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### Title

THE ADSORPTION OF ACETYLENE ON THE (111) CRYSTAL FACE OF PLATINUM; DETECTION OF TWO CHEMICALLY DIFFERENT ADSORPTION STATES BY LOW-ENERGY ELECTRON DIFFRACTION

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### Author

Stair, P.C.

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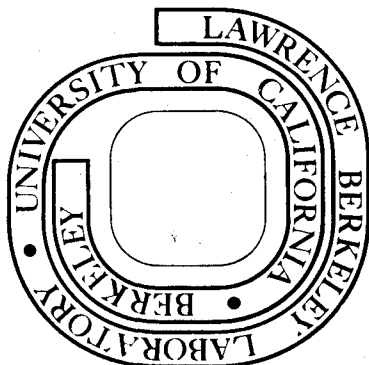
P. C. Stair and G. A. Somorjai

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The Adsorption of Acetylene on the (111) Crystal Face of  
Platinum; Detection of Two Chemically Different Adsorption  
States by Low-Energy Electron Diffraction

by

P. C. Stair and G. A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,  
and Department of Chemistry, University of California,  
Berkeley, California 94720

The chemisorption of acetylene on the Pt(111) single crystal surface has been studied using low-energy electron diffraction (LEED) by several workers.<sup>1,2</sup> It has been well established under conditions of low acetylene exposure to a clean surface in ultra-high vacuum that the adsorbed acetylene forms a well ordered overlayer structure with a diffraction pattern characteristic of a (2x2) unit mesh (Fig. 1). We have measured, for the first time, the diffraction beam intensities from the adsorbed layer as a function of electron energy in the range of 10-100 eV for use in surface crystallography. This data indicates that the adsorption takes place in two steps: first, acetylene adsorbs at 300K into a metastable state followed by chemical conversion into another more stable state upon heating to ~400K. Both structures show the characteristic (2x2) diffraction pattern with no apparent change in position or in shape of the diffraction spots during the transformation. Thus, the two adsorption states are distinguishable only through changes in the diffraction beam intensity profiles (I vs eV curves). Via LEED crystallography, we are able, for the first time, to monitor in detail a structural-chemical change in an adsorbate system that is also catalytically important.

The experiments were all carried out in an ultra-high vacuum LEED-Auger apparatus using (111) orientation single crystal platinum samples. The cleaning procedure and the photographic intensity measurement technique have been previously described.<sup>3</sup> The acetylene, which had been purged of acetone in a molecular sieve, dry-ice cooled trap, was introduced into the vacuum chamber via a stainless steel needle pointed at the sample. Although the exposures have not been determined accurately, it was found that at 300K a well ordered  $C_2H_2$  overlayer that exhibits a (2x2) surface structure was obtained only at low exposures ( $\sim 1$  Langmuir), in agreement with earlier work.<sup>2</sup> The adsorption and ordering characteristics as well as the observed chemical change were independent of exposure to the electron beam. Further details on the experimental technique will be reported elsewhere.<sup>4</sup>

Measured diffraction intensity profiles are shown for the metastable room temperature state in Figure 2. The diffraction beam labeling and incident angle designation follow Jona's convention.<sup>5</sup> This structure is stable for several hours at 300K, and the peak positions, relative intensities and shapes in the profiles are well reproduced from one adsorption experiment to the next. Upon heating to 400K for one hour then cooling to 300K the intensity profiles have transformed to those shown in Figure 3. The transformation also takes place at 300K but requires more than 24 hours for completion. The Auger traces show the same amount of carbon for both structures implying no acetylene desorption.

Detailed analyses of the curves obtained at normal incidence ( $\theta = 0$ ,  $\phi = 0^\circ$ ) show (Fig. 2a and 3a) several important changes. The 68 eV peak in the  $(0 \sqrt{1/2})$  beam has shifted and broadened into a complex peak spanning

between 40 eV and 70 eV as the transformation from the less stable first structure to the more stable second structure occurs. Similarly for the  $(1/2 \overline{1/2})$  beam, the peak at 30 eV is shifted 10 volts to 20 eV; the double peaks at 56 eV and 66 eV shift and change intensity becoming a strong peak at 62 eV and a much weaker one at 50 eV, and the valley at 40 eV becomes a peak. If we compare I vs eV curves for the two structures at  $\theta = 4^\circ$  (Figs. 2b and 3b) for the  $(0 \overline{1/2})$  beam, a large peak at 40 eV shifts slightly to 36 eV while a new, high intensity peak appears at 55 eV; a significant change in the shape of the profiles for the  $(1/2 \overline{1/2})$  beam takes place at between 20 eV and 60 eV. Finally the structure between 30 eV and 40 eV in the  $(1/2 0)$  beam is much reduced with the appearance of a new structure between 40 eV and 60 eV. Similar marked changes occur in the fractional order beams at  $\theta = 10^\circ$  and  $\theta = 16^\circ$  along with some smaller shifts accompanied by peak ratio changes in the (00) beam profiles.

These drastic differences in the I vs eV curves indicate changes in the surface structure of acetylene that must be due to a change in the chemical bonding of the acetylene to the platinum (111) surface. Thus, adsorbed acetylene undergoes a chemical transformation on the metal surface upon heating to 400K that is accompanied by transition from one ordered surface structure to another both having the same unit cell. We have also measured the intensity profiles of adsorbed ethylene, methylacetylene and propylene which chemisorb with the same (2x2) surface periodicity as acetylene on the (111) platinum surface. The intensity curves obtained upon ethylene adsorption are virtually identical to those we have measured for the more stable acetylene structure. Comparing the intensities from adsorbed propylene and methylacetylene in those parts of

the I vs eV curves most sensitive to the observed structural transformation, we find nearly identical changes between methylacetylene and propylene as occur with acetylene upon heating to 400K.

Detailed structure analysis by means of dynamical LEED calculations can be carried out and should identify the molecular geometry of the adsorbed hydrocarbons that give rise to the experimental diffraction beam intensity profiles. These calculations are in progress and their results will be reported at a later date. However, our experimental observations provide some basis for speculation as to the nature of the structural and chemical changes in the ordered acetylene overlayer. It appears that acetylene is undergoing a carbon-carbon bond expansion during its transformation on the platinum (111) crystal face. The less stable surface structure that forms first at 300K is more weakly bound and only slightly distorted from its free molecule configuration. The stable structure would then be more tightly bound to the platinum with a shorter platinum-carbon bond distance and a weaker, more elongated carbon-carbon bond. In fact, preliminary results from LEED intensity calculations confirm the sensitivity of the intensity profiles to the carbon-platinum distance and seem to indicate changes in this distance for the two acetylene structures in the direction that is indicated by our model.<sup>6</sup>

With the completion of detailed geometrical structure calculations we should be able to construct a complete picture of the adsorption mechanisms of several hydrocarbon molecules ( $C_2H_2$ ,  $CH_3C\equiv CH$ ,  $C_3H_6$ ). It appears that studies of chemical changes in the adsorbed layer by LEED can provide insight into the dynamics of adsorption and chemical bonding to surfaces.

Acknowledgement

We are grateful to Dr. L. L. Kesmodel for helpful discussions in the course of this work. This work was supported by the U. S. Energy Research and Development Administration.



References

1. A. E. Morgan and G. A. Somorjai, J. Chem. Phys., 51, 3309 (1969).
2. W. H. Weinberg, H. A. Deans and R. P. Merrill, Surf. Sci., 41, 312 (1974).
3. P. C. Stair, T. J. Kaminska, L. L. Kesmodel and G. A. Somorjai, Phys. Rev. B, 11, 623 (1975).
4. P. C. Stair and G. A. Somorjai (To be published).
5. F. Jona, IBM J. Res. Develop., 14, 444 (1970).
6. L. L. Kesmodel (Private communication).

## Figure Captions

- Fig. 1 Low-energy electron diffraction patterns from the clean platinum (111) crystal face (above) and the acetylene on platinum overlayer (below). Both pictures are for normal incidence and 68 volts.
- Fig. 2 a) I-V profiles from the less stable acetylene structure at normal incidence.  
b) I-V profiles from the less stable acetylene structure at  $\theta = 4^\circ$ .  
Note: The dotted lines indicate the reproducibility of the data.  
The large dots indicate the points of scaling factor changes.
- Fig. 3 a) I-V profiles from the more stable acetylene structure at normal incidence.  
b) I-V profiles from the more stable acetylene structure at  $\theta = 4^\circ$ .  
Note: The dotted lines indicate the reproducibility of the data.  
The large dots indicate the points of scaling factor changes.

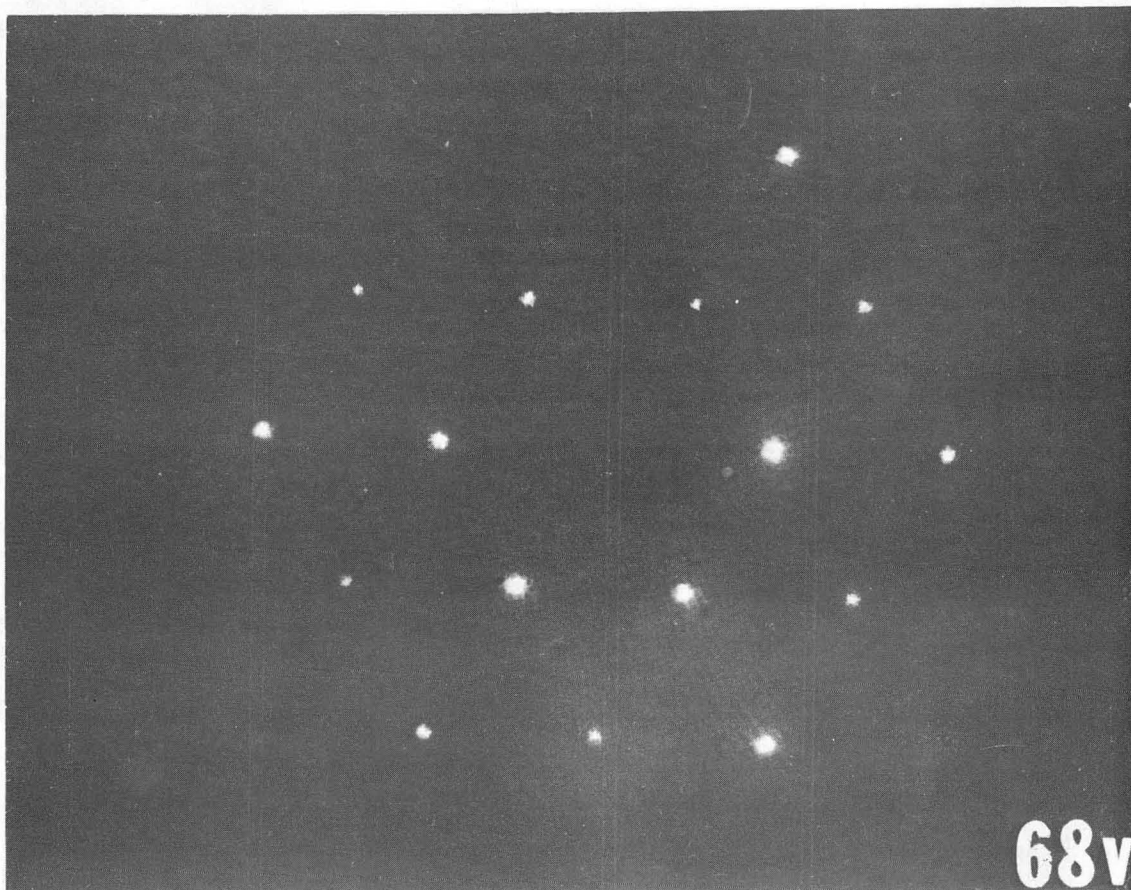
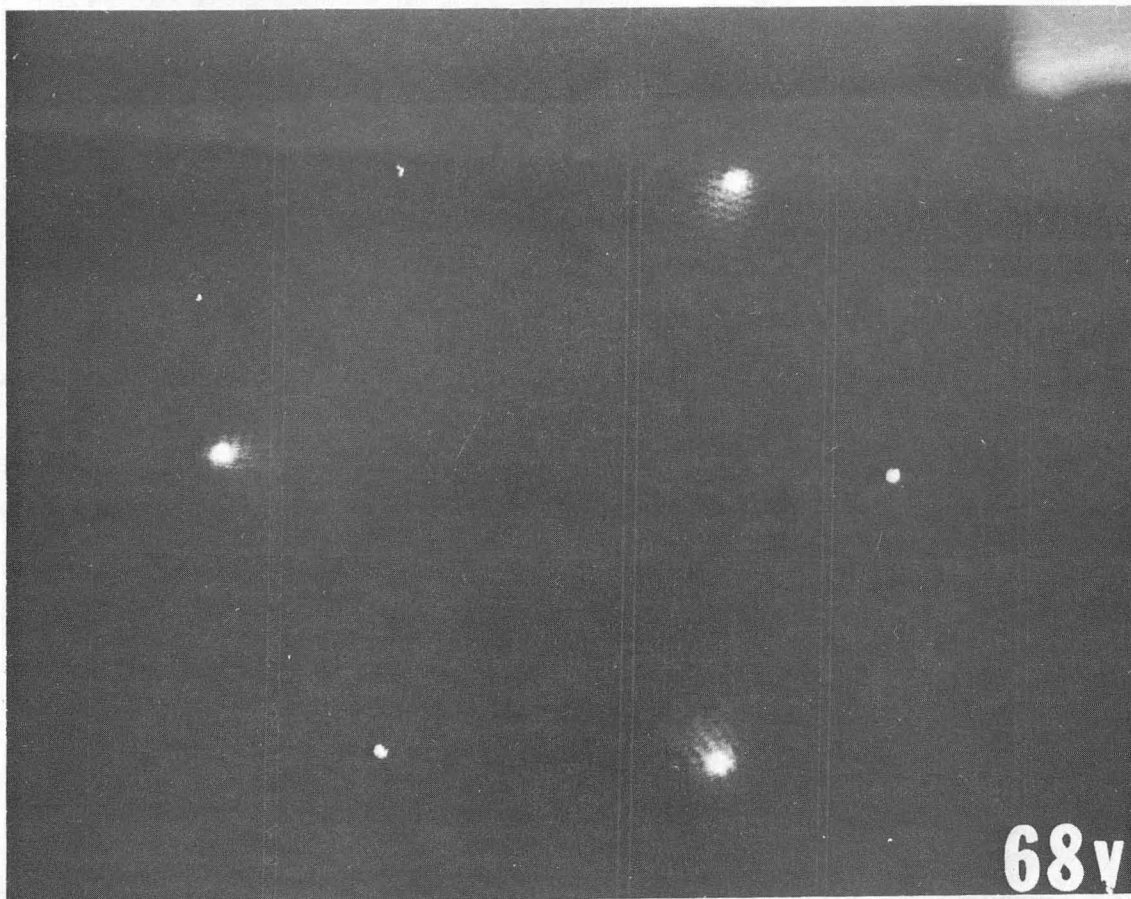
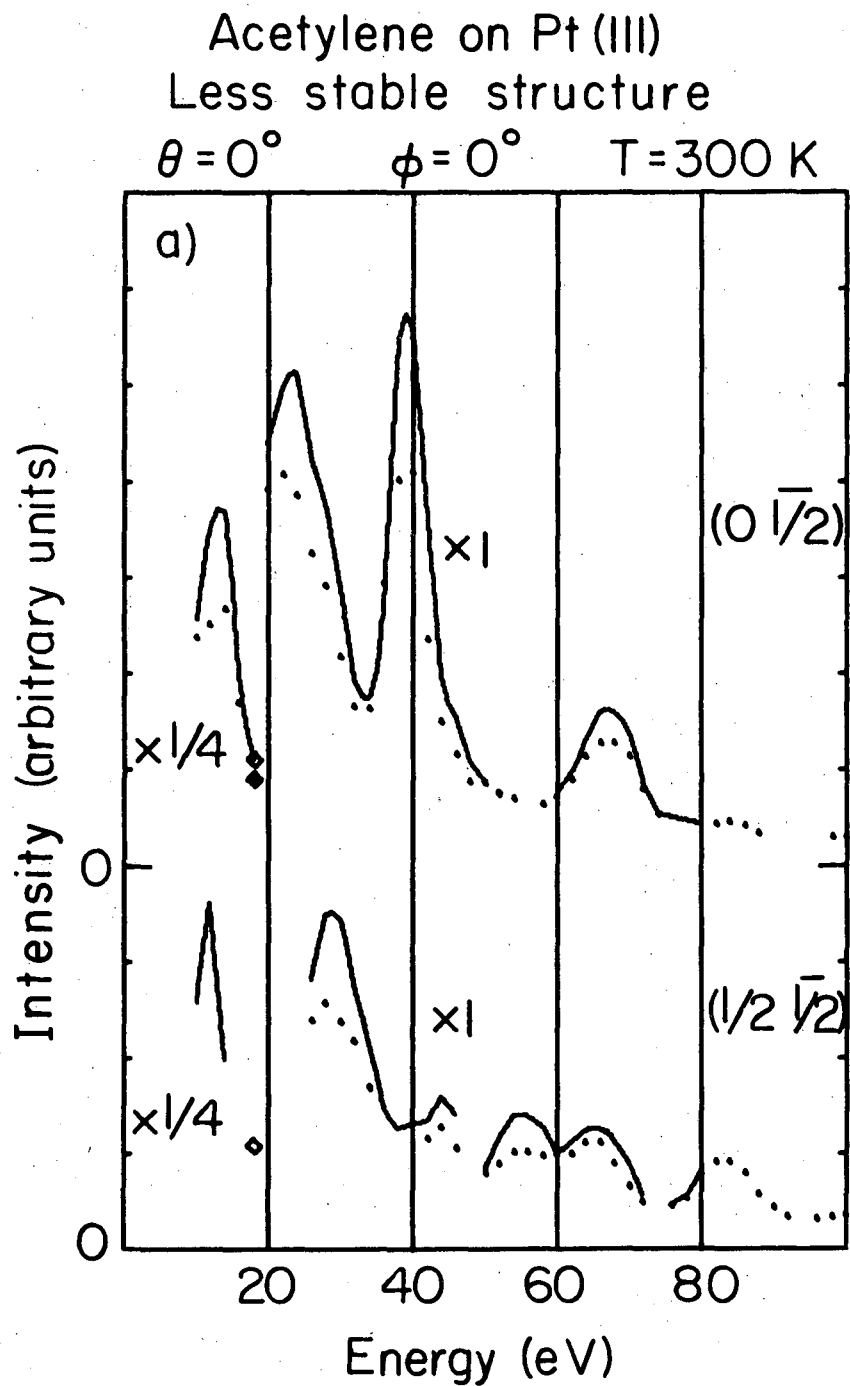


Fig. 1

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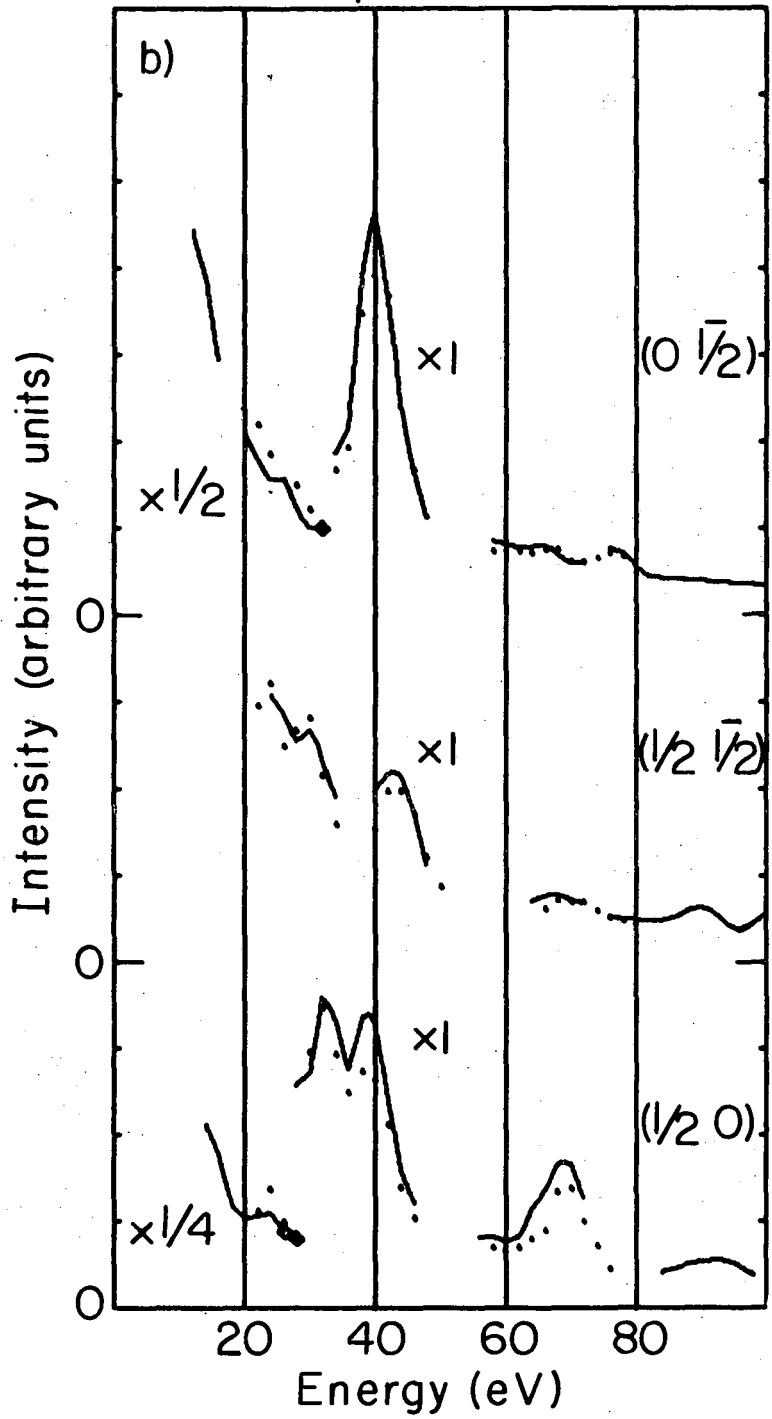


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Fig. 2a

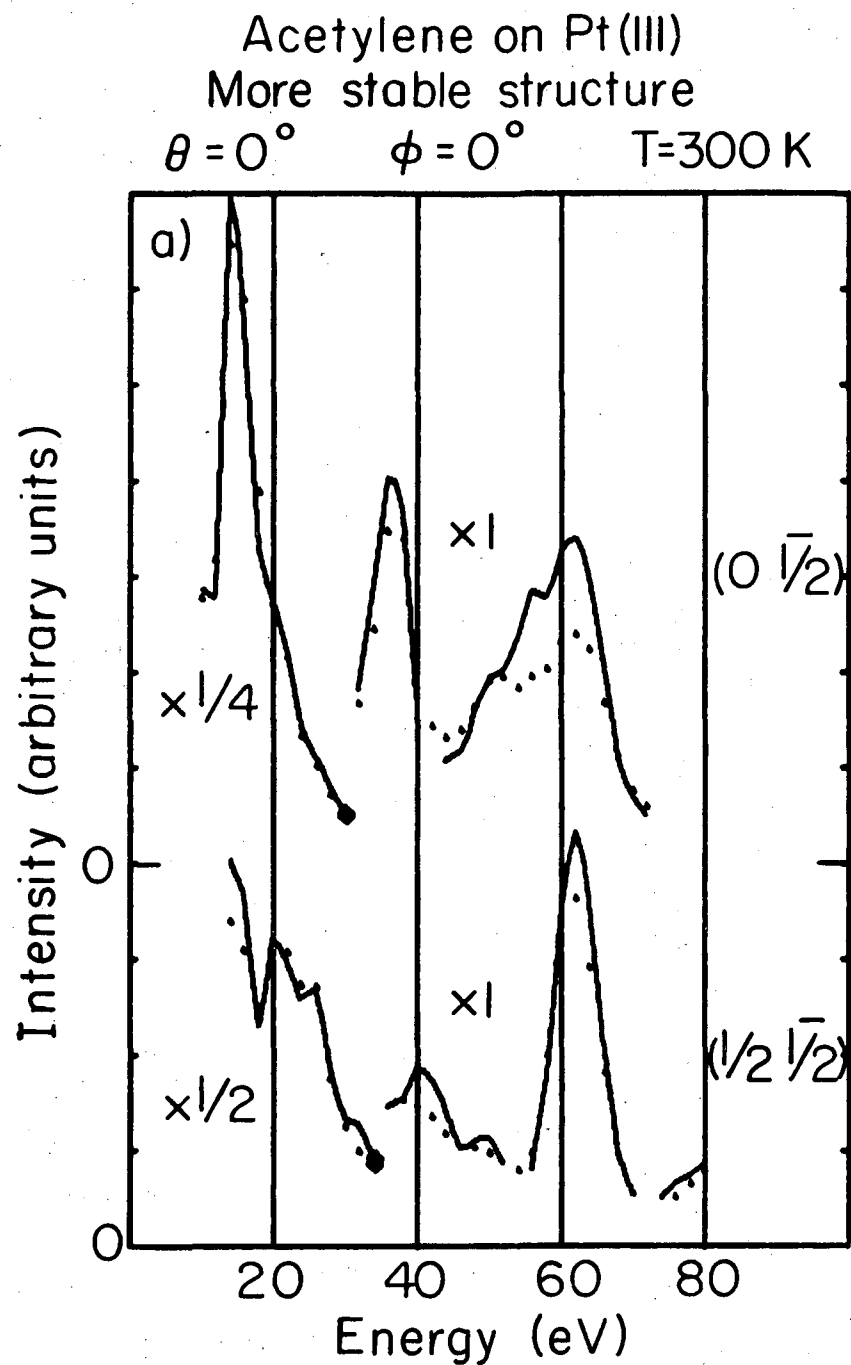
Acetylene on Pt(111)  
Less stable structure

$\theta = 4^\circ$     $\phi = 0^\circ$     $T = 300 \text{ K}$



XBL 763-6654

Fig. 2b

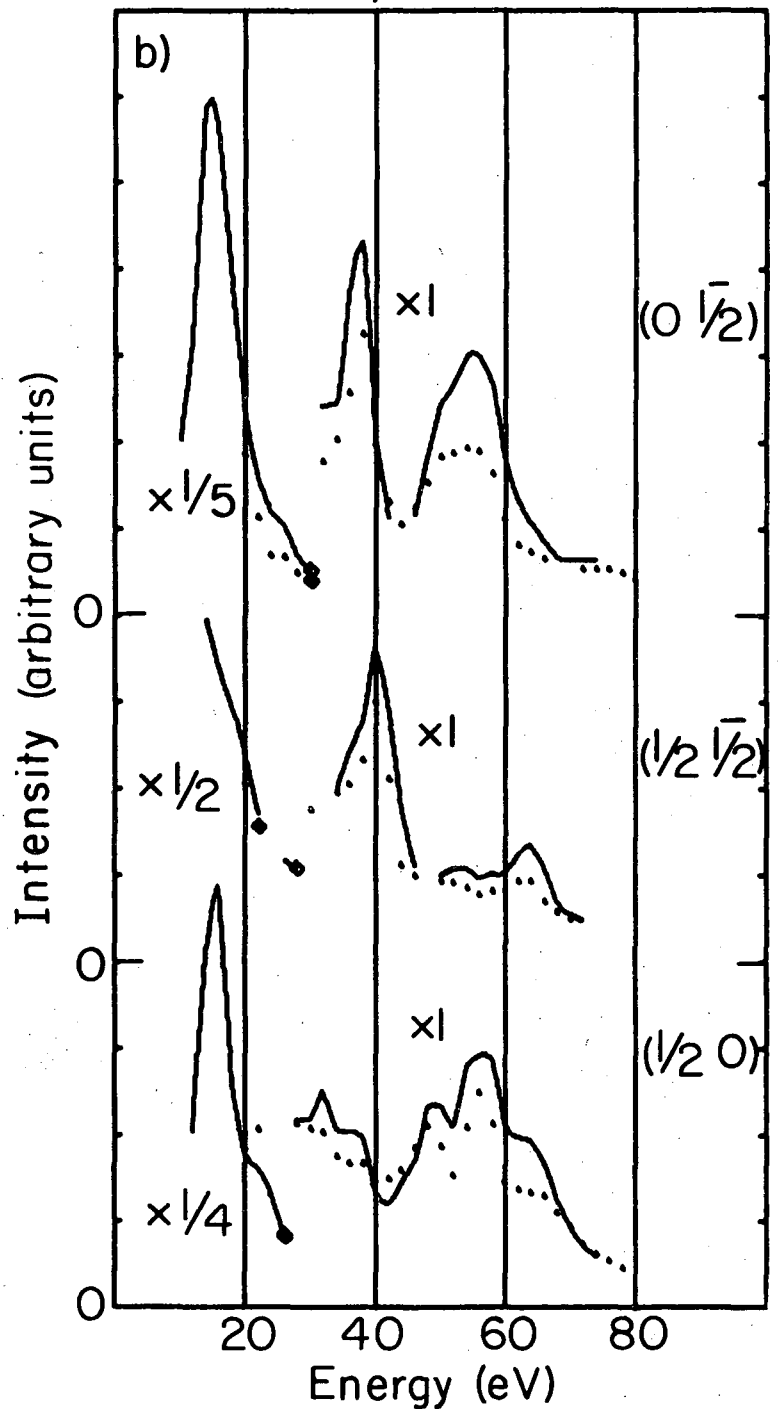


XBL 763-6655

Fig. 3a

Acetylene on Pt(111)  
More stable structure

$\theta = 4^\circ$   $\phi = 0^\circ$   $T = 300$  K



XBL763-6656

Fig. 3b

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