references 64 and 76-85). In addition, prior to this work, IRAS studies have been almost exclusively limited to adsorbates on monometallic substrates with exceedingly few studies on adsorbates on metal overlayers [84,85]. These single crystal studies, however, have demonstrated the usefulness of IRAS as a technique for studying both the surface structure and reactions of adsorbates on these surfaces.

The aforementioned surface structure studies have been primarily concerned with the structure of the adsorbed CO and the dynamics of the CO-metal

interaction. The typical goals of these studies have been to determine the CO bonding configuration (linear, bridged, or hollow), temperature and coverage effects, as well as CO binding energies [78-87]. Some of these studies [78,80,83,86] have addressed the preferential bonding of CO to different sites on a surface or on different surfaces. In general, these studies could be described as being fundamental experiments on the nature of the bond between CO and a single-crystal metal surface and the factors that affect the CO stretching frequency on these surfaces.

IRAS studies of adsorbate molecule reactions (both inter- and intramolecular) are less common than the CO structure studies, but show an important capability of IRAS [88-91]. The ability of IRAS to follow the reactions of molecules on a surface has direct, obvious applications in the study of catalysts. These studies have demonstrated that the effect of modifiers, as well as factors affecting active sites and intermediates, can be evaluated [88-91].

In this work, studies have been conducted using IRAS to study bimetallic surfaces. Cu overlayers on Rh(100) and Ta(110) substrates have been studied and will be compared to results obtained previously for Cu overlayers on different substrates. In addition, Ni, Co, S and mixed Co/S overlayers have been studied on a Mo(110) substrate. These studies have shown that by using CO as a probe molecule, information can be obtained about the structure of the admetal - substrate interface. In addition, the nature of the chemisorptive bond between the carbon monoxide molecule and the metal substrate has been further evaluated and the different components involved will be assessed. The results discussed in this

work will demonstrate the utility of using IRAS to study metal-metal interfaces and will provide new insights into the nature of the CO-substrate bond in bimetallic systems.

EXPERIMENTAL

Surface Analytical Techniques

There has been an enormous growth in the study of solid surfaces and likewise in the number of techniques available for their study in the past three decades. It was not until the early 1960's that sufficient technological advances had been made to allow UHV conditions to be routinely achieved, and to allow the high resolution measurement of electron energies from several KeV down to a tenth of an electron volt. The most commonly used methods of surface analysis use photons, electrons or ions as excitation sources and detect the electrons, ions or molecular fragments ejected from the surface [4-7]. In this chapter, the surface analytical techniques used in this study (XPS, AES, LEED, TPD and IRAS) will be discussed. The chapter will conclude with a discussion of the requirements for UHV and the UHV system used in this study, and finally a discussion of the techniques used to prepare the samples for analysis. This discussion is not meant to be an in depth description of these topics, but is only meant to provide sufficient background information to elucidate the procedures used to collect the data presented in this work.

X-Ray Photoelectron Spectroscopy (XPS) In the typical XPS set-up, photons in the 1-2 KeV energy range are directed toward and absorbed by a sample in a UHV chamber. Although these photons will penetrate $\sim 1\mu\text{m}$ into the sample, XPS is still a surface sensitive technique. The surface sensitivity of XPS (and all other

electron spectroscopies) is due to the limited escape depth of electrons. Fig. 2 shows the inelastic mean free path length for electrons of varying energies. It is clear from this figure that electrons with energies between ~ 100 & 1000 eV (typical values for XPS measurements) have escape depths ≤ 10 monolayers (~ 30 Å). In XPS, electrons that are bound at energies less than that of the incident photon can be ejected from the sample as photoelectrons upon photon absorption. This process is illustrated in fig. 3. The energy of the ejected photoelectron is determined by the difference between the energy of the incident photon and the binding energy of the electron. Conversely, the binding energy of the electron can be determined by subtracting the kinetic energy of the photoelectron from the energy of the incident photon.

$$E_B = h\nu - E_K \quad (\text{eqn. 1})$$

For metals, the binding energy is usually related to the fermi level, giving:

$$E_B = h\nu - E_K - \phi \quad (\text{eqn. 2})$$

where ϕ is the work function of the metal surface. Since XPS directly measures the binding energies of the core levels, chemical speciation is inherent to XPS measurements. Thus, shifts in peak binding energies give useful information about the bonding of the atom involved. The ability to obtain chemical state information is the most valuable attribute of this technique [7].

The XPS instrumentation used in this work is shown schematically in fig. 4 and has been discussed in detail elsewhere [10]. The source was a Perkin-Elmer model 04-548 dual anode x-ray source and detection was via a Perkin-Elmer model 10-360 spherical capacitor analyzer. This instrument has a resolution of ~ 1 eV

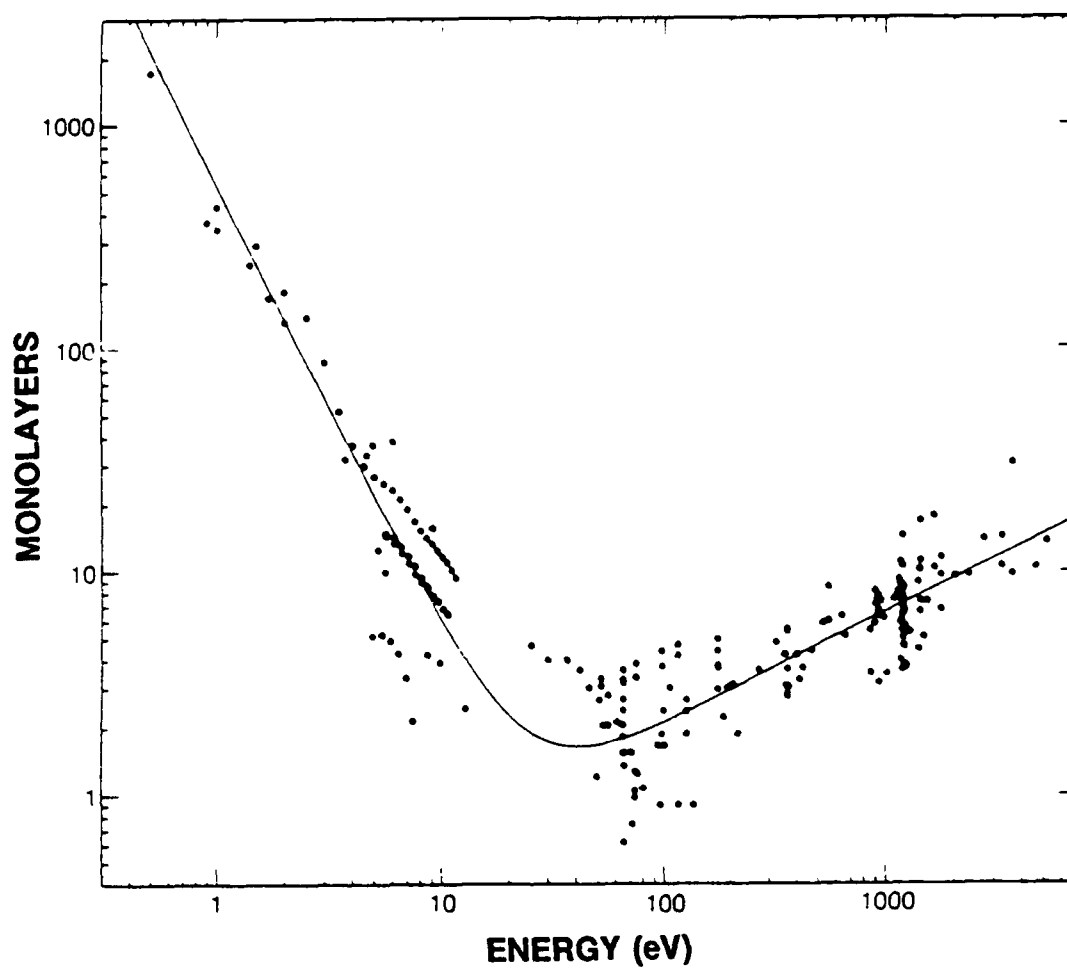


Fig. 2: Plot of electron inelastic mean free path as a function of electron energy after Seah and Dench [92].

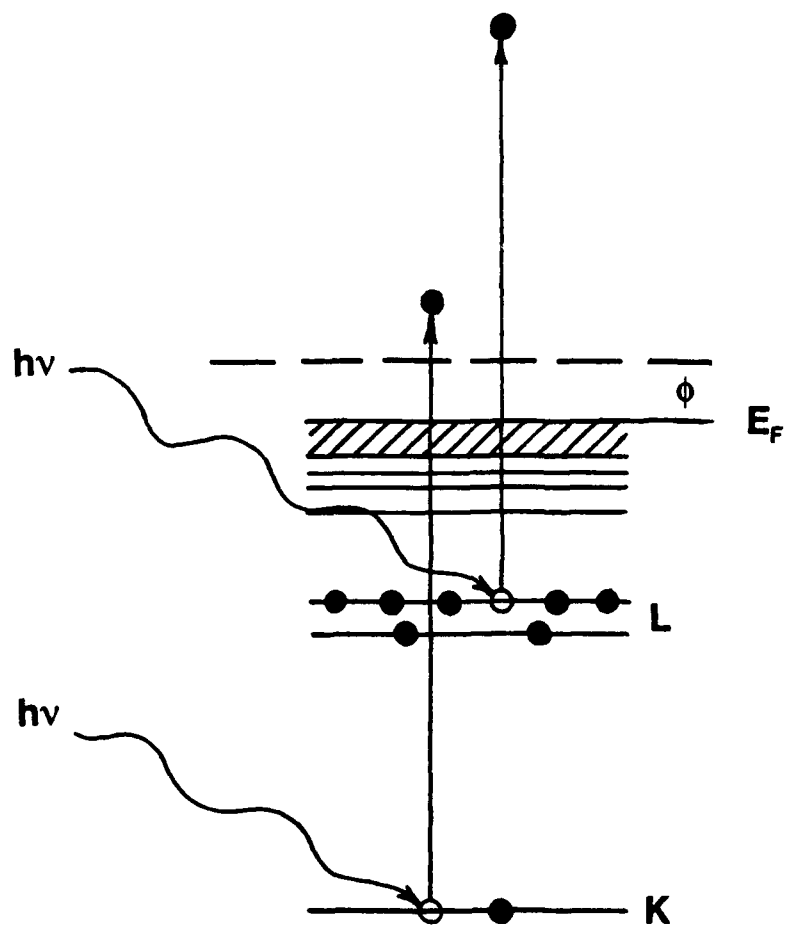


Fig. 3: Schematic diagram of x-ray induced photoemission.

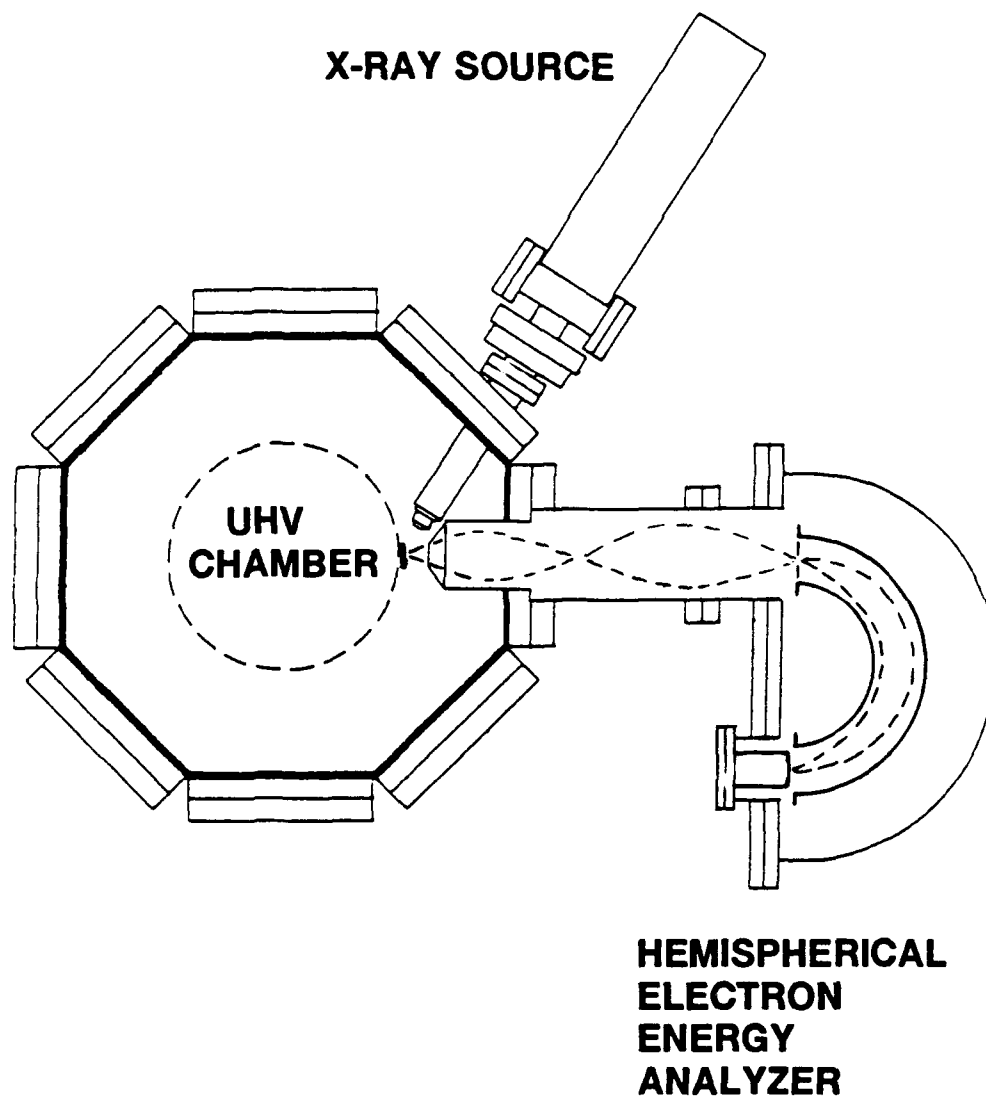


Fig. 4: The arrangement used to collect XPS spectra.

FWHM and an accuracy of ~ 0.05 eV.

Auger Electron Spectroscopy (AES) The principle use for AES is surface elemental analysis. The surface is bombarded with an electron beam (typically 2-3 KeV) that will induce the ejection of electrons in a manner that is essentially identical to the creation of photoelectrons in XPS. To stabilize the resulting charged atom, its electrons will rearrange with an electron from a higher lying energy level filling the vacancy in the core level. The energy difference between the two levels (which must be accounted for due to the law of conservation of energy) will either be dissipated as an ejected photon of characteristic energy (fluorescence) or by the ejection of an additional (Auger) electron. This process is shown schematically in fig. 5. For a KLL Auger transition the energy of the ejected Auger electron is given by:

$$E_{KLL} = E_K - E_{L1} - E_{L2} \quad (\text{eqn. 3})$$

where E_i is the binding energy of the i^{th} energy level. For energy differences on the order of a hundred to a couple thousand eV, the Auger process will dominate and occur for at least 90% of the initial core vacancies created.

The main advantages to using AES, rather than XPS to determine surface elemental composition, are the greater speed of data acquisition and the greater sensitivity of AES [7]. This increase in sensitivity is due in part to the higher luminosity of an electron gun compared to an x-ray source, and also to the high transmission of the cylindrical mirror analyzer (CMA) that is typically used to collect Auger spectra (see fig. 6). The main disadvantage with AES is its limited ability to provide chemical speciation information [7].

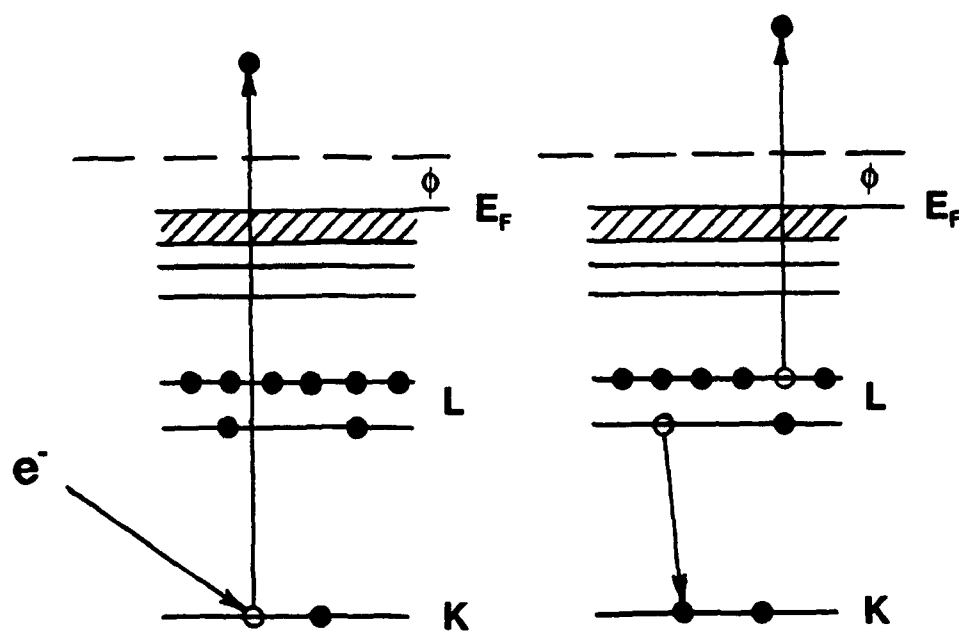


Fig. 5: A schematic illustration of the Auger process.

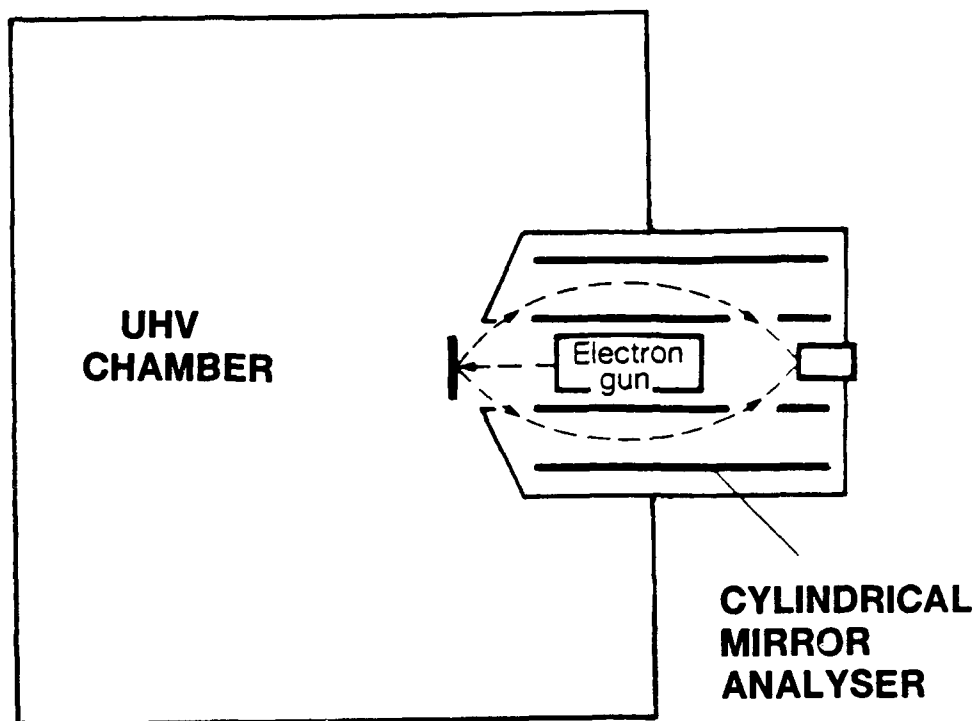


Fig. 6: Typical experimental arrangement for AES.

The AES instrumentation used in this work was a Perkin-Elmer model 15-155 CMA with a concentric electron gun. The CMA was interfaced to a PC compatible computer via the Perkin-Elmer model 137 interface which collects the signal digitally in a pulse counting mode rather than in an analog fashion with a lock-in amplifier.

Low Energy Electron Diffraction (LEED) When studying bimetallic systems using single crystal metal substrates, the ability to study surface order is advantageous and often necessary. The most commonly used technique to probe the atomic order of a surface is LEED. Fig. 7 illustrates the arrangement of a typical LEED apparatus. The central electron gun directs a focused monoenergetic e^- -beam of variable energy toward the sample. These electrons will scatter elastically off the sample and (due to the wave nature of the electron) form a diffraction pattern. Thus, the LEED pattern observed is a reciprocal space projection of the surface structure onto the LEED screen.

In the studies of metal overlayers on single crystal metal substrates discussed in this work, knowing the structure of the overlayer (or lack thereof) relative to the substrate provides valuable information about the surface coverage and bonding interactions of the overlayer. The LEED instrumentation used in this work was a Perkin-Elmer model 11-020 rear-view LEED optics. The design of this apparatus is essentially identical to that shown in fig. 7. The only difference between rear-view and standard LEED optics is that for rear-view optics one views the back of the phosphor screen via a window in the base plate of the assembly rather than the front of the screen via a window elsewhere in the UHV chamber.

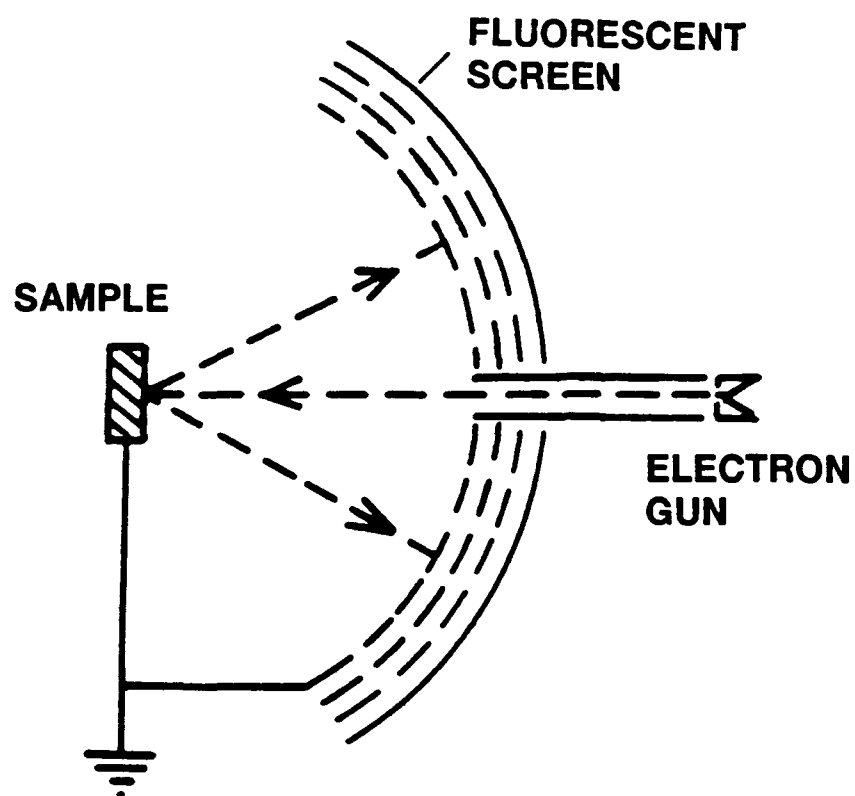


Fig. 7: Diagram of a typical LEED apparatus.

Temperature Programmed Desorption (TPD) One of the most frequently used techniques in surface science and catalysis is TPD [93]. It is commonly used to determine adsorbate surface coverage and binding energy. Data acquisition involves heating a sample and monitoring the desorption products with a mass spectrometer. The rate dependence of desorption of the adsorbed material from the surface can be described by the general form of the Arrhenius equation

$$-\frac{d\theta}{dt} = \nu \theta^n \exp(-E_d/RT) \quad (\text{eqn. 4})$$

where θ is the adsorbate surface coverage, ν is the pre-exponential (frequency) factor, n is the desorption order, E_d is the activation energy for desorption, R is the gas constant and T is the sample temperature. Although fractional desorption orders are possible, the three most common desorption orders are zero, first and second. Since pumping speed is usually high compared to the desorption rate, the temperature at which a peak is observed in the TPD spectrum corresponds to a maximum in the desorption rate. Therefore, by equating the derivative of the Arrhenius equation to zero at $T = T_{\max}$ one can obtain equations for different order rates in terms of the peak temperature. Thus, for first order desorption the equation is :

$$E_d/RT_{\max}^2 = \nu (dt/dT) \exp(-E_d/RT_{\max}) \quad (\text{eqn. 5})$$

and for second order desorption the equation is:

$$E_d/RT_{\max}^2 = 2 \nu \theta_{\max} (dt/dT) \exp(-E_d/RT_{\max}) \quad (\text{eqn. 6})$$

where dt/dT is the heating rate (β). It is clear from these equations that $T_{\max}$ is constant/increasing with increasing adsorbate coverage for first/second order

desorption, respectively. For first order desorption, Redhead derived an easily applicable approximation to determine E_d from T_{max} , ν and β [94].

$$E_d = R T_{max} [\ln(\nu T_{max}/\beta) - 3.46] \quad (\text{eqn. 7})$$

By choosing an appropriate value for ν , this equation is easily solvable. The usual choice for ν is 10^{13} s^{-1} .

To accurately interpret TPD results, one first must determine the order of the desorption process. As discussed earlier, shifts in peak desorption temperature with changing coverage are instructive. In addition, the shape of the desorption peak can give useful information about desorption order [95]. In general, zero-order desorption peaks tend to have a long leading edge and end abruptly. First and second order desorption peaks, on the other hand tend to be more Gaussian in shape with first order peaks being asymmetric toward their leading edge and second order peaks being asymmetric toward their trailing edge.

The TPD apparatus used in this work consisted of a UTI model 100c quadrupole mass spectrometer that was enclosed in a shield of a design similar to that described by Smentkowski and Yates [96]. The purpose of the shield is to act as a skimmer, allowing only those adsorbates present on the front face of the crystal into the mass spectrometer for detection and mass analysis. The linear temperature ramp was provided by a Hewlett-Pakard 6259B DC power supply controlled by a PC compatible computer. The software controlling the heating ramp, sweeping the mass spectrometer and storing the data, was developed in this lab. The heating rates used for CO and metal TPD in this work were 5 and 10 K/sec, respectively.

Infrared Reflection Absorption Spectroscopy (IRAS) In order to use IR spectroscopy to detect the vibrations of a molecule adsorbed on a surface, there are several conditions that must be met. The first is that the adsorbed molecule must have a vibrational mode that is dipole allowed and has a non-zero dipole moment. In addition, the combination of adsorbate concentration and dipole oscillator strength must be such that the absorption will be detectable above background noise. If we assume that the molecule in question satisfies the above criteria, then the question of detectability turns to the molecule substrate interaction and the interaction of the IR radiation with the adsorbate-substrate interface.

The absorption of IR radiation by a molecule adsorbed onto a surface will be determined by the electromagnetic field experienced by the molecule. Due to the close spatial relationship of the molecule to the substrate (relative to IR wavelengths), the field experienced by a molecule adsorbed on a metal substrate is dominated by the dielectric response of the metal. The dielectric response of the metal substrate will, therefore, determine the optimum conditions to detect the absorption of IR radiation by the adsorbed molecule.

Most metals have dielectric constants in the IR region that make them almost perfect reflectors of IR light. If reflection IR is attempted at normal incidence, however, a standing wave will be created with a node on the surface and a node to anti-node distance of $\geq 10^4 \text{ \AA}$ (both components of the electric field would be parallel to the surface and would thus undergo a phase change of 180° upon reflection). Thus, the electric field has no intensity at the surface and does not

reach a maximum until $\geq 10^4 \text{ \AA}$ above the surface (this is at least 1000 times the height of the average adsorbate) [97].

For reflection at non-normal incidence [64,76,77,97] (see fig. 8), on the other hand, only one component of the incident IR light would be polarized parallel to the surface (s) and would therefore undergo a 180° phase shift and cancel out. The other component of the incident radiation (p), however, is in the plane of incidence (normal to the surface) and therefore only experiences a small phase shift for most angles. As the angle of incidence approaches 90° , the phase shift rapidly increases to a value of 180° at grazing incidence. These phase shifts (see fig. 9) are a direct result of the boundary conditions that exist at the metal interface and can be treated theoretically on a macroscopic level using Fresnel's equations [98,99]. These equations are written in terms of the amplitude (r) and phase (δ) of the reflected wave with respect to the incident wave in terms of the complex index of refraction of the surface ($\tilde{n} = n + ik$). However, since $n^2 + k^2 \gg 1$ in the IR spectral region, the equations for the light reflected from a clean surface can be simplified to:

$$R_s = r_s^2 = \frac{(n - \sec\phi)^2 + k^2}{(n + \sec\phi)^2 + k^2} \quad (\text{eqn. 8})$$

$$R_p = r_p^2 = \frac{(n - \cos\phi)^2 + k^2}{(n + \cos\phi)^2 + k^2} \quad (\text{eqn. 9})$$

$$\Delta = \delta_p - \delta_s = \arctan \left(\frac{2 k \tan\phi \sin\phi}{\tan^2\phi - (n^2 + k^2)} \right) \quad (\text{eqn. 10})$$

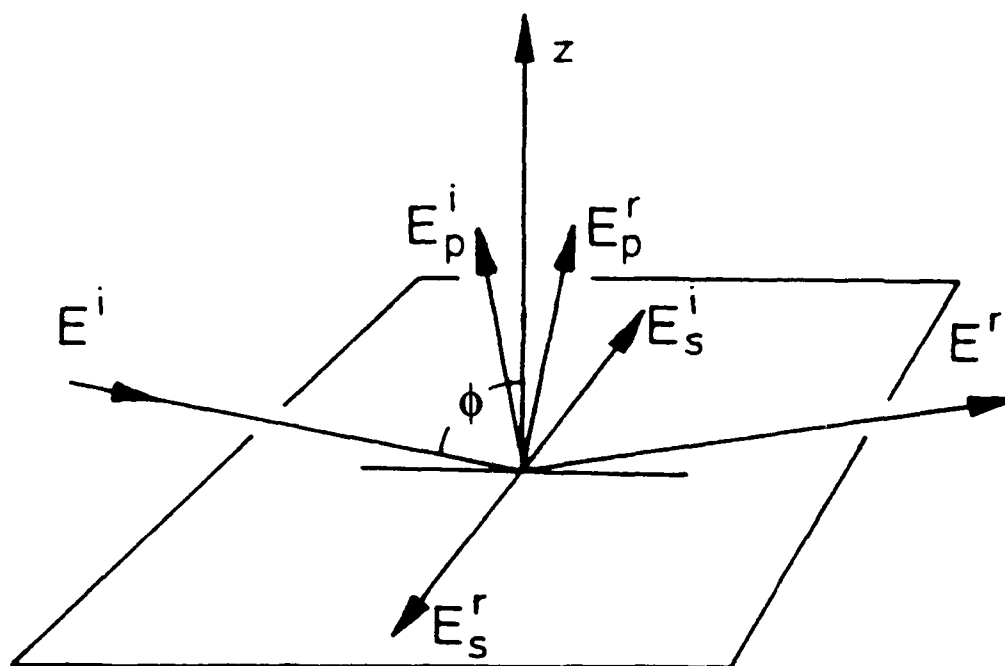


Fig. 8: Geometric considerations for reflection at non-normal incidence.

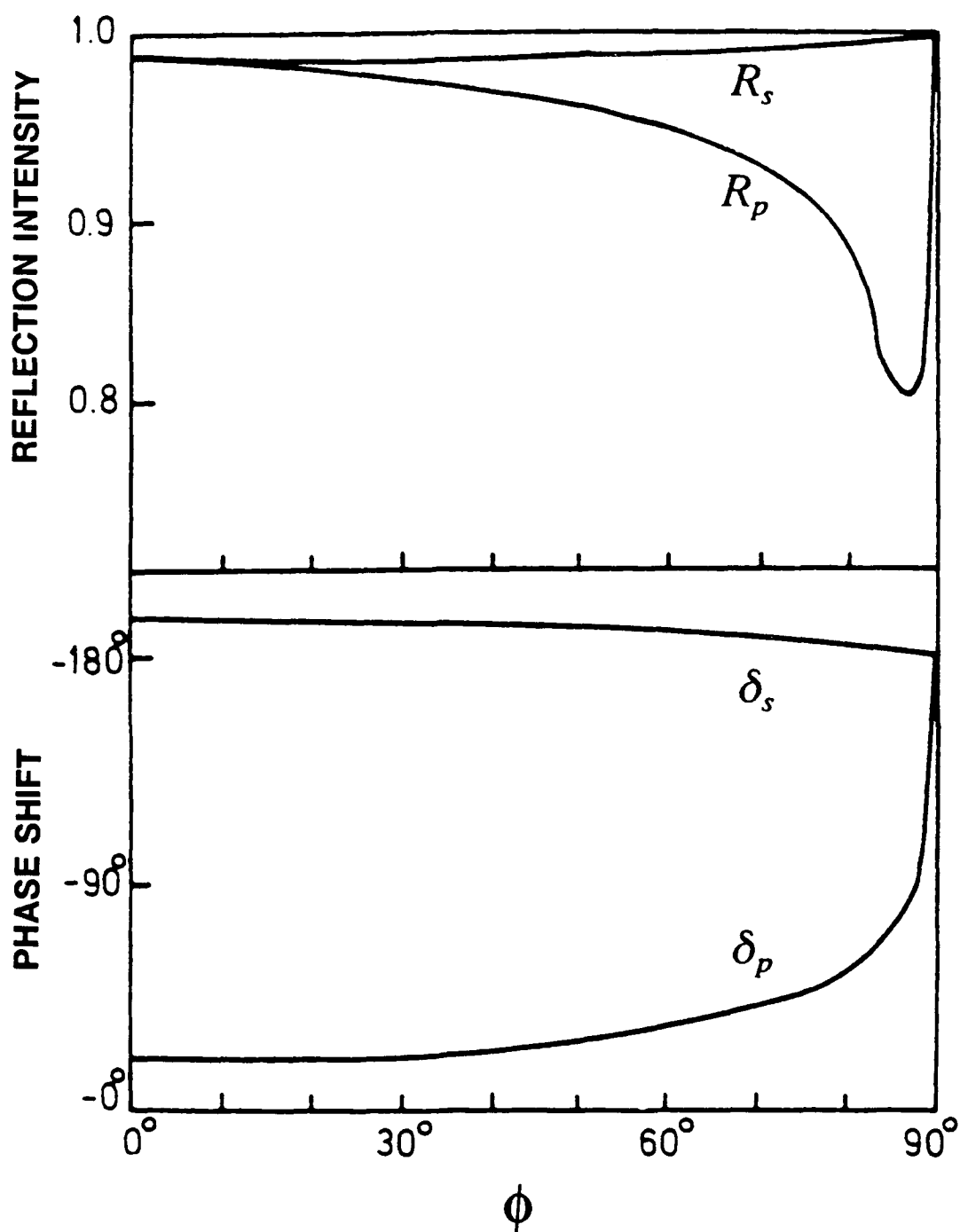


Fig. 9: Phase shifts and reflection intensities as a function of angle of incidence (ϕ).

where R_s and R_p are the reflected intensities of the s and p components of the light, respectively, δ_p and δ_s are the phase shifts and ϕ is the angle of incidence of the incident beam relative to the surface normal. The small phase shifts induced in the p polarized light lead to constructive interference in the incident and reflected waves and create a standing electromagnetic wave on the surface. The amplitude of the field is a maximum at high (but not grazing) angles of incidence as can be seen in fig. 10. The net result is a field that is anisotropic with almost all of its intensity normal to the surface. This results in the selective excitation of modes that have components of their dynamic dipole normal to the surface. To better determine the optimum angle of incidence, a surface intensity function can be calculated. Since absorption is proportional to the square of the field strength and the path length of the wave traversing through the adsorbate (the number of molecules excited) is proportional to the secant of the angle of incidence, the function has the form $(E/E_0)^2 \sec \phi$ and predicts an optimum angle of approximately 87° as is shown in fig. 10. In summary, for molecules adsorbed on a metal surface, only molecular vibrations with a component of their dynamic dipole normal to the surface are observable, only the p component of the IR light can interact with the adsorbed molecules and the highest sensitivity will occur at near grazing angles of incidence [64,76,77,97]. It does need to be mentioned, however, that highly dispersed metal crystallites supported on high area oxides do not have these constraints. Since these studies are conducted in the transmission mode and the wavelength of IR light is much larger than the average particle size, both components of the electric field can produce a measurable absorbance and all

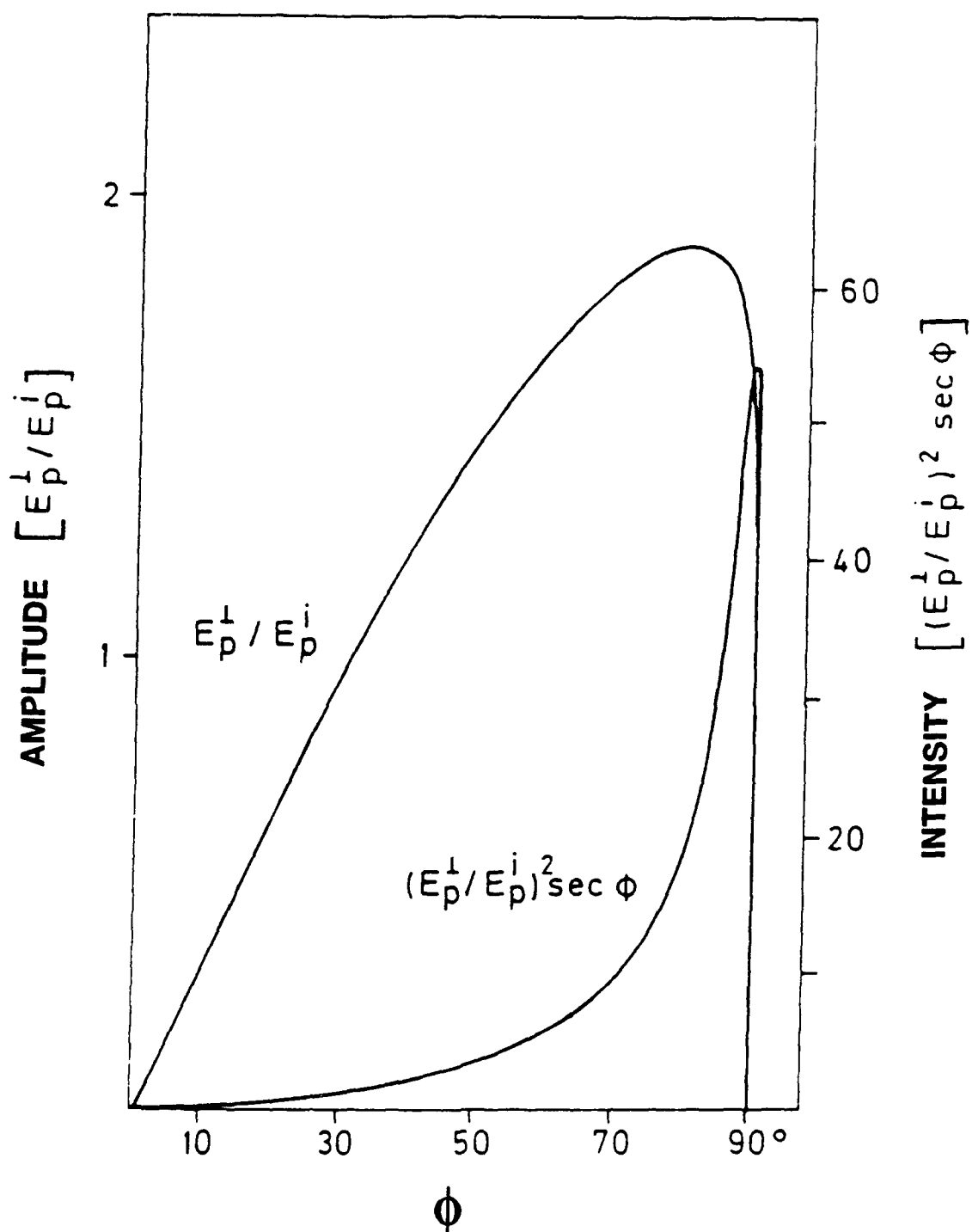


Fig. 10: The amplitude and intensity of the surface field as a function of incidence angle (ϕ).

dipole allowed vibrational modes of the adsorbed molecules will be active due to their random orientation in the field.

The discussion so far has only dealt with the interaction of the IR electric field with the molecule-sample interface. There are additional, practical, instrumentation aspects that also influence one's ability to detect the absorbance of IR radiation by an adsorbed molecule. For adsorbates on metal surfaces, the most serious problem is the low intensity of the absorption bands. A monolayer of a strong absorber like CO will only give an absorbance of approximately 1% of the total detected intensity while weak absorbers like hydrocarbons have absorbencies of 0.3%. If one wishes to detect 1% of a monolayer of an adsorbate, then the spectrometer will need to have a high enough signal-to noise ratio to allow one to tell the difference between a signal that is <0.01% of the total absorbance intensity and background (i.e. a S/N ratio of $>10^4$). In addition to a low signal strength, there are also problems arising from absorptions due to atmospheric gases in the optical path or due to gases present in the IR cell if one is studying reactions of gases on surfaces. This is particularly important when trying to study bands in the 3700 - 3200 cm^{-1} and 1900 - 1200 cm^{-1} regions where water vapor bands can be several orders of magnitude more intense than the absorption signal of interest.

The chief hinderance to detectability that arises from the spectrometer itself is noise. The three main sources of instrument noise are source noise, detector noise and fluctuation or drift noise. The nature of the first two sources is implicit, the third is a collection of problems such as background drift, vibration (vacuum pump, modulator, scanning monochromator, etc), power supply

irregularities, etc. Fluctuation noise can not be reduced just by increasing the intensity of the source, the sensitivity of the detector or increasing measurement time. Spectral averaging can help, but the best solution for fluctuation noise is to reduce each of the sources as much as possible. Since detector noise is by definition independent of the incident signal intensity, it will dominate in regions where the incident intensity is low, i.e. at long wavelengths ($>1000\text{ cm}^{-1}$). Source noise is the result of the random nature of the emission process and is proportional to the square root of the source power. Thus increasing source intensity will reduce this contribution to instrument noise. To sum things up, the bottom line is that the major, limiting constraint when using IR spectroscopy to study adsorbed molecules is sensitivity. It limits which molecules can be studied and what the minimum surface concentration is to be able to detect them if they are present. Sensitivity problems also limit the spectral range for most experiments to the mid-IR where sources and detectors are sensitive enough to detect these absorbencies above the background noise.

The IR spectrometer used in this work was a Mattson Cygnus 100 FT-IR spectrometer. The source was a globar in a water cooled enclosure and detection was via a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. This spectrometer contains a KBr beam splitter and cube-corner mirrors in the interferometer. A schematic diagram of the spectrometer and optical path through the sample cell is shown in fig. 11. The spectra in this work were collected with 4 cm^{-1} resolution in a single reflection mode at an incident angle of 85° . The number of scans per spectrum was 320, giving an acquisition time of ~ 2.5 minutes.

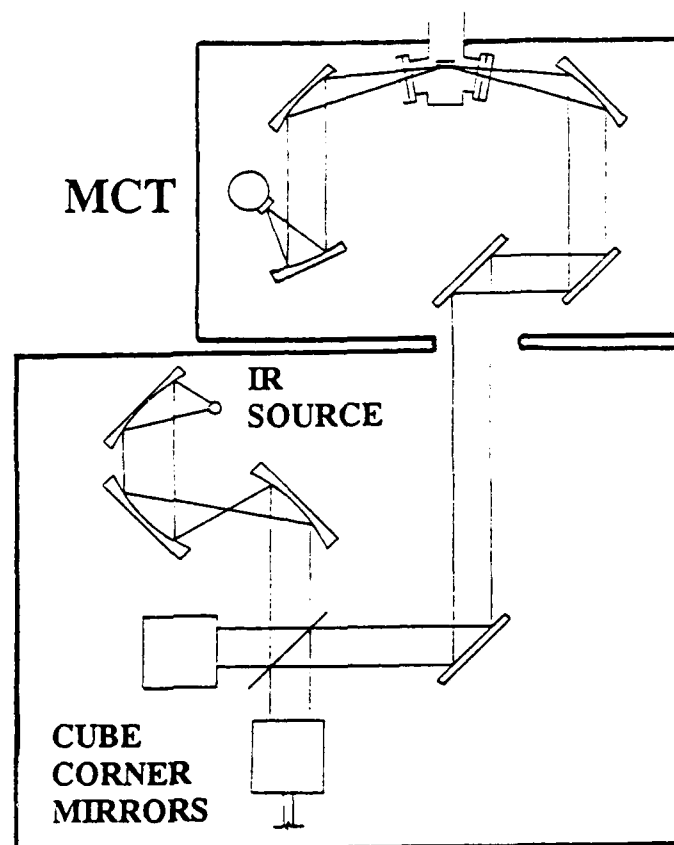


Fig. 11: Diagram of IR spectrometer optical path.

Ultra-High Vacuum (UHV) System

The experiments discussed in this work were conducted in a custom built UHV chamber. This instrument is shown in fig. 12 and is very similar in design to another chamber in this research group that has been discussed in detail elsewhere [10]. The system was constructed of 304 stainless steel and was octagonal in shape. The arrangement of the surface analytical equipment is shown schematically in a cross sectional view through the octagonal UHV chamber (see fig. 13). The sample manipulator was positioned on top of the chamber and the IR cell is located below it. The system was pumped with a Balzers 330 l/s turbomolecular pump in combination with a titanium sublimation pump (TSP) to obtain a typical base pressure of $<5 \times 10^{-10}$ torr. The sample manipulator allowed lateral motion of the sample in any direction up to 1.5" off the center line of the chamber. In addition, the sample manipulator provided an 18" throw in the vertical direction to move the sample from the UHV analysis part of the instrument to the IR sample cell. Rotation of the sample around the center line (vertical axis) of the chamber was accomplished via a differentially pumped rotary seal on top of the sample manipulator assembly.

The IR cell (see fig. 14) was fitted with bakeable, UHV compatible CaF_2 IR windows and was pumped with a Balzers 56 l/s turbomolecular pump. In addition, there was a doubly differentially pumped sliding seal located between the cell and the UHV chamber. The sliding seal allowed for IR spectral acquisition at pressures up to 1 atm while maintaining UHV conditions in the main chamber. An MDC gate valve was located between the sliding seal and main chamber to eliminate out-

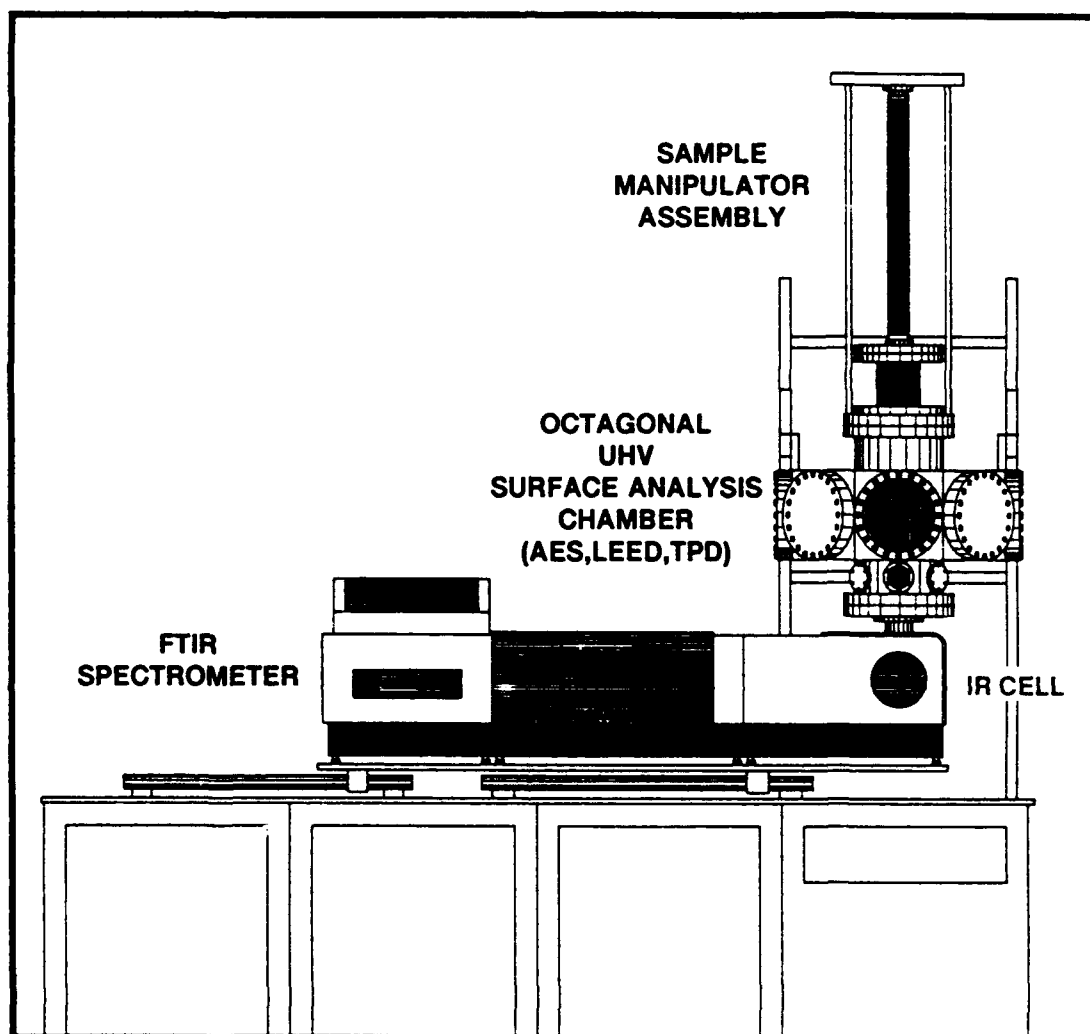


Fig. 12: Combination UHV/FT-IR instrument.

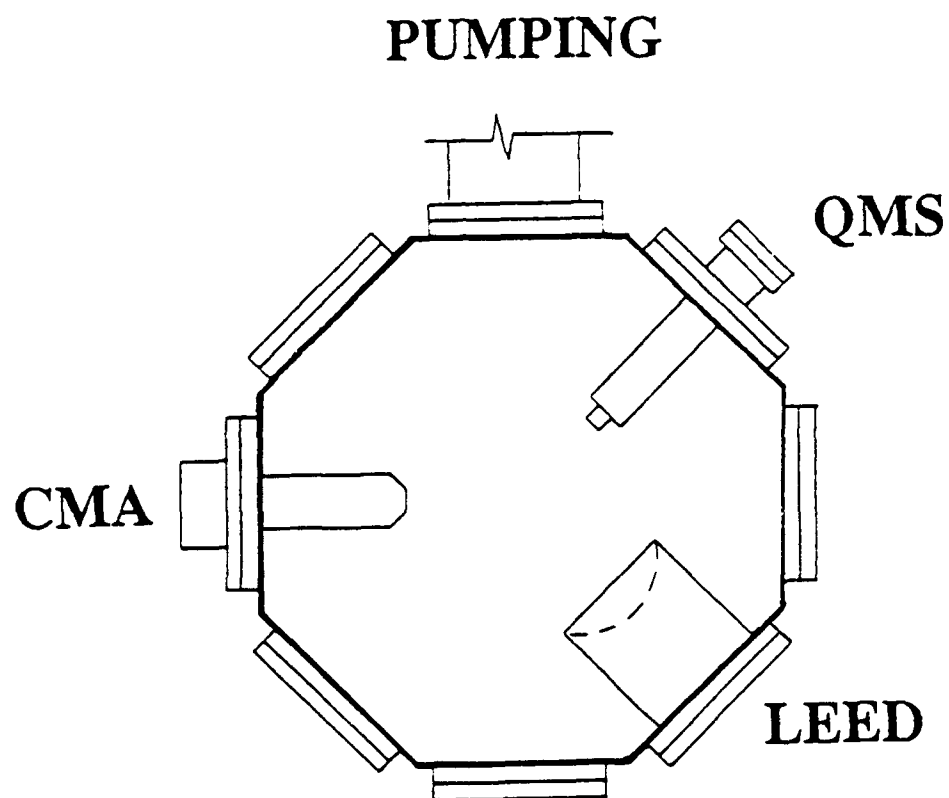


Fig. 13: Arrangement of surface instrumentation.

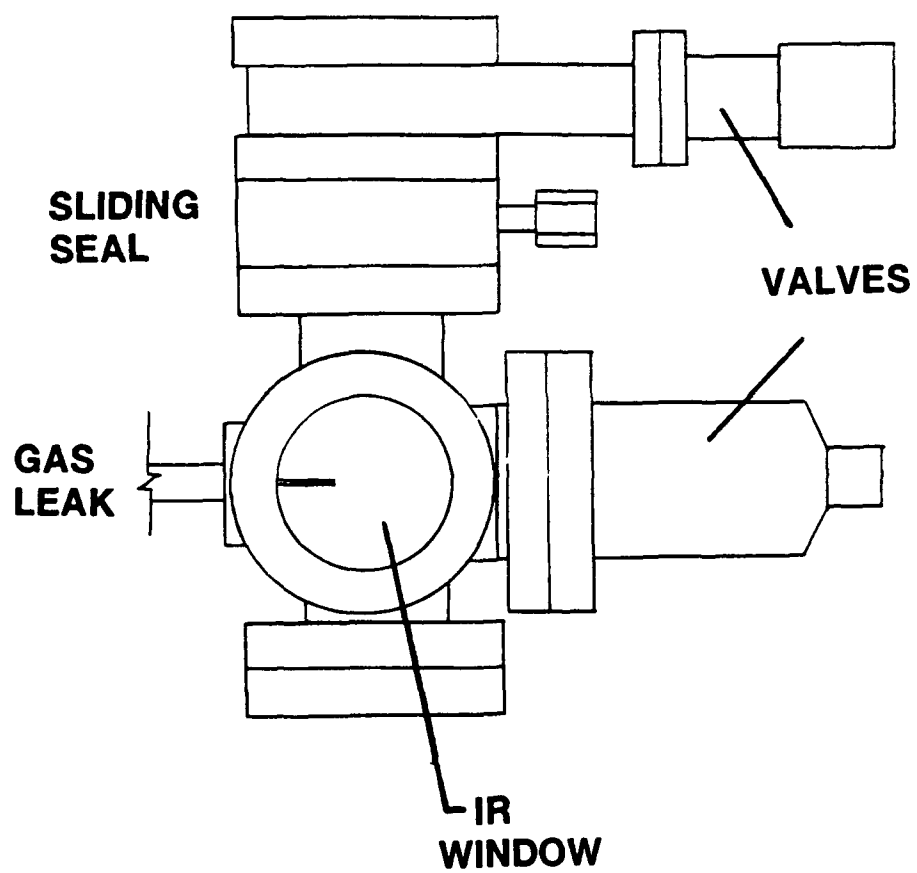


Fig. 14: Combination UHV/elevated pressure IR cell.

gassing from the IR cell into the main UHV chamber after the sample probe was disengaged from the sliding seal and moved up into the main UHV chamber. The sample could be exposed to the desired adsorbate gases via a Varian variable leak valve. If higher pressures were desired, the IR cell could be isolated from the turbomolecular pump and back-filled to the desired pressure via a valved gas line leading to gas handling manifold. The gas manifold could be fitted with up to five different gases and was pumped with an Alcatel model 2004a rough pump. To minimize cross contamination, the manifold could also be pumped to $\sim 1 \times 10^{-8}$ torr with an attached 20 l/s ion pump. Pressure in the IR cell was monitored with a nude ion gauge for pressures between 1×10^{-9} and 9×10^{-4} torr. For pressures between 1 mTorr and 10 Torr, an MKS 10 torr barratron gauge was used.

The sample was attached to a probe that was designed such that it allowed experiments to be conducted in the IR cell at temperatures ranging from 80 K to 1200 K and at pressures ranging from 1×10^{-10} torr to 1 atm. Since sample cooling was accomplished by filling the inner tube with liquid nitrogen, the probe (see fig. 15) was built as a Dewar with two concentric tubes. A rough pump was used to maintain vacuum between the two tubes to minimize heat conduction. This double wall Dewar construction was necessary to achieve sample cooling, yet still maintain approximately ambient temperatures on the outer wall of the probe. Ambient outer probe wall temperatures were necessary to allow access to the IR cell because the sliding seal separating the main and sample chambers was fitted with spring loaded teflon seals. The walls of the probe were 304 stainless tubes with outer diameters of 5/8" and $1.000" \pm 0.005"$. The tight tolerances on the outer probe tube were

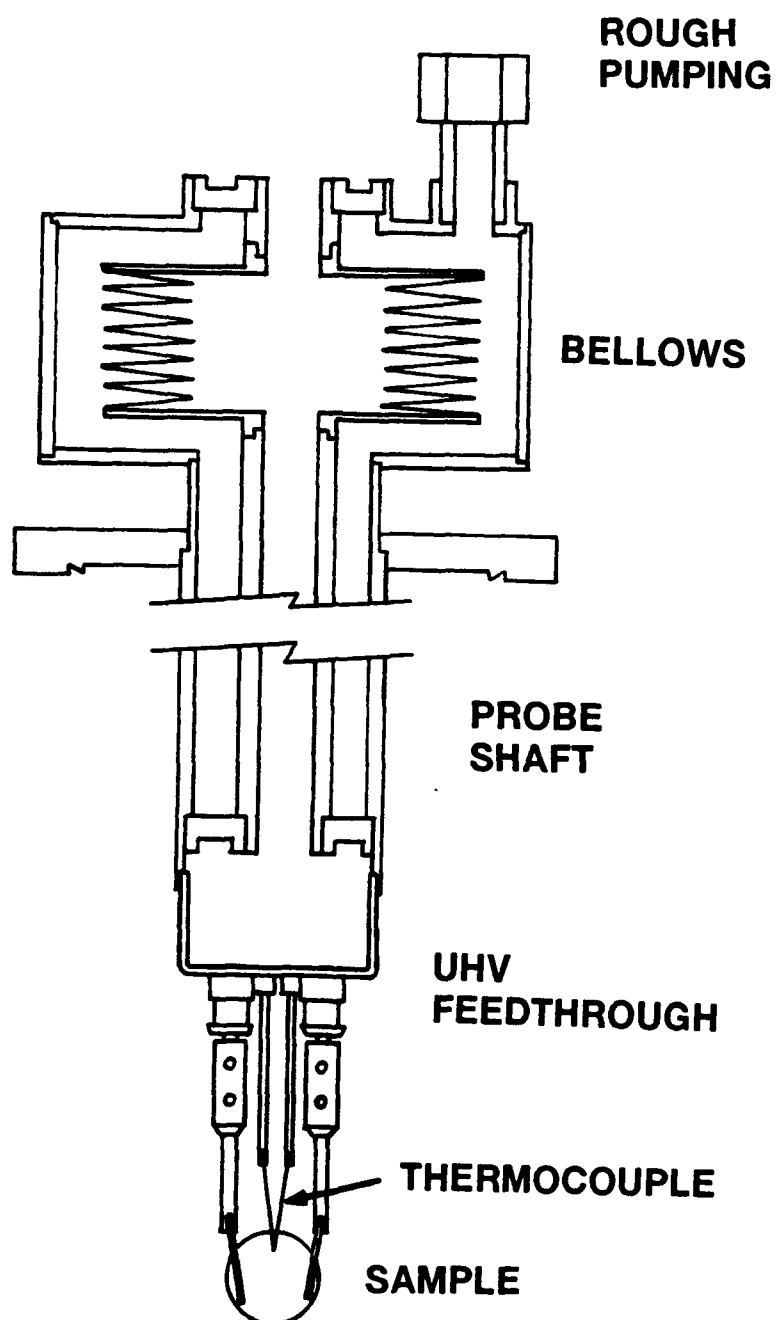


Fig. 15: Schematic diagram of sample probe.

necessary to allow the probe to seal properly in the sliding seal located between the main and IR chambers. A bellows was welded between the inner tube and the outer tube at the top of the probe to relieve the stress that would occur due to the contraction of the inner tube relative to the outer when filled with liquid nitrogen. A UHV compatible combination thermocouple/power feedthrough was attached to the bottom of the probe to allow resistive heating of the sample and temperature measurement. The sample was attached to the probe via two 0.020" dia Ta wires spot-welded to the back of the sample as shown in fig. 15. The temperature of the sample was measured with 0.005" or 0.003" dia W / 5% Re - W / 26% Re thermocouple wire spot-welded to the back of the sample between the two heating wires.

Sample Preparation

The samples studied in this work all consisted of single crystal substrates onto which were deposited metal overlayers, carbon monoxide and in one study hydrogen sulfide. The single crystals used were approximately 1 cm in diameter and 1-2 mm thick. Before any of the studies could be begun, the single crystal substrates had to be cleaned in the UHV chamber. The general procedures [100] used to clean the substrates used in this study (Rh(100), Mo(110) and Ta(110)) were as follows: First, the sample was heated repeatedly to ~1200K to desorb the majority of the contaminants. The treatment that followed depended on the

contaminant remaining on the surface, but was typically further heating and/or oxidation cycles.

For the Rh sample, after the initial heating the usual contaminant would be carbon which could be removed by repeatedly cycling between oxidation (1×10^{-6} torr O_2 at ~ 900 K for 300 sec) and annealing (1400 K for 15 sec) cycles. The annealing step would flash the oxygen off the surface and cause any sub-surface carbon present to migrate to the surface where it could be burned off in the next oxidation cycle. This was continued until AES showed a clean surface with no visible contaminants (< 1 atom percent).

For the Mo and Ta samples, the usual contaminant left after the initial resistive heating was oxygen. In refractory metal samples like these the oxygen desorption temperature is quite high ($\sim 1800 - 2000$ K for Mo and $\sim 2200 - 2500$ K for Ta). In addition, oxygen will form a bulk oxide with Ta. Therefore, to remove the oxygen contaminants from these samples electron beam heating was necessary. The sample would be biased to +1000 V in close proximity ($\sim 2-5$ mm) to a tungsten filament. The current was increased in the W filament until electron emission occurred. The Mo and Ta samples were heated with emission currents of 200 and 320 mA (200 and 320 Watt), respectively. The e^- -beam heating was held at temperature for $\sim 5-15$ sec in each cycle. During e^- -beam heating, the sample was cooled with liquid nitrogen to keep the feedthrough and copper legs cool. Again, these heating cycles were continued until AES showed a clean surface with no visible contaminants.

Once the sample has been cleaned, cleanliness can be maintained for short periods of time just by keeping the sample under UHV conditions. Simple kinetic theory can be used to show that molecules with ambient thermal kinetic energy have an arrival rate of approximately 10^{20} molecules $\text{cm}^{-2} \text{s}^{-1}$. For the average sample, this means that at 3×10^{-10} torr it would take approximately 5 hours for a complete monolayer of contaminants to form. On the other hand, the surface will only stay clean ($< 1\%$ of a monolayer) for ~ 3 minutes. These calculations have assumed a sticking probability of 1, which is too high for many of the background gases (hydrogen for example) present in a UHV system with the sample at ambient temperatures. A more typical time would be 5-10 minutes.

Metal deposition was accomplished by wrapping a wire (0.005" dia) of the desired metal around a W filament (0.010 - 0.020" dia) which was resistively heated until the metal sublimed. Prior to use, the metal evaporator was outgassed extensively. No measurable contaminants accumulated on the surface during metal deposition (unless noted otherwise). Metal overlayer coverage was determined from the overlayer/substrate AES ratio which was calibrated against the metal TPD results. To deposit sulfur onto the surface, the sample was dosed with H_2S . Heating to > 500 K caused the H_2S to decompose with the hydrogen desorbing, leaving only S on the surface. The H_2S was cleaned by freezing the H_2S in liquid nitrogen and then vacuum distilling off the dissolved gases. The CO used in this work was obtained from Matheson, was 99.99% pure and was used without further purification. Gas exposures in this work are given in terms of Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ torr} \cdot \text{sec}$).

RESULTS

The main purpose of this work was to study the properties of model bimetallic systems. The primary technique used in these studies was IRAS; however, the use of TPD, LEED and AES was necessary to help understand these systems. The results of studies conducted on Cu/Rh(100), Cu/Ta(110), Ni/Mo(110), Co/Mo(110), S/Mo(110) and Co/S/Mo(110) are presented in this section.

Cu/Rh(100)

The IR spectra of CO adsorbed onto various coverages of Cu (θ_{Cu}) on a Rh(100) substrate are shown in fig. 16. The sample temperature during Cu deposition was 100K. 10 L of CO was dosed at 85K without annealing the Cu/Rh(100) surface. The spectrum of CO on clean Rh(100) is also presented for reference. The peak at 2087 cm^{-1} together with a shoulder at 2079 cm^{-1} correspond to on-top CO and that at 1952 cm^{-1} to bridge-bound CO. The detailed results and discussion of CO chemisorption on Rh(100) can be found in reference 83.

Fig. 16 shows that Cu deposition induces a new CO vibrational feature whose frequency red shifts with increasing Cu coverage. This feature is identified as CO adsorbed on Cu because its intensity increases as the coverage of Cu increases. Furthermore this feature is the only feature present at $\theta_{\text{Cu}} > 1$ and its disappearance at elevated temperatures correlates with the desorption of CO from

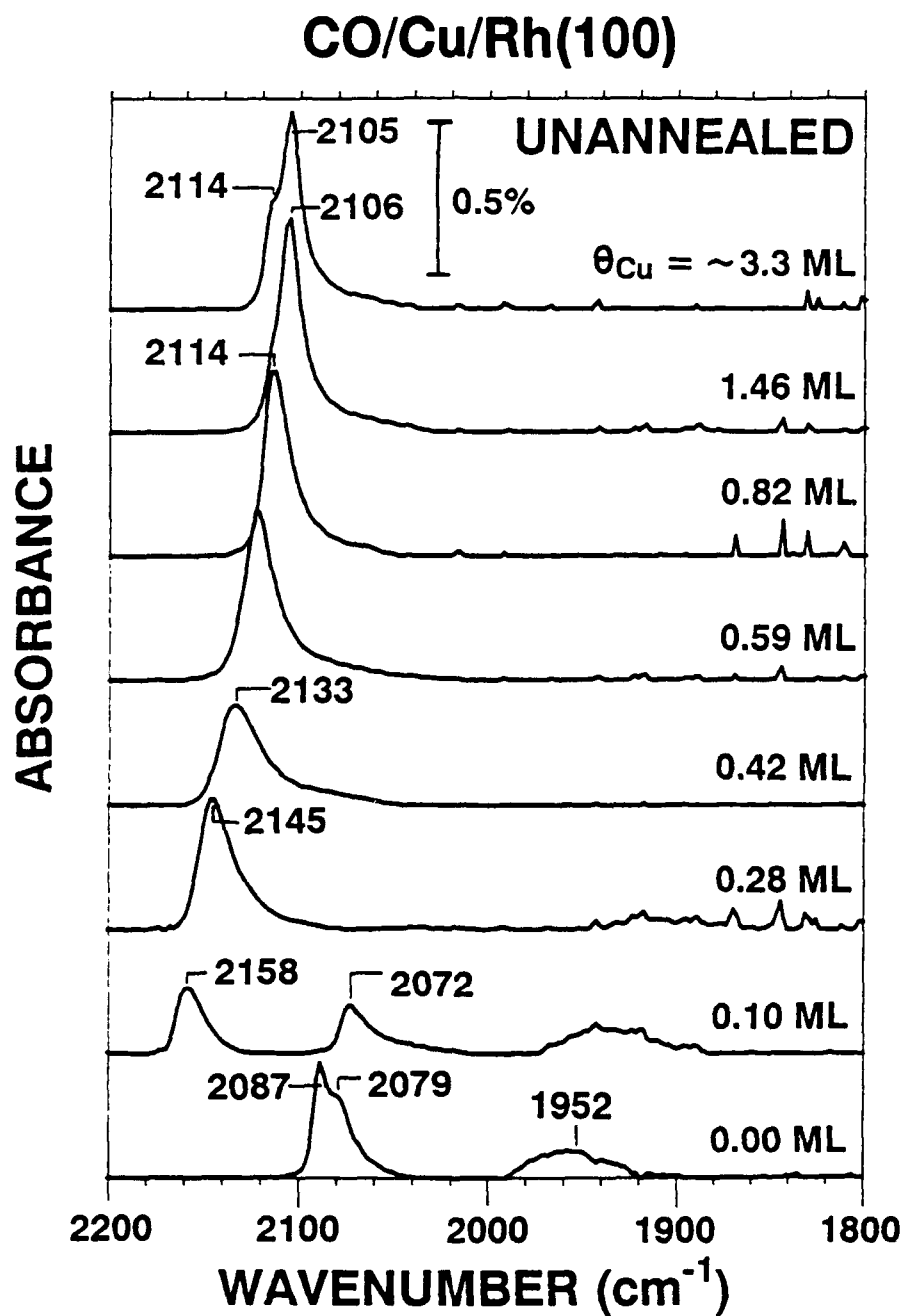


Fig. 16: IR spectra of CO on unannealed Cu/Rh(100) surfaces at 90K.

Cu [46]. Fig. 17 shows the CO spectra from Cu/Rh(100) surfaces annealed to $\sim 900\text{K}$.

One noteworthy point about Figs. 16 and 17 is that at low Cu coverage, the adsorbed CO exhibits a vibrational frequency higher than that of gas phase CO (2143 cm^{-1}). The frequencies for CO on the 0.1 ML unannealed and annealed Cu/Rh(100) surfaces are 2158 cm^{-1} and 2155 cm^{-1} , respectively. Extrapolations of the data to $\theta_{\text{Cu}} = 0$ yield the singleton frequencies of 2166 and 2162 cm^{-1} for the unannealed and annealed Cu/Rh(100) surfaces, respectively. Another noteworthy point is that even at Cu coverages up to ~ 3 ML, the CO stretching frequency is $\sim 2100\text{ cm}^{-1}$. This is markedly higher than for CO on Cu(100) ($\sim 2080\text{ cm}^{-1}$) and implies that 3 monolayers of Cu is not yet bulk-like (at least with respect to CO chemisorption).

Fig. 17 also shows that annealing the Cu/Rh(100) surface to $\sim 900\text{K}$ leads to the development of a peak at 2095 cm^{-1} which appears at 0.28 ML and becomes well-defined at 0.59 ML. This peak is quite distinct and its frequency remains essentially unchanged as θ_{Cu} increases. This peak has a characteristic full width at half maximum (FWHM) of 4 cm^{-1} at an instrumental resolution of 1 cm^{-1} . A typical FWHM for CO chemisorbed on metal surfaces is $\sim 20\text{ cm}^{-1}$; however, a FWHM of 4 cm^{-1} has been observed previously for CO chemisorbed on Cu(100) [101]. The 2095 cm^{-1} peak is only seen when the Cu/Rh(100) surface is annealed to temperatures above 300K with its intensity increasing as the annealing temperature is increased (see fig. 18).

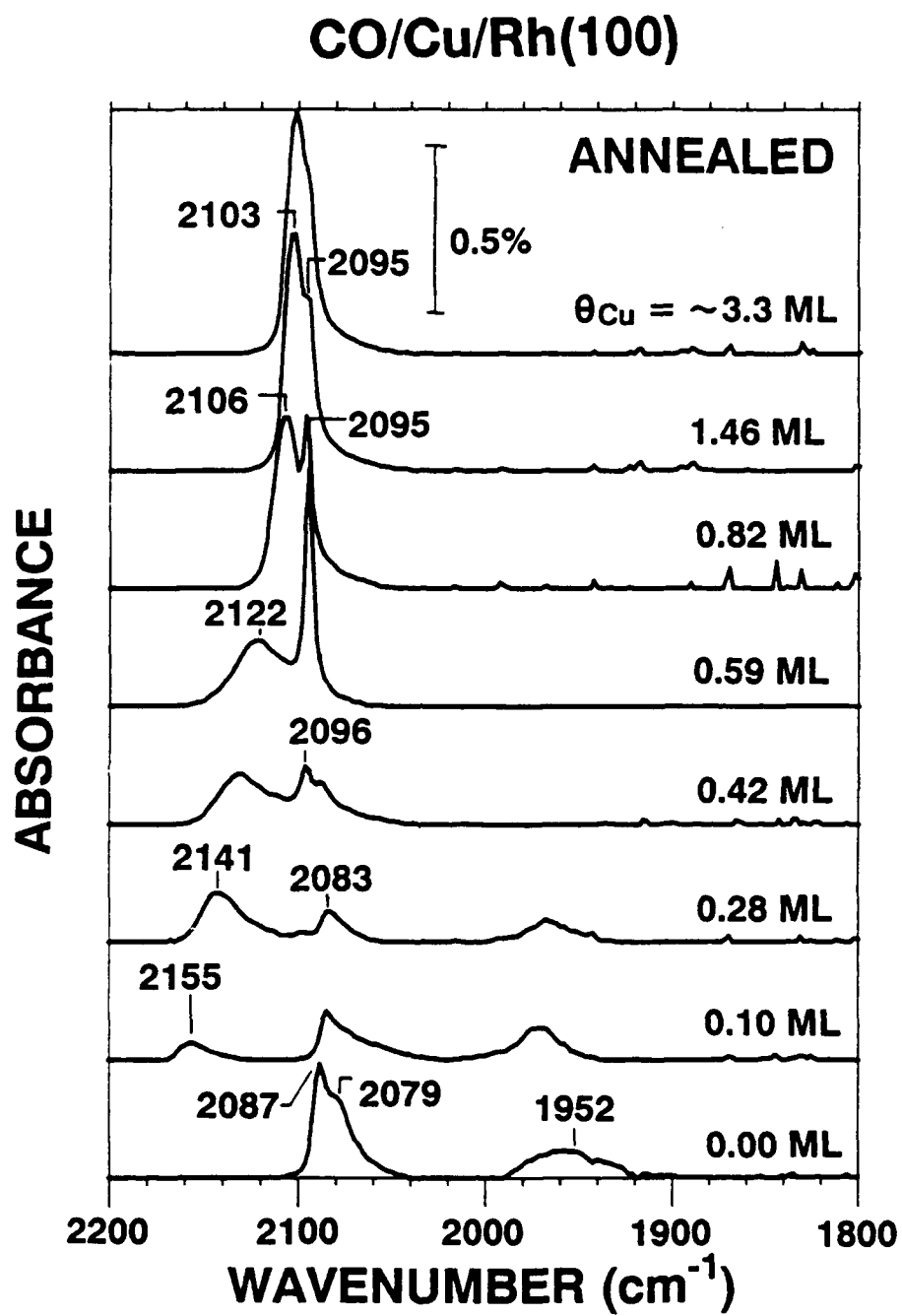


Fig. 17: IR spectra of CO on annealed Cu/Rh(100) surfaces at 90K.

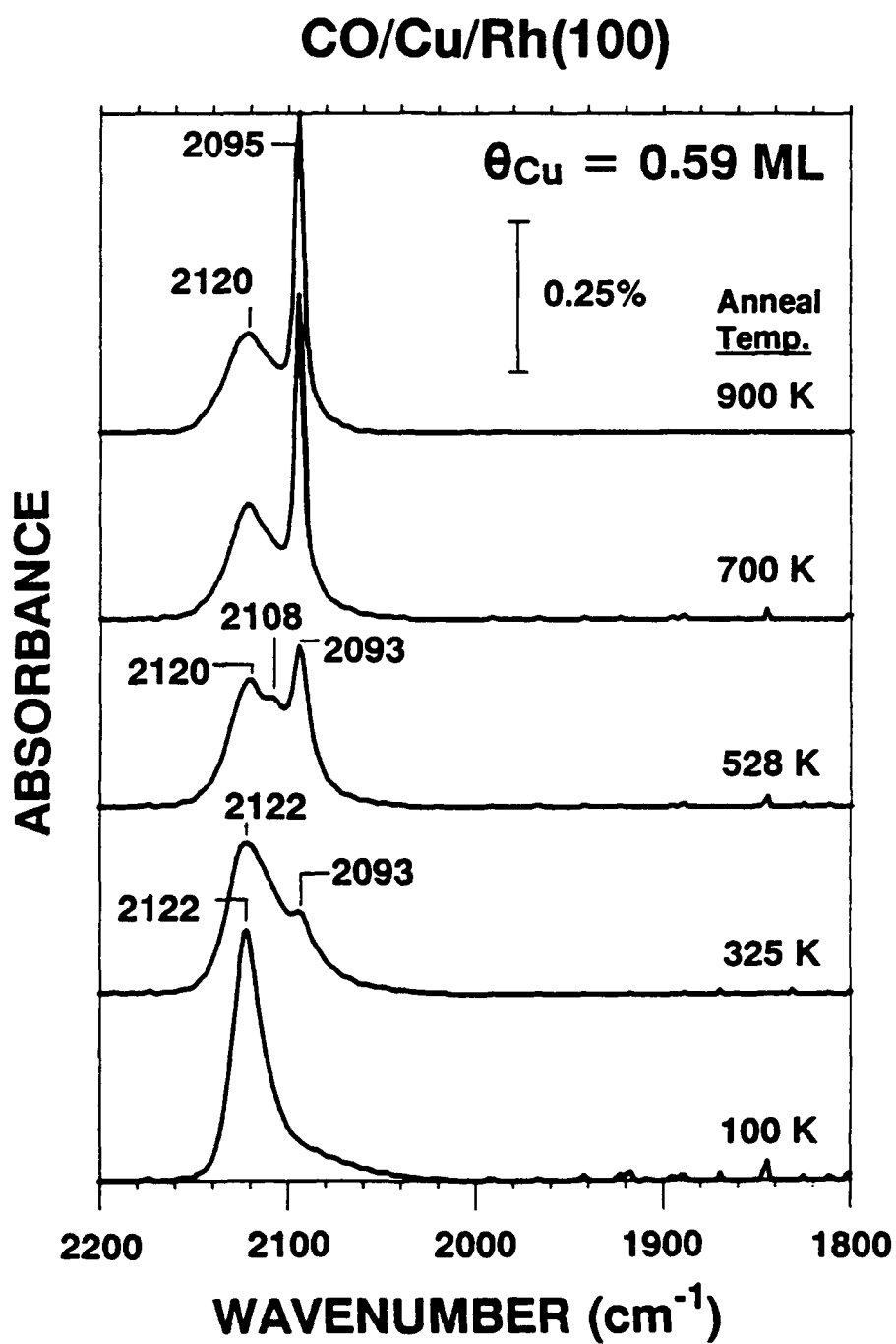


Fig. 18: IR spectra of CO on 0.59 ML Cu on Rh as a function of annealing temperature. CO exposure and spectral acquisition were at 90 K.

Fig. 18 shows the effect that annealing the Cu/Rh(100) surface has on the CO spectra. The Rh(100) surface was first covered with 0.59 ML of Cu at 100K and then annealed to the indicated temperatures. 10L CO was dosed at 85K after each anneal, and the IR spectrum was then acquired at 85K. Fig. 18 clearly shows that the 2095 cm^{-1} peak emerges at an annealing temperature of 325K. Annealing the Cu/Rh(100) surface further increases the intensity of the 2095 cm^{-1} peak at the expense of the 2120 cm^{-1} peak's intensity. Our LEED studies showed that submonolayer Cu on Rh(100) yields only the (1x1) pattern of the substrate. In addition, annealing above 300K significantly decreases the background intensity. A recent XPS study has shown that upon annealing 1.05 ML Cu/Rh(100) to temperatures from 300 K to 700 K, the $\text{Cu}(2p_{3/2})$ core level remains unchanged [55]. This indicates that the Cu atoms in the pseudomorphic layer do not alloy with Rh below 700K. Therefore the 2095 cm^{-1} peak, which gradually becomes well-defined with annealing between 300 and 700K, likely does not correspond to CO adsorbed onto a Cu-Rh alloy. In addition, the 2095 cm^{-1} CO peak cannot arise from CO on Rh since this feature is prominent at $\theta_{\text{Cu}} > 1\text{ ML}$. Also the desorption temperature associated with the 2095 cm^{-1} peak correlates with that of CO from Cu surfaces. Finally, fig. 17 clearly shows that at a Cu coverage of 0.42 ML, both CO-Rh and the 2095 cm^{-1} CO-Cu features are evident.

In fig. 19 we present the integrated absorption intensity of the CO peaks on Rh and Cu as a function of θ_{Cu} for the unannealed and annealed Cu/Rh(100) surfaces from figs. 16 and 17, respectively (the integrated intensities are normalized with respect to the intensity for saturation CO on clean Rh(100)). For

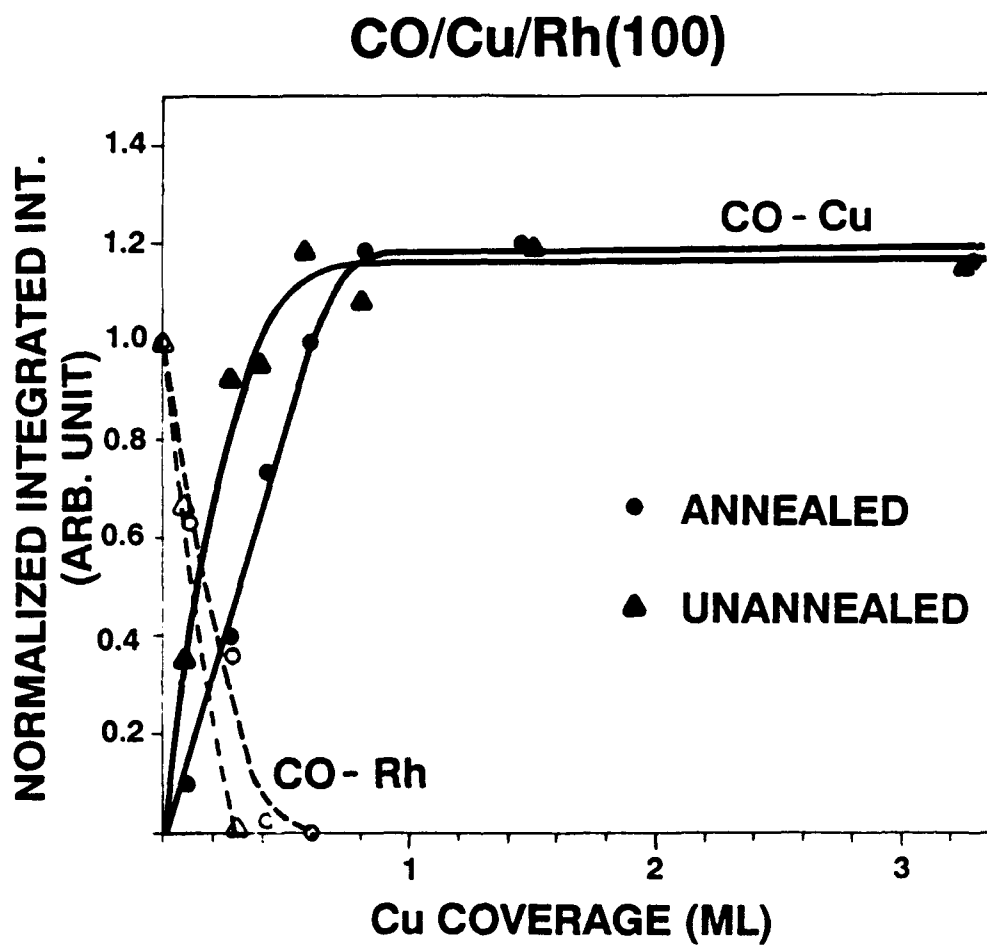


Fig. 19: The normalized integrated intensities of the CO on Cu and Rh atoms as a function of Cu coverage from the spectra in figures 16 and 17.

the purposes of these comparisons, the CO cross-sections are all assumed to be approximately equal. Fig. 19 shows a strong attenuation of the vibrational intensity of CO on Rh as Cu is deposited. At $\theta_{\text{Cu}} = 0.42$ ML, IRAS shows that no CO on Rh(100) is detected. That is, the Rh sites for CO adsorption have either been blocked by the Cu or the CO on the Cu, or the intensity of the low frequency peak is screened by the high frequency CO. On an annealed Cu/Rh(100) surface, the intensity of the linear CO peak on Rh decreases to zero at $\theta_{\text{Cu}} = 0.59$ ML. A marked attenuation of the chemisorption of hydrogen or CO by metal overlayers has been observed previously in TPD spectra [29].

Fig. 20 shows spectra of CO on 0.1 ML Cu on Rh(100) (previously annealed to $\sim 900\text{K}$) as a function of CO exposure. It is clear that at low CO exposure, linear CO-Rh appears first and then bridge-bound CO-Rh. At 4 L of CO, a CO-Cu feature appears. At 6 L CO exposure, the integrated intensity of CO-Cu increases and that of linear CO-Rh decreases. The decrease in the linear CO-Rh integrated intensity is accompanied by a considerable reduction in the overall peak width. The sequence in which the peaks appear suggests the binding energy ordering $E_{\text{Cu}} < E_{\text{B}} < E_{\text{L}}$, where E_{Cu} , E_{B} and E_{L} represent the binding energies of CO-Cu, bridge-bound CO-Rh and linear CO-Rh, respectively. It also suggests that even at 90 K, CO has a high mobility on the surface, allowing it to migrate to the preferred bonding sites.

The IR spectra of various exposures of CO on 0.74 ML Cu on Rh(100) are shown in fig. 21. The Cu/Rh(100) surface overlayer was annealed to $\sim 900\text{K}$ prior to CO exposure at 90 K. Fig. 21 indicates that two peaks (corresponding to CO adsorbed onto different 2-D domains of Cu) are evident for all CO exposures. Both

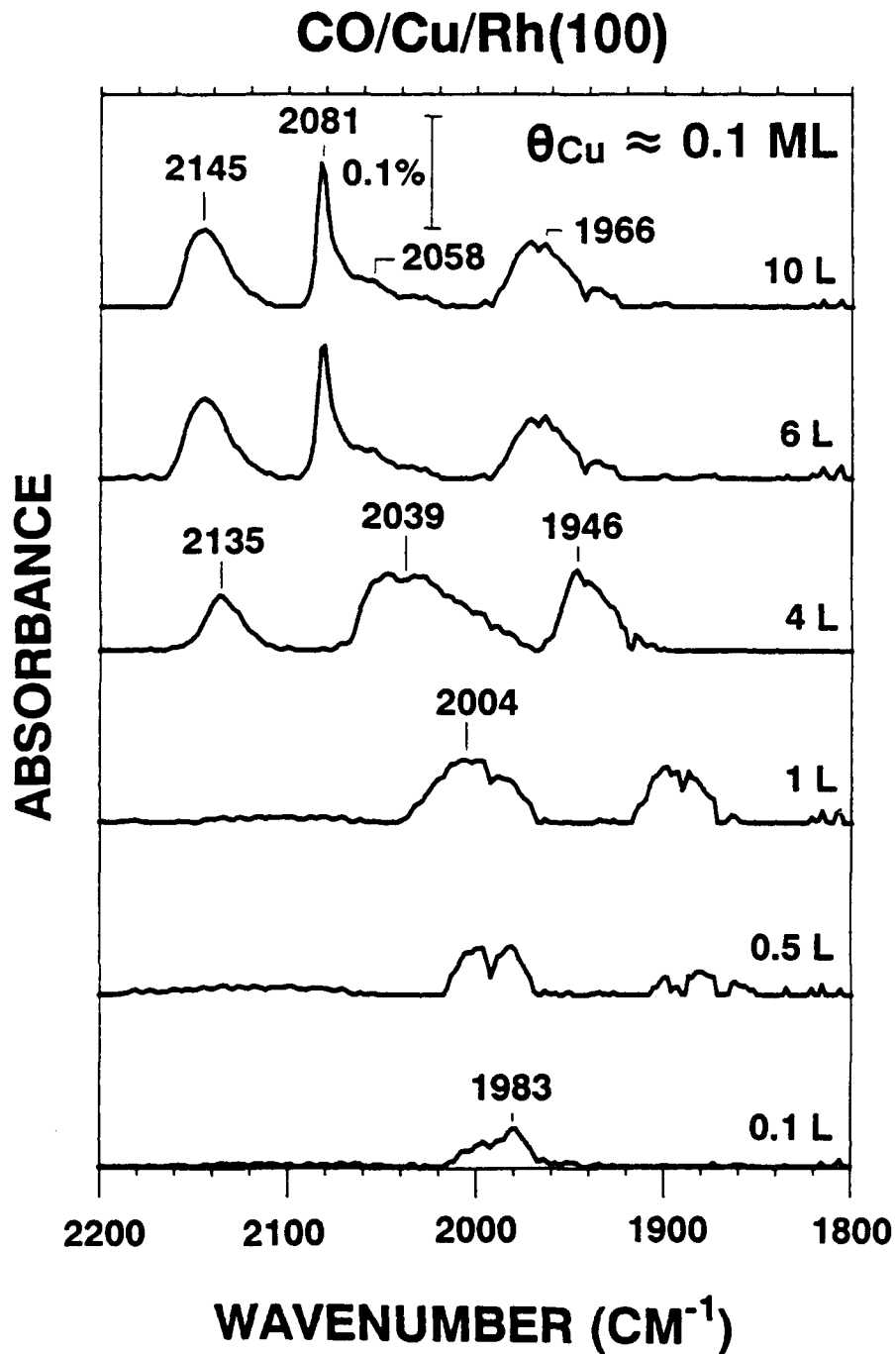


Fig. 20: IR spectra of CO on 0.1 ML of Cu on Rh(100) at 90 K as a function of CO exposure.

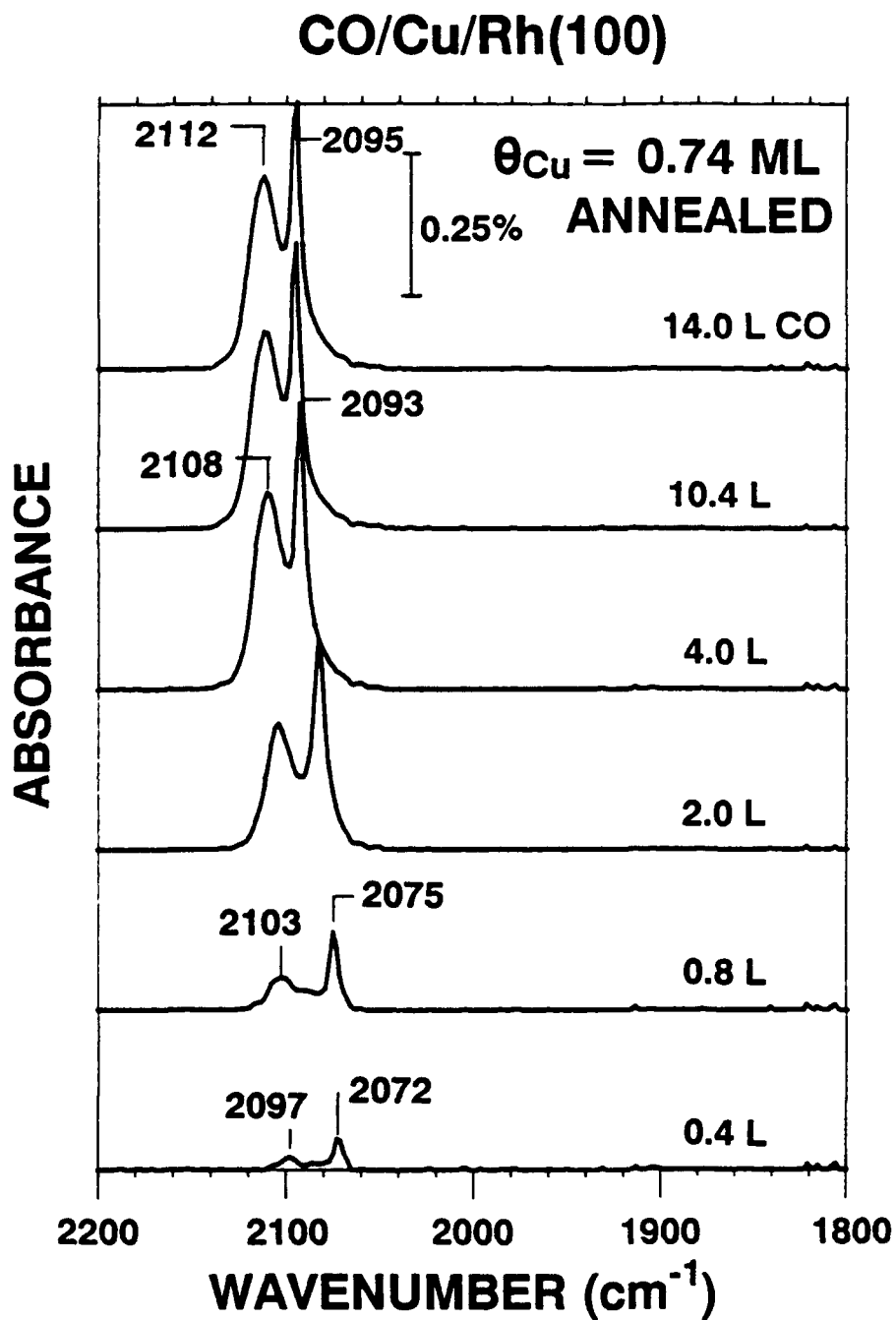


Fig. 21: IR spectra of 0.74 ML of Cu on Rh(100) at 90 K as a function of CO exposure.

frequencies increase as the CO coverage increases, due to a decrease of back-donation to the CO molecule from the substrate as the CO surface density increases and/or an increase in dipole-dipole coupling [64,76,77]. At saturation CO exposure, the frequencies of the high and low frequency peaks have increased by 17 and 26 cm^{-1} , respectively. At 4 L CO exposure, the total integrated CO intensity saturates; however, the frequency of the high frequency peak continues to shift upwards slightly. This slight shift in the high frequency peak is likely due to the adsorption of additional CO. The fact that the integrated intensity does not increase correspondingly indicates a change in the CO cross section as the CO exposure is increased beyond 4L. This, in turn, is likely due to compression (depolarization) of the CO layer at these coverages.

The spectra of CO on Cu/Rh(100) as a function of temperature are shown in figs. 22, 23 and 24. Fig. 22 shows the IR spectra of CO on ~ 0.1 ML Cu on a Rh(100) surface. For these spectra, the Cu was deposited onto the sample and the surface was exposed to 10 L of CO at 100K. The IR spectra were collected at the indicated sample temperatures. Previous studies of CO adsorption on Rh(100) have shown that the peak for CO-Rh will only be seen at a frequency of $\sim 2085 \text{ cm}^{-1}$ or lower with typical linear and bridging frequencies of 2085 and 1970 cm^{-1} , respectively [83]. For monolayer or lower Cu coverages, on the other hand, the CO-Cu peak will be seen at $\sim 2090 \text{ cm}^{-1}$ or higher. Therefore, the peak at $\sim 2150 \text{ cm}^{-1}$ corresponds to CO adsorbed on Cu, while the peaks at ~ 2040 and 1930 cm^{-1} correspond to CO on linear and bridging Rh sites, respectively.

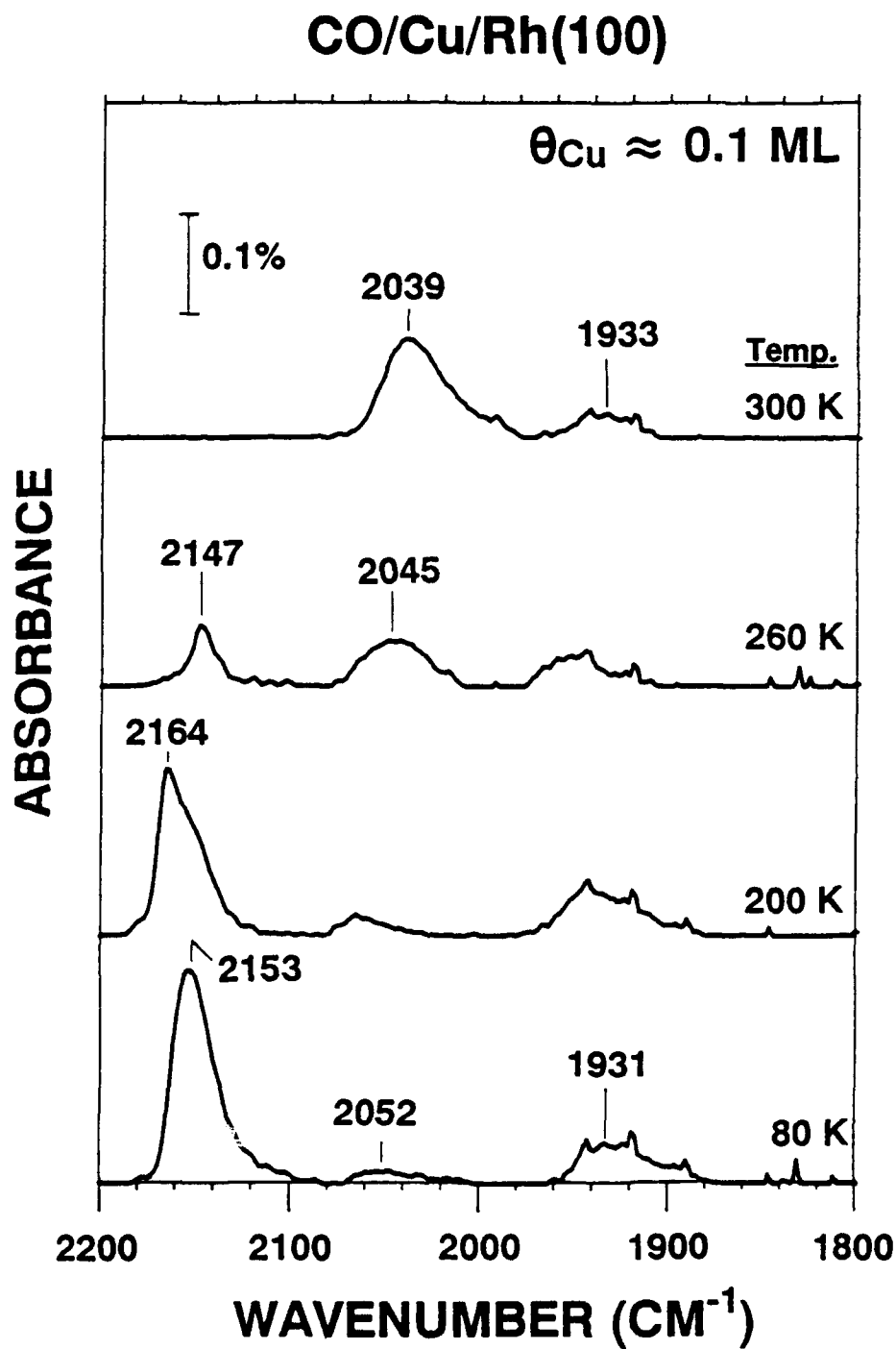


Fig. 22: IR spectra of saturation CO on 0.1 ML of Cu on Rh(100) at the indicated temperatures.

For fig. 23, a Cu coverage of 0.59 ML was evaporated onto Rh(100) at 100K, annealed to 900K, cooled to 83K, and then dosed with 10L CO. From 83K to 135K, the spectra remain essentially unchanged. At 173K, the intensity of the 2095 cm^{-1} peak has decreased and its frequency has red shifted. At temperatures above 213K, the intensity of both peaks decreases. It is noteworthy that the 2095 cm^{-1} peak intensity begins to attenuate at a lower temperature than does the intensity of the 2122 cm^{-1} peak. This result suggests either a lower CO binding energy or a lower CO diffusion activation energy on the ordered domains relative to the disordered domains. However, as discussed above, the adsorption results of fig. 21 show a higher population of CO in the 2095 cm^{-1} peak compared to the 2120 cm^{-1} peak for low exposures of CO. Thus it appears that the activation energy for CO diffusion on the surface, rather than the intrinsic binding energies, controls the relative populations of CO in the two adsorption sites upon CO exposure or upon heating. In other words, the competition between the ordered and disordered domains for CO upon exposure and heating is governed by kinetics rather than thermodynamics.

It is noteworthy that concomitant with the disappearance of CO on Cu, a small amount of CO on Rh appears (see fig. 23). The appearance of CO on Rh indicates either a spillover of CO from the Cu sites to the Rh sites or the desorption of the CO that had been screening the CO-Rh feature. It is unlikely that the appearance of this feature is due to an "intensity sharing" since its peak frequency is 80 cm^{-1} lower than that of the 2095 cm^{-1} peak, even at very low CO coverages ($<0.07\text{ ML}$) (see fig. 21). A detailed discussion will be presented later.

Fig. 24 shows the IR spectra for saturation CO on 1.19 ML of Cu on the

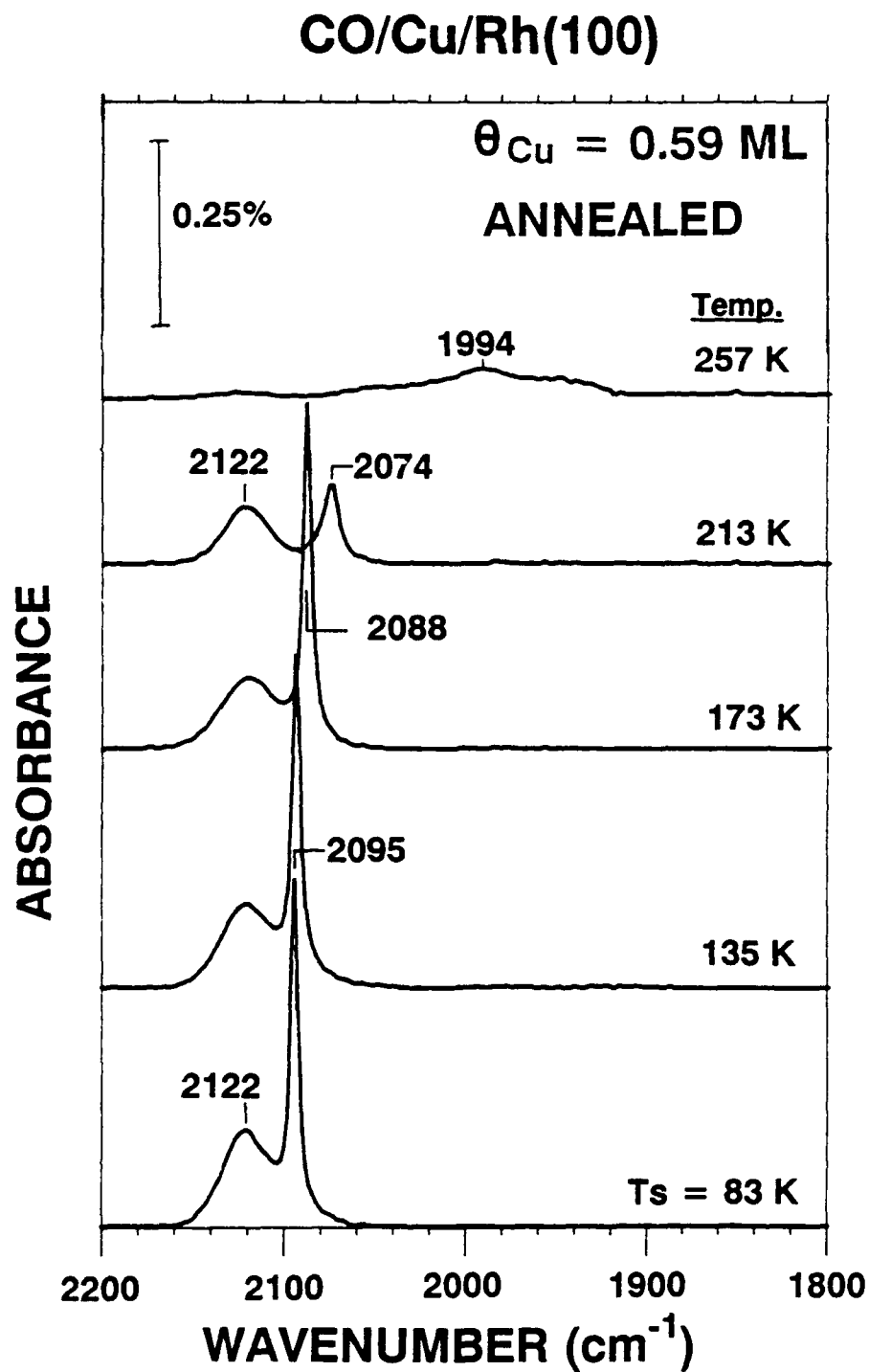


Fig. 23: IR spectra of CO on 0.59 ML of Cu on Rh(100) as a function of sample temperature.

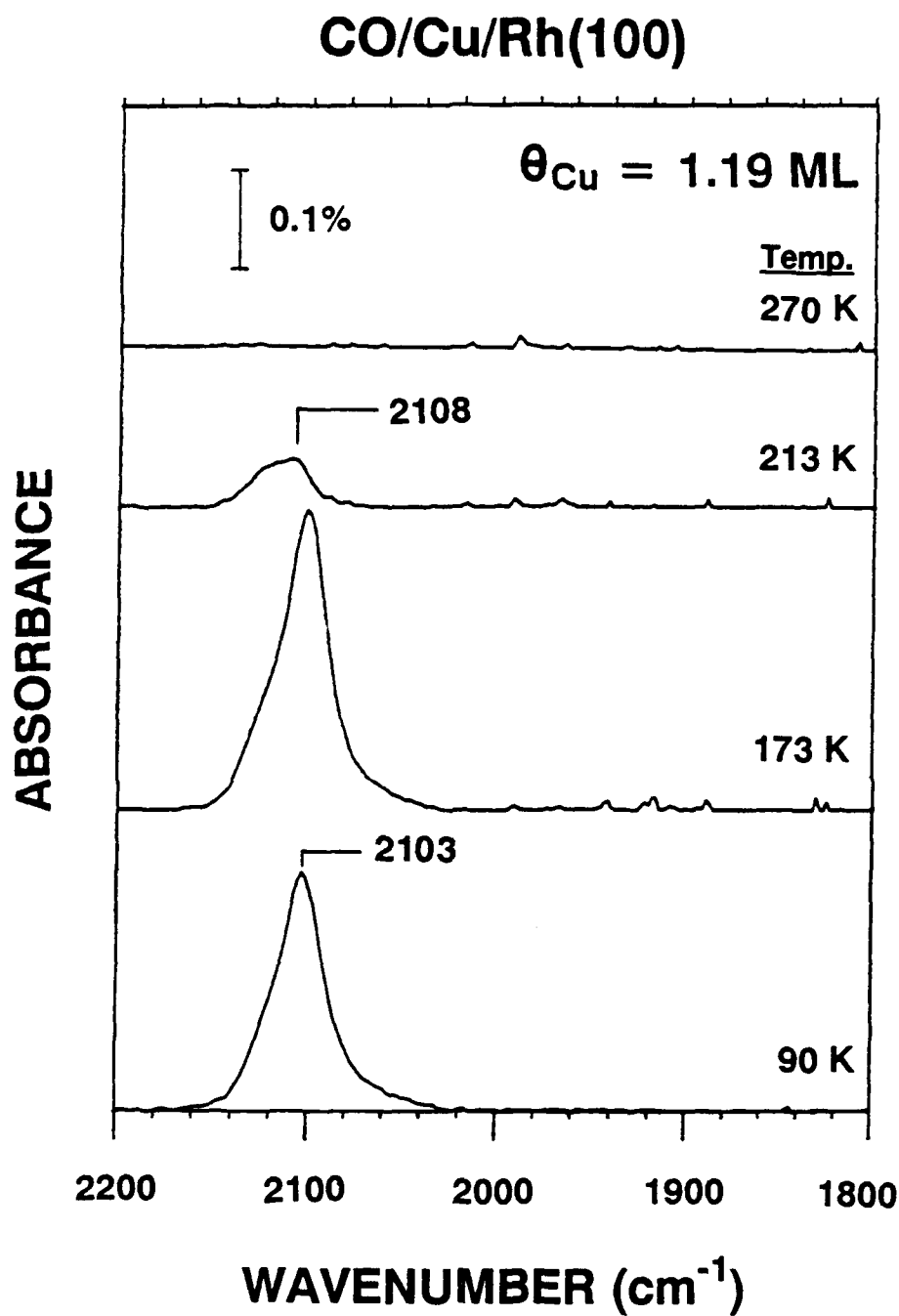


Fig. 24: IR spectra of CO on 1.19 ML of Cu on Rh(100) at the indicated temperatures.

Rh(100) substrate. The sample was annealed to 900 K and then cooled back down to 90 K prior to CO exposure. The spectra were acquired at the indicated temperatures. It is clear from these spectra that as the sample temperature is increased above ~ 200 K that CO begins to desorb from the Cu sites on the surface and that by 270 K no CO remains on the surface. The fact that no CO stretching features are present at 270 K implies that there are no exposed Rh sites available for CO adsorption. The peak assignments discussed above can be corroborated by comparing the temperature dependent IR spectra (figs. 22 - 24) to the CO TPD spectra from Cu/Rh(100).

The CO TPD spectra for various coverages of Cu on Rh(100) (from reference 34) are shown in fig. 25. The sample was annealed to 900 K prior to CO exposure at 100 K. The desorption state induced by Cu adatoms becomes apparent at 260K and peaks at 310K.

In fig. 26, the IR spectra of CO on Cu/Rh(100) at a high Cu coverage are presented. Cu was evaporated onto the Rh(100) surface at 100K, annealed to 871K and followed by a 10 L CO exposure at 85K. Based on previous work [5], the morphology of Cu after this treatment is known to be two uniform (2-D) layers covered with 3-D clusters. The spectrum at 85K shows peaks at 2103 cm^{-1} and 2076 cm^{-1} , with no indication of a peak at 2095 cm^{-1} . The peak at 2076 cm^{-1} , which is not observed at low Cu coverage (<2 ML), apparently corresponds to CO adsorbed on 3-D Cu clusters. This frequency (2076 cm^{-1}) has been reported for CO on Cu(100) and Cu(111) [76,79,101]. Fig. 26 shows that upon flashing the sample to 215K, the peak at 2076 cm^{-1} disappears, while the peaks at 2085 and 2103 cm^{-1}

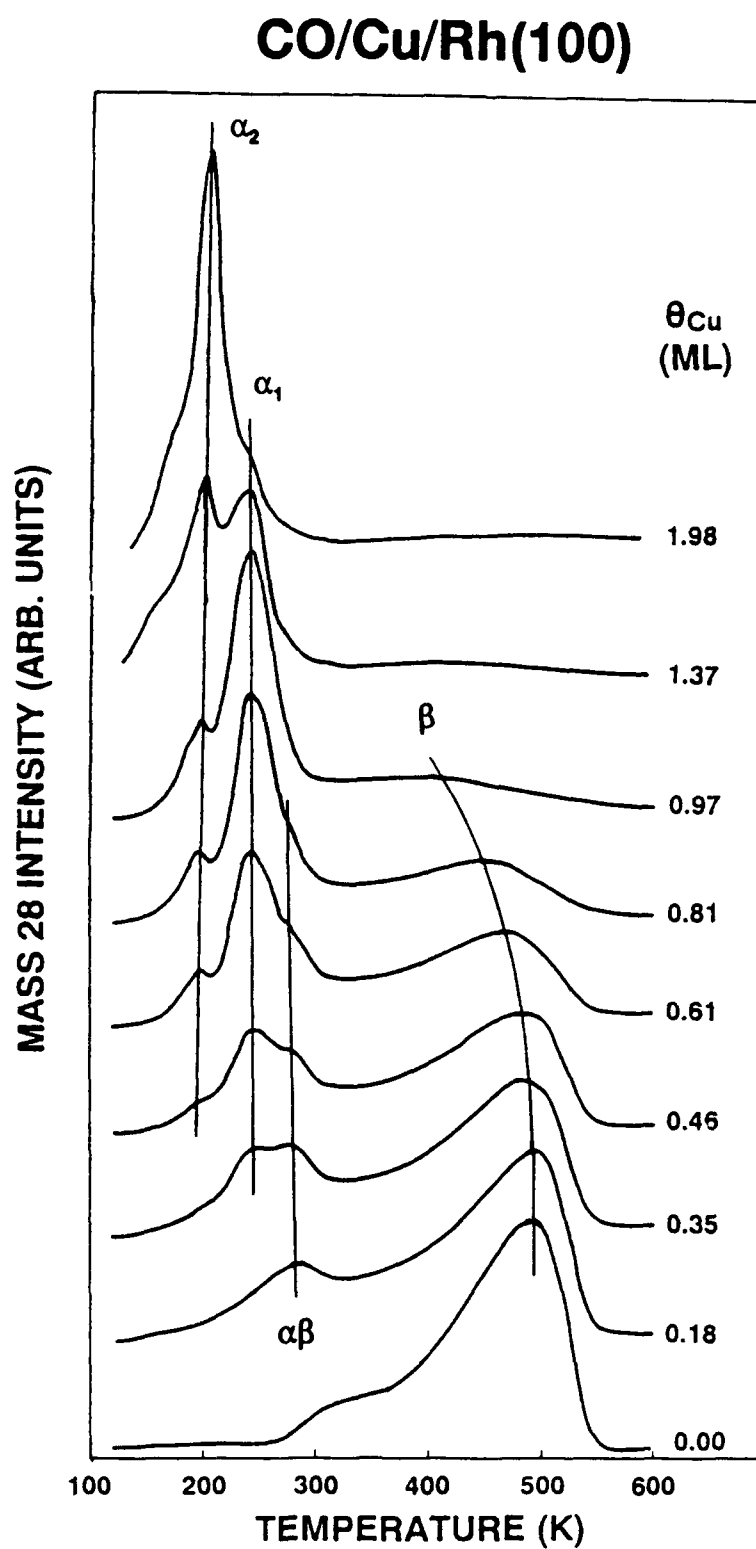


Fig. 25: CO TPD spectra from Cu/Rh(100) after Jiang and Goodman [34].

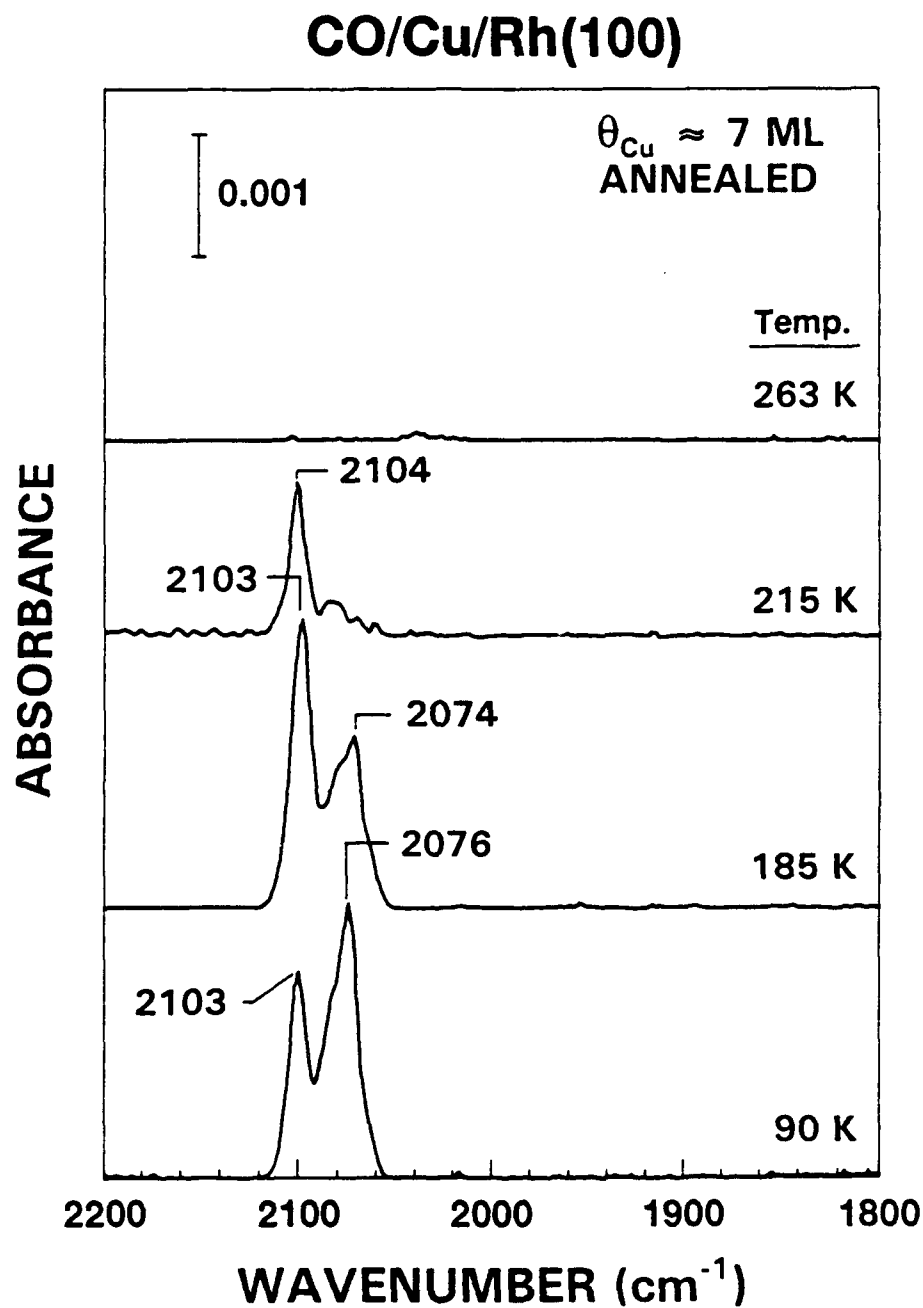


Fig. 26: IR spectra of CO on ~ 7 ML of Cu on Rh(100) at the indicated temperatures.

remain. The disappearance of the peak at 2076 cm^{-1} is due to thermal desorption of CO from 3-D clusters. Upon heating to 263K, all CO desorbs from the surface.

Cu/Ta(110)

CO TPD spectra from Cu/Ta(110) surfaces are shown in fig. 27. Following a saturation CO exposure on a clean Ta(110) surface, there were no CO desorption features for temperatures between 100K and 1500K. Fig. 27a shows the CO desorption spectra from Cu overlayers which were annealed to 900K prior to receiving a saturation CO exposure at 90K. At low Cu coverages, 2 peaks are present at $\sim 210\text{K}$ and $\sim 230\text{K}$ (α_1 and α_2). For coverages greater than 1ML, the α_2 peak persists with a new peak at $\sim 180\text{K}$ (α_3) growing in and eventually becoming dominant. The α_1 and α_3 states likely correspond to CO desorption from the pseudomorphic overlayer and 3-D clusters, respectively. The origin of the α_2 peak is uncertain, but could correspond to CO desorption from the Cu/Ta interface between the substrate and 2-D or 3-D Cu islands. For fig. 27b, the Cu was deposited onto the surface at 100K prior to a saturation (20L) CO exposure at 90K. For submonolayer Cu coverages, there is a decrease in CO desorption temperature as the Cu coverage increases. This likely reflects the coalescence of Cu into 2-D islands. Extrapolating the CO desorption temperatures to zero Cu coverage yields a temperature of $\sim 275\text{K}$. This would be the expected desorption temperature of CO from individual Cu atoms on a Ta(110) surface. For Cu coverages $\geq 1\text{ML}$, CO desorption occurs at 180K, which is very similar to that observed for Cu(111). This

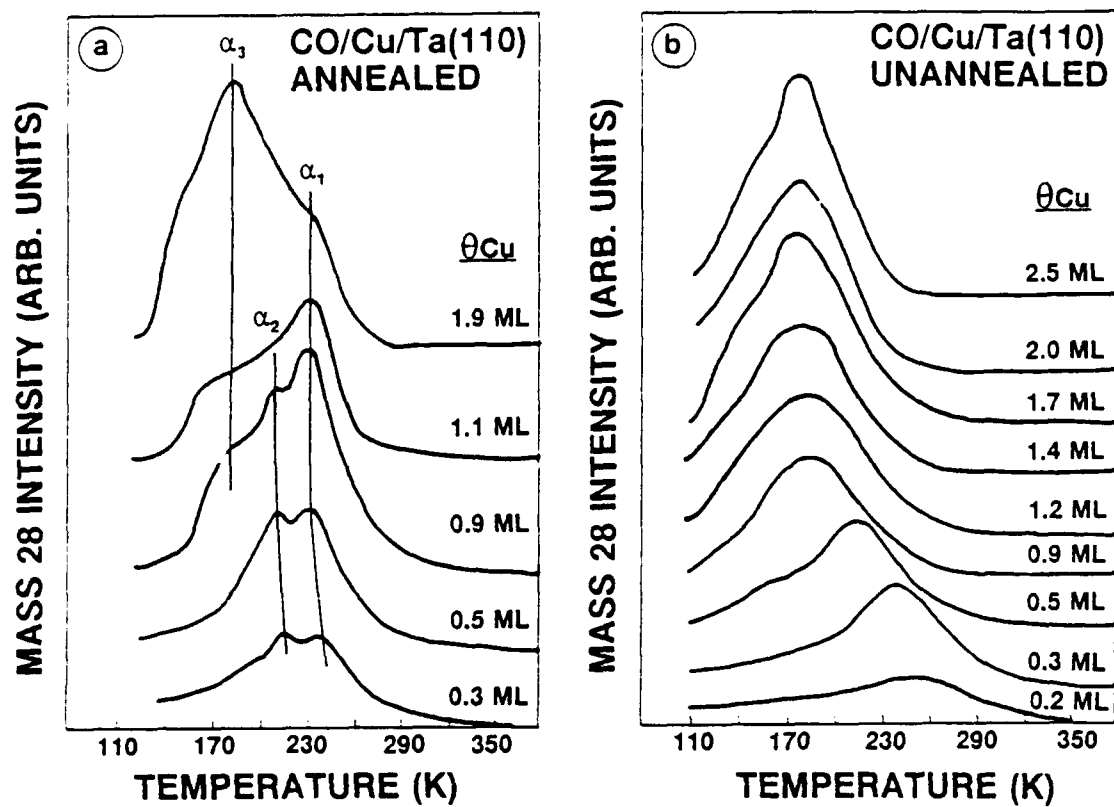


Fig. 27: CO TPD from Cu/Ta(110) as a function of Cu coverage. The Cu was deposited at 90 K and either annealed to 900 K (a) or left unannealed (b) prior to a saturation CO exposure at 90 K.

is likely due to the formation of 3-D Cu clusters.

IR spectra for CO adsorbed on different Cu coverages on the Ta(110) substrate are shown in fig. 28. In fig. 28a, Cu deposition, CO dosing and spectral acquisition were all conducted at 90K. In fig. 28b, the Cu was deposited at 90K, annealed to 900K and then cooled to 90K for the saturation CO exposure and spectral collection. CO adsorbed on Ta(110) gives a broad, weak feature at $\sim 2100 \text{ cm}^{-1}$ indicating that although CO does not desorb from Ta(110) at temperatures $< 1500\text{K}$, CO adsorption at 90K is not entirely dissociative. The large width of the CO-Ta(110) IR peak suggests considerable inhomogeneity in the adsorbed CO. This could be due to the atomic C and O that are also present on the surface due to CO dissociation. In fig. 28a, it is noteworthy that at a Cu coverage of 0.1 ML, the CO-Ta peak is no longer visible. This feature is apparently greatly attenuated by the CO-Cu overlayer as has been seen for other Cu overlayer systems [85,102]. In fig. 28b, the proximity of the CO-Ta and CO-Cu peaks makes it difficult to determine precisely at what Cu coverage the CO-Ta peak is completely attenuated. The spectra for unannealed Cu overlayers in fig. 28a show a continuous red-shifting of the CO peak from $\sim 2123 \text{ cm}^{-1}$ to $\sim 2106 \text{ cm}^{-1}$ as the Cu coverage is increased from 0.1 ML to 2.0 ML, approaching the value observed for CO adsorbed on Cu(111) ($\sim 2070 \text{ cm}^{-1}$) [103]. The 30 cm^{-1} difference is significant; however, the observed frequencies of $\sim 2100\text{-}2110 \text{ cm}^{-1}$ are similar to those seen for CO adsorption on stepped Cu surfaces and supported Cu films [104]. In the annealed films shown in fig. 28b, on the other hand, the value of the CO peak is constant at 2095 cm^{-1} for Cu coverages between 0.3 and 0.9 ML. The constant frequency of this peak as the

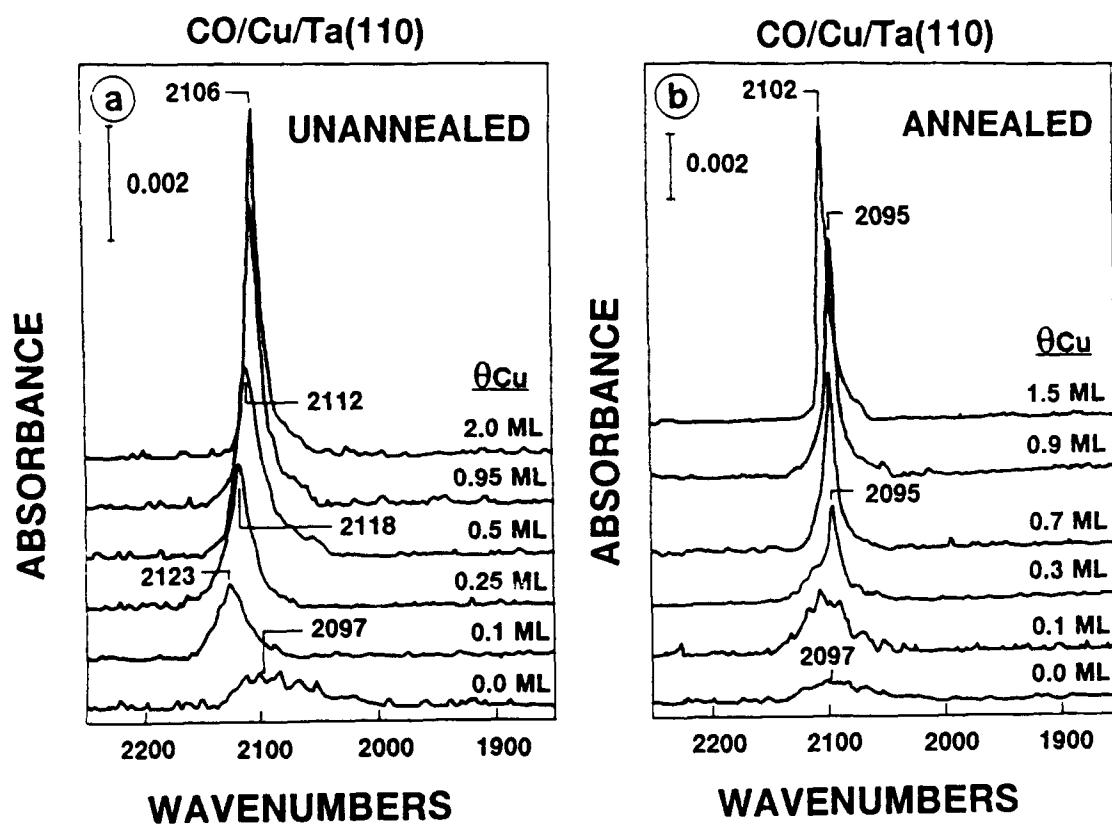


Fig. 28: IR spectra of CO on Cu/Ta(110) at 90K as a function of Cu coverage.

Cu coverage is increased suggests CO adsorption onto 2-D islands that are increasing in size via growth at the island edges. The CO IR peak shifts to 2102 cm^{-1} for CO on 1.5 ML of annealed Cu, reflecting the phase transition seen by LEED at this coverage. In addition, the annealed CO/Cu/Ta(110) peaks are, in general, narrower than the unannealed CO/Cu/Ta(110) peaks. This is attributed to the inhomogeneous broadening of the unannealed spectra due to the non-uniformity of these films.

Fig. 29 shows the CO exposure dependence of the CO IR features for annealed Cu overlayers. In both figs. 29a and 29b, the IR spectra show a shift to higher frequency which is typical of CO adsorption as the CO coverage is increased. It is, however, contrary to the slight shift to lower frequency that is observed for CO on Cu(111) [103]. A coverage dependent shift toward higher frequency with an increase in CO coverage has been observed previously for supported Cu monolayers [84] and different Cu crystal faces [105]. The coverage induced frequency shift is usually attributed to a decrease in back-donation as CO coverage increases or to an increase in dipole-dipole coupling [64,76]. An additional feature at a lower frequency is present in fig. 29b for low CO exposures. This low frequency feature blue shifts at a higher rate than the high frequency peak, and at saturation CO exposure is only visible as a slight shoulder on the main high frequency peak (2102 cm^{-1}). Due to the proximity of the two peaks, there is likely a strong transfer of intensity from the low frequency peak to the high frequency peak [106,107]. As the CO coverage increases, this effect will increase due to the increased proximity of the CO molecules and the decrease in the separation between the peak frequencies.

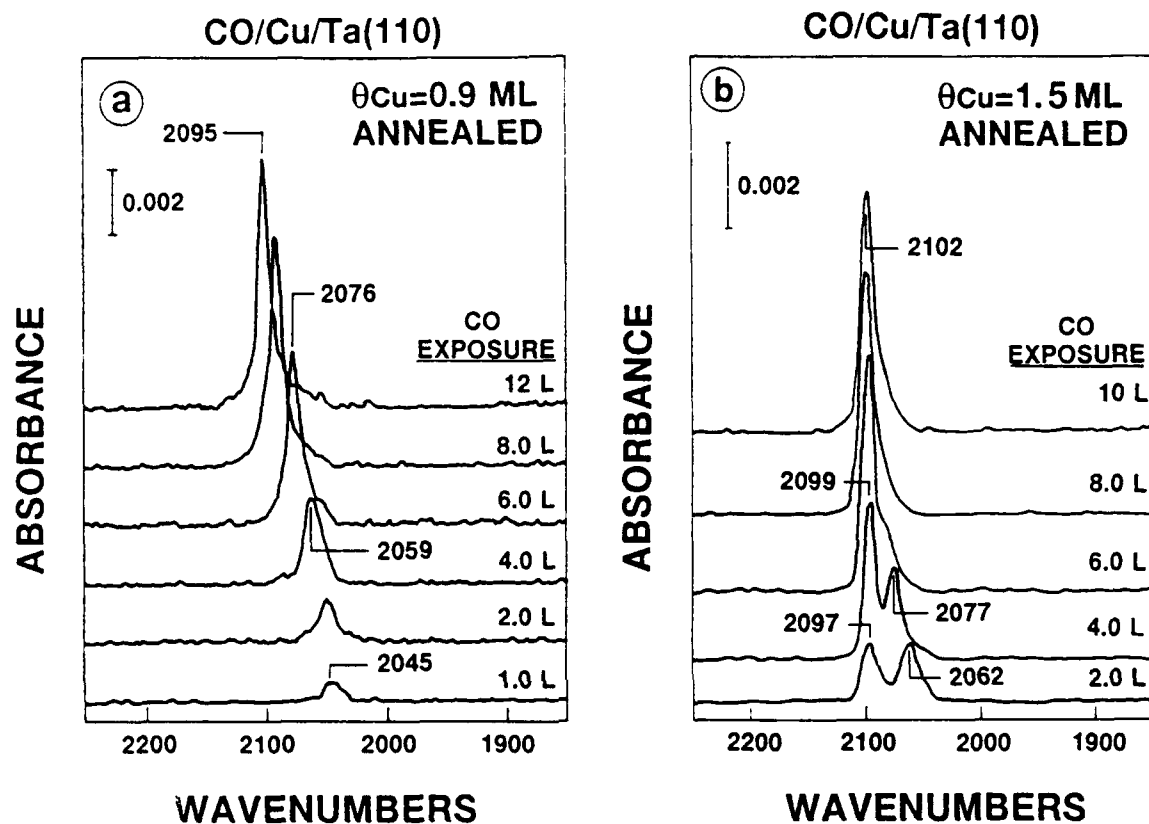


Fig. 29: IR spectra of CO on Cu/Ta(110) as a function of CO exposure at 90K.

Thus, it is very likely, even at saturation CO coverage, that the low frequency peak is the majority surface species.

IR spectra of CO on Cu/Ta(110) as a function of sample temperature are shown in figs. 30 and 31. For submonolayer Cu on Ta(110), fig. 30 shows a slight blue shift in the CO stretching frequency as the CO coverage decreases. In addition, the spectra in figs. 30a and 30b at ~ 0.1 ML and ~ 0.33 ML, respectively, show a decrease in the CO desorption temperatures as the Cu coverage is increased. In addition, fig. 31a ($\theta_{\text{Cu}} \sim 1.8$ ML) shows a desorption temperature of approximately 190K. This decrease in desorption temperature as the copper coverage increases is in agreement with the TPD data shown in fig. 27b. Figs. 31a and 31b again show the effect of annealing the Cu overlayer prior to CO adsorption. In fig. 31b, the low frequency shoulder that was present in fig. 29b for low CO exposures is present at elevated temperatures where the CO coverage is reduced. The CO peak in fig. 31a shifts slightly to lower frequency as the CO coverage decreases. This is in agreement with the exposure dependence observations shown in fig. 29a but is contrary to the shift seen in fig. 30 for submonolayer Cu films.

Ni/Mo(110)

Fig. 32 shows the IR spectra of CO on Ni/Mo(110) at the indicated Ni coverages (θ_{Ni}). The Ni was deposited onto Mo(110) at 100 K and annealed to 900K. The CO exposure (saturation) and IR spectral acquisition were carried out at 90K. CO adsorbed on Mo(110) ($\theta_{\text{Ni}} = 0$ ML) shows a single peak with a stretching

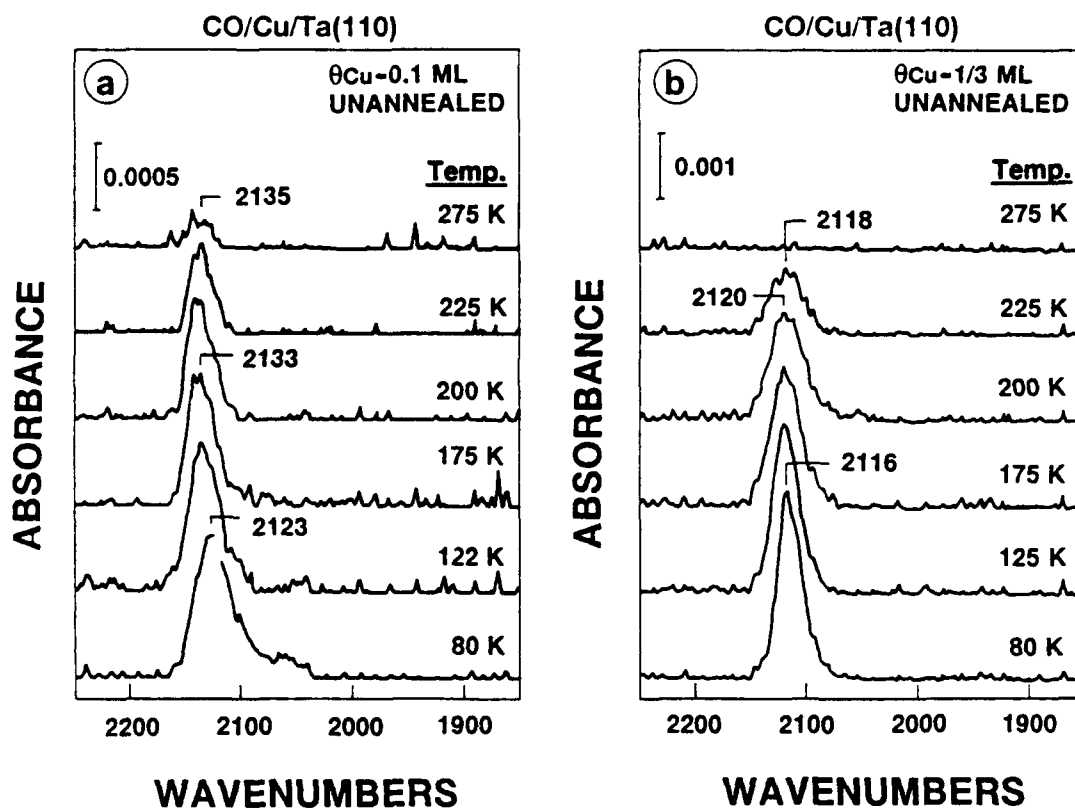


Fig. 30: IR spectra of CO/Cu/Ta(110). Cu deposition and CO exposure were at 90 K with spectral acquisition at the indicated temperatures.

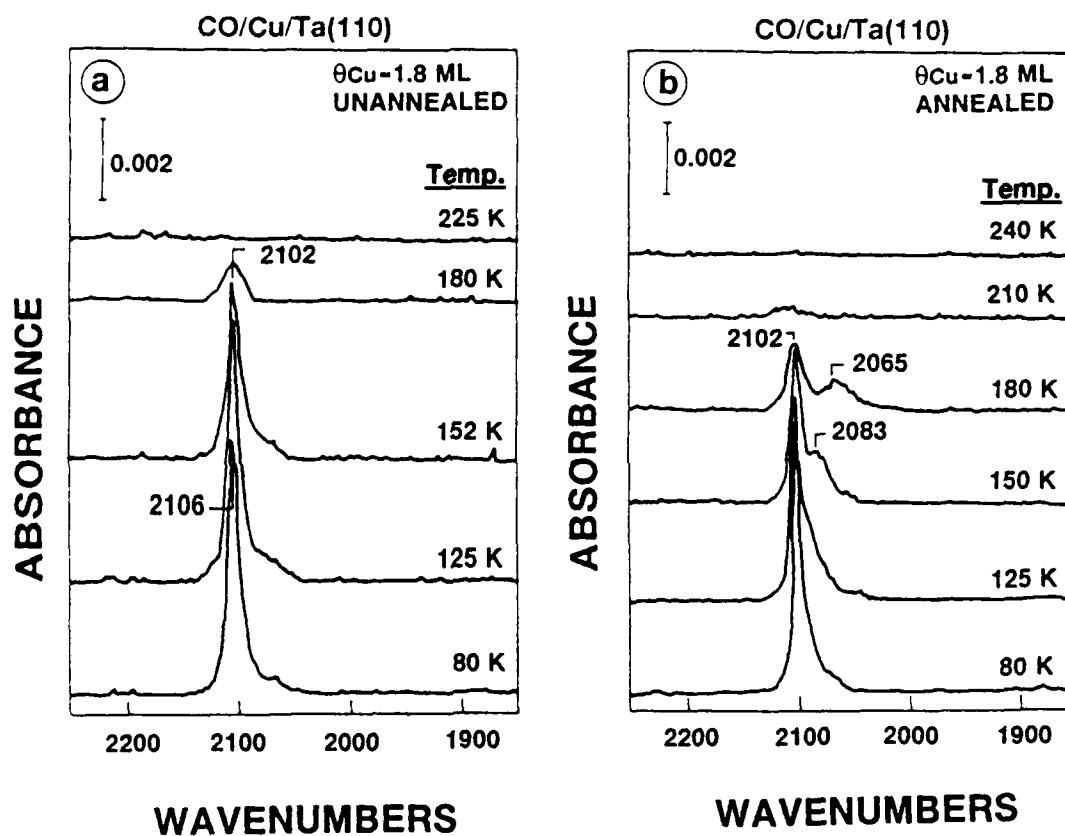


Fig. 31: IR spectra of CO/Cu/Ta(110). The Cu was deposited at 100K and either left unannealed (a) or annealed to 900K (b) prior to CO exposure at 90K and spectral acquisition at the indicated temperatures.

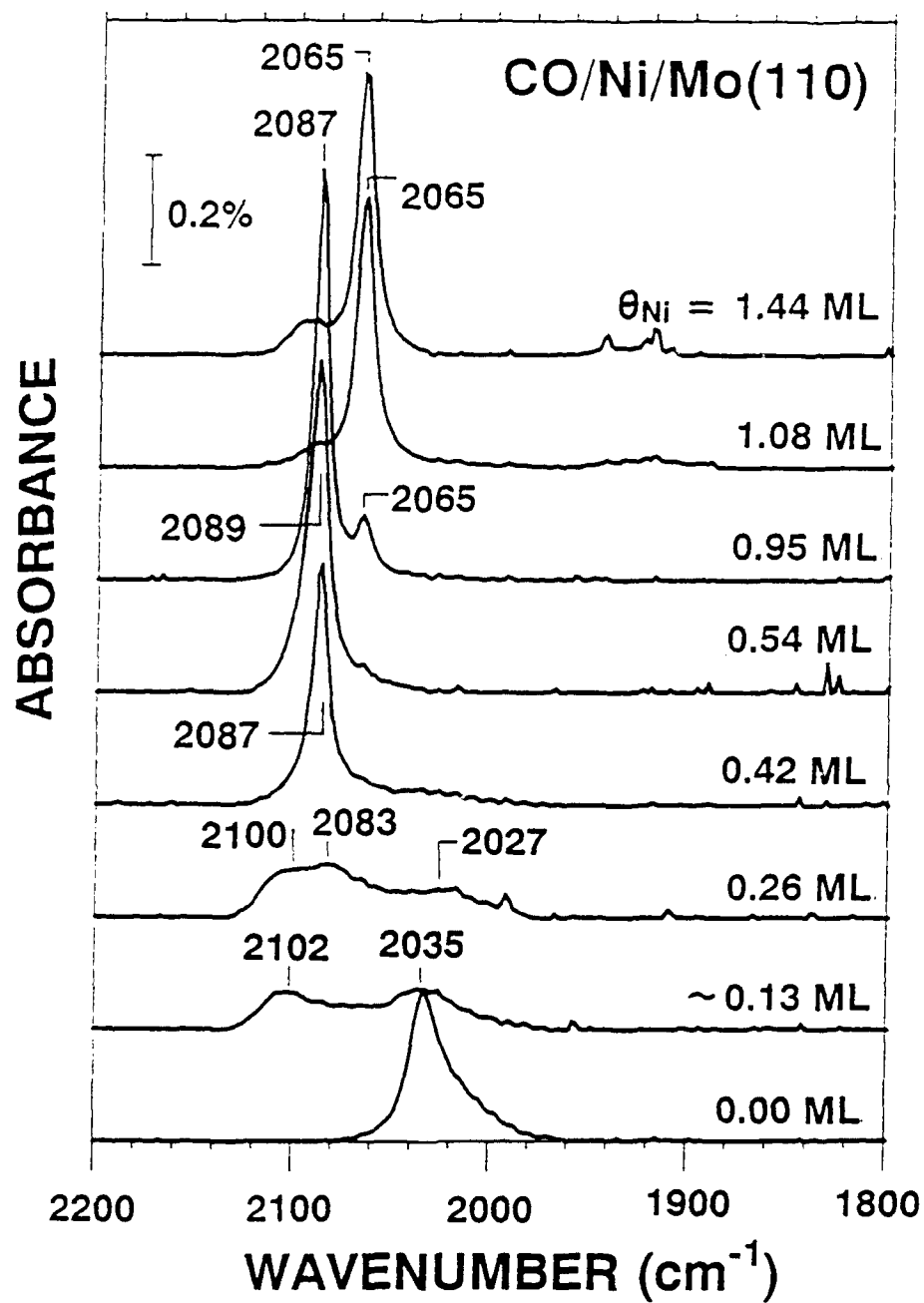


Fig. 32: IR spectra of CO on Ni/Mo(110) at the indicated Ni coverages.

frequency of 2035 cm^{-1} . As the Mo surface is covered with Ni, this peak is greatly attenuated, and disappears by $\theta_{\text{Ni}} = 0.54\text{ ML}$. At $\theta_{\text{Ni}} = 0.26\text{ ML}$, two peaks arise at 2100 and 2083 cm^{-1} . As θ_{Ni} increases from 0.42 to 0.95 ML , the spectra exhibit a peak at 2087 cm^{-1} and its intensity increases with the peak frequency remaining essentially unchanged. At $\theta_{\text{Ni}} = 0.95\text{ ML}$, another peak appears at 2065 cm^{-1} . By $\theta_{\text{Ni}} = 1.08\text{ ML}$, the 2065 cm^{-1} peak has become predominant, and the 2087 cm^{-1} peak is markedly attenuated. The frequencies of these two peaks are higher than that of linear-CO adsorbed on a Ni(111) surface (2054 cm^{-1}) [78], and therefore are assigned to CO bound linearly to the Ni overlayers. It is evident from fig. 32 that at $\theta_{\text{Ni}} = 0.95\text{--}1.08\text{ ML}$, the intensity of the high frequency peak decreases with a concomitant intensity increase in the low frequency peak, while the peak frequencies of the two peaks remain essentially unchanged. It is also noteworthy that both peaks are sharp and symmetric with a full width at half maximum (FWHM) of 10 cm^{-1} , indicating excellent order in the adsorbed CO molecules and consequently implying well-ordered Ni atoms.

LEED observations show that the abrupt spectral change at $\theta_{\text{Ni}} = 0.95\text{--}1.08\text{ ML}$ correlates with a surface phase transition from an (8×2) to (7×2) Ni overlayer structure. The (8×2) pattern (shown schematically in fig. 33) is assigned with respect to the $\langle 001 \rangle$ and $\langle \bar{1}\bar{1}0 \rangle$ Mo lattice parameters, following a previous assignment for the same structure of Ni/Mo(110) [27]. The (7×2) phase has a similar structure but with six satellite spots (instead of seven) between two integral spots along the $\langle 001 \rangle$ direction. From $\theta_{\text{Ni}} = 0.42$ to 0.95 ML , the Ni/Mo(110) surface exhibited the (8×2) pattern. The (7×2) pattern was observed at $\theta_{\text{Ni}} \geq 1.08\text{ ML}$. The

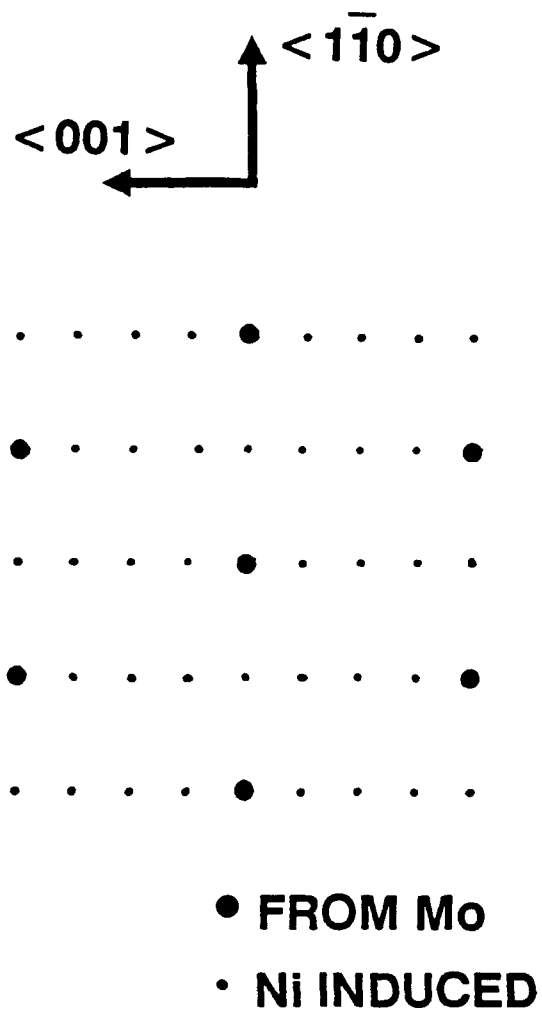


Fig. 33: A schematic representation of the (8X2) LEED pattern.

Ni coverages for the (8x2) and (7x2) structures are 1.250 and 1.286 ML, respectively [27]. The surface density of a Ni(111) surface would correspond to 1.303 ML. Therefore, the (8x2) and (7x2) Ni phases are more densely packed than the Mo(110) surface (25% and 29%, respectively), but are less dense than a Ni(111) surface (4% and 1%, respectively). In a recent study, the (8x2) to (7x2) transition also was found at $\theta_{\text{Ni}} = \sim 0.74\text{--}1.29$ ML for Ni deposition on Mo(110) at room temperature [27]. The (8x2) phase, however, was reported to be metastable, and unobserved by LEED for Ni deposition at $T > 600$ K [27]. The appearance of these structures at submonolayer Ni coverages suggests island formation on the Mo(110) surface.

In fig. 34, the Mo(110) surface was covered with 1.29 ML of Ni at 90 K, and then flashed to the indicated temperatures. The annealed surface was exposed to 10 L of CO at 90 K followed by IR spectral acquisition. Fig. 34 shows peaks at 2097 and 2058 cm^{-1} . Annealing to higher temperatures increases the intensity of the 2058 cm^{-1} peak with its frequency shifted to 2068 cm^{-1} . This intensity increase is at the expense of the 2097 cm^{-1} peak's intensity. At annealing temperatures higher than 675 K, the spectra are essentially identical to the spectrum at 1.44 ML in fig. 32. LEED observations showed that the deposition of Ni at 90 K attenuated the substrate spots and increased the background intensity significantly, indicating a disordered Ni overlayer. Annealing above 500 K decreased the background intensity considerably and yielded the (7x2) pattern. The IR spectral changes in fig. 34 correlate well with the LEED results and reflect the formation of the ordered (7x2) structure from a relatively disordered Ni overlayer. During this surface ordering, the peak frequencies for the ordered and disordered

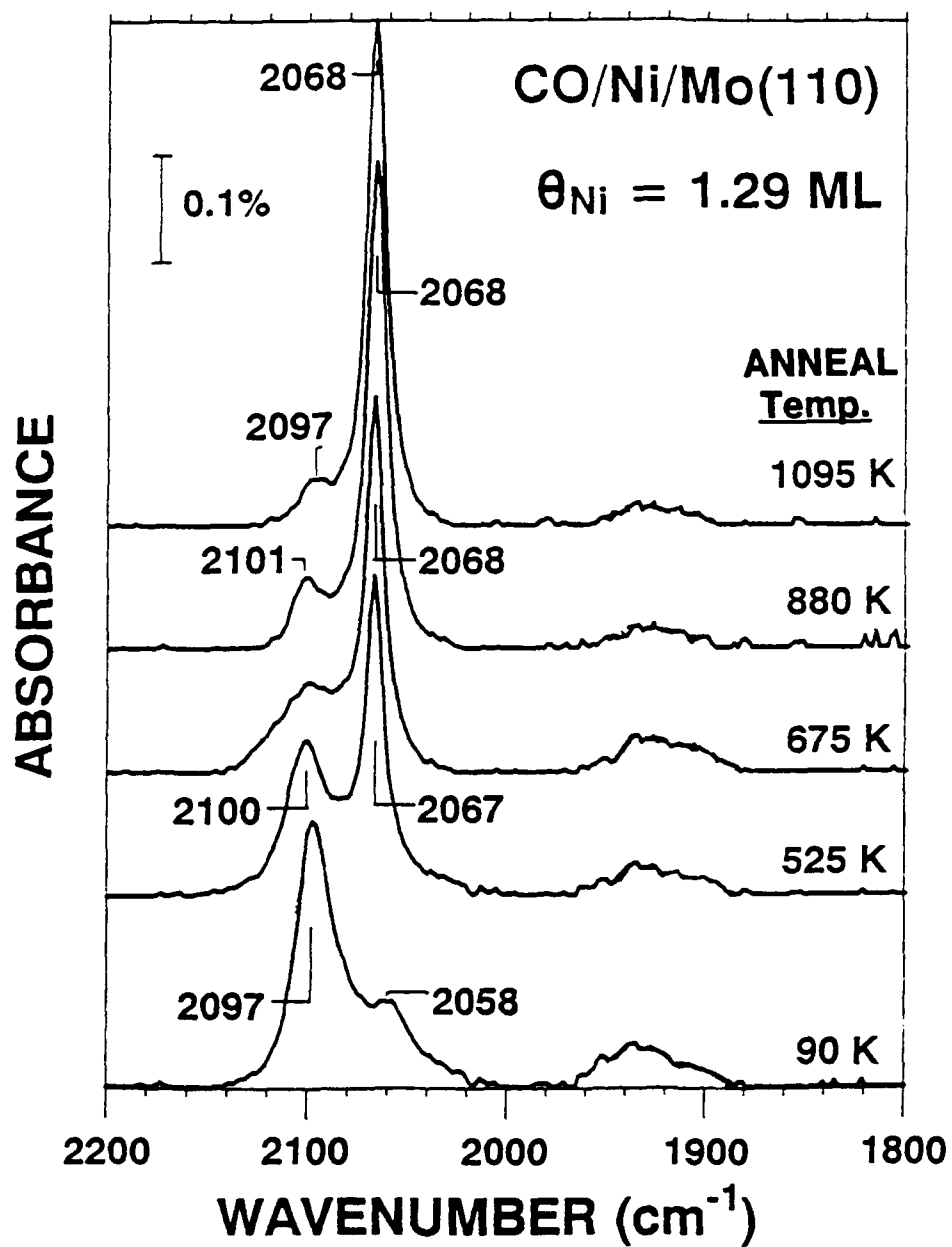


Fig. 34: IR spectra of CO on Ni/Mo(110) at 90K as a function of the annealing temperature of the Ni/Mo(110) surface.

phases are essentially unchanged. The broad peak at $\sim 1932\text{ cm}^{-1}$ is interpreted as bridge-bound CO on the Ni overlayer [78].

IR spectra of CO on Ni/Mo(110) as a function of sample temperature are shown in figs. 35 and 36. For these figures, the Mo(110) surface was dosed with Ni at 100 K, flashed to 1100 K, cooled to 90 K for a saturation CO exposure and then heated to the indicated temperatures for spectral acquisition. The peak at 2068 cm^{-1} in fig. 35 corresponds to CO adsorbed on a (7X2) Ni overlayer (see fig. 34). As the sample temperature is increased to 288 K, this peak gradually shifts toward lower frequency and increases in intensity. This intensity increase is due to the desorption of enough CO to reduce the dipole-dipole coupling and dephasing that result from the high CO surface density at saturation exposure. Further heating causes a fairly rapid red shift in the CO stretching frequency as the remaining CO desorbs from the surface between 330 and 360 K.

In fig. 36, the two main features present at 2066 and 1908 cm^{-1} are due to CO adsorption on the (7X2) overlayer and on 3-D clusters, respectively. These features show a temperature dependent red-shift similar to that observed in fig. 35. CO begins desorbing at $\sim 200\text{--}250\text{ K}$ and desorption is completed between 350 and 390 K. A comparison of the spectra from the (7X2) overlayers shown in figs. 35 and 36 gives a desorption temperature of $\sim 360\text{ K}$. This is in good agreement with TPD results [24].

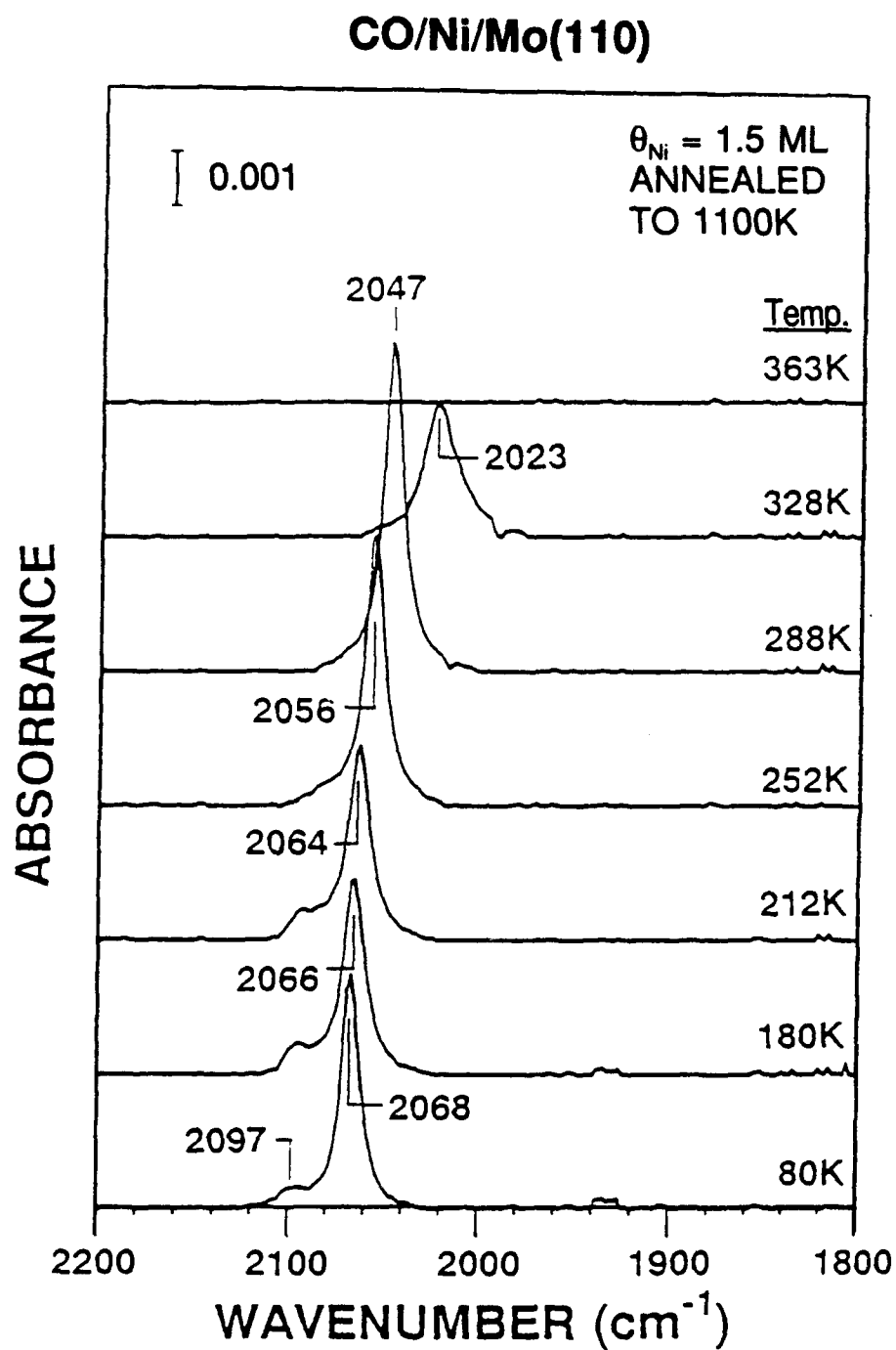


Fig. 35: IR spectra of CO on 1.5 ML of Ni on Mo(110). CO exposure was at 90K with spectral acquisition at the indicated temperatures.

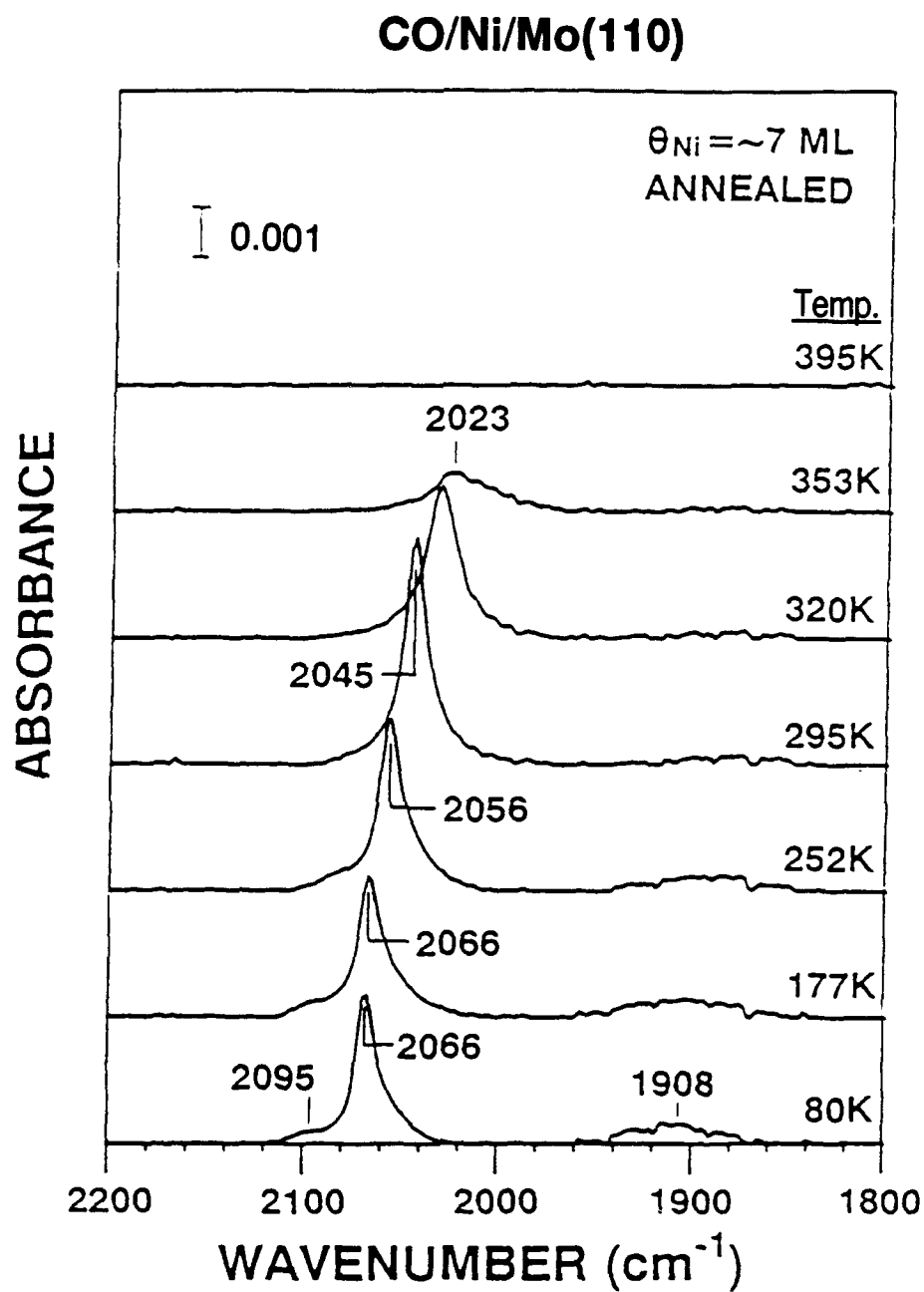


Fig. 36: IR spectra of CO on $\sim 7 \text{ ML}$ of Ni on Mo(110). CO exposure was at 90 K with spectral acquisition at the indicated temperatures.

Co/Mo(110)

Fig. 37 presents the IR spectra of CO on Co/Mo(110) at the indicated Co coverages (θ_{Co}). The Co was deposited onto the Mo(110) surface at 100 K, heated to 900 K, then dosed with 10 L of CO at 90 K, and the IR spectra acquired. The pseudomorphic to (8x2) phase transition is clearly reflected in the spectra as θ_{Co} increases from 1.02 to 1.69 ML. Co is known to form a pseudomorphic structure on Mo(110) for Co coverages less than 1 ML, i.e., the Co atoms assume the Mo(110) substrate lattice [27,35]. At $\theta_{\text{Co}} \geq 1$ ML, an ordered structure appears and is assigned as (8x2). The Co coverage of the (8x2) structure is 1.250 ML [35], and is, therefore, 25% more densely packed than the pseudomorphic structure and 2% less densely packed than the Co(0001) plane. A similar transition (pseudomorphic to (8x2)) has also been observed for the Co/W(110) system [31,108]. CO adsorbed on the pseudomorphic and (8x2) phases shows peaks at 2074 and 2052 cm^{-1} , respectively. As the intensities of the two peaks change, the peak frequencies remain essentially unchanged. The peak at 2035 cm^{-1} corresponds to CO adsorbed on the Mo surface. The small peak at 2095 cm^{-1} is associated with trace surface C from dissociated CO on the Co overlayers [35]. The FWHM for the low frequency peak at $\theta_{\text{Co}} = 1.94$ ML is 10 cm^{-1} .

In fig. 38, the Mo(110) surface was covered with 1.29 ML of Co at 90 K, and then flashed to the indicated temperatures. Each annealed surface was exposed to 10 L of CO at 90 K followed by IR spectral acquisition. As the surface is annealed above 535 K, a peak at 2050 cm^{-1} appears and becomes dominant at the expense

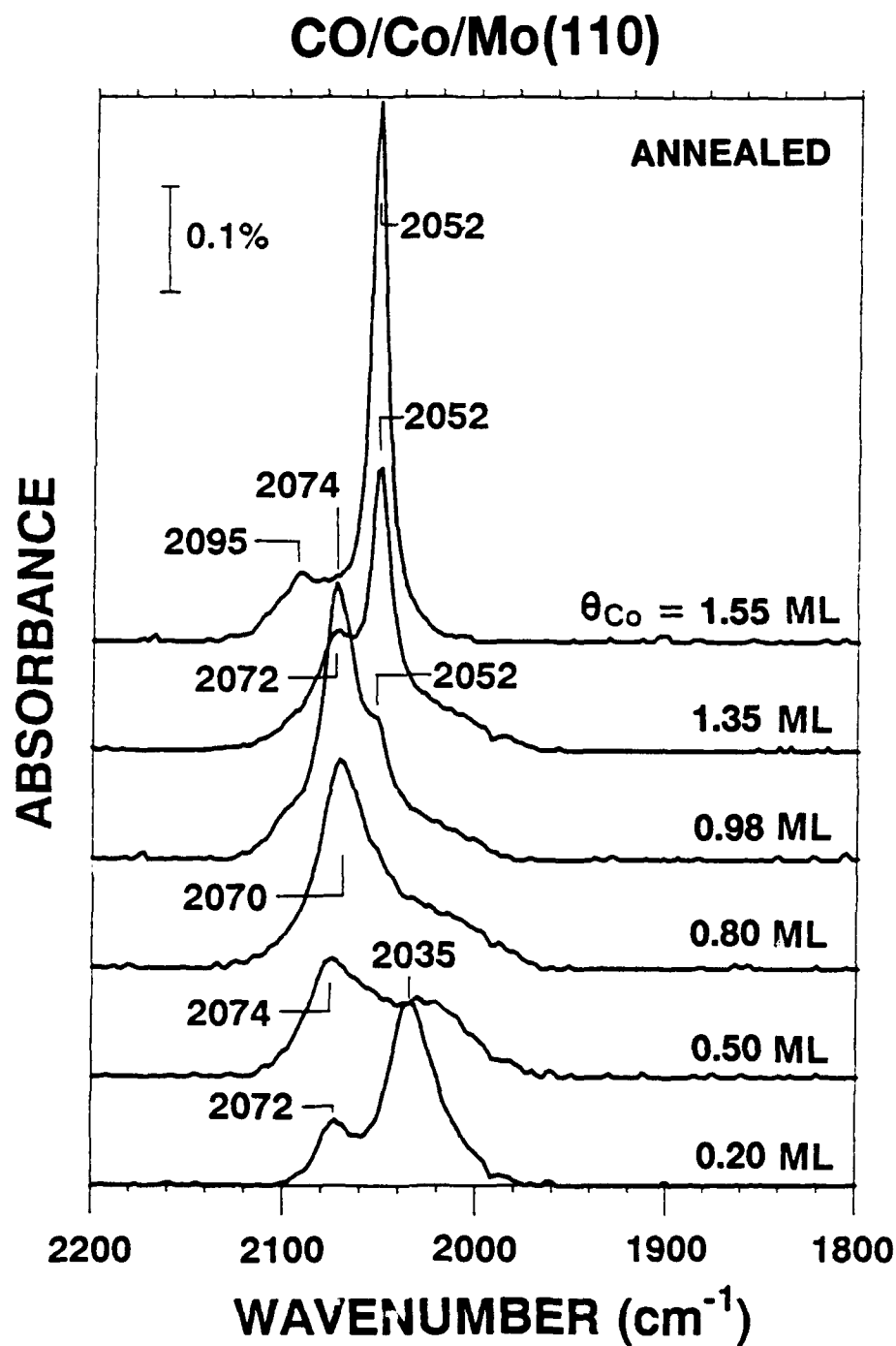


Fig. 37: IR spectra of CO on Co/Mo(110) at 90K at the indicated Co coverages.

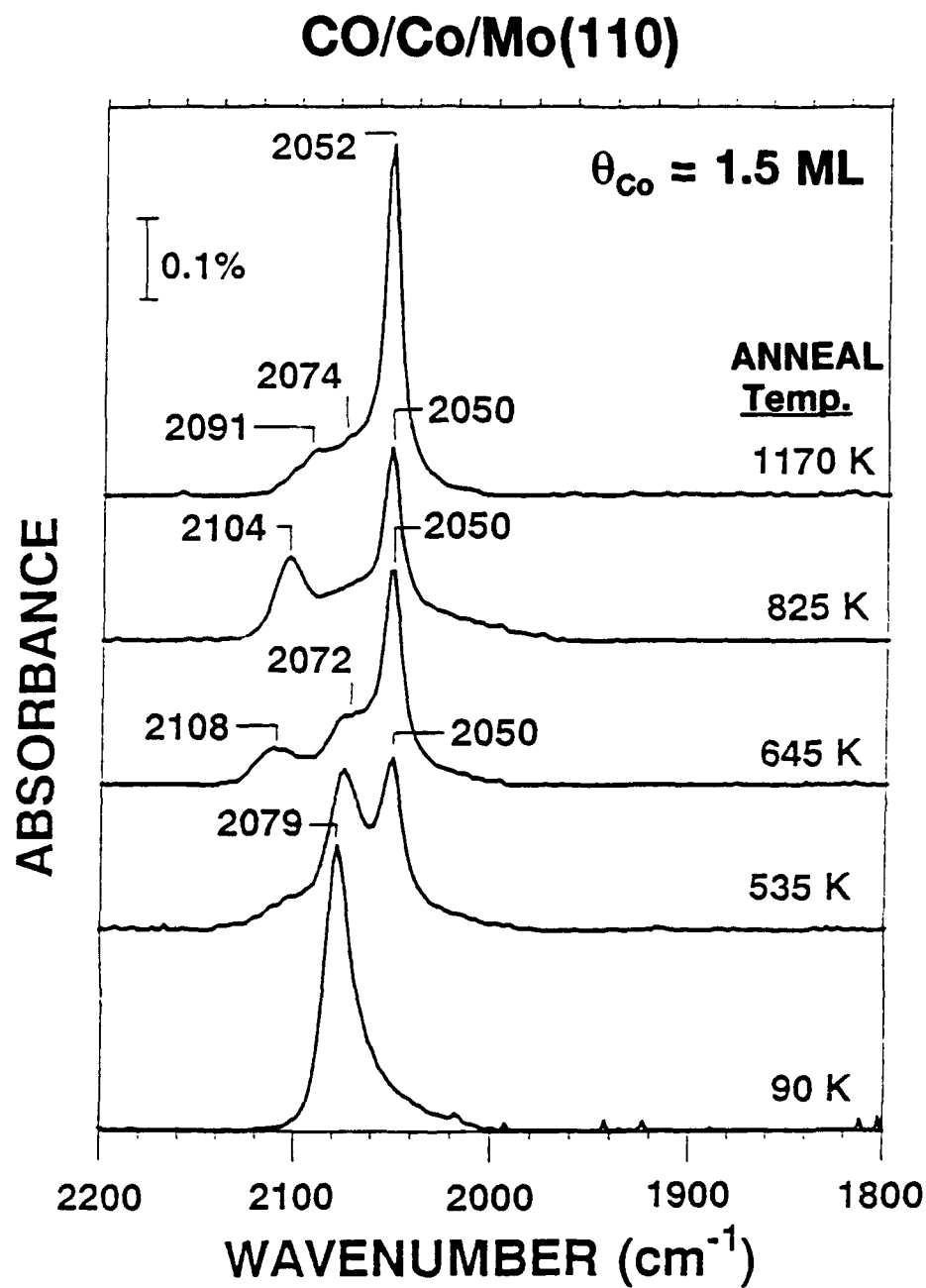


Fig. 38: IR spectra of CO on Co/Mo(110) at 90K as a function of the annealing temperature of the Co/Mo(110) surface.

of the 2073 cm^{-1} peak's intensity. LEED observation demonstrated that annealing above 500 K decreased the background intensity and yielded an (8×2) pattern. Similar to the Ni/Mo(110) system, as discussed above, the correlation of the IR spectral changes in fig. 38 with the LEED results indicates the formation of an ordered (8×2) structure from a relatively disordered Co overlayer. The high frequency peaks at $\sim 2100\text{ cm}^{-1}$ are associated with CO adsorbed in the vicinity of dissociated CO. CO has been shown to dissociate on ultra-thin Co films on a Mo(110) substrate, with subsequent recombination and desorption at $\sim 950\text{ K}$ [35].

IR spectra of CO on Co/Mo(110) as a function of temperature are shown in fig. 39. The Co was deposited at 100 K and annealed to 1100 K prior to a saturation CO exposure at 90 K. The two features present in the 100 K spectrum at 2079 and 2025 cm^{-1} correspond to CO adsorbed on Co and the clean Mo substrate, respectively. The decrease in FWHM and increase in peak height of the CO-Co feature as the temperature is increased from 100 to 180 K is again due to either an increase in the order of the CO adsorbed on these domains, or to a reduction in the dephasing and dipole-dipole coupling that occurs at high CO coverages. As the sample temperature is increased to $\sim 340\text{ K}$ the CO-Co feature disappears, indicating that the CO adsorbed on these sites has desorbed. The Co remaining on the clean Mo surface desorbs at $\sim 380\text{ K}$.

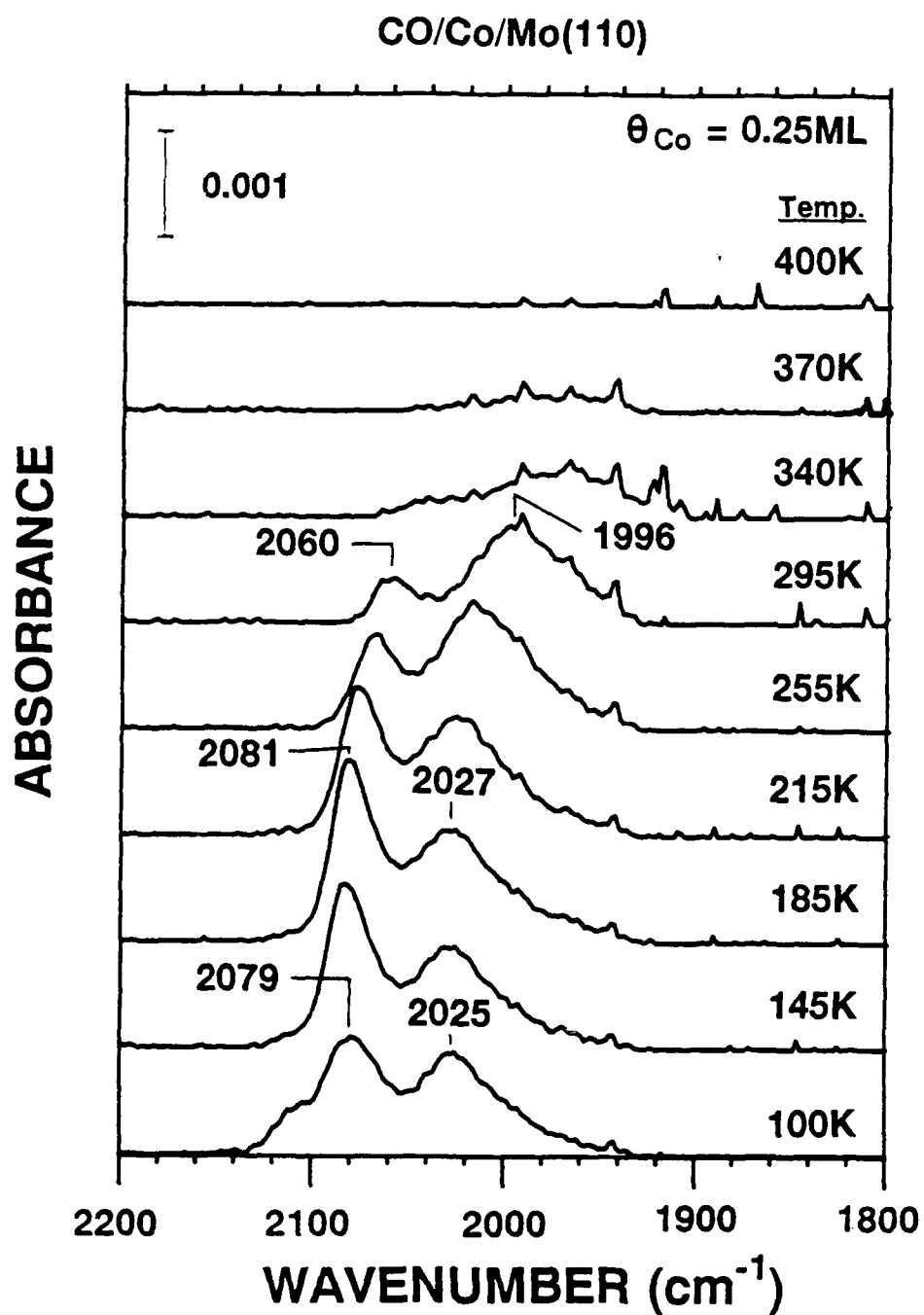


Fig. 39: IR spectra of CO on 0.25 ML of Co on Mo(110). CO exposure was at 90 K with spectral acquisition at the indicated temperatures.

S/Mo(110)

IR spectra of CO adsorbed on various coverages of S on a Mo(110) surface are shown in fig. 40. The sulfur was deposited by exposing the sample to H_2S at 90 K. Subsequent heating to ~ 1400 K causes the H_2S to decompose into H_2 (which desorbs at 400 - 500 K) and elemental S. The spectra were then acquired at 90 K after a saturation CO exposure. Fig. 41 shows the peak positions and total integrated peak area for the spectra in fig. 40. As the sulfur coverage is increased from 0.0 to ~ 0.35 ML, the CO peak position shifts from 2035 to ~ 2010 cm^{-1} . At a sulfur coverage of 0.29 ML, a new peak appears at 2037 cm^{-1} . The intensity of this peak increases with further increases in S coverage. At a sulfur coverage of 0.5 ML, this new peak has a frequency of 2045 cm^{-1} and is the only peak observable.

The sulfur coverages were determined from the $c(2\times 2)$ LEED pattern (see fig. 42) that was observed for the highest S coverage obtainable using the above S deposition method. A $c(2\times 2)$ LEED pattern has a coverage defined to be 0.50 ML. The S coverage assignment is further supported by a $p(2\times 2)$ LEED pattern at $\theta_S = 0.25$ ML. Previous work on S/Mo(110) supports the use of these LEED pattern to establish S coverage on Mo(110) [109]. The continuous shift of the CO-Mo peak from 2035 to ~ 2010 cm^{-1} as the sulfur coverage is increased from 0.00 to ~ 0.35 ML can be explained by a simple site blocking mechanism. Fig. 41 shows that as the S coverage is increased from 0.00 to ~ 0.3 ML, the total integrated CO intensity decreases to approximately 75% of its original value. This implies a 25% reduction

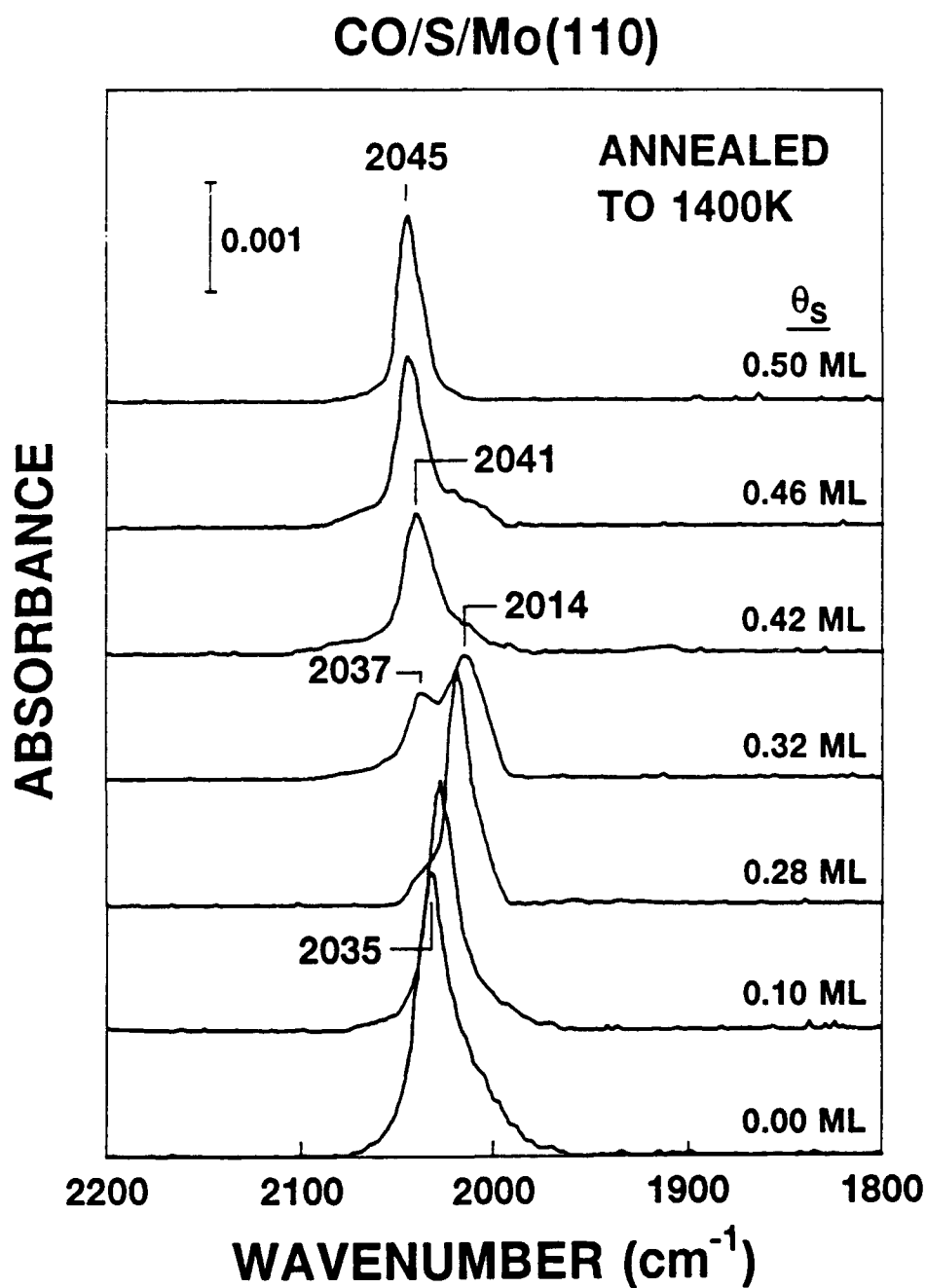


Fig. 40: IR spectra of CO on Mo(110) surfaces at 90 K with the indicated sulfur coverages.

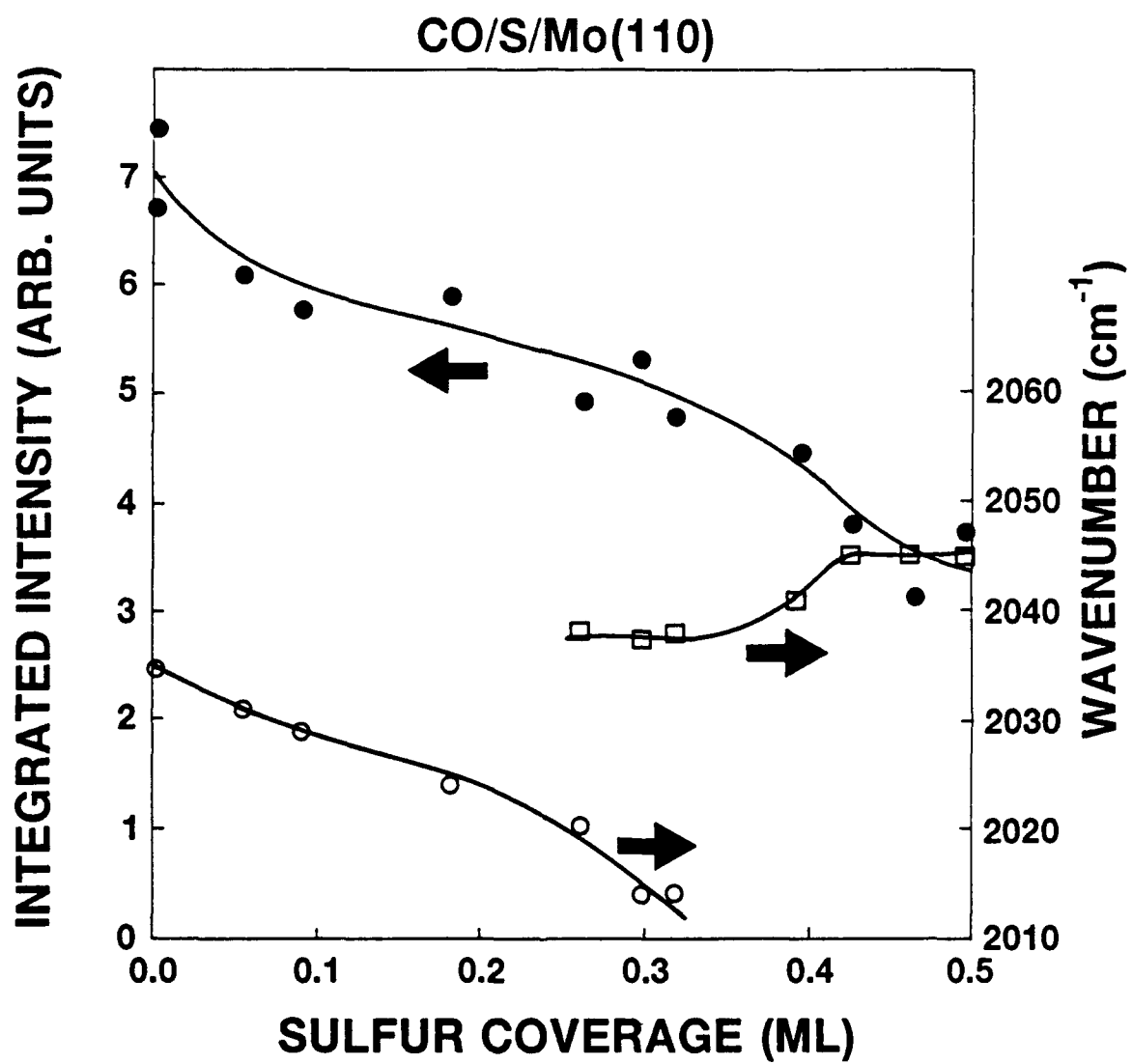


Fig. 41: Peak positions and integrated intensities for the spectra shown in figure 40.

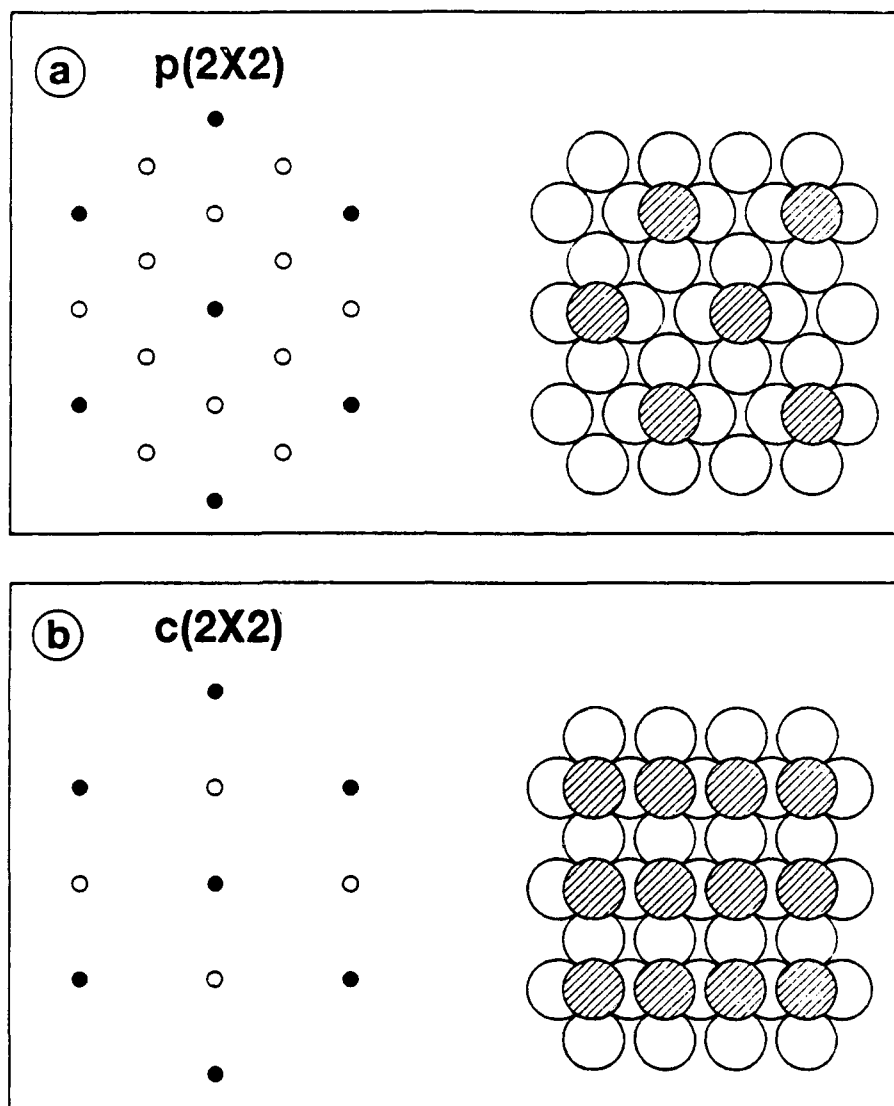


Fig. 42: Representations of the $p(2 \times 2)$ and $c(2 \times 2)$ LEED patterns and corresponding real space structures.

in CO coverage and a S coverage of 0.25 ML. This is in reasonable agreement with the ~ 0.3 ML S coverage and a site blocking mechanism. To further explore CO coverage changes as a function of S coverage, CO TPD spectra were obtained as a function of S coverage (see fig. 43). This figure also shows a decrease in CO as S coverage is increased. The CO TPD results indicate that at a S coverage of 0.2 ML, the CO coverage is only $\sim 75\%$ of the amount on clean Mo(110). These TPD results are in good agreement with the IR results and indicate a simple site blocking mechanism for sulfur coverages up to ~ 0.3 ML.

The constant red shift in the CO peak position as S coverage increases reflects the site blocking nature of the adsorbed S. It is well known that on almost all surfaces, CO peak frequencies shift as CO coverage changes [64,76,77]. This shift is typically toward higher frequency as CO coverage increases and is usually explained as being due to a reduction in 2π backdonation upon increasing CO coverage [64,76,77]. This was also seen to be true for CO adsorption on S/Mo(100) surfaces. Figs. 44-46 show the exposure dependence of CO adsorption at S coverages of 0.20, 0.35 and 0.50 ML, respectively. For these figures, the Mo(110) sample was exposed to H_2S at 90 K and then flashed to 1400 K to desorb the hydrogen and anneal the overlayer. CO exposure and IR spectral acquisition were at 90 K. For all three S coverages, there was an approximately 10 cm^{-1} increase in the CO stretching frequency as the CO coverage was increased to saturation (10 L). It is likely, therefore, that the decrease in peak frequency seen in fig. 41 as S coverage is increased to ~ 0.3 ML is due to a decrease in CO coverage.

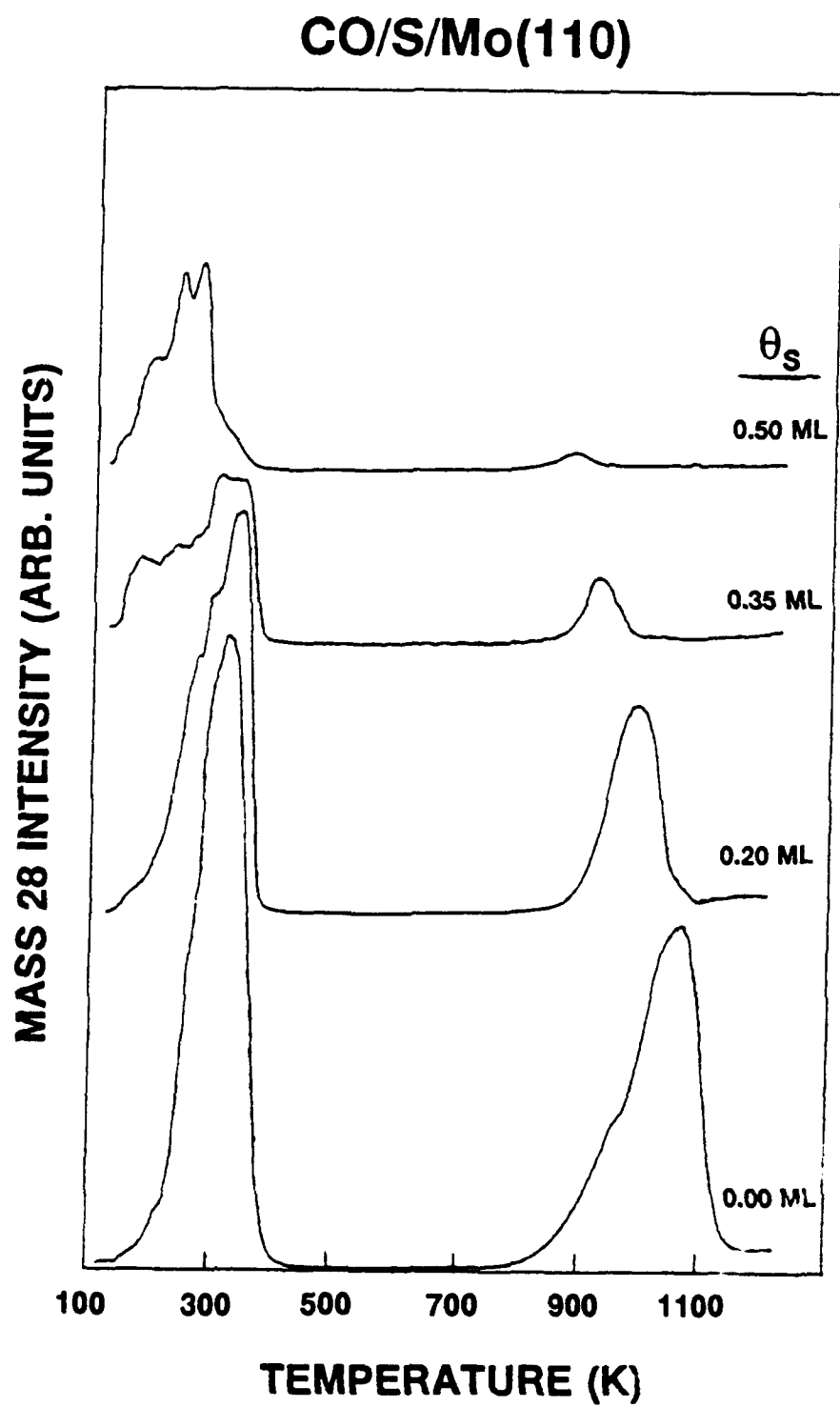


Fig. 43: CO TPD from S/Mo(110) as a function of S coverage.

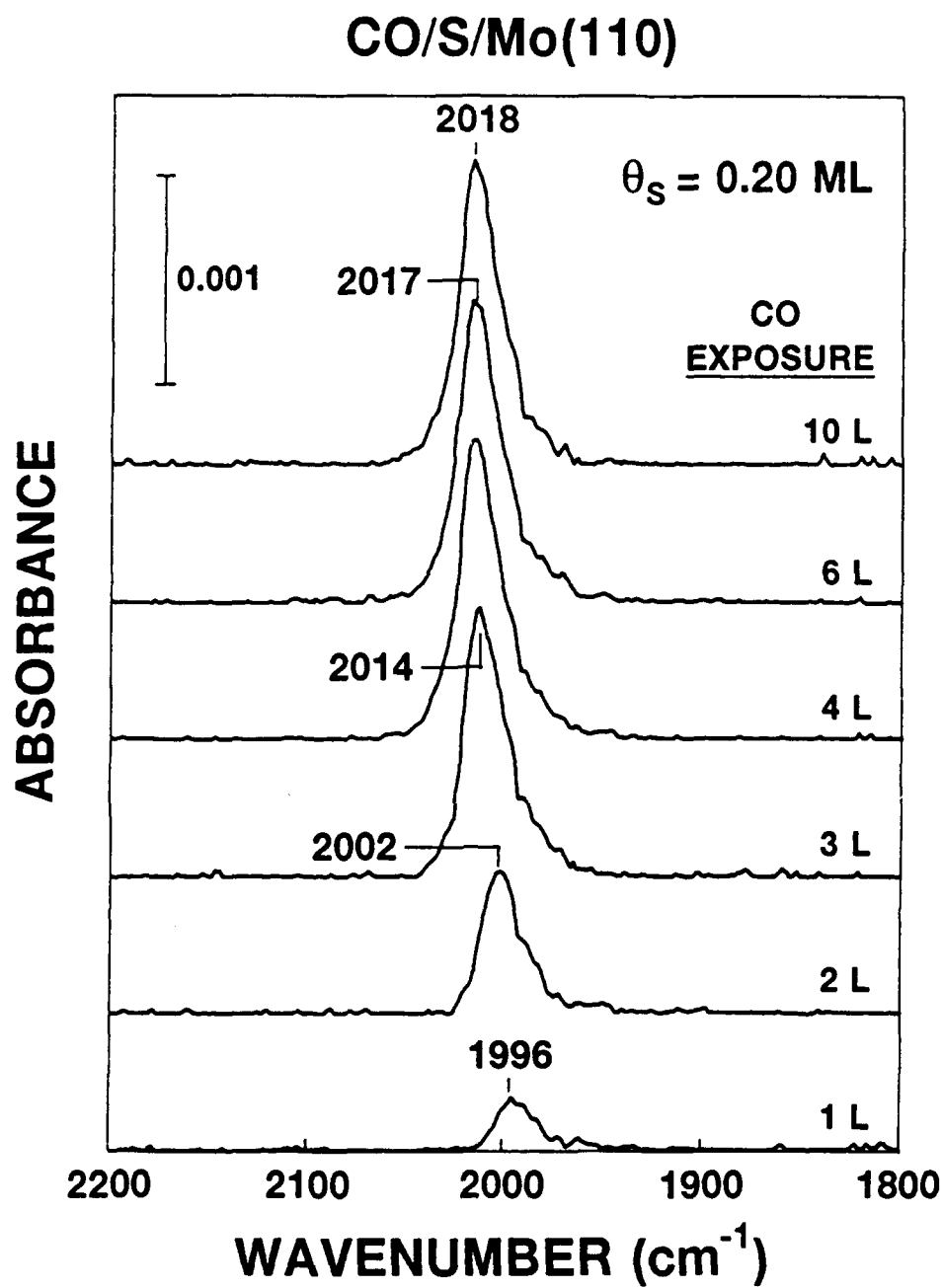


Fig. 44: IR spectra of CO adsorbed on 0.20 ML of S on Mo(110) at 90 K as a function of CO exposure.

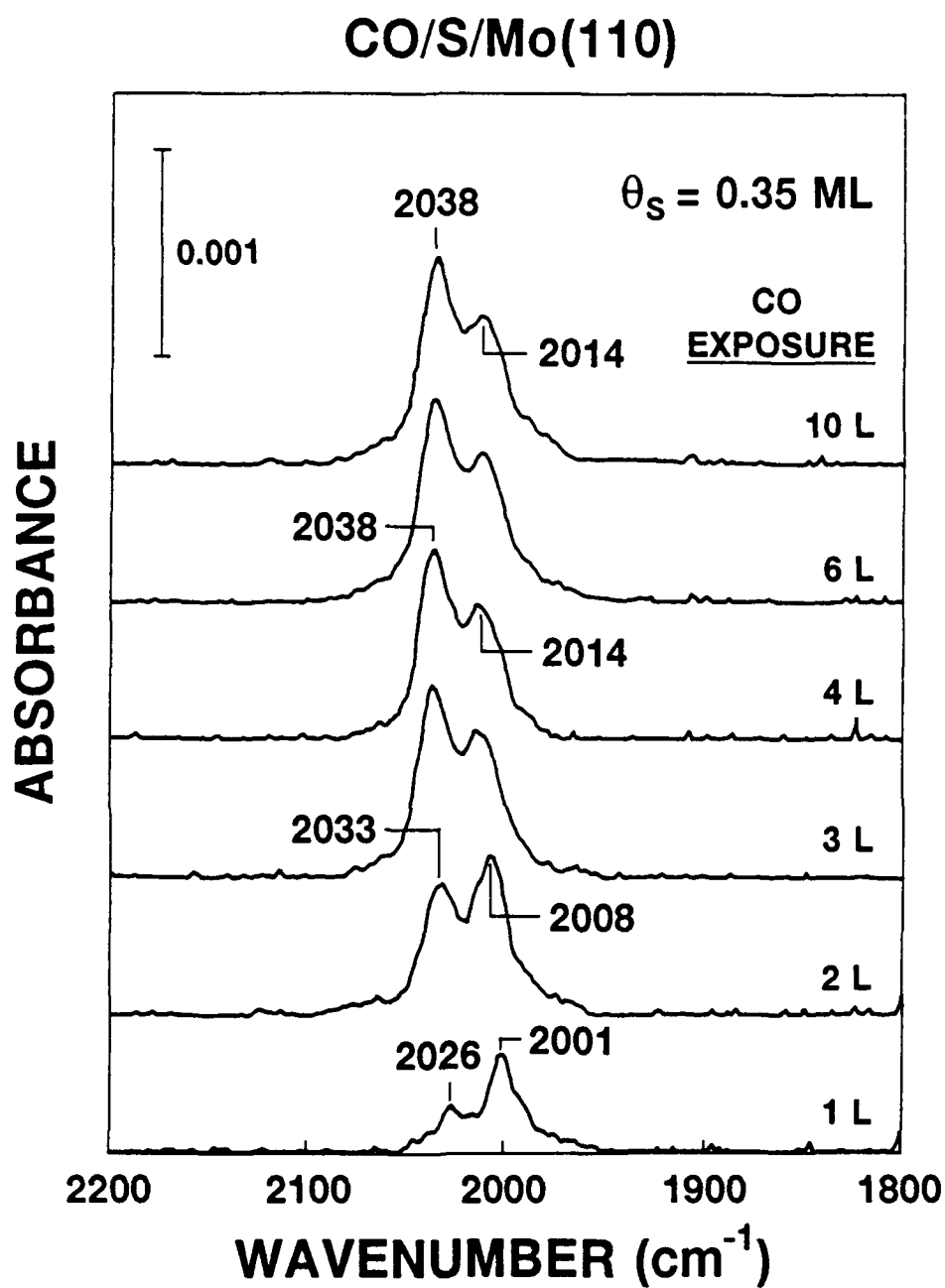


Fig. 45: IR spectra of CO adsorbed on 0.35 ML of S on Mo(110) at 90 K as a function of CO exposure.

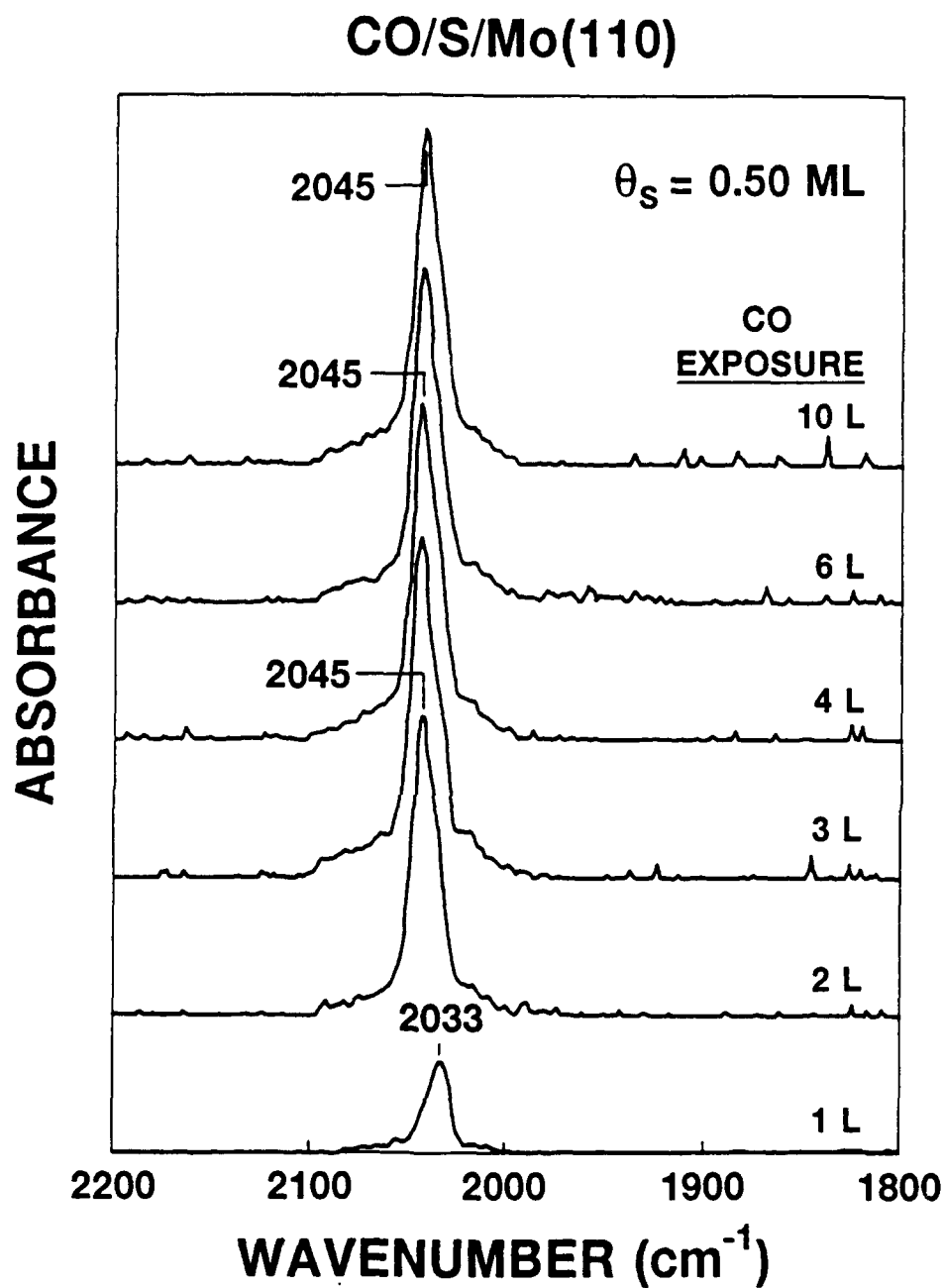


Fig. 46: IR spectra of CO adsorbed on 0.50 ML of S on Mo(110) at 90 K as a function of CO exposure.

For S coverages >0.25 ML, on the other hand, the new peak that appears at $\sim 2040\text{ cm}^{-1}$ is likely due to the electron withdrawing nature of S. As the sulfur coverage is increased above 0.25 ML, $c(2\times 2)$ islands begin to form and eventually coalesce to cover the entire surface at a S coverage of 0.5 ML. Assuming that the most likely position for S atoms on the Mo(110) surface is in the hollow sites [109], real space surface structures corresponding to the $p(2\times 2)$ and $c(2\times 2)$ LEED patterns can be deduced and are shown in fig. 42. It is apparent from the structure shown in fig. 42b for 0.5 ML of S on the Mo(110) surface that the likely sites for CO adsorption would be on top between two S atoms, or bridging two Mo atoms with four adjacent S atoms. Due to the steric crowding at the a-top site, it is likely that the preferred site would be the bridging one. The stretching frequency for CO adsorbed on this surface, however, is at 2045 cm^{-1} . This is a rather high frequency to be associated with a bridge-bound CO. In a previous HREELS study of CO adsorption on S/Ni(100), CO adsorbed on a $c(2\times 2)$ S structure was observed to have a frequency of 2115 cm^{-1} and was attributed to adsorption in a four-fold Ni hollow between four S atoms with highly reduced backdonation into the 2π orbital due to the adsorbed sulfur [110]. It is therefore possible that the peak at 2045 cm^{-1} could be due to CO adsorption bridging between two Mo atoms with the unusually high frequency being due to the electron withdrawing effect of the adjacent sulfur atoms.

IR spectra of CO on S/Mo(110) as a function of sample temperature are shown in figs. 47-49. For these figures, the Mo(110) surface was exposed to the H_2S at 90 K and flashed to 1400 K to desorb the hydrogen and anneal the overlayer. CO

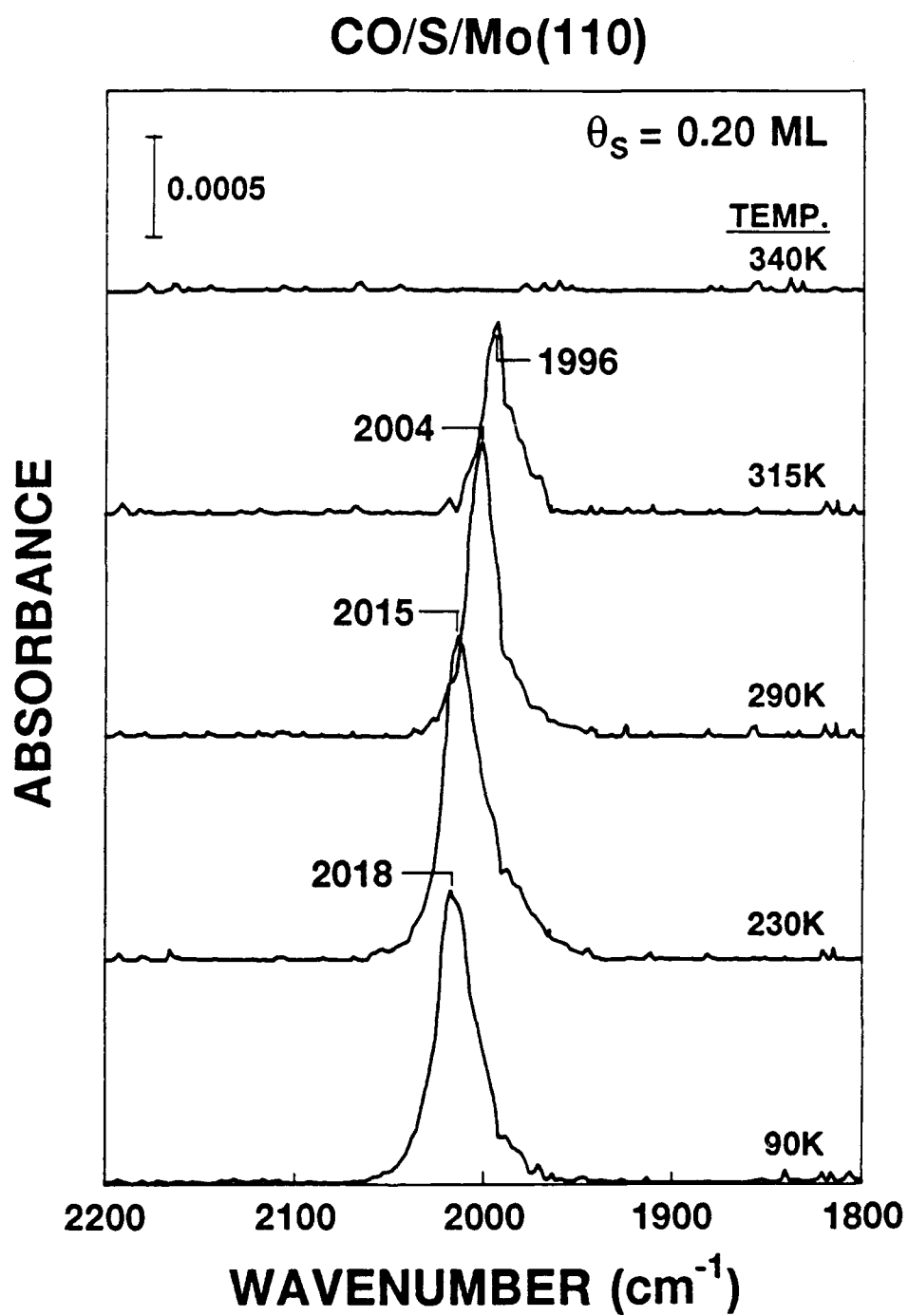


Fig. 47: IR spectra of CO on 0.20 ML of S on Mo(110). CO exposure was at 90 K with spectral acquisition at the indicated temperatures.

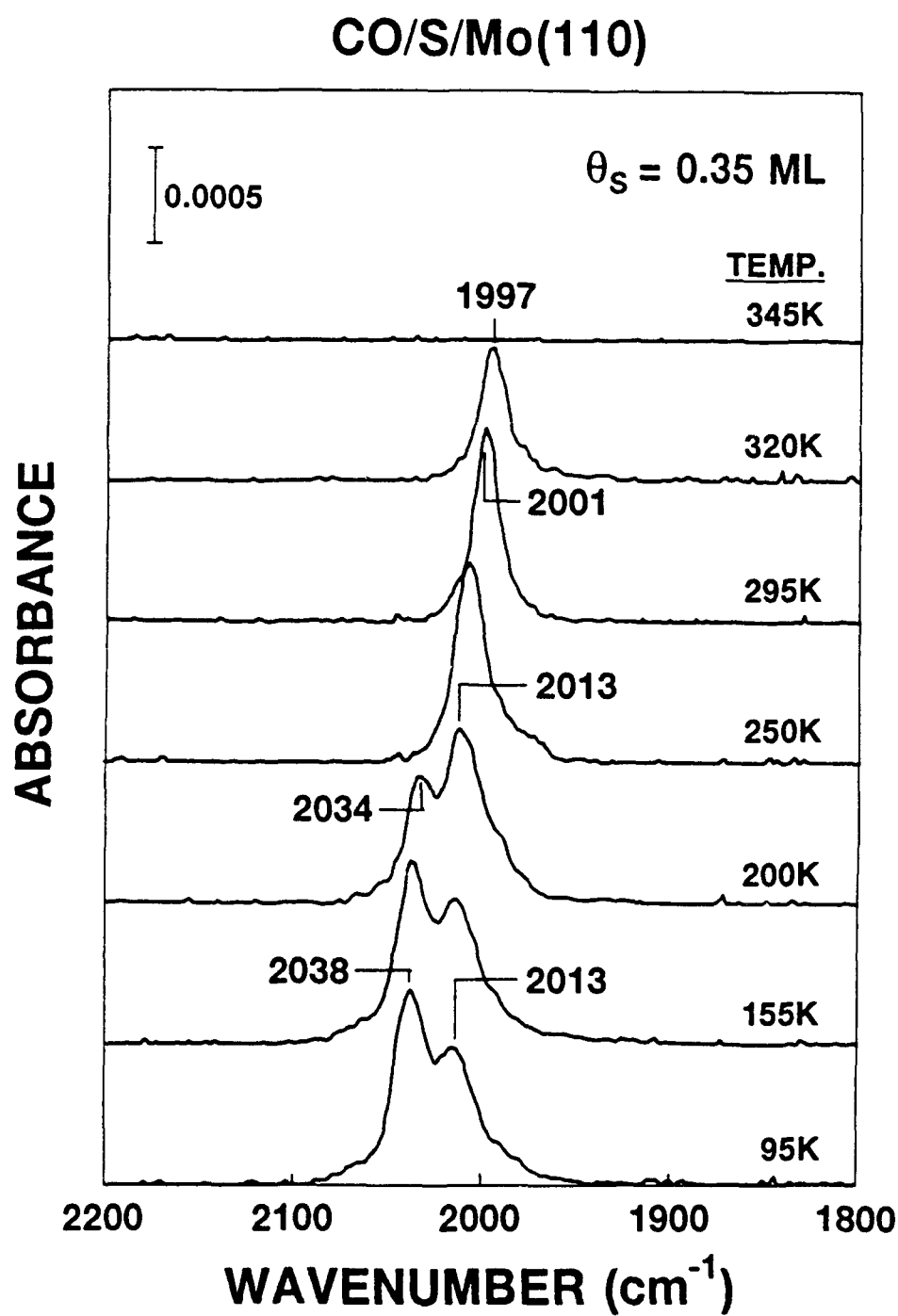


Fig. 48: IR spectra of CO on 0.35 ML of S on Mo(110). CO exposure was at 90 K with spectral acquisition at the indicated temperatures.

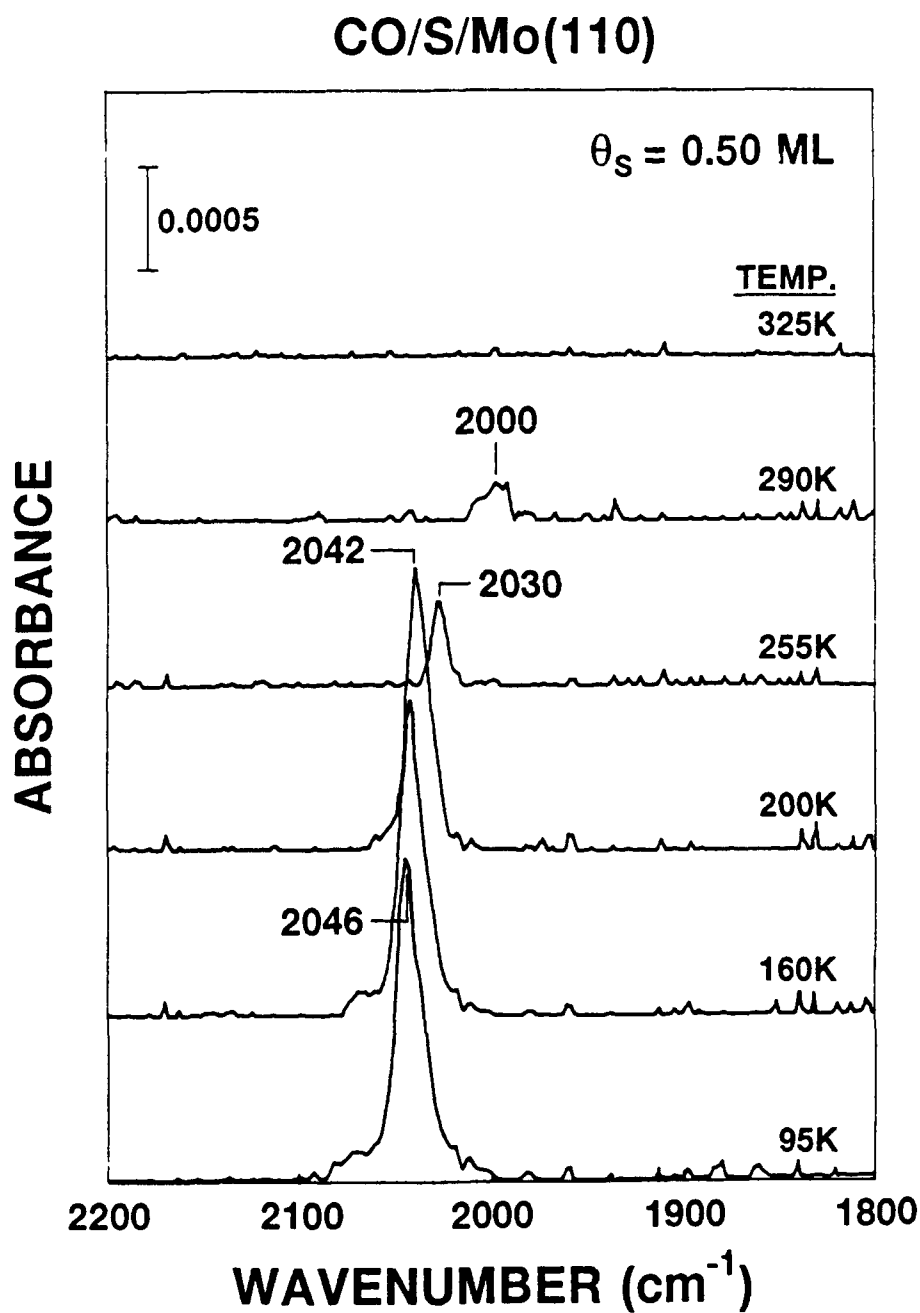


Fig. 49: IR spectra of CO on 0.50 ML of S on Mo(110). CO exposure was at 90 K with spectral acquisition at the indicated temperatures.

exposure was at 90 K and spectral acquisition was at the indicated temperatures. All three figures show the expected red shift in stretching frequency as the CO coverage is reduced due to desorption. The desorption temperatures indicated in the IR data are in excellent agreement with the TPD data shown in fig. 43. For S coverages of ~ 0.35 ML or below, molecular desorption occurs at 330 K, however; for 0.5 ML of S, desorption occurs at 300 K. This decrease in desorption temperature for CO adsorbed on S/Mo(110) surfaces with S coverages in excess of 0.35 ML is a further indication of a sulfur interaction withdrawing charge from the Mo surface. As discussed above, the electron withdrawing effect of the adsorbed S will reduce the charge donation from the Mo atoms to the adsorbed CO. This will lead to a weaker metal-CO bond (lower desorption temperature). The lower desorption temperature for CO bound to the c(2X2) S phase compared to CO bound to the p(2X2) phase is clearly evident in fig. 48. Applying the Redhead approximation and assuming a frequency factor of 10^{13} gives bond energies of 20.1, 20.1 and 18.2 Kcal/mole for CO adsorbed molecularly on clean Mo(110), the p(2X2) overlayer and the c(2X2) overlayer, respectively. These bond energies further reinforce earlier indications that in the p(2X2) S overlayer, the S merely acts as a site blocker without noticeably affecting the bonding of the CO to the Mo surface. For the c(2X2) S overlayer, however, the S electronically perturbs the surface changing the bonding of the S to the Mo surface. Thus, the c(2X2) 0.50 ML S overlayer both induces a bridgebound CO adsorption peak at 2045 cm^{-1} , and also decreases the binding energy of the CO adsorbed on these sites.

There is an additional effect that occurs when S is adsorbed onto a Mo(110) surface. Dissociative CO adsorption is reduced. This result has been observed previously [111], and is clearly evident in the CO TPD spectra shown in fig. 43. Increasing S coverage not only decreases the amount of dissociatively adsorbed CO, but also facilitates the recombinative dissociation of the CO. In the previous study, the reduced dissociative adsorption was explained as being due to an increase in desorption probability, not a decrease in the desorption rate constant [111]. The lower CO desorption temperatures at higher S coverages observed in this work are in qualitative agreement with this earlier study. The lack of CO dissociation on the c(2X2) S overlayer was observed in the IR spectra of the CO adsorbed on this surface. Repeated adsorption-desorption cycles showed no IR features due to C build up ($\sim 2100 \text{ cm}^{-1}$) on this surface. On the p(2X2) S or clean Mo(110) surfaces, on the other hand, adsorption-desorption cycles produced a pronounced peak at $\sim 2100 \text{ cm}^{-1}$, due to carbon buildup.

Co/S/Mo(110)

The data discussed above for CO adsorption on S/Mo(110) was a starting point for the studies of CO adsorption on Co/S/Mo(110). As a second step in the evaluation of the interactions involved in the Co/S/Mo(110) system, S deposition on Co/Mo(110) surfaces was studied. Fig. 50 shows the IR spectra of CO adsorbed onto a S/Co/Mo(110) surface with various S coverages. 0.5 ML of Co was deposited onto a clean Mo(110) surface at 100 K and flashed to 1100 K prior to H₂S exposure at

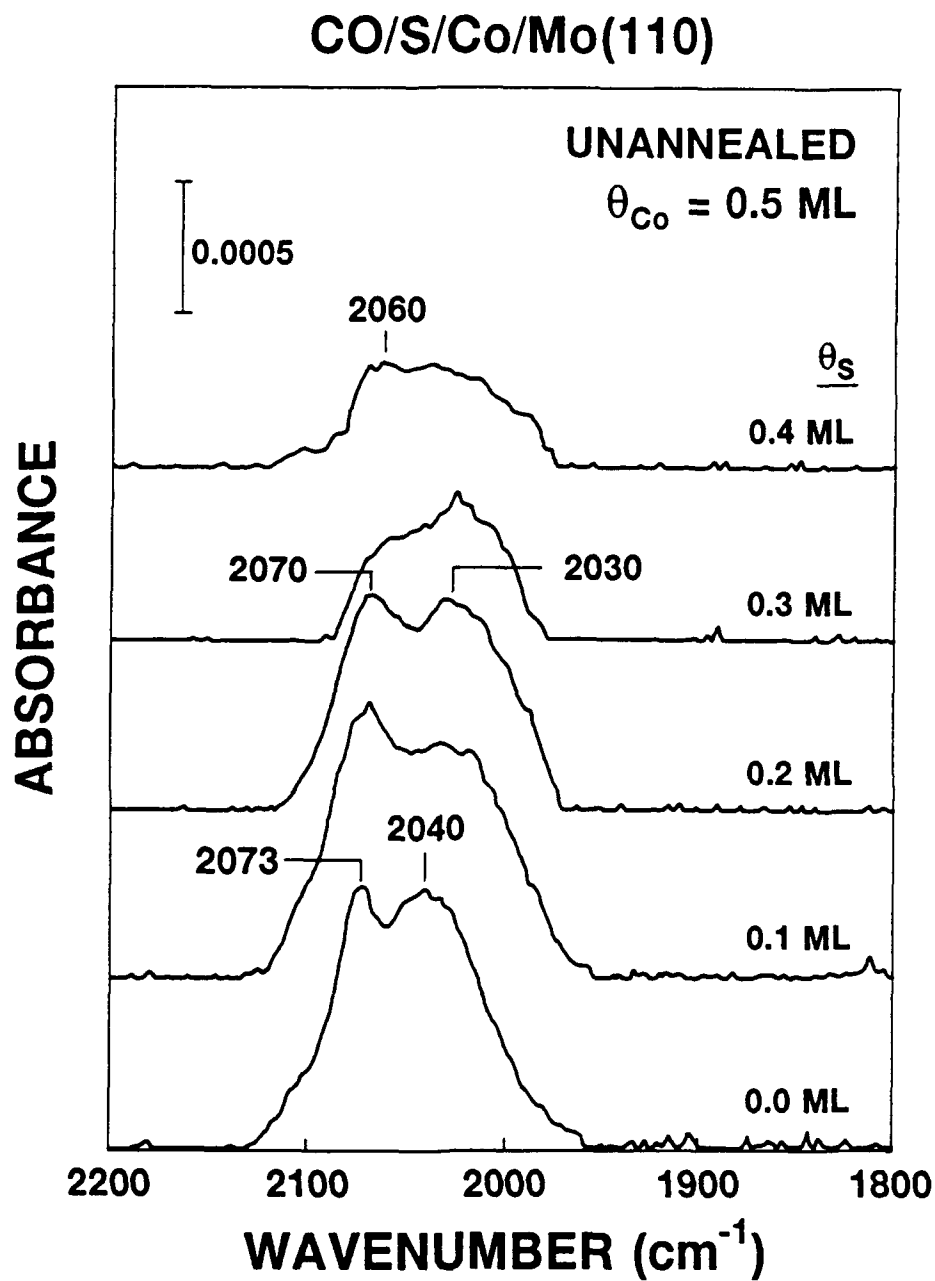


Fig. 50: IR spectra of CO adsorbed on S/Co/Mo(110) at 90 K with varying sulfur coverages.

90 K. The resulting surface was flashed to 500 K to desorb the hydrogen prior to CO exposure and spectral acquisition at 90 K. The two features at 2073 and 2041 cm^{-1} for the non-sulfided surface are due to CO adsorption on Co islands and the Mo substrate, respectively (see fig. 37). As the S coverage is increased, both peaks shift toward lower frequency, broaden and are reduced in intensity. This likely results from a site blocking interaction of the S on the Co/Mo substrate. Fig. 51 shows the IR spectra of CO adsorbed on the same surfaces shown in fig. 50 after they were annealed to 1100 K. As the S coverage is increased, the peak corresponding to CO adsorbed on Co (2073 cm^{-1}) is rapidly attenuated. The CO-Mo feature, on the other hand, shows an increase in intensity at low S coverages before being attenuated as the S coverage is further increased. This implies that annealing causes the S atoms to migrate on the surface such that they poison the Co sites preferentially to the Mo sites. To more clearly illustrate the effects of annealing on the S/Co/Mo(110) surface, IR spectra acquired after annealing to different temperatures are shown in fig. 52. The clean Mo(110) surface was dosed with 0.5 ML of Co and annealed to 1100 K. This was followed by an exposure to 1.5 L of H_2S (enough to form a 0.25 ML S layer after heating) and annealing to the indicated temperatures. CO exposure and spectral acquisition were at 90 K. This figure shows that increasing the annealing temperature from 500 K to 800 K increased the intensity of the CO-Co feature at the expense of the CO-Mo feature. The feature at $\sim 2100 \text{ cm}^{-1}$ is due to small amounts of C on the Mo surface due to dissociative adsorption on the Co adatoms. Annealing to higher temperatures (950 - 1100 K), however, caused a marked reduction in the intensity of the CO-Co feature with an

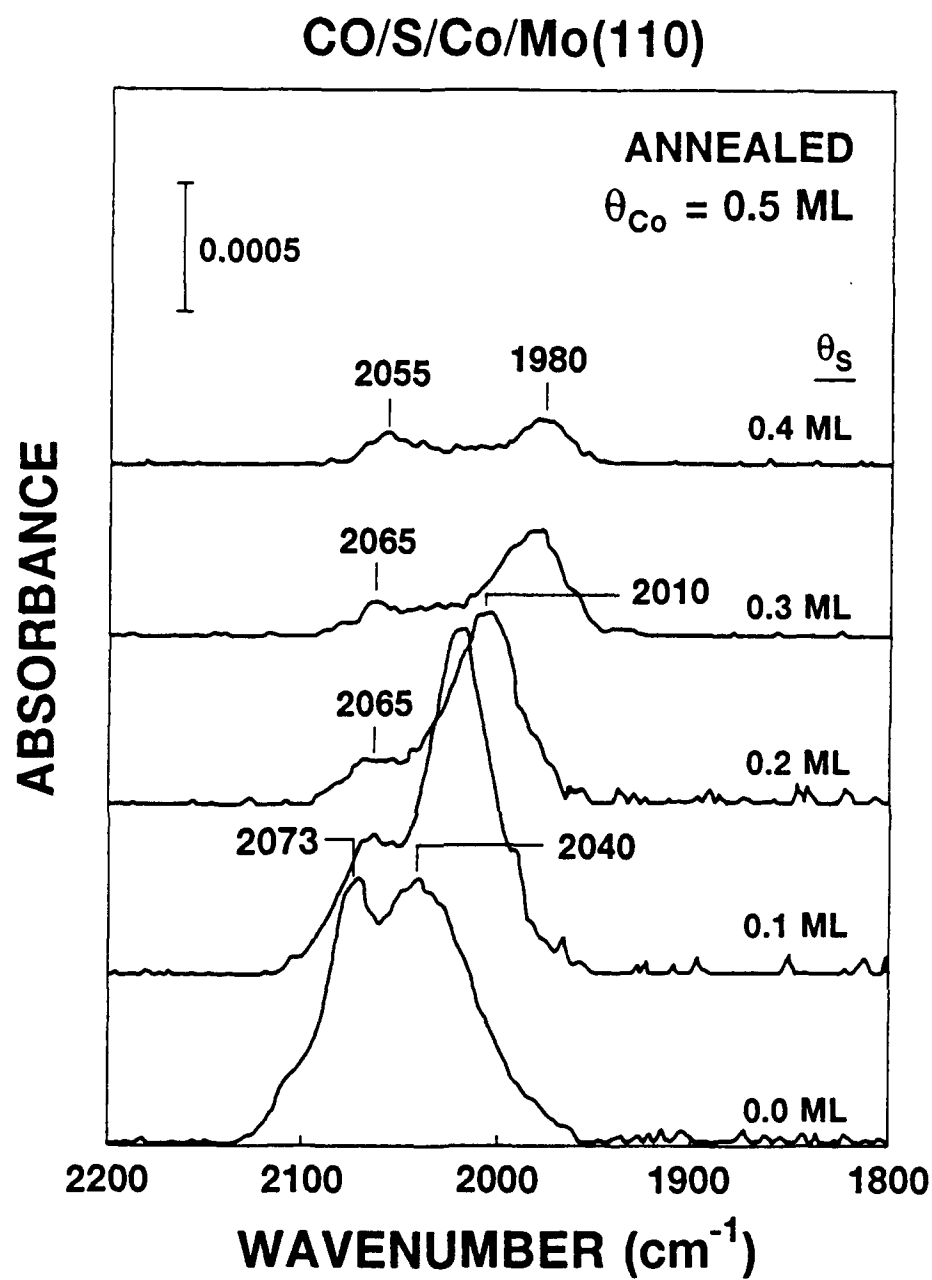


Fig. 51: IR spectra of CO adsorbed on an annealed S/Co/Mo(110) surface at 90 K with various sulfur coverages.

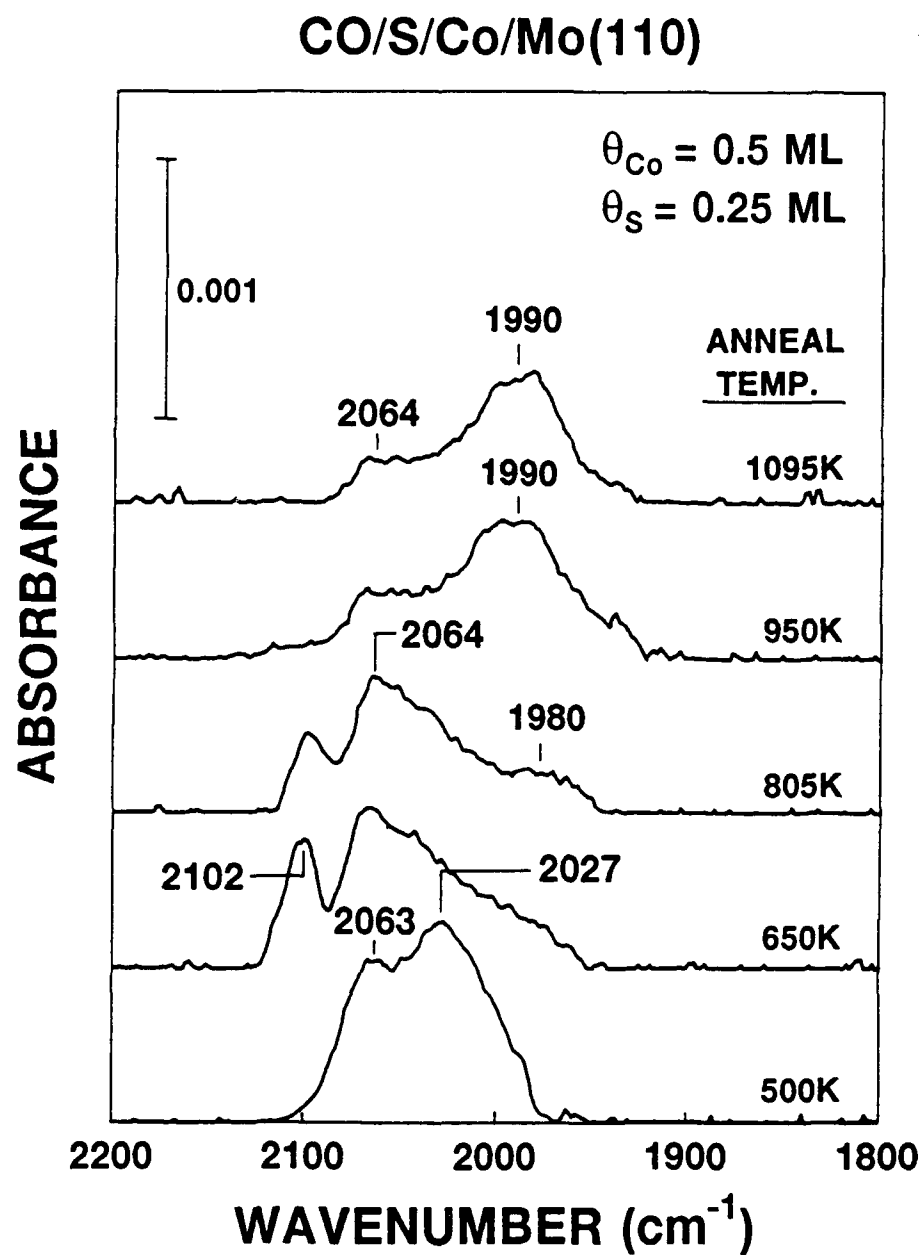


Fig. 52: IR spectra of CO adsorbed on S/Co/Mo(110) at 90 K after annealing the surface to the indicated temperatures.

increase in the CO-Mo feature. This seems to indicate that the preferential poisoning of the Co sites does not occur until the surface is annealed to a sufficiently high temperature.

Another direct example of the interaction between S and Co on a Mo(110) surface is shown in fig. 53. 1.5 ML of Co was deposited onto the clean Mo(110) surface and annealed to 1100 K. This procedure creates the (8X2) Co overlayer structure discussed earlier (see fig. 37). This surface was exposed to 1.5 L of H₂S at 90 K, flashed to the indicated temperature, and cooled back to 90 K for CO exposure and spectral acquisition. The feature at 2048 cm⁻¹ is due to CO adsorption on the (8X2) Co overlayer. The frequency shift (4 cm⁻¹) and reduced intensity of this peak compared to the peak at 2052 cm⁻¹ for CO on the clean (8X2) Co overlayer (see fig. 37) is related to the site blocking nature of the un-annealed S overlayer. Annealing the surface to higher temperatures drastically attenuates the peak at 2048 cm⁻¹ with two new peaks growing in at 2085 and 2016 cm⁻¹. The peak at 2016 cm⁻¹ correlates well with the feature observed previously for a 0.25 ML S coverage on Mo(110) (see fig. 40). It is also possible that this feature could correspond to CO adsorbed on domains of clean Mo(110). Figs. 37 and 39 imply that if ~1/2 of the Mo(110) surface were exposed, that the frequency of CO adsorbed on these clean Mo(110) domains could be ~2020-2010 cm⁻¹. Either way, the appearance of this feature necessitates 3-D cluster formation of the Co overlayer. Thus the peak at 2085 cm⁻¹ is likely due to CO adsorption on S modified 3-D Co clusters. The actual S coverage on these Co clusters depends on whether or not there is any S remaining on the Mo(110) surface. The feature at ~2100 cm⁻¹ is due

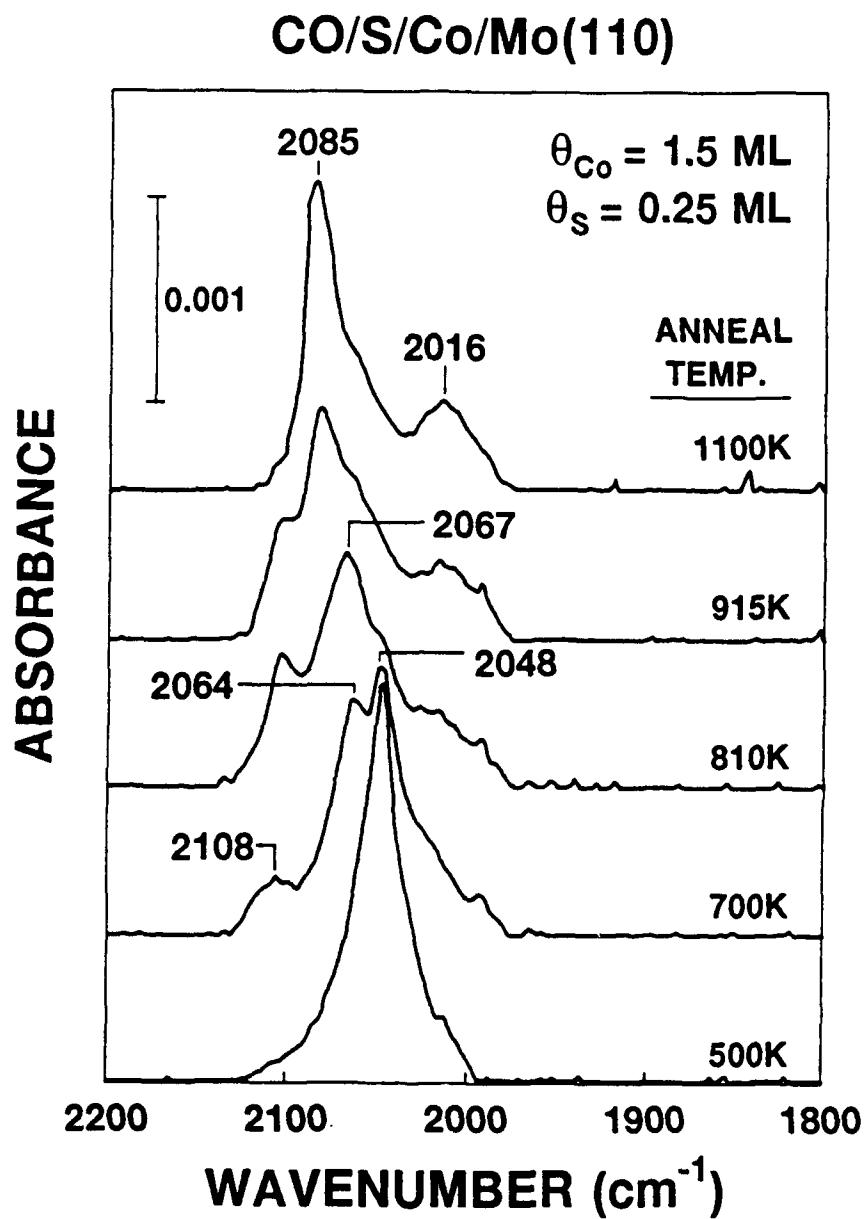


Fig. 53: IR spectra of CO adsorbed at 90 K on S/Co/Mo(110) as a function of annealing temperature.

to slight C contamination due to a small amount of dissociative CO adsorption on Co.

The complex interactions between Co, S and Mo were further studied by depositing Co on S/Mo(110) surfaces. Figs. 54 and 55 show the IR spectra of CO on unannealed and annealed Co/S/Mo(110) surfaces as a function of Co coverage, respectively. For these figures, the clean Mo(110) surface was exposed to 0.8 L of H₂S (enough to form 0.15 ML of S after heating) and flashed to 1400 K prior to Co deposition at 90 K. For fig. 55 the sample was flashed to 1100 K prior to CO exposure and spectral acquisition at 90 K, whereas for fig. 54 the sample was not heated prior to CO exposure. Fig. 54 clearly shows the buildup of Co on the surface with the feature due to CO-Co replacing the feature due to CO-Mo. There is no real interaction between the Co overlayer and the S/Mo(110) substrate, the Co just covers the surface.

In fig. 55, on the other hand, it is clear that annealing the surface to 1100 K causes intermixing of the Co and S/Mo(110). This is clearly evident from the fact that the feature at $\sim 2020\text{ cm}^{-1}$ arising from CO adsorbed on p(2X2) S domains on the Mo(110) surface never disappears, but just shifts to lower frequency as the Co coverage is increased to 0.5 ML. The apparent shift in frequency of this peak to 2027 cm^{-1} as Co coverage is increased to 1.5 ML is likely due to S migration to the deposited Co overlayers. Thus, the resulting feature at 2027 cm^{-1} is most likely due to CO adsorbed on clean Mo(110) domains (see figs. 37 and 39). The sharp feature at 2052 cm^{-1} corresponding to domains of (8X2) Co on clean Mo(110) (see fig. 37) also supports the migration of S on the surface. In addition, the

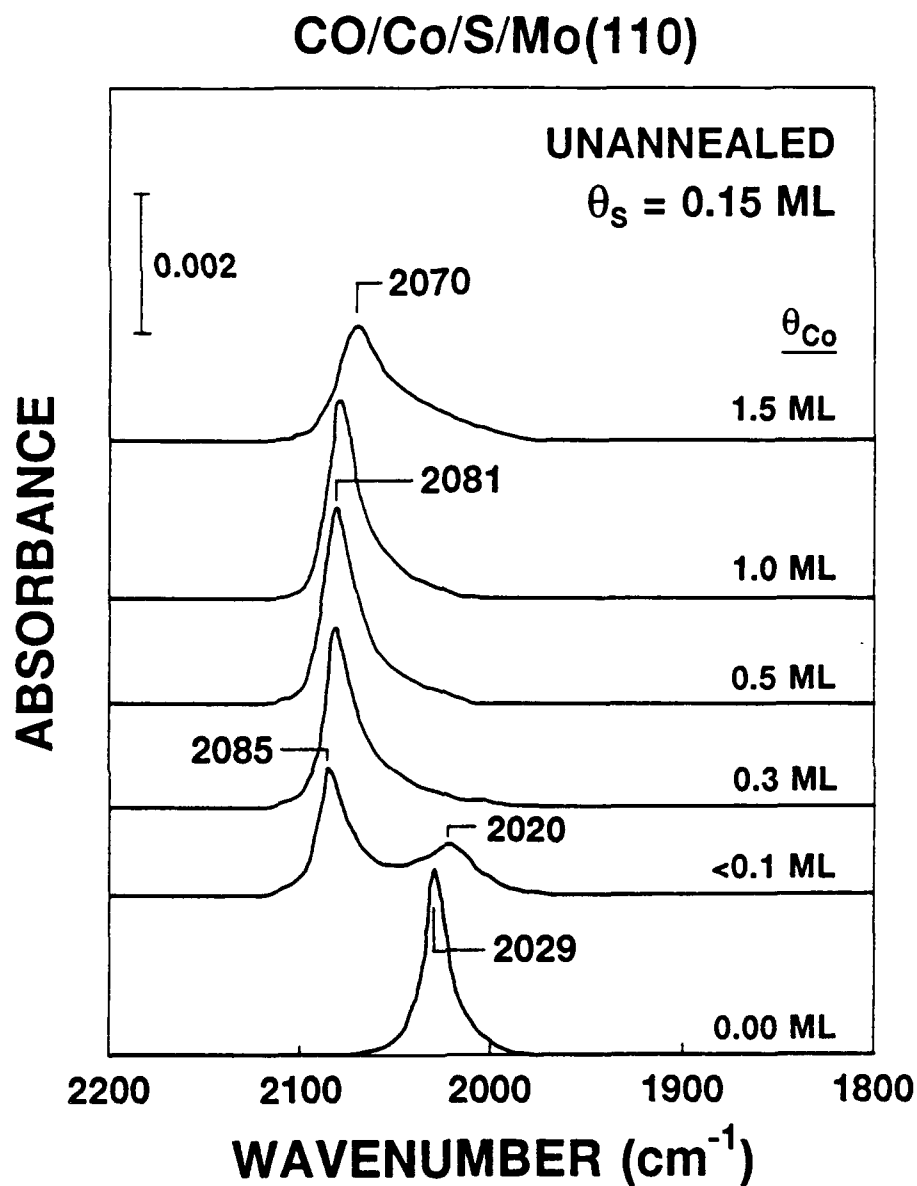


Fig. 54: IR spectra of CO adsorbed on unannealed Co/S/Mo(110) surfaces at 90 K as a function of Co coverage.

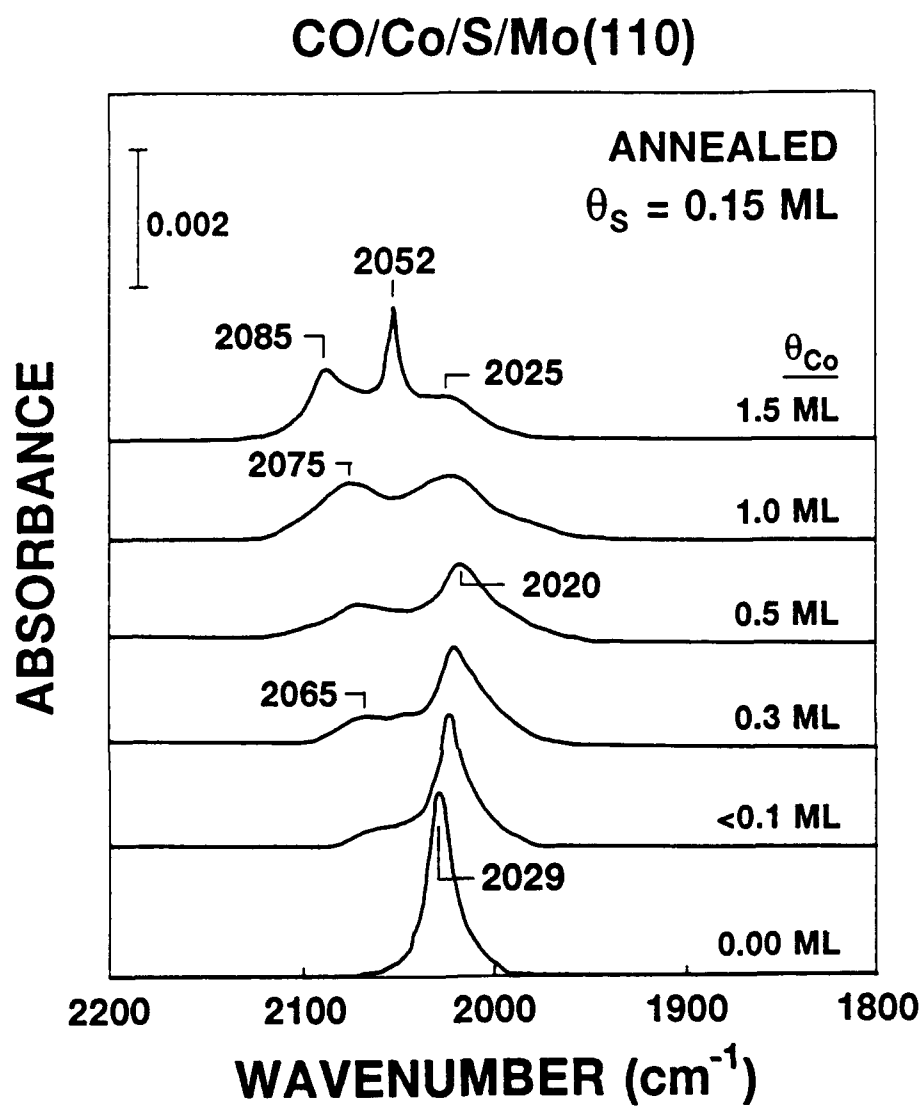


Fig. 55: IR spectra of CO adsorbed on annealed Co/S/Mo(110) surfaces at 90K as a function of Co coverage.

feature at 2087 cm^{-1} is in good agreement with the peak at 2085 cm^{-1} in fig. 53 corresponding to CO adsorbed on sulfided 3-D Co clusters. All of these features point to the fact that annealing the surface to 1100 K induces migration of the Co and S into distinct domains.

The IR spectra of CO adsorbed on unannealed and annealed Co overlayers on the $c(2\times 2)$ S/Mo(110) surface are shown in figs. 56 and 57. For these figures, the Mo(110) sample was saturated with H_2S and flashed to 1400 K to desorb the hydrogen and anneal the S overlayer to form the $c(2\times 2)$ S film. This surface was dosed with the indicated Co coverage and either annealed to 1100 K or not heated prior to CO exposure and spectral acquisition at 90 K (figs. 57 and 56, respectively). In fig. 56, the buildup of Co on the surface is clearly evident with the feature at $\sim 2070\text{ cm}^{-1}$ due to CO-Co replacing the feature due to CO-Mo. This figure is quite similar to fig. 54 in that there is apparently no real interaction between the Co overlayer and the S/Mo(110) substrate at 90 K, the Co just covers the surface.

The results shown in fig. 57, however, are quite different. Just as was observed in fig. 55, annealing the surface to 1100 K causes the Co and S to segregate and/or interact on the Mo(110) surface. An intriguing aspect of this figure is that up to a Co coverage of $\sim 0.3\text{ ML}$, there are no CO stretching features that appear to be due to CO adsorbed on Co. The two peaks present in the 0.3 ML Co spectrum are most likely due to CO adsorption on the $c(2\times 2)$ S/Mo(110) surface and $p(2\times 2)$ S domains. For higher coverages of Co, a feature due to CO adsorption on Co is finally observable. The two features present in the 1.0 and 1.5 ML Co spectra are due to CO adsorbed on S modified Co domains and on $p(2\times 2)$ S/Mo

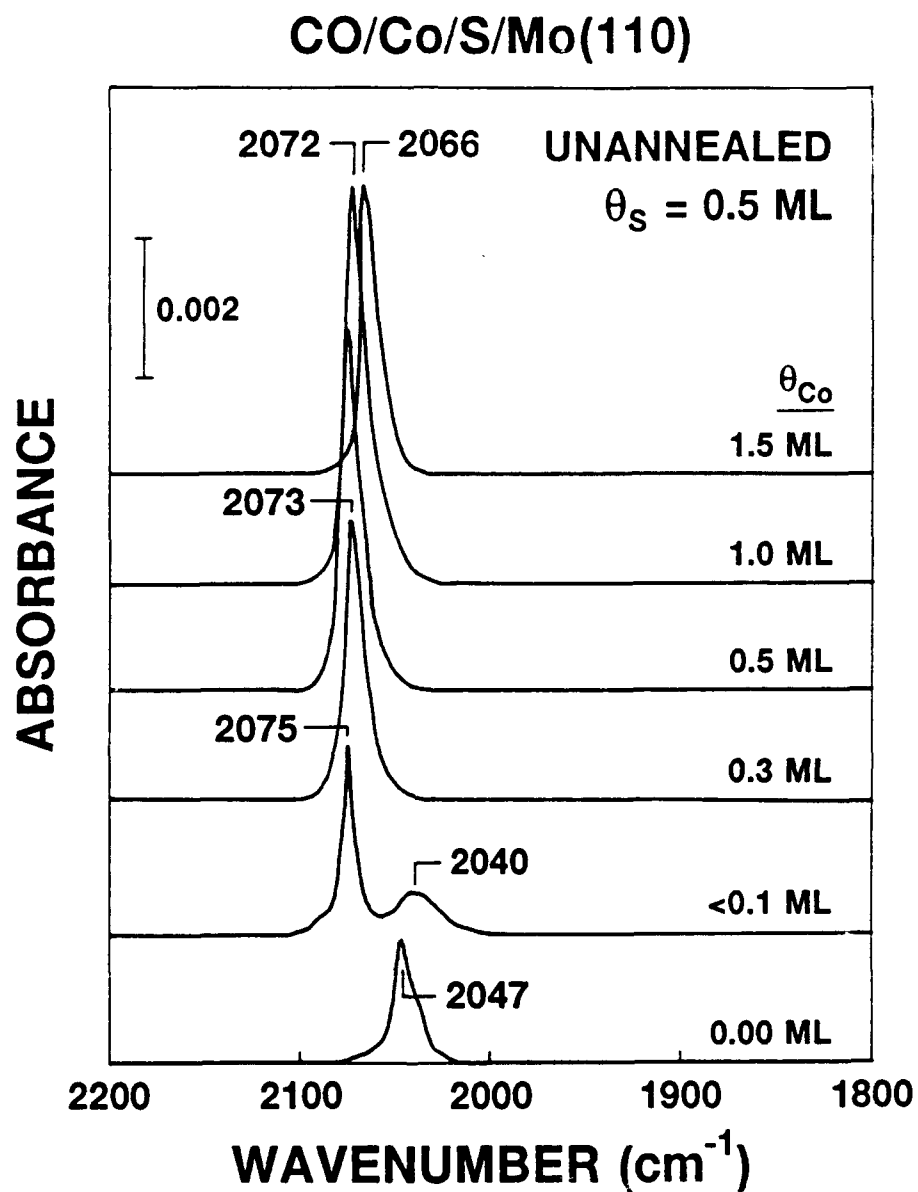


Fig. 56: IR spectra of CO adsorbed at 90 K on unannealed Co/S/M(110) surfaces at various Co coverages.

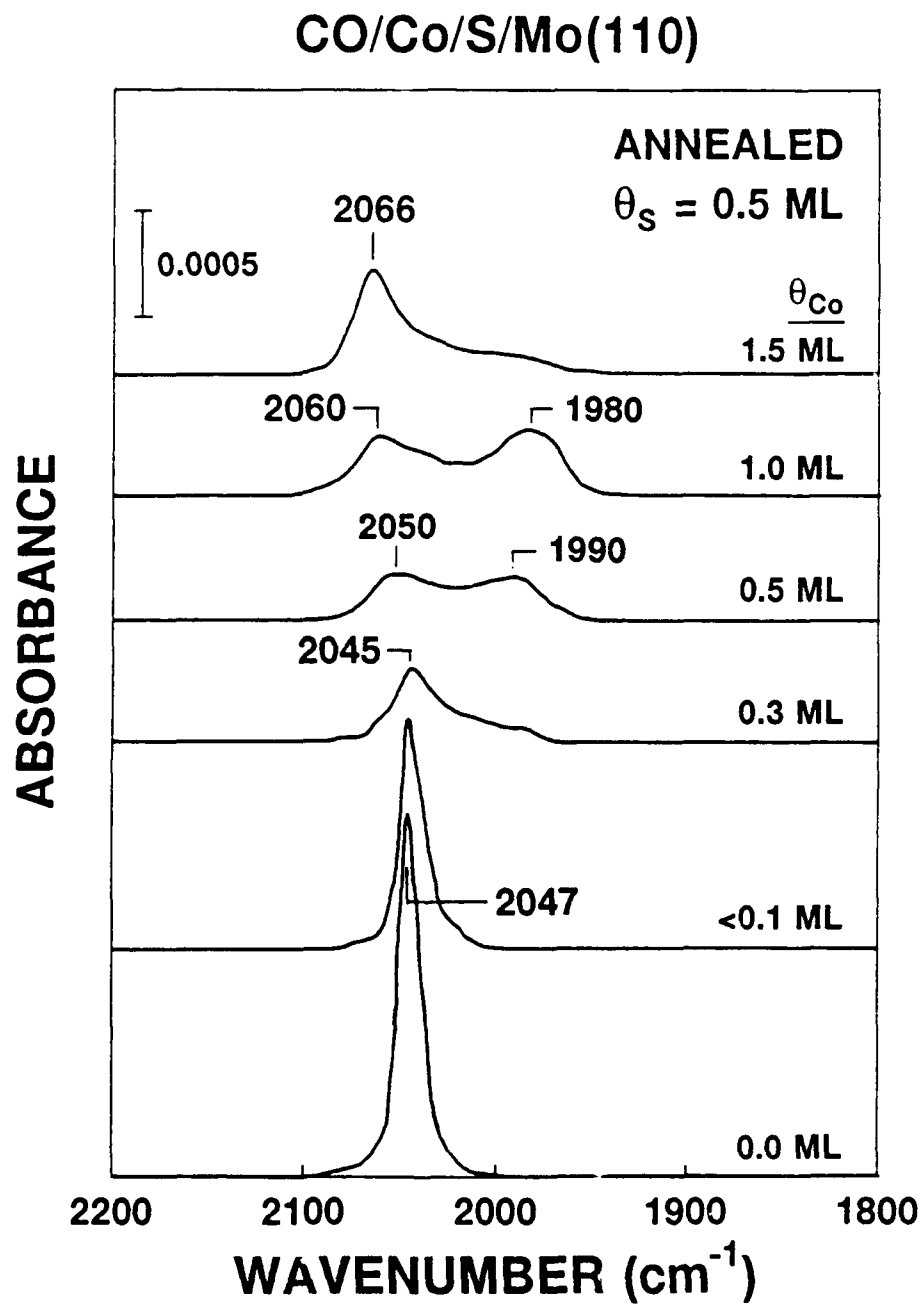


Fig. 57: IR spectra of CO adsorbed at 90 K on annealed Co/S/Mo(110) surfaces at various Co coverages.

domains. The spectra for 1.0 and 1.5 ML of Co in fig. 57 are very similar to the spectrum observed on fig. 51 for 0.4 ML of S on the Co/Mo(110) surface. The spectra in fig. 57 have a higher intensity for the CO-Co peak, however, due to the larger amount of Co on the Mo(110) surface in this figure.

The temperature dependence of the features in the 1.5 ML Co spectrum from fig. 55 are shown in fig. 58. The CO stretching features in these spectra show the expected red-shifts as the CO coverage in the domains associated with each feature is reduced due to desorption. As the sample temperature is increased from 100 K to 250 K, the feature at 2086 cm^{-1} decreases in intensity and finally is no longer visible. This implies that the CO adsorbed on sulfided 3-D Co clusters desorbs between 200 and 250 K. Concomitant with the decrease in intensity of the 2086 cm^{-1} peak is an increase in the intensity of the feature at 2025 cm^{-1} . This likely does not represent a migration of CO to the Mo sites, but probably represents a reduction in the screening of these sites due to the desorption of the CO on the sulfided 3-D Co cluster sites. Increasing the sample temperature from 250 K up to 350 K causes the CO adsorbed on the (8X2) Co domains to desorb. Finally, the remaining CO on the Mo(110) domains desorbs between 350 and 400 K.

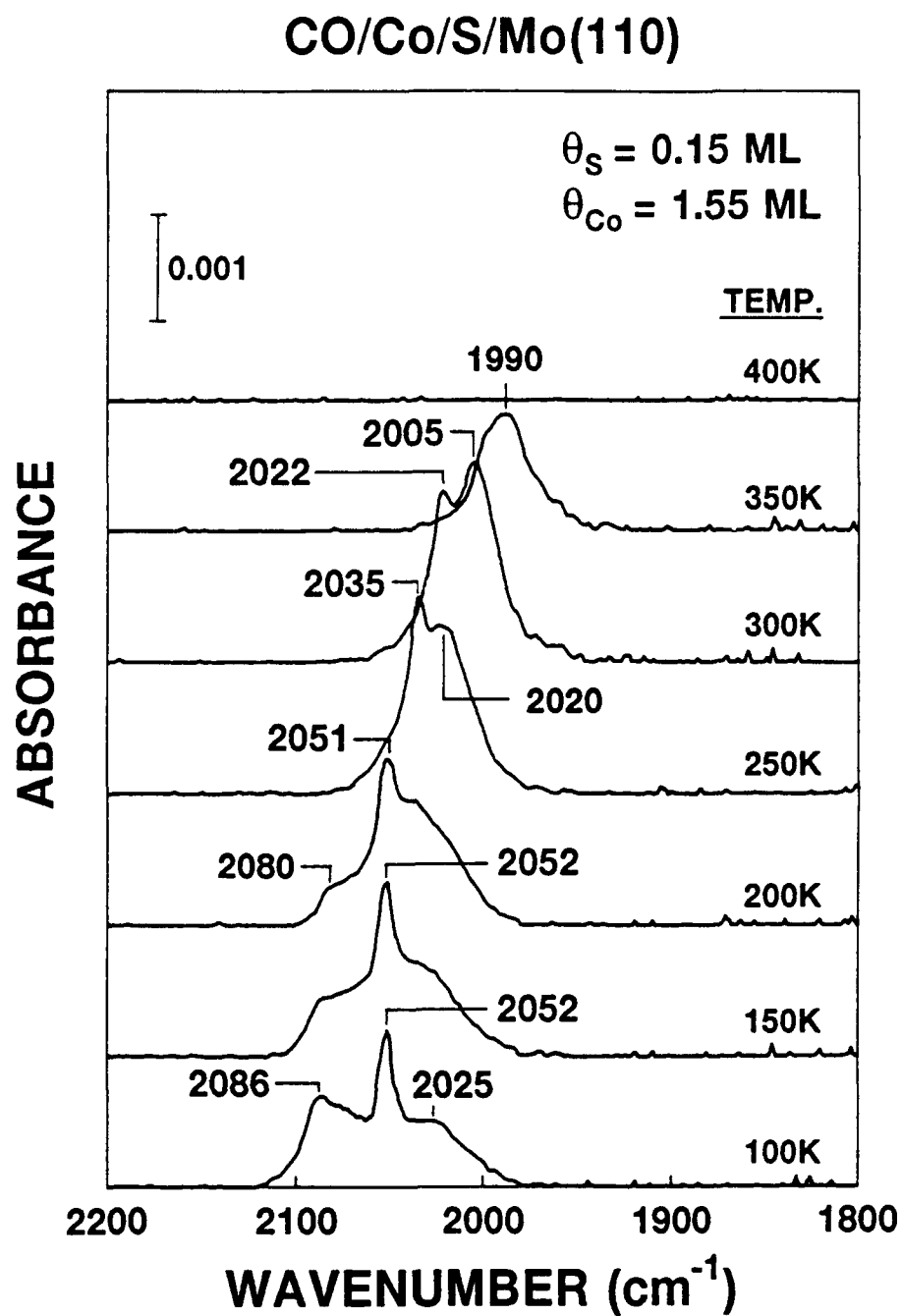


Fig. 58: IR spectra of CO on 1.5 ML of Co on S/M(110). CO exposure was at 100K with spectral acquisition at the indicated temperatures.

DISCUSSION

The close relationship between the electronic, structural and chemisorptive properties of bimetallic systems necessitates an understanding of the electronic properties of these systems before a thorough understanding of their chemisorptive properties is possible. Therefore, since the stretching frequency of an adsorbed CO molecule is influenced (if not determined) by its chemisorptive bond to the metal substrate, a detailed discussion of the bonding interactions between the overlayer and substrate atoms in bimetallic systems is a necessary prelude to a discussion of CO chemisorption on these surfaces.

Overlayer-Substrate Bonding

The results of the IRAS studies of CO adsorption on Cu overlayers presented in this work provide valuable information necessary for an understanding of the chemical properties of these overlayer systems. IRAS studies of CO adsorbed on Cu/Ru(0001) [84,85] as well as Cu(100) [79] and Cu(111) [103] have been conducted previously. In addition, Cu overlayers on Ta, Mo, Re, Ru, Rh and Pt have been studied using TPD [20-24,34,43,102] and XPS [47,55-57,112,113]. A comparison of the results of these studies allows the formation of a model explaining the chemisorptive properties of Cu overlayers on metal substrates.

Previous XPS studies have shown that the atoms in a monolayer of Cu on Ta(110) [112], Mo(110) [56] and Re(0001) [47,113] have a higher Cu(2p_{3/2}) binding

energy than the surface atoms in Cu(100). These results indicate that electronic charge is transferred from the overlayer Cu atoms to the Ta, Mo and Re substrate atoms upon bond formation. For Cu monolayers on Ru(0001) [55], Rh(100) [55] or Pt(111) [57], on the other hand, the Cu($2p_{3/2}$) energy level is shifted toward lower binding energy. The removal of charge from a Cu atom to form a bond with the substrate will increase the energy necessary to remove a core electron in the XPS measurement leading to a shift toward higher binding energy. The opposite effect will lead to a shift toward lower binding energy. Shifts in core-level binding energies, however, must be regarded cautiously since changes in the screening of the core hole (final state effects) could give rise to the observed shifts. Several factors indicate that charge transfer is the primary source of the core level binding energy shifts. For example, the magnitude and direction of the charge transfer between overlayer and substrate atoms, observed with work function measurements [25,61-63], support the UPS [57,59,60,114,115] and XPS [47,55,56,113] results. This correlation among work function, UPS and XPS measurements implies that charge transfer is indeed the operative mechanism leading to the observed XPS binding energy shifts.

These charge transfer effects have been interpreted in terms of a model where the different metals are designated as being electron rich or electron poor. Metals on the left hand side of the transition series, which are deficient in d electrons (e.g. Ta, W, etc.), are designated as electron-poor whereas metals on the right hand side, which have a more than half-filled d-band (e.g. Pd, Pt, etc.), are designated as being electron rich. Upon bond formation, charge transfer occurs

from the electron-rich metal to the electron-poor metal. For Cu, the interactions can be explained by using the $3d^{10}4s^1$ electronic configuration to designate Cu as having a half-filled valence band. When a Cu monolayer is deposited onto an electron-rich substrate, e.g. Ru(0001), Rh(100) or Pt(111), for example, the Cu($2p_{3/2}$) binding energy will shift toward lower energy [55,57], as can be seen in fig. 59a. Likewise, when Cu is deposited onto a substrate that has a less than half occupied valence band (electron poor relative to Cu) charge transfer will occur from Cu to the substrate. These trends are clearly reflected in fig. 59a for Cu films and have been observed likewise for Ni [50,56], Pd [47,50,56] and Ag [116] films on various transition metal substrates.

Fig. 59b shows the desorption temperatures for a monolayer of Cu from several substrates. The higher desorption temperature observed for Cu on Pt(111) likely reflects the alloying that occurs between Cu and Pt. Since the desorption temperature of the Cu overlayer is a good qualitative measure of the bond strength between the Cu and the substrate, this figure indicates that Cu overlayers are bound less tightly to Re than to metals on either end of the transition series. These bond strength differences correlate well with the charge transfer trends shown in fig. 59a. The greater the magnitude of charge transfer, the greater the bond strength between the overlayer and the substrate. It is important to notice that for certain cases the bond is formed by charge transfer from the Cu overlayer to the substrate and in others by the Cu accepting charge from the substrate. Thus, this comparison between copper desorption temperature and Cu($2p_{3/2}$) binding energy shift shows that charge transfer between the overlayer and the substrate plays an

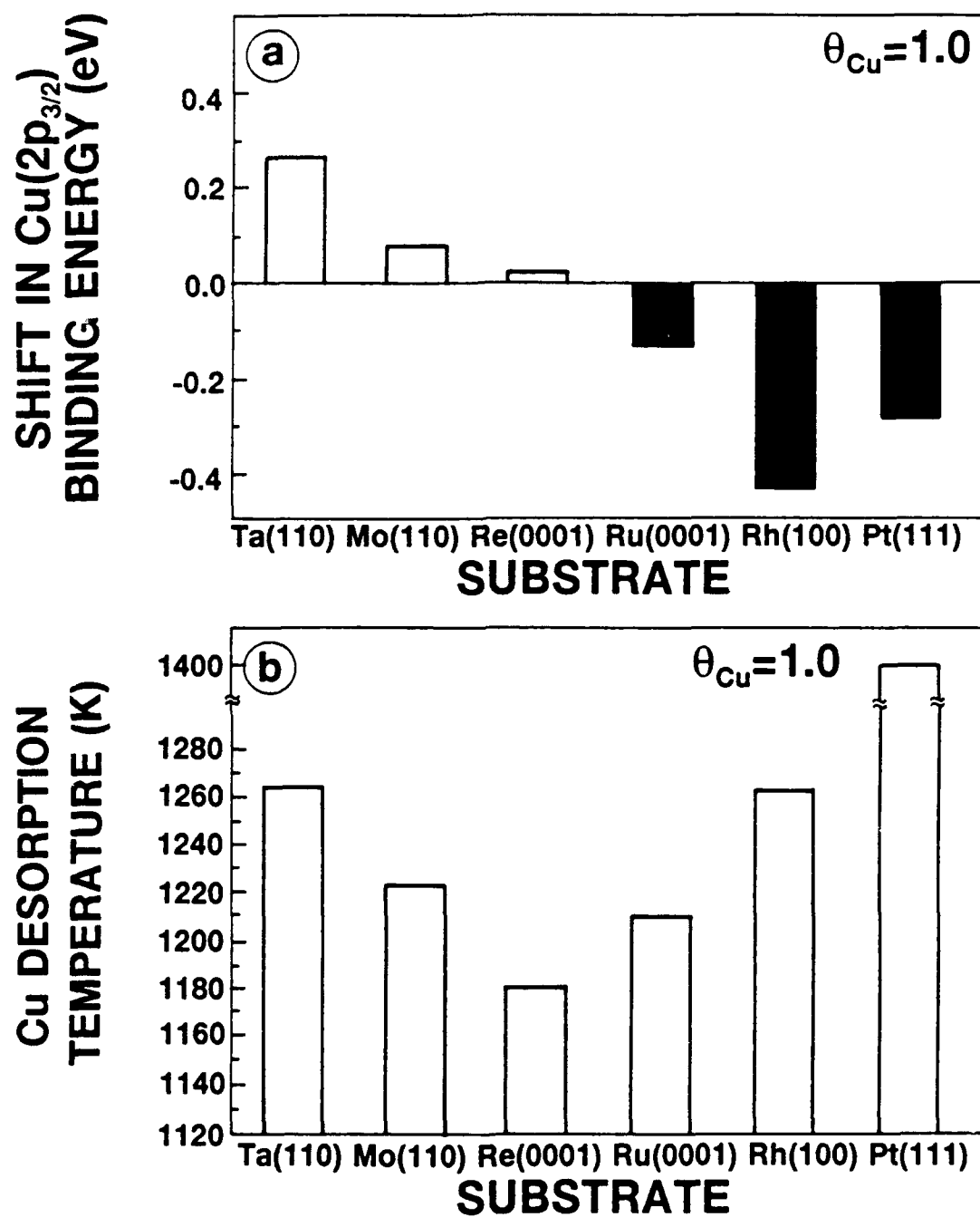


Fig. 59: A comparison of the shift in the Cu(2p_{3/2}) binding energy and the Cu desorption temperature for Cu monolayers on different substrates.

important role in determining the overlayer-substrate cohesive bond strength. This correlation between the overlayer binding energy shift and the overlayer-substrate bond strength is a general phenomenon and has been observed for Pd and Ni overlayers as discussed elsewhere [47,50].

A charge transfer explanation of bond strength was originally proposed ~50 years ago for intermetallic alloys and follows generalized Lewis acid-base theory ([52] and references therein). The application of Lewis acid-base theory to transition metals predicts that those metals with more than half-filled d-bands will behave as Lewis bases and those with few d electrons would behave as Lewis acids. Metals with half-filled valence bands, like Cu, are considered to be amphoteric, exhibiting both acidic and basic properties depending upon the bonding counterpart. *In addition*, Lewis acid-base theory predicts that the strongest interactions will be between metals at opposite ends of the transition series (i.e. a strong acid interacting with a strong base). This description agrees very well with the data presented in fig. 59 for Cu overlayers and likewise for Ni and Pd overlayers [47,50]. Although this description of metal-metal bonding interactions satisfactorily explains the bond strengths between overlayer and substrate atoms [47,50,56] as well as the heats of formation of intermetallic compounds ([52] and references therein), it incorrectly predicts the charge transfer between the bonding metals in bulk alloys to be in the direction opposite to that indicated by classical electronegativities.

Thus, a different theory of bond formation for bulk alloys has been developed based on the transformation of the metallic Wigner-Seitz cells into the alloy Wigner-Seitz cell with an associated redistribution of electron density ([51] and

references therein). For bulk intermetallic alloys, this explanation is preferred since it predicts charge transfer to occur in the direction predicted by bulk electronegativities. Recent self-consistent density-functional theory calculations and Mössbauer experiments suggest that charge transfer in bulk alloys does occur from the electropositive metal to the electronegative metal during alloy formation [117-119]. Although this explanation is consistent with the experimental evidence for bulk alloys, it is clearly contrary to the results presented here and elsewhere [47,50,56] for monolayer metal films supported on metal substrates.

The bonding between overlayer and substrate atoms has recently been described in terms of electronegativity differences between the two metals [47,50,56]. However, because of the charge transfer observed with XPS, the electronegativities of the ultra-thin 2-D films have been re-evaluated [47,50,56]. Electronegativity is typically defined as a measure of the ability of an atom or molecular orbital to attract electrons [120,121]. The electronegativities of bulk transition metals tend to increase from left to right across the transition series [122]. It is well known, however, that the anisotropic environment present at a surface can have pronounced effects on the surface atoms. The lower coordination number of a surface atom as well as changes in the geometrical arrangement of its neighbors will likely cause changes in the orbital hybridization of these atoms [120,121]. Photoemission studies of pure metals have clearly shown that surface and bulk atoms have different electronic properties [123]. Thus, it is not surprising that the electronegativities of surface atoms can be quite different from those of bulk atoms. XPS measurements of charge transfer between surface and substrate

atoms can, therefore, be used to establish a qualitative scale of surface electronegativities. These data have been presented elsewhere [50] and yield the general trend that surface electronegativities increase from right to left across a transition series. This trend is exactly opposite to the trend observed for bulk electronegativities. Thus, these recent interpretations, based on the concept of surface electronegativities [47,50] as well as on the generalized acid-base theory of Brewer [52], can be used to explain the bonding and charge transfer trends observed with XPS in a variety of monolayer metal systems. Therefore, although a complete theoretical understanding of surface atomic bonding interactions is lacking, it is clear that overlayer-substrate bond formation can be thought of in terms of electron donor-electron acceptor interactions with electronic charge being reduced on the electron rich component and increased on the electron poor component. In addition, the magnitude of the charge transfer between the overlayer and substrate atoms has been shown to be related to the bond strength between the overlayer atoms and the substrate (see fig. 59) [47,50].

CO Chemisorption

The changes in the electronic properties of the overlayers that were discussed in the previous section should be reflected in the chemical properties of the surface. The chemisorptive properties of carbon monoxide as well as its involvement as a reactant in many catalytic reactions make it an ideal molecule for chemisorption studies on bimetallic surfaces. Fig. 60 is a comparison of the

desorption temperatures of CO adsorbed on monolayer Cu films and the shift in the $\text{Cu}(2p_{3/2})$ binding energy induced by the adsorption of CO. The Cu monolayers which have withdrawn charge from the substrate (shifted toward lower binding energy) show a larger CO-induced shift compared with the Cu monolayers that donated charge to the substrate (shifted toward higher binding energy). The CO-induced shift is always toward higher binding energy, indicating that, when CO is adsorbed, charge flows from the Cu overlayer. It is noteworthy, however, that the CO desorption temperatures shown in fig. 60, which are proportional to the strength of the Cu-CO bond, do not correlate with the CO induced shift.

The nature of the CO-substrate chemisorptive bond has been the subject of numerous studies, both experimental and theoretical. The conventional description of CO chemisorption is based on the Blyholder model [67] where CO-metal bonding is thought to occur via donation of charge from the CO 5σ orbital to an unoccupied metal orbital and by backdonation from the metal d orbitals into the unoccupied 2π orbital of CO. It is generally assumed that as the CO-substrate bond strength increases, the amount of back-donation must also increase. This increase in back-donation into the 2π orbital destabilizes the intermolecular C-O bond and is believed to be a cause of the dissociative adsorption of CO that occurs in very strongly bound CO-metal systems. Subsequent studies by Messmer et al. [124,125] attempted to correlate the electronic and vibrational properties of adsorbed CO. These authors proposed a model where the forward- and back-donation of charge (as described by Blyholder) is valid for strong adsorption systems (i.e. transition metals with partially filled d bands), but that in weak adsorption systems, such as

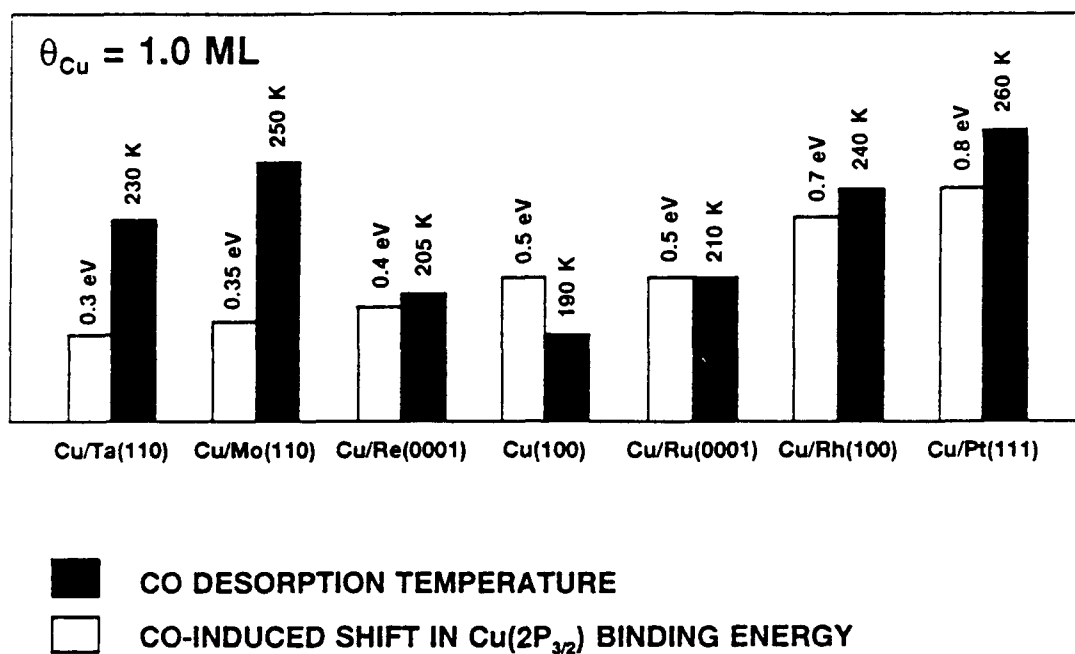


Fig. 60: A comparison of the desorption temperatures of CO adsorbed on monolayer Cu films and the shift in the $\text{Cu}(2p_{3/2})$ surface binding energy induced by the adsorption of the CO.

noble metals, a different bonding mechanism is operative. It is suggested that 5σ donation necessitates donation into an empty level to form a strong bond. Thus, since Cu is a noble metal and has a $d^{10}s^1$ electron configuration, no completely empty states are available. Therefore, bonding is proposed to occur primarily via a metal p-state charge transfer into the 2π orbital with little direct interaction between the CO and the metal d orbitals [125]. Additional theoretical calculations for CO adsorbed on Cu clusters support this explanation [68]. These calculations have indicated that the CO chemisorptive bond is dominated by the transfer of electron density from occupied metal orbitals into the unoccupied 2π orbital of the CO molecule.

This theory of the chemisorptive bonding interaction between CO and a Cu substrate has been used in the evaluation of the CO/Cu/Ru(0001) system [126]. It was proposed that the bonding interaction between CO and Cu must depend on the degree of 4s occupancy. Angle resolved ultraviolet photoemission spectroscopy results identified the existence of Cu(3d)-Ru(4d) interface states in the Cu/Ru(0001) system and showed that these states shift together toward higher binding energy upon CO adsorption [126]. Therefore, it was concluded that the CO-Cu interaction did not involve any appreciable hybridization with metal d orbitals but rather resulted from the formation of a CO(5σ)-Cu(4s) bond. The authors suggested that the increase in the CO-Cu bond strength for monolayer Cu on Ru compared to pure Cu was due to a reduction of charge on the Cu 4s orbital, possibly due to: (1) Cu being less electronegative than Ru and thus donating charge to Ru, (2) CO induced polarization of the Cu 4s orbitals away from the surface toward the substrate due

to the presence of the adsorbed CO, and (3) backdonation from Cu into empty CO orbitals [126].

The data presented in fig. 60 support the reduction of charge on Cu upon CO adsorption. However, as can be seen in fig. 59a, XPS studies have shown that a surface monolayer of Cu is not less electronegative than Ru and that for a monolayer of Cu on Ru(0001), charge is not transferred from Cu to Ru [50,55], but vice versa. Thus, (1) is not a valid explanation for the increased CO bond strength on supported Cu monolayers. The CO induced Cu($2p_{3/2}$) binding energy shifts shown in fig. 60 are consistent with either a CO induced polarization of the Cu orbitals toward the substrate or backdonation of charge from Cu to CO. However, the changes in the CO desorption temperatures do not coincide with the linear increase seen for the CO induced shift as the substrate is changed from Ta to Pt. Instead, the CO desorption temperature (which is related to the strength of the CO-Cu bond) is lowest for Cu and increases as the substrate is moved away from the center of the transition series. The increase in CO-Cu binding energy for Cu monolayers on electron-rich substrates has been discussed previously and has been attributed to an increase in the ability of the Cu atoms to backdonate charge into the CO 2π orbital leading to a stronger CO-Cu bond [50,56]. The increase in CO-Cu binding energy for Cu monolayers on electron-poor substrates, on the other hand, is not consistent with a model where an increase in 2π backdonation leads to an increase in CO-metal bond strength.

Recent theoretical calculations for CO adsorbed on different sized Cu clusters indicate that there are two main contributions to Cu-CO bonding: intra-

species charge polarization and inter-species charge transfer [65,69]. The inter-species charge transfer has two main components: CO- σ to metal charge donation and metal to CO- π charge backdonation. Of these, the metal to CO- π backdonation has been shown to be more important in CO-metal bond formation [65,68,69,125]. Most previous discussions of CO-metal bonding [67,124,125], however, have neglected the importance of the polarization of the metal and CO charge densities to produce an attractive dipole-dipole interaction. The polarization of metal charge away from the CO is a result of the necessity of reducing the repulsive charge superposition interaction between the CO-5 σ and metal-s charge distributions during bond formation between Cu and CO. Thus, it is possible that the increase in the CO-Cu bond strength for Cu monolayers on electron poor substrates could be a direct consequence of the charge transfer from the Cu to the substrate. This would increase the net charge polarization of Cu electron density away from the CO leading to a stronger dipole-dipole inductive bond between the CO and Cu. Therefore, it appears that the two main factors affecting CO-metal bond strength are: (1) the amount of π -backdonation and (2) the polarization interaction between the CO dipole and the partial positive charge on the metal center. The combination of these effects determines the trend seen in fig. 60. The trends shown in fig. 60 should be verifiable through a comparison of the shifts in the IR stretching frequency of the adsorbed CO.

The stretching frequency of saturation CO adsorbed on a well-ordered Cu monolayer on Rh(100) and Ta(110) is 2095 cm^{-1} as can be seen in figs. 18 & 29. An identical frequency has been observed previously for Cu/Pt(111) [102]. This

frequency, however, is quite different from the 2075 cm^{-1} value observed for CO on Cu(111) [105]. In fig. 61, the stretching frequencies and desorption temperatures of CO adsorbed on several monolayer Cu films are compared. From this figure, it is apparent that the stretching frequency of the CO adsorbed on these Cu films correlates well with the CO desorption temperature. The fact that there is a correlation between the CO stretching frequency (which is proportional to the strength of the C-O bond) and the CO desorption temperature (which is related to the strength of the Cu-CO bond) is surprising since fig. 60 shows that the CO desorption temperature does not correlate with the CO-induced shift in the $\text{Cu}(2p_{3/2})$ binding energy (which is proportional to the amount of π -backdonation).

The typical view of the CO-substrate interaction is that an increase in π -backdonation should cause a decrease in the C-O stretching frequency [67-69,124,125]. However, it is clear from figs. 60 and 61 that the stretching frequency of CO adsorbed on supported Cu monolayers does not correlate with the amount of π -backdonation (as measured by the CO-induced shift). A correlation between the CO stretching frequency (C-O bond strength) and the CO desorption temperature (Cu-CO bond strength), was observed previously for a limited number of supported Cu overlayers [102] and is found to still be valid for the additional data presented in this work. However, this correlation is difficult to explain using simple molecular orbital theory models. Previous calculations have indicated that the CO stretching frequency is influenced by the following: (1) π -backdonation, (2) the interaction of the CO dipole and the electronic charge distribution around the metal atom, and (3) the repulsion occurring when the CO molecule stretches in the

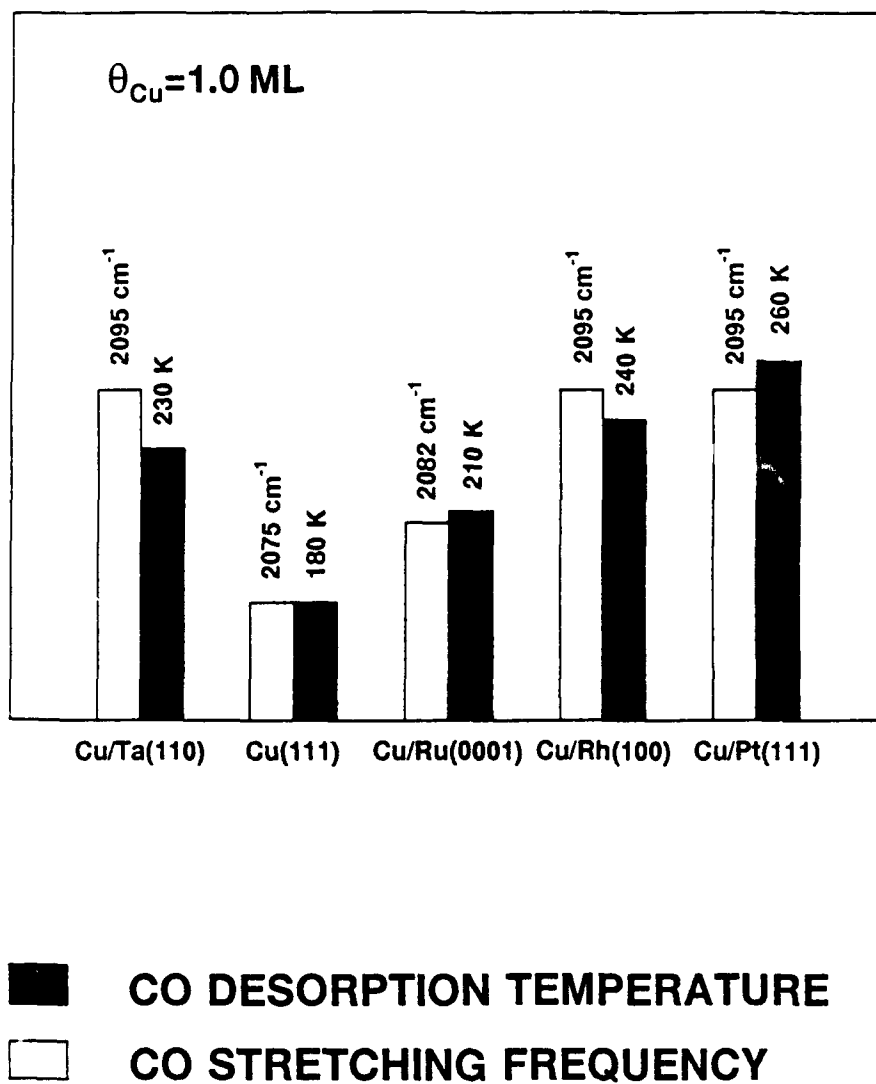


Fig. 61: A comparison of the stretching frequencies and desorption temperatures of CO adsorbed on monolayer Cu films on various substrates.

presence of a rigid surface (the "wall effect") [69,70,127]. Overall, π -backdonation dominates (in agreement with theory [65,69,70]) and gives rise to a vibrational frequency lower than that of gas phase CO (2143 cm^{-1}). However, the data shown in fig. 61 imply that the CO stretching frequency is also influenced by the polarization interaction between the CO dipole and the charge density on the metal center. A tighter Cu-CO bond necessitates a shorter Cu-CO bond length. A shorter Cu-CO bond length yields a greater repulsive interaction between the CO dipole and the charge density on the metal center, which in turn leads to an increase in the observed CO stretching frequency. It is the complex combination of all of these effects that determines the trend seen in fig. 61. It should be noted that the two main features apparently affecting the CO stretching frequency (π -backdonation and polarization interaction) are the same factors discussed earlier that apparently dominate the CO-Cu bond strength. Additional studies with other metal overlayers need to be conducted to determine if the effects observed here only occur for Cu films or if they can be generalized to other overlayer systems.

Surface Structure

As an initial comment on the use of CO adsorption to study surface structure, it should be mentioned that IR peak intensities frequently do not accurately represent the true concentration of surface species. "Intensity transfer" [64,107,127] and "screening" [102,106,129,130] effects can significantly perturb the observed IR peak intensities. The "intensity transfer" effect is a strong dipole-

dipole coupling between CO molecules adsorbed on a surface that results in the transfer of intensity from a low frequency mode to a high frequency mode [64,106,107]. This effect is most evident when the vibrational modes are separated by less than a hundred wavenumbers. A good example of this effect is in the spectra of co-adsorbed $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ where the observed IRAS peaks are at equal intensity for a 5% $^{12}\text{C}^{16}\text{O}$ / 95% $^{12}\text{C}^{18}\text{O}$ mixture [106]. In addition, a suppression in the IRAS intensity of a CO-Pt(111) peak has been observed when CO is co-adsorbed with a highly polarizable species like CH_3OH , H_2O or Xe [1128]. The polarizable species can induce a considerable shielding of the local electric field around the CO molecule, "screening" its dipole moment. More importantly, this effect has also been observed for CO adsorbed on submonolayer Cu and Ag on Pt(111) [102,129], Cu on Ru(0001) [84,85] and Ni on Mo(110) [130]. Due to the polarizability of the overlayer adatoms upon CO adsorption, the CO-adatom ensembles are effective at screening the intensity of chemisorbed CO on the overlayer-free substrate [102,129]. The relative importance of "intensity transfer" and "screening" can be determined by the frequency separation between the peaks for the different adsorption sites and the polarizability of the overlayer.

For CO adsorption on all of the bimetallic systems studied in this work, attenuation of the substrate peak was evident. As expected, it was always stronger for unannealed (more dispersed) overlayers. This is clearly shown in fig. 19 for Cu/Rh(100) where the CO-Rh peak on the unannealed surface is attenuated to zero at a Cu coverage that is at least 0.2 ML lower than necessary for an annealed surface. The polarizability of the overlayer adatoms makes "screening" the most

likely cause of the intensity attenuation, however, the proximity of the peaks in certain of these systems (Cu/Ta(110) for example) means that "intensity transfer" can not be ruled out. In the final analysis, it is not terribly important from a practical standpoint to determine with absolute certainty which of these effects is occurring. The truly important observation is to note that it is occurring so the intensity perturbations can be qualitatively evaluated to allow a meaningful interpretation of the data.

There are several interesting features in the IRAS spectra of CO adsorbed on ultra-thin Cu films that have been presented in this work. In fig. 16, it is noteworthy that the CO adsorbed on 0.1 ML of Cu on Rh(100) shows a peak at 2155 cm^{-1} which is higher than that of gas phase CO (2143 cm^{-1}). An unusually high CO stretching frequency (2138 cm^{-1}), although not blue-shifted, has been observed in a previous study of CO adsorbed onto 0.03 ML of Cu on a Ru(0001) surface and was interpreted to correspond to CO adsorbed on single Cu atoms [85]. In addition, in a recent study of CO adsorbed on ~ 0.1 ML of Cu on Mo(110), a feature was observed at $\sim 2160\text{ cm}^{-1}$ [131]. The high intensity of the peaks arising from CO on low coverages of Cu on Rh(100) when compared to the Cu surface concentration is due to the screening effect discussed above. The high stretching frequencies for the CO adsorbed on these sites suggest a considerable reduction in 2π backdonation. In a previous XPS study of the Cu/Rh(100) system, it was observed that for low Cu coverages, the $\text{Cu}(2p_{3/2})$ peak is shifted toward lower binding energy, indicating an increase in electron density on the Cu [55]. When CO is adsorbed, however, the $2p_{3/2}$ peak shifts toward higher binding energy [55]. Work on the Cu/Ru(0001)

system indicates that there is a net charge transfer from the Cu overlayer to the Ru substrate upon CO adsorption [126]. It is, therefore, likely that there is a strong polarization interaction between the adsorbed CO molecules and the isolated metal adatoms. In addition, fig. 25 shows that the CO TPD feature associated with the <0.2 ML Cu films on Rh(100) has a desorption temperature ($\sim 280\text{K}$) that is higher than for either bulk Cu or monolayer Cu films [34]. This is in complete agreement with the CO adsorption model discussed in the previous section which stated that the increased repulsive polarization interaction that results from a shortening of the Cu-CO bond (tighter bond - higher desorption temperature) should lead to an increase in the CO stretching frequency.

It is well known, and intuitively obvious, that the deposition of metal overlayers at liquid nitrogen temperature will typically form a disordered overlayer since the atoms impinging on the surface cannot migrate across the surface to find the most favorable adsorption sites. Annealing these disordered overlayers will supply the energy necessary to allow the atoms to move around on the surface to find the most favorable adsorption sites. For many systems these annealed overlayers will be pseudomorphic with respect to the substrate. The spectra presented in this work indicate that by using CO as a probe molecule, the resulting IRAS spectra are sensitive to these changes. A good example of this can be seen in fig. 18 for the Cu/Rh(110) system. It is clear from this figure that annealing the surface to higher temperatures increases the intensity of the sharp peak at 2095 cm^{-1} at the expense of the peak at 2120 cm^{-1} . In addition, as mentioned earlier, annealing reduced the background intensity, implying the formation of an ordered

pseudomorphic Cu overlayer. However, the appearance of the new feature in the IR spectra is a much more definitive indicator of the formation of the ordered overlayer. In addition, some qualitative information about the quality of the ordered overlayer is obtainable. The fact that a peak is still evident at 2120 cm^{-1} indicates that not all of the Cu on the surface has been incorporated into the ordered overlayer. The amount is exaggerated by intensity sharing, however. Allowing for this would give a rough estimate of ~80-90% of the Cu overlayer being ordered.

This type of disorder-order phase transition is also observable for Ni and Co overlayers on a Mo(110) substrate (figs. 34 and 38). For these overlayer systems, the formation of an ordered overlayer upon annealing films ~1-2 ML thick is easily observable by the formation of multi-diffraction spots in the LEED patterns from the annealed surfaces. The IR spectra from CO adsorbed onto these surfaces indicate that annealing to ~1100 K produces an almost complete ordering of the overlayers. From the intensity remaining in the peak attributable to disordered admetal domains, it is possible to estimate that at least 90-95% of these overlayers adatoms are in ordered domains. For these disorder $\rightarrow$ order phase transitions, the IR peak shift is toward lower frequency. In other words it is toward the value obtained on the bulk ordered surfaces.

These examples show the utility of using IRAS with CO as a probe molecule to study the structure of these model bimetallic systems. A further, and perhaps more significant, example of the ability of this technique to provide information about surface structure is shown in figs. 28b, 32 and 37. These figures of annealed

Cu/Ta(110), Ni/Mo(110) and Co/Mo(110) surfaces all show the pseudomorphic $\rightarrow$ pseudo-close packed phase transitions that occur on these surfaces. It is the higher packing density of these pseudo-close packed overlayers that gives rise to the multiple diffraction patterns observed. The (9X2), (8X2) and (7X2) LEED pattern observed correspond to overlayer coverages of 1.22, 1.25 and 1.29 ML, respectively (1 ML is defined as 1 overlayer atom per substrate atom). As mentioned earlier, the Ni/Mo(110) system exhibits an order-order phase transition from an (8X2) phase to a (7X2) phase. Thus, the density difference between the different surface structures is only 3%. The two structures, however, are unambiguously identified by their CO peaks at 2087 and 2065 cm^{-1} . Similarly, the CO IR spectra clearly characterize the pseudomorphic $\rightarrow$ (9X2) and pseudomorphic $\rightarrow$ (8x2) overlayer structural transitions of Cu/Ta(110) and Co/Mo(110), respectively.

The ability to use CO as a molecular probe for phase transitions obviously results from a different CO bonding strength and/or configuration on the different metal overlayer structures, as well as the intrinsic high resolution of IRAS. During the structural phase transitions, the changes in electronic and structural properties of the metal overlayers induce a frequency shift in the adsorbed CO. The phase change may result in an alteration of the CO-CO inter-molecular spacing and consequently change molecule-molecule interactions, such as dipole-dipole coupling [64]. In addition, changes in the electronic properties of the overlayer could alter substrate-CO interactions, such as charge backdonation from the metal overlayers to the adsorbed CO. However, any effect due to the overlayer geometric change is expected to be negligible based on the following. (a) As mentioned above, the

density difference between the Ni (8x2) and (7x2) phases is only 3%, while the difference between the Co pseudomorphic and (8x2) phases is 25%. This corresponds to a change of only 1.5% and 12% in the respective lattice constants. These small variations (0.05 and 0.38 Å) are expected to have little effect on the molecular interactions. (b) It can be seen in fig. 32 that the integrated intensity and the full widths at half maximum for the spectra at 0.95 and 1.08 ML are invariant during the phase transition. This further discounts the possibility that CO adsorbed on the two phases has significantly different molecule-molecule interactions.

It is well known that as CO coverage increases, the increase in molecular interactions usually results in a decrease in IR intensity (due to depolarization) and an up-shift in frequency (due to dipole-dipole coupling) [64]. The abrupt frequency shifts observed during the phase transitions are, therefore, attributed mainly to changes in the electronic properties of the metal overlayers. During the phase transitions, the overlayer density increases to approach that of the corresponding bulk metal surface. The work function of and the CO desorption temperature from the metal overlayers also increase to approach those for a Ni(111) or Co(0001) surface [27,35]. As the Ni or Co overlayers change from strained structures to relatively relaxed ones ((8x2) to (7x2) for Ni and (1x1) to (8x2) for Co), the strain-induced electronic perturbations of the overlayer atoms are reduced. Thus, the backdonation from the metal overlayer to the CO 2π orbital increases, and the C-O stretch frequency is consequently red-shifted. This work shows a red-shift of 20

to 30 cm^{-1} as the surfaces change from relatively open to relatively close packed structures ((8x2) to (7x2) for Ni and (1x1) to (8x2) for Co).

During the phase transitions on Ni/Mo(110) and Co/Mo(110), the stretching frequency of CO adsorbed on each phase remains virtually unchanged (see figs. 28, 32, 34, 37 and 38). This strongly implies a 2-D island growth mechanism of the phases, with two dimensional phase expansion at the island edges. The configuration and bond strength of CO at the island interiors would thus be preserved during the phase transition. This mechanism has also been observed in the disorder-pseudomorphic transition of Cu/Rh(100) as discussed above (see fig. 18) and appears to be general for all the phase transitions at metal-metal interfaces which we have addressed to date. In an early study of CO adsorption on a Ru(0001) surface, the CO within the ordered CO islands of the $\sqrt{3} \times \sqrt{3}$ R 30° structure showed a different frequency from the CO at the island edges [132]. In the present work, each ordered phase is represented by a single, highly symmetric peak. Therefore, the contribution of CO at the island edges is negligible. However, the IR peaks at 2100 and 2083 cm^{-1} at $\theta_{\text{Ni}} = 0.26\text{ ML}$ in fig. 32 may correspond to CO adsorbed on small islands and island edges. As Ni coverage is further increased to 0.42 ML , the spectrum shows only a single peak for the (7x2) structure, indicating that the islands have grown in size and the fraction of the CO adsorbed at the edges has become small. The present work does not yield quantitative information on island size.

Sulfur is a common contaminant and has been shown to have a pronounced effect on the adsorption of CO [110,111,133]. These effects are clearly evident in

the IRAS spectra of CO adsorption on S/Mo(110) presented earlier. The spectra shown in fig. 40 reflect the dual nature of adsorbed S. It can act as both a site blocker and/or an electron withdrawing agent. The fact that S can affect CO adsorption in both a site blocking [133] and electron withdrawing [110] fashion has, of course, been observed before. However, the fact that these effects can be observed in the CO IRAS spectra is another example of the utility of this technique. In figs. 40 and 41, it is clear that from a sulfur coverage of ~ 0.25 ML up to a coverage of ~ 0.35 ML that both $p(2 \times 2)$ and $c(2 \times 2)$ S domains exist on the surface at the same time. The lack of an abrupt change as the S coverage is increased, implies that this is not really a phase transition from the $p(2 \times 2)$ structure to the $c(2 \times 2)$ structure, but rather, just the gradual filling in of the $p(2 \times 2)$ overlayer lattice structure with additional S atoms to give the $c(2 \times 2)$ structure. This filling in of the $p(2 \times 2)$ lattice, however, does not occur randomly. The almost constant frequency for CO adsorbed on the $c(2 \times 2)$ sites implies that upon annealing the additional S tends to aggregate to form domains with the $c(2 \times 2)$ structure amongst domains that retain their original $p(2 \times 2)$ structure. The $c(2 \times 2)$ domains will expand via nucleation at their edges until the entire surface is covered with a $c(2 \times 2)$ S overlayer.

Co promoted MoS_2 hydrodesulfurization (HDS) catalysts are extensively used in refineries to remove S from the crude oil feed stock. MoS_2 itself can be used for this reaction, but the addition of Co can increase the activity of the catalyst by an order of magnitude. There have been several different explanations given for this increase in activity upon Co addition. Two of these involve whether the Co-

MoS₂ interaction is one of the Co truly acting as a promoter that perturbs the MoS₂ catalyst forming the so called Co-Mo-S structure at the edges of the MoS₂ crystallites [134-137], or whether the Co-MoS₂ interaction actually forms a highly dispersed Co₉S₈ phase that is the active component of the catalyst [138,139]. These studies have all attempted to determine the nature of active component in the real supported complex catalysts. There have been very few studies attempting to understand the effects of cobalt on more easily tractable model single crystal bimetallic systems. A recent study [140] of Co/S/Mo(100) has shown that annealing causes the sulfur to migrate on top of the Co. This migration, however, did not significantly affect the thermal desorption of Co from the surface [140].

The studies of CO adsorption on S/Co/Mo(110) and Co/S/Mo(110) surfaces presented in this work were an attempt to understand the Co-S-Mo interaction using a model single crystal system. In the experiments on S/Co/Mo(110) surfaces, S appears to act almost entirely as a site blocker. In figs. 50 and 51, it is obvious that increasing the sulfur coverage decreases the intensity of the CO features and leads to red shifts in their stretching frequencies. In addition, fig. 51 strongly indicates that this site blocking effect occurs preferentially at the Co sites. There does appear to be an activation energy barrier to the migration of the S on the surface that leads to the preferential poisoning of the Co sites at lower S coverages. Fig. 52 shows that at an annealing temperature of 800 K, the majority of the Co sites are still available for CO adsorption. But upon annealing to ≥ 950 K, the intensity of the Co peaks is drastically reduced. In addition to the major role S plays as a site blocker on S/Co/Mo(110) surfaces, there is evidence in fig. 53

that it can also exhibit electron withdrawing effects. The feature at 2085 cm^{-1} in this figure is to be due to CO adsorption on sulfided Co 3-D clusters. This is a higher frequency than is seen for CO adsorbed on clean Co clusters.

For the Co/S/Mo(110) surfaces, it was again possible to see effects attributable to both site blocking and electron withdrawal. Fig. 55 shows the effects of increasing the Co coverage on a S/Mo(110) surface with a fairly low S coverage (0.15 ML). At a cobalt coverage of 1.5 ML, the annealed surface has three features observable that can be attributed to CO adsorption on clean Mo(110), (8X2) Co/Mo(110) and sulfided 3-D Co clusters. This indicates that essentially all of the S has migrated to the Co clusters giving a high enough S concentration to electronically perturb these sites as evidenced by their CO stretching frequency at 2087 cm^{-1} . The assignment of the peak at 2052 cm^{-1} to CO adsorption on domains of (8X2) Co on the Mo(110) substrate was corroborated by LEED observations of this surface which did indeed show a faint (8X2) multidiffracton pattern.

The surface used for the spectra shown in fig. 57 was the closest to the actual catalyst that was obtainable in this study. The substrate was an annealed c(2X2) S/Mo(110) surface which can be thought of as roughly approximating the surface of a MoS_2 crystallite. Increasing Co coverages are then added to this surface and annealed (sintered) prior to CO exposure to probe the available adsorption sites. Fig. 57 shows that up to Co coverages of $\sim 0.3\text{ ML}$ there are no CO adsorption features associated with the Co adatoms. At coverages of 0.5 ML and above features due to Co are visible and at a Co coverage of 1.5 ML, sulfided Co makes up the main adsorption feature. It is unlikely that this type of promoter

loading would ever be used in an actual catalyst. A typical value for the real catalysts is a 1:3 Co to Mo ratio [134], which implies a Co surface coverage of 33% or 0.3 ML. For this Co coverage, as stated before, there are no IR features due to CO adsorbed on Co. It is, therefore, quite unlikely that a Co site on this type of surface could be the active catalytic site. Thus, from this data it must be concluded that a more likely explanation of the increased catalytic activity of Co promoted MoS₂ would be that the active site is a Co promoted Mo-S site.

As a final point, it is noteworthy that in all the co-adsorption systems studies in this work with IRAS, multiple peaks have been observed. These results imply that there is a segregation of the adatoms into 2-D (and sometimes 3-D) islands and that the different domains are distinguishable by the stretching frequency of adsorbed CO. It is also important to again restate the fact that despite the sensitivity of the vibrational frequency of CO to its electronic and chemical environment, the peak areas should not be assumed to be representative of the relative populations of the indicated features.

SUMMARY AND CONCLUSIONS

This dissertation has discussed recent studies that were conducted using CO IRAS to study well defined bimetallic surfaces. Information has been obtained about the interaction between CO and the surface as well as details about the structure of the deposited metal overlayers. It is the inherent high spectral resolution of IRAS combined with the localized nature of the CO-substrate interaction that makes these observations possible.

Several interesting features have been observed in the systems studied for this dissertation and are summarized as follows.

1. The chemisorption bond between CO and an overlayer metal atom consists primarily of two components: a π -backdonation and a polarization interaction component. The magnitude and relative contributions of these two interactions determine the bond strength and stretching frequency of the adsorbed CO.

2. For low coverages (<0.3 ML) of Cu on Rh(100) and Cu on Mo(110) [131], the vibrational frequency of adsorbed CO is higher than the gas phase CO stretching frequency. This blue shift was not, however, observed for CO adsorbed on Ni/Mo(110) or Co/Mo(110). The blue shift is believed to correspond to CO adsorbed on well dispersed Cu that is polarized due to CO-Cu-substrate interactions.

3. 3-dimensional Cu clusters, 2-dimensional pseudomorphic Cu overlayers and isolated Cu atoms on a Rh(100) surface are characterized by their CO stretching frequencies at 2074, 2095 and $\sim 2160\text{ cm}^{-1}$, respectively.

4. Disorder $\rightarrow$ order and order $\rightarrow$ order phase transitions lead to abrupt changes in the stretching frequency of adsorbed CO. This was clearly observable in the disorder $\rightarrow$ (1X1) transition for Cu/Rh(100), the disorder $\rightarrow$ (7X2) transition for Ni/Mo(110), the disorder $\rightarrow$ (8X2) transition for Co/Mo(110), the (1X1) $\rightarrow$ (9X2) transition for Cu/Ta(110), the (1X1) $\rightarrow$ (8X2) transition for Co/Mo(110) and the (8X2) $\rightarrow$ (7X2) transition for Ni/Mo(110). The growth of the domains of these structures apparently follows a mechanism of two dimensional island expansion via nucleation of the adatoms at the island edges.

5. The IRAS studies of S/Mo(110) and Co/S/Mo(110) presented in this work have shown that S can act as both a site blocker and electron withdrawing agent with respect to CO adsorption on these surfaces. Annealing mixed S and Co overlayers induces migration and segregation of the components into domains that are identifiable by the stretching frequency of adsorbed CO. Sulfided Co, (8X2) Co, c(2X2) S, p(2X2) S and clean Mo(110) domains are all observable.

6. The spectra obtained from the 0.3 ML Co - c(2X2) S Mo(110) surface suggest that the increased catalytic activity of the Co promoted MoS₂ catalyst is due to a Co promoted Mo-S site as the active site.

This dissertation has shown that IRAS studies using CO as a probe molecule, when used in conjunction with traditional surface analytical techniques, can provide valuable information on surface structure. It has been shown for the first time that

the stretching frequency of chemisorbed CO is sensitive to phase transitions in the substrate surface. However, due to intensity transfer and screening effects, great care must be used when attempting to infer relative abundances of the different phases from the CO IR spectra. Therefore, although it has some limitations, IRAS using CO as a probe molecule is an extremely valuable surface analytical tool that can be used to gain information on surface structure and the nature of adsorption sites in mixed overlayer systems.

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VITA

William Kevin Kuhn

Birth:

August 11, 1962, Frankfurt, Germany

Address:

4782 James Cir. #C, Huntington Beach, CA 92649

*Education:*Ph.D. in Chemistry, Texas A&M University, College Station, Tx
December 1992.M.S. in Chemistry, University of Hawaii, Honolulu, HI
December 1986.B.S. in Chemistry (with distinction), University of Hawaii, Honolulu, HI
May 1984.*Professional Experience:*

Officer in US Air Force working on PhD in analytical chemistry 8/89-8/92.

Officer in US Air Force working in an environmental water analysis lab
1/87-7/89.Teaching assistant in the Chemistry Department of the University of Hawaii
9/84-12/86.*Publications:*

15 publications and 8 in preparation.

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