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ABSTRACT

The adsorption and desorption of oxygen, carbon monoxide, deuterium and ethylene has been studied over rhenium films using thermal desorption spectroscopy, low energy electron diffraction and Auger electron spectroscopy. The films, obtained by evaporating rhenium onto a platinum (111) single crystal, grow over the substrate forming (0001) basal plane rhenium surfaces. Oxygen chemisorbs on this film, forming an ordered structure, consisting of three (2x1) overlayer domains and giving a saturation coverage of half a monolayer of atomic oxygen. CO chemisorption is mainly molecular, although some dissociation occurs at temperatures above about 700K. A complicated LEED pattern is obtained when saturating the surface at 150K with CO, but it changes to a (2x2) or (2x1) structure upon heating. Also, CO chemisorption can be modified by predissociated CO or preadsorbed oxygen on the rhenium surface. Deuterium desorbs in three peaks, starting at temperatures as low as 150K. Ethylene desorbs partially intact at around 250K, the rest decomposing and yielding hydrogen, that appears as two main peaks at 357K and 460K during thermal desorption. We conclude that epitaxially grown films may be an alternative to single crystals for studying chemisorption over well ordered surfaces.

INTRODUCTION

Chemisorption studies are usually carried out at low pressures (10^{-8} - 10^{-6} torr) using single crystal surfaces of materials. The question arises how one would study the surface chemistry of substances that are not readily available in single crystal form. It is desirable to determine the chemisorption properties or the reactivity on ordered surfaces because the surface chemical bonds of adsorbates are structure sensitive. It appears that by epitaxial deposition of thin layers of metals on single crystal surfaces of other metals one may be able to study the surface chemistry of those solids that cannot readily be obtained as single crystals because of their high reactivity (Cs, Na, B, U, just to mention a few).

In order to compare the chemisorption properties of thin epitaxial deposits with those of single crystal surfaces we have explored the surface chemistry of rhenium films that were epitaxially deposited on platinum (111) single crystal surfaces.

The chemisorptive properties of rhenium crystal surfaces have been studied under ultra-high vacuum conditions by several authors. O_2 , CO, NO, H_2O , H_2 , C_2H_4 and C_2H_2 adsorption at room temperature over Re (0001) single crystals have been characterized using different surface science techniques [1-7]. Adsorbed oxygen dissociates on the surface even at room temperature, forming an overlayer that has been proposed to be a surface oxide [1]. Carbon monoxide adsorbs on top of the metal atoms and remains molecular up to 500 K, where desorption of some of the molecules takes place. At 600 K a small fraction of carbon and oxygen is present on the surface, products of CO dissociation, and they recombine at 800 K and

desorb [1-4]. Hydrogen exhibits second order desorption kinetics, with activation energies of 20 Kcal/mole [5]. Ethylene partially decomposes upon adsorption at room temperature, and subsequent H₂ thermal desorption shows two additional decomposition temperature regimes at about 425 and up to 700 K [6]. Results on stepped surfaces [2,5,8] and foils [9-11] have also been reported.

In the present study we investigated the chemisorption of small molecules at 150 K over crystalline rhenium films grown over platinum (111) single crystal surfaces. The films grow epitaxially, with the hexagonal (0001) orientation so the resulting rhenium surfaces resemble that of the basal plane of single crystals. In fact, the adsorption results obtained here agree very well with those previously reported for Re (0001). Adsorbed oxygen orders, forming a (2x2) or (2x1) overlayer, and does not desorb up to 1000K. CO adsorbs molecularly and also orders on the surface, but between 5 and 10% dissociates above 700K (the rest desorbs at lower temperatures). The dissociated carbon and oxygen atoms then recombine and desorb at around 800K. The adsorption of CO can be modified by preadsorption of dissociated CO or O₂. Also, due to the low adsorption temperatures, we were able to observe additional desorption states for H₂ and C₂H₄ to those reported in the literature [5,6].

EXPERIMENTAL

Most of the experimental details of the apparatus used for this work has been described in detail previously [12,13]. Briefly, it consists of a ultra-high vacuum (UHV) chamber evacuated with a six inch diffusion pump together with a cryotrap, to achieve base pressures of $6-8 \times 10^{-10}$ torr. The residual gas is composed mainly of air, coming from a virtual leak in the manipulator, and did not affect the results of the experiments reported here. The system was equipped with a four grid retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a glancing electron gun for AES that provides beam currents below $5 \mu\text{A}$, with a beam size of up to 1 mm diameter. A UTI mass spectrometer was used for thermal desorption spectroscopy (TDS). The chamber also have a Bayard-Alpert ion gauge for pressure measurements, an ion sputtering gun for crystal cleaning, three Varian leak valves for controlled introduction of gases, and an environmental cell that allow us to isolate the crystal from UHV conditions and expose it to atmospheric pressures of the desired gases. The XPS spectra were obtained in a second chamber equipped with a high pressure cell and a Mg X-ray source and double pass cylindrical mirror analyzer [14].

A Pt (111) single crystal, in the form of a thin disc about 1 cm diameter and less than 1 mm thickness, was used as the substrate for rhenium deposition. The crystal was spotwelded to a sequence of 0.020" diameter platinum and 0.060" diameter gold wires, and finally clamped to two thick copper rods. This arrangement permits heating of the crystal resistively to above 1300 K without significant heating of any other part of the chamber [13]. One of the gold wires was also in contact with an electrically isolated liquid nitrogen

reservoir, that made possible to cool the sample below 150K in less than five minutes. The temperature was measured using a chromel-alumel thermocouple pair spotwelded to the edge of the crystal, and the readings were calibrated against the isobutane-isobutene equilibrium constant, as described elsewhere [15].

Rhenium was deposited on the platinum substrate by evaporating it from a 0.020" diameter Re wire, located 3-4 cm away, by heating it resistively up to about 2500K. The main impurities of the resulting film were carbon and/or oxygen. Carbon could be removed by burning it at 750K using stoichiometric amounts of O₂. Oxygen was cleaned by either reacting it with carbon containing molecules, like ethylene, or by mild argon ion sputtering.

High purity gases were used as supplied: H₂ (99.99%, Matheson), D₂ (99.95% chemical purity, 99.5% isotopic purity, Matheson), O₂ (99.9%, Matheson), CO (99.5%, Matheson), and ethylene (99.9%, Matheson). They were introduced into the chamber through a leak valve that had a 1/8" diameter doser attached pointing directly to the crystal. Since only experiments at saturation coverages are reported here, no particular care was taken for measuring accurate exposures. They were estimated using the ion gauge, and were of the order of 30 L (1L = 10⁻⁶ torr·sec) unless otherwise indicated.

RESULTS AND DISCUSSION

The Clean Surface.

Rhenium was deposited on a Pt (111) single crystal substrate by evaporation from a Re filament, as mentioned in the experimental section. Other methods of deposition were tried, including the use of a planar magnetron sputtering gun and the decomposition of dirhenium decacarbonyl deposited under UHV, but these methods were not as reliable as the evaporation technique [16].

The films grow in a layer by layer mode, as indicated by distinctive breaks in the plots of Auger signal intensities versus time of deposition [16]. Thick enough films were grown, so that no platinum peaks were detected by AES. This corresponded to at least a 10 Å thickness (about 3 layers), but much thicker layers were generally deposited to avoid possible changes in the surface properties due to the presence of the platinum underneath. The resulting surface, after cleaning and annealing to 1000K, displayed a hexagonal LEED pattern characteristic of the rhenium basal plane, indicating epitaxial growth of the film. Since the interatomic distances for both metals are similar, the dimensions of the LEED patterns did not change while covering the platinum surface with rhenium (The atomic radii are 1.39 Å for Pt and 1.37 Å for Re). The films were stable upon heating up to about 1100K, but at higher temperatures Re diffused into the Pt crystal bulk.

Auger peak ratios.

An attempt was made to use Auger spectroscopy for quantitative measurements of coverages of various adsorbates. As mentioned earlier, a

retarding field analyzer was used. The signal was recorded as the second derivative of the current through the screen, by adding a small ac voltage (10 V peak to peak) to the retarding field, and filtering the signal at twice the frequency of that modulation, as is commonly done [17]. The primary electron beam had an energy of 1700 eV and the incident angle was 60° to the surface normal.

The spectra for clean Pt and Re, recorded with these settings, are shown in fig. 1. Due to the low resolution, the 161 and 167 eV Re peaks are unresolved, and only one peak at 168 eV is obtained [18]. Other Re peaks are at 178, 217 and 227 eV. The intensity of the peaks, measured as the peak to peak heights, were compared to the Pt ones before the Re deposition. The signal ratio obtained was $\text{Re}(217\text{eV})/\text{Pt}(237\text{eV}) = 0.46$ (fig. 1). From this calibration, the relative cross sections for carbon and rhenium can be estimated. Those values are available for platinum, since a ^{14}C radiotracer technique was recently used in our laboratory to obtain the signal ratio $\text{C}(273\text{eV})/\text{Pt}(237\text{eV}) = 1.61 (\pm 15\%)$ [19].

Finally, a value for the relative cross section of oxygen was estimated in different ways, all based on the carbon to oxygen ratio. Auger spectra of CO saturated rhenium and platinum surfaces were recorded. Also, during the rhenium cleaning process, AES before and after high temperature flashing provided the difference value for the C and O signals, due to desorbing carbon monoxide from recombination. The average over many of these measurements gave a value for the ratio of $\text{C}(273\text{eV})/\text{O}(515\text{eV}) = 1.60$. A list of cross sections obtained for the different Auger peaks, referred to $\text{Re}(168\text{eV})$, is presented in table I. These numbers are only reliable to within 20-30%. They will be used later to estimate absolute coverages.

Oxygen adsorption.

Oxygen adsorbs at temperatures as low as 150K. Once adsorbed, no desorption was observed up to 1100K. An apparent (2x2) LEED pattern was observed at all temperatures above 150K, and it became sharper with increasing exposure of the surface to the electron beam. The O(515eV)/Re(217eV) Auger ratio was 1.2, suggesting a saturation coverage value close to one. As a result of this high coverage, the LEED pattern could be reinterpreted as due to the superposition of three (2x1) domains, as has been proposed previously [1]. This interpretation yields a saturation coverage of at least 0.5, to be compared with the literature value of $\theta_{\text{sat}}=0.4$ [20].

There is evidence suggesting that oxygen dissociates upon adsorption on rhenium. X-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy [1,10,21] clearly indicate the presence of atomic oxygen on the surface. We have used XPS to corroborate the previously reported results [22]. An oxygen 1s peak at 530 eV binding energy (fig. 2a) was observed, characteristic of atomic oxygen. However, no shift in the Re 4f peaks was observed when compared to the signal from the metal, indicating that no oxide was formed [16,22]. In any case, this chemisorbed layer is very stable not only towards heating in vacuum, but also when exposed to high pressures of hydrogen. The oxygen covered surface remains unaltered even after a 1 atm H₂ treatment for several minutes, while heating up to 700K. Finally, further chemisorption of other molecules on the oxygen saturated rhenium surface was almost totally inhibited.

The formation of rhenium oxides when exposing Re(0001) to low pressures of oxygen under UHV has been reported by Ducros and coworkers [1]. They based their conclusion in an observed shift of 1.1 V in the Re

4f XPS signal upon oxygen dosage. However, the oxide thickness was reported to be about 2 Å, and the composition between Re₂O and ReO. This surface oxide would then yield a very small signal that would be obscure by that coming from the metallic bulk; the shoulder at higher binding energies in the spectra are very hard to see. We did not observe any extra features in the Re 4f spectra after low pressure O₂ exposures, but were able to form several oxides after atmospheric treatments, including a state which displayed a 1 V shift in the Re 4f peaks after 1 atm O₂ at close to room temperature [16,22]. We therefore concluded that the result obtained under UHV corresponded to the formation of a chemisorbed oxygen layer, and no oxide formation was detected.

CO adsorption.

Carbon monoxide adsorption was studied using LEED, AES, TDS and XPS. The thermal desorption of CO from the rhenium film is very similar to the one reported in the literature for Re (0001) [1-3,5] (fig 3a). Two α states are seen at low temperatures, with maxima at 335 and 415K, and one β state at high temperature, with maximum at 810K. The temperature for maximum desorption of these peaks correspond to activation energies of 19, 24 and 44 Kcal/mole respectively, as calculated using Redhead equations (assuming first order desorption for the α states, $\nu_1=10^{13} \text{ s}^{-1}$, and second order for the β state, $\nu_2=10^{-2} \text{ cm}^2/\text{s}$, and $\theta_0=10^{14} \text{ molec}/\text{cm}^2$) [23]. The β state peak at temperatures identical to where carbon and oxygen recombine during the cleaning process, and it is believed to correspond to desorption of dissociated carbon monoxide. Since the heating rate in these experiments was 30 K/sec, the α states could not be well resolved. However, changes in thermal desorption peak shape could be brought about

in several ways. The spectrum shown in fig. 3a was obtained after exposing the surface to 30L CO. Much higher doses (more than 1000L) increased the relative amount of CO in the low temperature desorption peak (335K). Also, if the surface was saturated with CO, flashed up to about 700K, and then cooled and resaturated with CO, a spectrum like that shown in fig. 3b was obtained. Finally, if the experiment was performed on a surface exposed to oxygen (half saturation coverage) prior to CO exposure, a TDS like the one in fig. 3c was seen. In this later case a small amount of CO₂ was also detected as a desorption product (fig. 3d).

A diffuse LEED pattern was obtained when the surface was saturated with CO at low temperatures (<150K). This pattern, represented schematically in fig. 4, is similar to the ones reported for Re(0001) [3], and Ru(0001) [24]. It is unstable, and disappears after prolonged exposure to the electron beam. When the surface is heated to 700K, the CO from the α state desorbs, leaving only dissociated carbon monoxide on the surface [4]. At this stage, an apparent (2x2) LEED structure is present, similar to the one reported for oxygen adsorption. Further adsorption of CO on this surface yields a combination of both patterns.

The CO saturation coverage is not well known. The LEED structure mentioned previously has been assigned to either $(\sqrt{3} \times \sqrt{3})R30^\circ$ ($\theta_{\text{sat}} = 0.65$) or three domains of $(\sqrt{3} \times 4)$ ($\theta_{\text{sat}} = 0.75$). Other studies report coverages between 0.45 and 0.5 [2,3]. Our Auger measurements, using a defocussed beam to avoid electron stimulated desorption, gave ratios of $C(273\text{eV})/Re(217\text{eV}) = 0.4$ and $O(515\text{eV})/Re(217\text{eV}) = 0.25$, corresponding to a saturation coverage of about 0.3. Further work is needed to obtain a more reliable value for this quantity.

The O_{1s} XPS spectrum obtained after CO saturation of the rhenium surface at room temperature is shown in fig. 2b. Two peaks at about 530.5 eV (from atomic oxygen) and 532 eV (from molecular CO) were observed. This means that some dissociation of CO may take place at room temperature, contrary to the results obtained by Ducros et al [1].

Results reported in the literature concerning heats of desorption of CO over transition metals are summarized in table II. They refer to experiments performed over the basal planes of the metals. Also, the values reported correspond to saturation coverages. Some molecular adsorption takes place over most metals, with heats of adsorption close to 25 -35 kcal/mole, regardless of the metal within the experimental errors. However, only the most reactive metals are able to dissociate some of the CO molecules, a phenomenon that is manifest in the thermal desorption experiments by the appearance of a second peak at around 900K. Mo and W belong to this group. Metals in the middle of the periodic table, on the other hand, are not able to break the C-O bond, unless an additive like potassium is used [25]. In this respect, rhenium behavior similarly to Mo and W, and approximately 5 - 10% of the total CO adsorbed dissociate at high temperatures, forming carbon and oxygen atoms on the surface that recombine and desorb around 810K.

Deuterium adsorption.

Deuterium adsorbs onto rhenium at temperatures below 150K. The thermal desorption of D_2 after saturation is shown in fig. 5. The peak at 335K corresponds to a previously reported state observed after H_2 adsorption over Re(0001) at room temperature [5]. There is also a shoulder in the high temperature side of the main peak that was also

seen in previous work. Finally, a third low temperature state starts to populate below the lowest temperatures we can obtain with our present experimental conditions. The corresponding activation energies for the second order desorption processes are <14, 19 and 20 Kcal/mole ($\nu=10^{-2}$ cm²/s, $\theta_0=1.5 \times 10^{15}$ molec/cm²).

The heats of adsorption of hydrogen on various metal crystal surfaces are summarized also in table II. In general, H₂ adsorbs over most metal surfaces, dissociatively at very low temperatures, and recombination and desorption of the resulting hydrogen atoms occurs close to 0°C. A molecular adsorption state has also been reported in some cases. No clear trend is observed for the heats of desorption, except perhaps the uniquely low values reported for Pt and Ir(111) surfaces [26,27], and the multiple states observed in the Mo and W(001) and Re (0001) surfaces [28,29].

Ethylene adsorption.

After low temperature saturation of the rhenium surface with ethylene, sometimes a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern would appear. However, this result was not reproducible, and most often no ordered structure would form. Thermal desorption after saturation exhibit partial decomposition of the ethylene. Hydrogen (m/e=2) and ethylene (m/e=27) desorption were followed, and the spectra are shown in fig. 6. Some intact ethylene desorbs giving a peak with maximum at 250K ($E_a < 14$ Kcal/mole), while the rest decomposes, giving hydrogen peaks at 357, 460 and 650K ($E_a = 21, 27$ and 38 Kcal/mole respectively, assuming 1st order desorption). The high temperature region of the H₂ TDS resembles spectra reported earlier on Re(0001) [5,6], but due to the lower adsorption temperatures used in our work, desorption of molecular ethylene could be detected, and an additional low temperature

peak is present in the H₂ TDS. The results reported by Ducros et. al., on the other hand, were performed at room temperature, and some hydrogen evolution was detected during adsorption.

The saturation coverage was estimated using AES. A ratio $C(273\text{eV})/Re(217\text{eV}) = 0.5$ implies a saturation coverage value of about 0.2, instead of $\Theta_{\text{sat}} = 0.13$, as reported by the French workers [6].

Ethylene chemisorption on Re may be compared with its adsorption on other metals. For Ag(111), the ethylene molecule lies flat on the surface almost undistorted at low temperature, until total molecular desorption occurs at 200K [30]. Most metals decompose ethylene at least partially yielding hydrogen gas. The decomposition generally takes place in several stages: for Pt, Rh and Pd(111), the formation of ethylidyne near room temperature has been reported [31]. In the case of Pt, some molecular desorption occurs at 285K, and hydrogen peaks are observed at 297, 492, 550, 641 and 704K in the TDS. This corresponds to the formation of ethylidyne and CH fragments, and to the total decomposition that leaves graphite on the surface respectively [31,32]. Similar processes have been reported for Ni and Ir(111) [33,34], although these systems have been less well characterized. Total decomposition with H₂ peaks at 280, 300 and 450K in TDS have been reported for W(100) [35,36]. In the case of Mo(100), molecular desorption occurs mostly at 150K, and decomposition yielding H₂ peaks at 350 and 460K [37]. Our results on Re(0001) are very similar to those obtained for molybdenum, as it would be expected.

CONCLUSIONS

In this work the adsorption of small molecules (O_2 , CO, D_2 and C_2H_4) on rhenium films was studied. Oxygen chemisorbs dissociatively, forming an ordered overlayer that passivates the surface from further adsorption. CO adsorption is molecular at low temperatures, but a small fraction dissociates above 700K. These dissociated species change the site distribution for additional CO uptake. Oxygen coadsorption also changes CO adsorption in a similar way. D_2 desorbs in three different temperature regions, starting at temperatures as low as 150K. Finally, ethylene desorbs partially intact, and the rest decomposes forming hydrogen (that desorbs giving three different peaks) and carbon (that remains on the surface). The activity of rhenium can then be placed in between that observed for Pt and Mo, with more similarities with the Mo case. Most of these results are in excellent agreement with those reported previously for Re(0001) single crystal surfaces. This means that epitaxially grown films may mimic the behavior of single crystal surfaces of the same orientation. Therefore, film growth could be an alternative for studying chemisorption on ordered surfaces, especially for cases when the material is highly reactive, where handling and cleaning of single crystals is difficult.

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FIGURE CAPTIONS

Fig. 1 Auger electron spectra of a clean Pt(111) single crystal and a rhenium film, using a retarding field analyzer. The incident electron beam energy was 1700 eV, at an incident angle of 60° . The field was modulated with a 10 V peak to peak ac voltage (2 V for energies under 110 eV).

Fig. 2 O_{1s} X-ray photoelectron spectra from a rhenium film surface after O_2 (a) or CO (b) saturation at room temperature.

Fig. 3 CO thermal desorption spectra from rhenium film surfaces. a) After CO saturation at 150K. b) After CO saturation at 150K, heating to 700K and CO saturation again at 150K. c) After O_2 adsorption to half saturation and posterior CO saturation at 150K. d) CO_2 trace for the same experiment as c). Heating rate ~ 30 K/sec.

Fig. 4 Schematic LEED pattern obtained after CO saturation of a Re film at 150K. The dark dots represent the rhenium surface, while the open circles are due to the CO overlayer. Heating rate ~ 30 K/sec.

Fig. 5 D_2 thermal desorption spectrum from a rhenium film after saturation at 150K. Heating rate ~ 30 K/sec.

Fig. 6 Ethylene and H_2 thermal desorption spectra from a rhenium surface saturated with ethylene at 150K. Heating rate ~ 30 K/sec.

Table I

Auger relative cross sections.

$V_{pp} = 10 \text{ V}$, $E_p = 1700 \text{ eV}$.

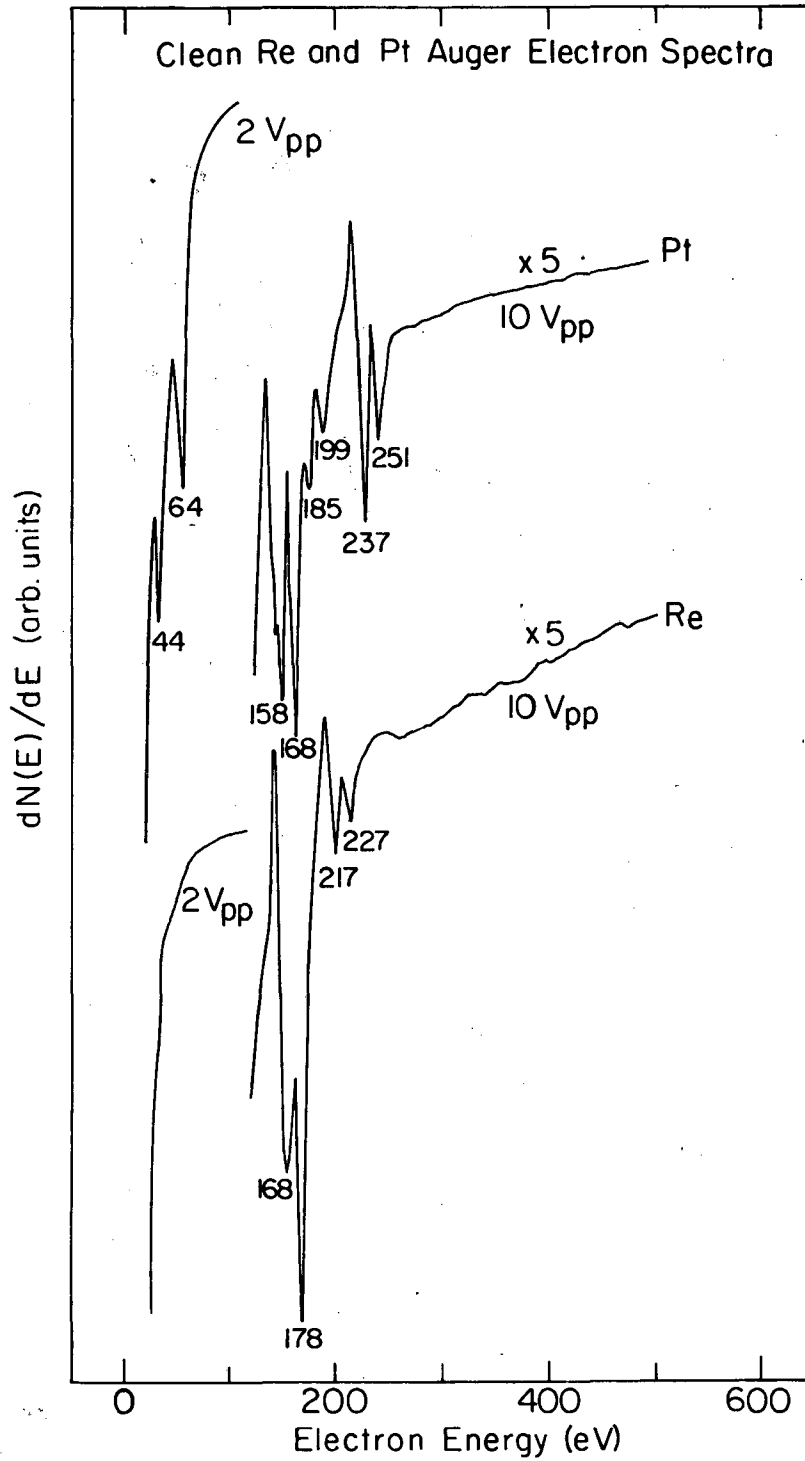
Peak	Relative cross section
Re(168eV)	1.00 (reference)
Re(217eV)	0.32±0.04
Pt(237eV)	0.7 ±0.2
C(273eV)	0.4 ±0.1
O(515eV)	0.25±0.07

Table II

Heats of desorption for CO and H₂ over the basal plane
of transition metal single crystals surfaces.^a

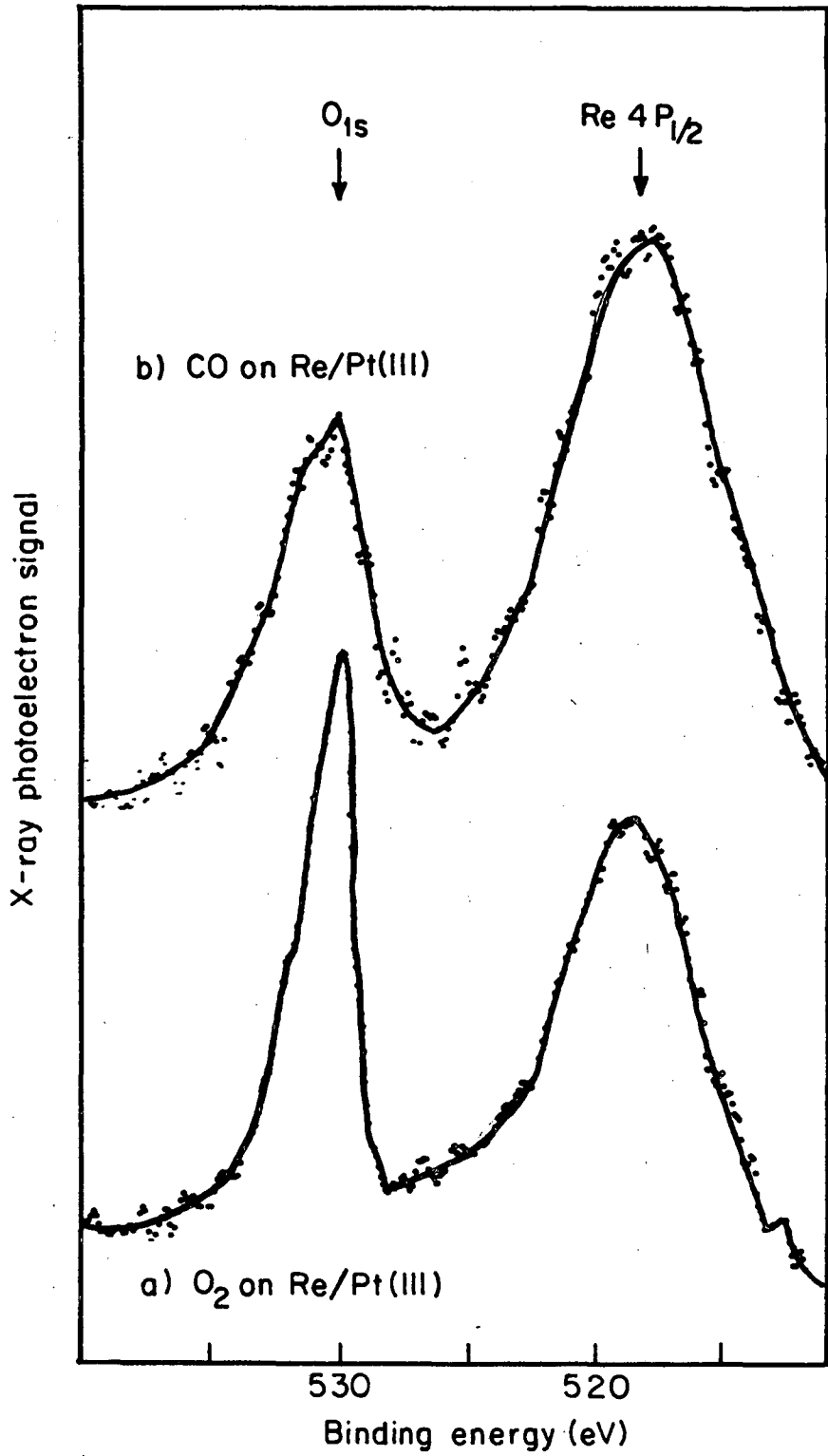
Surface	CO		H ₂		Reference
	Molecular	Dissociated	Molecular	Dissociated	
Mo(100)	~25	85	16	20,27	28,38,39
W(100)	~25	83,86	11	14,22,30,37	29,40
Fe(100)	20,24	50	18	24	26,41
Ru(0001)	23,28	—		15	42
Co(0001)	25	—		16	43,44
Rh(111)	32	—		19	45,46
Ir(111)	39			9	27,47
Ni(111)	26	—	<20	23	48
Pd(111)	34	—		23	49,50
Pt(111)	28	—		~7,9.5	51,52
Cu(111)	12	—			53
Ag(111)	5	—			54
Re(0001)	19,24	44	<14	19,20	our work

a) ΔH_d , in kcal/mole.



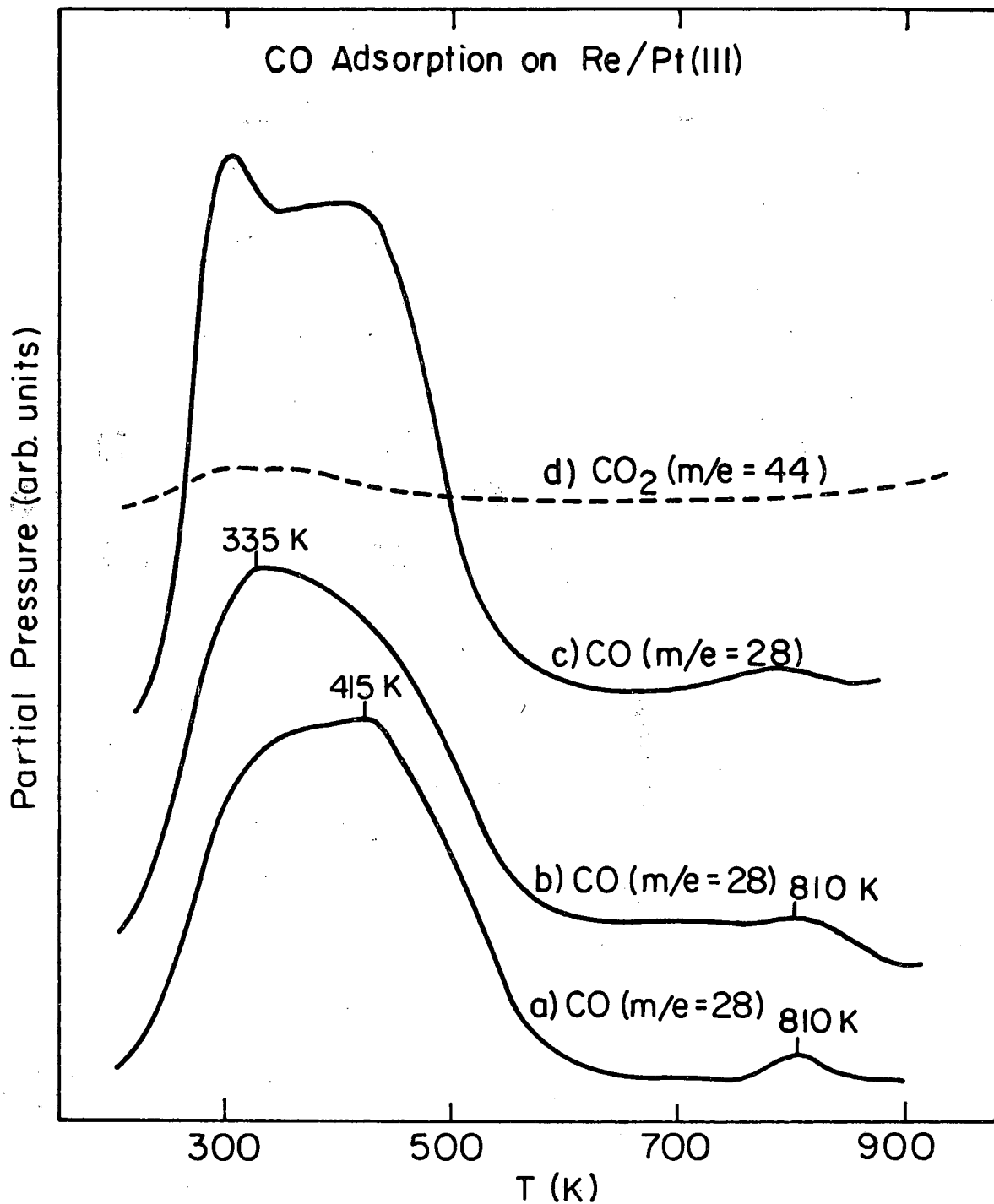
XBL 843-6703

Fig. 1



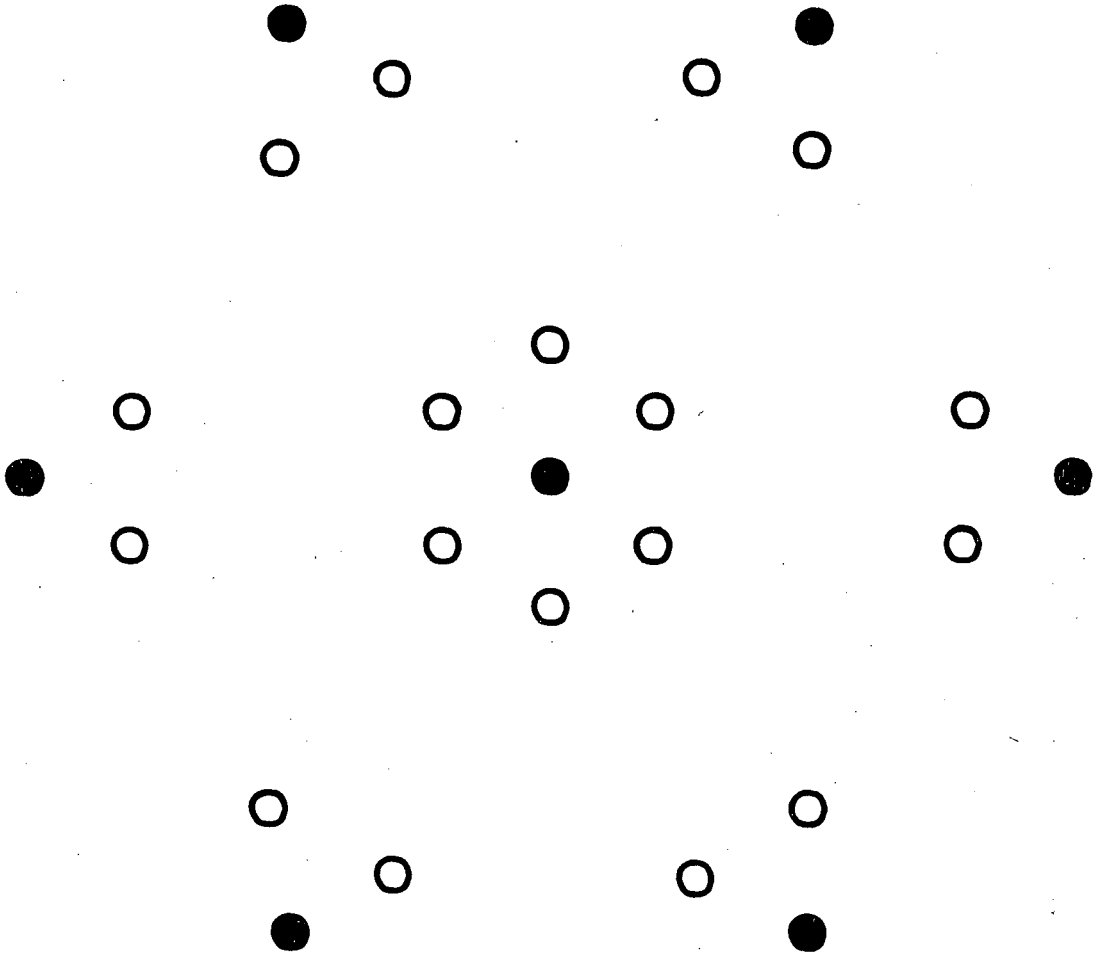
XBL 849-7358

Fig. 2



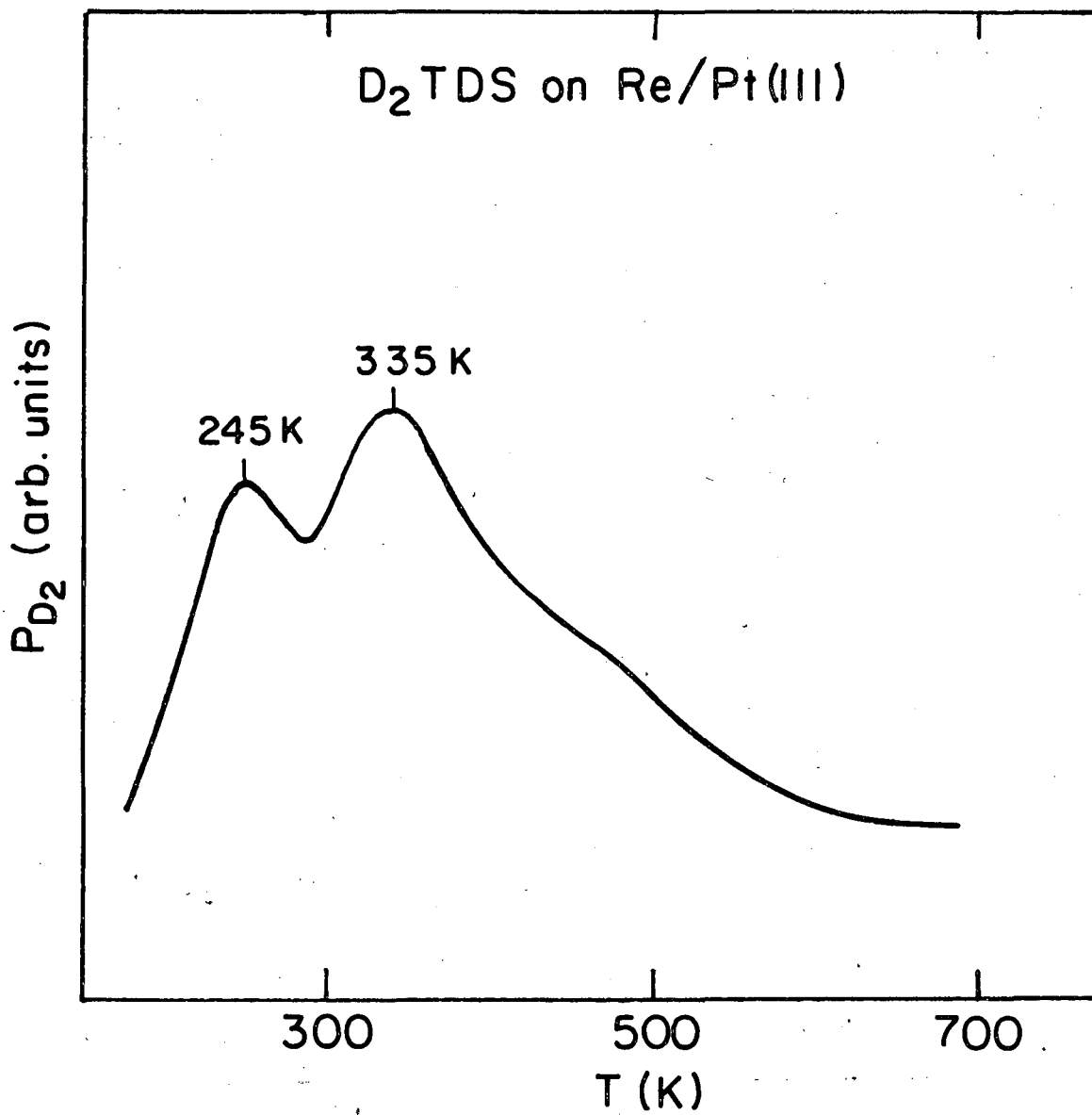
XBL 843-6704

Fig. 3



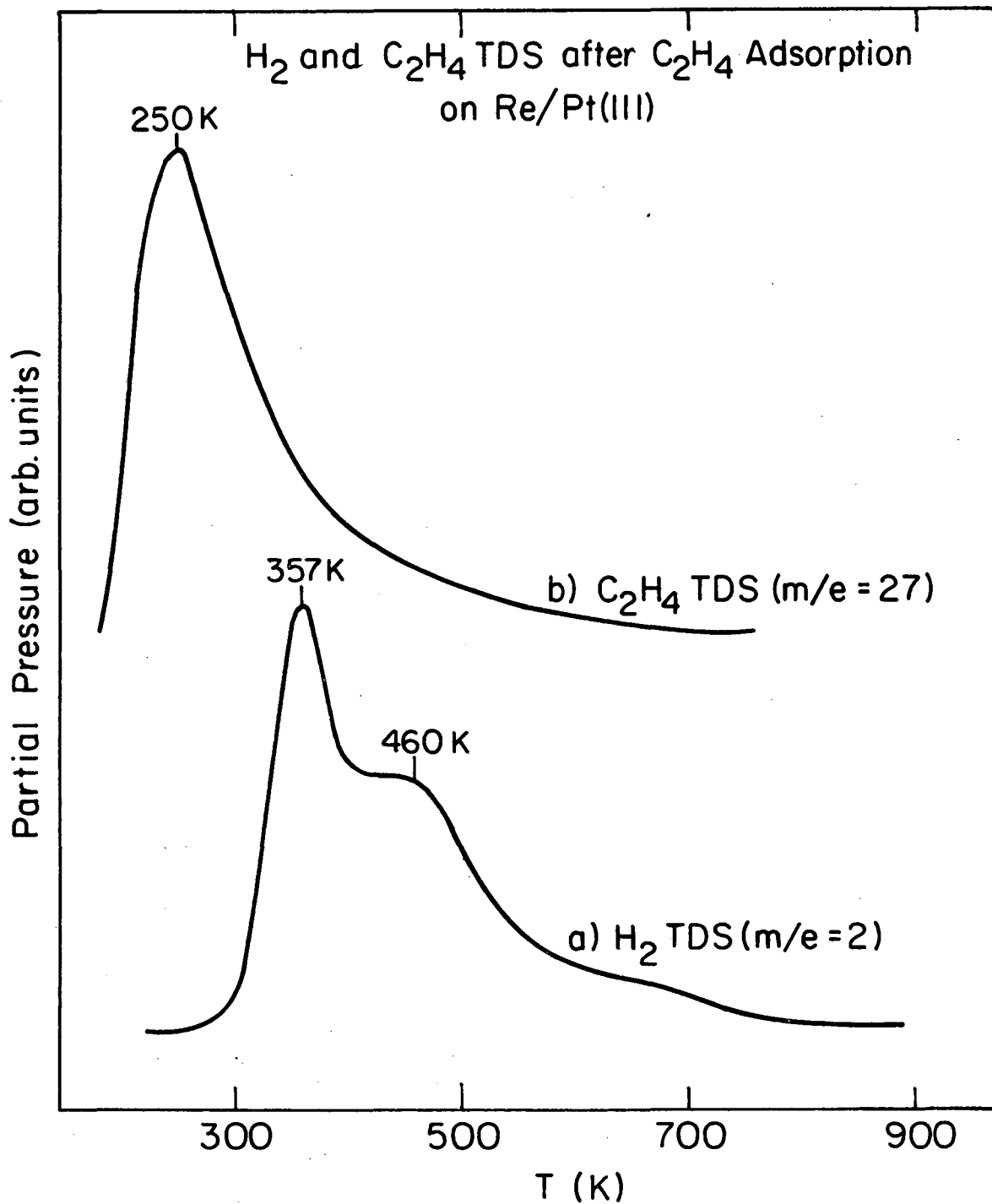
XBL 843-6707

Fig. 4



XBL843-6705

Fig. 5



XBL 843-6706

Fig. 6

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