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Author

Kesmodel, L.L.

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

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The Surface Structure and Bonding of Acetylene
to the Platinum (111) Surface

by

L. L. Kesmodel, 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

ABSTRACT

Analysis of low-energy electron diffraction beam intensities for a (2×2) chemisorbed overlayer of acetylene on the Pt(111) surface shows that the molecules are adsorbed in two-fold bridge positions at a distance of 1.8 ± 0.1 Å above the topmost plane of platinum atoms. We suggest a model for the chemisorption bonding in light of these results.

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.¹ We find that the method is able to rather easily distinguish between competing model geometries of the metal-hydrocarbon system and that the optimum bonding arrangement gives calculated I-V profiles which are in excellent agreement with experiment.

The exposure of a clean Pt(111) surface at 300 K under ultra-high vacuum conditions to C_2H_2 gas gives rise to a (2×2) LEED diffraction pattern with sharp fractional-order spots indicative of long-range order in the overlayer. 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.² 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.³ 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-C₂H₂ 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 (2×2) or (2×1) packing of C₂H₂ 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.⁴ The Pt geometry and scattering parameters were the same as those used previously for the clean surface⁵ 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 C₂H₂ scattering potential will be reported elsewhere.⁶ 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 calculation⁷ for C₂H₂ 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 varied between 1.3 and 2.5 Å in 0.2 Å intervals. The C-C distance was allowed to expand from the triple-bond (gas phase C_2H_2) distance of 1.20 Å, to the single-bond distance of 1.54 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. We are, therefore, unable to rule out a possible C-C bond expansion upon adsorption although the relative intensities show slightly better agreement with experiment for the triple-bond, as opposed to the single-bond, distance.

The results of these calculations are summarized in Figs. 2-3. Figure 2 shows a comparison of the I-V curves for various planar orientations at the optimum z-distance of 1.9 Å above the substrate with the (2×2) translational symmetry and the C-C distance of 1.20 Å. The (2×1) arrangements gave poor agreement with experiment. Figure 2 shows clearly that the preferred position of the molecule is a two-fold orientation (B1) with the molecule coordinated to four Pt atoms. Analysis of two additional fractional-order ($0\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}$) and two integral-order beams ($1\bar{1}$ and $0\bar{1}$) also favors this geometry in each case. The results for geometries A2 and C2 (not shown) are very similar to those for A1 and C1, respectively. Figure 3 compares theory and experiment for the B1 geometry for three fractional-order beams. There is good agreement in peak positions, line shapes, and relative intensities. The absence of

the peak near 50 eV in the ($\frac{11}{22}$) beam experimental curve can be explained by a small contraction to $z = 1.8 \text{ \AA}$, and a comparison with the integral order beams also slightly favors the $1.8 \text{ \AA}$ over the $1.9 \text{ \AA}$ spacing.

We conclude that acetylene is chemisorbed on Pt(111) with the local bonding arrangement indicated in Fig. 4. This result is of considerable interest because it argues against popular notions of acetylene adsorption on transition-metal surfaces which propose either an acetylene π complex coordinated to a single metal atom (model geometry A1 or A2) or a di- σ complex in which each of the two carbon atoms form a σ -bond with a different metal atom⁸ (model geometry B2). In particular, the di- σ model has often been cited in connection with the mechanism of dehydrogenation of ethylene (C_2H_4) to an acetylenic species upon adsorption with the ligand molecular orbitals in an sp^2 hybrid configuration. Our results suggest instead that the two sets of acetylene π orbitals are relatively intact upon adsorption of the molecule and are symmetrically directed (perpendicular to the C-C axis) towards two platinum atoms with forward electron donation to empty Pt hybrid orbitals. The geometry is also favorable for possible retro-dative bonding involving electron donation from occupied Pt d orbitals back to empty acetylene antibonding π^* orbitals. Precisely this type of bonding is found to occur in bimetallic metal-alkyne complexes.⁹ We emphasize that such localized orbital concepts of chemisorption on a metal surface should be viewed with due caution, and realistic electronic structure calculations for these systems would be of considerable interest. In ultraviolet photoemission studies¹⁰ of acetylene on Ni(111), however, no strong changes in the molecular configuration were observed between condensed and chemi-

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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° -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 geometry (B1, $z = 1.9 \text{ \AA}$) to experiment (dashed line) at normal beam incidence.
- Fig. 4. Bond lengths (in $\text{\AA}$) and angles for the Pt(111)-(2x2)- C_2H_2 system. The C-C distance (double bond shown here) and the hydrogen atom positions are not accurately known.

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Figure 1

Pt(III) - (2x2) - C₂H₂

XBL 75II-9634

Figure 2

XBL 7511-9635

Figure 3

Figure 4

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