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BEAM STUDIES OF MOLECULAR PROCESSES ON METAL SURFACES.(U)

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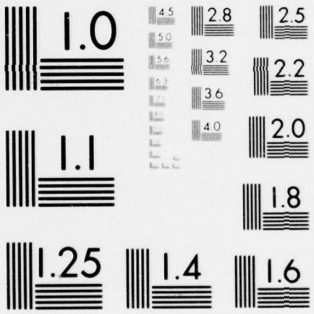

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(10) **Robert L. Palmer**

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The isosteric heats of adsorption of NO and O_2 have been studied on epitaxially grown Pt(111) using elastic helium scattering as the surface coverage probe. The measured isosteric heats for NO and O_2 are 21 and 26 kcal/mole, respectively. The data also indicate a pre-exponential factor for NO desorption of less than 2×10^7. ←

10 to the 7th power

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Beam Studies of Molecular Processes on Metal Surfaces

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Studies of molecular processes on surfaces are motivated by a variety of interests in interface phenomena including catalysis, corrosion and high altitude drag coefficients. Molecular beam studies of gas-surface interactions have been particularly fruitful for probing the details of molecular processes such as adsorption, desorption, energy transfer and chemical reaction. When an atom or molecule collides with a surface it can interact in a number of ways. It may be reflected elastically, partially or completely accommodated or physi- or chemisorbed. Among other things, the energy transfer to the surface varies from zero in the case of elastic reflection to 100 percent for complete accommodation and adsorption.

Since adsorption is the first step in heterogeneous catalysis while accommodation coefficients (energy transfer) are of interest in aerodynamics, a study of the parameters that affect the rate of adsorption of gases on metal surfaces is of particular interest in both of these seemingly unrelated areas. We have used molecular beams to study the adsorption of gases such as O_2, N_2, H_2, CH_4, C_2H_x, NH_3, CO, CO_2 and others on both single-crystal and polycrystalline surfaces of metals such as Ag, Au, Ni, Fe, Co, Pd, Pt, and Mg. We have found that for some gas/surface systems the adsorption probability (sticking coefficient S), is strongly affected by the physical structure of the surface. Generally speaking, clean, single-crystal surfaces have the lowest sticking probabilities, while rough, polycrystalline surfaces are more likely to partially or fully accommodate or adsorb incident molecules. While this may be due, in part, to multiple collisions on microscopically rough surfaces, subtle changes in the electronic structure of surfaces at step edges and other "low coordination" sites can have a significant influence on the sticking coefficient of molecular species.

Using molecular beams to measure adsorption probabilities as a function of incident angle and kinetic energy, some idea of the gas/surface interaction potential can be obtained. In some cases the adsorption step has an activation barrier that can be overcome most effectively by translational energy while, for others, the barrier is most effectively overcome by internal (vibrational) energy. The importance of this information lies in the ability to modify the surface in such a way as to increase or decrease the activation barrier and thereby vary the sticking coefficient to suit the particular circumstance. The electronic structure is influenced by both the elemental composition and physical structure of the surface. Sticking coefficients can be lowered by as much as an order of magnitude by eliminating surface structures such as steps, grain boundaries, etc.

The molecular beam technique has long been recognized as the most direct way to study the interaction of molecular and atomic species. Many important studies of the chemical interaction of atoms, molecules, radicals and charged species have been carried out in the gas phase using the beam method. Eastermann and Stern first applied the beam technique to the study of atomic interactions on surfaces some fifty years ago. Their diffraction results were quite significant because they demonstrated the wave properties of particles at a time when de Broglie's hypothesis was a revolutionary concept in physics. However, the value of this and subsequent molecular beam scattering studies on surfaces suffered from the lack of any real ability to characterize the actual surface where the scattering event occurred. Even cleaved crystals such as those used by Eastermann, et al. were subject to adsorption of gases from the vacuum ambient. This was assumed to occur rapidly in the vacuums used in these early experiments since no diagnostic techniques were available for measuring the chemical and physical nature of the vacuum/surface boundary. Before 1964, attempts to study molecular scattering from metal surfaces were largely unsuccesful. Neither diffraction, nor other features one would expect when scattering atoms from smooth, single-crystal metal surfaces were observed in experiments up to that time.

In 1964, Joe N. Smith, Jr. and Howard Saltsburg, working at General Atomic in San Diego, began a series of experiments in which they scattered molecular beams from single-crystal gold and silver surfaces that were grown epitaxially in situ. Even in the absence of ultra-high-vacuum, these surfaces could be maintained clean by growing the crystal continuously during the experiment at a fast rate compared with the surface contamination rate. Their results were quite impressive, showing a high degree of specular scattering as expected from an ideal single-crystal surface and repeatability of the results from crystal to crystal. These results spurred both experimental and theoretical interest in gas-surface interactions and considerable fruitful work has subsequently been carried out on a wide variety of metal surfaces. Carefully prepared surfaces of bulk crystals as well as deposited single-crystal films have both been used to give results that appear to approach the ideal, contaminant and defect-free surface required for studies of molecular interactions with surfaces.

This ability to produce well-characterized surfaces led, very naturally, to broadening the scope of molecular beam studies to include the investigation of chemical as well as physical interactions. A number of studies of surface catalyzed chemical reactions, usually on transition metal surfaces, have been performed using molecular beams. Almost all of this work has been reported during the period from 1970 to the present so that this field is really very new. Because of the fundamental nature of molecular beam studies, the systems studied have been those involving rather simple chemical reactions where one hopes to be able to identify each step in the reaction mechanism, and to determine the respective rate parameters. Catalytic reactions studied to date using molecular beams include H_2/D_2 exchange on Pt(111) (Refs. 1,2), Ni(111) (Ref. 3) and Cu(100) (Ref. 4) and Cu(110) (Ref. 4); D_2, CO and C_2H_x oxidations on Pt(111) (Refs. 1,5,6) and Pd(111) (Ref. 7) and HCOOH decomposition on Pt foil

(Ref. 8). Despite the rather straightforward nature of these reactions, both experimental results and interpretations of the data by researchers in this field have often been in disagreement, especially in the earlier work. Researchers are now more familiar with the techniques involved with conducting beam studies of chemical interactions on surfaces and, in particular, with the interpretation of kinetic measurements using phase-lock methods and modulated beams. In many cases the apparent discrepancies between experiments can be explained in terms of artifacts in the measurement technique. Also, the importance of a very careful analysis of the chemical kinetics with respect to alternative reaction models is now more fully appreciated. Real world chemical kinetics do not always follow the rate laws one expects from a very simplified evaluation of a particular reaction scheme. When a careful evaluation of the boundary conditions assumed in the kinetic analysis of a reaction model is made and compared with the actual conditions of the experiment a different conclusion is often reached than that presented in textbook examples. For example, when a diatomic molecule like O_2, D_2, etc., is adsorbed dissociatively on a surface the equilibrium balance between the gas phase and the surface coverage of species A_2 is usually written

$$p_A(1-\theta_A)^2 = k\theta_A^2$$

for the reaction

$$A_2(g) \leftrightarrow 2A(s)$$

so that the surface coverage, θ_A, varies as the half power of the partial pressure, p_A. This relation is valid only in the absence of a competing surface reaction for the removal of A atoms. If, for example, the surface reaction is a simple one of the form

$$A(s) + B(s) \rightarrow AB(g)$$

then the surface coverage of A(s) may vary from half order in p_A to first order in p_A, depending on the relative rates of the competing reactions. This makes it impossible to distinguish between alternate reaction mechanisms, e.g., Rideal versus Langmuir, without precise knowledge of the surface coverages and the rate constants of the competing reaction paths in a given experiment.

Other factors that can further complicate the kinetics of real surface/adsorbate systems include coverage dependent heats of adsorption, the effects of "precursor" states in the adsorption/desorption process, and phase changes in the adlayer with coverage.

Since our early work on H_2/D_2 exchange on Ni(111), we have stressed the relationship between adsorption and desorption, i.e., that these processes are just time reversals of the same process so that microscopic reversibility applied in general and detailed balance can be applied when the kinetics of adsorption and desorption are compared at the same temperatures. Shannabarger has pointed out that because of this relationship between adsorption and desorption, precursor states should play an important role in desorption kinetics in an analogous way to that observed in studies of adsorption using beams and other techniques (Ref. 9). It is now being recognized that precursor states do indeed affect adsorption/desorption kinetics in real systems and that it is likely that the interpretation of flash desorption data as well as reaction kinetics are often significantly affected by these states. Molecular beam studies of adsorption are perhaps the most effective way of studying these precursor intermediates, and the importance of these studies to surface chemistry is even clearer now than when they were first begun. Further studies of this type will be of great help in clarifying results obtained by other experimental techniques such as flash desorption and kinetic measurements of surface catalytic reactions.

The foregoing discussion points up the need for more progress in unifying the various areas of surface chemistry. Molecular beam and other recent experiments in surface chemistry have produced a number of surprises that were not anticipated from our rather simplified understanding of the gas-surface boundary. Although the pioneering concepts established early in this century by Langmuir, Knudsen, and others have provided a good framework for understanding the gas-surface interface, further development in this area is clearly needed. In particular, emphasis should be placed on developing the broader implications of results obtained in specialized areas of study such as molecular beam scattering, flash desorption, field ion microscopy, and chemical reaction kinetics on single-crystal surfaces. Efforts are now underway to codify the results of various well-characterized surface studies with significant improvements in the theory of reaction rates, including chemisorption and catalysis being the likely result.

Recently, we have been using molecular beams to study the chemistry of NO_x (N_2O, NO, and NO_2) on Pt(111) surfaces. This work is still in progress, but some of our results can be reported now. While the catalysis of NO_x on platinum is related to applied areas such as pollution control in automotive exhausts, our interest is to characterize the interaction of NO_x with platinum and other group VIII metals in a rather fundamental way.

One technique that can be applied uniquely to single-crystal surfaces is the use of helium beam scattering to measure adsorbate coverages. The technique depends on the fact that adsorbed molecules scatter helium atoms inelastically, whereas the clean surface reflects some fraction of the helium atoms elastically into a well-defined specular ray. This provides a means of probing the surface of coverage and the technique becomes quantitative if the scattering cross section of the adsorbate can be determined. This method has been used to determine the isosteric heats of adsorption of NO_x and O_2 on Pt(111). Figure 1 gives data obtained for helium scattering from Pt(111) as a function of O_2 pressure and, hence, oxygen coverage on the surface at several surface temperatures. Replotting this data as oxygen pressure versus reciprocal surface temperature at constant coverage (helium attenuation) we obtain the isosteric heat of adsorption. This is done in Figure 3 for 50 percent helium attenuation which is approximately 20 percent oxygen coverage using appropriate scattering dimensions for oxygen and helium. Similar attenuation data for NO is plotted in Figure 2 and Figure 3 also gives the Clausius-Clapeyron plot for NO, also at 50 percent attenuation.

We first observe that the isosteric heat of adsorption for oxygen is unusually low when compared with other methods that yield values typically in the range 40 to 70 kcal/mole. To understand this result we must consider the method in more detail. Since we rely on inelastic scattering for the detection of adsorbates, the possiblity exists that some of the chemisorbed oxygen may not give rise to inelastic scattering, either because it is tightly bound and/or because it lies below the uppermost surface layer and is shielded from scattering with incident helium atoms. A further complication is that oxygen can exist in both atomic and molecular states on platinum and we have no a priori way of determining from helium scattering alone which state we are probing. We assume from the measured slope (26 kcal/mole) that we are dealing with a chemisorbed state and, hence, probably oxygen atoms although this is by no means unequivocal. One more factor to consider is that the effective scattering cross section of loosely bound species may be significantly enhanced because of their greater mobility on the surface.

Considering these factors, we are most likely probing a rather loosely bound oxygen species on Pt(111) (either O_2 or O atoms) at high total coverage and tightly bound oxygen atoms lying below the topmost surface layer are shielded from scattering by helium atoms and not detected.

The chemisorption of NO data of Figure 2 indicates an isosteric heat of adsorption of 21 kcal/mole. Surprisingly, for nondissociative adsorption, the pre-exponential of the desorption rate can be calculated from the data to be

$$S\nu_o = 2 \times 10^7$$

where S is the initial sticking coefficient for NO on Pt(111). Since $S \leqslant 1$, the pre-exponential is quite low, in the range normally expected for dissociative adsorption where desorption involves a concerted process. We speculate at this point that chemisorbed NO, while perhaps not completely dissociated, is bound to the surface at both the nitrogen and oxygen atoms, i.e., lying down rather than erect as in the case of CO adsorption. The chemisorption of NO_2 is consistent with the process

$$NO_2(g) \rightarrow NO(s) + O(s) \quad .$$

Strenuous attempts were made to react all three species, N_2O, NO, and NO_2 with CO without success. No CO_2 reaction product could be observed by the molecular beam technique. The upper limit of reaction probability is less than 10^{-3} per CO collision with the target surface. While this does not preclude the detection of reaction by other more sensitive techniques, the result is surprising for the case of CO + NO_2 since CO reacts rapidly with surface oxygen atoms on Pt(111). Evidently the presence of NO(s) inhibits the reaction between O(s) and CO(s). Experiments are planned to study the reaction CO + O_2 + NO to verify the inhibition effect of NO on the oxygen rate of CO.

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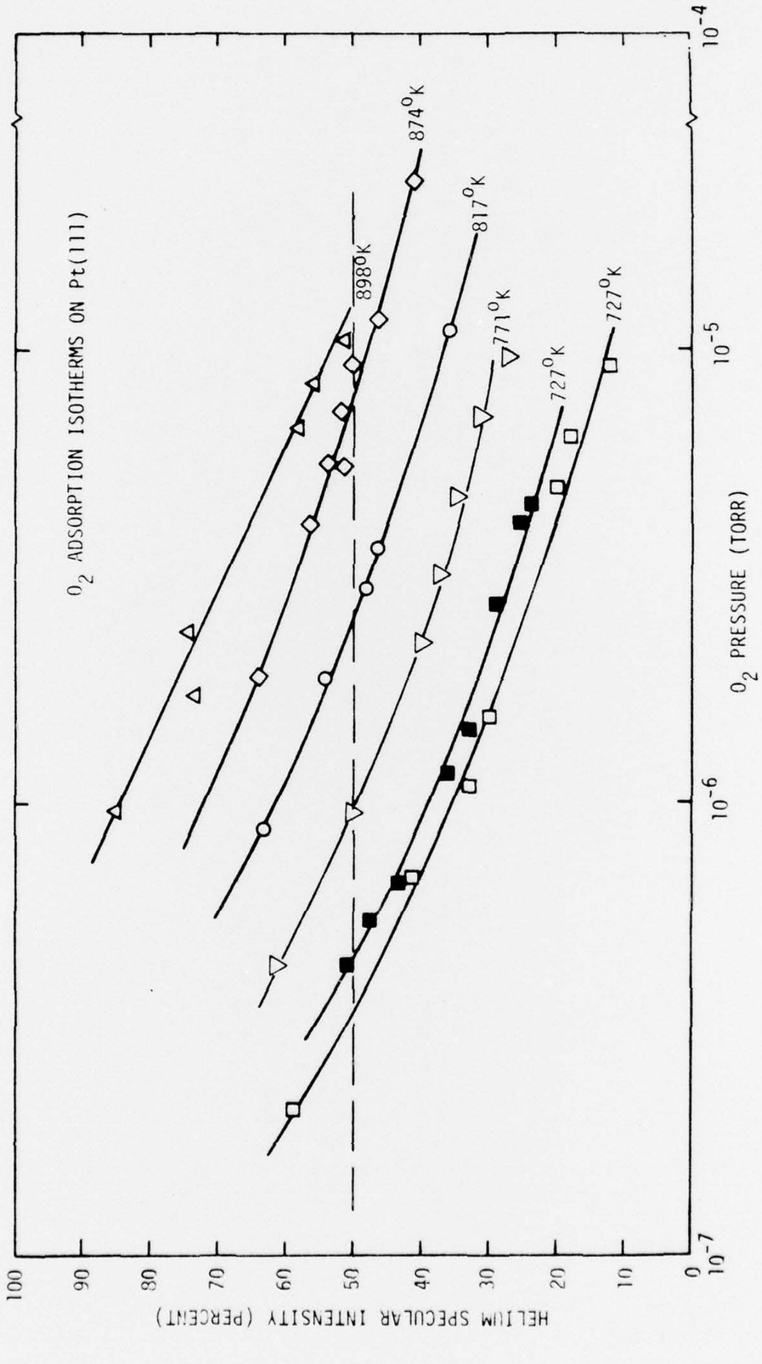
O$_2$ ADSORPTION ISOTHERMS ON Pt(111)
898°K
874°K
817°K
771°K
727°K
727°K
HELIUM SPECULAR INTENSITY (PERCENT)
100
90
80
70
60
50
40
30
20
10
0
O$_2$ PRESSURE (TORR)
10^{-7}
10^{-6}
10^{-5}
10^{-4}

Figure 1

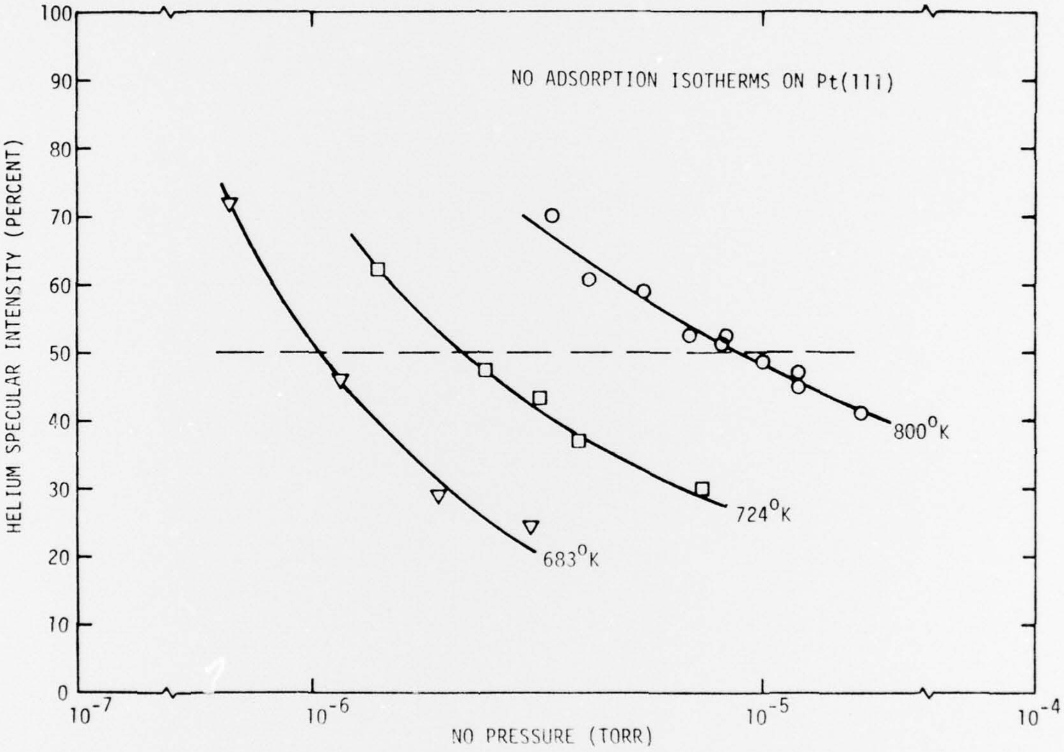
NO ADSORPTION ISOTHERMS ON Pt(111)
HELIUM SPECULAR INTENSITY (PERCENT)
100
90
80
70
60
50
40
30
20
10
0
10^{-7}
10^{-6}
10^{-5}
10^{-4}
NO PRESSURE (TORR)
800°K
724°K
683°K

Figure 2

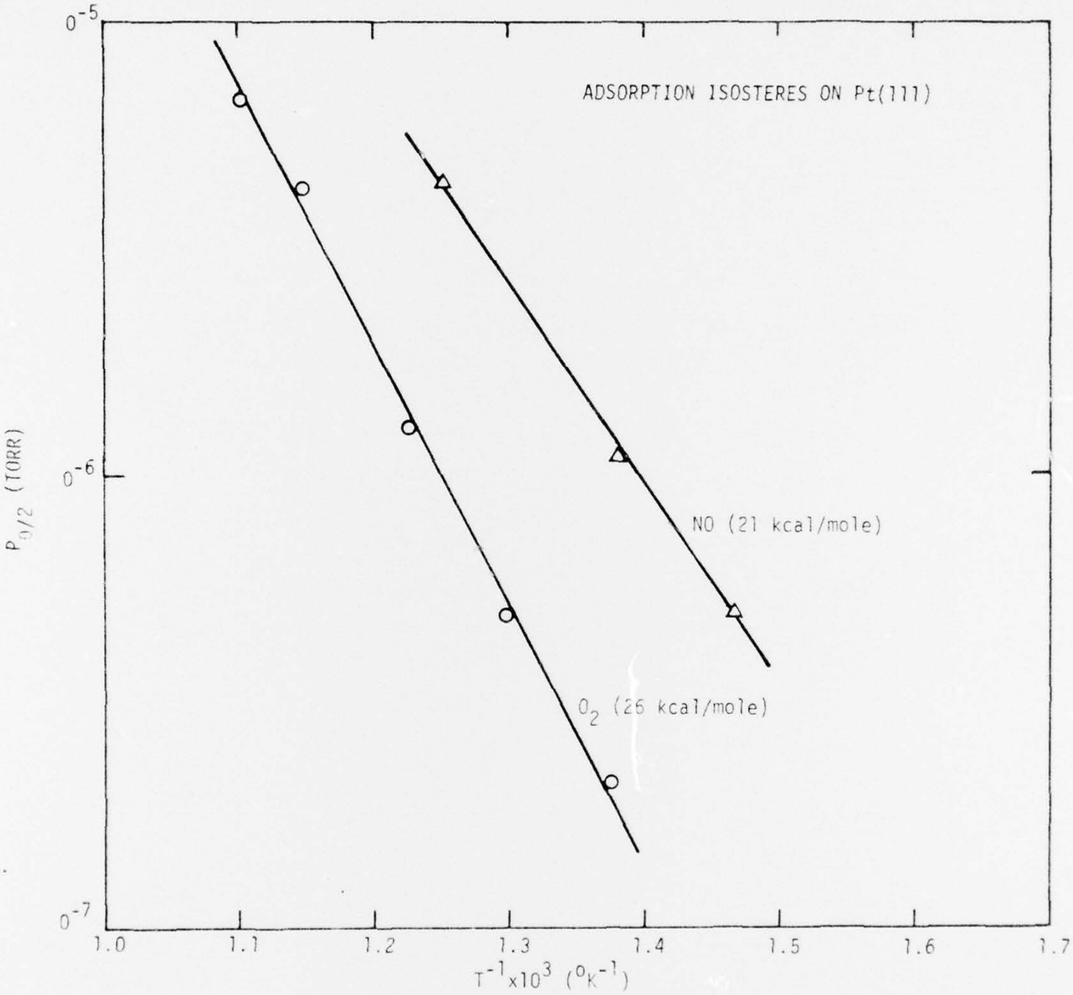
ADSORPTION ISOSTERES ON Pt(111)
NO (21 kcal/mole)
O2 (26 kcal/mole)
0-5
0-6
0-7
Pθ/2 (TORR)
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
T-1x10^3 (°K-1)

Figure 3

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