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L. H. Dubois and G. A. Somorjai

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THE CHEMISORPTION OF CO AND CO_2 ON Rh(111) STUDIED BY
HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY

By

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Abstract

We have applied the techniques of high resolution electron energy loss spectroscopy (ELS), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED) to a study of CO and CO_2 chemisorption on the Rh(111) single crystal surface. The vibrational spectra of carbon monoxide indicate two distinct binding sites (atop and bridged) whose relative populations and vibrational frequencies are determined by both the substrate temperature and the background pressure. TDS measurements show the bridge bonded CO to have an approximately 4 kcal/mole lower binding energy to the surface than the species located in the atop site. Surface pretreatment also had a marked effect on CO adsorption: oxygen and carbon both inhibited carbon monoxide chemisorption and weakened the metal-adsorbate bond strength. Hydrogen had no observable effects. The adsorption of carbon dioxide yields virtually identical spectra to that of chemisorbed CO, indicating dissociative adsorption. By combining the present data with earlier infrared and inelastic electron tunneling spectroscopic studies, a consistent set of force constants for the two types of chemisorbed carbon monoxide can be calculated.

Introduction

The bonding of carbon monoxide to transition metals is one of the most studied chemisorption systems in surface science. The interaction of CO with metal atoms or with clusters of metal atoms is also well understood by inorganic chemists. As a result of these detailed studies of CO, comparisons between surfaces and metal cluster carbonyls can now be made. The bonding of carbon monoxide to rhodium is of special interest since this metal catalyzes the hydrogenation of CO in both heterogeneous and homogeneous media. The formation of small hydrocarbons from either CO and H_2 or CO_2 and H_2 over supported[1] and unsupported[2] rhodium surfaces is well known. Furthermore, rhodium carbonyls catalyze the hydroformylation of olefins and produce ethylene glycol from mixtures of hydrogen and CO[3]. Because of the importance of this metal we have chosen to explore the vibrational spectrum of both CO and CO_2 chemisorbed on a Rh(111) single crystal surface.

The classic picture of carbon monoxide bonding to metals is by electron transfer from the 5σ orbital of CO to the metallic d orbitals and by backbonding of the metallic electrons into the empty $2\pi^*$ orbital of the adsorbate. This scheme has been used by both surface scientists and inorganic chemists to explain the infrared spectra of chemisorbed carbon monoxide and of metal carbonyls. Since the electron density in the CO antibonding orbital has increased, the carbon-oxygen stretching frequency should decrease below the gas phase value of 2143 cm^{-1}. Furthermore, as the CO is bound to an increasing number of metal atoms this frequency should drop even further as shown in the IR spectra of model organometallic compounds of known molecular struature. It is generally assumed that species with C-O stretching frequencies above 2000 cm^{-1} correspond to

linearly bonded CO, frequencies between about 1860 and 2000 cm^{-1} belong to bridge bonded species and those below approximately 1860 cm^{-1} are for face bridging or three-fold coordination.[4] The validity of this rule has not yet been well tested on single crystal surfaces. Furthermore, the presence of other either electron donating or withdrawing substituents on the surface can alter the CO electron density and will certainly shift the observed stretching frequencies.

Much effort has gone into understanding the vibrational spectrum of carbon monoxide chemisorbed on rhodium. More than 20 years ago Yang and Garland performed the first infrared studies using highly dispersed rhodium particles supported on an inert alumina substrate.[5] They provided convincing evidence for a species of the form $Rh(CO)_2$, a gem dicarbonyl, whose IR spectrum showed a doublet at 2095 and 2027 cm^{-1}. The presence of linear ($\sim$2060 cm^{-1}) and bridge bonded (1925 cm^{-1}) forms were also demonstrated. More recent investigations [4,6-10] agree extremely well with these early experiments except that the C-O vibration of the multiply coordinated species was found to lie near 1860 cm^{-1} in most cases. Supported rhodium cluster carbonyls of known structure have also been studied and analogous stretching frequencies in the 1800 to 2100 cm^{-1} region were reported.[11,12] Substrate adsorption below 1000 cm^{-1} masked all Rh-CO vibrations. Both transmission and reflection IR studies employing evaporated rhodium films yield similar results.[4] Due to the high density of Rh atoms, no species of the form $Rh(CO)_2$ were formed, however. This is expected to be the case on the (111) surface as well. Weak adsorptions between 400 and 575 cm^{-1} were seen and are indicative of metal-adsorbate stretching and bending vibrations. Inelastic electron tunneling spectroscopic (IETS) measurements on alumina supported rhodium particles [13-15] add little new structural information except that peaks in the 400-600 cm^{-1} region

have been definitely assigned to Rh-CO bending and stretching modes. Ibach[16] has shown that high resolution electron energy loss spectroscopy (ELS) and IR spectroscopy yield analogous information and therefore one would expect similar results from the present investigation .

The structure of CO adsorbed on rhodium surfaces has also been studied by low energy electron diffration. The first reported LEED experiments on the Rh(111)/CO system were carried out by Grant and Haas in 1970.[17] These results have only recently been expended and systematized.[18,19] At room temperature CO forms a $(\sqrt{3}x\sqrt{3})R30°$ structure at exposures near 0.5 L (1L=1 Langmuir= 10^{-6} torr sec.). At intermediate coverages a "split" (2x2) pattern is visible and can be explained by double diffraction from a hexagonal overlayer of molecular CO. The spot splitting decreases as the overlayer compresses into a closest packed configuration and finally a (2x2) LEED pattern is visible. Thermal desorption spectra yield only molecular CO desorbing from the surface ($E_d\approx31$ kcal/mole)[18,19] and show no evidence for CO dissociation under ultrahigh vacuum conditions.

The effects of surface pretreatment on the chemisorption of CO on rhodium have also been considered previously. Early infrared experiments showed that hydrogen had little affect on the CO/rhodium vibrational spectrum.[5] More recent studies indicate a slight decrease in the gem dicarbonyl $(Rh(CO)_2)$ species upon hydrogen exposure.[8,20] However, no evidence for changes in either the LEED patterns or the thermal desorption spectra of CO adsorbed on Rh(111) were found after exposing the surface to gaseous hydrogen.[18] Infrared studies on O_2/CO co-adsorption show an increase in the concentration of the gem dicarbonyl species[5,6,8] and a decrease in the concentration of the bridge bonded species relative to the linear species.[5,8] Small shifts in the C-O stretching vibrations to higher frequencies have also been reported.[21] The

formation of CO_2 at higher pressures and elevated temperatures has been seen as well.[2,5,22] Carbon pretreatment from the thermal decomposition of acetylene had a marked decreasing effect on the rate of methane formation from CO/H_2 mixtures over a polycrystalline rhodium foil.[2] Furthermore, CO thermal desorption spectra show a shift of 30 K to lower binding energy on these same pretreated surfaces.

Castner, et al showed that CO and CO_2 produced an identical series when either gas was chemisorbed of both LEED patterns and thermal desorption spectra on the Rh(111) surface.[18] They interpreted these findings in terms of carbon dioxide dissociation into adsorbed CO and oxygen. Further studies on stepped rhodium surfaces are in full agreement with this interpretation.[23] Recent catalytic experiments on rhodium foils indicate that CO_2 does indeed dissociatively chemisorb and is extremely reactive toward hydrogen.[2] For a more complete review of earlier work on the chemisorption of CO_2 on various rhodium surfaces, see Reference 24.

In this study we have combined high resolution ELS with LEED and thermal desorption spectroscopy (TDS) to present a rather complete picture of CO and CO_2 chemisorption on the Rh(111) single crystal surface. The vibrational spectra of carbon monoxide indicate two distinct binding sites (atop and bridged) whose relative populations and vibrational frequencies are a strong function of both substrate temperature and background pressure. TDS measurements show the bridge bonded CO to have a lower binding energy to the surface than the species located in the atop site, and therefore this species can be selectively removed from the rhodium crystal. Surface pretreatment also had a marked effect on CO adsorption: oxygen and carbon both inhibited carbon monoxide chemisorption and weakened the metal-adsorbate bond strength. Hydrogen had no observable effects. The adsorption of carbon dioxide yields virtually identical spectra to that of

chemisorbed CO, again indicating dissociative chemisorption. Finally, by combining the present data with earlier IR and IETS studies a consistent set of force constants for the two types of chemisorbed carbon monoxide can be calculated.

Experimental

Experiments were carried out in an all stainless steel ultrahigh vacuum chamber built in two levels. The upper portion contains the standard single crystal surface analysis equipment (four grid LEED/Auger optics, glancing incidence electron gun and quadrupole mass spectrometer). Crystal cleaning by cycles of argon ion bombardment and annealing were also performed in this location. After dosing, the sample was lowered into the high resolution electron energy loss spectrometer by an extended travel precision manipulator. The monochromator and analyzer are identical 127° cylindrical sectors mounted on a rotatable base. The design is similar to that of Froitzheim, et al.[25] In the present series of experiments the angle of incidence was fixed at 70° to the surface normal. The elastic scattering peak had a full width at half maximum between 80 and 100 cm^{-1} and a maximum intensity of 1×10^5 counts per second. The vacuum chamber is lined with layers of μ metal and silicon-iron shielding to reduce stray magnetic fields. The upper and lower levels are also separated by μ metal. The base pressure in the system was maintained at 1×10^{-10} torr with two sputter ion pumps and a titanium sublimation pump. Neither gas exposures nor background pressures were corrected for ion gauge sensitivity.

The procedures for sample preparation, mounting and cleaning have been described previously.[18] Briefly, the rhodium single crystal rod was

oriented to $\pm$ 1/2° using x-ray back reflection and a 1mm thick disc was cut by spark erosion. After mechanical polishing the sample was spot welded to etched tantalum foil and mounted inside the UHV chamber. The Rh(111) crystal was cleaned by a combination of argon ion bombardment (1000-2000 eV) followed by annealing in vacuum ($\sim$900 K) and O_2/H_2 cycles to remove carbon, sulfur and boron.

Results and Discussion

A. CO Chemisorption on Clean Rh(111)

The adsorption of CO on Rh(111) at 300 K produced a series of well ordered LEED patterns in excellent agreement with previous studies.[18,19] The vibrational spectra of chemisorbed CO as a function of coverage is shown in Fig.1. At very low exposures (less than 0.1 L) only one peak at 1990 cm^{-1} is observed in the C-O stretching region and no ordered LEED pattern is found. By comparison with the infrared spectra of relevant organorhodium compounds[26,27] and with matrix isolated metal carbonyls,[28] one can assign this loss to the carbon-oxygen stretching vibration of a linearly bonded species. This peak shifts to higher frequency as the coverage is increased. Possible causes for this include local field effects,[29,30] vibrational coupling[30] and dipole-dipole interactions.[31] Currently one is lacking a complete understanding of the forces involved and most likely a combination of all three mechanisms is present. The result of these effects is a decrease in the rhodium-carbon backbonding and a weakening of the metal-adsorbate bond. This is clearly shown in Fig.1 by a shift in the rhodium-carbon stretching vibration for this linearly bonded species from 480 cm^{-1} to lower frequency as the coverage is increased. Thermal desorption spectra of CO from Rh(111) (Fig.2)[32] also show a weakening of the metal-adosrbate bond at high

surface coverage, again in agreement with previous studies.[18,19] No other vibrations corresponding to Rh-C=O bending modes were observed and therefore by invoking the normal dipole selection rule[16] we conclude that the carbon-oxygen bond is perpendicular to the surface.

At larger than 0.4 to 0.5 L CO exposures a small shoulder near 1870 cm^{-1} appears. Again by comparison with relevant model compounds, we can assign this peak to the carbon-oxygen stretch of a bridge bonded species. Unlike the loss near 2000 cm^{-1}, this peak grows at essentially constant frequency, never varying more than $\pm$ 5 cm^{-1}. By a CO exposure of 1.0 L the rhodium-carbon stretch has significantly broadened and split into two losses. The new low frequency peak appearing at approximately 400 cm^{-1} corresponds to the metal-carbon stretch for the bridge bonded species. This weaker bond to the substrate for the new species can be correlated with the low temperature desorption peak appearing at high exposures in the thermal desorption spectra of Fig.2. Assuming first order desorption kinetics and a pre-exponential factor of 10^{13} sec^{-1}, the binding energy difference between these two sites is found to be approximately 4 kcal/mole. Again the bridge bonded species is perpendicular to the surface since no bending or asymmetric stretching modes were observed.

Since Castner, et al[18] found the (2x2) LEED pattern at room temperature to be stable only at relatively high gas pressures, we have explored the vibrational spectrum of chemisorbed CO up to 1×10^{-5} torr. This series of spectra is shown in Fig.3. Once again the carbon-oxygen stretch for the atop site continues to shift to higher frequency as a function of coverage and reaches a limiting value of 2060 to 2070 cm^{-1}. The rhodium-carbon stretch of the linear species simultaneously decreases to 420 cm^{-1}. The 1870 cm^{-1} loss due to the bridge bonded species remains at a constant frequency with increasing coverage,

however.   The presence of gem dicarbonyl species cannot be ruled out here due to the limited resolution of ELS, but seem unlikely because of the high density of metal atoms on the (111) surface[4] that would lead to extreme crowding of CO molecules in the dicarbonyl configuration.

The high coverage values of the C-O stretching frequencies measured here are in excellent agreement with most of the earlier infrared studies of carbon monoxide adsorption on both supported[4-12] and unsupported[4] rhodium samples. The small differences in the reported stretching frequencies are due to dispersion and support effects. Representative infrared and ELS data for the CO-rhodium system are summarized in Table I.

The chemisorption of carbon monoxide on Rh(111) is completely reversible. As the background CO in Fig.3 is pumped away the carbon-oxygen stretching vibtation for the bridge bonded species decreases in intensity and the metal-carbon and carbon-oxygen stretching vibrations for the atop site shift back into their original positions. The bridge bonded species can be selectively removed from the substrate by slowly heating the crystal to approximately 360 K. This is shown in Fig.4a, where we have exposed the Rh(111) surface to an essentially infinite amount (>1000 L) of CO at 300 K and then evacuated the system. As the crystal is slowly heated, the 1870 cm^{-1} peak, due to the more weakly bound bridged species, decreases first and the carbon-oxygen stretch for the atop species shifts to lower frequency. This is entirely consistent with the thermal desorption spectra of Fig.2 which show a lower binding energy for bridge bonded carbon monoxide. The second series of spectra in Fig.4b were obtained in the presence of 1×10^{-5} torr of CO and at much higher temperatures. Once again the

multiply coordinated species desorbs first. No CO decomposition was detected under any of the conditions employed in our experiments ($p \leq 1 \times 10^{-5}$ torr CO, $T \leq 600$ K).

The present high resolution ELS spectra can be well correlated with earlier LEED studies on Rh(111).[18,19] The $(\sqrt{3}x\sqrt{3})R30°$ LEED pattern observed at a 0.5 L CO exposure probably is due to an ordered array of CO molecules sitting in atop sites since the vibrational spectrum shows only a single peak in the carbon-oxygen stretching region at 2010 cm^{-1} (see Fig.5a). At intermediate CO exposures we see a compression of this hexagonal overlayer until at pressures of $\sim 1 \times 10^{-6}$ torr where a closest packed carbon monoxide overlayer has formed. This yields a (2x2) LEED pattern and a surface coverage of 3/4. A real space model for this substrate-overlayer combination is shown in Fig.5b. The ratio of atop to bridge sites is two to one and is in agreement with the intensity ratio found in the vibrational spectrum. The relative populations of the two surface species could not be accurately measured from the thermal desorption spectra due to the asymmetric peak shapes. Relaxation processes occuring in the overlayer during the desorption process also complicate the determination of the coverages of the two types of CO species. Between these two limiting coverages we see a continuous growth of both peaks and a shift in the loss above 2000 cm^{-1}, consistent with the compression of the carbon monoxide overlayer.

Pritchard[34] has shown that by slightly "relaxing" the overlayer structure, local site adsorption can be obtained without altering the diffraction pattern. Such effects may be taking place on Rh(111) and are consistent with the vibrational spectra. Further evidence for local site adsorption can be seen in Table I, where a comparison of the present results with earlier IR studies is

shown. Linearly bonded carbon monoxide molecules have C-O stretching frequencies between 2000 and 2100 cm^{-1}, regardless of the support or the dispersion. Similarly, bridge bonded species lie in the 1850-1900 cm^{-1} region. Finally, the recent photoemission studies of Braun, et al on the Rh(111)/CO chemisorption system show no evidence for adsorbate bond formation.[35]

We are currently carrying out a LEED sturctural analysis of the ($\sqrt{3}$x$\sqrt{3}$)R30° and (2x2) diffraction patterns to determine the positions of the adsorbed molecules.

B. CO Chemisorption on Pretreated Rh(111)

Sexton and Somorjai showed that surface pretreatment had a marked effect on the rate of hydrocarbon formation from H_2/CO mixtures over polycrystalline rhodium foils[2]; oxidation enhanced the methanation rate while surface carbon inhibited product formation. We have studied the effects of hydrogen, oxygen and carbon on the CO vibrational spectra[a], H_2 pre-adsorption or post-adsorption at 300 K had no significant effect on either the CO vibrational spectra or the thermal desorption spectrum (Fig.6b). Earlier LEED,[18] TDS,[18] and IR[5,8,20] studies also showed no effects at 300 K. Furhtermore, no room temperature rhodium-hydrogen stretching vibrations were observed, even at H_2 exposures up to several thousand Langmuirs. Finally, no changes were seen after heating the crystal to 600 K in 1x10^{-5} torr of a 3:1 H_2/CO mixture for 30 minutes.[36]

The effects of preadsorbed oxygen on the carbon monoxide vibrational spectrum is shown in Fig.7. O_2 chemisorption on Rh(111) is dissociative at 300 K yielding a single metal-oxygen stretching vibration at 520 cm^{-1} and a second order thermal desorption maximum.[18,37] This peak only remains as a shoulder on the more intense rhodium-carbon stretch as the CO coverage is increased. The formation of bridge bonded carbon monoxide is strongly inhibited in the presence of chemisorbed

oxygen and the atop sites seem to saturate with CO by an exposure of only 1 L. It appears that pre-adsorbed oxygen blocks some of the surface sites so that CO cannot adsorb in many of the atop and bridged positions. Since oxygen is strongly electron withdrawing, the extent of rhodium-carbon backbonding has decreased and the C-O stretch has shifted approximately 50 cm^{-1} to higher frequency. The strength of the metal-adsorbate bond is determined by the electron density in both the 5σ and $2\pi^*$ molecular orbitals of carbon monoxide and should therefore decrease as well. Consistent with this is a decrease of at least 30 cm^{-1} in the metal-carbon stretch and a lowering of the thermal desorption temperature by approximately 40 K (see Fig.6c). The smaller thermal desorption peak area is also in agreement with fewer CO molecules on the surface in the presence of chemisorbed oxygen.

At CO pressures near 5×10^{-7} torr a small shoulder at 1860 cm^{-1} appears and the bridge bonded species begins to form. By 5×10^{-6} torr of CO the Rh-O stretch is absent and bridge bonded carbon monoxide is definitely present. Furthermore, the metal-carbon and carbon-oxygen stretching vibrations have shifted into more "normal" positions (ν_{Rh-C} = 430 cm^{-1}, $\nu_{C=O}$ = 1860, 2070 cm^{-1}). Oxygen is soluble in bulk rhodium at elevated termparatures and therefore may be residing beneath the surface.[18,22,23,37] Alternatively, the chemisorbed oxygen could slowly react with CO and desorb from the surface as CO_2.[18] No CO_2 was observed in the thermal desorption spectrum, however. This is not surprising since oxygen will diffuse into the bulk of the crystal rather quickly at these temperatures. Once the near surface region becomes oxygen rich, CO_2 will form in measurable quantities.[22]

These results are in qualitative agreement with earlier infrared studies:[5,8,21] shifts in the carbon-oxygen stretching vibration to higher

frequency   are seen and the population of the linearly bonded species relative to the bridge bonded species has increased. Similar site changes and energy loss peak shifts have been observed in CO/O co-adsorption studies on both Ni(100)[38] and Ru(001).[39] The post-adsorption of oxygen on a CO saturated surface showed no effects. This is consistent with the low pressuure CO oxidation studies carried out over rhodium wires by Campbell and White.[22] Adsorbed carbon monoxide strongly inhibited oxygen adsorption and therefore decreased the reaction rate.

The Rh(111) surface was covered with carbon by decomposing 5×10^{-7} torr of either acetylene or ethylene at 1100 K for 10 minutes and subsequent flashing to 1200 K. Pre-adsorbed carbon has a very strong inhibiting effect on carbon monoxide chemisorption as shown in Fig.9. This is the same effect it had on the methanation rate.[2] The low inelastic scattering intensity indicates relatively small CO coverages while the broad eleastic peak and high background level are indicative of poor ordering. Consistent with this is a high background intensity in the LEED pattern and a decrease in the CO thermal desorption peak area (Fig.6d). The carbon overlayer is covering most of the crystal face so that there are only a few sites open for CO chemisorption The slightly more intense 1890 cm^{-1} peak indicates that chemisorption of the linearly bound species is inhibited more than chemisorption of the bridge bonded species.

There is also an electronic interaction between the carbon overlayer and the adsorbed carbon monoxide molecules, since the vibrational peaks have shifted slightly and the termal desorption temperature has dropped about 10 K (Fig. 6d). This altering of the CO-metal bond has also been observed in CO/hydrocarbon co-adsorption studies on other group VIII metals.[40]

C. CO_2 Chemisorption on Clean Rh(111)

Carbon dioxide chemisorption on Rh(111) yields a series of vibrational

spectra identical to those shown in Figs. 1 and 3 for CO adsorption. The only

difference appears to be that an approximately ten-fold higher exposure of CO_2

is needed to form the same surface structures.[18,24] As shown in the previous

section, the rhodium-oxygen stretch has a relatively low intensity and is probably

hidden beneath the metal-carbon peak. Our results are consistent with earlier

single crystal experiments showing an identical series of both LEED patterns

and thermal desorption spectra for the chemisorption of either CO or CO_2.[18,23]

These results lead to the conclusion that CO_2 dissociatively chemisorbs on Rh(111)

to adsorbed CO and oxygen. This is also in agreement with other TDS[23], IETS,[41]

and IR[8] studies on stepped and supported rhodium surfaces. Furthermore,

by utilizing both ELS and TDS to study isotopically labeled [13]CO_2 we have shown

that the adsorbed CO species is not derived from the ambient CO, but is the

result of CO_2 dissociation.[24]

D. Vibrational Analysis of the Rh/CO System

Infrared spectroscopic studies on supported metal catalysts have an

inherently high resolution, but are limited by support adsorption below 1000 cm^{-1}.

Therefore metal-carbon stretching and bending vibrations are obscured. IR

studies on either well characterized single crystal surfaces or evaporated films

are limited, at present, to transitions with large dipole derivatives and therefore

these same vibrations are not visible. Also, observation of modes parallel to

the surface is prohibited by the normal dipole selection rule.[16] High resolution

ELS allows one to scan the entire infrared region of the spectrum with high

sensitivity, but is hindered by relatively low resolution and again by the normal di-

pole selection rule. Inelastic electron tunneling spectroscopy has neither of

these drawbacks. However, peaks in the vibrational spectrum are shifted due to the geometry of the tunnel junction. Here the presence of the upper lead electrode in the Al-Al$_2$O$_3$ - Pb junction broadens and shifts the vibrational frequencies due to an image dipole effort.[42] By combining the present ELS results at high CO coverage with earlier IR[9] and IETS[15] studies we can now calculate a consistent set of force constants for the Rh/CO system. For the species that gives rise to the losses at 420 and 2070 cm^{-1} we assume a linear triatomic molecule of the form Rh-C=O and take relevant bond lengths from Rh$_6$(CO)$_{16}$.[43] Using a valence force model[44] one can easily obtain the force constants for the Rh-C and C-O stretching vibrations as well as that for the Rh-C=O bending modes. The results of these calculations are shown in Table II. A comparison of the observed and calculated values for the ^{13}C labeled species is indicative of the accuracy of these calculations.

Similar results can be obtained for bridge bonded carbon monoxide. Here we assume C$_{2V}$ summetry for a species of the form $\begin{smallmatrix} O \\ \| \\ C \\ Rh \quad Rh \end{smallmatrix}$ and to a first approximation neglect all bending modes. The results of these calculations are displayed in the second half of Table II. The agreement between the observed and calculated values for the isotopically labeled CO is not as good here due to the absence of bend-stretch interactions. Since we have neglected the bending modes in the force constant equations for the bridge bonded species, we can solve for the Rh-C-Rh bond angle and thus determine the rhodium-carbon bond length. This angle is calculated to be 88° and if we assume a Rh-Rh nearest neighbor distance of 2.69Å, we find a Rh-C bond length of 1.93Å. This is in good agreement with both LEED studies for CO bridge bonded to Pd(100)[45] and with the x-ray structure of several organometallic rhodium clusters.[46]
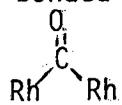
Summary and Conclusion

By combining the present ELS, TDS and LEED experiments with earlier

studies we can now present a fairly complete picture of CO and CO_2 chemisorption

on Rh(111). At very low exposures a single species is present on the surface

located in an atop site $(\nu_{Rh-C} = 480 \text{ cm}^{-1}, \nu_{C-O} = 1990 \text{ cm}^{-1})$. As the coverage

increases the bonding to the surface becomes weaker $(\nu_{Rh-C}$ decreases, $\nu_{C=O}$

increases, TDS peak maximum shifts to lower temperatures). This process

continues until an approximately 0.5 L ($\sim$5 L for CO_2) exposure where a $(\sqrt{3}x\sqrt{3})R30°$

LEED pattern is seen and all of the adsorbed CO molecules are linearly bound

to individual rhodium atoms. Above this coverage a second, bridge bonded species

begins to form $(\nu_{Rh-C} \simeq 400 \text{ cm}^{-1},$ $\overline{\nu_{C=O} = 1870 \text{ cm}^{-1}})$ and the "split" (2x2) LEED pattern indicates a

loosely packed hexagonal overlayer of CO molecules which compresses upon further

exposure. Throughout this intermediate coverage region there is a mixed layer

of atop and bridge bonded CO species. Two peaks are visible in the TDS spectra

with the bridge bonded carbon monoxide having an approximately 4 kcal/mole lower

binding energy$_\wedge^{\text{to the surface}}$than the species located in the atop site. Finally, by a back-

ground pressure of approximately $1x10^{-6}$ torr CO at 300 K , a (2x2) LEED pattern

forms whose unit cell consists of three carbon monoxide molecules--two atop and

one bridged, in agreement with the two-to-one peak ratio found in the ELS.

The high coverage values of the $\overset{C-O}{\text{stretching}}$ frequencies for the two types of chemisorbed

carbon monoxide $(\nu_{bridge} = 1870 \text{ cm}^{-1}, \nu_{atop} = 2070 \text{ cm}^{-1})$ are in excellent agreement with

previous infrared studies (see Table I).

The pre-adsorption of hydrogen had no effect on CO chemisorption on

Rh(111) as evidenced by both TDS and high resolution ELS. Oxygen and carbon

blocked many sites for CO chemisorption and weakened the metal-adsorbate inter-

action (ν_{Rh-C} decreases, $\nu_{C=O}$ increases, TDS peak maximum shifts to lower temperature). CO_2 dissociatively adsorbed to form chemisorbed CO and oxygen.

LEED and TDS studies on the interaction of carbon monoxide with the hexagonally closest packed faces of other Group VIII metals show numerous similarities. CO almost always forms a $(\sqrt{3}x\sqrt{3})R30°$ diffraction pattern at low coverages.[47] This LEED pattern compresses through a number of intermediate steps into a hexagonal closest packed overlayer of carbon monoxide molecules.[19,47] This is the case despite varying electronic configurations and different metal-metal distances. Similar metal-adsorbate bond energies have been measures as well.[18] The vibrational spectra show tremendous differences, however. Both nickel [48] and palladium[49] form multiply coordinated species at low CO exposures and the atop species are only seen at high coverage. The CO chemisorption behavior on Rh(111) and Pt(111)[50] are the opposite; here the atop sites populate first and predominate at low CO exposures. Bridge bonded species begin to form at intermediate coverages. Ruthenium is totally different; only a single carbon-oxygen stretching vibration is present at all coverages.[51] The reasons for these differences in the nature of CO bonding to the various transition metal surfaces will have to be explored further in the future.

Acknowledgements

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TABLE I — Selected Vibrational Frequencies for Carbon Monoxide on Rhodium [a]

Surface	Technique	ν_{Rh-C} $\delta_{Rh-C=O}$	$\nu_{3\text{-fold}}$	ν_{bridge}	ν_{atop}	$\nu_{Rh-(CO)_2}$
Rh(111) [b]	ELS	430		1870	2070	
Rh/Al$_2$O$_3$ [9]	IR			1870	2070	2031, 2101
Rh/SiO$_2$ [21]	IR			1890-1900	2040-2065	1990-2020, 2080
evaporated Rh film [33]	Transmission IR	400-575		1852,1905	2055	(2111)
Rh/Al$_2$O$_3$ [15]	IETS	413, 465, 600		1721 [c]	1942 [c]	1942 [c]
Rh$_2$(CO)$_8$ [26]	solution, IR			1845, 1861		2061, 2086
Rh$_4$(CO)$_{12}$ [27]	solid. IR	393, 423 488		1848		2028-2105
Rh$_6$(CO)$_{16}$ [27]	solid, IR	413, 427 513	1770			2016-2077

a) all frequencies in cm^{-1}
b) this study
c) peaks shifted due to the geometry of the tunnel junction (see page 14 of text and Ref. 42)

TABLE II   <u>CO on Rhodium, Vibrational Analysis</u>

Species	Mode	$^{12}CO_{(observed)}$	Force Constants		$^{13}CO_{(observed)}$	$^{13}CO_{(calculated)}$
linear	ν_{Rh-C}[a]	430	K_{Rh-C}	$2.52\ ^{md}/Å$	$-$[d]	425
$\overset{\displaystyle O}{\underset{\displaystyle Rh}{\overset{\|}{\underset{\|}{C}}}}$	$\delta_{Rh-C=O}$	469	K_β	$0.607^{md}\ Å/rad^2$	454	455
	$\nu_{C=O}$[c]	2070	$K_{C=O}$	$16.4\ ^{md}/Å$	2024	2020
bridged	ν_{Rh_2-C}[a] (symmetric)	420	K_{Rh_2-C}	$2.38^{md}/Å$	$-$[d]	414
$\overset{\displaystyle O}{\underset{\displaystyle Rh\ \ Rh}{\overset{\|}{\underset{\diagup\diagdown}{C}}}}$	ν_{Rh_2-C}[b] (asymmetric)	605			589	584
	$\nu_{C=O}$[c]	1870	$K_{C=O}$	$13.3\ ^{md}/Å$	1832	1826
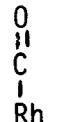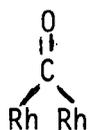
a) by ELS, this study
b) by IETS[15]
c) by IR[9]
d) not a resolvable shift by ELS

1) Vibrational spectra of CO chemisorbed on a clean Rh(111) surface at 300 K as a function of exposure. Note the shift in both the 480 and 1990 cm^{-1} losses with increasing coverage.

2) Thermal desorption spectra of CO from an initially clean Rh(111) surface.[32] The high temperature peak corresponds to the atop sites while the low temperature peak which grows in at larger CO exposures belongs to the bridge bonded species.

3) Vibrational spectra of CO chemisorbed on Rh(111) at 300 K as a function of pressure.

4) Temperature dependence of the CO on Rh(111) vibrational spectrum;

    a. infinite exposure (>1000 L) to CO;

    b. spectra run under 1x10^{-5} torr CO. Note the desorption at the bridge bonded species first, in agreement with the TDS spectra of Fig.2.

5) Real space representations of CO chemisorbed on a Rh(111) surface:

    a. ($\sqrt{3}$x$\sqrt{3}$)R30° overlayer structure visible at low exposures;

    b. (2x2) structure seen at relatively high background pressures.

6) The effects of surface pretreatment on the thermal desorption spectrum of CO from Rh(111);

    a. clean surface;

    b. pretreated in hydrogen;

    c. pretreated in O_2; and

    d. pretreated with carbon.

7) The effects of preadsorbed oxygen on the CO on Rh(111) vibrational spectrum.

8) The effects of preadsorbed carbon from the thermal decomposition of ethylene on the CO on Rh(111) vibrational spectrum.
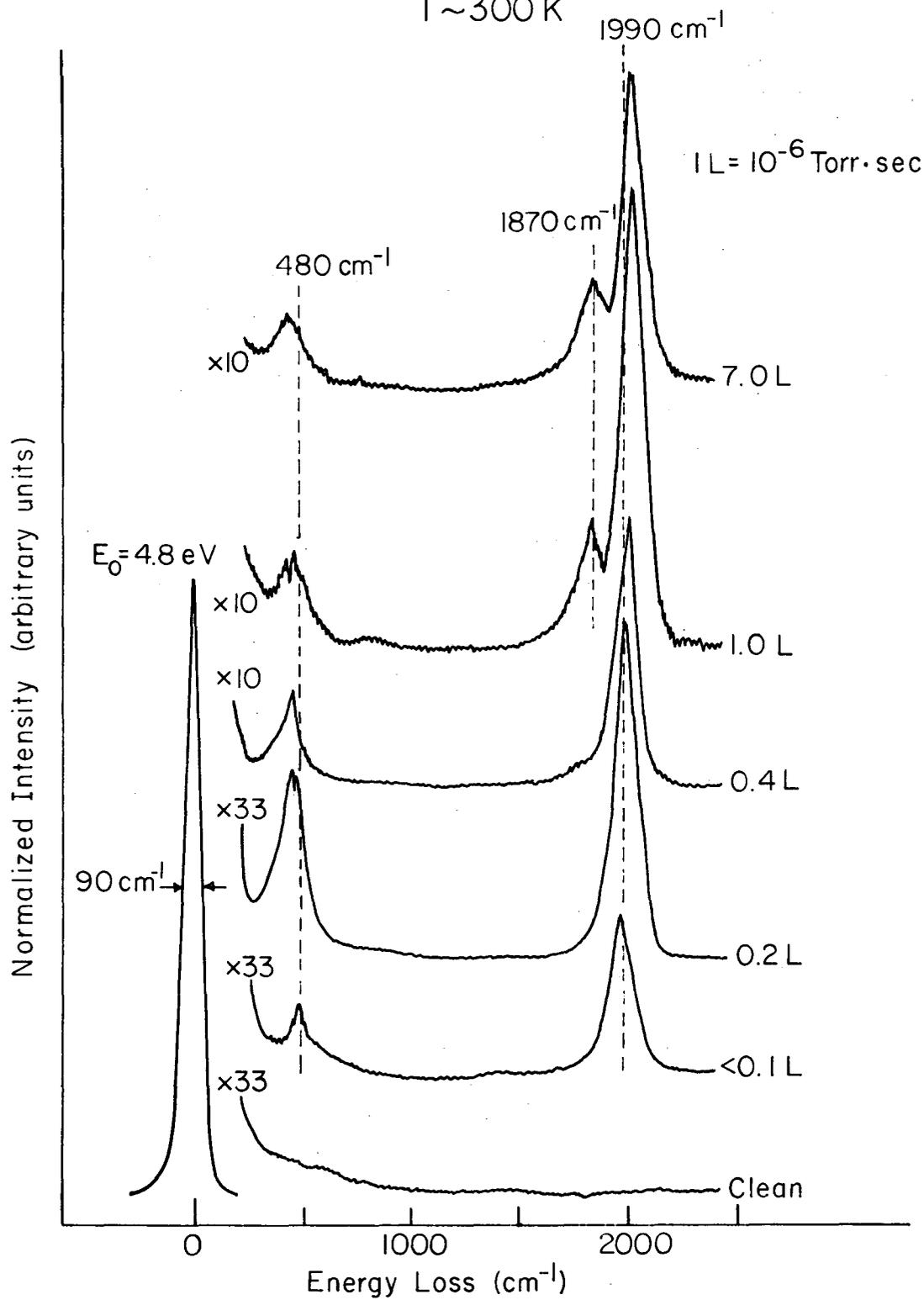
Fig. 1

XBL 793-5880
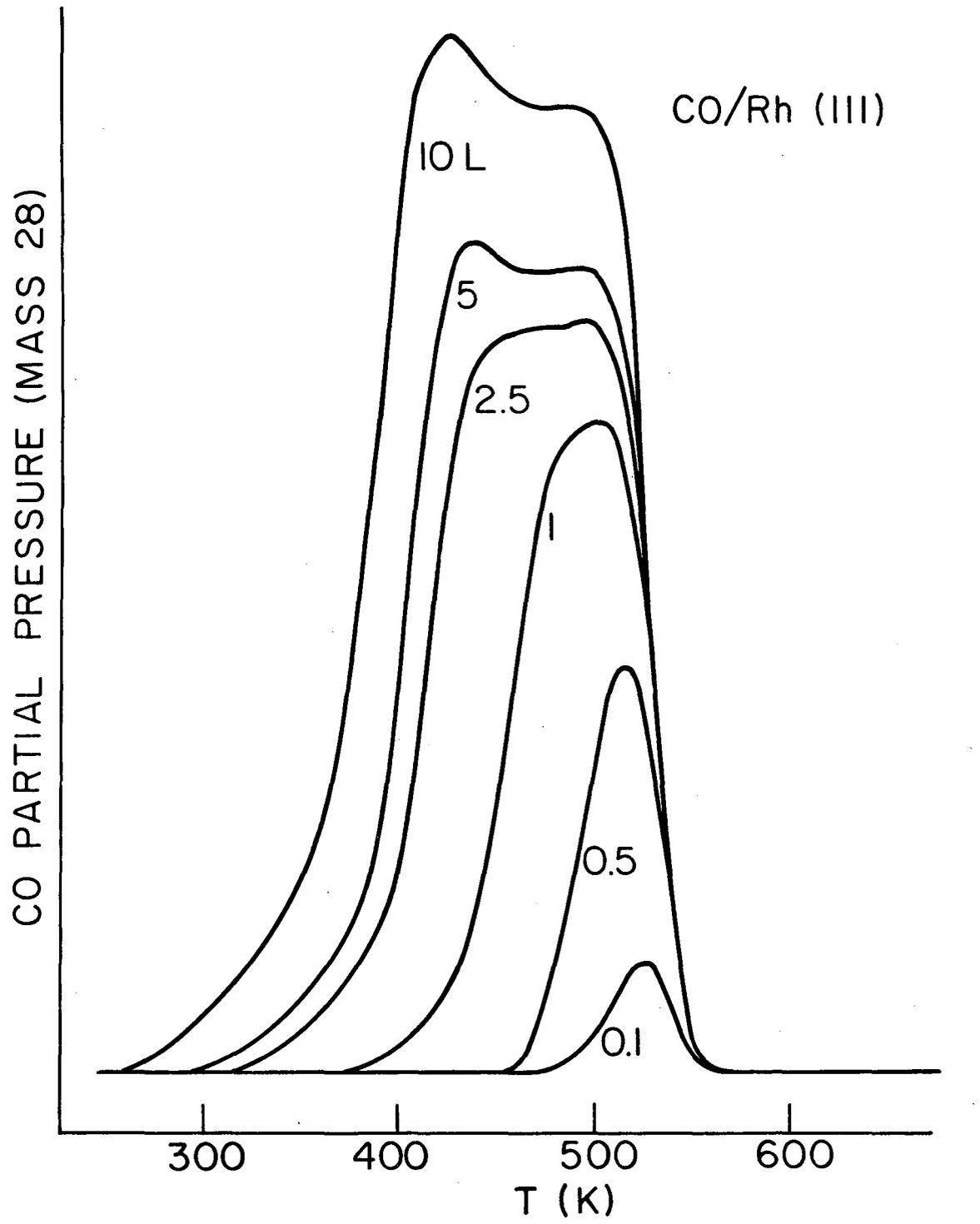
Fig.2

XBL 788-5563A
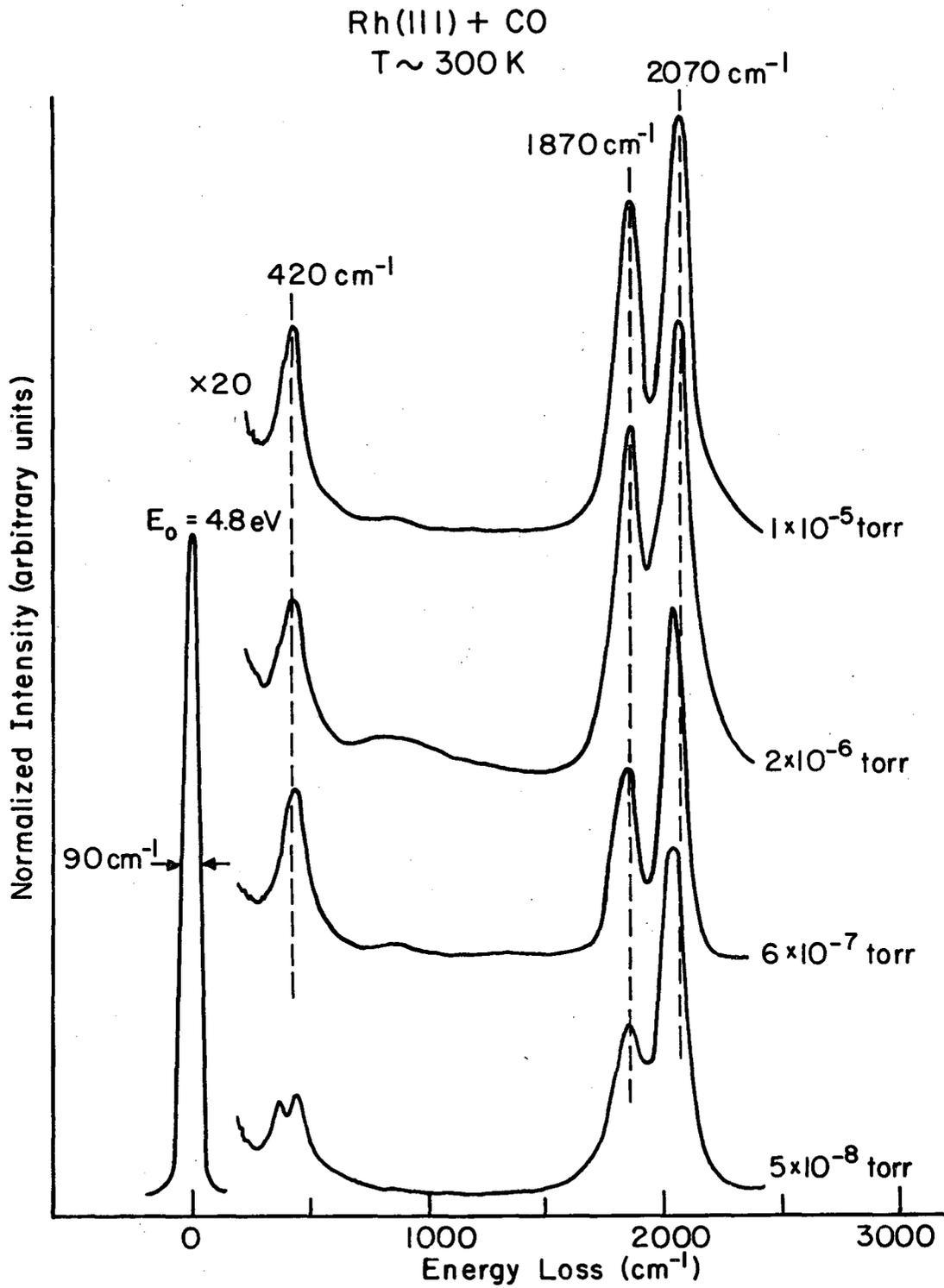
Rh(III) + CO
T ~ 300 K

Fig.3

XBL 793-5879

Rh (III) + CO : Temperature Dependence
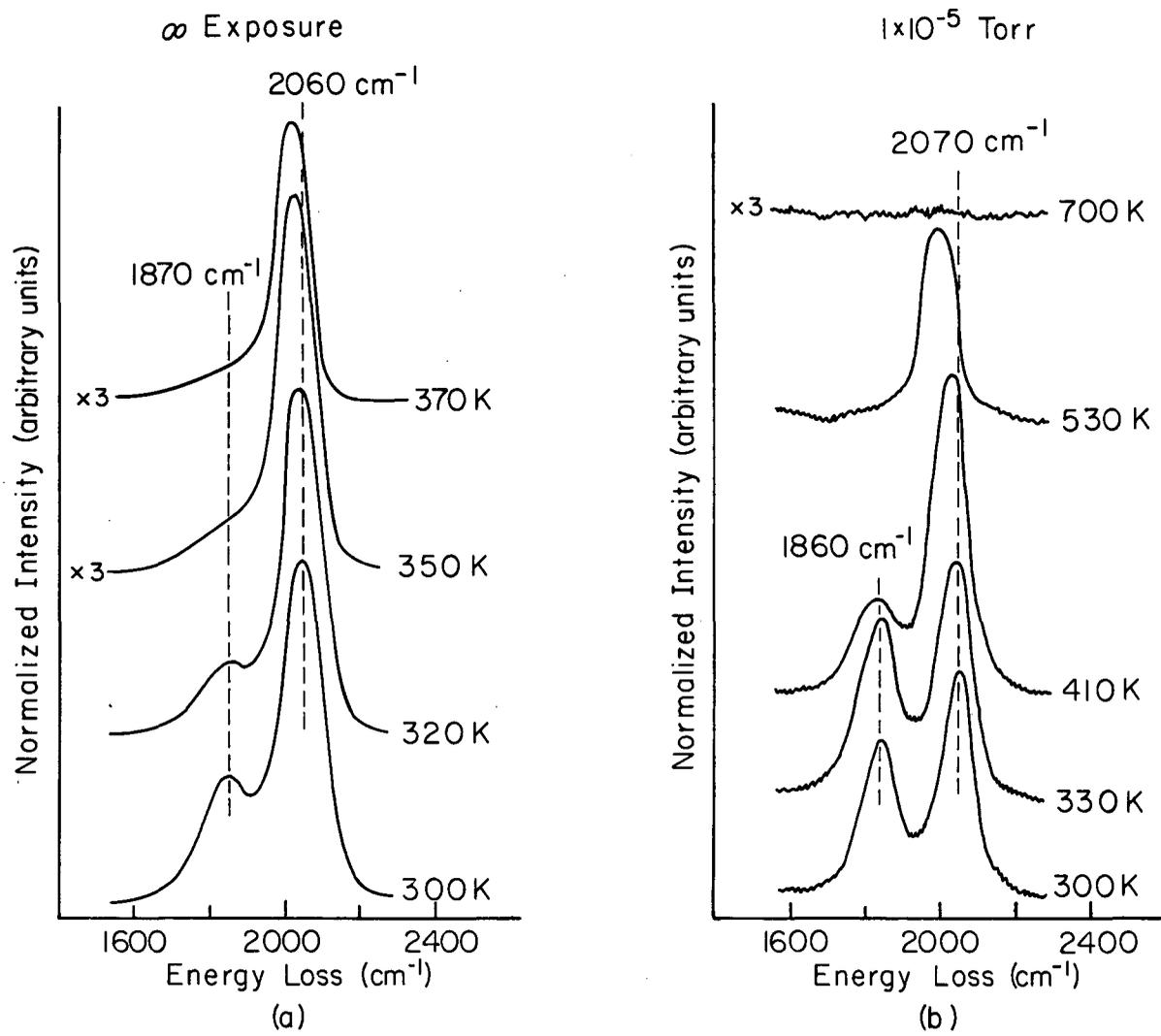
Fig. 4
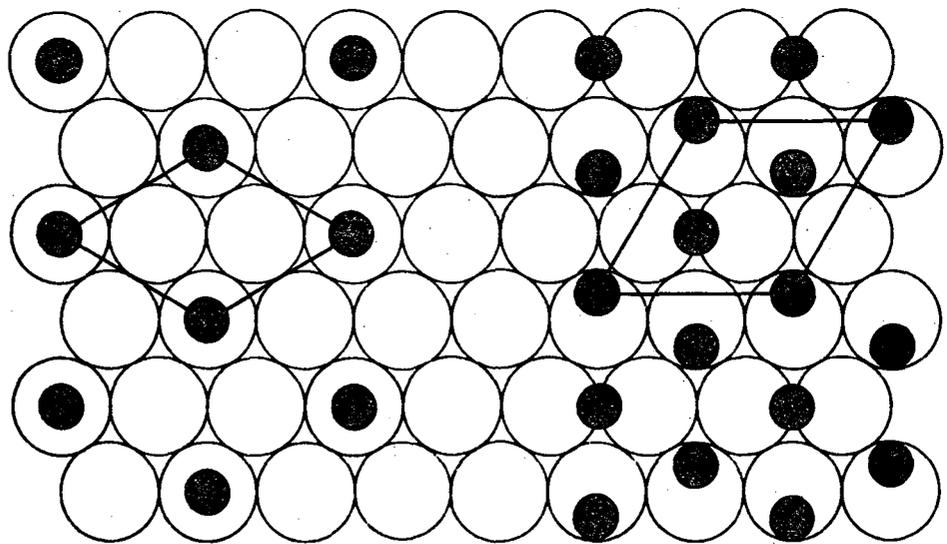
$(\sqrt{3} \times \sqrt{3})R\,30$
$\theta = 1/3$
a.

(2×2)
$\theta = 3/4$
b.

XBL795-6248

Fig.5

PRE-TREATED Rh (III) + 0.2 L CO
T_ads ~ 305 K

Fig.6

XBL795-6252

Fig. 7

XBL 793-5973

Fig.8