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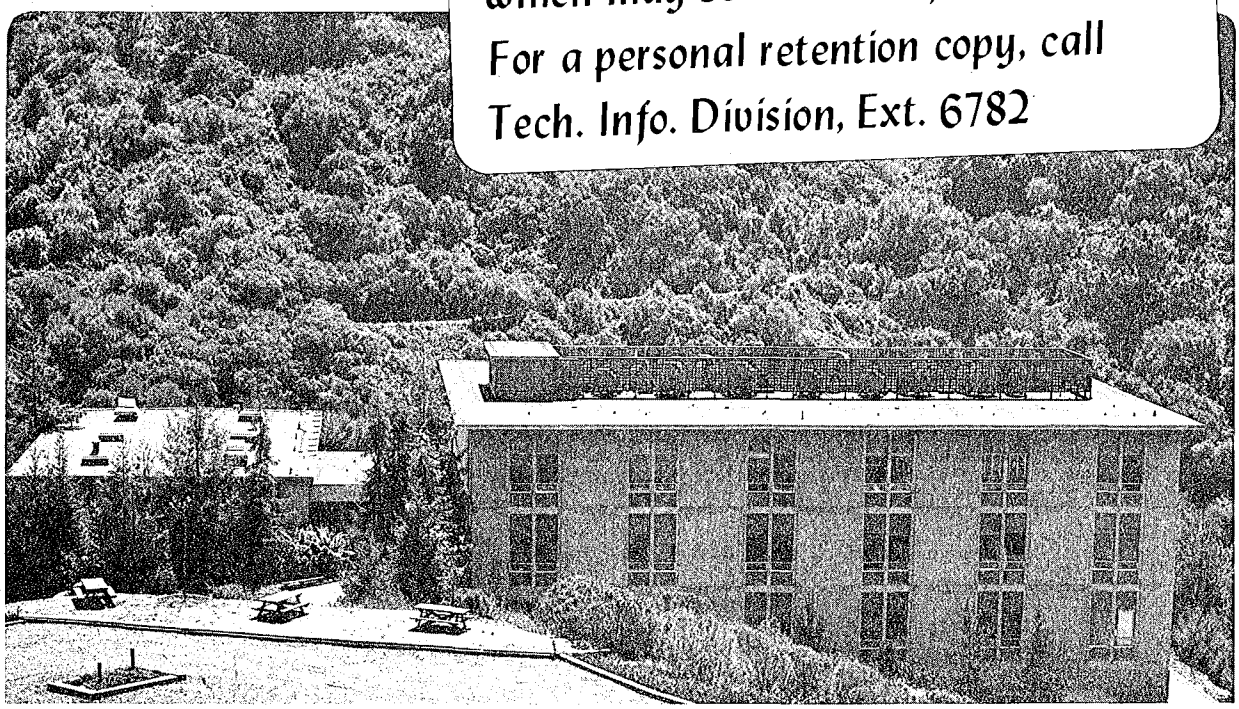

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# EVIDENCE FOR CO DISSOCIATION ON RHODIUM SURFACES

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Abstract

Carbon monoxide adsorbs molecularly on rhodium surfaces at 300K, but if the rhodium samples are heated in the presence of carbon monoxide, there is evidence for carbon-oxygen bond breaking at step and/or defect sites. The effects of step and defect site density, subsurface oxygen concentration, and oxygen dissolution into the rhodium lattice on CO dissociation are discussed.

Recent work by Yates, Williams, and Weinberg[1] (hereafter referred to as YWW) has questioned about the probability of carbon monoxide dissociation on rhodium surfaces. They used a combination of isotope exchange, Auger electron spectroscopy (AES), and thermal desorption mass spectroscopy (TDS) to show that the probability of CO dissociation on the flat Rh(111) single crystal surface is neglegible. We are in agreement with this result and have previously shown that carbon monoxide adsorption and desorption from both the Rh(111)[2,3] and Rh(100)[2] surfaces is molecular. We disagree, however, with their conclusion--based on the results from the Rh(111) surface--that CO dissociation is neglegible on <u>all</u> rhodium surfaces. A great deal of experimental evidence indicates that CO dissociates on rhodium surfaces with irregularities (steps, kinks, and defects) at elevated temperatures. In this letter we will summarize these studies which indicate CO dissociation occurs on both stepped[5,7,8] and polycrystalline[9] rhodium surfaces and discuss the relationship of these results to those of YWW.

When a CO TDS experiment is performed by adsorbing carbon monoxide on a clean rhodium surface at or below 300K, all detected CO desorption (m/e=28) occurs below 550K. (See References 1-3, 5, and 8-11 for examples of typical spectra.) This is the case for all rhodium surfaces studied to date: flat,[1-3,10] stepped,[5,8] kinked,[12] and polycrystalline.[9,11] In all cases this peak is attributed to the desorption of molecular carbon monoxide. For stepped, kinked, and polycrystalline rhodium surfaces, these results can be misleading and

Encl. - Figures 1 and 2

complimentary AES or high resolution electron energy loss (ELS) studies are needed in order to obtain a more complete understanding of the CO/Rh chemisorption system.

We have previously shown that if carbon monoxide is adsorbed on a clean, stepped rhodium surface and the crystal subsequently heated to 675K to desorb all of the molecular CO, AES studies indicate that carbon is still present on the surface.[5] This carbon disappears when the sample is heated above 975K in vacuum. This surface carbon can also be removed by heating the rhodium sample to 1000K in $1 \times 10^{-7}$ torr of oxygen (a standard crystal cleaning procedure). The temperature dependence of the carbon AES signal from CO adsorption on a Rh(331) single crystal surface at 270K is shown in Figure 1. Although TDS studies indicate that most of the carbon has been desorbed as CO by heating to 675K, the carbon AES signal does not noticeably decrease. This is probably due to the different AES cross-sections for carbon and CO, as suggested by Marbrow and Lambert.[8] Our original explanation for the presence of surface carbon (which we still believe is correct) is that CO molecularly adsorbs at room temperature; but as the crystal is heated during the TDS experiments, both desorption and dissociation of the adsorbed species occurs. Usually a high temperature CO TDS peak due to the recombination of surface carbon and oxygen species is seen on surfaces which dissociate CO.[13] However, no high temperature CO desorption peak is observed on rhodium because the oxygen produced during CO dissociation will diffuse into the rhodium lattice rather than recombine with the surface carbon and desorb as CO. Oxygen diffusion into bulk rhodium has been well documented by a

number of research groups in recent years.[2,4-6] If the oxygen concentration in the near surface region is increased by either pretreating the rhodium sample with oxygen or by dissociatively adsorbing carbon dioxide, then some of the carbon present on the surface after desorption of the molecular CO will recombine with oxygen and desorb as CO near 850K.[5] In the absence of excess surface oxygen, carbon will diffuse into the rhodium sample above 900K (see Figure 1). We have previously reported a similar high temperature CO thermal desorption peak from the chemisorption of carbon monoxide on CO and $CO_2$ pretreated polycrystalline rhodium samples.[9] YWW have neglected the effects of oxygen dissolution into the rhodium lattice in the discussion of their results.

We would like to emphasize that in the course of our experiments we have not found any evidence for the dissociative adsorption of CO on rhodium, as YWW have attributed to us, but rather CO adsorption is molecular below 300K and dissociation only occurs as the rhodium sample is heated.[5]

Recent CO and oxygen chemisorption experiments on several rhodium surfaces have produced results which support our original findings. A similar high temperature CO desorption peak was observed during TDS studies on a Rh(110) surface after a high temperature pretreatment in carbon monoxide.[8] The (110) surface can be indexed as a Rh(S)-[2(111)x(111)] surface which means that it has two atom wide (111) terraces separated by one atom high steps.[14] High resolution ELS studies of CO chemisorption on the stepped Rh(331) surface show that CO is molecularly adsorbed at 300K. There is an energy loss peak

(molecular vibration) at 1930 $cm^{-1}$ which can be assigned to the C≡O stretch of molecular CO associated with step atoms.[7] This peak disappears when the rhodium surface is heated to 450K, which is well below the temperature of the molecular CO TDS peak (500-575K, depending on the initial coverage and heating rate). Unfortunately no low frequency rhodium-carbon stretching vibration was reported. (This mode could be hidden beneath the relatively intense Rh-CO stretch at 430 $cm^{-1}$.[3]) However, these results are consistent with molecular CO adsorption at 300K followed by dissociation at step sites at elevated temperatures. Finally, infrared studies by Primet[15] have shown that carbon monoxide is dissociated on highly dispersed rhodium particles supported on a zeolite or alumina base.

On polycrystalline rhodium filaments, a high temperature CO desorption peak was not detected after CO pretreatment.[11] Differences in subsurface oxygen concentration and/or experimental conditions could be causing this discrepancy. Unfortunately, in situ AES measurements were not made in these experiments, so it could not be determined whether CO dissociation was occurring but was not detected by TDS due to oxygen dissolution into the rhodium sample.

A detailed study of oxygen adsorption on Rh(111) shows that chemisorbed oxygen begins to diffuse into the rhodium lattice at 400K and at least 40% of the saturation oxygen coverage (as determined by AES) must be adsorbed before oxygen desorption is detected.[4] This evidence supports our earlier statement that no high temperature (~850K) desorption peak from dissociated CO is observed from either the clean stepped or polycrystalline rhodium surfaces. Oxygen

dissolution into the rhodium lattice is depleting the surface oxygen concentration before it has a chance to recombine with carbon and desorb as CO.

When carbon monoxide is adsorbed on Rh(111) at 300K and the surface heated to 675K, we did not detect any surface carbon by AES; but occasionally a small amount of CO desorption was detected near 850K.[12] This high temperature peak was only seen on Rh(111) surfaces which had previously undergone several oxygen pretreatments (from either cleaning or oxidation studies) before the CO TDS experiments were performed. The amount of CO desorbed at this temperature was much smaller than the amount observed under similar conditions from stepped surfaces and could easily be accounted for by defect sites present on the surface. (The crystal was oriented to within $\pm 0.5$ degrees.) The extent of CO desorption in the high temperature peak could be enhanced by annealing the Rh(111) single crystal in carbon monoxide as shown in Figure 2. The Rh(111) crystal was annealed for 10 min. in $1 \times 10^{-7}$ torr of CO at 670K, then cooled in vacuum. The peak at 530K is due to the desorption of molecular CO from the adsorption of background CO on the surface during the cooling process while the peak at 830K is due to the recombination of surface carbon and oxygen. We have reported a similar enhancement on polycrystalline rhodium foils.[9]

In the YWW CO isotope exchange experiments where the Rh(111) crystal is heated in a flowing mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$, they only conclusively show that the low temperature CO desorption peak (~550K) is from molecular not dissociated CO. They only report results for

temperatures less than 800K, well below the desorption temperature of dissociated CO on stepped[5] or polycrystalline[9] rhodium surfaces (~850K). After pumping out the CO mixture and flashing the Rh(111) crystal to 850K in vacuum to remove the chemisorbed CO, YWW observe a significant carbon AES signal (~1/3 monolayer). These results actually support CO dissociation because the temperature range of the isotope exchange experiments is high enough for CO dissociation and oxygen penetration into the rhodium lattice to occur but not high enough for the recombination and subsequent desorption of dissociated CO. YWW suggest that trace hydrocarbon impurities in their vacuum system may also be responsible for the carbon deposition.

The CO TDS experiments of YWW on clean Rh(111) produced no high temperature CO desorption peak, in agreement with previous results.[2,3,10] CO adsorption on a Rh(111) surface which had been annealed in CO showed a slight attenuation of the low temperature molecular CO desorption peak but no desorption from a high temperature state. The slight attenuation of molecular CO desorption would be expected from a blockage of CO adsorption on a small number of sites (steps and/or defects?) due to CO dissociation at these sites during the CO pretreatment. YWW did not indicate whether AES was used to determine if carbon remained on the surface after the carbon monoxide pretreatment. There are several possible explanations why YWW did not observe a high temperature CO desorption peak. The oxygen concentration in the near surface and/or bulk regions of their rhodium crystal may be different than ours. Since the subsurface oxygen concentration can control the extent of oxygen dissolution, this could have a

significant effect on whether the oxygen atoms produced from CO dissociation dissolve into the rhodium lattice or recombine with carbon and desorb as CO. Because of the oxygen "threshhold effect" on rhodium surfaces (discussed in Reference 4), much longer annealing times in CO would be required on the low step and defect site density (111) surface than on a stepped surface or polycrystalline foil. The longer annealing times are necessary to generate a sufficient oxygen concentration in the near surface region to insure recombination with carbon and desorption as carbon monoxide, but YWW only employed CO pretreatment times similar to those we employed on polycrystalline Rh foil.[9]

As mentioned earlier, we only observed the high temperature CO desorption peak after previous oxygen treatments. Also, we found that a much higher sensitivity (x200) than shown in YWW's Figure 6 was needed to easily observe the high temperature (~850K) CO desorption peak from the Rh(111) surface. YWW state that they can easily detect 0.05 monolayer of dissociated CO. However, the integrated intensity of the high temperature CO desorption peak in Figure 2 after an extensive CO pretreatment is only 0.005 monolayer. This value was obtained by comparing the area of the high temperature CO TDS peak (lower trace) to the molecular CO TDS peak (upper trace) and using an initial carbon monoxide sticking coefficient of 0.5[4]. Thus we are not surprised that the dissociation of CO was not observed by YWW. This amount of carbon monoxide is consistent with the defect density expected from a $\pm 0.5$ degree misorientation of the crystal.

In summary, we believe that CO adsorption on rhodium surfaces is molecular at 300K but that CO can dissociate at step or defect sites upon heating the rhodium sample in the presence of carbon monoxide. In the course of our experiments we have studied numerous different rhodium samples in three different ultra-high vacuum systems and have obtained reproducible results under a variety of controlled conditions. For YWW to conclude that CO dissociation cannot occur on stepped or polycrystalline rhodium surfaces based only on their results on Rh(111) is tenuous at best in light of the very low step and defect site density on this surface, the effect of oxygen dissolution into the rhodium lattice and alternate interpretations of their results presented here.

Acknowledgment

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Figure Captions

1. Auger electron spectra of CO chemisorption on the Rh(331) single crystal surface as a function of substrate temperature. Peak energies are in eV.

2. CO TDS spectra (m/e = 28) after the adsorption of 0.1 L of CO (upper trace) on Rh(111) at 270K. After this surface is heated to 670K for 10 min. in 1 x $10^{-7}$ torr of carbon monoxide and cooled in vacuum, the high temperature CO desorption becomes clearly visible (lower trace). The peak at 530K is due to the desorption of residual CO which absorbed on the surface during the cooling process.

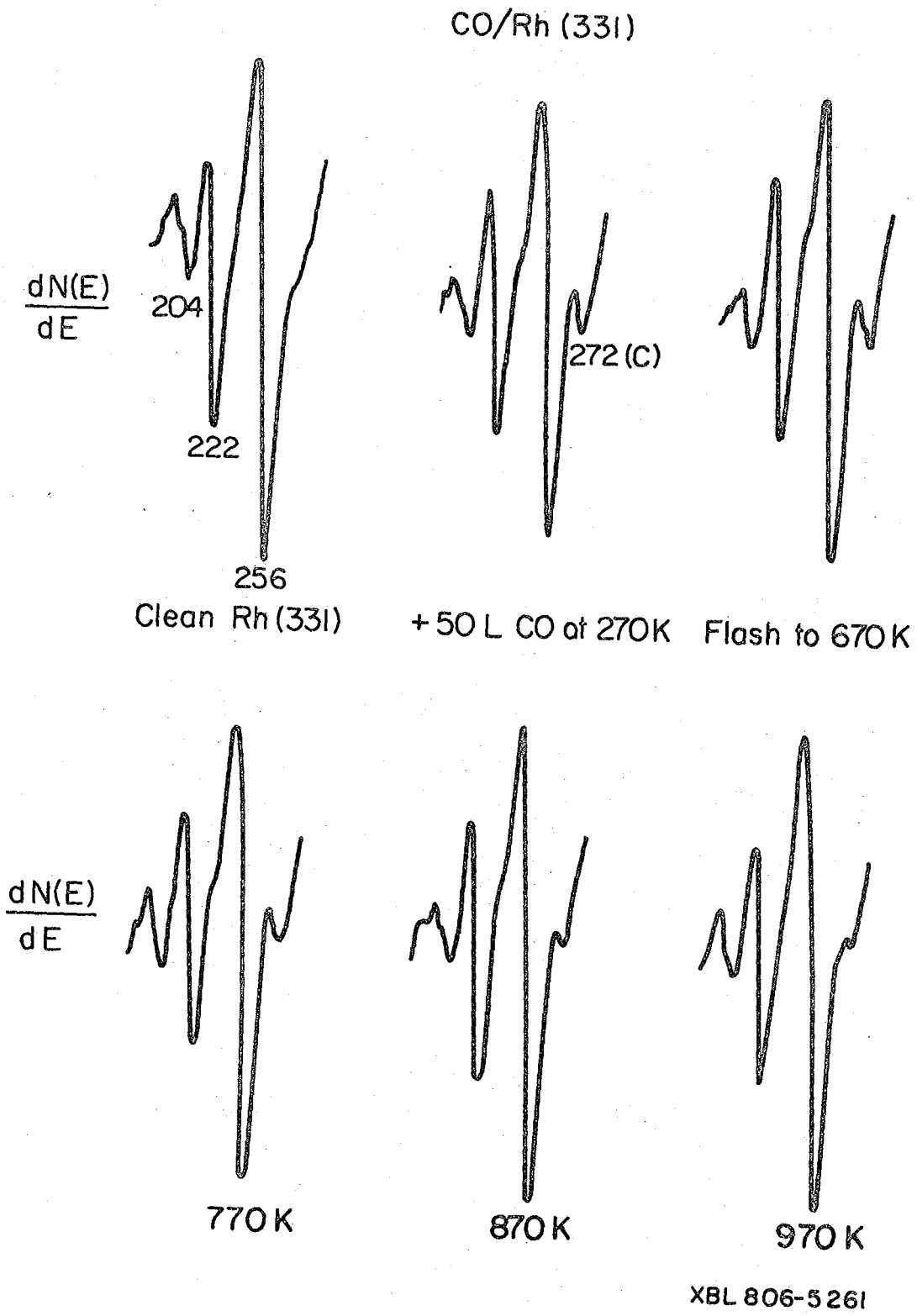
CO/Rh (331)
dN(E)/dE
204
222
256
272 (C)
Clean Rh (331)
+50 L CO at 270K
Flash to 670K
dN(E)/dE
770K
870K
970K
XBL 806-5261

Fig.1

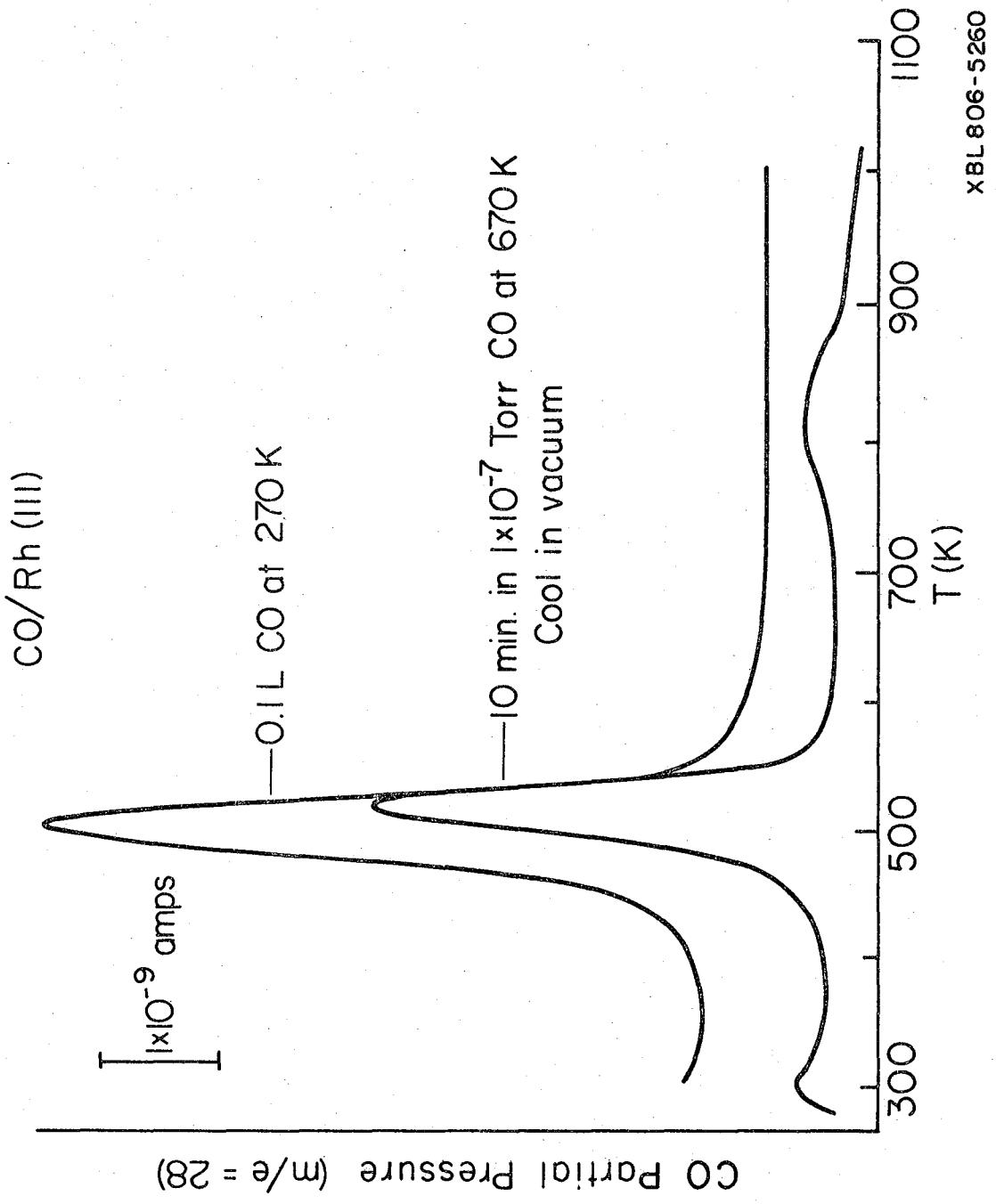
CO/Rh (111)
0.1 L CO at 270 K
10 min. in 1x10^-7 Torr CO at 670 K
Cool in vacuum
1x10^-9 amps
CO Partial Pressure (m/e = 28)
300
500
700
900
1100
T (K)
XBL 806-5260

Fig.2

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