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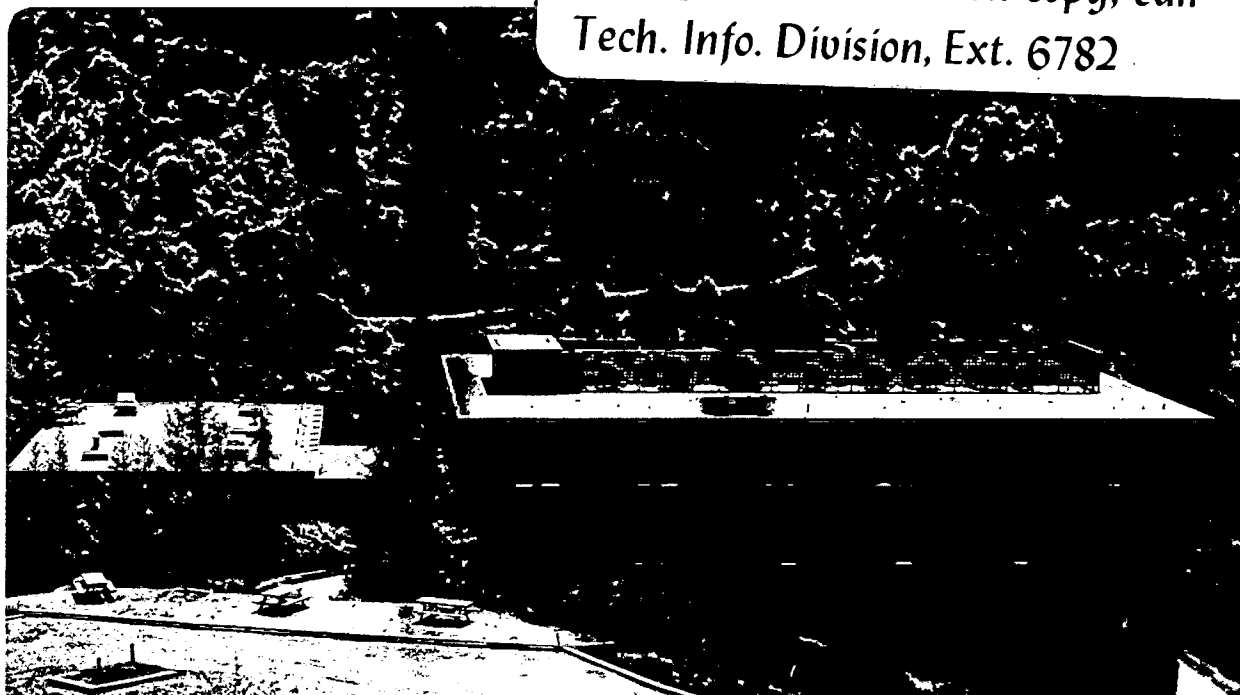
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THE STRONG INFLUENCE OF POTASSIUM ON THE ADSORPTION OF CO

ON PLATINUM SURFACES: A TDS AND HREELS STUDY

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Abstract

The chemisorptive properties of carbon monoxide on the Pt(111) crystal face were observed to change markedly in the presence of potassium. Upon deposition of half a monolayer of potassium the saturation coverage adsorption energy of CO increased from 27 to 39 kcal/mole. High resolution electron energy loss spectroscopy (HREELS) showed a 475 cm^{-1} decrease in the bridge bonded CO vibrational frequency to as low as 1400 cm^{-1}, while CO preferentially occupied bridge bonded rather than linearly bonded surface sites in the presence of potassium. These large variations appear to be caused by enhanced electron back-donation from the platinum into the $2\pi^*$ antibonding orbitals of CO.

Introduction

Potassium and other alkali metals, which are often used as additives in many catalytic systems [1,2], have been shown to change the binding energy of reactive molecules to metal surfaces. On nickel, the heats of adsorption of both H_2 and CO increase with the addition of potassium to the surface [3], while on iron, alkali metals decrease the sticking probability and increase the dissociation probability of CO [4]. Several laboratories have shown that potassium increases the sticking probability of O_2 on platinum [5,6] and promotes oxide formation on iron surfaces [6]. In addition, studies by Ertl et al [7] on iron surfaces indicate that the heat of adsorption of N_2 increases by 3 kcal/mole in the presence of potassium.

As a result of these alkali induced chemisorption changes, under actual catalytic conditions, the relative surface concentration and dissociation probability of CO, H_2, O_2, and N_2 should be significantly altered, affecting both reaction mechanism and product distribution. With these ideas in mind we have studied the chemisorption of CO to a platinum surface in the presence of potassium.

A substantial increase in adsorption energy and significant shifts in the site selectivity were observed for CO co-adsorbed with submonolayer amounts of potassium on the Pt(111) crystal surface. In addition, a continuous decrease in the CO stretching vibrational frequency was observed with decreasing CO coverage and/or increasing potassium coverage. A decrease in CO vibrational frequency to as low as 1400 cm^{-1} was observed, the lowest stretching frequency reported for CO on metal surfaces to date. These results are attributed to a substantial back-donation of electrons from platinum into the antibonding orbitals of CO.

Experiments

Experiments were performed in two separate ultrahigh vacuum (UHV) systems with base pressures of 1×10^{-10} torr. All thermal desorption studies were performed in an ion pumped UHV chamber equipped with a single pass cylindrical mirror analyser (CMA) for Auger electron spectroscopy (AES), a 4-grid low energy electron diffraction (LEED) system, and a quadrupole mass spectrometer (QMS) for thermal desorption spectroscopy (TDS).

All vibrational spectra were obtained in an ion pumped UHV chamber built in two levels. The upper portion of the chamber contained standard vacuum surface analysis equipment (four grid LEED/AES retarding field optics, glancing incidence electron gun, and QMS). The lower level contained the high resolution electron energy loss spectrometer (HREELS) as described elsewhere [8].

Two different platinum crystals (99.998% purity) were cut to (111) orientation, mounted, and cleaned using standard procedures. Both systems were equipped with a "Saes Getters" potassium source mounted about 3 cm from the sample surface. Deposition rates were routinely on the order of 0.2 monolayers/minute, with the platinum crystal held at room temperature. The potassium monolayer (Θ_K) coverage calibration is described in detail elsewhere [5]: $\Theta_K=1$ at 5.5×10^{14} K atoms/cm^2, or about one third the atomic density of the platinum (111) face.

For the thermal desorption experiments shown in Figure 1, atomic potassium was deposited onto a clean Pt(111) surface held at room temperature. After potassium coverage determination by AES, the surface was exposed to 10L of CO (1 Langmuir=10^{-6}torr sec) from a molecular doser, to give a saturation coverage ($\approx5\times10^{14}$ CO molecules/cm^2). The sample was then heated at 30 K/sec, and the intensity of the desorbing CO (mass 28) was recorded by the QMS as a function of temperature.

Results

In Figure 1, the thermal desorption spectra for saturation CO coverages on the Pt(111) surface are shown for various potassium coverages. At $\Theta_K=0.05$, the CO desorption peak maximum, originally at 400K, began to shift to higher temperatures. As the potassium coverage is increased to $\Theta_K=0.2$, the CO thermal desorption peak broadens substantially on the high temperature side. By a potassium coverage of $\Theta_K=0.4$, the desorption peak maximum shifts to 600K. For potassium coverages in excess of $\Theta_K=0.5$, the maximum CO coverage, as determined by TDS peak integration, decreases markedly, but the peak position remains at about 600K. There is residual desorption centered at 420K, even for multilayer potassium deposits, causing some spectra to appear to be the result of two separate CO binding states. However, from control experiments, this 420K residual peak was shown to be due to crystal back, edge and/or support effects. Thus, despite the appearance of two separate peaks at high potassium coverages, the contribution from the potassium covered surface is a single, sometimes broad, desorption peak, as will become clearer below. No other CO peaks were seen with multilayer potassium deposits, nor was carbon or oxygen found by AES to remain on the surface after heating to 650K, indicating no significant irreversible CO dissociation.

In Figure 2, the room temperature HREELS vibrational spectra for saturation coverages of CO are shown as a function of potassium coverage. In the HREELS experiment, the potassium coverage was varied by depositing about a monolayer, then annealing to a specified temperature, thereby desorbing potassium, to achieve the desired coverage [5]. The surface was then exposed to >10L CO and HREELS spectra were taken. On the clean Pt(111) surface, the $1875cm^{-1}$ peak, usually attributed to the stretching vibration of CO bridge bonded between two platinum atoms, is about one half as intense as the $2120cm^{-1}$ peak, attributed to CO bonded linearly on top of a surface platinum atom [9].

The relative intensity of the two vibrational states varies continuously with potassium coverage such that the peak heights are nearly equal at $\Theta_K=0.10$. The bridge site vibrational loss intensity becomes more than twice that of the linear site at $\Theta_K=0.3$. We interpret this shift in intensity as a shift in CO occupation from the linear site to the bridge site. This trend continues with increasing potassium coverage, and by $\Theta_K=0.6$ the linear site is unoccupied with only bridged CO sites remaining.

In addition to the change in site occupancy, the vibrational frequency of the linear CO species gradually decreases from $2120cm^{-1}$ for the potassium-free surface, to $2000cm^{-1}$ as the potassium coverage is increased to $\Theta_K=0.3$. The vibrational frequency of the bridge bonded CO species is seen to shift even more substantially to $1565cm^{-1}$, at a coverage of $\Theta_K=0.6$, compared to $1870cm^{-1}$ on the clean Pt(111) surface.

The low frequency region of the spectra are partially obscured due to tailing of the elastic peak. It does show, however, a platinum-carbon stretching frequency at $475cm^{-1}$ for potassium-free Pt(111), which broadens as both top and bridge sites become occupied, shifting to $435cm^{-1}$ by a potassium coverage of 0.1 monolayers. No K-Pt, K-C, or K-O vibrations were observed. The K-O vibrational spectra from co-adsorbed potassium and oxygen on Pt(111) will be discussed in a future paper [10].

The thermal desorption spectra for various CO exposures on Pt(111) at a constant potassium coverage of $\Theta_K=0.3$ are shown in figure 3. At low CO exposures (<0.1L) the temperature of the CO desorption peak is centered between 580-600K. As the coverage is increased, the CO desorption peak broadens to lower temperatures. After CO exposures of >2L, the FWHM expands to 200K, compared to only 80K at $\Theta_K=0$. It is interesting to note

that the desorption peak broadens continuously and does not indicate two distinct peaks.

In Figure 4 we see the change in CO vibrational spectra for various CO coverages with $\Theta_K=0.3$. The reported temperatures indicate the temperatures at which the crystal was annealed for several seconds prior to recording the spectra; all spectra were obtained at 300K. This heating process is used to vary the CO coverage: the higher the annealing temperature, the lower the CO coverage. Since the $\Theta_K=0.3$ coverage was obtained by annealing a monolayer of potassium to 700K, no noticeable potassium desorption was detected in the temperature range studied here. As seen in figure 4, the linear CO species (with a frequency of 2000cm^{-1}) completely desorbs by 400K. The bridged species (1725cm^{-1}) maintains approximately the same vibrational peak intensity, although some peak broadening and decrease in frequency ($\Delta\nu\simeq40$cm^{-1}) does occur. This should be contrasted with CO desorption from clean Pt(111), where only bridged species (1870cm^{-1}) desorb by 400K, and all linear species (2120 cm^{-1}) are left chemisorbed. The asymmetric broadening of the bridge bonded peaks at 1725, 1685, and 1605 cm^{-1} toward lower frequency, combined with high frequency tailing of the 1550 and 1520 cm^{-1} peaks may indicate the occupation of an additional adsorption site on the Pt(111) surface, possibly a three-fold hollow position. Upon further heating the intensity and the stretching frequencies of the multiply bonded species continue to decrease. By 525K only a small fraction of a monolayer of CO is left adsorbed with a stretching frequency located at 1400cm^{-1}. This is lower than any previously reported CO vibrational stretching frequency.

Discussion

Our results indicate that the CO thermal desorption and vibrational frequency behavior are significantly altered by submonolayer coverages of

preadsorbed potassium on the Pt(111) surface. The dominant effects resulting from the coadsorption of CO and potassium are:

a. A 200K increase in temperature of the CO desorption peak maximum occurs as potassium coverage is increased to near a monolayer (Figure 1). Assuming first order desorption kinetics and a preexponential factor of 1.25×10^{15} sec^{-1} as determined by Campbell et al [11], this corresponds to a heat of desorption increase from 27 to 39 kcal/mole.

b. As the potassium coverage is increased from zero to 0.6 of a monolayer, the bridge bonded CO stretching mode at saturation coverage decreases by 310 cm^{-1}.

c. When the CO coverage is decreased at a constant potassium coverage of $\Theta_K=0.3$, the bridge bonded CO stretching mode decreases by 325 cm^{-1}. Simultaneously, an increase of 200K in the FWHM of the CO desorption peak occurs at high coverages.

d. A change in the relative occupancy of the two adsorption sites present on the Pt(111) surface at saturation CO coverages occurs as potassium coverage is increased, favoring the higher coordination bridge bonded sites over the linear site (Figure 2).

The accepted model for the bonding of carbon monoxide to metal atoms involves a synergistic electron transfer from the highest occupied molecular orbital of CO (5σ) to the metal, along with back donation of metal electrons into the lowest unoccupied molecular orbital ($2\pi*$) of CO [12-14]. It is known that on metal surfaces the metal-carbonyl vibrational frequencies and bond energies depend on the work function and crystallographic face of the metal, as well as on the CO coverage of the surfaces [15]. Back donation weakens the carbon-oxygen bond, lowering its vibrational frequency, and strengthens the metal-carbon bond energy. Changes in a metal's local surface electronic structure should change the extent of back donation.

We believe that enhanced electron back-donation from the platinum into the

$2\pi^*$ antibonding orbital of CO, due to the presence of potassium, is the dominant factor causing the large changes in the adsorption energy, vibrational frequency, and site selectivity of adsorbed CO. The response of the surface to a potassium atom is best understood as electron transfer from the potassium to the platinum valence bands. This is combined with electrostatic screening of the resultant positive charge by the metal electrons. From our results, this effect appears to be delocalized over a few interatomic distances. Also, adsorbed CO, by taking up excess charge, may permit an increase in the degree of potassium ionization.

The CO heat of desorption increase from 27 to 39 kcal/mole with increasing potassium coverage is in accordance with enhanced back-bonding orbital occupancy. Likewise, the 310 cm^{-1} decrease of the bridge bonded CO vibrational frequency at saturation CO coverage, as potassium coverage is increased from 0 to 0.6 monolayers, would also be a result of an increase in backbonding orbital occupancy. If direct interactions between the adsorbed potassium and CO were the dominant factor inducing the changes, different HREELS and TDS results would have occured at low potassium coverages. This will be discussed in a future paper [16].

The 325 cm^{-1} decrease in the bridge bonded vibrational frequency as CO coverage is decreased (at constant potassium coverage) can also be rationalized by the backbonding model. We propose that this effect is due mostly to a competition between the adsorbed CO molecules for the excess platinum valence electrons provided by the fixed number of potassium adatoms. At low CO coverages, each CO may interact with a larger fraction of the excess electron density. This is also supported by the single broad CO thermal desorption peak for saturation CO coverages at a potassium coverage of $\Theta_K=0.3$ (figure 3). At any point during the CO desorption process, those CO molecules which remain

on the surface become more tightly bound, and their stretching frequency decreases. This is reasonable as surface electron transfer processes take 10^{-14}-10^{-15} seconds, while the thermal desorption experiment occurs on a time scale of about 30 seconds. Contributions to this 325 cm^{-1} decrease due to dipole-dipole interactions between the adsorbed CO molecules cannot be distinguished from backbonding effects, but electron back-donation appears to be the dominant contribution.

The change in relative occupancy of the surface sites is more difficult to rationalize. Recently Nieuwenhuys [14] has shown a correlation between the work function of a metal surface and the degree of electron backdonation: the lower the work function, the higher the electron spillover into the backbonding orbital. Also on many lower work function metal surfaces CO sits preferentially on the bridged site. This indicates that the bridged site permits more extensive d_{Pt} to $2\pi^*_{CO}$ electron overlap than the linear site. Another factor influencing site selectivity could be the energetically favorable decrease in the dipole separation of CO and its image achieved by moving from a linear top site to a bridged or threefold hollow site.

The catalytic implications of the results shown above, especially the weakened CO bond, are significant. An increase in the electron back-donation from a metal increases the probability of both the hydrogenation of the weakened CO molecule and the dissociative adsorption of CO. For the Fischer-Tropsch reaction (CO + H_2 → hydrocarbons), an increase in the rate of CO dissociation will increase the carbon and oxygen surface coverage relative to that of hydrogen. Work in the past [1,17] on catalytic hydrocarbon reactions have shown a preference for longer chain hydrocarbons as well as oxygenated products when alkali oxides were added to catalysts. More exact reaction studies, combined with atomic level surface characterizations such

as those presented here, will eventually lead to a more fundamental understanding of promoter effects in catalysis.

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References

1. M.E. Dry, T. Shingles, L.J. Boshoff and G.J. Oosthuizen, J. Cat. 15, 190 (1969).

2. A. Ozaki and K.I. Aika, in A Treatise on Nitrogen Fixation, p169, eds. R.W.F. Hardy, F. Bottomley and R.L. Burns, Wiley 1979.

3. J. Benziger and R.J. Madix, Surface Sci. 94, 119 (1980).

4. G. Broden, G. Gafner and H.P. Bonzel, Surface Sci. 84, 295 (1979).

5. E.L. Garfunkel and G.A. Somorjai, submitted to Surface Sci.

6. G. Broden, G. Pirug and H.P. Bonzel, Chem. Phys. Lett. 73, 506 (1980).

7. G. Ertl, M. Weiss and S.B. Lee, Chem. Phys. Lett. 60, 391 (1979).

8. L.H. Dubois and G.A. Somorjai, Surface Sci. 91, 514 (1980).

9. H. Froitzheim, H. Hopster, H. Ibach and S. Lehwald, Appl. Phys. 13, 147 (1977).

10. J.E. Crowell, E.L. Garfunkel and G.A. Somorjai, to be published.

11. C.T. Campbell, G. Ertl, H. Kuipers, and J. Segner, Surface Sci. 107, 207 (1981).

12. G. Doyen and G. Ertl, Surface Sci. 43, 197 (1974).

13. R.P. Eischens, S.A. Francis and W.A. Pliskin, J. Phys. Chem. 60, 194 (1956).

14. G. Blyholder, J. Phys. Chem. 68, 2772 (1964).

15. B.E. Nieuwenhuys, Surface Sci. 105, 505 (1981).

16. J.E. Crowell, E.L. Garfunkel and G.A. Somorjai, to be published.

17. T.P. Wilson, W.J. Bartley and P.C. Ellgen, to be published.

Figure Captions

Figure 1: Thermal desorption spectra of saturation exposures of CO on Pt(111) as a function of preadsorbed potassium.

Figure 2: Vibrational spectra of the saturation CO coverage chemisorbed on Pt(111) at 300K as a function of preadsorbed potassium.

Figure 3: Thermal desorption spectra of CO from Pt(111) predosed with 0.3 monolayers of potassium as a function of CO coverage.
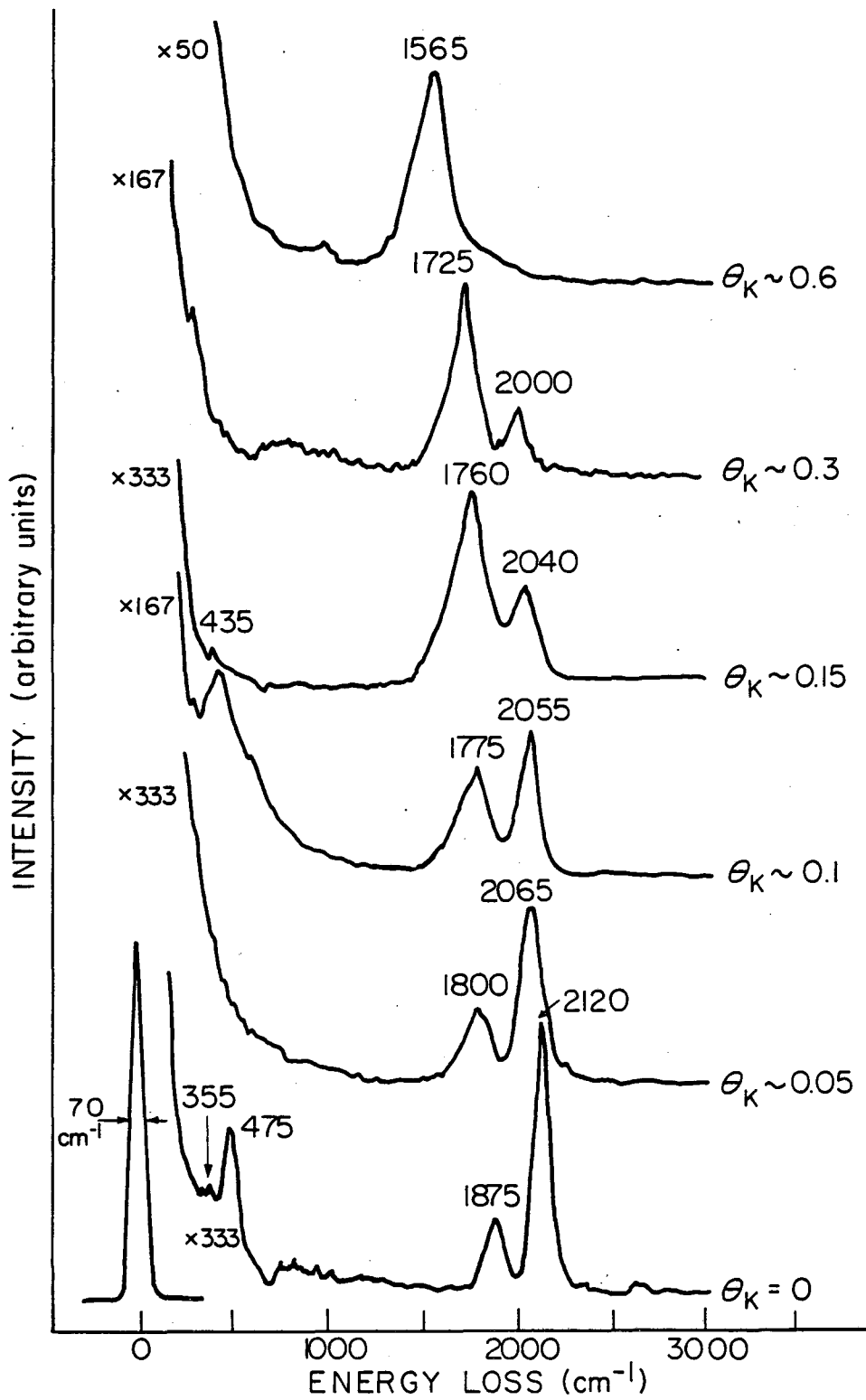
Figure 4: Vibrational spectra of CO chemisorbed on Pt(111) predosed with 0.3 monolayers of potassium as a function of substrate temperature (ie, CO coverage).
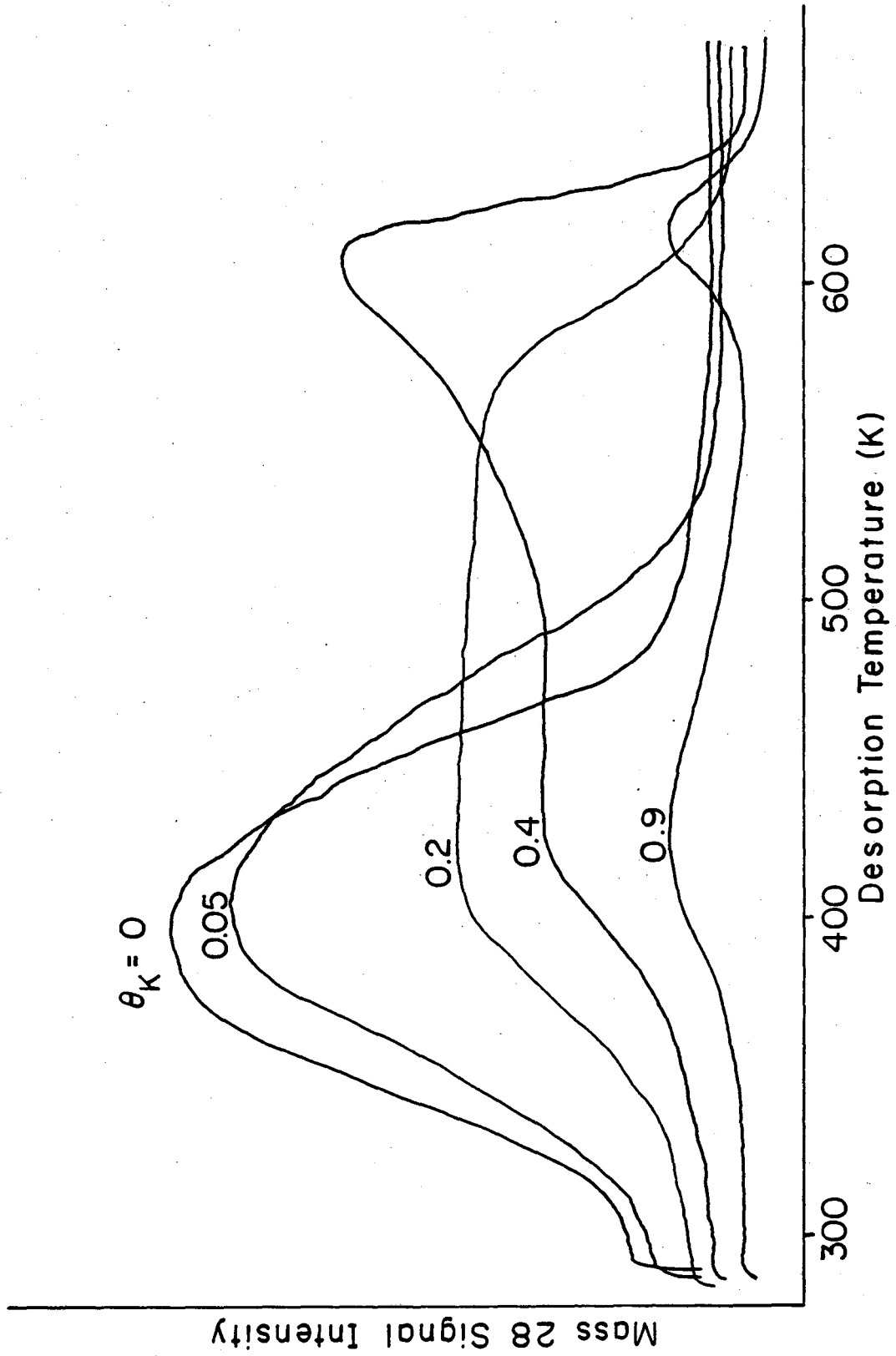
Fig.1

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Fig.2
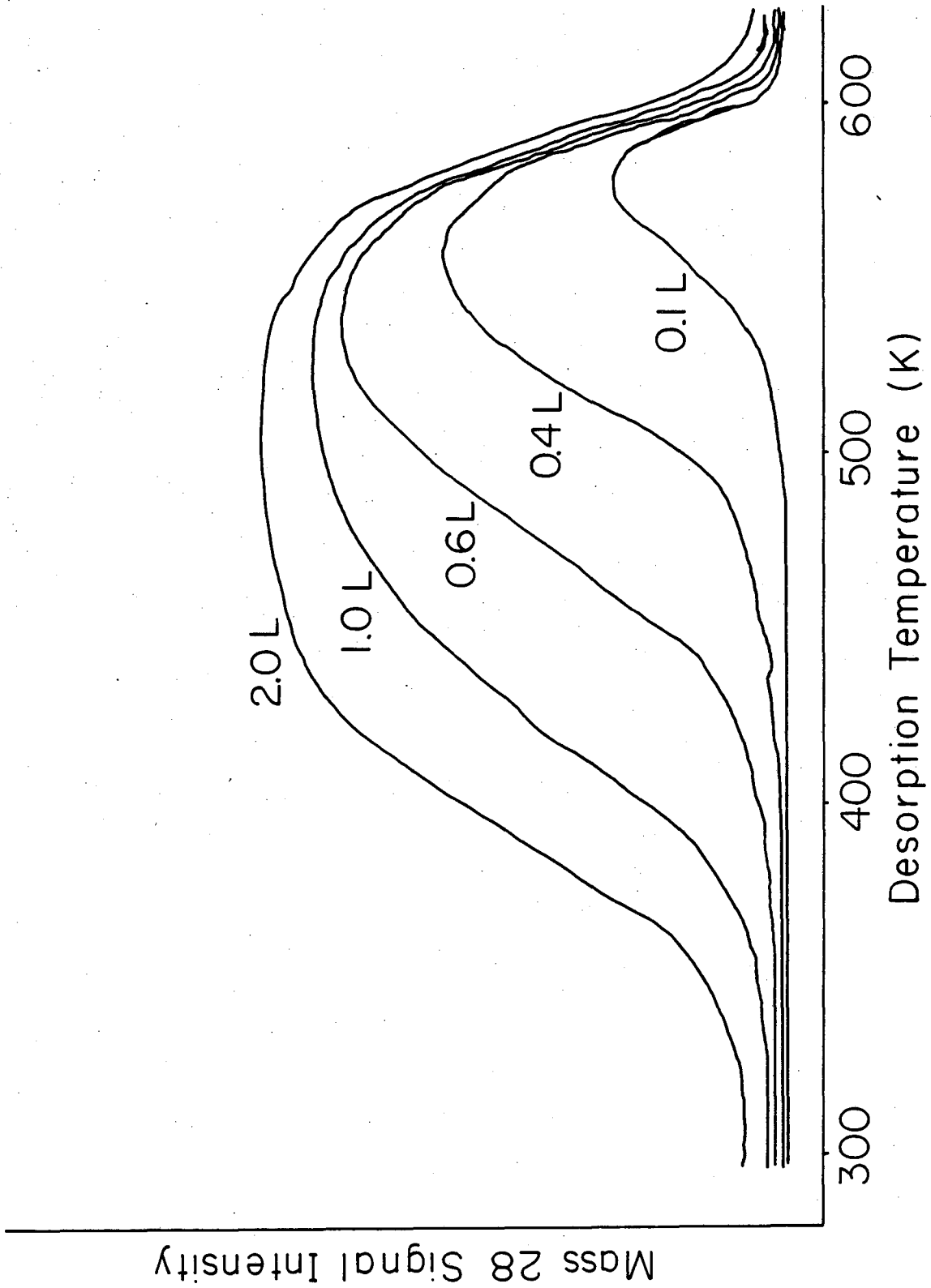
Fig. 3

XBL 819-6462

CO COVERAGE DEPENDENCE ON Pt(III)/K ($\theta_K \sim 0.3$)

XBL 819- 6627

Fig.4