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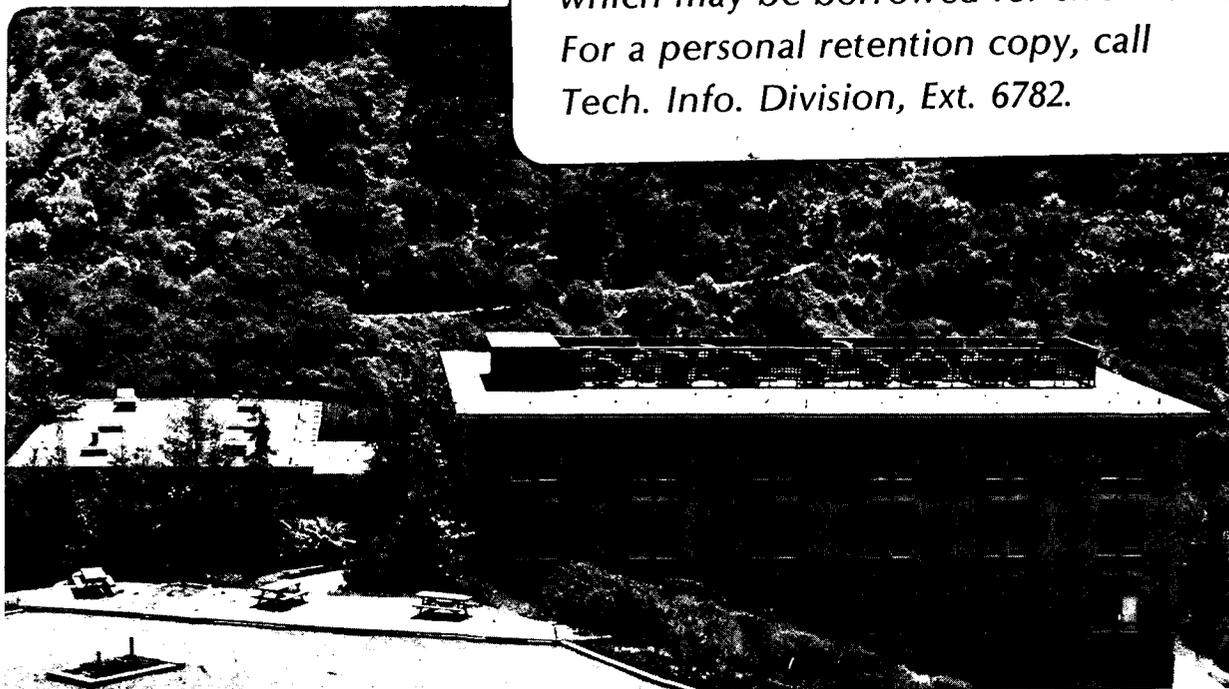
THE EFFECT OF POTASSIUM ON THE CHEMISORPTION OF
CARBON MONOXIDE ON THE Rh(111) CRYSTAL FACE

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THE EFFECT OF POTASSIUM ON THE CHEMISORPTION OF
CARBON MONOXIDE ON THE Rh(111) CRYSTAL FACE

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ABSTRACT

The adsorption of CO on the clean and potassium-predosed Rh(111) crystal surface has been studied using TPD and HREELS. When 10 percent of a monolayer of potassium is preadsorbed, the thermal desorption spectrum of CO broadens up to 100K higher temperature. In the presence of 10-36 percent of a monolayer of coadsorbed potassium, two new high temperature desorption maxima develop due to dissociation of CO. The CO stretching vibrations decrease continuously with either increasing potassium coverage or decreasing CO coverage. Substantial population and adsorption sequence shifts in site occupancy from the atop to the bridge site occur as a function of increasing potassium coverage. The results indicate both strengthening of the M-C bond and weakening of the C-O bond in the presence of potassium, due presumably to increased electron occupancy of the $2\pi^*$ -orbital of CO. Broadening and asymmetry of the vibrational peaks suggest the proximity of the CO molecules to the potassium adatoms influences the chemisorption behavior, although nonlocal interactions are also indicated.

1. Introduction

The coadsorption of alkali atoms with molecular adsorbates on transition metal surfaces is important both in surface science and in heterogeneous catalysis. By altering the extent of charge transfer between an adsorbed molecule and a metal surface, the nature of the bonding between these species can be explored. One method of influencing the metal-molecule interaction, especially for adsorbates such as CO, is by coadsorbing electronegative [1] or electropositive [2] atoms with the molecule. Spectroscopic investigations can reveal the bonding changes induced by the coadsorbed adatoms, elucidating the nature of the interaction. In turn, the role these adatoms play in modifying the chemical bonding at surfaces has important consequences in heterogeneous catalysis. In particular, electropositive atoms such as potassium and electronegative atoms such as sulfur can profoundly affect both the selectivity and rate of several reactions, including the hydrogenation of CO [3-7], the ammonia synthesis [8,9], and hydrocarbon reforming reactions [10,11].

The interaction of CO with transition metals shows empirical trends in both adsorption energy and dissociation behavior [12]. In particular, for a given row, the farther to the left in the periodic table a transition metal lies, the greater is the probability that CO will dissociate on this surface. Furthermore, the borderline or transition from dissociative to molecular adsorption moves to the left as one moves down the periodic table [13]. In an earlier study on Pt(111) [2], we showed that CO chemisorption is strongly affected by coadsorbed potassium. The binding energy increases dramatically with

increasing potassium coverage (as indicated by thermal desorption studies), while the C-O bond strength decreased markedly (as indicated by changes in the CO stretching frequency). Concurrent with these metal-CO bonding changes was a shift in site occupancy of the CO molecules from predominately single metal atom coordination sites to predominately multiply-coordinated adsorption sites. However, no evidence for CO dissociation was seen. The work reported here involves a similar study of the coadsorption of CO and K on Rh(111) using principally temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). The rationale for investigating Rh(111) is that this surface does not dissociate CO at low pressures [14], but its position in the periodic table suggests that the nature of CO adsorption on this surface, associative or dissociative, may be extremely sensitive to alkali promotion.

2. Experimental

The experiments were performed in a two level ultra-high vacuum chamber. The upper level was equipped with a retarding field analyzer for LEED and AES analysis, a glancing incidence electron gun, sputtering capabilities, and a quadrupole mass spectrometer for TPD studies. The HREEL spectrometer, mounted in magnetic shielding, occupies the lower level. The chamber is ion, titanium sublimation, and diffusion pumped with a base pressure typically less than 10^{-10} torr. The Rh(111) sample, oriented and polished on both sides, was mounted on 0.25 mm Ta support wires and attached to an extremely stable long-travel manipulator. The sample was heated resistively

and the temperature measured by a chromel-alumel thermocouple spot-welded to the back face of the crystal. The HREEL spectrometer consists of two identical 35 mm cylindrical sectors with 0.20 mm \times 4.0 mm slits as the entrance and exit apertures, and is similar to other designs [15]. The angle of incidence was 60° from the surface normal, and the total scattering angle fixed at 120°. The incident energy was 2-5 eV. Typical system resolution (FWHM of the elastic peak) for specular reflection from the clean or CO covered Rh(111) surface is 40-50 cm⁻¹ (5-6 meV) with greater than 10⁵ cps in the elastic peak. All spectra have been normalized to the elastic peak height shown. The power supply used for supplying the spectrometer voltages is easily adjusted and characterized by low-noise, high stability, and rapid response [16].

The Rh(111) sample was cleaned on both sides using a combination of chemical treatment with oxygen at elevated temperatures (3×10^{-7} torr O₂, 950-1250K), Ar⁺ sputtering (0.5-1.0 kV, 8 μ A), and annealing (1000-1400K) in vacuum. Care was taken to remove boron, carbon, oxygen, and sulfur impurities as observed by Semancik et al. [17]. AES, LEED, and HREELS were used to insure the surface was clean and well-ordered.

Potassium atoms were deposited onto the Rh(111) sample by heating a commercial SAES Getter source which consists of a powdered mixture of potassium chromate and a zirconium-16 percent aluminum alloy getter, enclosed in a tantalum dispenser. The K doser was positioned 6-8 cm from the sample, and dosing rates varied between 0.05 and 0.10 monolayers per minute. Potassium coverages were calibrated using LEED, AES, and TPD yield, and are described elsewhere [18]. A monolayer of potassium on Rh(111) corresponds to a surface density of

5.8×10^{14} atoms/cm², or $\theta_K = 0.36$ potassium atom per surface rhodium atom.

All experiments described here were performed at 300K. All exposures of CO were achieved by backfilling the chamber; exposures are uncorrected for ion gauge sensitivity.

3. Results

While the adsorption of CO on clean Rh(111) has been characterized by LEED, TPD, and HREELS [19]; only the TPD and HREELS results will be summarized here. The desorption of CO from Rh(111), shown in Fig. 1, is characterized by a single desorption peak. The peak maximum decreases as a function of CO exposure from 516K at low exposures to 482K at near-saturation exposures (at a linear heating rate of 15K/s). At high coverages, a low temperature shoulder develops. This desorption behavior of decreasing desorption temperature and observation of a low temperature shoulder with increasing coverage has been observed previously [20,21] and is believed to be due to repulsive lateral interactions between the CO molecules and population of lower energy binding sites at high coverage.

Vibrational spectroscopy using electron energy losses shows that at low exposures only a single C-O stretching vibration with a frequency characteristic of CO adsorption on an atop site is observed. This is shown in Fig. 2. Associated with this 2016 cm⁻¹ vibration is a low frequency mode at 468 cm⁻¹ due to a metal-carbon stretch of this linearly-bonded molecule. Bonding at a bridge site begins to populate at higher exposures with an initial C-O stretching frequency

of 1835 cm^{-1} . Both sites continue to populate with increasing exposure, and quickly a new vibration assigned to the metal-carbon stretching mode of the bridge bonded species becomes discernable at 383 cm^{-1} . Note that both C-O stretching vibrations increase in frequency with increasing exposure; this has been shown for a number of systems to be due predominately to dipole-dipole coupling [22]. Similar vibrational spectra for this system have been seen previously [23,24].

When CO is adsorbed onto a potassium predosed Rh(111) surface, dramatic changes in the CO TPD and HREEL spectra occur. In Fig. 3, representative TPD spectra are shown for saturation CO exposure on Rh(111) at 300K as a function of predosed potassium coverage. In these experiments the back face of the crystal was masked by adsorbing multilayers of potassium prior to CO exposure; CO does not adsorb on pure potassium multilayers [2]. When the Rh(111) surface is predosed with small amounts of potassium ($\theta_K < 0.10$), the CO desorption spectra only broaden to higher temperature. The degree of broadening is dependent on the potassium coverage. Once a critical potassium coverage is reached ($\theta_K \approx 0.10$), two new desorption states at 630 and 700K become populated. These new states are present in addition to the broadened lower temperature state such that CO desorbs continuously from 325 to 725K at this potassium coverage. New states at 630 and 700K continue to grow in intensity with increasing potassium coverage as the lower temperature state(s) dramatically decrease in intensity. At potassium coverages near saturation (e.g. see $\theta_K = 0.33$ in Fig. 3), only desorption from the 700K state occurs. This state decreases further with increasing potassium coverage.

Earlier studies by Yates et al. [14] have shown that CO does not dissociate on clean Rh(111) at low pressures, hence the low temperature desorption peak is due to first order molecular desorption. In order to elucidate the nature of the high temperature desorption states observed at large potassium coverages, we have recently adsorbed isotopically labelled CO and followed any isotopic mixing that occurs as a function of CO exposure, potassium coverage, and heating rate [19]. In this experiment, a mixture of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are adsorbed on the potassium dosed Rh(111) surface at 140K. The desorption of several species, including all possible CO isotopes (i.e. amu 28, 29, 30, and 31) are followed as the sample is heated linearly. If CO does dissociate on the potassium dosed surface, we expect scrambling of the isotopes to occur. For potassium coverages large enough that the 630 and 700K states are populated, we observe enhanced desorption of the mixed products $^{13}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ from these states. This does not occur for the lower temperature states, nor does it occur for the clean surface or for low coverages of potassium [19]. When the potassium coverage reaches nearly completion of the first layer and CO desorption only occurs at 700K, considerable scrambling occurs for this state. These results verify that these higher temperature desorption states, only present at relatively high potassium coverages, are due to recombination of carbon and oxygen atoms on the surface, produced from the dissociation of adsorbed CO.

When the higher temperature states become populated in the CO TPD spectra, significant changes also occur in the potassium desorption behavior [18]. Potassium TPD on Rh(111), when examined without other adsorbates, is similar to alkali desorption from several other transition

metals [c.f. 25-27]. On Rh(111), it is characterized by a desorption maximum near 1100K at low coverages ($\theta_K < 0.02$). The maximum desorption rate shifts rapidly to lower temperature with increasing coverages and peaks at 500K at completion of the first monolayer. The second layer desorption maximum then begins growing in at 350K. When CO is coadsorbed with small potassium coverages, this desorption behavior is unchanged as all the CO desorbs prior to any potassium desorption. However, once a critical potassium coverage is obtained such that the two high temperature CO desorption states are present, no potassium desorbs until 700K. This is in contrast to potassium desorption without coadsorbates, where desorption at much lower temperatures occurs. Curiously, for larger potassium coverages, all the additional desorption intensity grows in sharply into this narrow desorption state near 700K. Near saturation of the first layer of potassium, much less CO can be adsorbed so desorption maxima at both 500K (i.e. clean surface behavior) and 700K (i.e. coadsorbed CO behavior) are observed in the potassium TPD spectrum. Similar behavior has been seen with coadsorbed oxygen, both on Rh(111) [18] and Pt(111) [27]. These results suggest a strong interaction at higher coverage between potassium and certain coadsorbates.

The effect of potassium on the adsorption of CO has also been studied by vibrational spectroscopy, as shown in Fig. 4. These spectra are for saturation CO exposure of a predosed potassium overlayer at 300K. One of the most striking features seen with even very small potassium coverages is the increased intensity in the bridge site CO stretching frequency. This trend continues with increasing coverage such that the bridge site intensity dominates and very little of the atop species is populated at

large potassium coverages (c.f. $\theta_K = 0.25$). In addition, the frequency of the CO stretching vibrations decrease as the potassium coverage increases. This shift is fairly uniform with potassium coverage, although at very small coverages only relative populations change. The frequency shift is more pronounced for the bridged species, decreasing by 145 cm^{-1} compared to 65 cm^{-1} for the atop site. The metal-carbon vibration also decreases in frequency with increasing potassium coverage, although only by 17 cm^{-1} up to $\theta_K = 0.25$. Furthermore, the intensity of all the CO vibrations decrease with increasing potassium coverage, as indicated by the relative scaling factors. This intensity decrease is more pronounced for the metal-carbon vibrations. From Fig. 2 we note that the intensity and frequency of the bridge bonded metal-carbon stretch are significantly less than that of the atop site, hence both changes seen with potassium coadsorption (i.e. decreased intensity and frequency of the observed ν_{M-C} mode) are consistent with increased population of a bridge bonded species.

One also sees in Fig. 4 that the CO stretching vibrations broaden significantly with increasing potassium coverage. This is seen more clearly in Fig. 5 where the M-C and C-O stretching vibrations are shown on an expanded scale. Note that even for very small potassium coverages there is considerable broadening, especially on the low frequency side of the peaks. As the potassium coverage increases, this trend continues, and as the average frequency of the peaks decrease, the broadening is seen to be extended to the high frequency side of the peak maxima as well. This broadening can be attributed to either population of additional sites, such as 3-fold hollow sites, or to the inhomogeneity in the bond strength of the CO molecules due to their proximity to

the potassium adatoms.

Figure 6 shows the vibrational spectra for CO with a small fixed potassium concentration as a function of CO exposure. Initial CO adsorption on a $\theta_K = 0.02$ potassium layer has a stretching frequency that is quite low, 1530 cm^{-1} , but the vibrational mode is broad and asymmetric. At slightly higher CO exposure (0.7L), modes near 1600 cm^{-1} populate in addition to those at 1530 cm^{-1} . The CO stretching region becomes quite broad even at this low coverage. With further CO exposure these modes remain populated as additional modes at higher frequency begin growing in. At this point (2.0L), similar behavior begins for the atop site (i.e. more than one vibrational mode becomes visible near 2000 cm^{-1}). However, as more CO is adsorbed, the intensities of the initially filled low frequency modes seem to decrease as the average peak frequencies begin to increase. This trend continues with further exposure as the atop site predominately fills. These spectra indicate that the first CO molecules on the surface feel a much greater perturbation due to potassium adatoms, with a large inhomogeneity in the CO bond strength. As the CO coverage increases, this inhomogeneity increases, indicating that the proximity of the CO molecules to the K adatoms strongly affects its bond strength. As additional CO adsorb, these low frequency modes decrease in intensity while further increases in the average CO frequency occur, indicating the effect per CO is decreasing. Interestingly, a metal-carbon mode does not become visible until the atop sites begin to be significantly populated. The dynamic dipole moment of the metal-carbon stretch perpendicular to the surface is expected

to decrease as the bond strength increases for a bridge or multiply coordinated CO molecule. This may explain why the metal-carbon vibration for the strongly perturbed CO molecules is difficult to observe.

A region of the vibrational spectrum for a coverage series similar to Fig. 6 is shown in Fig. 7. Here the C-O stretching frequency region is shown on an expanded scale as a function of CO coverage at a predosed potassium coverage of $\theta_K = 0.03$. At low exposure, the stretching vibration is quite broad, extending from 1500-1700 cm^{-1} . An increase of $\sim 100 \text{ cm}^{-1}$ in the peak width occurs with further exposure (0.7L), increasing the asymmetry as modes near 1655 cm^{-1} begin to populate. The relative intensity of the most strongly perturbed CO molecules begins to decrease with increasing exposure, as shown at 1.7 and 20L. The peak maxima also shift considerable. Similar trends, though less dramatic, occur for the atop site vibrations. These spectra, like those in Fig. 6, suggest both local and nonlocal interactions. The local interactions dominate at small CO exposures, as evidenced by the asymmetric band filling sequence and the strongly perturbed vibrational frequencies observed. Nonlocal interactions are apparent at large CO exposures, indicated by large continuous shifts in the peak frequency and dramatic reduction in the intensity of the most strongly perturbed CO molecules.

At a larger potassium coverage ($\theta_K = 0.10$), the local effects are not nearly so dramatic, as shown in Fig. 8. The major change observed as the CO coverage increases is a continuous increase in the CO stretching frequency, shifting from 1500 to 1790 cm^{-1} . As this shift occurs, little broadening occurs, suggesting that the inhomogeneity in the CO frequencies

is much less. Similar to that seen in Fig. 6, a metal-carbon vibration does not become distinguishable until an atop site stretching vibration is observed.

4. Discussion

Preadsorbed potassium dramatically affects the chemisorption behavior of CO on Rh(111), as evidenced by the changes seen in the TPD and HREEL spectra. The most significant results are summarized as follows:

- (i) The CO desorption spectrum broadens up to 100K higher temperature as a function of potassium coverage, for $\theta_K < 0.10$.
- (ii) For $0.10 < \theta_K < 0.36$, two new desorption maxima at 630 and 700K are observed and are due to recombination of carbon and oxygen produced by dissociation of adsorbed CO.
- (iii) The presence of CO alters the desorption behavior of potassium for $\theta_K > 0.10$, increasing the potassium binding energy as much as 12 kcal/mole.
- (iv) As the potassium coverage increases from zero to 0.25 of a monolayer, the CO stretching modes at saturation coverage decrease by 145 cm^{-1} for the bridge site and 65 cm^{-1} for the atop site. Concurrently, the broad single M-CO vibration decreases by 17 cm^{-1} .
- (v) The relative occupancy of the two adsorption sites changes considerably with increasing potassium coverage, favoring the bridge site over the atop site.
- (vi) The width of the stretching vibrations increase as the potassium coverage increases.

(vii) The CO stretching vibration observed at submonolayer CO coverages in the presence of low concentrations of potassium ($0.02 \leq \theta_K \leq 0.10$) is 335 cm^{-1} less than the lowest vibration observed for CO adsorption on clean Rh(111). Dramatic broadening and asymmetry is also observed at these low CO and potassium coverages.

The bonding of carbon monoxide to transition metal surfaces is believed to be synergistic with electron donation from the 5σ -orbital of CO to partially empty metal orbitals, and simultaneous backdonation of charge from metal orbitals into the empty $2\pi^*$ -orbitals of CO. The σ bonding strengthens both the metal-carbon and carbon-oxygen bonds, while the backdonation strengthens the M-CO interaction but weakens the C-O bonding. On surfaces, the metal-carbonyl vibrational frequencies and bond energies depend on the crystallographic orientation of the metal (i.e. the site symmetry), the metal work function (a measure of the surface basicity), and the CO coverage [28]. Enhanced backdonation decreases the CO stretching frequency, increases the M-CO stretching frequency, and strengthens the metal-carbon adsorption energy. Additionally, backdonation requires suitably oriented d-orbitals on the metal; recent studies indicate that bridge sites have better π -orbital overlap with CO, allowing greater backdonation [29-31]. Specifically, work function measurements for CO on Pt(111) show an abrupt change from decreasing to increasing work function with initial population of bridge sites in addition to atop sites [29], while calculations suggest $d_M - 2\pi^*_{CO}$ overlap is greater for bridge sites [30,31].

The large changes in the desorption behavior, the vibrational frequencies, and the site occupancy of adsorbed CO in the presence of

potassium can all be attributed to enhanced backdonation of electrons from the metal into the $2\pi^*$ -orbital of CO. Potassium is expected to lower the work function of the rhodium surface. This allows greater electron spillover into the the backbonding orbital [28], of which bridge sites permit more extensive $d_M - 2\pi^*_{CO}$ orbital overlap [29-31]. Enhanced electron density into this conjugate orbital increases the metal-carbonyl bond strength, increasing both the CO heat of desorption and the ν_{M-CO} vibrational frequency. Enhanced occupancy of this orbital also weakens the C-O bond, leading to a decrease in the ν_{CO} frequencies. Whether this enhanced backdonation is due solely to electrostatic effects [30,32], or involve primarily other contributions [31] is not directly measured here; the results only indicate the strength of the bonds involved. Recent metastable quenching experiments [33] also indicate enhanced occupation of the $2\pi^*$ -orbital of CO in the presence of potassium.

An important aspect of the effects seen with additives such as potassium or sulfur is the spatial extent of the interaction. The results presented here provide evidence for both short- and long-range electronic effects. The results presented in Figures 6 and 7 strongly suggest that local or even direct interactions occur for initially adsorbed CO. The asymmetry and broadening also seen at relatively small CO and potassium coverages indicate further that the proximity of the CO molecules to the potassium adatoms is important: the closer the species, the more pronounced is the perturbation. Once a significant amount of CO has been adsorbed at these low potassium coverages, additionally adsorbed CO molecules can no longer occupy sites closer than a few interatomic spacings, yet their frequency is strongly altered. Furthermore, the intensity of initially

occupied sites decrease with increasing CO coverage. Both these results can be explained by suggesting that potassium can affect more than its nearest and next-nearest neighbors. Furthermore, it is difficult to explain the gradual frequency shift observed with increasing CO coverage seen in Figures 6-8 without invoking long-range interactions. Note that some broadening occurs with increasing CO coverage, but much less than expected if the additional CO molecules did not strongly influence the already adsorbed CO vibrational frequencies. The HREELS data discussed here and the gradual broadening seen as a function of CO coverage in TPD [19] strongly indicate that nonlocal electronic changes occur, and that as additional CO molecules are adsorbed, the effect of potassium per CO decreases. These conclusions are based on both the TPD and HREELS data. Changes in the electron scattering cross-section or in the shape of the CO molecular potential well with CO coverage or in the presence of potassium are not well understood, but could possibly account for the vibrational data. However, these changes would not additionally account for the dramatic changes seen in the TPD spectra.

The effects seen here for CO and potassium on Rh(111) are not as large in magnitude of frequency shifts and heat of adsorption changes as seen on Pt(111), although the trends are quite similar [2]. However, unlike that seen for Pt(111), CO does dissociate on potassium promoted Rh(111). The role these additives play in promoting CO hydrogenation reactions is clearly complicated. Potassium certainly enhances CO dissociation in some cases, leading to reduced methanation and higher molecular weight products [5]. But CO insertion reactions are also more facile in the presence of alkalis in homogeneous catalysis [34], and may also be an important mechanism in heterogeneous Fischer-Tropsch

reactions, as alkalis also enhance the formation of olefins and oxygenated molecules [35, 36]. For either mechanism, a change in relative concentrations of CO and H on the surface will alter product distribution.

5. Conclusions

Potassium preadsorption on Rh(111) has been shown to significantly alter the chemisorptive properties of CO. The heat of desorption increases while the C-O stretching frequencies decrease in the presence of preadsorbed potassium. Additionally, a dramatic shift in intensity from the atop to the bridge site occurs with increasing potassium coverage. The site-filling sequence observed as a function of CO exposure is also altered even for very low levels of coadsorbed potassium. The changes observed suggest enhanced occupation of the $2\pi^*$ -orbital of CO in the presence of potassium, leading to a weakening in the C-O bonding with simultaneous strengthening of the M-C bonding. Occupation of higher coordination sites leads to better $d_M-2\pi^*CO$ orbital overlap, and is common for low work function surfaces. Local interactions seem to be evident at low CO coverages, but the entire CO layer is affected at even small potassium coverages, suggesting long-range electronic effects. If the potassium coverage is large enough, CO dissociation can occur, most likely during the desorption process [19].

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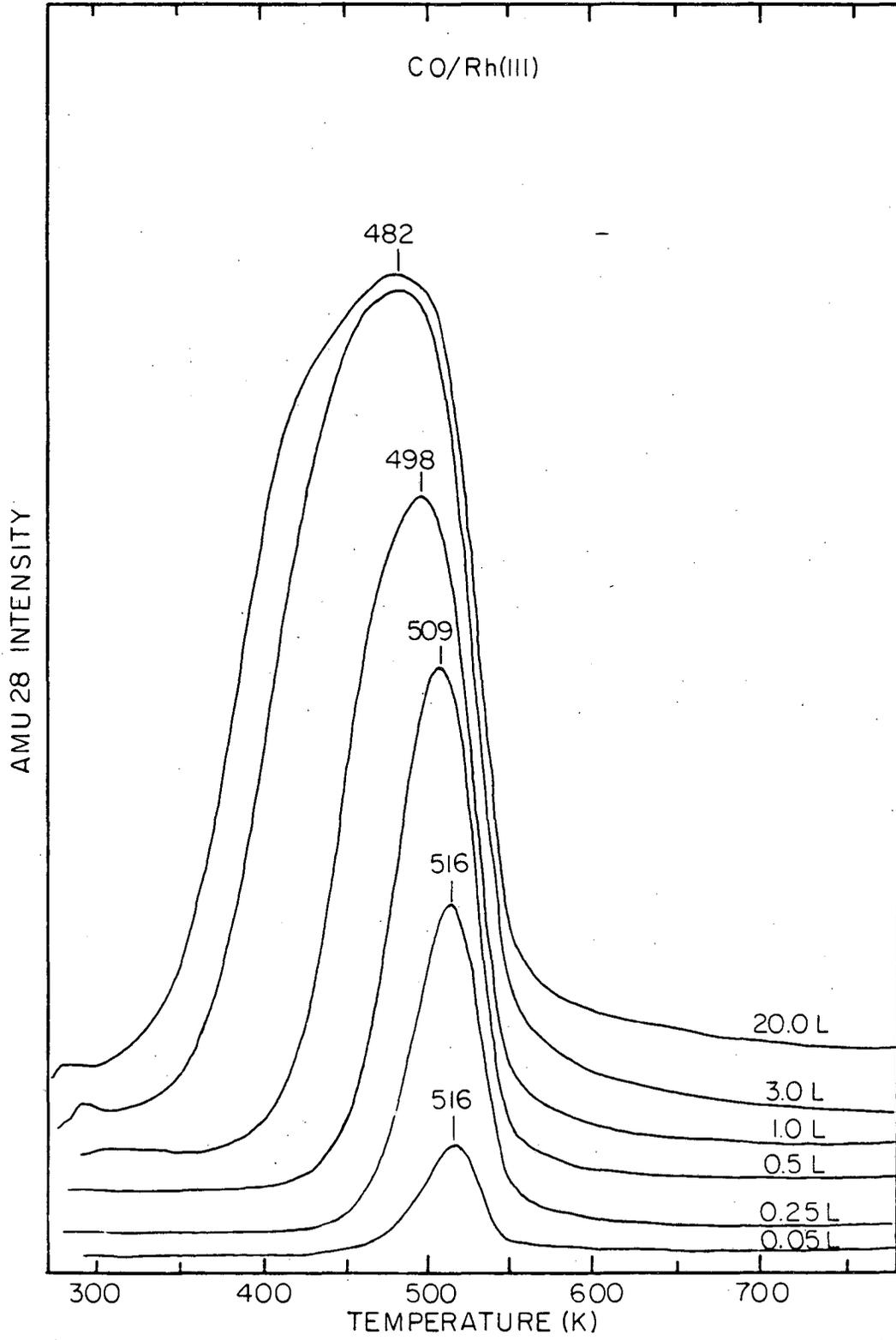
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FIGURE CAPTIONS

- Fig. 1. TPD spectra of CO on Rh(111) following adsorption near 300K measured as a function of CO exposure. The heating rate used was linear at 15K/sec.
- Fig. 2. Vibrational spectra obtained using HREELS for CO chemisorbed on Rh(111) at 300K, recorded as a function of CO exposure.
- Fig. 3. TPD spectra of CO following saturation adsorption at 300K on a Rh(111) surface predosed with the potassium coverage specified. The heating rate used was linear at 15K/sec. A coverage of $\theta_K = 0.36$ potassium atom per surface rhodium atom corresponds to a surface density of 5.8×10^{14} atoms/cm².
- Fig. 4. HREEL spectra for saturation CO adsorption at 300K on a Rh(111) surface predosed with varying amounts of potassium.
- Fig. 5. Portions of the vibrational spectrum obtained on an expanded scale for saturation CO adsorption at 300K on a Rh(111) surface predosed with potassium. Three different potassium coverages are shown.
- Fig. 6. HREEL spectra of CO adsorbed on a potassium predosed Rh(111) surface obtained as a function of CO exposure at a constant potassium coverage.
- Fig. 7. Vibrational spectra of CO adsorbed at 300K on a Rh(111) surface predosed with potassium, as a function of CO exposure. The CO stretching vibrations are shown on an expanded scale.
- Fig. 8. HREEL spectra of varying exposures of CO on a Rh(111) surface predosed with potassium.



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Fig. 1

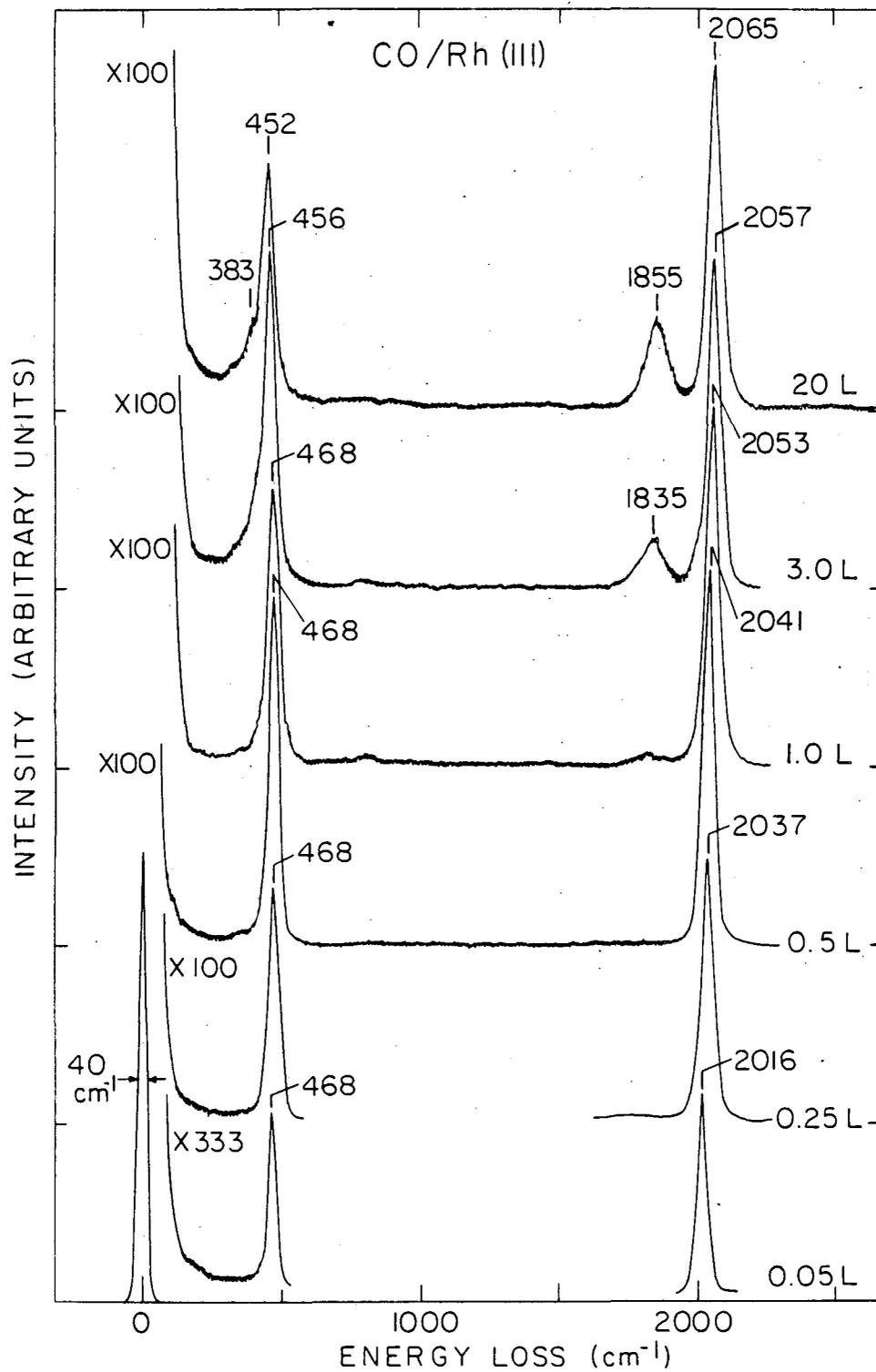
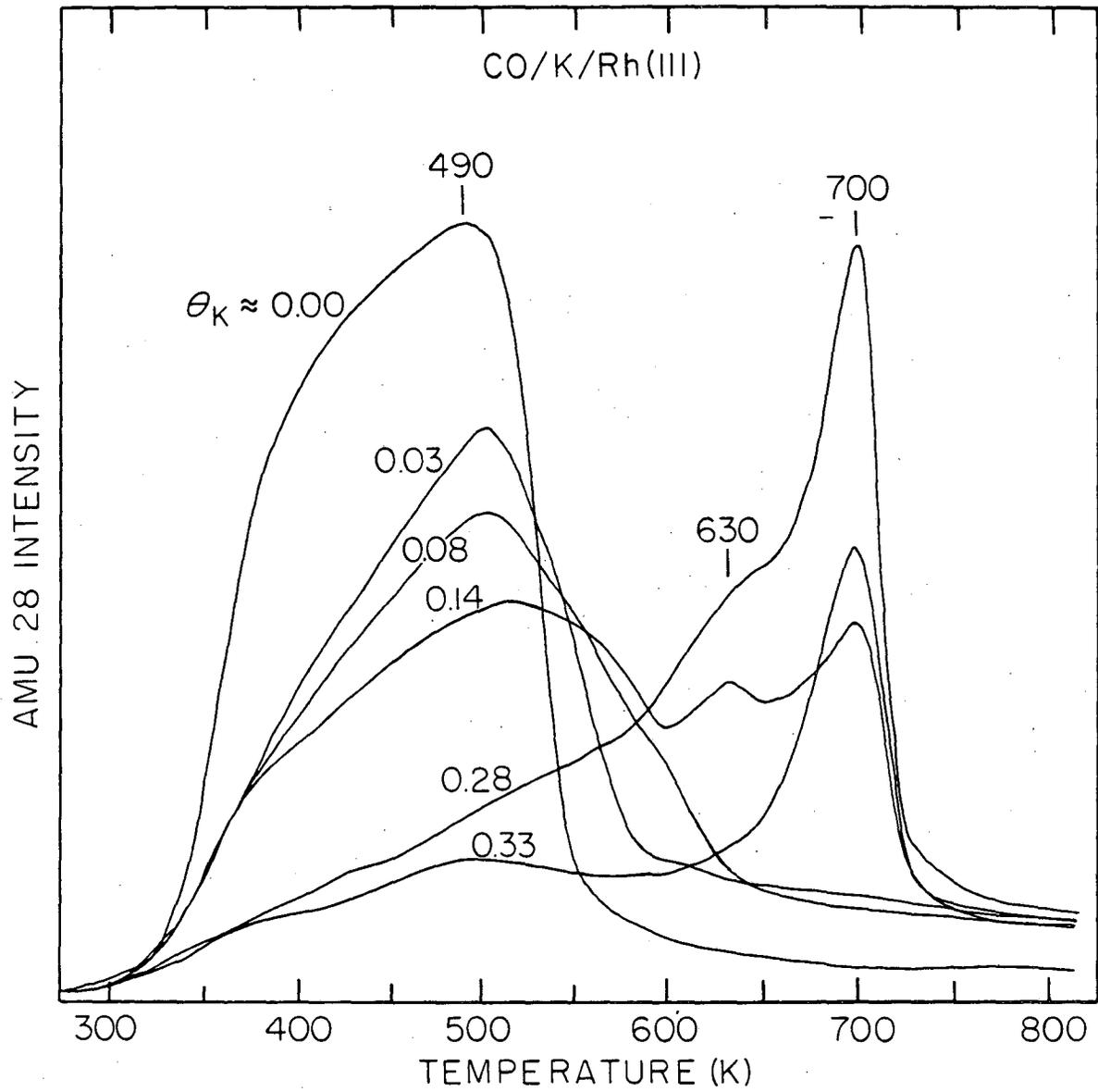


Fig. 2



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Fig. 3

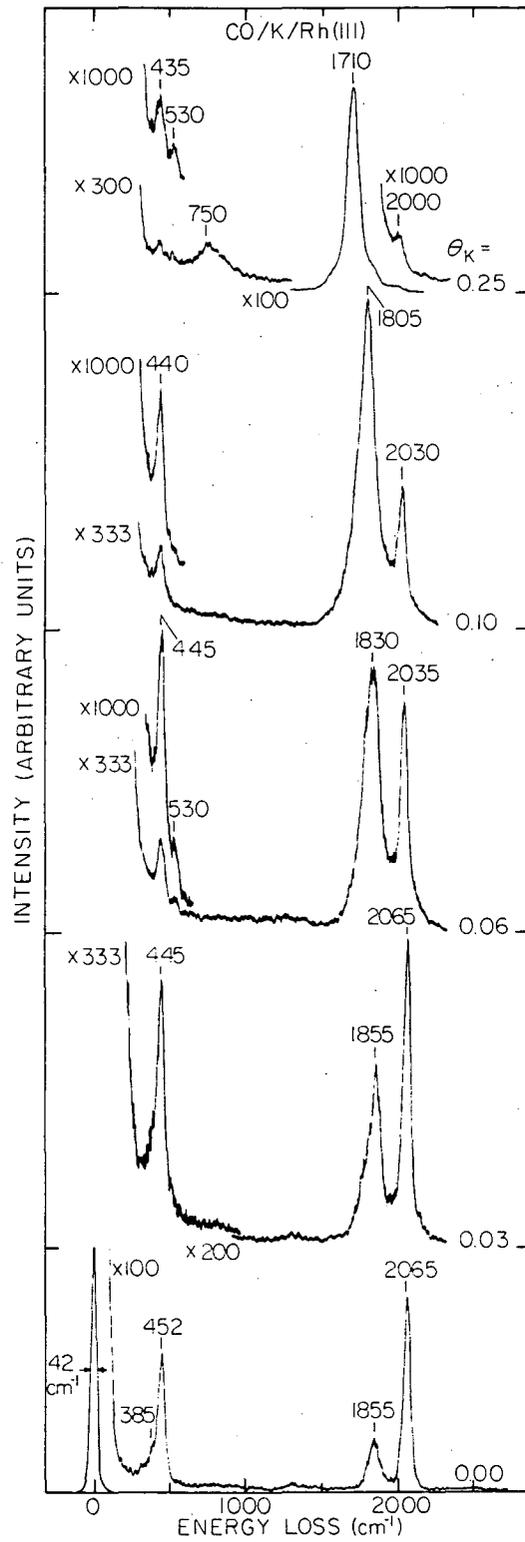


Fig. 4

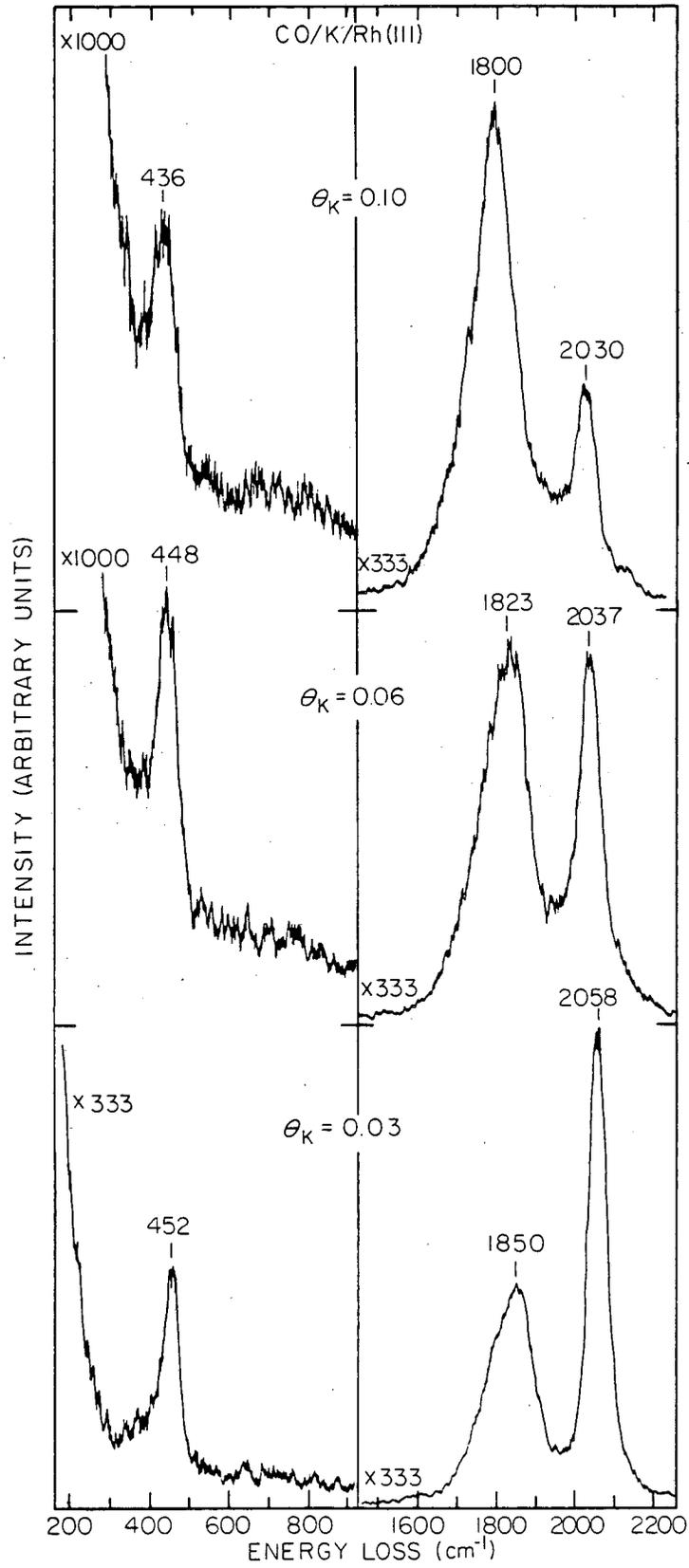


Fig. 5

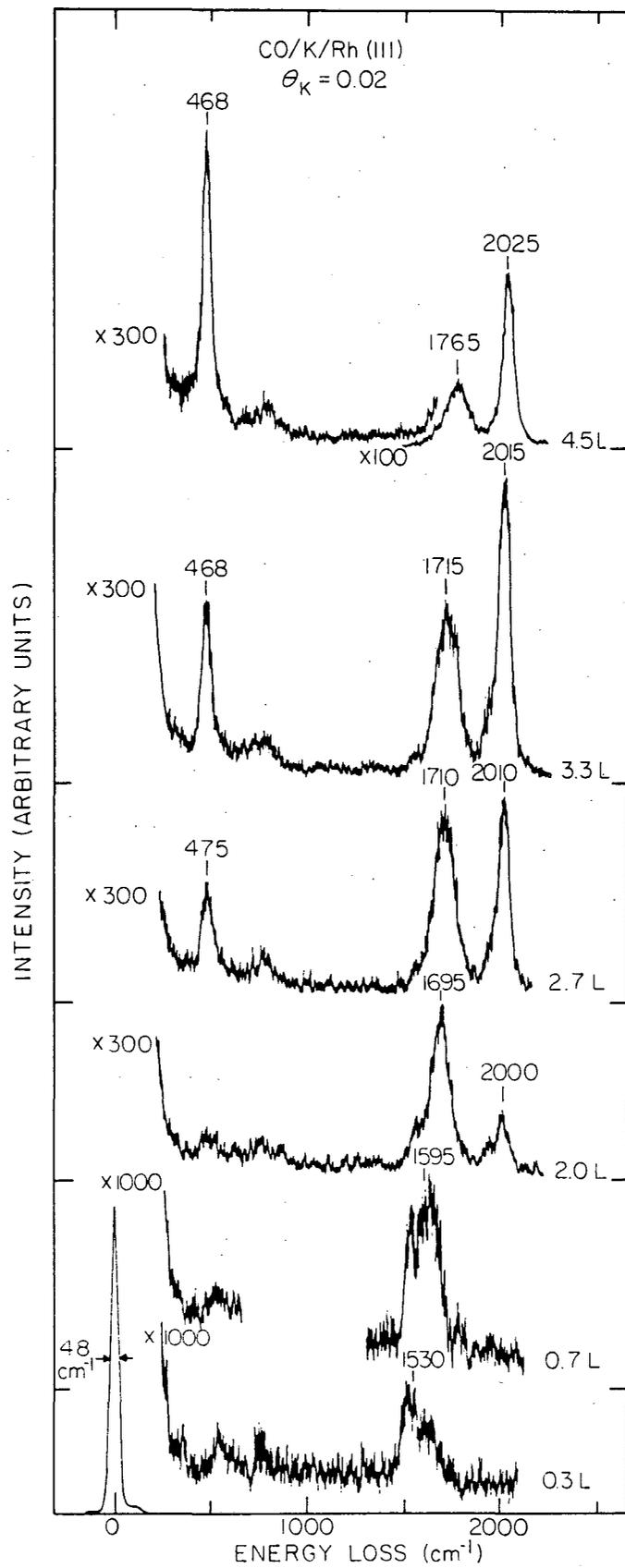


Fig. 6

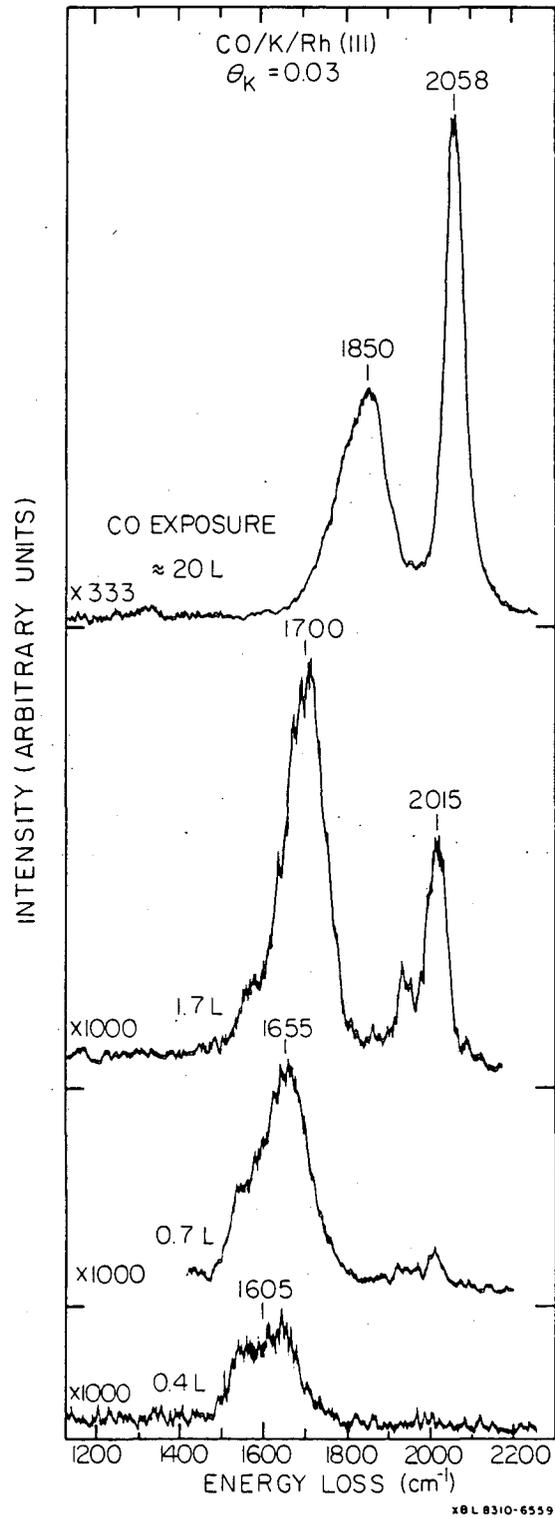


Fig. 7

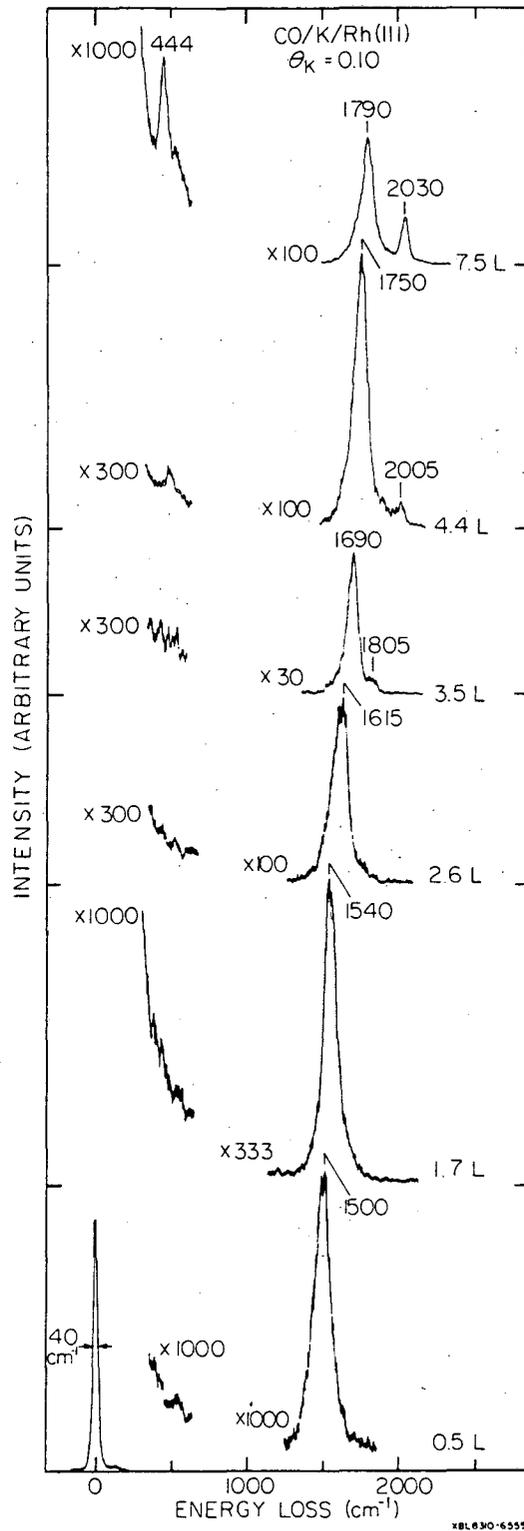


Fig. 8

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