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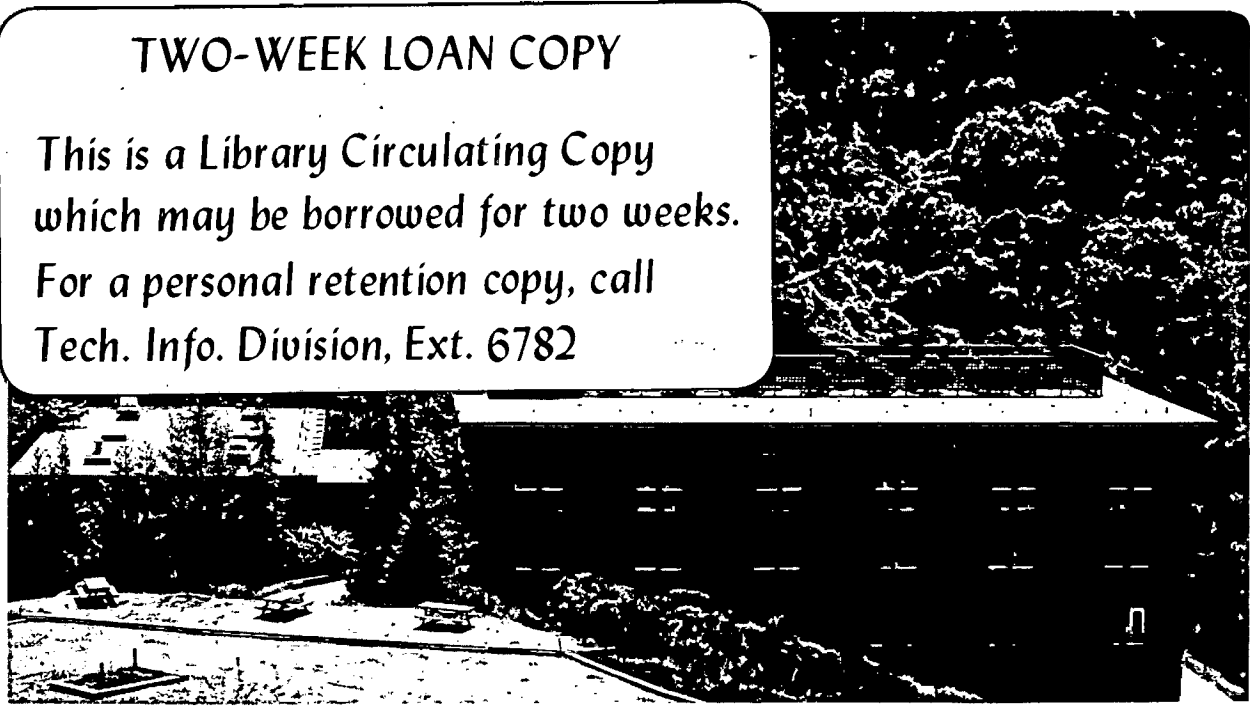
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Coordination Chemistry of Metal Surfaces-
Carbon Monoxide Chemisorption States on Pt(111)
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Abstract

A simple experimental blank procedure is described whereby the chemistry associated with single crystal metal surfaces can be unambiguously differentiated from chemistry associated with the sides or back of the crystal or the large inner surface of a conventional ultra high vacuum chamber. Using this blank procedure along with chemical and spectroscopic information, the two CO chemisorption states for a real, carefully prepared Pt(111) surface are ascribed to imperfection sites (terminal Pt-C-O) and to the (111) platinum sites (bridging Pt_x-C-O). The generality of this experimental and interpretational approach to characterization of chemisorption states is discussed.

7/20/79

Coordination Chemistry of Metal Surfaces--
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Sir:

Delineation of the coordination chemistry of metal surfaces with defined crystallography under "clean" conditions is now a viable and extremely active research activity.¹⁻³ Here we describe a valuable experimental procedure to insure that chemistry ascribed to the flat, crystallographically defined surface is, in fact, just that chemistry--particularly for experiments based on thermal desorption⁴ and chemical displacement^{3,5} reactions. Through such experiments, we have shown that surface imperfections,⁶ invariably present even in carefully prepared crystal samples, play an important and detectable role in the spectroscopic and chemical behavior of a real crystal surface. In addition, we call attention to an alternative interpretation of vibrational spectroscopic data for such conceptually simple systems as chemisorbed CO on the close-packed platinum (111) surface.

A common observation in spectroscopic, diffraction and thermal desorption studies is the apparent presence of two or more chemisorbed states even at coverages that are substantially lower than one half monolayer. Consider the well studied example of CO on the Pt(111) surface. All results from thermal desorption studies are identical within experimental error⁷: there are two well separated desorption curves, one of variable intensity at 180°C which shifts to 150°C as initial CO surface coverage increases and one of relatively fixed intensity and position at approximately 240°C (Figure 1). With substantial CO coverage, the former desorption peak is the larger (ca. 80-90% of the total CO desorption). The higher temperature desorption peak is present in thermal desorption experiments with Pt(111) after 15-30 minute exposures of the crystal to the ambient atmosphere of 10^{-10} to 10^{-11} torr which atmosphere largely consists of H₂ and CO. The major desorption peak has been ascribed uniformly to

a CO chemisorption state on a Pt(111) surface and the minor peak has been variously associated with desorptions from other parts of the ultra high vacuum system, to the edge areas of the crystal and to the ubiquitous imperfections⁶ of a real Pt(111) surface. We have established the last explanation to be the correct one.

In our surface studies,³ thermal desorption⁴ and chemical displacement^{3,5} reactions play a major role in establishing the surface coordination chemistry. Without an experimental blank, there is a major uncertainty as to whether observed thermal desorptions or chemical displacements occur at the crystallographically defined surface of the very small metal crystal.⁸ We have devised a blank experiment based on a crystal, of the metal in study, that has the flat exposed face of experimental study covered by a layer of gold (in the platinum system, the blank was prepared from a conventional platinum crystal wafer by vapor deposition of a thin copper layer followed by a thin gold layer--the sides and back of the crystal were masked during the deposition). By using such metal crystal blanks, we have found it possible to establish with certainty the origin of any molecules displaced in thermal desorption or chemical displacement reactions from metal surfaces. Only in three cases have we seen any chemistry associated with the gold surface in the temperature range of 25 to 400°C: methyl isocyanide expectedly was chemisorbed strongly on gold with a thermal desorption maximum at ~130°C, pyridine behaved similarly, and CH₃CN desorbed at ~90°C.

Our blank studies demonstrated that the observed thermal desorption of CO from the Pt(111) surface is totally associated with the real exposed crystal surface--not with the sides or back of the crystal or other parts of the vacuum system. The gold plated crystal blank experiment showed no CO desorption in the 25 to 400°C region. Accordingly, the desorption maximum at 240°C must be ascribed to thermal desorption from the front surface of the prepared crystal; and because of the high temperature of this desorption process, desorption from surface imperfection sites is the logical process for this desorption phenomenon. It may be of electronic and structural sig-

nificance to the issue of imperfection sites that a stepped Pt crystal (e.g. Pt 6(111) x (111)) exhibits a more intense 240°C thermal desorption maximum and a less intense peak in the 150-180°C range.^{7,9} Crystals with steps and kinks behave similarly.^{7b} (Thus, there is no evidence of different activation energies for CO desorption from steps and kinks). Likewise, for comparable exposures of CO, the intensity of the energy loss peak at 2080 cm.⁻¹ is much greater from the stepped surface(6(111)x(111)) than from the (111) surface.^{7a} That is, as steps are added to the imperfections which are always present, the intensity of the loss at 2080 cm.⁻¹ compared to the 1850 cm.⁻¹ loss increases. We suggest that the most common imperfections on a carefully prepared, cleaned and annealed Pt(111) surface will be steps and kinks.

Since there is a significant (ca. 10-20%) concentration of chemisorbed CO at imperfections on the Pt(111) surface and since there is a substantial difference, about 5 kcal./mole, in the activation energies for desorption from the (111) surface and for imperfection sites, vibrational studies should detect (resolve) both states. The first detectable state should be the more tightly bound state associated with CO at imperfection sites. In fact, two states are detected by electron loss studies¹⁰ -- the first to appear in the energy region characteristic of losses due to CO stretching excitation is a loss at 2080 cm.⁻¹ and the second at 1850 cm.⁻¹, regions characteristic of terminal M-CO and bridging M_x-CO metal carbonyls, respectively. The current interpretation of these data is that CO first chemisorbs on single platinum atoms in the (111) plane (terminal and linear M-C-O) and at higher coverages bridging sites are occupied. However, CO chemisorption apparently occurs first at bridging sites on the (111) surfaces of the closely related metals, nickel and palladium, a stereochemical feature fully consonant with coordination chemistry principles since maximal interaction of the CO carbon atom with surface metal atoms should lower most effectively the surface potential energy at low CO surface coverages on close packed (111) or (001) surfaces.^{11,12}

In the interpretation of the vibrational data for CO on Pt(111), serious consideration should be given to the possibility that the energy loss at 2080 cm.^{-1} arises from CO chemisorbed at imperfections on a real Pt(111) crystal face,¹³ and that the CO chemisorbed on the Pt(111) plane has a CO stretching frequency at 1850 cm.^{-1} a region characteristic of a bridging carbonyl--as expected by analogy to the CO chemisorption states on Ni and Pd(111) surfaces and from coordination chemistry principles.^{11,12}

In addition, we submit that another feature of the vibrational data for CO on Pt(111) supports the thesis that CO is on bridging sites (the state associated with the 1850 cm.^{-1} loss) for platinum atoms in a (111) environment. For a given chemisorption state of a molecule or a molecular fragment on a metal surface, the average binding energy for the molecules bound to metal atoms in environments characteristic of the prepared surface plane should decrease generally to some small but detectable degree as the separation between individual surface molecules decreases (i.e. as the surface coverage increases). In some instances these slight energy changes may be detectable spectroscopically. In sharp contrast, chemisorption states of molecules on imperfection sites of a well prepared crystal surface should be less perturbed by coverage changes--the imperfections sites generally will not be ordered, contiguous or subject to correlation effects. For the general case of CO chemisorption states, characteristic of the prepared metal surface plane, electron transfer from metal to π^* CO orbitals should be less extensive as CO coverage increases and the ν_{CO} characteristic of this state should increase--available data from electron loss and infrared reflectance studies of CO on metal surfaces can be so interpreted.^{7a,10} Thus, the chemisorption state which gives rise to the nearly coverage invariant 2080 cm.^{-1} energy loss for CO on Pt(111) is best ascribed to CO at surface imperfection sites. The chemisorption state which yields the lower energy (1850 cm.^{-1} - 1880 cm.^{-1}) CO stretching loss whose position is coverage dependent with a shift to higher energy with increasing coverage is best ascribed to CO bridge bonded to platinum atoms in a (111) surface environment.

Although imperfections on single crystal surfaces present substantial difficulties in the interpretation of chemical and spectroscopic data for chemisorption states, we believe that the above described blank experiments coupled with a careful assessment of the coordination chemistry as a function of surface crystallography can eventually unravel the intimate features of metal surface coordination chemistry. The implications presented here for platinum surfaces have substantial breadth, e.g., formally analogous phenomena have been established for the chemisorption of benzene on a Pt(111) surface.¹⁵ In contrast, we have not sensed apparent chemisorption states due to crystal imperfections on Ni(111) with a variety of small molecules--a result in keeping with the greater ease of preparing "nearly" perfect surfaces with nickel than with platinum. In the specific case of CO on nickel, both the (111) surface and a stepped surface show a single desorption maximum, at temperatures separated by only 20°C.¹⁶ Therefore, thermal desorption experiments would not detect step-like imperfections on a Ni(111) surface.

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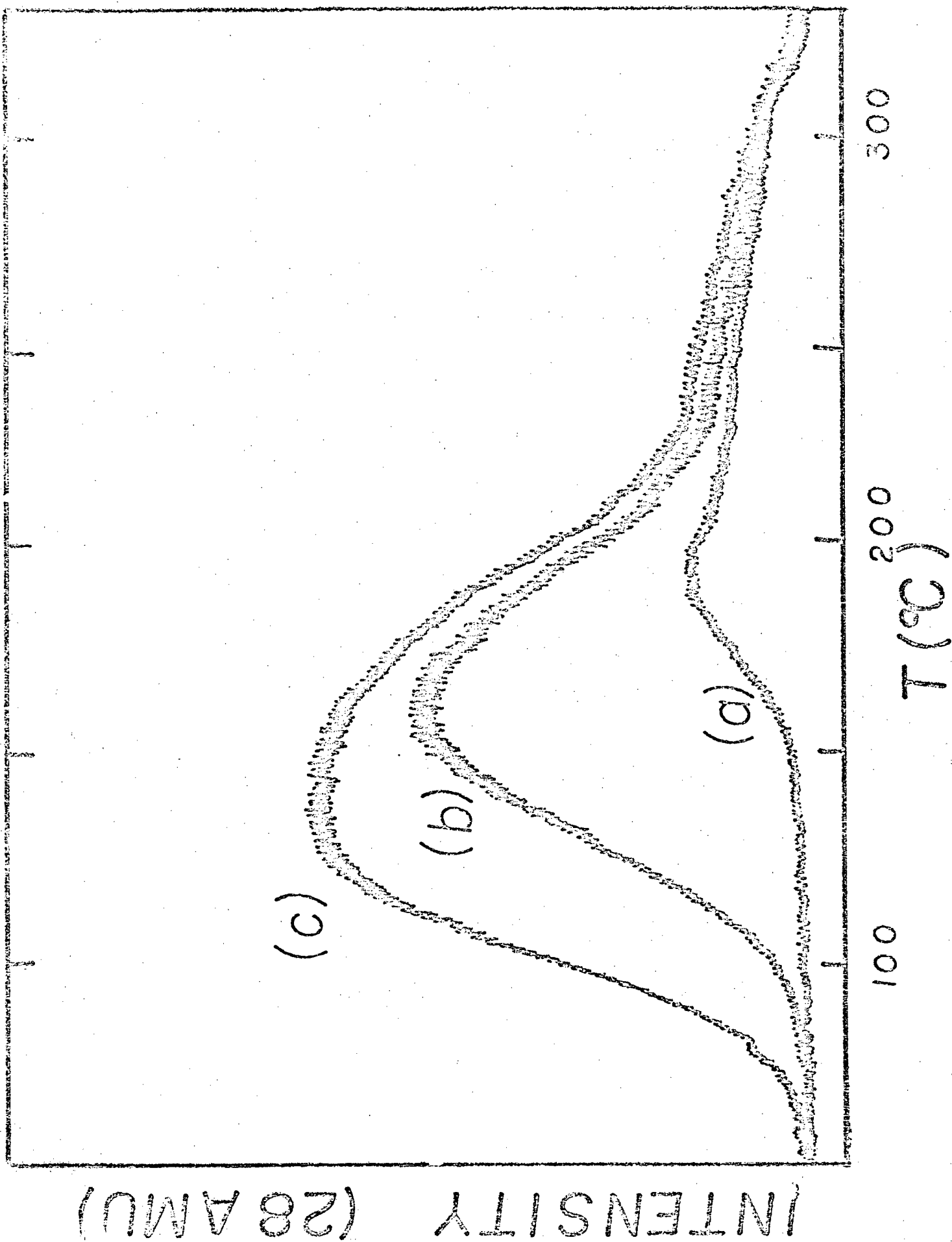
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Figure 1. Thermal desorption spectra for CO from a Pt(111) crystal surface. In (a) is shown the spectrum obtained for mass 28 after exposure for 50 minutes to the ambient gas present in the vacuum chamber. Spectra for CO desorptions from CO states with coverages of 0.1 and 0.2, as measured from Auger intensities, are given in (b) and (c), respectively.



INTENSITY (28 AMU)

T (°C)

300

200

100

(a)

(b)

(c)

References and Notes

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- (7a) Hopster, H.; Ibach, H. Surf. Sci. 1978, 77, 109.
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(13) There has been a reluctance to consider this possibility because of the relatively large intensity of the 2080 cm.^{-1} loss. However, there need be only a factor of five difference in the oscillator strengths for CO bound at imperfection and at (111) sites to account for the apparent intensity discrepancy. There are experimental data in molecular coordination chemistry that clearly show such differences in oscillator strengths are possible and commonly found¹⁴ in CO coordination chemistry.

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(15) These studies, to be published, show that benzene chemisorption on Pt(111) is largely thermally reversible. The thermal desorption studies clearly show there are two distinct chemisorption states. Neither was detected in the blank experiment. The more strongly bound state is ascribed to benzene on Pt(111) and the more weakly to benzene bound at or near imperfection sites.

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