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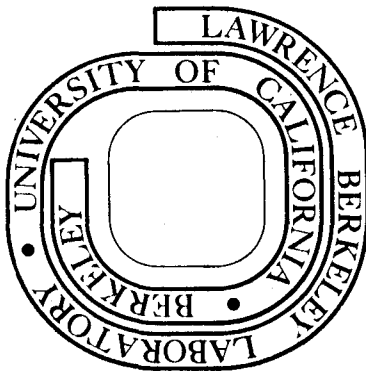
L. L. Kesmodel, P. C. Stair, R. C. Baetzold, and  
G. A. Somorjai

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THE SURFACE STRUCTURE AND BONDING OF ACETYLENE  
TO THE PLATINUM (111) SURFACE

by

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ABSTRACT

Analysis of low-energy electron diffraction beam intensities for a  $(2 \times 2)$  chemisorbed layer of acetylene on the Pt(111) surface shows that the molecules are adsorbed in either a three-fold position or a two-fold bridge position at a distance of  $1.95 \pm 0.10 \text{ \AA}$  above the topmost plane of platinum atoms.

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In recent years the technique of low-energy electron diffraction (LEED) beam intensity-voltage (I-V) analysis (surface crystallography) has been used primarily to determine bonding geometries for (unreconstructed) clean metal surfaces and simple overlayer systems of chemisorbed atoms. Here we wish to report the first such investigation of an ordered overlayer of molecules on a surface, the hydrocarbon acetylene ( $C_2H_2$ ) associatively chemisorbed on the (111) surface of platinum.<sup>1</sup> We find that the method can distinguish between competing model geometries of the metal-hydrocarbon system and that the optimum bonding arrangement gives calculated I-V profiles which are in consistently good agreement with experiment for several incident beam angles and a large number of fractional and integral-order beams.

The exposure of a clean Pt(111) surface to  $C_2H_2$  gas at 300 K under ultra-high vacuum conditions followed by gentle heating to 400 K for one hour gives rise to a (2x2) LEED diffraction pattern with sharp fractional-order spots indicative of long-range order in the overlayer.<sup>2</sup> The LEED beam intensities from the  $C_2H_2$  overlayer were measured photographically at several incident beam angles for energies 10-200 eV. The experimental apparatus, single crystal platinum sample, cleaning procedure and the photographic technique have been previously described.<sup>3</sup> The gas was introduced into the vacuum chamber via a stainless steel needle directed at the crystal surface. Although gas exposures have not been accurately determined, it was found that at 300 K a well-ordered  $C_2H_2$  overlayer was obtained only at low exposures (~1 Langmuir), in agreement with earlier work.<sup>4</sup> The adsorption and ordering characteristics of  $C_2H_2$  were independent of the electron beam. However, the fractional-order beams lost intensity

under electron beam exposure at a rate approximately proportional to the incident beam current. The electron beam exposure was therefore limited so that the maximum loss in fractional-order beam intensity was about 5% during the period of photographic data collection (2 min).

The surface structure analysis was carried out by comparing calculated I-V profiles from models of the Pt-C<sub>2</sub>H<sub>2</sub> geometry to the experimental results. The model geometries considered were the likely ones in which the C-C axis of the molecule is parallel to the surface plane with the molecule oriented in various symmetric ways with respect to the substrate atoms (Fig. 1). The observed three-fold symmetry of the diffraction pattern could arise from three 120°-rotated domains of either (2x2) or (2x1) packing of C<sub>2</sub>H<sub>2</sub> on the substrate, and both types of translational symmetry were considered in the analysis. The calculations employed a multiple-scattering theory using a beam representation and the layer-doubling method.<sup>5</sup> The Pt geometry and scattering parameters were the same as those used previously for the clean surface<sup>6</sup> with the exception of the electron damping (imaginary part of the potential) which was taken as 2.5 eV.

Details of the construction of the C<sub>2</sub>H<sub>2</sub> scattering potential will be reported elsewhere.<sup>7</sup> Trial calculations showed that the inclusion of H scattering produced negligible changes in the I-V profiles, and the H atoms were therefore neglected in the structure analysis (the scattering cross-section of hydrogen is about 15% that of carbon in the energy range 15-90 eV). The C atom scattering potentials were constructed from a self-consistent field molecular-orbital calculation<sup>8</sup> for C<sub>2</sub>H<sub>2</sub> and then spherically averaging the potential within spheres centered on each of

the two C atoms. The I-V profiles were calculated in the energy range 15-90 eV using 5 partial-wave phase shifts for each atomic species and a convergent number of atomic layers and beams.

For each of the planar orientations shown in Fig. 1 the z-distance of the molecule above the surface was initially varied between 1.3 and 2.5 Å in 0.2 Å intervals and was later refined to 0.1 Å intervals in the optimum range 1.8-2.1 Å. The C-C distance was allowed to expand from the triple-bond (gas phase  $C_2H_2$ ) distance of 1.20 Å to the double-bond distance of 1.34 Å, but the calculated I-V profiles were found to be insensitive to this variation, exhibiting only minor changes in relative intensities and peak positions.

The I-V profiles were calculated for a large number of fractional and integral-order beams at incident beam angles of  $\theta=0^\circ$ ,  $4^\circ$ ,  $8^\circ$  and  $16^\circ$ ; the results are summarized in Figs. 2-4. Figure 2 shows a comparison of the I-V curves for various planar orientations at the z-distance of 1.9 Å above the substrate with the (2x2) translational symmetry and the C-C distance of 1.20 Å. The (2x1) arrangements gave poor agreement with experiment. Due to intensity averaging over equivalent  $120^\circ$ -rotated domains the I-V profiles for geometries A1 and C1 are virtually identical to those for A2 and C2, respectively. The B1 and B2 profiles are very different, however, due to the lower symmetry of the B site. As illustrated in Fig. 2 the best agreement is found for the B1 and C2 (or C1) orientations with poor agreement for the A1, A2 and B2 geometries. The C1 geometry, however, in which the two carbon atoms have different atomic environments appears quite unfavorable from a carbon-platinum bonding viewpoint and is rejected for that reason. Figures 3-4 show several additional comparisons of theory

and experiment for the B1 and C2 geometries. Visual evaluation of the I-V profiles over all angles and diffraction beams rates the B1 and C2 geometries as the most favorable. An objective, computerized analysis<sup>7</sup> of the profiles with regard to peak positions, line shapes and relative intensities is consistent with the visual rating and further indicates that the C2 geometry is somewhat more favorable than the B1 geometry. The A1, A2 and B2 arrangements can be ruled out.

We conclude that acetylene is chemisorbed on Pt(111) in one of two possible local bonding modes at a z-distance of  $1.95 \pm 0.10 \text{ \AA}$  above the top-most plane of platinum atoms. In the most likely bonding mode (C2) the molecule is centered on a triangular site, the carbon atoms are equivalent by symmetry, and relevant C-Pt distances are  $2.25 \text{ \AA}$  and  $2.59 \text{ \AA}$ . In the other possible bonding mode (B1) the molecule is in an approximately two-fold position with each carbon coordinating to three platinum atoms, C-Pt distances being  $2.47 \text{ \AA}$  and  $2.65 \text{ \AA}$ . The C2 mode of bonding is found to occur in various trimetallic metal-alkyne complexes whereas a bridging structure analogous to B1 occurs in bimetallic complexes.<sup>9,10</sup> On the other hand, popular notions of acetylene adsorption on transition-metal surfaces have involved an acetylene  $\pi$ -complex coordinated to a single metal atom (model geometry A1 or A2) or a di- $\sigma$  complex in which each of the two carbon atoms forms a  $\sigma$ -bond with a different metal atom<sup>11</sup> (model geometry B2). In particular, the di- $\sigma$  model has often been cited in connection with the mechanism of dehydrogenation of ethylene ( $\text{C}_2\text{H}_4$ ) to an acetylenic species upon adsorption with the ligand molecular orbitals in an  $\text{sp}^2$  hybrid configuration. Although these bonding modes could be operable in the less stable acetylene overlayer,<sup>2</sup> our results show that



they are not the favored bonding arrangements on the platinum (111) surface.

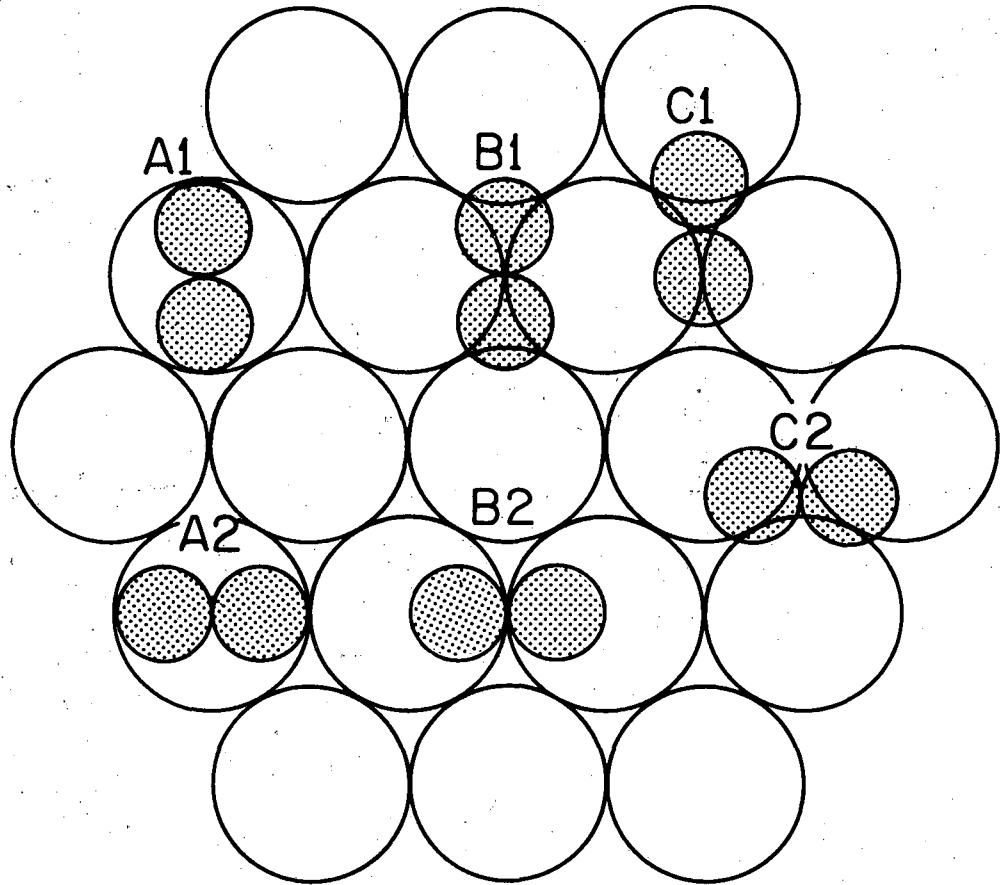
This work was carried out under the auspices of the U. S. Energy Research and Development Administration. We wish to thank N. Bartlett, L. Falicov, K. N. Raymond and H. F. Schaefer for helpful discussions on various aspects of this research.

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Figure Captions

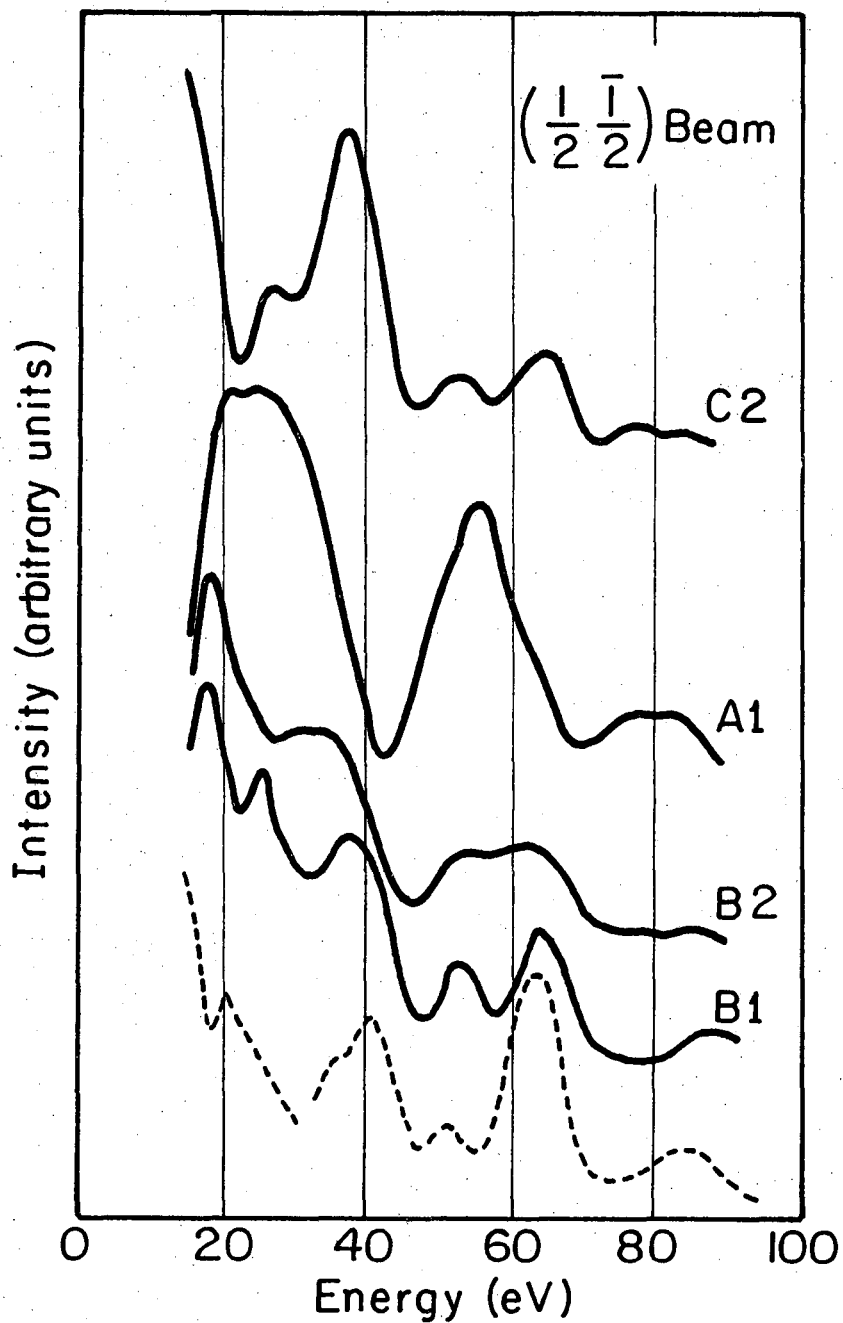
- Fig. 1. Trial geometries of  $C_2H_2$  on the Pt(111) surface. Positions A, B, C refer to coordinations to one, two or three neighboring Pt atoms. The labels 1 and 2 distinguish  $90^\circ$ -rotated molecules.
- Fig. 2. Comparison of calculated I-V profiles (solid line) for the trial geometries ( $z=1.9 \text{ \AA}$ ) to experiment (dashed line) at normal beam incidence.
- Fig. 3. Comparison of calculated I-V profiles (solid line) for the optimum geometries (B1, C2;  $z=1.9 \text{ \AA}$ ) to experiment (dashed line) at normal beam incidence.
- Fig. 4. Comparison of calculated I-V profiles (solid line) to experiment (dashed line) at incident angle  $\theta=4^\circ$ . Other conditions as in Fig. 3.



XBL 7512-10,012

Figure 1

Pt(III) - (2x2) - C<sub>2</sub>H<sub>2</sub>



XBL 7511-9634

Figure 2

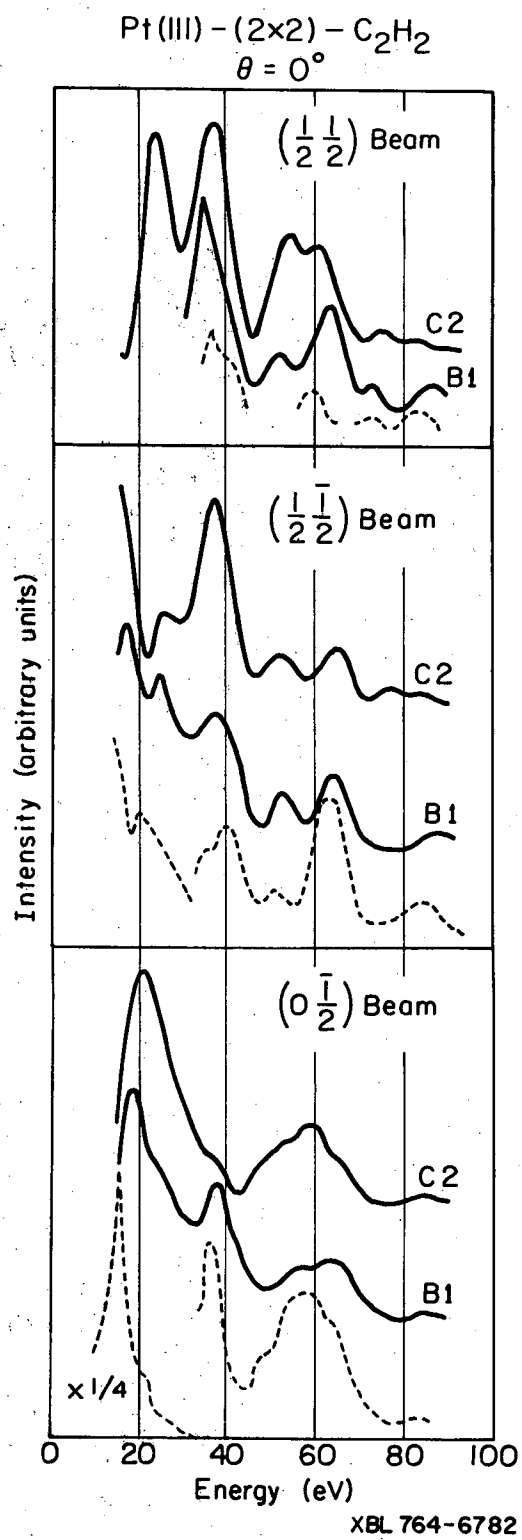
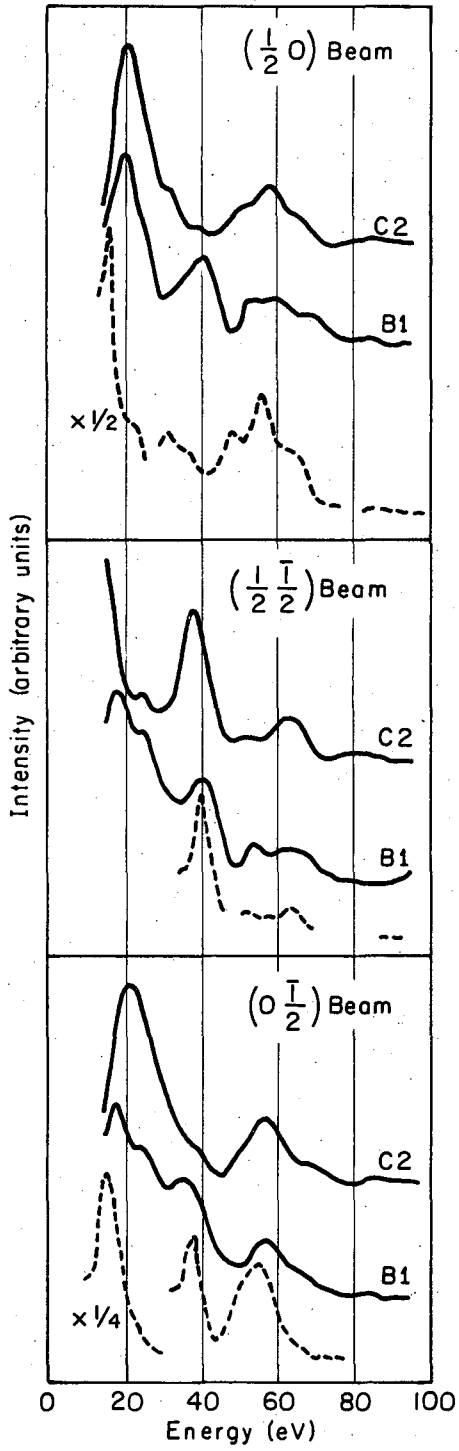


Figure 3

Pt(III) - (2x2) - C<sub>2</sub>H<sub>2</sub>  
 $\theta = 4^\circ$



XBL764-6783

Figure 4

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