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ADSORPTION ON Pt(111) AND Pt(100)

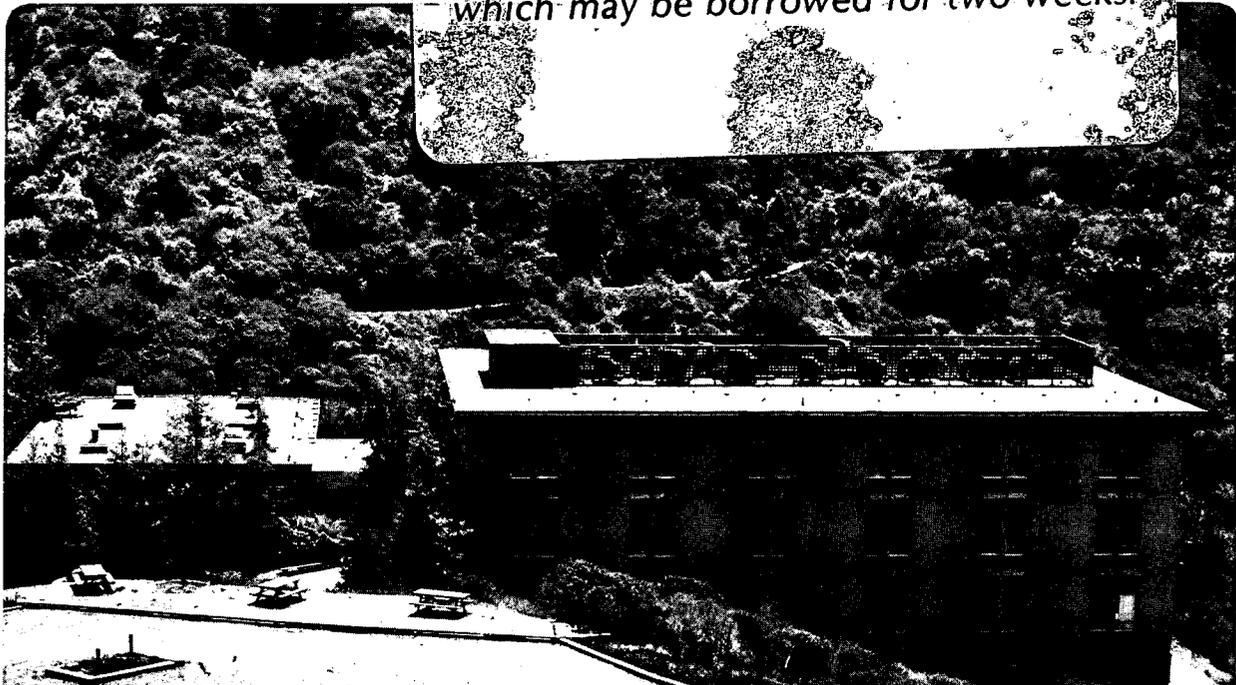
G.N. Derry and P.N. Ross

April 1984

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ABSTRACT

Oxygen adsorption on Pt(111) and Pt(100) was investigated using a Kelvin probe to measure adsorbate induced work function changes. The variation of  $\Delta\phi$  with  $\theta$  was linear ( $p = 0.103$  debye/atom) on Pt(111) even up to  $\theta_{\max} \sim 7 \times 10^{14}$  atoms  $\text{cm}^{-2}$ . On Pt(100), there was an abrupt increase in  $\Delta\phi$  at low coverage ( $< 1 \times 10^{14}$  atom  $\text{cm}^{-2}$ ) which was presumed to be adsorption at defect sites ( $p = 0.62$  debye/atom). Sticking coefficients were calculated from the rate of change of the work function with time. For room temperature adsorption on Pt(111), the sticking coefficient followed the functional form  $S_0(1 - \vartheta)^2$ ,  $\vartheta = \theta/\theta_{\max}$ , and  $S_0 = 0.038$ . On Pt(100) the functional dependence was more complex with an initial increase in  $S$  (from  $S_0 = 0.042$ ) to a of  $\sim 0.1$ , then an approximately quadratic decrease as the coverage increased to saturation. The maximum coverage observed in room temperature dosing of either surface was  $\sim 3 \times 10^{14}$ . However, dosing at 200–300°C at  $10^{-5} - 10^{-4}$  torr induced coverages as high as  $7-9 \times 10^{14}$  on both surfaces. The isosteric heat of adsorption was measured from

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equilibrium isotherms and found to be  $232 \pm 36 \text{ kJ mol}^{-1}$  with a coverage dependence less than the experimental precision. For Pt(111), it is postulated that population of the high coverage state proceeds via the activated process of direct dissociation, whereas the unactivated room temperature process is via the molecularly adsorbed precursor. For Pt(100), population of the high coverage state involves activated transitions in the Pt surface structure which require further study.

## I. Introduction

The adsorption of oxygen on a platinum surface has been the subject of numerous studies. These efforts have produced a great deal of information, but there are many unanswered questions remaining. Most recent investigations have been done using single crystal surfaces, and the present work is on two of the low index planes, namely Pt(111) and Pt(100). The  $O_2$ /Pt(111) system has been more extensively studied and is somewhat better understood than  $O_2$ /Pt(100).

Recent studies of oxygen adsorption on Pt(111) have yielded fairly consistent results. Gland and co-workers [1,2] have investigated this system with thermal desorption, LEED, UPS and EELS. They have identified a molecularly adsorbed species below ~150 K surface temperature and dissociated oxygen adsorbed above ~150K. Monroe and Merrill [3] used AES and LEED to study the kinetics of adsorption for oxygen on Pt(111) at 373 K and 658 K surface temperatures. Campbell, et al. [4] used molecular beam scattering of  $O_2$  from a Pt(111) surface, along with thermal desorption, LEED and AES. All three investigators reported that adsorption occurs via dissociation of a molecular precursor state and that the coverage by atomic oxygen saturates at 0.25 monolayer. The reported initial sticking coefficients are consistent (0.04-0.06), but there is a discrepancy in the variation of sticking coefficient with coverage [3,4]. Gland [1] also found that greater than saturation coverage was induced by external atomization of the oxygen. More recently, this high coverage oxygen on Pt(111) has been observed by Steininger, et al. [5] (induced by electron beam dissociation of

adsorbed molecules), by Dahlgran and Hemminger [6] (induced by  $\text{NO}_2$  dosing), and by Derry and Ross [7] (induced by elevated temperature and  $\text{O}_2$  pressure). These three groups all concluded, using different techniques, that the high coverage oxygen and low coverage oxygen are chemically the same. The implication of these high coverage reports is that population of the (111) surface above  $\sim 0.25$  monolayer requires a different (presumably activated) pathway for dissociation than the molecular precursor route followed initially.

Oxygen adsorption on Pt(100) exhibits more complex behavior than on Pt(111) and previous studies are in lesser accord. One complicating factor is that the stable form of the clean Pt(100) surface is reconstructed [8]. It was shown by Helms, et al. [9] and Pirug, et al. [10] that a clean, metastable Pt(100)-(1x1) surface could be prepared and that this surface is more reactive to oxygen than the reconstructed surface. Studies of oxygen on this reconstructed Pt(100) surface have been performed by Kneringer and Netzer [11] and by Barteau, et al. [12] using thermal desorption and LEED, but the results of these early studies were inconsistent, e.g., the thermal desorption lineshapes were very different and Barteau, et al. reported a significantly higher saturation coverage. The inconsistencies were reconciled by recently reported studies [7,13] which showed that different conditions of surface temperature and oxygen pressure caused the differences in both saturation coverage and TDS lineshape. As in the case of the (111) surface, room temperature dosing with  $\text{O}_2$  resulted in saturation coverages well below a monolayer, but elevated temperatures and relatively high dosing pressures ( $10^{-3}$  Pa) produced coverages

approaching a monolayer. The thermal desorption spectra for the near monolayer oxygen on (100) are much more complex than for the (111) surface, but XPS analysis indicated the high coverage state was still a chemisorption state on top of the Pt surface (as opposed to an anionic state in the Pt surface). Barteau, et al. attributed the high saturation coverage at elevated surface temperature and pressure to a reduction in the "clean-off" (by CO and/or H<sub>2</sub> in the residual gas of the UHV system) reactions at these conditions of dosing. While these clean-off reactions are important, and appear to account for some reports of very low oxygen sticking coefficients [14], they are not necessarily the primary factor that limits saturation coverage under normal dosing conditions. For example, on the reconstructed (100) surface, Norton and co-workers [13] reported very low sticking coefficients ( $S < 10^{-4}$ ) for room temperature dosing which they claimed were not due to clean-off effects, but represented the relatively unreactive nature of the reconstructed surface. Norton and co-workers also presented a very extensive analysis of the complex thermal desorption lineshapes observed from Pt(100) surfaces at high oxygen coverages. They suggested three different equilibrium states of oxygen form on Pt(100) in relative concentrations that depend on temperature and pressure and that the complex lineshape results from transitions between these states. The most strongly held state (last to desorb in TDS) was presumed to be at the relatively numerous defects in the reconstructed surface which occur due to the buckled nature of this surface [8]. The two high coverage states were characterized by different surface dipoles (from work function measurements) and by displacement of Pt atoms from their

positions in the metallic surface (from Rutherford backscattering measurements). However, in spite of these extensive prior studies, several fundamental issues in the  $O_2/Pt$  interaction remain unresolved, particularly with respect to the kinetics and energetics. The strong effect of surface temperature on the sticking coefficient reported in the recent studies is not understood. The large difference in sticking coefficient between the reconstructed and the (1 x 1) surface of Pt(100) was not explained by Norton and co-workers. It is particularly puzzling that the reconstructed surface, which is an hexagonal close-packed overlayer on the square-net substrate, should have an initial sticking coefficient orders of magnitude lower than that reported by others for Pt(111). Therefore, we felt that a further examination of oxygen adsorption on both Pt(111) and (100) in the same apparatus was warranted.

Measurement of work function changes occurring upon adsorption is a valuable supplement to electron spectroscopy and thermal desorption in the study of gas/surface interactions. Several methods have been used to measure work function changes, but the most advantageous method for our purposes is the vibrating reed capacitor (Kelvin probe). It has high sensitivity, and most importantly can be used in the presence of the adsorbing gas. The ability to measure the work function change dynamically during oxygen dosing should minimize the "clean-off effect" [12] and permit one to make equilibrium coverage determinations. We present here a study of oxygen adsorption on Pt(111) and Pt(100) using a Kelvin probe in the conjunction with the other techniques of XPS and

TDS as in our previous study [7]. We used crystal pre-treatment procedures that produced a reconstructed (100) surface in a LEED system in our laboratory, but surface structure was not confirmed since the UHV chamber used in this work did not have LEED optics. We report here both kinetic constants (sticking coefficients) and equilibrium coverages derived from work function measurements. The equilibrium coverages at variable temperature were used to calculate the isosteric enthalpy of adsorption. The influence of surface structure on the kinetics and thermodynamics of oxygen adsorption was examined by comparing the results for the two low index planes.

## II. Experiment

The basic features of the apparatus used here have been described in detail previously [7]. Briefly, it consists of an ultra-high vacuum chamber (base pressure  $\sim 10^{-8}$  Pa) equipped with x-ray and UV sources, a hemispherical electron spectrometer, a quadrupole mass spectrometer, and an ion gun. For the present study, we added a vibrating reed capacitor (Kelvin probe) to measure changes in the contact potential difference induced by chemisorption.

The Kelvin probe used in this work is the same as that described by Besocke and Berger [15]. The oscillations of this device are piezo-electrically driven. The signal is drawn from the sample and measured by lock-in techniques. Biasing the probe to null the signal provides a measure of the contact potential difference. The surface of the reference electrode is evaporated gold, which is reported [16] to be stable in oxygen pressures many orders of magnitude higher than any used here. Since the signal is measured at the sample rather than the reference electrode, there are significant problems with noise pick-up,

especially if the sample needs to be heated concurrently with the measurement. Heating the sample with a DC battery (with output current controlled by a simple transistor circuit) enclosed in a grounded metal box made the experiment possible, but the noise problems were still not eliminated. The temperature could not be measured simultaneously with the contact potential difference and thus had to be checked periodically to insure stability.

The temperature was measured with a Pt-Pt/Rh thermocouple spotwelded to the side of the crystal. Sample heating was accomplished by a small 40 W heater. The samples, cut to expose the (100) face and the (111) face, are the same as those used in reference [7]. The surfaces were cleaned in vacuo by argon ion sputtering, heating in oxygen, and high temperature annealing.

The oxygen used for surface cleaning and for adsorption experiments was introduced through a tube attached to a precision leak valve. The sample was positioned separately for dosing, for Kelvin probe use, and for thermal desorption to correlate contact potential difference change with oxygen coverage. To make equilibrium measurements, however, the sample must remain positioned at the Kelvin probe, so the entire vacuum system was brought to the desired oxygen pressure. There may have been some masking of the surface by the reference electrode resulting in a lower effective pressure [17] at the sample surface than at the ionization gauge used to measure the system pressure. This effect would be most pronounced at the lowest dosing pressures.

The contact potential difference (CPD) change,  $\Delta\phi$ , for oxygen chemisorption was measured as a function of coverage for a wide range

of exposure conditions. The experiments were performed by first positioning the clean surface in front of the vibrating reference electrode and measuring the CPD. The sample was then moved for dosing and exposed to oxygen so as to induce the desired coverage. After re-positioning the surface at the Kelvin probe, the CPD was measured again, and a thermal desorption spectrum for oxygen was then recorded leaving a clean platinum surface. Finally, the sample was again moved to the probe and the CPD measured to check reproducibility of the clean surface measurement (average discrepancy was ca. 8 mV). The change due to adsorption,  $\Delta\phi$ , is simply the difference of these measurements, while the relative coverage is obtained by integrating the area under the thermal desorption curves. Calibration of the absolute coverage was achieved using the absolute calibration of Norton, et al. [18] in conjunction with thermal desorption of saturation coverages of CO on the same clean surfaces in the same geometry.

### III. Results

Figure 1 presents  $\Delta\phi$  vs. coverage data for oxygen of Pt(111). Data points for coverages less than  $\sim 4 \times 10^{14}$  atoms/cm<sup>2</sup> were obtained by exposing the clean surface at 370 K to an oxygen pressure of  $\sim 1.3 \times 10^5$  Pa for varying exposure times. The higher coverage data were obtained by dosing with the surface held at  $\sim 570$  K, using various exposure times and pressures in the  $10^{-4}$  -  $10^{-3}$  Pa range. There is no apparent discontinuity in the slope between the low and high coverage regions in the  $\Delta\phi - \theta$  data, although at the very highest coverages (near monolayer) the curve seems to flatten. These data indicate that the adsorption induced work function change is linear with coverage. The

usual interpretation of this result is that the adsorbate atoms constitute a set of discrete dipoles and the effects of each can simply be added together. Approximating the net dipole moment as the result of sheets of charge, the Helmholtz equation

$$p = \frac{\Delta\phi}{4\pi h}$$

can be used to calculate the dipole moment per adatom. The line in Fig. 1 is a least-squares fit to the data, and the slope of this line yields a dipole moment of  $p = 0.103$  debye/atom.

The  $\Delta\phi$ - $\theta$  data for oxygen on Pt(100) are shown in Fig. 2. For coverages less than  $2.7 \times 10^{14}$  atoms/cm<sup>2</sup>, the adlayer was obtained by dosing with  $1.3 \times 10^{-5}$  Pa oxygen and a surface temperature 370 K for varying exposure times. At higher coverages, the data were obtained by dosing with the surface held at ~570 K using various exposure times and pressures in the  $10^{-4}$  -  $10^{-3}$  Pa range. The work function behavior was clearly much different on the (100) surface than on the (111) surface. The initial adsorption of oxygen resulted in a much sharper increase of  $\Delta\phi$  up to ~200 mV at  $\theta \sim 0.1$  monolayer. For higher coverages,  $\Delta\phi$  increases linearly with coverage. Similar behavior has been reported before [19,20] and is usually associated with adsorption onto steps. The line through the higher coverage points is again a least-squares fit and its slope yields a dipole moment of  $p = 0.128$  debye/atom. A least-squares fitting procedure was deemed unnecessary for the initial adsorption data because there are only a few points and  $\Delta\phi = 0$  at  $\theta = 0$

by definition. The empirical line drawn in Fig. 2 was used to approximate the conversion of work function change to coverage and to estimate the dipole moment per atom,  $p \sim 0.62$  debye/atom. This is a much larger dipole moment than for the (111) surface or for the (100) surface at high coverage.

The results of a different type of experiment are shown in Fig. 3. In this case, the clean surface was positioned in front of the reference electrode, a baseline CPD is established, and the surface exposed to oxygen at  $2.3 \times 10^{-6}$  Pa with CPD monitored continuously. The sample was at ambient temperature.  $\Delta\phi$  was obtained by digitally subtracting the baseline CPD from the CPC versus time curve, and the time and oxygen pressure were used to calculate the exposure in torr-sec(L). The results for the first 1500 sec of dosing on Pt(111) are presented in Fig. 3. Since  $\Delta\phi$  is linear with coverage, Fig. 3 is essentially the coverage versus exposure. The conversion is made using Fig. 1 and the right-hand vertical axis in Fig. 3 shows the coverage values explicitly for convenience. The derivative of the curve in Fig. 3 yields the sticking coefficient.

The same experimental method was applied to  $O_2$ /Pt(100) and the result for the first 1250 seconds is shown in Fig. 4. In this case, the exposure pressure was  $4.8 \times 10^{-7}$  Pa. The simple linear relationship of  $\Delta\phi$  with coverage was not observed on this surface. There is a change in the slope, as seen in Fig. 2, and even the depiction as two straight lines is obviously an approximation. The coverage scale on the right-hand axis of Fig. 4 is based on the low coverage line in

Fig. 2, and should be valid (to the extent that this line represents the  $\Delta\phi$  versus  $\theta$  behavior) for the data to the left of the arrow

If the temperature of the sample is higher than the temperature required for the onset of desorption, then equilibrium between adsorption and desorption can be achieved and equilibrium coverages measured. The equilibrium coverage can be obtained by measuring the change in work function as function of time and taking the time invariant value as the equilibrium value. We could thus determine the coverage for a series of oxygen pressures at constant surface temperature and construct an equilibrium isotherm. In practice, these measurements turned out to be problematic because the Kelvin probe was prone to malfunction in the vicinity of the heated sample. It was possible, however, to collect data for  $O_2/Pt(111)$  and generate a family of three isotherms, despite a significant amount of scatter in the data.

These results are shown in Fig. 5. The data were collected at three surface temperatures:  $T_s = 668$  K,  $T_s = 726$  K, and  $T_s = 784$  K. The horizontal axis is the coverage, derived from the  $\Delta\phi$  measurements. The vertical axis gives the pressure measurements, using a logarithmic scale simply to fit any orders of magnitude change onto the same plot. Because of the degree of scatter in the data, we cannot determine the functional form of the isotherms. It is clear by inspection, however, that they are at most only weakly non-linear on the  $\ln P$  scale, so we have used linear regression as a means of averaging the data. The least-squares fit lines are shown in Fig. 5. From these families of isotherms we can calculate the isosteric enthalpy of adsorption from the Clausius-Clapeyron relation.

$$\Delta H_{st} = -R \ln(P_1/P_2) / \left( \frac{1}{T_2} - \frac{1}{T_1} \right) .$$

We use this equation to calculate  $\Delta H_{st}$  from various pairs of lines in Fig. 5 at several coverages. There were no consistent trends apparent in the change of  $\Delta H_{st}$  with coverage, indicating that any coverage dependence of the adsorption enthalpy was masked by scatter in the isotherms. We therefore quote an average value of the enthalpy for the coverage range sampled (1 to  $6 \times 10^{14}$  atoms  $\text{cm}^{-2}$ ),  $\Delta H_{st} = 232 \pm 36$  kJ/mole.

#### IV. Discussion

The change of the work function induced by oxygen adsorption on Pt(111) is linearly proportional to the coverage. The straightforward interpretation of this observation is that each adsorbed atom is acting like an individual dipole and that the discrete dipoles can simply be summed to yield a surface dipole layer with a net moment. This adequately explains the linear dependence on coverage but provides no information about the microscopic structure of the dipole. The dipole moment calculated from the Helmholtz equation is  $p = 0.103$  debye/atom which corresponds to very small charge transfer ( $\sim 0.01$  e) for reasonable bond lengths. It is difficult to assess the meaning of this because the Helmholtz equation and the point dipole model are both crude approximations. The observation of a constant slope for  $\Delta\phi$  vs  $\theta$  over the entire coverage range tends to indicate that the Pt-O bonding

does not change with coverage, even at coverages which approach an atomic monolayer. This is in agreement with previous studies [5-7] of oxygen at high coverages on Pt(111).

In the case of oxygen adsorption on Pt(100), there was a large change in  $\Delta\phi$  for initial adsorption at low coverage. This sort of abrupt change has been reported previously for oxygen adsorption on Pt(S)-[9(111)x(111)] [20] and on W(S)-[10(110)x(011)] [19]. The interpretation of this phenomenon is that initial adsorption occurs at the steps and adsorption at a step causes a larger change in the dipole moment. This latter contention is corroborated by the change in work function with step density: Besocke, et al. [21] found a dipole moment per step atom of 0.6 debye for platinum, which is very similar to the moment we find here for initial oxygen chemisorption on Pt(100). Kesmodal, et al. [22] outlined a qualitative explanation of this "inverse dipole" associated with step sites. It is extremely likely that we have the same effect for oxygen adsorption on the reconstructed surface of Pt(100). The number of defect sites estimated from Fig. 2 ( $1 \times 10^{14} \text{ cm}^{-2}$ ) is not an unreasonable defect concentration in terms of the dislocation model [8] of the hexagonal overlayer. Norton and co-workers [13] also concluded that the initial adsorption onto Pt(100) was at defect sites (which they called the  $\beta_3$  state) at concentrations comparable to what we found in this work.

The work function changes shown in Fig. 2 clearly indicate that  $\Delta\phi$  was a single-valued function of  $\theta$  on the (100) surface (as it was on the (111) surface), in contrast to the work function data reported by Norton and co-workers [13]. They reported a more complex relation

between  $\Delta\phi-\theta$ , i.e.,  $\Delta\phi$  depends not only on the coverage but also on the surface temperature and dosing pressure, which they attributed to the formation of distinct surface phases. We found that within the reproducibility of any single measurement ( $\pm 25$  mV) the work function change depended only on the total oxygen coverage and not on the conditions of formation for that coverage. The major differences appear to occur at coverages above ca.  $8 \times 10^{14}$  atoms  $\text{cm}^{-2}$  where the transitions between their states labelled  $\beta_2$  and  $\beta_3$  occurred. At lower coverages there appears to be excellent agreement where common dosing conditions were used, e.g., dosing at 670 K at  $5 \times 10^{-3}$  Pa resulted in a coverage of  $8 \times 10^{14}$  atoms  $\text{cm}^{-2}$  and  $\Delta\phi = 460$  mV in both studies. The experimental procedures were not identical in the two works, e.g., our work function changes were made during dosing at constant surface temperature and not during thermal desorption as in [13], which may account for some differences. However, the differences in the maximum achievable surface coverage and the maximum observed work function change remain as essential discrepancies between the two works.

The linear region for  $\Delta\phi-\theta$  on the (100) surface at high coverage can be interpreted in the same manner as the data for the (111) surface. The dipole moment per adatom is slightly larger on the (100) surface, but it is not possible to draw conclusions about the Pt-O charge transfer on the basis of dipole moments alone. The constant slope for  $\Delta\phi$  vs.  $\theta$  in the high coverage region indicates that the Pt-O bond does not change with coverage even at coverages approaching a monolayer. In this sense, the Pt-O bonds on (100) and (111) are similar. This

conclusion is consistent with our XPS results [7] but at variance with the conclusions by Norton and co-workers [13].

As stated in section III, the curve in Fig. 3 can be digitally differentiated to obtain the sticking coefficient at near ambient temperature. The results of this operation is shown in Fig. 6, where the sticking coefficient is plotted as a function of coverage. The jagged nature of the curve is the result of accentuation of small fluctuations in the data by differentiation. Digital smoothing before and after the differentiation was applied to achieve the result shown in Fig. 6. The value of the initial sticking coefficient found from Fig. 6 is  $S_0 = 0.038$ . This is in fairly good agreement with the previous results of  $S_0 = 0.048$  [3] and  $S_0 = 0.06$  [4]. The smooth curve in Fig. 6 is a plot of the function  $S = S_0(1 - \vartheta)^2$ , where  $\vartheta = \theta/\theta_{\max}$ , and it is clear that this is in very good agreement with the data. Monroe and Merrill [3] observed a linear dependence, whereas Campbell, et al. [4] fit their data with a quadratic decrease of  $S$  with coverage, in agreement with the present work. It is interesting that such a simple function fits the observed behavior so well, although it cannot be used to unambiguously deduce any specific adsorption mechanisms.

The same procedure was employed to extract the sticking coefficient vs coverage from the data in Fig. 4 for the (100) surface and the results are shown in Fig. 7. This curve is smoother, probably because the CPD changes themselves were much larger in this case. The magnitude of the initial sticking coefficient is in agreement with our previous result [7] obtained by TDS and is in fact somewhat larger. This is not

surprising since the kelvin probe can access extremely low coverage data not available in a TDS experiment. The decrease of the sticking coefficient with coverage was more rapid for  $O_2/Pt(100)$  than it was for  $O_2/Pt(111)$ . This is consistent with our conclusion that initial adsorption on Pt(100) is onto defect sites due to the relatively high concentration of defects on the reconstructed (100) surface [8].

Another interesting feature of Fig. 7 is that the sticking coefficient increased initially reaching a maximum and then decreased with higher coverage. This is very unusual behavior and has only been reported to our knowledge once before [23] for oxygen on Ni(111). We are evidently not seeing the same phenomenon, however, because Winkler, et al.

observed the maximum at much higher coverage and stated that the effect is most pronounced on the smoothest surfaces. The behavior is clearly not an artifact of the differentiation process, since a small "induction period" can be seen even in the original data in Fig. 4. That it is an experimental artifact can not be entirely ruled out, but we are unaware of any experimental difficulties that would produce this effects. The mechanism invoked by Winkler, et al., that sites with adsorbed oxygen promote adsorption into adjacent sites, is unlikely since our maximum occurred at such a low coverage ( $<0.01$  monolayer). A qualitative tentative explanation consistent with the data is that dissociative chemisorption into a small number of very active defect sites occurs via a weakly adsorbed transient molecular state. The rate of adsorption into the active sites would then be limited by the surface concentration of the transient state. At the low oxygen pressure which

was used, one would expect a slow (~10 sec) increase in the population of this state until equilibrium is attained. Competing with this increase, there is a decrease in the rate of adsorption due to loss of active sites as they are filled by dissociative chemisorption. Thus, there should be an initial increase through a maximum followed by a decrease in the sticking coefficient, in agreement with Fig. 7.

If the initial adsorption on the Pt(100) surface is onto defect sites whose number may be as high as ca.  $2 \times 10^{14}$ , then it is clear from the data in Fig. 7 that the sticking coefficient at room temperature for oxygen onto the close-packed regions of the reconstructed surface is very low,  $<0.003$ , and about an order of magnitude lower than for the (111) surface. A similar conclusion can be inferred from the results of Norton and co-workers [13], although their data indicate an even greater difference in sticking coefficient between (100) - (1 x 1) or (111) and the reconstructed (100) surface. There is at least qualitative consensus from different groups that the adsorption of oxygen onto the reconstructed surface of Pt(100) at room temperature is significantly slower than onto any other low index surface. Quantitative consensus has been problematic due in part to the "clean-off" effect, but may also be a more fundamental problem due to the very nature of the reconstructed surface. The detailed analysis of LEED patterns [8] for the (100) surface indicates that four different reconstructions have been observed that are related to the simultaneous presence of multiple domains on the surface. Steps in the surface appear to affect which reconstruction unit cell is observed via the

occurrence of selected domains. Variations in the reconstruction unit cell means variable arrangements of the hexagonal overlayer, yielding different slip fault densities (slip faults are the origin of the relatively high concentration of defect sites on the reconstructed surface). One should expect, therefore, that relatively minor variations in cutting the Pt crystal (off the [100] zone axis) or variations in mechanical polishing could lead to large differences in slip fault densities on the clean, annealed (100) surface, and this seems to be an important factor in conflicting observations with this surface.

Finally, we consider the kinetics of adsorption onto the (111) surface and the relation to the isosteric heat of adsorption. A major point to emphasize about this result is that it is a true equilibrium thermodynamic measurement and therefore not dependent on any model. It would have been desirable to measure the coverage dependence of the adsorption enthalpy, but the scatter in the data prevented this. The change in  $\Delta H$  with coverage must be fairly small, however, or it would be observable within the precision of the experiment. This conclusion is consistent with the results of Campbell, et al. [4] and with the data in Fig. 1. The isosteric enthalpy,  $\Delta H$ , is equivalent to the desorption energy in the case of activationless adsorption. Using our measured  $\Delta H$  value and various kinetic parameters derived from the literature [2,4], we used a precursor state model [24,25] to try to reproduce the desorption lineshape for the high coverage oxygen seen previously [7] on Pt(111). This attempt was unsuccessful, showing that incorporation of a precursor state does not alone explain all the thermal desorption data. Next, we inserted a coverage dependent energy [24,25], using our

measured enthalpy for the average desorption energy and a parameterized interaction energy. For a variation with coverage well within the error range of  $\Delta H$ , the major features of the TDS lineshape for high coverage  $O_2/Pt(111)$  (asymmetry, lower  $T_p$ , broadening) were reproduced. Thus, there is strong evidence that lateral interactions become particularly important effects at high coverage, and that the precursor state is not necessarily involved in the adsorption reaction at high coverage.

We agree with the suggestion made previously by Campbell, et al. [4] that at coverages of the (111) surface above  $\sim 0.25$  monolayers the dissociation step becomes activated, and adsorption probably proceeds via a route other than the molecular precursor, i.e., direct dissociation. That is why either elevated temperature (and pressure) or external atomization is required to achieve high coverages. We do not, however, offer any additional explanation as to why the activationless adsorption process becomes so kinetically hindered at the relatively low coverage of  $\sim 0.25$  monolayers. We have shown that there is no change in the chemical state of the oxygen adatom (not at defect sites) as a function of coverage, so that the deactivation mechanism must be related to other factors. In the case of the (100) surface, where high coverage of the surface also requires elevated temperature, a description of the energetics of the oxygen interaction must include transitions in the Pt structure as well. That such transitions occur is clearly indicated in the work of Norton and co-workers [13], and it is clear that these transitions are activated processes that require elevated temperature,

but the details of the transitions, e.g., to the degree that the CO induced transitions on the (100) surface were elucidated by Ertl and co-workers [26], will require further study.

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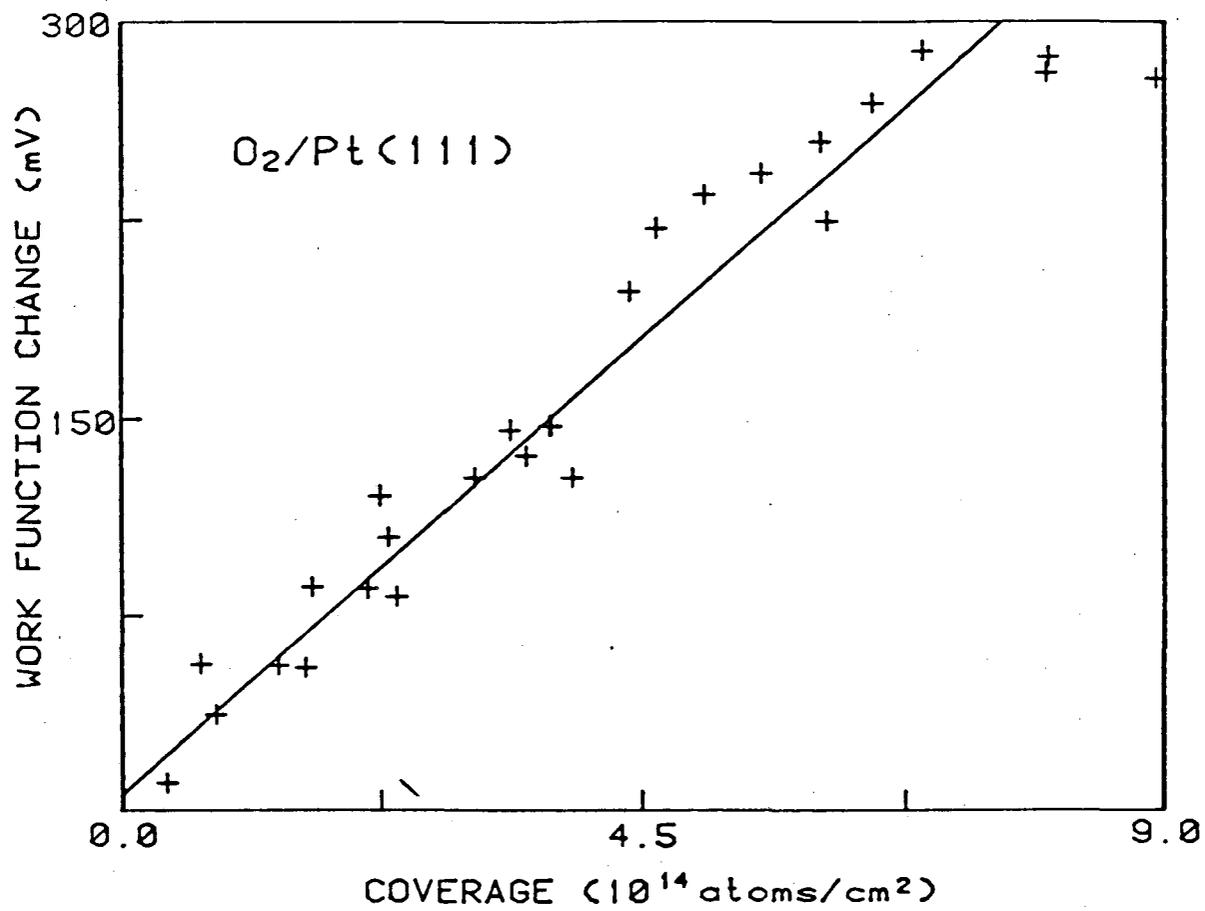
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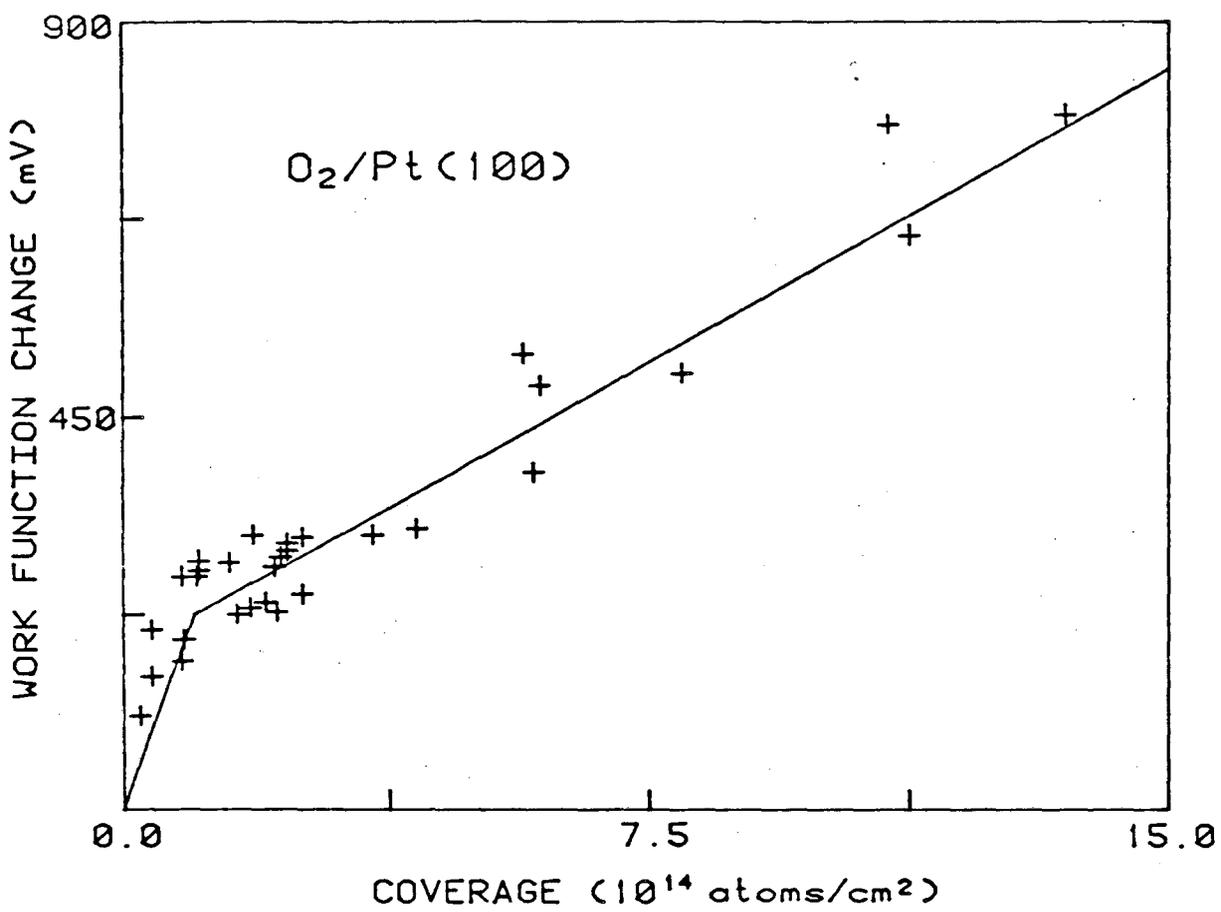
## Figure Captions

- Fig. 1. Work function change induced by oxygen adsorption on Pt(111) for a range of oxygen coverages.
- Fig. 2. Work function change induced by oxygen adsorption on Pt(100) for a range of oxygen coverages.
- Fig. 3. Change in Pt(111) work function with time at a constant oxygen pressure ( $2.3 \times 10^{-6}$  Pa,  $T \approx 300$  K); calibrated coverage is shown at right.
- Fig. 4. Change in Pt(100) work function with time at a constant oxygen pressure ( $4.8 \times 10^{-7}$  Pa,  $T \approx 300$  K); calibrated coverage is shown at right.
- Fig. 5. Equilibrium isotherms for three surface temperatures of Pt(111) and a wide range of oxygen pressures.
- Fig. 6. Sticking coefficient on Pt(111) as a function of coverage, derived digitally from the data in Fig. 3; smooth curve is a quadratic model.
- Fig. 7. Sticking coefficient on Pt(100) as a function of coverage, derived digitally from the data in Fig. 4.



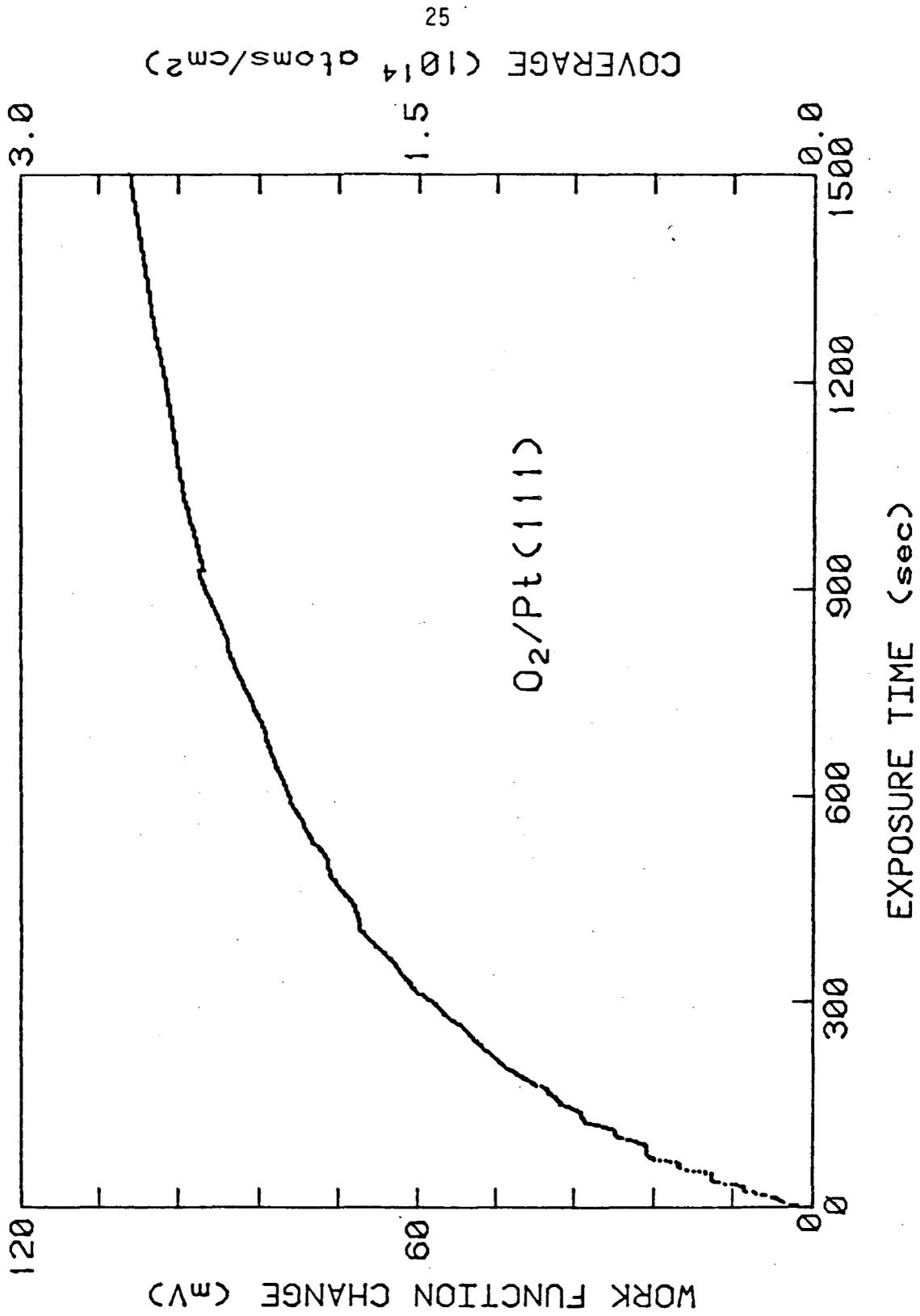
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Fig. 1



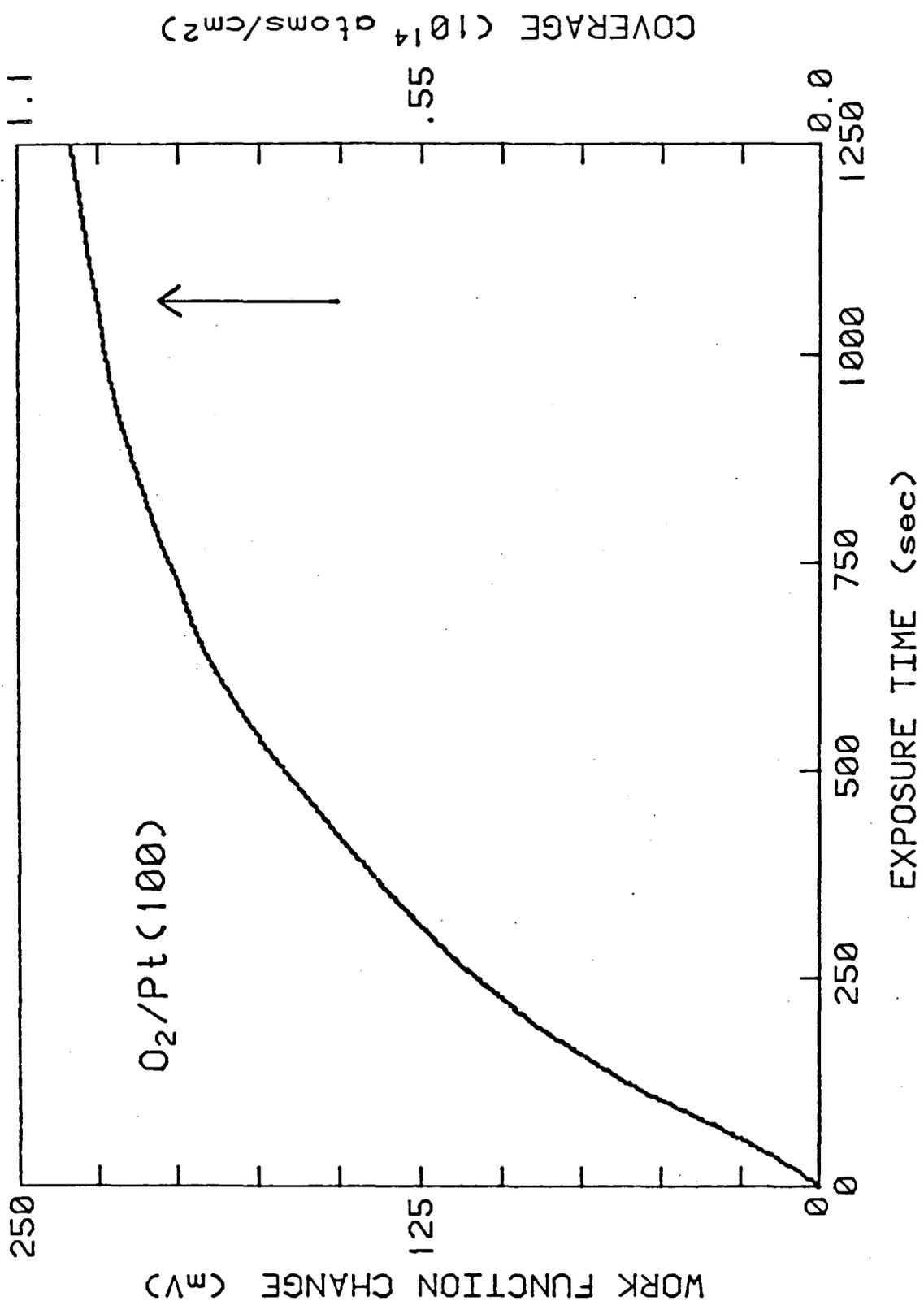
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Fig. 2



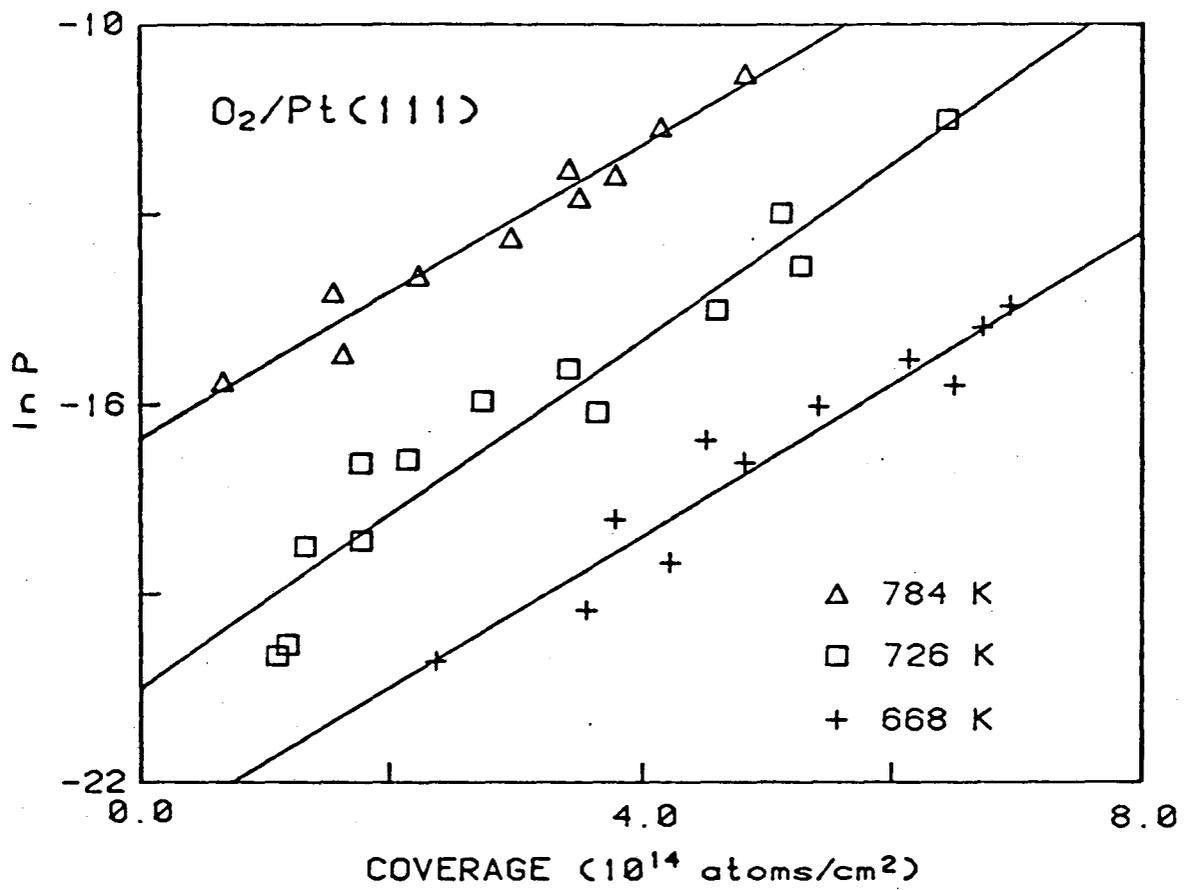
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Fig. 3



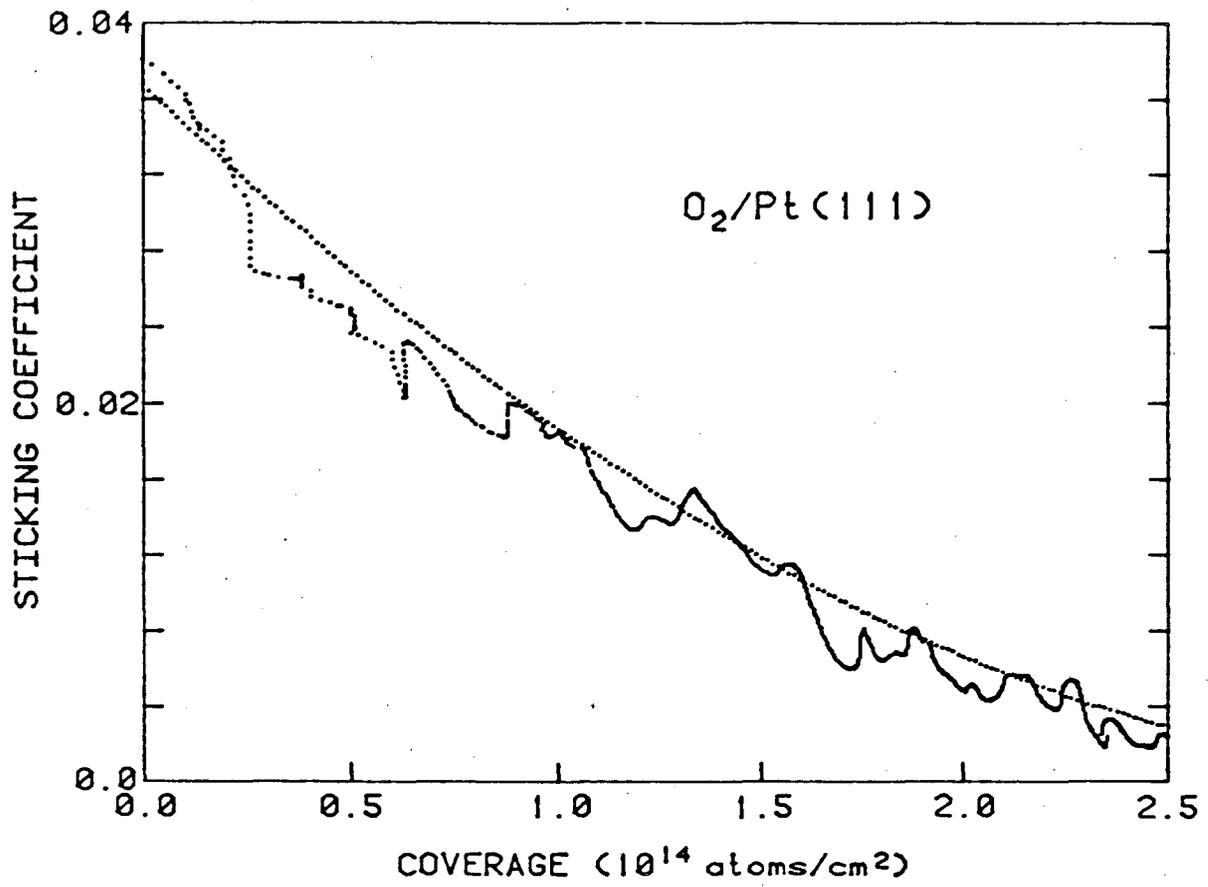
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Fig. 4



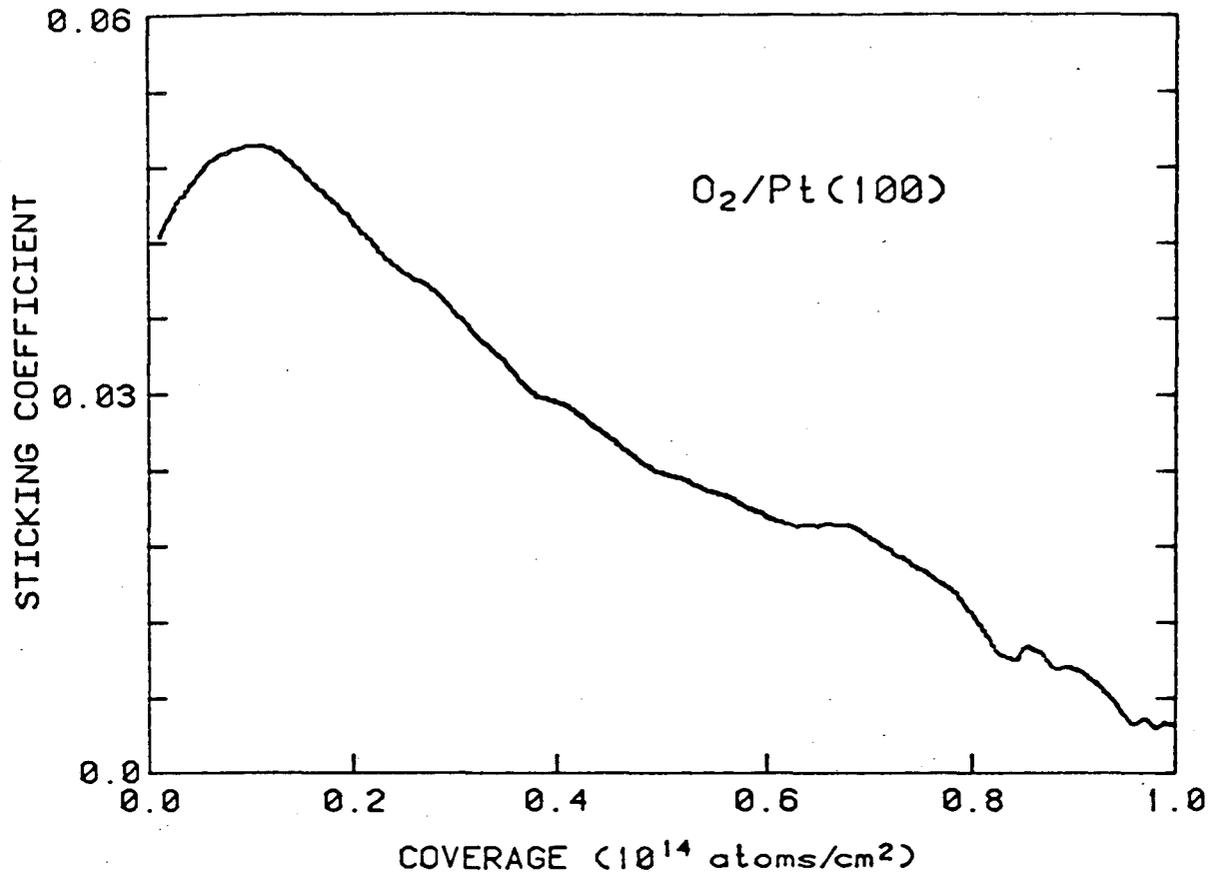
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Fig. 5



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Fig. 6



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Fig. 7

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