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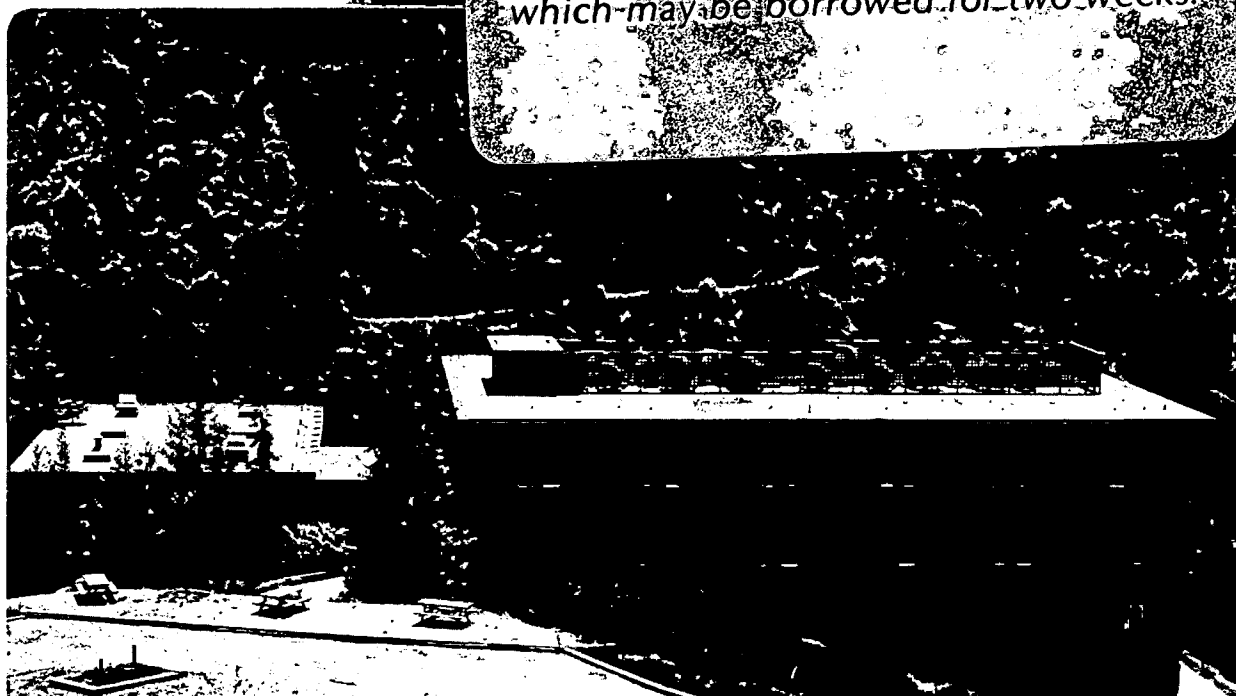
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POTASSIUM CO-ADSORPTION INDUCED DISSOCIATION OF CO ON THE RH(111)
CRYSTAL SURFACE: AN ISOTOPE MIXING STUDY.

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Abstract.

The formation of $C^{13}O^{18}$ from a mixture of $C^{13}O^{16}$ and $C^{12}O^{18}$ proves unequivocally that molecular CO dissociates on Rh(111) when potassium is co-adsorbed. The presence of a surface complex between the alkali metal and the CO is confirmed by the simultaneous desorption of potassium and CO. A minimum of 0.08 potassium atoms per surface Rh atom is necessary to induce any CO dissociation. A maximum of three CO molecules are observed to dissociate per potassium atom.

INTRODUCTION

The influence of alkali metals on the chemisorptive properties of CO are dramatic. It is, in fact, one of the most important and interesting examples of the ability of additives to modify the chemical properties of surfaces. Previous investigations on the Rh(111) [1] and Pt(111) [2] using electron energy loss spectroscopy (EELS) have demonstrated that alkalis cause considerable carbon-oxygen bond weakening and strengthening of the M-CO surface bond. This was concluded from observed changes in the corresponding bond vibrational frequencies, namely, substantial decreases in the C-O stretching frequencies and slight increases in the M-C vibrational frequencies. Furthermore, on both surfaces, temperature programmed desorption (TPD) spectra of CO shifts to higher temperatures indicating increased desorption energy in the presence of potassium. This shift of desorption peak to higher temperatures is continuous on Pt(111) with increasing K concentration, but distinct higher temperature states are apparent when CO is adsorbed with K on Rh(111). The origin of these potassium induced desorption states is unclear; they may be due to first order molecular desorption of CO with the change in desorption temperature corresponding to the observed increase in the M-C stretch in EELS. Alternatively, these states may be due to second-order atom-recombination reactions of carbon and oxygen on the surface produced by alkali induced CO dissociation. It should be emphasised that the vibrational spectroscopy data does not indicate whether CO bond cleavage occurs since no significant M-O or M-C vibrations were detectable. However, an unequivocal method of deciding if a molecular desorption peak arises from dissociated adspecies is to

use isotope mixing measurements. In these experiments, an alkali pre-dosed surface is exposed to a known mixture of $C^{13}O^{16}$ and $C^{12}O^{18}$ and the desorption products monitored at 28, 29, 30 and 31amu. The appearance of a 31amu signal indicates that isotopic scrambling has occurred which must indicate high temperature CO dissociation on the surface.

The purpose of this paper is to examine whether CO is dissociated in UHV in the presence of K on Rh(111). Previous studies by Yates and co-workers have shown that below 800K, CO does not dissociate at low pressure ($\sim 2 \times 10^{-6}$ torr CO) on clean Rh(111). Isotope scrambling in the presence of K would demonstrate that alkalis not only weaken the C-O bond but can ultimately lead to its rupture. Our isotope studies clearly indicate that co-adsorbed potassium induces the dissociation of CO. At an optimum potassium coverage $\theta_K = 0.1$, as much as three CO molecules may dissociate per potassium.

2. EXPERIMENTAL.

The experiments were performed in an ultra-high vacuum system equipped with a retarding field analyser for LEED analysis, a glancing incidence electron gun for Auger excitation, sputtering capabilities, and a quadrupole mass spectrometer for TPD studies. The chamber is maintained at base pressures, typically less than 1×10^{-10} torr with an ion and titanium sublimation pump. The sample, a Rh(111) single crystal oriented and polished on both sides, was mounted on 0.25mm Ta support wires. The sample was resistively heated and the temperature measured by a chromel-alumel thermocouple spot-welded to the back face of the crystal. The sample was cleaned on both sides by a combination of chemical treatment with oxygen, Ar^+ sputtering and annealing in vacuum.

LEED and AES were used to ensure that the crystal was clean and well ordered.

Potassium atoms were deposited onto the Rh(111) surface by heating a commercial getter source (SAES) positioned ~5cms from the sample. Potassium coverages were calibrated using LEED, AES and TPD yield as described elsewhere [4]. A monolayer of potassium corresponds to a surface density of 5.8×10^{14} atoms/cm²; a surface coverage (θ_K) of 0.36 potassium atoms per surface rhodium atom.

The sample was typically dosed at 140K with potassium, followed by CO exposure using a variable leak valve and directional doser. The CO gas exposures (either C¹²O¹⁶ or a mixture of C¹³O¹⁶ and C¹²O¹⁸) are uncorrected for ion gauge sensitivity. The TPD results were obtained by heating the sample linearly as a function of time and monitoring the desorbing species. The change in pressure of several masses were simultaneously recorded versus either time or temperature using a microcomputer.

3. RESULTS.

Representative TPD spectra for saturation CO exposures (C¹²O¹⁶) on Rh(111) at 300K as a function of pre-dosed potassium coverage are shown in figure 1. In these experiments, back face adsorption of CO was masked by pre-dosing multilayers of potassium onto the back face prior to CO exposure; CO does not adsorb on pure potassium multilayers at low pressure. Initially, the effect of K is to broaden the desorption peak for the clean sample to higher

temperatures. However, when a critical potassium coverage is reached ($\theta_K=0.1$), two new desorption states become populated. These states occur at 630 and 700K at a heating rate of 15K/sec. These states grow in intensity with increasing potassium coverage as the low temperature molecular state decreases in intensity. Desorption occurs only from the high temperature 700K state at coverages near saturation (e.g. $\theta_K=0.33$ in figure 1). At coverages greater than $\theta_K=0.36$, no CO desorption is observed at 10L exposure.

The origin of these high temperature states is discernable by adsorbing isotopic mixtures of CO. Figure 2 shows the TD spectra for surfaces predosed at 140K with potassium and exposed to 10L of a mixture of $C^{13}O^{16}$ and $C^{12}O^{18}$. Shown are the signals at 29, 30 and 31 amu which were monitored simultaneously. Notice that $C^{13}O^{18}$ desorbs at each of the three desorption states. Adsorption of isotopic CO on the clean Rh(111) surface indicates that 6.5% of the adsorbed CO desorbes as $C^{13}O^{18}$. Similar results by Yates et al [3] suggest that a portion of the desorbing CO are dissociated by the mass spectrometer ionizing filament. Hence, the small peak at 500K in the 31amu TPD spectrum is not indicative of any surface scrambling for this state

From figure 2, it is immediately obvious that the percentage of desorption of CO at 31amu is larger for the two high temperature states. This indicates that these states arise from a process which involves C and O scrambling and hence from dissociated CO.

It should be pointed out that the spectra in figure 2 include contributions from the crystal back face (which was not alkali dosed and hence does not dissociate CO). However, this contribution could

be measured by masking the crystal front face by saturating it with potassium. Data shown subsequently have been corrected for back face contributions.

The proportion of CO dissociating on the surface is shown versus potassium coverage in figure 3. The proportion of dissociation is near zero until $\theta_K=0.10$, where a sharp rise occurs and nearly all the CO has dissociated for a potassium coverages, $\theta_K \sim 0.10$. A criterion for whether dissociation has taken place can be related to the isotopically labelled TPD spectra by defining a scrambling parameter:

$$p = \frac{A_{31}}{\sqrt{A_{29} A_{30}}}$$

where A_n is the area under the 700K peak at n amu. A value of p of zero indicates that the carbon and oxygen are completely correlated, i.e. no dissociation has taken place. Conversely, $p=1$ indicates total randomization of the carbon and oxygen. However, since some $C^{13}O^{18}$ is produced by the hot electron emitting filament in the mass spectrometer ioniser the minimum value of p (no surface scrambling) is 0.14. Isotopic scrambling takes place when p exceeds this value. In the limit of complete scrambling (in which the dissociated atoms are completely mobile on the surface), p tends to unity. Intermediate values imply that, although dissociation takes place, the mobility of the atoms is small such that they have a higher probability of recombining with the atom to which they were originally attached. For constant CO exposure (i.e. saturation exposure) as a function of

K coverage (fig. 4a), p increases from zero at $\theta_K=0$ to a maximum of 0.6 at $\theta_K \sim 0.1$, and then slowly decreases with increasing θ_K . Similarly, at a constant K coverage of 0.3 as a function of CO exposure, as shown in figure 4b, a maximum in p occurs at an exposure of 2L. Significant changes in the potassium TPD spectra accompany changes in these high temperature states due to dissociated CO. Potassium TPD on clean Rh(111) is characterized by a desorption maximum near 1100K at low coverages ($\theta_K \sim 0.02$). The maximum desorption rate shifts rapidly to lower temperatures with increasing coverages and peaks at 500K at completion of the first layer ($\theta_K = 0.36$). The second layer desorption maximum then begins to grow in at 350K [4]. When CO is coadsorbed with low coverages of potassium (i.e. $\theta_K \leq 0.10$), this desorption behavior is unchanged as all the CO desorbs prior to any potassium desorption. However, once a critical potassium coverage is reached such that the two high temperature CO desorption states are present indicating that CO dissociation has occurred, no potassium desorbs until 700K (at a heating rate of 15K/sec). Figure 1 shows a typical desorption spectrum observed in this potassium coverage range when CO is coadsorbed. The desorption maximum is identical to that of the highest CO desorption state (700K), suggesting an interaction between K and the dissociated CO species. For K exposures near saturation of the first layer, much less CO can be adsorbed and potassium desorption maxima at both 500K (i.e. clean surface behavior) and 700K (i.e. coadsorbed CO behavior) are observed in the K TPD spectrum. Similar behavior has been seen with coadsorbed oxygen, both on Rh(111) [4], Pt(111) [5] and Ni(111) [6]. Attempts to observe the desorption of potassium oxides

(i.e. KO, K₂O, KO₂) were made, but no signals from these species were detected. Very small amounts of CO₂ were detected at 700K.

4. DISCUSSION.

Preadsorbed K broadens the coadsorbed CO desorption spectrum by 100K for $\theta_K < 0.10$, and induces new desorption states in the potassium coverage range $0.10 < \theta_K < 0.36$. Isotopic mixing measurements have demonstrated that these high temperature states are due to recombination of carbon and oxygen produced by the dissociation of adsorbed CO. The extent to which scrambling of the isotopically labelled CO molecule occurs depends on both K coverage and CO exposure.

From the plot of the fraction of CO dissociated as a function of K coverage (fig. 3) demonstrates that the effect of the alkali on the number of molecules dissociating is very pronounced. Over 80% of the adsorbed CO dissociates at $\theta_K = 0.15$. Using the CO saturation coverage of $\theta_{CO} = 0.75$ for the clean Rh(111) surface, it is possible to determine the number of CO molecule which dissociate per adsorbed K atom. Such a curve is plotted in figure 5 as a function of K coverage. Up to three CO molecules dissociate per coadsorbed potassium atom at a coverage $\theta_K = 0.1$, a very marked effect indeed. The curve rapidly attains a maximum, followed by a gradual decrease. This suggests that, (1) a critical potassium coverage (i.e. potassium separation) is needed to induce CO dissociation, and (2) site blocking by potassium at higher coverages limits CO adsorption. This results in the ratio CO_{diss}/K decreasing slowly as the potassium coverage increases. These competitive effects result in a peak maximum. Recent calculations by Norskov et al

[7] suggests that sites adjacent to the alkali should be very strongly affected by the alkali, whereas the second nearest neighbours experience a much reduced effect. These results are consistent with our data since the number of CO molecules that dissociate is that which would be expected to pack adjacent to an isolated K molecule.

The simultaneous desorption of CO and K in the high temperature state as shown in figure 1 indicates that that potassium and either C or O (or both) are associated with one another, and that the rate limiting step is the decomposition of this surface complex.

Measurement of the scrambling parameter yields a value of p considerably larger than that expected for molecular desorption, confirming that the highest temperature states are indeed due to dissociated CO. The behavior as a function of CO exposure can be explained by assuming that isolated C or O atoms (or both species) have some mobility on the Rh(111) surface. At low CO coverages (fig. 4b) the C and O adatoms from different molecules are sufficiently remote from each other that the probability of scrambling is small. As the CO coverage increases, the fragments from different molecules come into closer proximity and can then scramble. At even higher coverages the atoms become less mobile, either since they are close packed or because they are associated with potassium and are thus immobilized, inhibiting significant scrambling.

Finally, it should be emphasized that EEL spectroscopy shows no evidence that potassium causes CO to dissociate on the Rh(111) surface [1] since no C-metal or O-metal vibrations are observed. TPD evidence clearly indicates that CO does indeed dissociate on a potassium pre-dosed

surface and the absence of any EELS evidence may be suggestive that the dissociation (and scrambling) occur as a concerted process.

5. CONCLUSION.

The coadsorption of potassium with CO on Rh(111) induces dramatic changes in the chemisorption properties of CO. Isotopic mixing measurements verify that CO dissociation occurs with co-adsorbed potassium ($\theta_K > 0.10$) but does not occur on the potassium-free Rh(111) surface. The simultaneous desorption of potassium and CO for the dissociated state indicates that direct interactions are responsible for CO dissociation, and that up to three CO molecules are dissociated per potassium atom.

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Figure Captions.

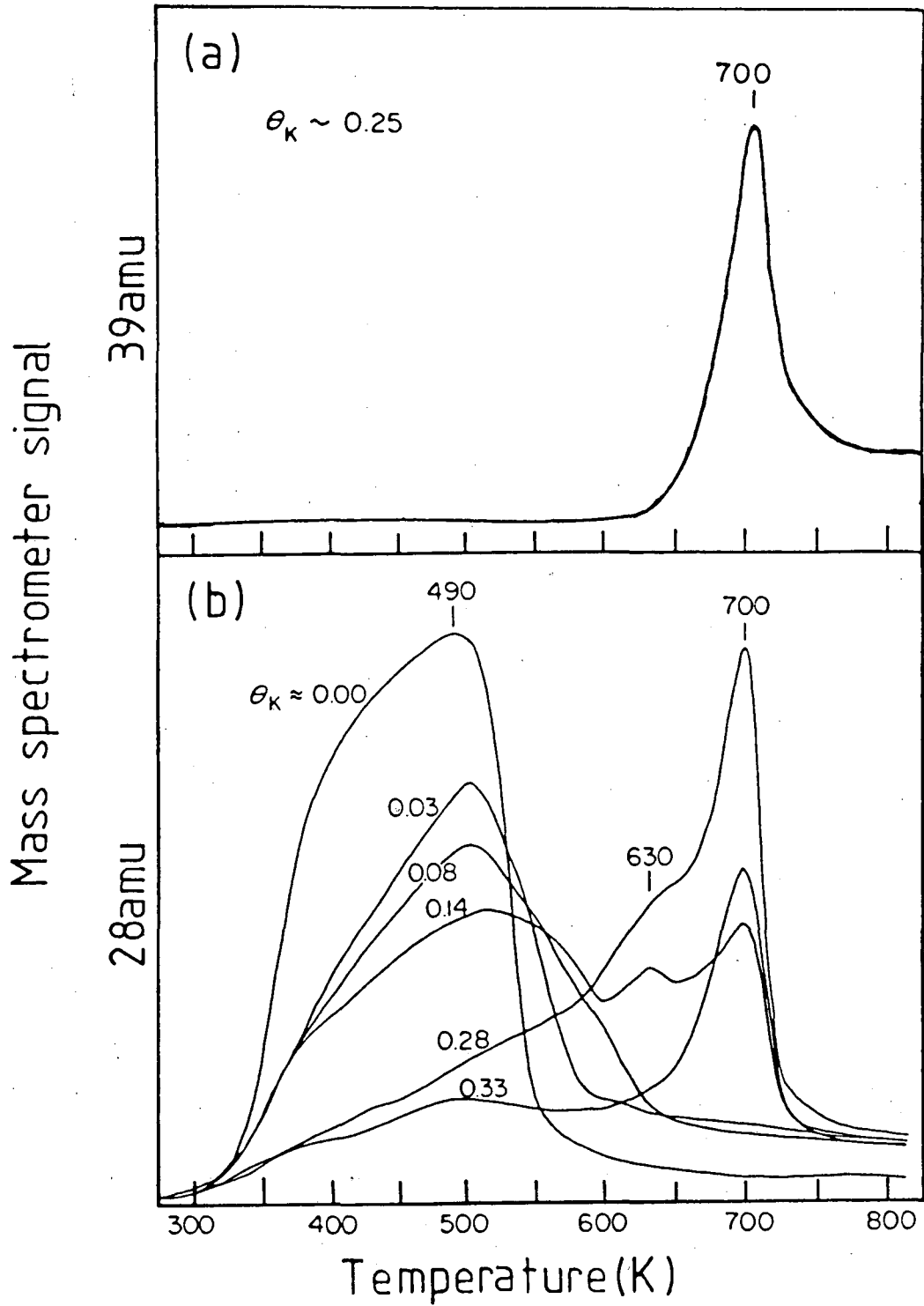
Figure 1. Thermal desorption spectra from co-adsorbed K and CO on Rh(111). (a) at 39amu for saturation CO and $\theta_K=0.25$ (b) at 28amu as a function of K dose for saturation CO exposure.

Figure 2. Thermal desorption spectra after dosing a mixture of $C^{13}O^{16}$ and $C^{12}O^{18}$ onto a potassium pre-dosed surface for $\theta_K=0.1$ and 0.32.

Figure 3. Plot of fraction of CO dissociated on Rh(111) as a function of potassium dose.

Figure 4. Plot of the variation of the scrambling parameter, p, as a function of (a) CO exposure (L) for a potassium coverage, $\theta_K=0.3$ (b) potassium coverage for saturation CO.

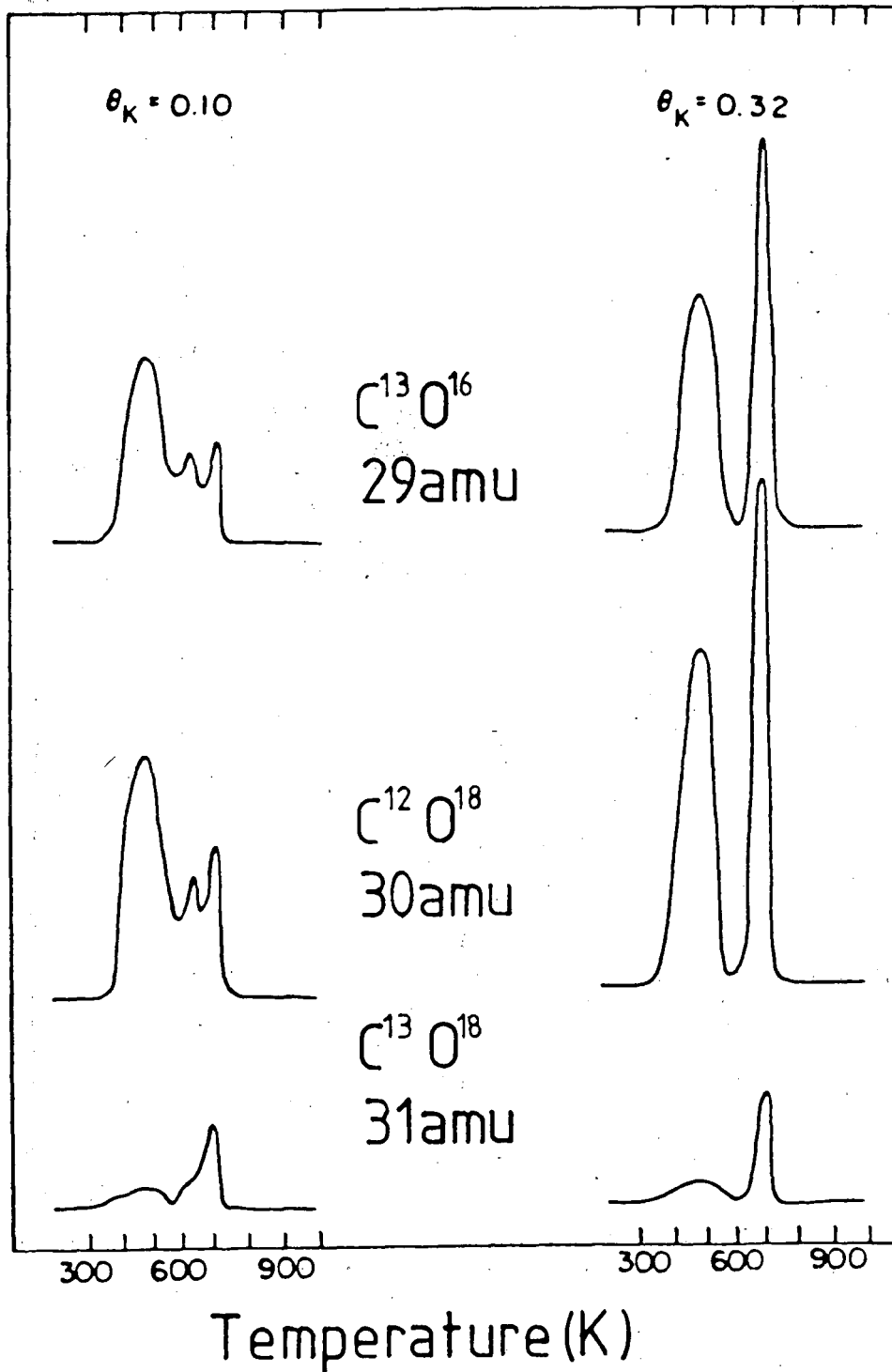
Figure 5. Plot of the number of CO molecules dissociated per potassium atom as a function of potassium coverage.



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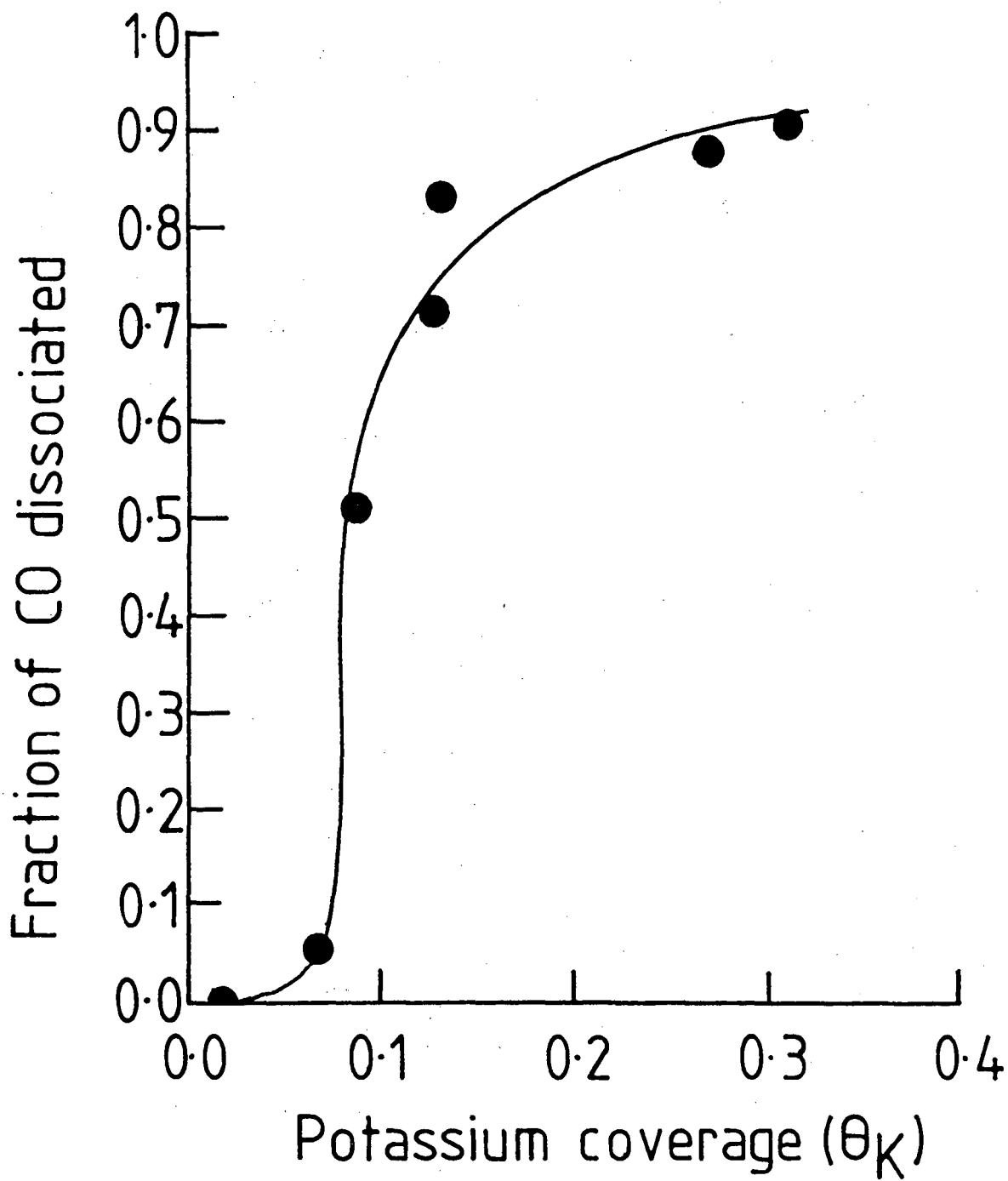
Figure 1

Mass spectrometer signal



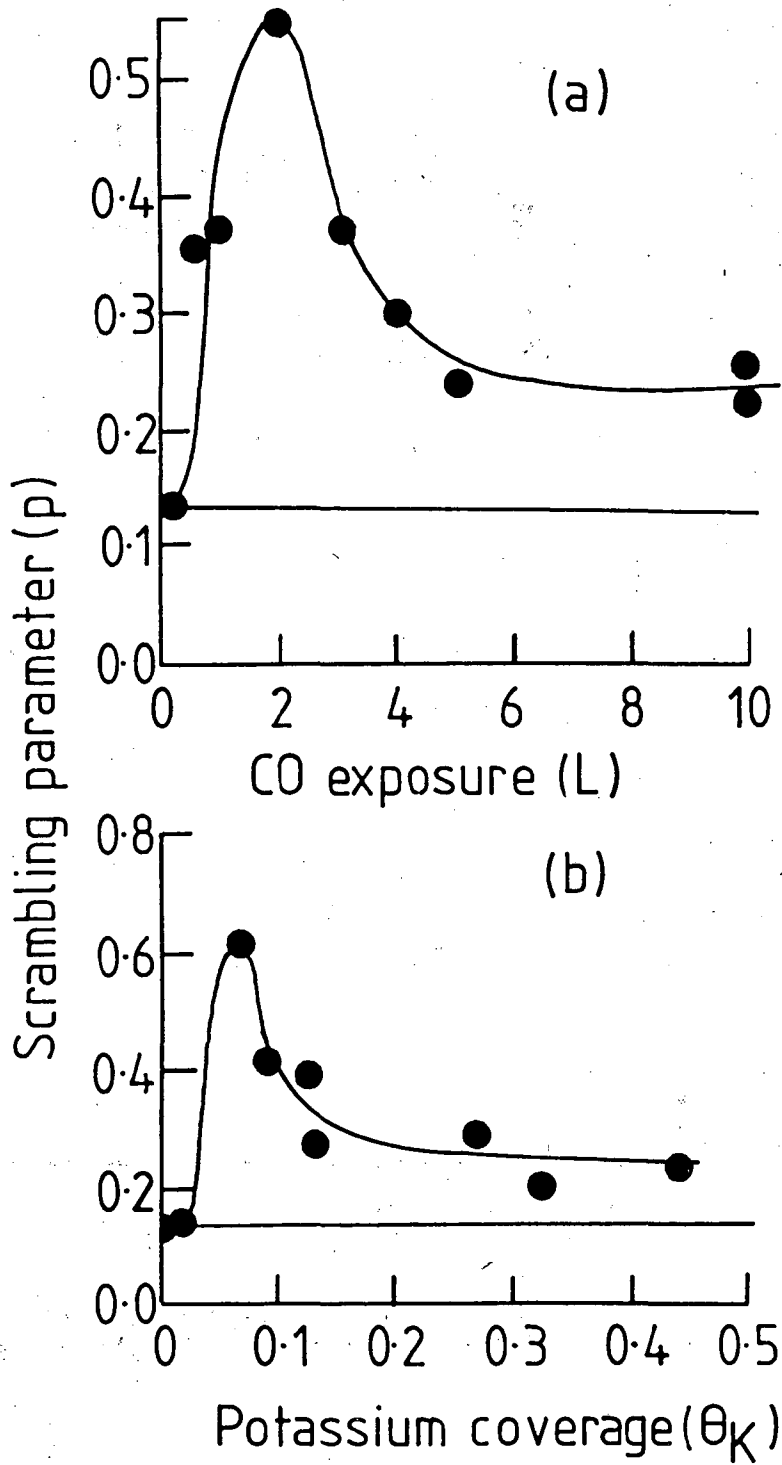
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Figure 2



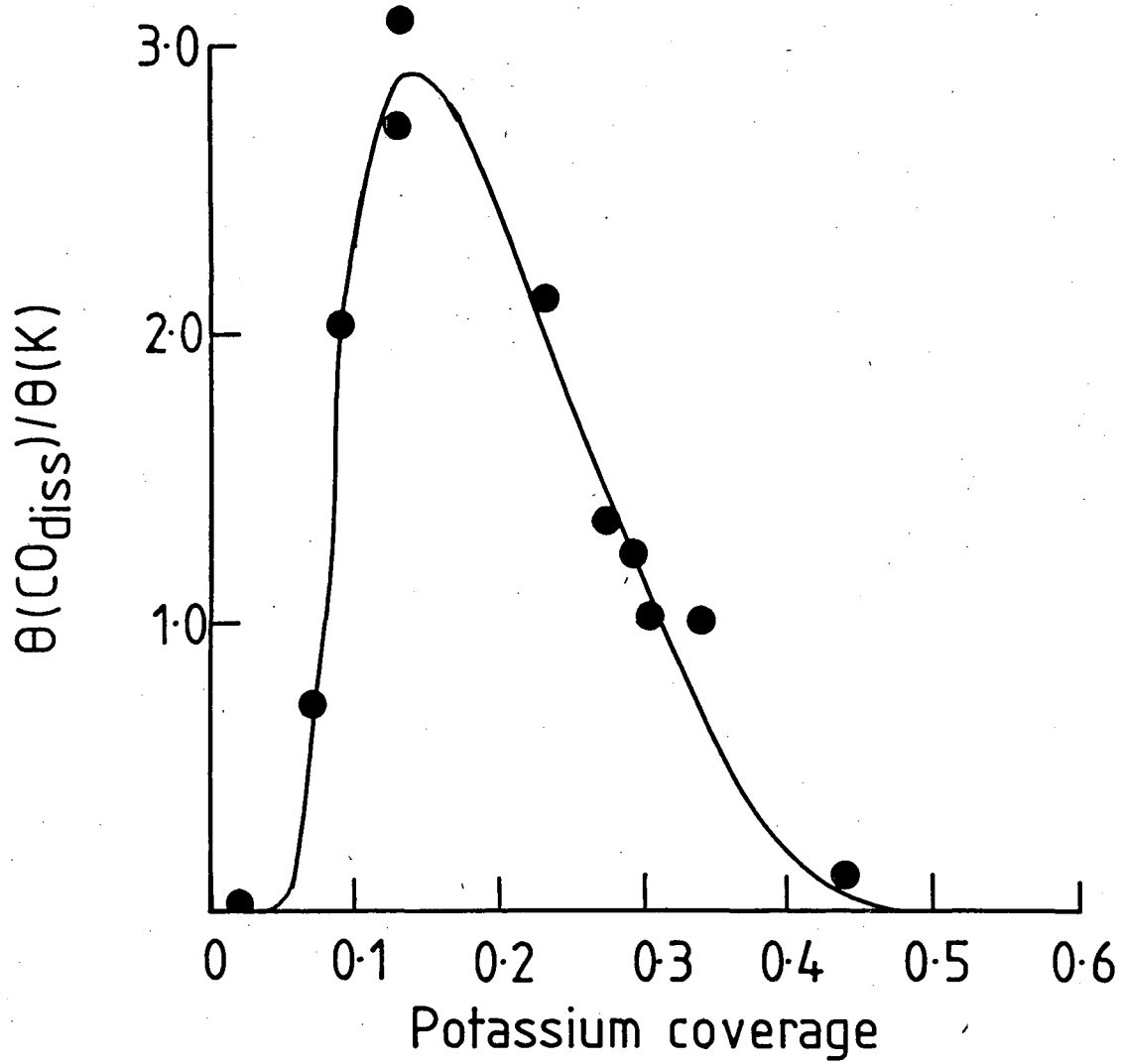
XBL 847-3014

Figure 3



XBL 847-3015

Figure 4



XBL 847-3016

Figure 5

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