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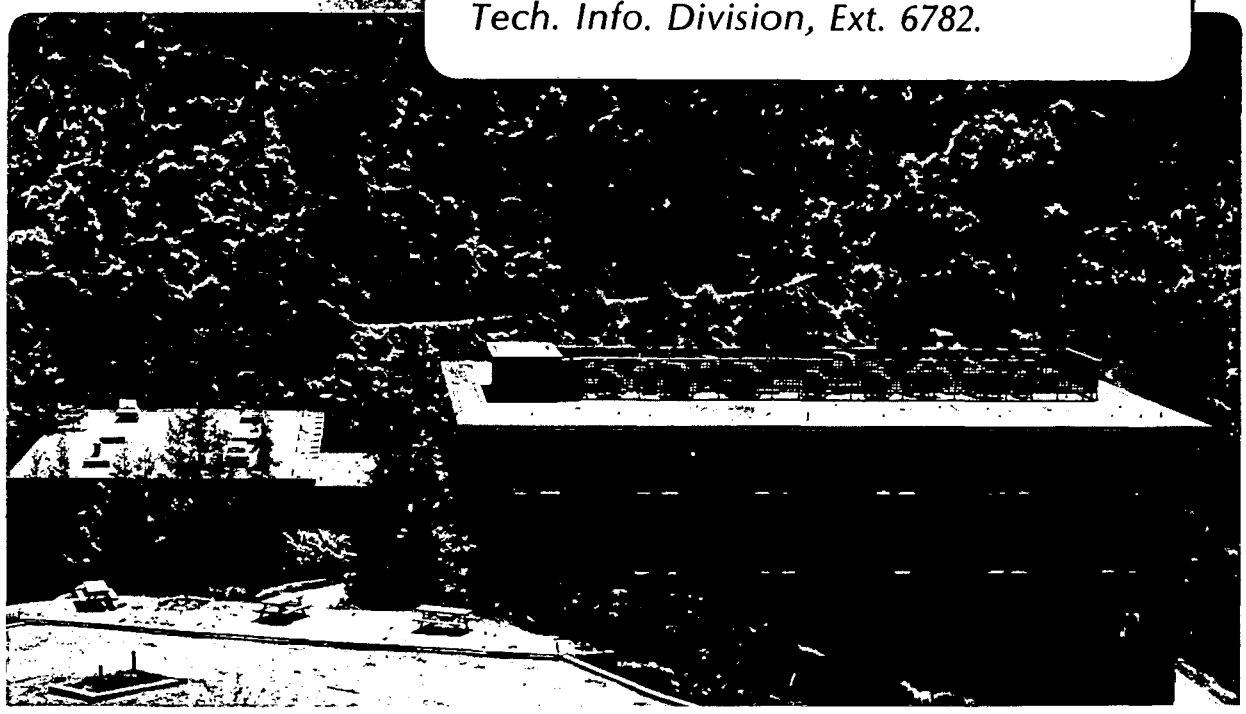

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THE COADSORPTION OF POTASSIUM AND CO ON THE Pt(111) CRYSTAL SURFACE:

A TDS, HREELS AND UPS STUDY

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ABSTRACT

The interaction of CO with a potassium covered Pt(111) surface is investigated using thermal desorption (TDS), high resolution electron energy loss (HREELS) and ultraviolet photoelectron (UPS) spectroscopies. When submonolayer amounts of potassium are preadsorbed, the adsorption energy of CO increases from 25 to 36 kcal/mole, while substantial shifts in the site occupancy from the linear to the bridged site are observed. The CO stretching vibrational frequencies are shown to decrease continuously with either increasing potassium coverage or decreasing CO coverage. A minimum CO stretching frequency of 1400 cm^{-1} is observed, indicative of a CO bond order of 1.5. The work function decreases by up to 4.5 eV at submonolayer potassium coverages, but then increases by 1.5 eV upon CO co-adsorption. The results indicate that the large adsorption energy, vibrational frequency and work function changes are due to molecular CO adsorption with a substantial charge donation from potassium through the platinum substrate and into the $2\pi^*_{CO}$ orbital.

1. INTRODUCTION

The interaction of alkali metal atoms with transition metal surfaces has received considerable attention in the past. Interest in these systems originated from the significant enhancement in electron emission upon alkali adsorption[1]. In addition to the now widespread use of surface alkali oxides to make low work function photocathodes, much research is presently focussed on alkali adlayer systems as thermionic converters[2].

An understanding of alkali induced phenomena on transition metal surfaces is also important due to their promoter action in heterogeneous catalysis[3,4]. In particular, potassium is used in two important catalytic reactions, the hydrogenation of carbon monoxide and the ammonia synthesis. In an attempt to understand the promoter effect, recent coadsorption experiments have shown that alkali metals change the chemisorptive characteristics of small reactive molecules (i.e. CO, H_2, N_2 and O_2) on catalyst surfaces. On iron and nickel surfaces, potassium appears to increase the heat of adsorption and the dissociation probability of CO, as well as decrease its sticking probability[5-7]. In addition, potassium increases the sticking probability of oxygen on platinum[8,9] and bismuth [10] and promotes oxide formation on iron[9], nickel[11] and bismuth[10] surfaces. Finally, both the heat of adsorption and the dissociation probability of N_2 increase on iron surfaces in the presence of potassium[12].

We have investigated the chemisorption of carbon monoxide on the platinum (111) surface in the presence of potassium. High resolution electron energy loss spectroscopy (HREELS) was used to determine the vibrational frequencies, thereby identifying the adsorption sites and relative site concentration of CO molecules when coadsorbed with potassium. Thermal desorption spectroscopy (TDS) provided information about changes in heats of adsorption of the coadsorbed system. Ultraviolet photoelectron spectroscopy (UPS) was utilized to determine

the work function change of the surface as a function of potassium and CO coverage.

It was found that submonolayer amounts of potassium increased the CO adsorption energy to the Pt surface while significantly affecting the CO site selectivity. The CO vibrational frequency, as determined by HREELS, was observed to decrease with decreasing CO coverage and/or increasing potassium coverage. CO vibrational frequencies as low as 1400 cm^{-1} were observed. Finally, UPS results show a 1.5 eV increase in the work function upon adsorption of CO on a potassium covered platinum surface, implying a significant charge transfer into the CO. All of the results will be shown to be consistent with a model of enhanced back-donation of electrons from the platinum into the $2\pi^*$ antibonding orbital of CO[13].

2. EXPERIMENTAL

Experiments were performed in three separate ultrahigh vacuum systems with base pressures of $\approx 1 \times 10^{-10}$ torr.

All thermal desorption studies were performed in an ion pumped UHV chamber equipped with a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a 4-grid retarding field analyzer (RFA) for low energy electron diffraction (LEED), a quadrupole mass spectrometer (QMS) for thermal desorption spectroscopy (TDS), and an argon ion sputtering gun for sample cleaning.

All vibrational spectra were obtained in an ion pumped UHV chamber built in two levels. The upper level contained the standard surface analysis equipment: an RFA for LEED and AES (with a glancing incidence electron gun), a QMS for TDS measurements as well as residual gas analysis, and an argon ion sputtering gun. The lower level contained the high resolution electron energy loss

spectrometer (HREELS) as described elsewhere[14]. The angle of incidence was ~ 72°; electrons were collected in the specular direction at a primary beam energy of 3-10 eV. Tuning was facilitated through use of a newly designed HREELS power supply[15]. Typical resolution was 85 cm^{-1} FWHM with 1-3 x 10^4 counts/sec in the elastically scattered peak. The full scale inelastic loss intensity is typically 1-3 x 10^2 counts/sec, however due to variations in the elastic peak intensity the peak areas are not directly comparable; the spectra have not been normalized.

The UPS spectra were obtained in an ion pumped UHV chamber equipped with QMS, LEED, argon ion sputtering gun, UV and X-ray sources and a double-pass CMA for AES, UPS and XPS. UPS excitation utilized the He(I) (21.4 eV) level, and data was collected with a multichannel analyzer.

Three different platinum crystals (> 99.998% purity) were cut to (111) orientation, mounted and cleaned using standard procedures. All systems were equipped with a "Saes Getters" potassium source mounted 3-5 cm from the sample[8]. During potassium deposition the crystal was maintained at ground potential and the potassium source was < 5V above ground, thus minimizing the accelerating potential. Typical deposition rates were on the order of 0.2 monolayer/minute with the crystal held at room temperature. No noticeable potassium diffusion into the platinum was recorded.

3. RESULTS

3.1 Potassium Adsorption on Clean Pt(111)

In a recent paper we note that potassium forms a hexagonal close packed monolayer (whose coverage we define to be $\Theta_K \equiv 1$) at 5.5 x 10^{14} K atoms/cm^2 on the Pt(111) surface[8]. This corresponds to 36% of the atomic density of the platinum surface layer. The thermal desorption spectra of potassium on

Pt(111) are shown in figure 1a. Assuming first order desorption kinetics and a preexponential factor of 10^{13} sec^{-1}, the large shift in desorption temperature with increasing K coverage shown here corresponds to a shift in the heat of desorption from 60 kcal/mole at $\Theta_K<0.1$ to 20 kcal/mole at $\Theta_K=1$, (see Figure 1b). This is generally attributed to depolarization effects in the potassium overlayer at higher coverages. A more exact determination of the preexponential factor would result in small changes in the calculated value of ΔH_{ads}. However, the trend of decreasing ΔH_{ads} with increasing K coverage would remain.

HREELS spectra of the pure K overlayer revealed no loss features. A simple calculation shows that such features should occur below 200 cm^{-1}, where tailing of the elatic peak obscures the spectrum.

3.2 CO Adsorption on Clean Pt(111)

The adsorption of CO on Pt(111) has been extensively studied in the past[16-22]. Figures 2a and b show our TDS and HREELS spectra for several CO coverages on Pt(111). These spectra agree well with other studies[20-22]. The thermal desorption spectra show there is one desorption peak whose maximum shifts to lower temperature and broadens with increasing coverage. Assuming the recently derived preexponential factor of 10^{13} s^{-1}, for CO adsorption on the flat Pt(111) surface[17], the heat of adsorption decreases with coverage from its low coverage value of 32 kcal/mole to 27 kcal/mole at saturation. It is now generally agreed that CO bonds with the carbon end toward the surface. The vibrational spectra show that CO adsorbs molecularly on the platinum surface in both linear (2100 cm^{-1}) or bridge-bonded (1870 cm^{-1}) configurations. The corresponding Pt-C stretches occur at 475 cm^{-1} and 355 cm^{-1} respectively. Furthermore, the CO is only linearly bonded at low coverages, while with increasing coverage the bridged position becomes partially occupied. Finally, the vibra-

tional frequency of the linearly bonded species increases by 30-40 cm^{-1} as the CO coverage is increased.

3.3 CO Adsorption on Potassium-Dosed Pt(111)

Substantial changes in the TDS, HREELS, and UPS spectra occur when potassium is co-adsorbed with CO on Pt(111). No ordered LEED patterns were observed with the co-adsorbed system.

3.3.1 Thermal Desorption Studies

Thermal desorption spectra for various CO exposures on Pt(111) at a constant potassium coverage are shown in Figures 3a, b and c. In Figure 3a with Θ_K=0.1 we see that at low CO exposures (< 0.1L) the desorption peak is centered around 490K, shifted by about 50K from clean Pt(111). The peak shifts to lower temperature and broadens as the CO coverage is increased. After > 5L exposure, the full width at half maximum (FWHM) of the desorption peak increases to ≈ 120K, and the peak is asymmetric. This trend of shifting peak and increasing FWHM becomes more apparent as the potassium coverage is increased. At Θ_K=0.2 (Figure 3b) the low exposure (< 0.1L) peak maximum is centered around 520K while it broadens to a FWHM of ~ 160K at saturation CO coverage. By Θ_K=0.3 (Figure 3c) the peak maximum has shifted as far as 590K for CO exposures less than 0.1L, and the saturation coverage desorption curve has broadened out considerably with the FWHM expanding to 200K. In these figures, it is evident that the desorption peak broadens continuously with both increasing CO exposure and increasing potassium coverage (up to Θ_K=0.5). The mechanism giving rise to the broad desorption peak will be discussed below.

Figure 4a shows the thermal desorption spectra for saturation CO coverages on the Pt(111) surface at various potassium coverages. Here we see the pronounced effect that potassium has on the CO heat of desorption. At Θ_K=0.05, the CO desorption peak maximum has already shifted toward higher temperatures

from the 400K peak maximum for clean platinum. This shift toward higher temperature continues for Θ_K=0.2 combined with substantial peak broadening on the high temperature side. By Θ_K=0.3, the FWHM is 200K and the peak maximum has shifted to nearly 600K. Above Θ_K=0.5 the maximum CO coverage decreased markedly as determined by TDS peak area, but the CO desorption peak mamximum remained at 610K. No CO was found to adsorb on potassium multilayers. A small amount of residual CO desorption (≈5% of saturation) centered at 420K, which was shown to be due to crystal back, edge and/or support effects, has been subtracted out of all spectra. Again, assuming a preexponential factor of 10^{13} s^{-1}[17] and first-order desorption kinetics, an increase from 400K to 610K in desorption rate maximum corresponds to a heat of adsorption increase from 25 to 36 kcal/mole. Finally, no significant irreversible CO dissociation was evident as no carbon or oxygen was found to remain on the surface by AES after heating to 650K.

We have also plotted the CO coverage vs. potassium coverage for 10L CO exposure in Figure 4b. It is seen that for room temperature exposure, the maximum coverage of CO at first increases slightly, then decreases at high potassium coverages. This is the result of the competing effects of an increase in CO binding energy due to potassium coadsorption, as well as a blocking of sites by the potassium. At low K coverage the increase in CO binding energy allows for tighter CO packing, which offsets the decrease due to the blocking of exposed Pt surface sites, that dominates at high K coverages.

3.3.2 High Resolution Electron Energy Loss Spectroscopy Studies

The effect of potassium on the vibrational spectrum of CO is illustrated in Figures 5 and 6. Figure 5 shows the room temperature HREELS vibrational spectrum for saturation exposures (> 10L) of CO as a function of potassium coverage. Potassium coverages were achieved by depositing a monolayer or more of potassium,

then heating the surface to achieve the desired coverage by desorption. The indicated potassium coverages were monitored with both TDS and AES calibrations[8]. One should remember that one potassium monolayer, Θ_K=1, has about one-third the atomic density of a Pt(111) surface layer.

As seen in Figure 5, a small addition of K has a marked effect on the CO vibrational frequency. Both the linear and bridged peaks shift to lower frequency compared to the potassium-free Pt/CO system. Already by $\Theta_K \approx 0.1$, the bridged CO stretching frequency has decreased by 100 cm^{-1} while the linear vibration has decreased by 65 cm^{-1}. Also note the change in relative peak heights of the linearly bonded CO versus the bridge bonded CO. This trend increases as K begins to cover more than 5% (i.e. $\Theta_K \approx 0.15$) of the platinum substrate. At $\Theta_K \approx 0.3$ the linear site intensity is much smaller than that of the bridged site. The ratio of these peaks now is nearly the inverse of the potassium-free Pt(111) case. By $\Theta_K \approx 0.6$, only one distinct peak is visible at 1565 cm^{-1}, although a high frequency tailing does exists. As will be examined in Figure 6, the large shift in frequency and lack of a linear species is not surprising at this lower CO coverage; the CO saturation coverage at $\Theta_K \approx 0.6$ is about one-half that of the previous K coverages, (see Figure 4b).

Figures 6a and b show the changes in the vibrational spectrum as the CO coverage is varied at a constant potassium coverage. In these figures the reported temperatures indicate those at which the crystal was annealed for several seconds prior to recording the spectra; all spectra were obtained at 300K. This annealing process is used to vary the CO coverage: the higher the annealing temperature, the lower the CO coverage (although the actual coverage was not determined). Since the partial monolayer potassium coverages were obtained by annealing a monolayer of potassium to at least 700K (e.g. annealing to 700K produced $\Theta_K \approx 0.3$), no noticeable potassium desorption was detected using this

process to vary CO coverage.

In Figure 6a we show the vibrational spectra as CO coverage is varied Θ_K= 0.07. In the room temperature spectra, both peaks are shifted slightly from the clean CO saturation coverage values (see Figure 2b). Only small variations occur until 400K, where the linear stretching frequency is decreased substantially. By 410K, both the linear and bridged species have the same peak height. Note that on clean Pt(111) at this temperature only the higher frequency species is present (see Figure 3b), while here both species are present. As the coverage is decreased, the peak height of the linear species continues to decrease faster than that of the bridged site. However the position of the stretching vibration has decreased more substantially for the bridged site than for the linear site (115 cm^{-1} vs. 25 cm^{-1}).

At a potassium coverage of Θ_K=0.05, lower than that shown in figure 6a, similar trends occur with coverage as discussed above, however both peaks decrease in peak height at nearly the same rate, becoming of the same intensity only at a very low coverage very near total desorption (425K). The frequency shifts are similar to those shown in Figure 6b, with an average frequency shift ~ 20 cm^{-1} less than at Θ_K=0.07.

The trend of decreasing stretching frequency and higher occupation of the bridge site continues for Θ_K=0.10 (not shown). In this case however, the linear and bridged peak heights are nearly the same at saturation CO coverage (see Figure 5). The bridged site dominates at CO coverages less that saturation. The stretching vibration decreases to a low of 1715 cm^{-1} for the bridged position with no linear species present after annealing to 435K.

Figure 6b shows the HREELS spectra for Θ_K=0.3. At this potassium coverage we see that most of the CO adsorbs in bridge bonded sites, while only a small amount of adsorption occurs in the linear site only at high CO exposures.

Both stretching frequencies are strongly affected by the potassium. The bridged CO stretching frequency at 1725 cm^{-1}, already substantially shifted at saturation coverage, continues to shift to lower frequency as the CO coverage is decreased. Notice that this shift is continuous with increasing temperature, but now the desorption process occurs over a broad temperature range as was evident in the corresponding TDS curves in Figure 3c. No spectra were taken on samples heated above 525K where further decreases on CO vibrational frequency might occur. The weakest CO stretching frequency recorded occurs at 1400 cm^{-1}: to our knowledge this is the lowest CO stretching frequency observed for CO bound to a metal.

We note that the existence of bridge bonded CO with a vibrational frequency of 1400 cm^{-1}, calls into question the conventional assignment of 1300-1500 cm^{-1} vibrational peaks as being due to carbonates and formates. On real catalysts they may instead be the result of multiply bonded CO adsorption on promoted sites. Also the large 470 cm^{-1} decrease in the bridge bonded CO stretching frequency raises the question of the nature of the C-O bond. The 1400 cm^{-1} CO frequency we observe for the CO/K coadsorbed system on platinum is characteristic of a molecule with a bond order of 1.2-1.5[23], compared with a bond order of 2.4 for free CO. Thus, the CO bond appears greatly stretched without dissociation of the adsorbed CO species.

3.3.3 Ultraviolet Photoelectron Spectroscopy Studies

We show UPS spectra for clean platinum (111) in figure 7a, for the platinum surface after adsorbing a third of a monolayer of potassium (Figure 7b), and for the same potassium covered surface after adsorption of 10L of CO (Figure 7c) (i.e. saturation CO coverage at $\Theta_K \approx 0.33$). At the top of this figure is the difference spectrum indicating the changes with CO adsorption. Of note here are the large work function variations. As potassium is adsorbed to a

coverage of $\Theta_K \approx 0.33$, the secondary electron emission cutoff energy, hence work function, decreases by 4-4.5 eV. This feature is typical for alkali adsorption on transition metal sufaces[24-26]. The work function usually decreases rapidly upon the adsorption of alkali metals, reaching a minimum value between 0.5 and 0.8 of a monolayer, then slowly rising to the bulk alkali value by the second layer, in our case at potassium coverages > 5.5×10^{14} atoms/cm^2.

In addition to the large increase and shift in the secondary electron emission yield, an attenuation of the platinum d-band emission just below the Fermi level is observed. Also, the K(3p) level becomes visible for $\Theta_K > 0.2$ Upon CO adsorption, the expected 4σ, 1π and 5σ energy levels of CO appear, accompanied by a further decrease in d-band emission just below the Fermi level. Here, the most significant feature appearing is the 1.5 eV increase in the work function of the surface. No conclusive evidence was found concerning the position of the 2π bonding level formed from the conjugation of Pt with the $2\pi^*$ molecular CO level.

4. DISCUSSION

The preadsorption of potassium has marked effects on the adsorption of CO on Pt(111). The major experimental findings can be summarized as follows:

i) The addition of submonolayer amounts of potassium continuously increases the heat of adsorption of CO on Pt(111) from 25 kcal/mole for clean Pt(111) to 36 kcal/mole for near monolayer coverages.

ii) Associated with the increase in heat of adsorption is a 310 cm^{-1} decrease in the stretching frequency of the bridge bonded CO molecules from 1870 cm^{-1} on clean Pt(111) to 1560 cm^{-1} with 0.6 monolayers of K coadsorbed.

iii) The CO thermal desorption peak broadens continuously to a maximum of 200K (FWHM) at saturation CO coverages as the potassium coverage is increased.

iv) At a constant potassium coverage, the CO vibrational frequencies for both linear and bridge adsorption sites decrease substantially with decreasing CO coverage.

v) On the potassium-free Pt(111) surface, CO prefers to occupy top adsorption sites while on the potassium-covered surface CO adsorbs preferentially on bridged sites.

vi) The work function of the Pt(111) surface decreases by 4-4.5 eV upon the adsorption of one-third of a monolayer of potassium, but increases by 1.5 eV when CO is coadsorbed.

These results can be interpreted by examining the electron acceptor character of CO and the changes in charge density at the platinum surface as potassium is adsorbed.

The bonding of carbon monoxide to metal atoms involves a synergistic electron transfer from the highest occupied molecular orbitals of CO (5σ) to the metal, and in turn metal electrons are backdonated into the lowest unoccupied molecular orbital ($2\pi^*$) of CO[27-29]. The backdonation of metal electrons into the $2\pi^*_{CO}$ orbital leads to a simultaneous strengthening of the M-C bond and a weakening of the CO bond, as seen in Figure 8a, where the $d_{Pt} - 2\pi^*_{CO}$ orbitals are in phase (bonding) between Pt and C, while being out of phase (antibonding) between C and O.

In our experiment changes in backdonation to CO are induced by using an electron donor, potassium (Figure 8b). Charge is transferred from the potassium to the platinum, with electrostatic screening of the resultant positive charge on the potassium by metal electrons. This polarization is displayed by the 4-4.5eV drop in work function upon potassium adsorption. Then, upon CO coadsorption, an enhancement (relative to clean Pt) of backdonation into the CO occurs as a result of the potassium induced surface charge density changes.

Two analogous rationale have been used to understand backdonation in similar systems and can be applied here. The first proposes that by a potassium induced change in the platinum surface valence band occupancy and a shifting of the CO molecular levels, a greater occupancy of the conjugate $d_{Pt} - 2\pi^*_{CO}$ orbitals is permitted. This hypothesis has been used to explain the potassium induced changes in the N_2 interaction with Fe(100)[12].

The second explanation assumes that a conjugate $d_{Pt} - 2\pi^*_{CO}$ orbital becomes fully occupied upon adsorption, but that the surface dipole component of the work function determines the relative contributions from the metal and $2\pi^*_{CO}$ orbitals, i.e. the spatial distribution of charge within the conjugate orbital. In the potassium-free, high work function case, most of the electrons in the orbital would be localized on the platinum atoms. On the potassium covered, low work function surface, however, the electrons in the $d_{Pt} - 2\pi^*_{CO}$ orbital would become less localized on the Pt, shifting their charge density more onto the C and O atomic positions, giving the conjugate orbital more $2\pi^*_{CO}$ character. Both models would account for the observed results of an increased Pt-C binding energy and decreased C=O vibrational frequency.

Theoretical calculations, combined with more exact UPS studies will be required to determine which of these effects, or others, is dominant in determining the observed results. Recent calculations of CO adsorbed on nickel[30] and lithium[31] clusters have shown that the $2\pi^*_{CO}$ orbital can also conjugate with s and p metal orbitals of the proper symmetry, and that CO vibrational frequencies below 1500 cm^{-1} can be predicted.

The 11 kcal/mole increase in adsorption energy of CO upon potassium coadsorption supports the model of enhanced electron backdonation. In addition to strengthening the metal-carbon bond, backdonation should also weaken the carbon-oxygen bond as noted above, lowering its vibrational frequency. This

indeed occurs since the vibrational frequency of bridge bonded CO at saturation coverage decreases by 310 cm^{-1} as the potassium coverage is increased to 0.6 monolayers.

Another effect of the platinum mediated potassium-CO interaction is the continuous and large decrease in both top and bridged site vibrational frequencies as the CO coverage is decreased at constant potassium coverage (see Figures 6a and b). This vibrational frequency observation has its thermal desorption analog in the continuous broadening of the desorption peaks in the $\Theta_K \approx 0.3$ TDS spectra (Figure 3c). Both of these effects support the model of electron backdonation, if one considers the CO molecules at various coverages as competing for the excess charge provided by a fixed number of potassium atoms to the platinum substrate. When less CO molecules are chemisorbed, at a fixed potassium coverage, the larger amount of backdonation per CO molecule leads to an increased adsorption energy and decreased vibrational frequency.

The change in CO adsorption site from linear to bridged with increasing potassium coverage is a striking effect. Nieuwenhuys has recently shown that the degree of electron backdonation increases with the lowering of the work function of a metal surface[29]. Our results not only indicate an increased heat of adsorption and decreased vibrational frequency due to the decreased work function, but also a change in CO site location. By continuously lowering the work function of the Pt surface by the adsorption of potassium, we are changing the most energetically favorable site location from top to bridged.

It must be noted that we cannot rule out the existence of the three-fold site CO molecule when the stretching frequencies decrease to their low coverage values. However, no clear evidence for the occupation of this site exists.

For the CO-CO interaction on clean Pt(111), as well as on many other surfaces, dipole-dipole interactions have been postulated. As discussed by Cross-

ley and King[20], the 40 cm^{-1} decrease of CO stretching frequency as the CO coverage is decreased on clean Pt(111) is due to a lessening of dipole-dipole coupling interaction. The corresponding contribution cannot be readily determined for the K-CO coadsorbed system, but we believe increased backdonation is the dominant contribution accounting for the 325 cm^{-1} decrease in the bridge bonded vibrational frequency as the CO coverage is decreased at Θ_K=0.3.

Although the idea of charge interactions has been proposed for other systems (for instance to explain the promoting effect of potassium for the catalyzed hydrogenation of CO[3,5,6] and for the ammonia synthesis[4,8] over iron, and CO interaction with alkali covered Ni(100)[9]), this is the first study that allows one to monitor significant changes in the magnitude of the backbonding effect without other complicating surface reactions occurring.

The possibility of direct bonding (either covalent or ionic) between K and CO on platinum can be ruled out by our observations. Figures 6a and b show that for a fixed potassium coverage, the CO stretching frequency merely increases gradually with increasing CO coverage. If direct K-CO interactions dominated, one would expect different vibrational frequencies for the CO molecules depending on their proximity to potassium adatoms. Once all CO sites closest to potassium atoms were occupied, the subsequently adsorbed CO molecules would find only clean platinum adsorption sites. This would give rise to multiple CO stretching peaks with wide variations in frequency. Although we do see some peak broadening, it is not enough to indicate significant bonding interactions.

Likewise, if direct K-CO interactions occurred, at low potassium coverages, the CO thermal desorption spectra should show two peaks, one at 600K for the K-CO species and one at 400K representative of potassium-free adsorption on Pt(111). This does not occur; we see a continuous increase in the high temper-

ature TDS tail with increasing potassium coverage. Within the range studied, CO molecules on the surface are seeing approximately the same "altered" substrate, regardless of their proximity to the K atoms. Thus the K-CO interaction appears not to be direct or localized, but delocalized over at least two or three interatomic distances.

The delocalization of interaction appears not to occur for other similar systems which have recently been studied. Multiple sites have been shown to exist in thermal desorption and photoelectron spectroscopy studies of CO on alkali covered Ni(100)[7] and Fe(110)[6], N_2 on K covered Fe(111) and (100)[12], and NO on K covered Pt(111)[32]. However, in most of these cases dissociative adsorption occurs first, followed by molecular adsorption on other surface sites. While we find that the adsorption of CO on the potassiumcovered platinum increases the work function, CO was found to decrease the work function of the potassium covered Fe(110) surface[6]. We believe that this effect in the K-CO-Fe system is most likely due to the formation of potassium oxide islands after the dissociation of CO. The interpretation of electron backdonation into CO is much more complex in the presence of dissociative adsorption and surface chemical reactions which are absent for our Pt-K-CO system.

Although the Pt(111)/K system studied here is different from the multicomponent surfaces used on actual industrial catalysts, the catalytic implications of our results are significant, especially with respect to CO hydrogenation reactions. The increase in backdonation strengthens the M-C bond and weakens the C-O bond, thus increasing the probability of hydrogenation. Furthermore, the increased binding energy means that the surface residence time of adsorbed CO will increase. Both these consequences should lead to the formation of longer chain hydrocarbons, as has been shown in previous catalytic studies[3,34].

5. SUMMARY

The chemisorption properties of carbon monoxide are significantly altered when adsorbed in the presence of potassium on Pt(111). The adsorption energy is increased by 11 kcal/mole and the CO vibrational frequencies decrease markedly. No dissociative adsorption was observed in our low pressure studies. These effects are explained by a simultaneous charge transfer from the potassium adatoms to the platinum substrate and an increase in backdonation from the platinum into the coadsorbed CO molecules. For a fixed potassium coverage, the CO molecules appear to compete for the "excess" charge donated by potassium. Direct bonding between coadsorbed CO and K is insignificant, unlike on Fe and Ni surfaces. Finally, a change in the CO site occupancy from top to bridge position is shown to occur with increasing potassium adsorption.

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Figure Captions

Figure 1: (a) Potassium thermal desorption spectra from Pt(111). The coverages are calibrated from TDS peak areas and AES signal intensities. The heating rate was 30 K/s. (b) The heat of adsorption versus coverage calculated from the data of panel (a). We assume first order desorption kinetics and a preexponential factor of 10^{13} s^{-1} (see text).

Figure 2: (a) TDS, and (b) HREELS spectra of CO on potassium-free Pt(111) for various CO coverages (expressed as exposure in (a), and as desorption temperature in (b). The heating rate was 30 K/s for all TDS spectra.

Figure 3: Carbon monoxide TDS spectra for various CO exposures after deposition of potassium in coverages of (a) $\Theta_K \approx 0.1$, (b) $\Theta_K \approx 0.2$ and (c) $\Theta_K \approx 0.3$ (the potassium coverage remains constant in each spectrum).

Figure 4: (a) CO thermal desorption spectra with various potassium coverages, after saturation CO exposures (≈10L). (b) Total CO coverage versus potassium coverage for room temperature CO exposures of 10L as determined from the average K and CO TDS peak areas and K AES signal intensities for several runs.

Figure 5: HREELS spectra for saturation CO exposures with various potassium coverages.

Figure 6: HREELS spectra for various CO coverages (expressed by the desorption temperature, see text) with constant potassium coverages of (a) $\Theta_K \approx 0.07$ and (b) $\Theta_K \approx 0.3$.

Figure 7: UPS spectra for (a) the potassium free Pt(111) surface, (b) the Pt(111) surface with $\Theta_K \approx 0.33$, and (c) the $\Theta_K \approx 0.33$ surface after exposure to 10L CO. In the upper right hand corner of the figure is plotted the (c)-(b) difference spectrum.

Figure 8: (a) A model of the electrom orbitals believed to interact most strongly in the bonding of CO to platinum. (b) A schematic diagram of electron transfer in the Pt(111)/K/CO system.

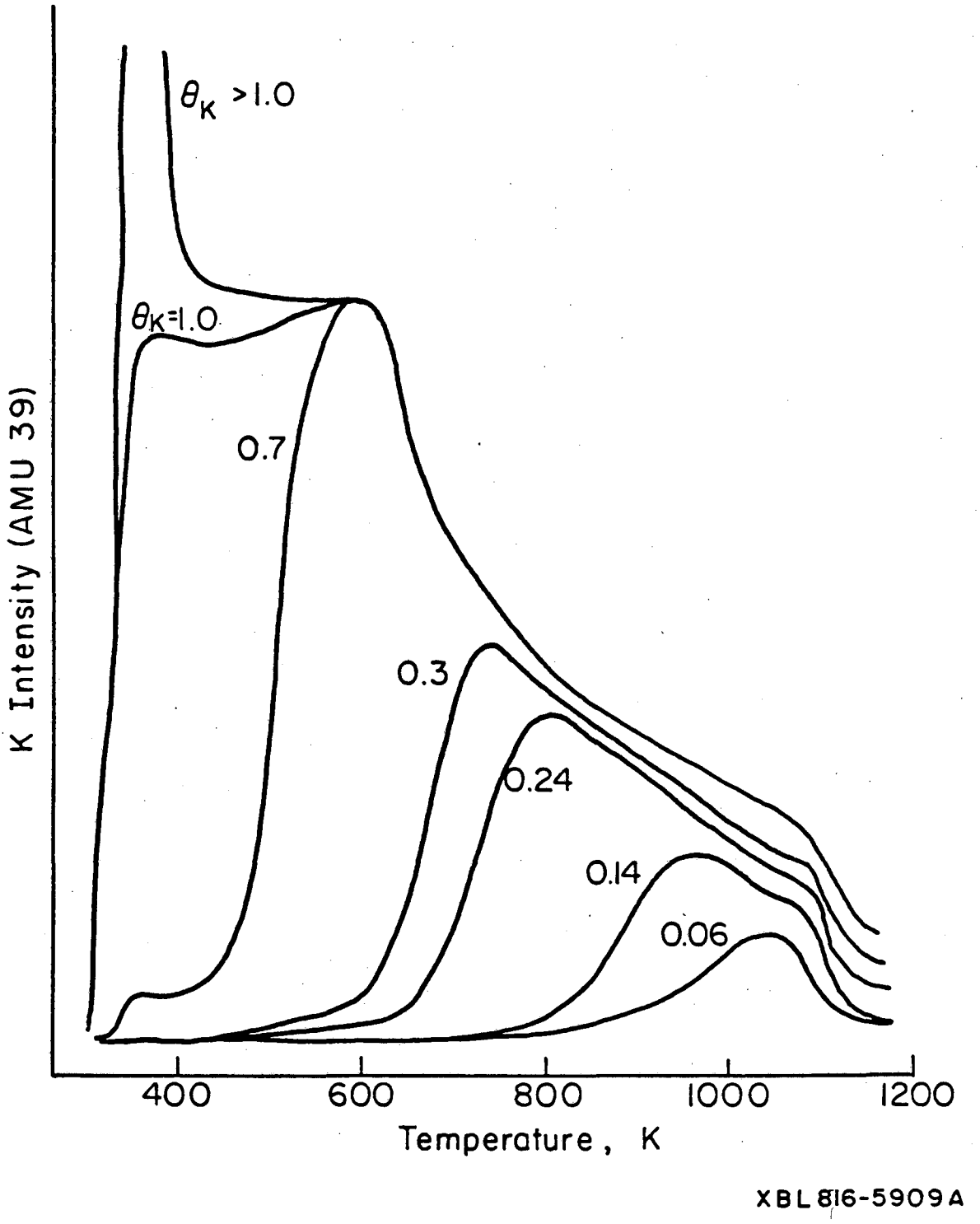

θK >1.0
θK=1.0
0.7
0.3
0.24
0.14
0.06
K Intensity (AMU 39)
400
600
800
1000
1200
Temperature, K
XBL 816-5909A

Fig. 1a

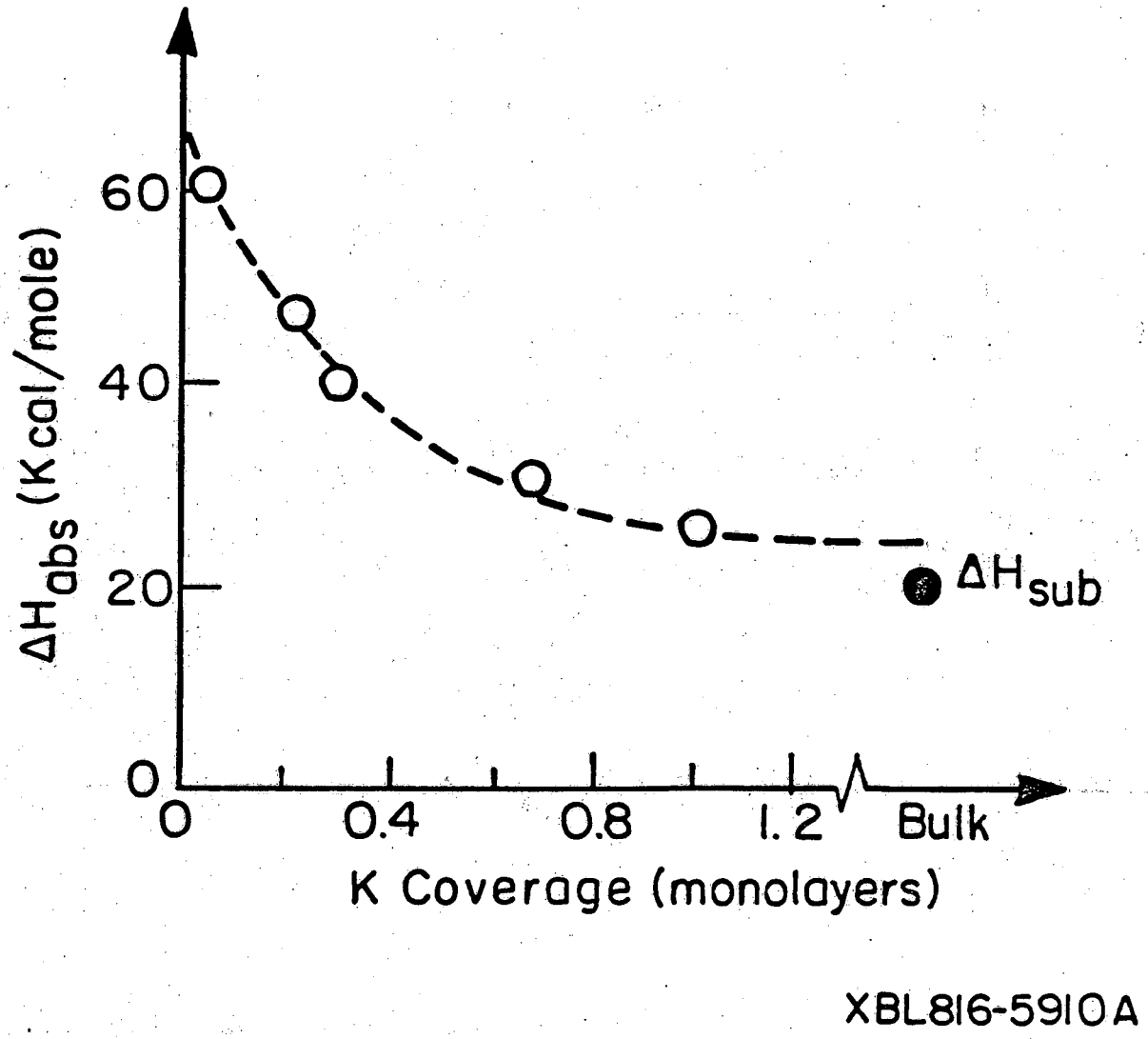

60
40
20
0
ΔH_{abs} (Kcal/mole)
ΔH_{sub}
0
0.4
0.8
1.2
Bulk
K Coverage (monolayers)
XBL816-5910A

Fig. 1b

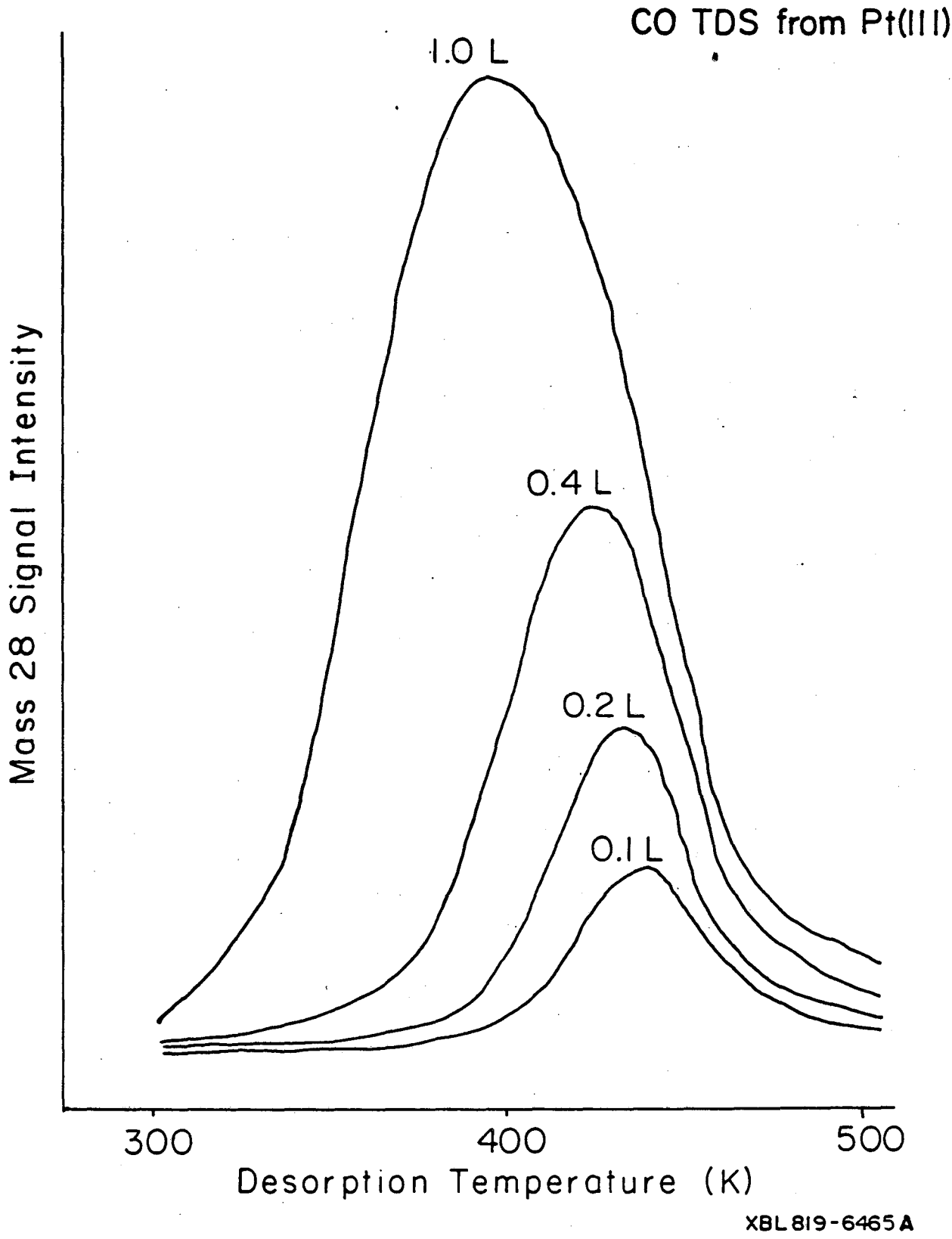

CO TDS from Pt(111)
1.0 L
0.4 L
0.2 L
0.1 L
Mass 28 Signal Intensity
300
400
500
Desorption Temperature (K)
XBL 819-6465 A

Fig. 2a

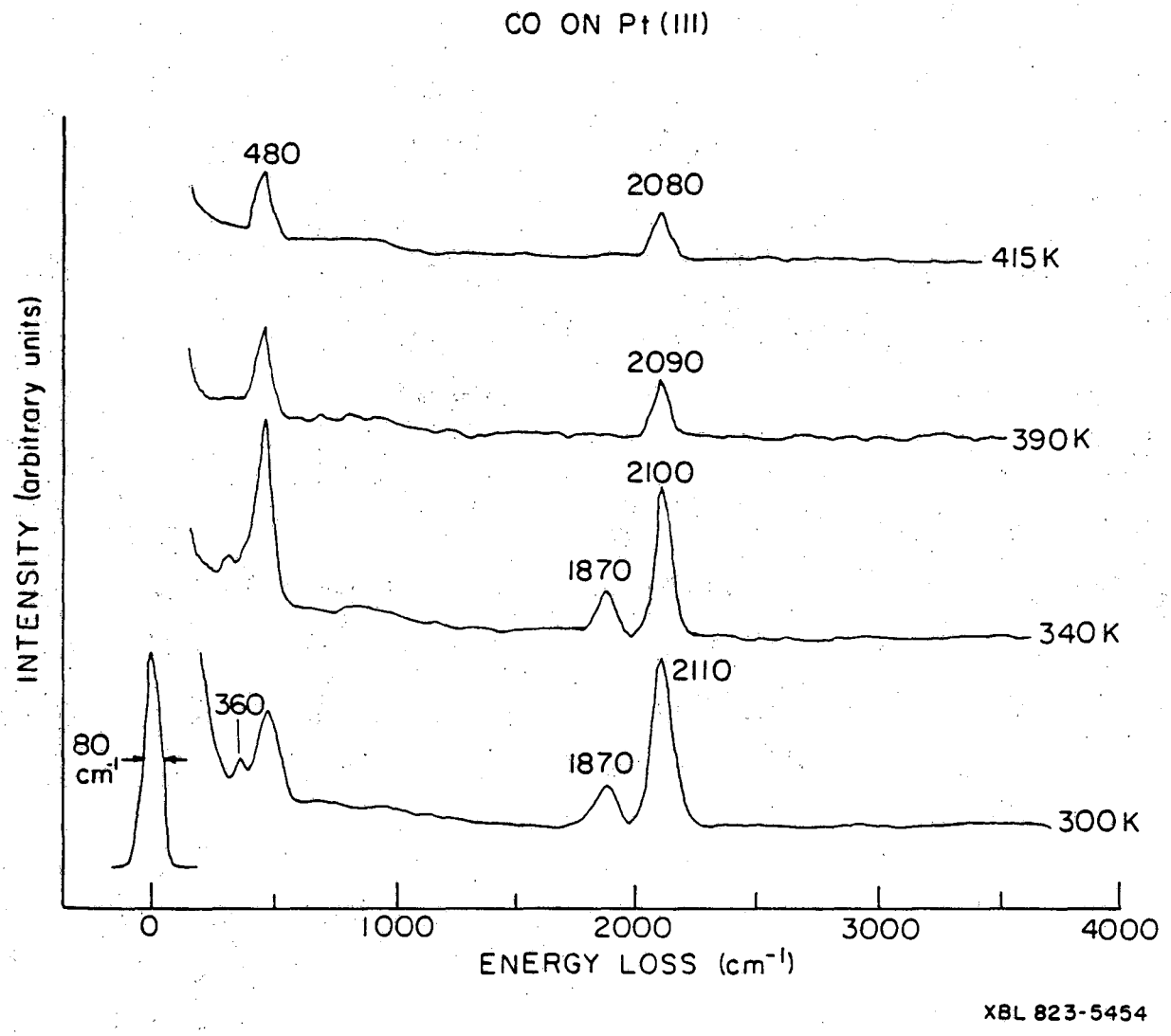
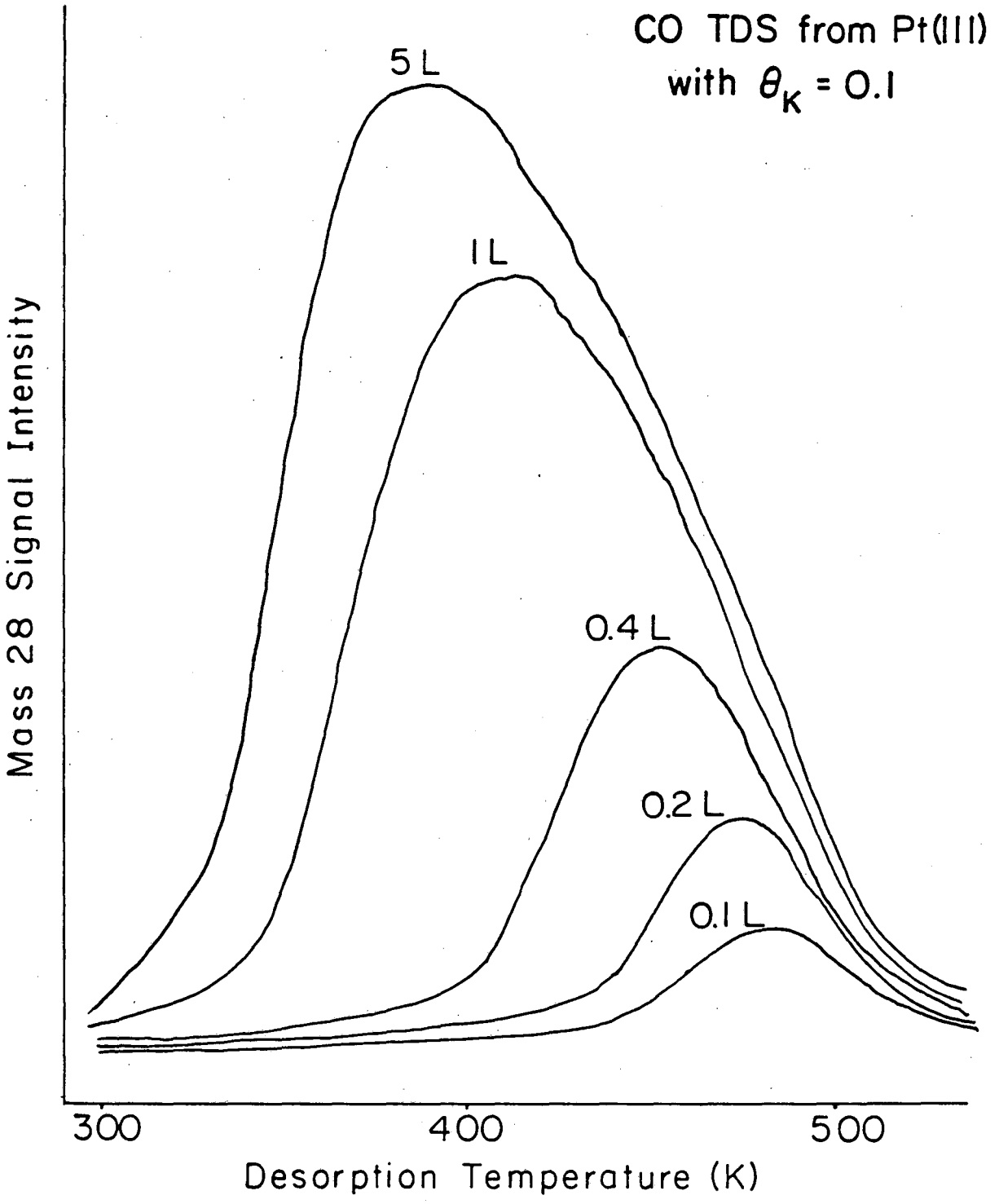

CO ON Pt (111)
480
2080
415 K
2090
390 K
2100
1870
340 K
2110
360
80 cm⁻¹
1870
300 K
INTENSITY (arbitrary units)
0
1000
2000
3000
4000
ENERGY LOSS (cm⁻¹)
XBL 823-5454

Fig. 2b



XBL 819-6464A

Fig. 3a

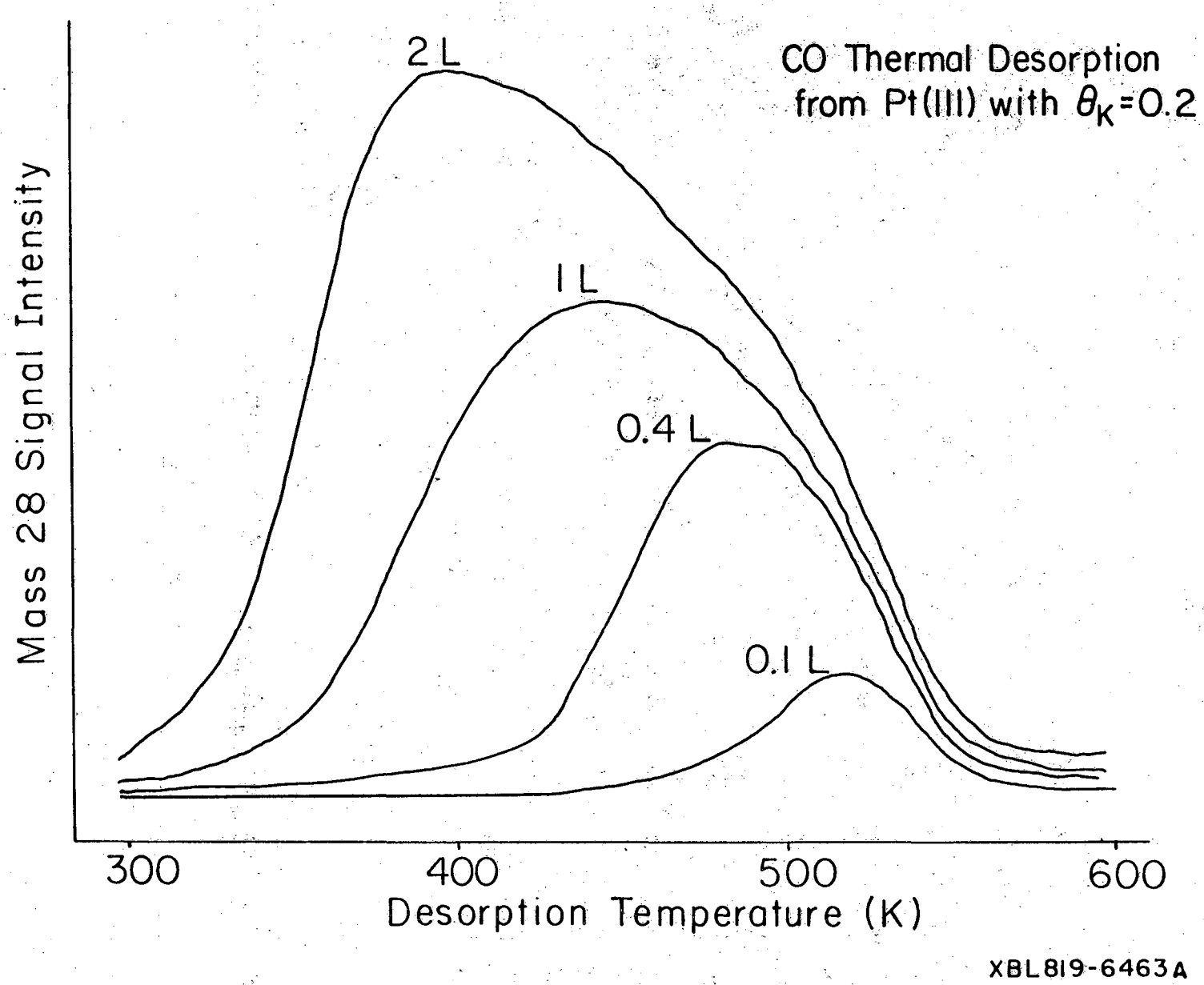

CO Thermal Desorption
from Pt(111) with θ_K=0.2
2 L
1 L
0.4 L
0.1 L
Mass 28 Signal Intensity
300
400
500
600
Desorption Temperature (K)
XBL819-6463A

Fig. 3b

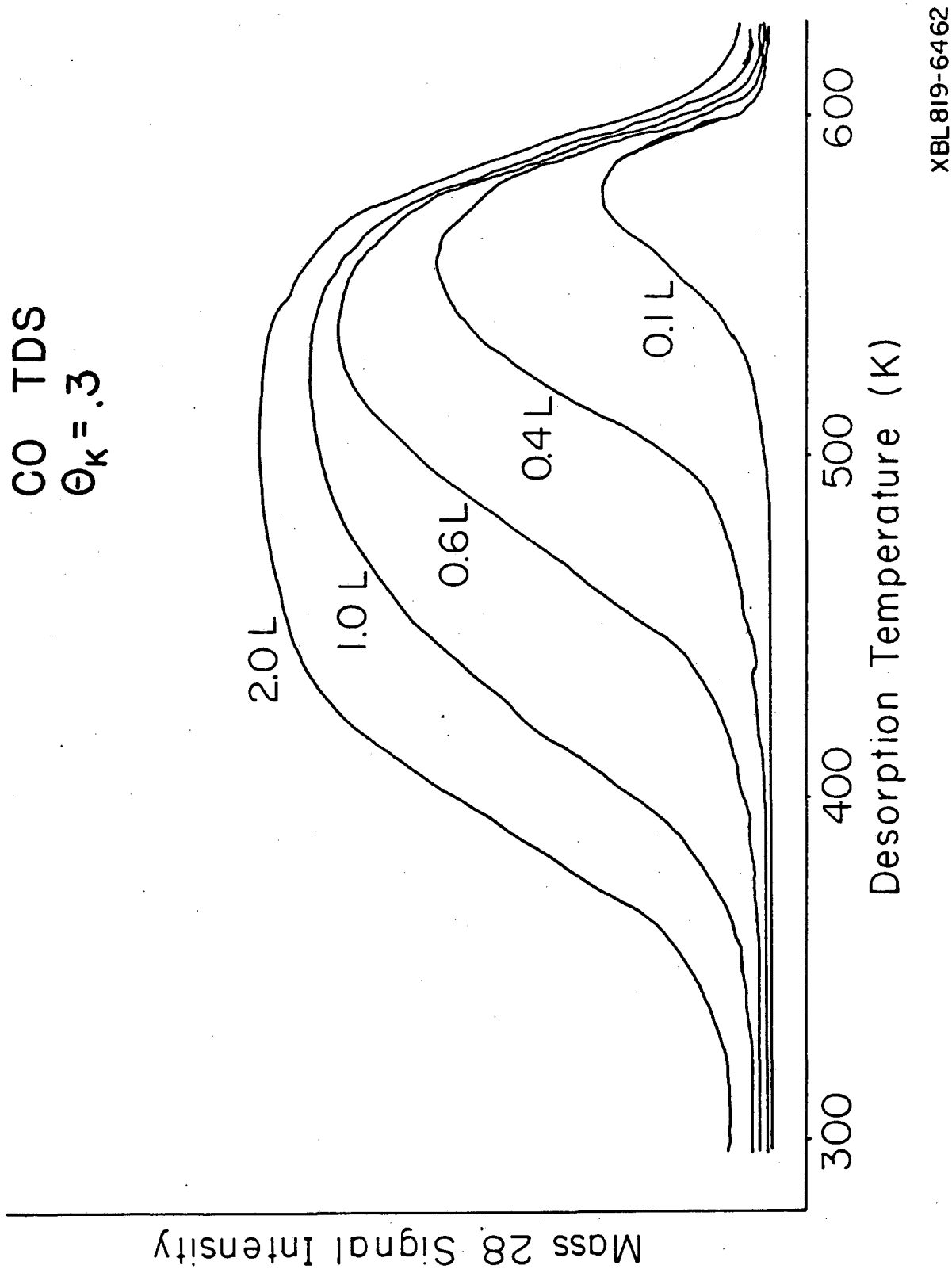
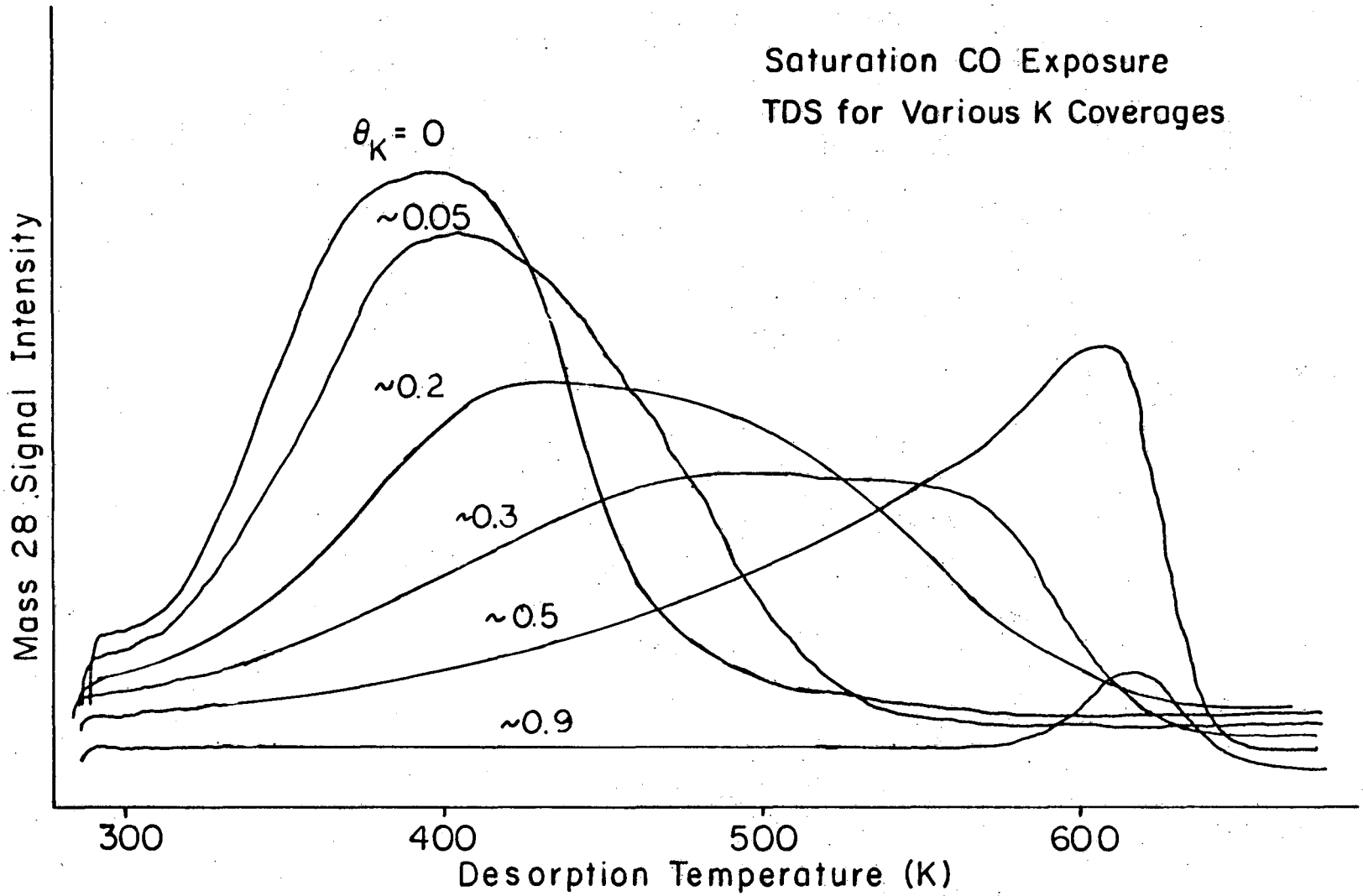

CO TDS
$\Theta_K = .3$
2.0 L
1.0 L
0.6 L
0.4 L
0.1 L
300
400
500
600
Desorption Temperature (K)
Mass 28 Signal Intensity
XBL 819-6462

Fig. 3c



XBL 819-6461B

Fig. 4a

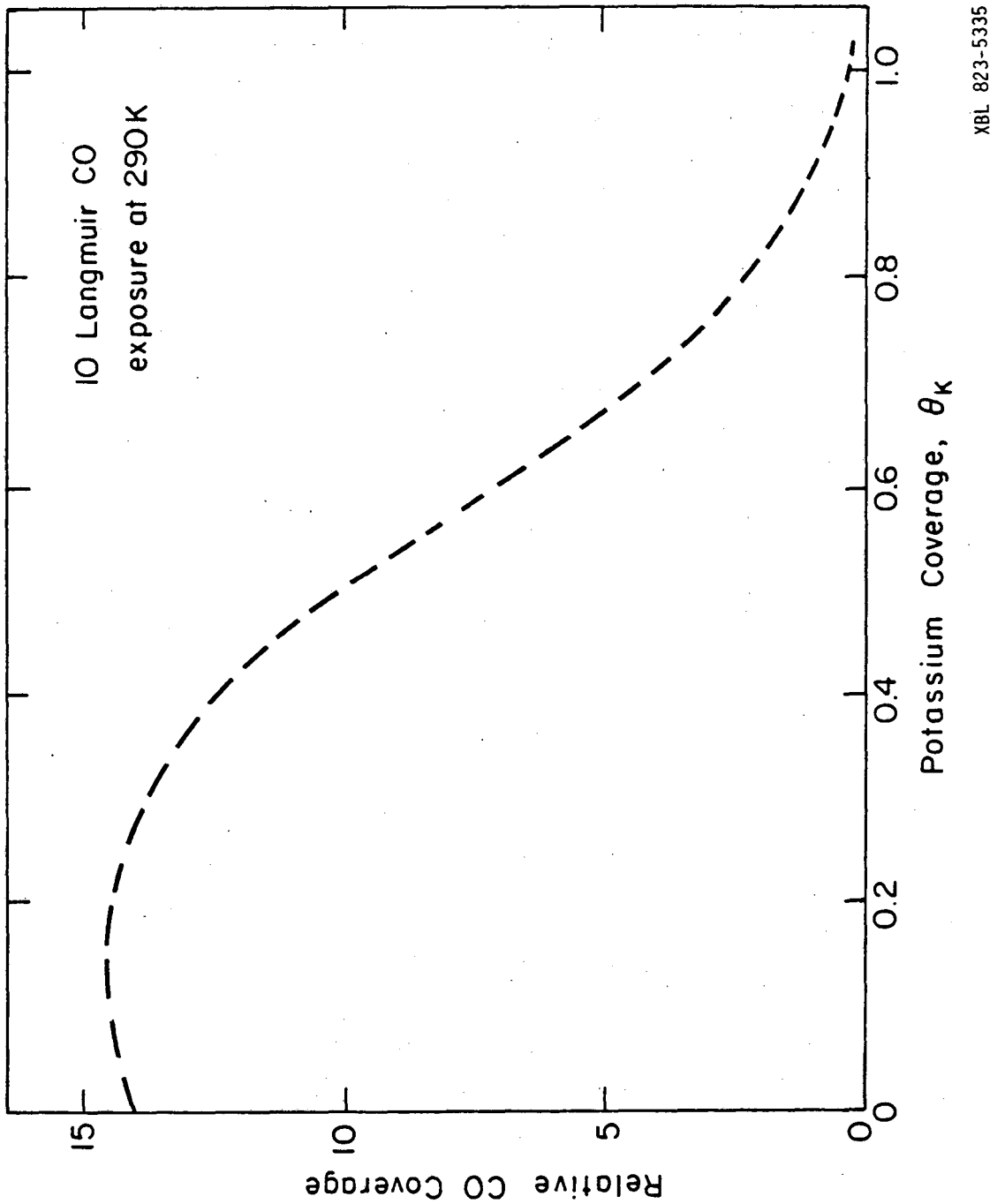

10 Langmuir CO
exposure at 290K
Relative CO Coverage
15
10
5
0
0
0.2
0.4
0.6
0.8
1.0
Potassium Coverage, θ_K
XBL 823-5335

Fig. 4b

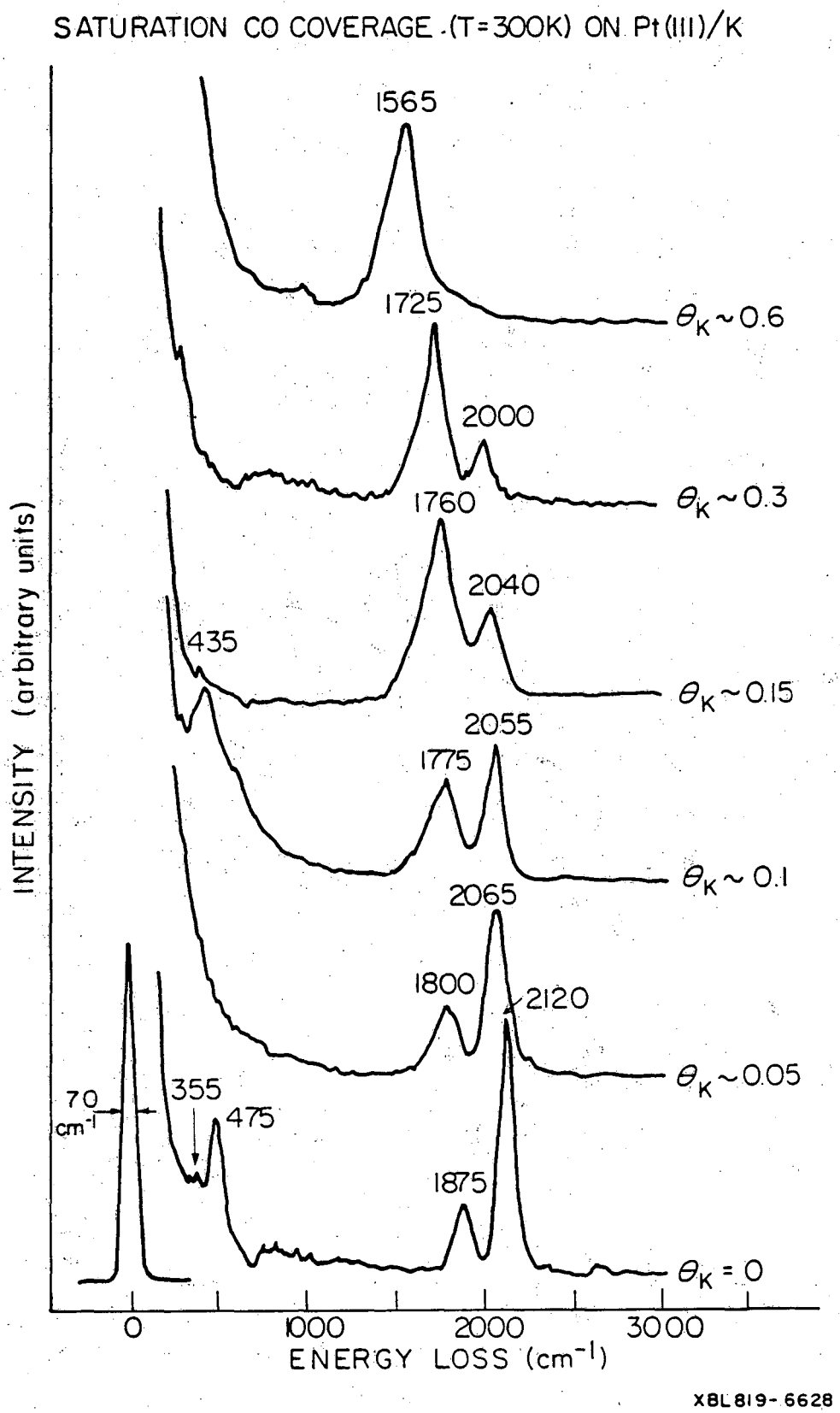

SATURATION CO COVERAGE (T=300K) ON Pt(111)/K
1565
1725
2000
1760
2040
435
2055
1775
2065
1800
2120
355
475
70
cm-1
1875
θK ~ 0.6
θK ~ 0.3
θK ~ 0.15
θK ~ 0.1
θK ~ 0.05
θK = 0
INTENSITY (arbitrary units)
0
1000
2000
3000
ENERGY LOSS (cm-1)
XBL819-6628

Fig. 5

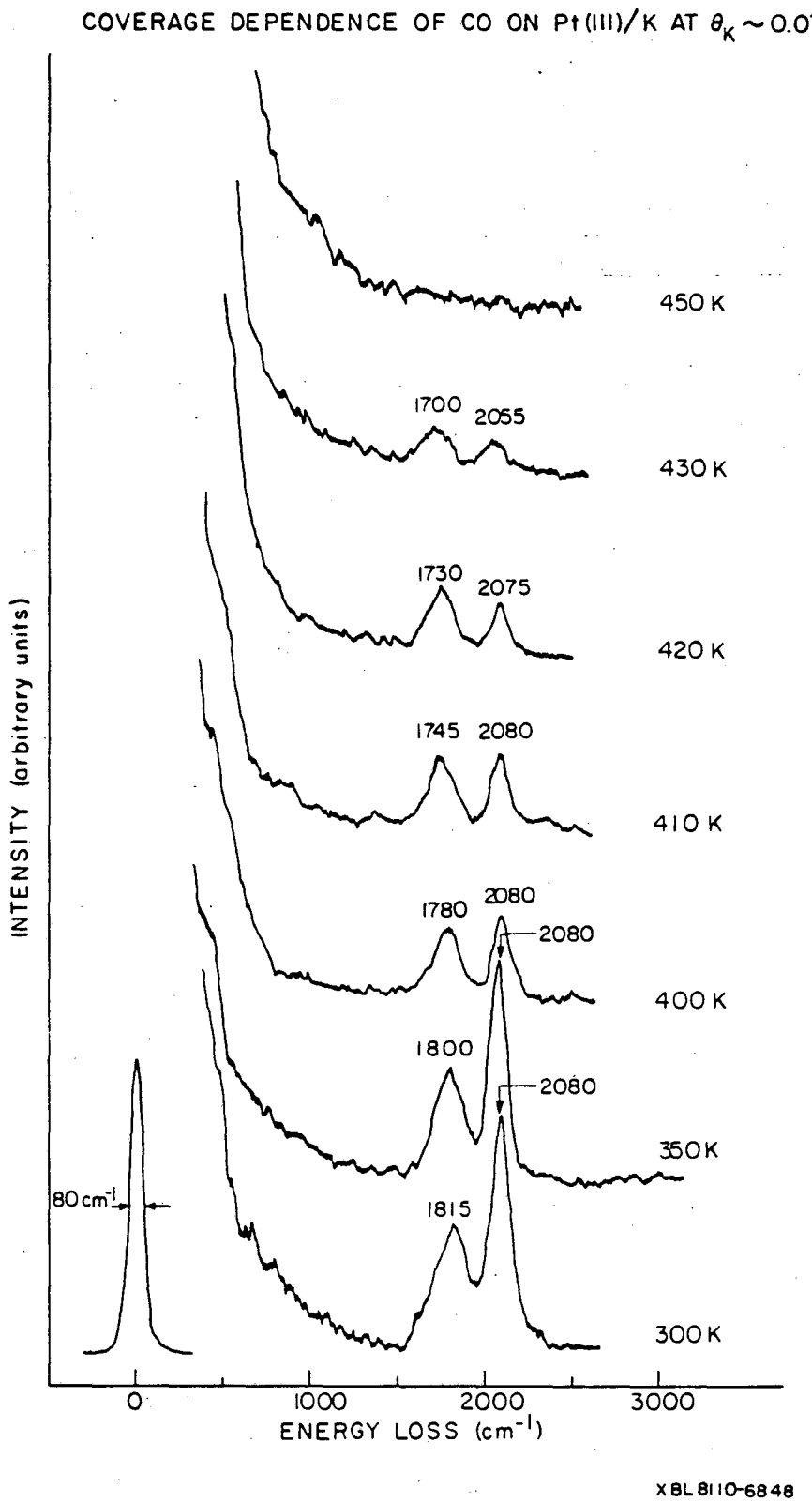

COVERAGE DEPENDENCE OF CO ON Pt(111)/K AT $\theta_K \sim 0.07$
INTENSITY (arbitrary units)
450 K
1700
2055
430 K
1730
2075
420 K
1745
2080
410 K
1780
2080
2080
400 K
1800
2080
350 K
80 cm⁻¹
1815
300 K
0
1000
2000
3000
ENERGY LOSS (cm⁻¹)
XBL 8110-6848

Fig. 6a

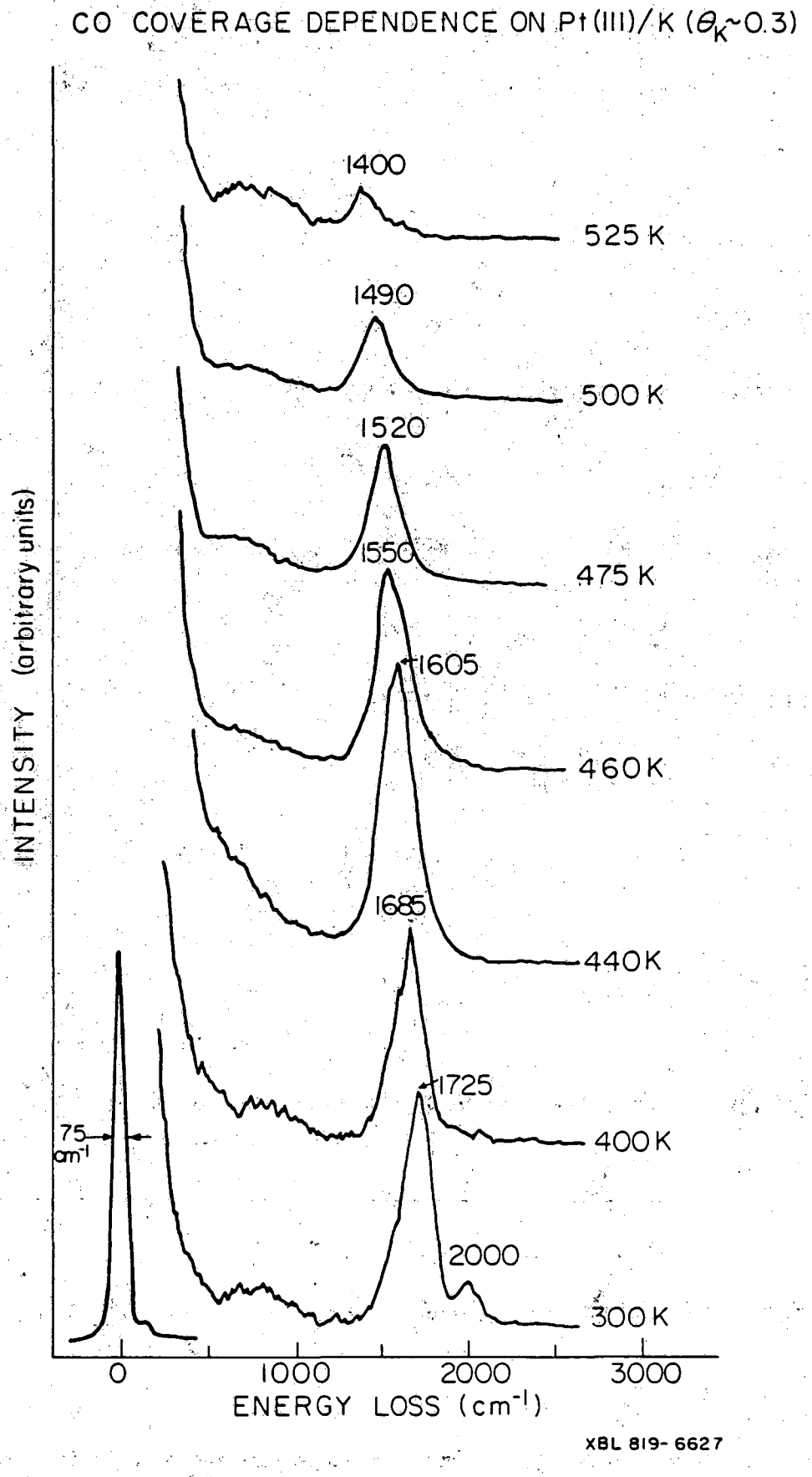

CO COVERAGE DEPENDENCE ON Pt(111)/K (θ_K~0.3)
1400
525 K
1490
500 K
1520
475 K
1550
1605
460 K
1685
440 K
1725
400 K
2000
300 K
75 cm⁻¹
INTENSITY (arbitrary units)
0
1000
2000
3000
ENERGY LOSS (cm⁻¹)
XBL 819-6627

Fig. 6b

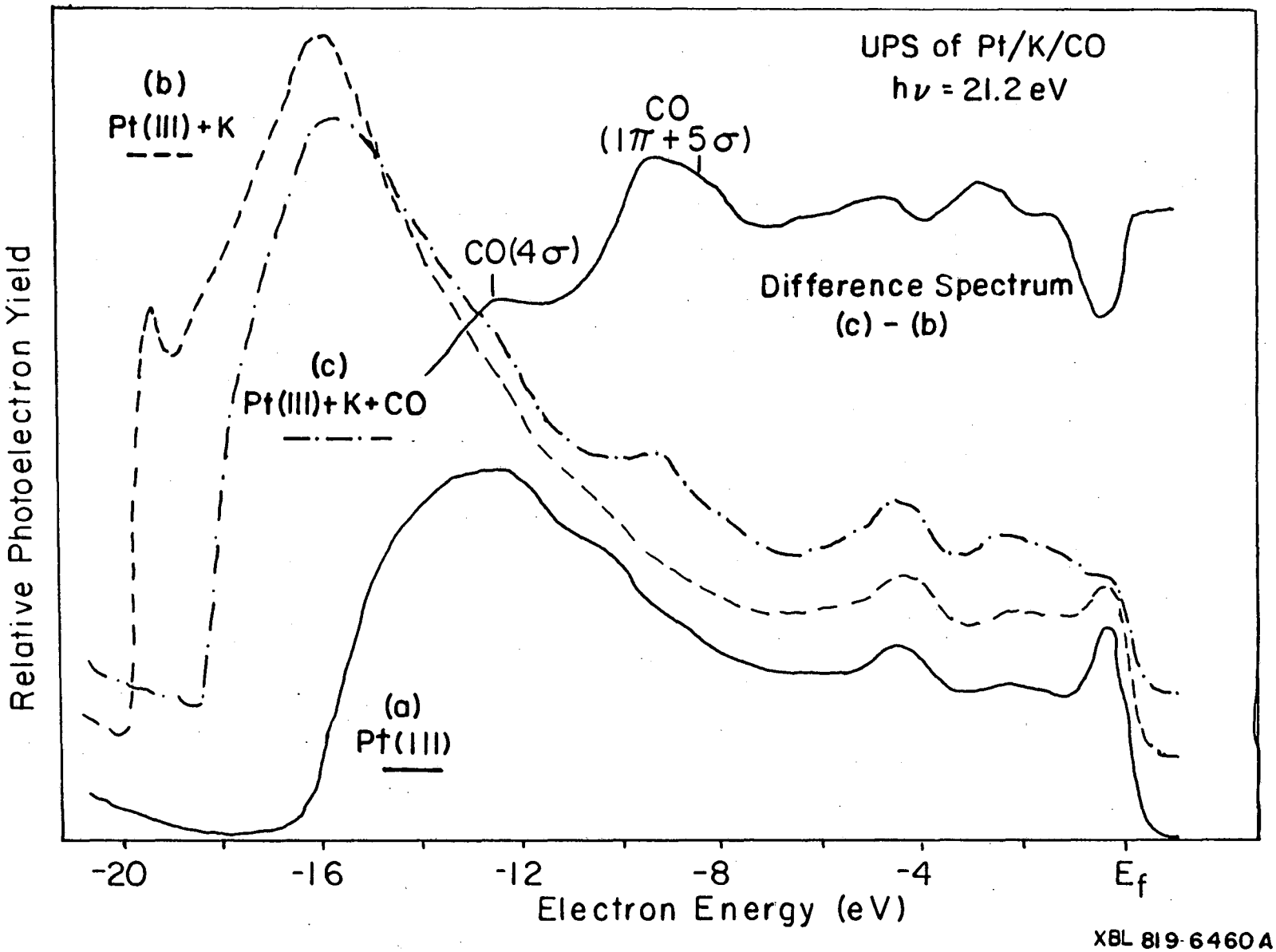

UPS of Pt/K/CO
hν = 21.2 eV
(b)
Pt(111)+K
CO
(1π+5σ)
CO(4σ)
Difference Spectrum
(c) - (b)
(c)
Pt(111)+K+CO
(a)
Pt(111)
Relative Photoelectron Yield
-20
-16
-12
-8
-4
Ef
Electron Energy (eV)
XBL 819-6460A

Fig. 7

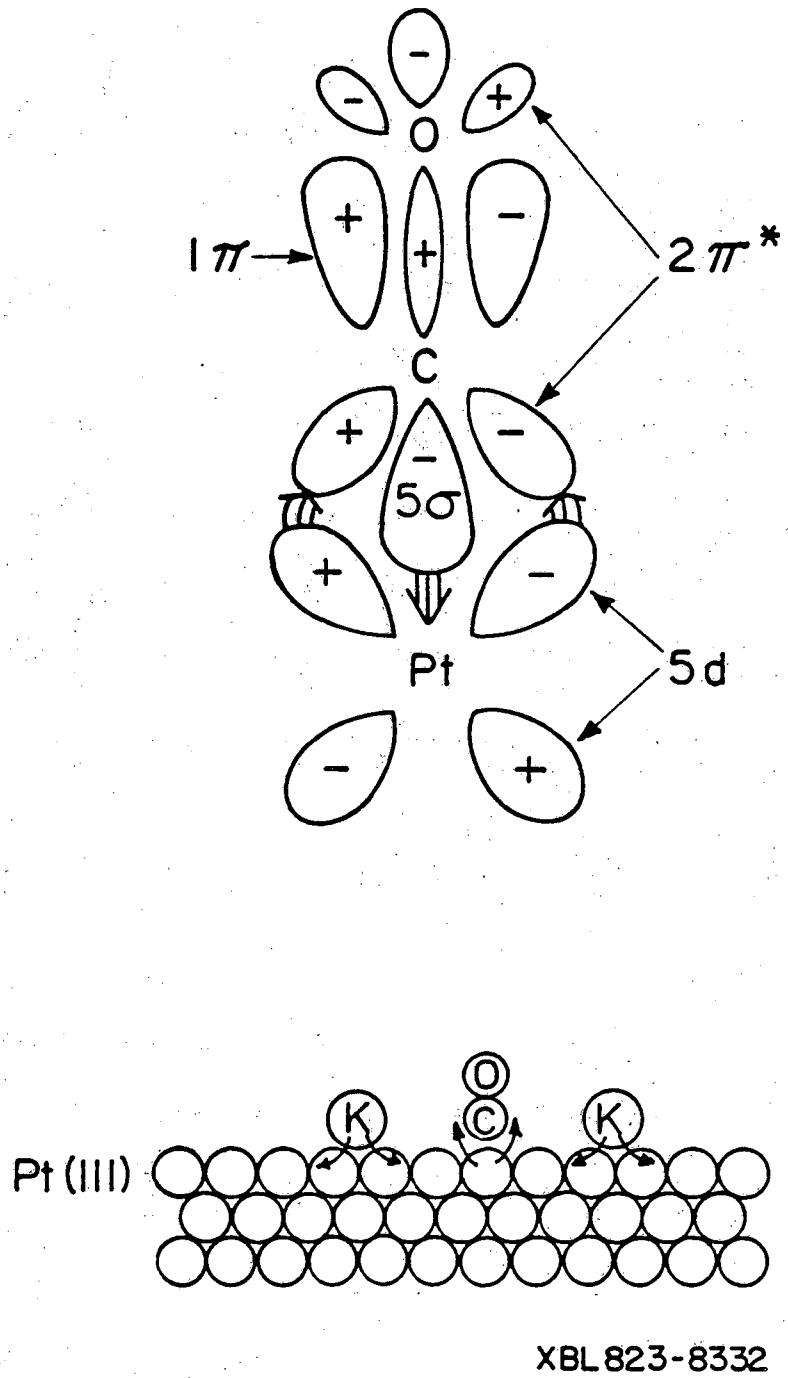


Fig. 8

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