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<sup>5</sup>D. R. Allum, P. V. E. McClintock, A. Phillips, and R. M. Bowley, to be published.

<sup>6</sup>The 1-mm cell incorporated a 2-mm-long medium-field ( $1 \text{ kV cm}^{-1}$ ) space on each side of the 1-mm high-field region. This arrangement facilitated temporal separation of the wanted signal from the gate-switching transients, and prevented high-field "leakage" into the gate or collector spaces.

<sup>7</sup>R. J. Donnelly, Phys. Lett. **39A**, 221 (1972).

<sup>8</sup>The high-field forms of  $\bar{v}(E)$  developed in Refs. 4 and 5 were based on a number of approximations which become poor for the higher values of  $E$  used in the present experiments. In particular, because of the different shape of  $f(v)$  at very large  $E$ , compared to that in small  $E$ , we have found it essential to compute  $\bar{v}$  by solving a Boltzmann equation, rather than by using the simpler approach via the concept of a relaxation time.

<sup>9</sup>R. M. Ostermeier, Phys. Rev. A **8**, 514 (1973).

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

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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 threefold position or a twofold bridge position at a distance of  $1.95 \pm 0.10 \text{ \AA}$  above the topmost plane of platinum atoms.

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 ( $\text{C}_2\text{H}_2$ ) 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  $\text{C}_2\text{H}_2$  gas at 300 K under ultrahigh vacuum conditions followed by gentle heating to 400 K for 1 h gives rise to a  $2 \times 2$  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  $\text{C}_2\text{H}_2$  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  $\text{C}_2\text{H}_2$  overlayer was obtained only at low exposures ( $\sim 1 \text{ L} = 10^{-6} \text{ Torr sec}$ ), in agreement with earlier work.<sup>4</sup> The adsorption and ordering characteristics of  $\text{C}_2\text{H}_2$  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- $\text{C}_2\text{H}_2$  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  $120^\circ$ -rotated domains of either  $2 \times 2$  or  $2 \times 1$  packing of  $\text{C}_2\text{H}_2$  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 scatter-

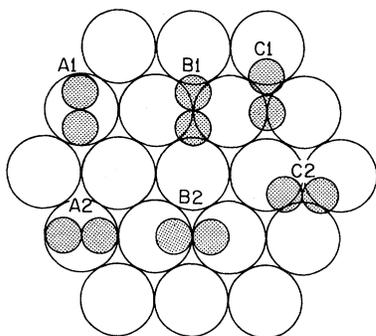


FIG. 1. Trial geometries of  $C_2H_2$  on the Pt(111) surface. Positions A, B, C refer to coordinations to one, two, or three neighboring Pt atoms. The labels 1 and 2 distinguish  $90^\circ$ -rotated molecules.

ing 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  $C_2H_2$  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  $C_2H_2$  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 five partial-wave

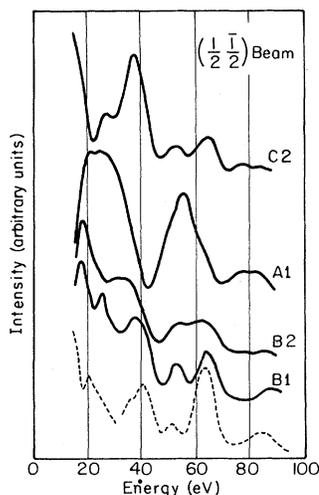


FIG. 2. Comparison of calculated  $I$ - $V$  profiles (solid line) for the trial geometries ( $z = 1.9$  Å) to experiment (dashed line) at normal beam incidence.

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  $2 \times 2$  translational symmetry and the C-C distance of 1.20 Å. The  $2 \times 1$  arrangements gave poor agreement with experiment. Because of 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, because of

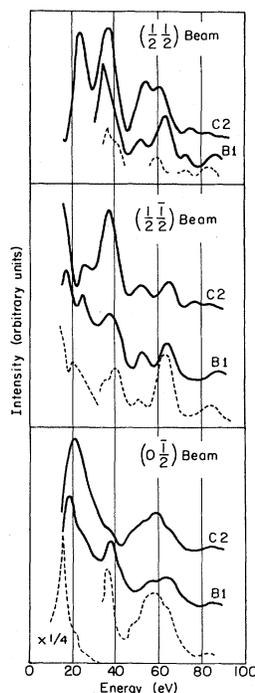


FIG. 3. Comparison of calculated  $I$ - $V$  profiles (solid line) for the optimum geometries (B1, C2;  $z = 1.9$  Å) to experiment (dashed line) at normal beam incidence.

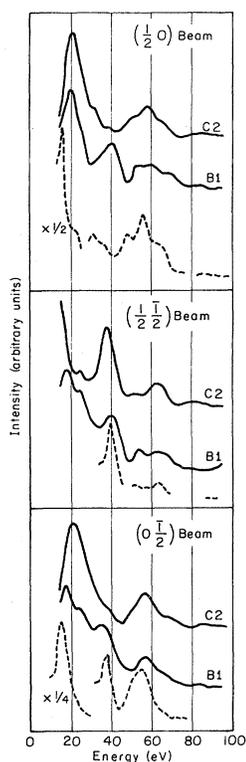


FIG. 4. Comparison of calculated  $I$ - $V$  profiles (solid line) to experiment (dashed line) at incident angle  $\theta = 4^\circ$ . Other conditions as in Fig. 3.

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 and 4 show several additional comparisons of the 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 topmost 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 and 2.59  $\text{\AA}$ . In the other possible bonding mode ( $B1$ ) the molecule is in an approximately twofold position with each carbon coordinating to three platinum atoms, C-Pt distances being 2.47 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 ( $C_2H_4$ ) to an acetylenic species upon adsorption with the ligand molecular orbitals in an  $sp^2$  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.

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<sup>1</sup>A preliminary report of this work was presented at the First Chemical Congress of the North American Continent, Mexico City, December, 1975 (unpublished).

<sup>2</sup>A less stable  $2 \times 2$  structure having different  $I$ - $V$  characteristics that is a precursor to the more stable structure analyzed herein has also been experimentally identified: P. C. Stair and G. A. Somorjai, to be published.

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## Evidence for the "Correlated Layer" Effect on the Effective Viscosity from Brownian Motion in a Ternary Liquid Mixture\*

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The translational diffusion coefficient of Brownian particles in the ternary liquid mixture water-ethanol-chloroform near a plait point has been studied by the autocorrelation spectroscopy method. It is found that the effective viscosity  $\eta_{\text{eff}}$  exhibits a strong anomaly close to the plait point. This anomaly can be explained in terms of the existence of a "correlated layer" of liquid mixture of thickness equal to the correlation length  $\xi$  on the surfaces of the Brownian particles.

According to mean-field theories,<sup>1,2</sup> first put forward by Fixman, the shear viscosity of a binary liquid would exhibit a strong anomaly proportional to the correlation length  $\xi$  when the critical mixing point is approached. However, this strong anomaly is never observed experimentally. Instead, various methods of viscosity determination<sup>3</sup> indicate that the anomaly is a weak one.

When Bal'tsevich, Martynets, and Matizen<sup>4</sup> and Martynets and Matizen<sup>5</sup> applied the method of microphotography to study Brownian motion in binary liquid mixtures, they observed the translational diffusion coefficient  $D$  to decrease by a factor of 4 in the phenol-water system<sup>4</sup> and by a factor of 2 in the methanol-cyclohexane<sup>5</sup> system near their critical mixing points. They explained the strong anomaly by assuming that the effective radii of the Brownian particles are increased by the formation of a "correlated layer" of binary liquid on their surfaces. The thickness of this correlated layer is probably of the same order of magnitude as the correlation length  $\xi$ . Unfortunately, their data were not accurate enough to allow a quantitative study. Subsequently, Giterman, Likht, and Steinberg<sup>6</sup> attempted to explain the anomaly by postulating a theory of "trapping" and "entrainment" of the particles by concentration fluctuations. They predicted  $D \sim (T - T_c)^{1.33}$  while the experimental data yield  $D \sim (T - T_c)^{0.2}$ .

Recently, Lyons, Mockler, and O'Sullivan<sup>7</sup> studied the translational diffusion coefficient of Brownian particles in the nitroethane-iso-octane system by the autocorrelation spectroscopy meth-

od and found a logarithmic divergence in the effective viscosity. Their data showed that the effects of the correlated layer, as advanced by Martynets and Matizen,<sup>5</sup> are small because they observed only a 35% increase in the effective viscosity near the critical mixing point. They argued that the correlated layer could be important only if the Brownian particles interact strongly with the fluid components and should be characteristic of the system studied.

In this work, I report observations which can be interpreted in terms of such a correlated layer by studying the Brownian motion near a plait point of a ternary liquid mixture using the autocorrelation spectroscopy method.

For a binary or a ternary liquid mixture with Brownian particles, the first-order electric field autocorrelation function is given by

$$|g^{(1)}(\tau)| = A_1 \exp(-\Gamma_1 \tau) + A_2 \exp(\Gamma_2 \tau), \quad (1)$$

where  $\Gamma_1$  and  $\Gamma_2$  are the linewidths due to Brownian motion and concentration fluctuations, respectively, and  $A_1$  and  $A_2$  are coefficients proportional to the corresponding scattering intensities. In the noncritical region where light scattering due to concentration fluctuations is weak compared with that due to Brownian motion, i.e.,  $A_1 \gg A_2$ ,

$$|g^{(1)}(\tau)| \approx A_1 \exp(-\Gamma_1 \tau). \quad (2)$$

In the critical region, light scattering due to concentration fluctuations becomes significant and Eq. (1) has to be used. Separating the two terms is difficult but the problem has been carefully studied by Lee and Chu.<sup>8</sup>