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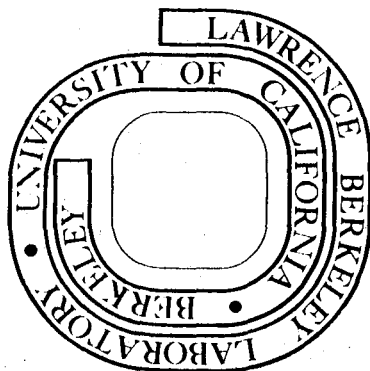
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THE SURFACE STRUCTURE AND BONDING OF (2X2) ACETYLENE OVERLAYERS  
ON PLATINUM (111): LEED INTENSITY ANALYSIS<sup>†</sup>

by

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ABSTRACT

The structure and bonding of (2x2) overlayers of acetylene on a platinum (111) surface has been studied by low-energy electron diffraction intensity-voltage analysis. A discussion is given of likely bonding modes and their stereochemical analogies in transition-metal clusters, multiple-scattering calculations and the construction of overlayer scattering potentials and the influence of electron scattering by hydrogen. The favored bonding geometry for the stable acetylene overlayer is found to be a triangular site at  $1.95 \pm 0.10 \text{ \AA}$  above the platinum surface (C-Pt distances of  $2.25 \text{ \AA}$  and  $2.59 \text{ \AA}$ ). We also report evidence that rehybridization of the adsorbed acetylene in terms of CCH angle-bending is weak to moderate ( $180^\circ \gtrsim \text{CCH angle} \gtrsim 150^\circ$ ).

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### INTRODUCTION

In a recent letter<sup>(1)</sup> we outlined the results of the first low-energy electron diffraction (LEED) study of molecular chemisorption by intensity-voltage (I-V) analysis. In this method, which has been rather widely applied to clean crystalline surfaces and atomic adsorbates, the surface geometry is determined by analysis of the beam intensities of slow electrons ( $10 \lesssim E \lesssim 200$  eV) diffracted from the surfaces of well-ordered systems under ultrahigh vacuum conditions.<sup>(2)</sup> Our study has dealt with the chemisorption of acetylene ( $C_2H_2$ ) that forms (2x2) overlayers on the platinum (111) crystal surface. A principal motivation for this work has been to show that definitive structural information on adsorbed molecules can be extracted from LEED I-V analysis; stereochemical arguments may then be employed to elucidate the nature of the chemical bonds in these heterogeneous systems.

In their recent experimental studies, Stair and Somorjai have reported the LEED I-V profiles for the acetylene-platinum system.<sup>(3)</sup> In particular, two different (2x2) structures of adsorbed acetylene were identified, which we refer to briefly as "stable" and "metastable" states and which have been interpreted as involving different chemical bonding.<sup>(3)</sup> The metastable (2x2) structure is observed to form initially at low exposure ( $\sim 1$  Langmuir =  $10^{-6}$  Torr-sec) of  $C_2H_2$  at room temperature but transforms in 1 h to the stable (2x2) structure upon gentle heating to  $100^\circ C$ . Both structures are characterized by the same (2x2) surface unit cell and involve the same carbon coverage as determined by Auger electron spectroscopic analysis. However, they are readily distinguishable by their different I-V characteristics.<sup>(3)</sup>

In this paper we present an extensive discussion of the I-V analysis of the stable acetylene overlayer and some preliminary remarks concerning the metastable system. The main results of this study as detailed in the later sections are the following: (i) the favored bonding-site for the stable structure is a 3-fold (triangular) position at a z-distance of  $1.95 \pm 0.1 \text{ \AA}$  above the topmost plane of platinum atoms (C-Pt distances of  $2.25 \text{ \AA}$  and  $2.59 \text{ \AA}$ ), and (ii) electron scattering by hydrogen significantly influences only the very low-energy (10-40 eV) region of the I-V curves; preliminary analysis of this region suggests that rehybridization of the adsorbed acetylene in terms of CCH angle bending is weak to moderate ( $180^\circ \geq \text{CCH angle} \geq 150^\circ$ ).

#### MODELS OF ACETYLENE CHEMISORPTION

The disposition and chemical state of unsaturated hydrocarbons on transition-metal surfaces has for many years been an unresolved problem of considerable interest in the fields of adsorption, adhesion and heterogeneous catalysis.<sup>(4)</sup> Competing models involving the formation of  $\pi$  complexes and  $\sigma$  complexes have been postulated for acetylene and ethylene chemisorption.<sup>(4)</sup> Generalizations of these models are also expected to apply to other unsaturated hydrocarbons on metal surfaces. In the present study of acetylene chemisorption on platinum we examine these various modes of bonding in the context of the high-symmetry bonding sites available on the (111) face of an f.c.c. crystal.

As illustrated in Fig. 1 we distinguish four sites designated as (a) one-coordinate  $\pi$ , (b) di- $\sigma$ , (c) bridging (sometimes referred to as  $\mu$ -bridging) and (d) triangular complexes. We have indicated for each site only those surface metal atoms expected to have significant metal-carbon

interaction. It is natural to discuss these surface geometries in terms of structural analogies in organometallic complexes. In these terms the one-coordinate  $\pi$  complex (a) involves the interaction of one or both sets of  $\pi$ -orbitals of the acetylene molecule with a single metal surface atom. The bridging site (c) utilizes both sets of  $\pi$ -orbitals to bond with two surface atoms; both (a) and (c) in principle entail little rehybridization of the molecule since essentially undistorted  $\pi$  orbitals would be involved.<sup>(5)</sup> However, the di- $\sigma$  bond (b) implies  $sp \rightarrow sp^2$  rehybridization and the formation of two carbon-metal  $\sigma$  bonds accompanied by large hydrogen cis-bending (CCH angle  $\sim 120^\circ$ ). This possibility has received serious consideration in the catalysis literature.<sup>(4)</sup> Finally, the triangular structure (d), commonly found in trinuclear metal-alkyne complexes, illustrates a mode of bonding loosely referred to in terms of both " $\sigma$ " and " $\mu$ " bonds.<sup>(6)</sup> As discussed below we find this triangular geometry to be the favored arrangement in the stable structure. In Table I we cite various organometallic compounds demonstrating the four geometries we have considered.<sup>(7)</sup>

Let us note that we have examined only high-symmetry structures having the C-C axis parallel to the Pt surface. We consider it unlikely that large distortions from planarity (e.g., "end-on" bonding characteristic of metal-carbonyls) would occur for chemisorbed acetylene as it leads to minimum overlap of bonding molecular orbitals. Furthermore, in previous work it was noted that a rather closely-packed layer of planar acetylene molecules is consistent with the observed (2x2) unit cell.<sup>(8)</sup> The possibility of dissociation of acetylene to CH fragments bound to the surface in a (2x2) configuration was ruled out based on experimental evidence to

be discussed below.

### INTENSITY CALCULATIONS

In this section we outline the calculational procedure for obtaining the reflected beam intensities for low-energy electron diffraction given a model geometry. In recent years the quantum-mechanical methods for treating the multiple-scattering of slow electrons from crystalline surfaces have become fairly standardized; we refer the reader to reviews on the subject for details of the LEED multiple-scattering theory.<sup>(9)</sup> Here we mention only the most important features of the calculation and some specific aspects pertaining to the scattering from an acetylene molecule.

#### Multiple-Scattering Method: General Features

An accurate description of the I-V profiles requires the consideration of several orders of (elastic) multiple-scattering of the electrons from the attractive (screened) Coulomb fields of the atomic nuclei, which by virtue of their periodic lattice arrangement and the wave-like behavior of the electrons ( $\lambda = h / \sqrt{2mE}$ ) give rise to diffraction effects.

In virtually all calculations the muffin-tin model<sup>(10)</sup> is employed, i.e., the scattering potential is taken to be spherically symmetric in the neighborhood of each atomic center and to be approximately constant in the interstitial region between muffin-tins. The assumption of sphericity, though inadequate for the general problem of valence electron behavior, is quite a good approximation at LEED energies: that is, in order to undergo back-scattering the LEED electron must experience the strong forces of the core-region of the atomic potential where the charge distribution is indeed spherically symmetric.

The scattering from the spherically symmetric atomic sites is given

by the conventional partial wave expansion<sup>(11)</sup> in terms of the phase shifts,  $\delta_\ell$ ,

$$f(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) e^{i\delta_\ell(k)} \sin\delta_\ell(k) P_\ell(\cos\theta) \quad (1)$$

where  $k = (2mE/\hbar^2)^{1/2}$  and  $P_\ell$  are the Legendre polynomials. The atomic scattering factor  $f(\theta)$  describes the amplitude and phase dependence of a scattering event on the scattering angle  $\theta$  from the forward direction.

The mathematical formulation of multiple-scattering processes involves essentially the products of single-scattering events given by Eq. (1) with the intermediate process of electron propagation. Due to efficient loss processes in the solid such as plasmon excitation, the mean free path  $\lambda_{ee}$  for the occurrence of an inelastic event is  $\sim 4-8 \text{ \AA}$  at LEED energies (20-200 eV). Since these large energy loss events ( $\Delta E \sim 10 \text{ eV}$ ) remove electrons from the observed elastic beams, we note that the electron propagation between scattering events is a highly-damped process. This electron beam attenuation is commonly treated as being isotropic and is described in terms of  $\lambda_{ee}$  or equivalently in terms of an imaginary contribution ( $\Sigma_i \sim 3 \text{ eV}$ ) to the scattering potential.

The main physical features of the calculation, then, are the elastic events parameterized by the phase shifts  $\delta_\ell$  (which are derived from the potential  $V(r)$  associated with each atomic site) and inelastic damping parameterized by  $\Sigma_i$ . Multiple scattering formulae essentially involve these parameters in various lattice summations. In particular, we have employed a beam representation and the layer doubling method.<sup>(12)</sup>

Finally, we note that we have used the "no-reflection" treatment of the barrier between vacuum and the solid surface; that is, we consider the

barrier to smoothly accelerate the incident electron in the direction normal to the surface and neglect reflections from the barrier itself. This approximation is valid for energies greater than about 30 eV.<sup>(13)</sup>

#### Scattering of Low-Energy Electrons from Platinum

The parameters describing the platinum scattering were the same as those used previously<sup>(14)</sup> with the exception of the electron damping  $\Sigma_i$  which was taken to be 2.5 eV in this work rather than the value of 4 eV used previously. The value of 2.5 eV gives a better description of fine structure in the I-V profiles for both the clean Pt and Pt-C<sub>2</sub>H<sub>2</sub> systems. The value of the constant potential between muffin-tin spheres (muffin-tin zero) was  $V_0 = 14.3$  eV below the vacuum level.<sup>(14)</sup> We have neglected the decrease in work function ( $\Delta\phi = 1.5$  eV) associated with acetylene adsorption. The platinum phase shifts (Ref. 14, Fig. 1) were derived from the band-structure potential used by Andersen and Mackintosh<sup>(15)</sup> for which the exchange contribution was given by the Slater formula.<sup>(16)</sup> (Eq. (3) below:)

#### Scattering of Low-Energy Electrons from Acetylene

Applying the muffin-tin model to acetylene, we consider spheres centered on each of the carbon and hydrogen atoms. Within these atomic spheres a spherical average of the potential is performed; the region outside the spheres (intermolecular) has a volume average which in our case was assumed equal to the platinum value  $V_0 = 14.3$  eV.

The electronic charge density in the molecule was calculated using molecular-orbital wave functions given by Palke and Lipscomb<sup>(17)</sup> in a self-consistent field treatment with a minimal basis set of Slater atomic orbitals. The electrostatic contribution to the potential energy was

calculated from Poisson's integral

$$\phi(\underline{r}) = \int \frac{\rho(\underline{r}') d^3r'}{|\underline{r}-\underline{r}'|} \quad (2)$$

employing the molecular charge density  $\rho(\underline{r})$  consisting of electronic and nuclear parts. The exchange potential was calculated from the local approximation due to Slater<sup>(16)</sup>:

$$V_x(\underline{r}) = -6 \left[ \frac{3}{8\pi} \rho(\underline{r}) \right]^{1/3} \quad (3)$$

Finally, contributions to the potential in the  $C_2H_2$  atomic spheres from substrate interaction was approximated by simple overlap of platinum potentials using standard methods.<sup>(10)</sup>

We have used overlapping atomic spheres on the carbon and hydrogen atoms; this departure from a strict muffin-tin treatment was made in order to include more of the electronic charge, a substantial portion of which lies outside of non-overlapping spheres. This problem has been dealt with earlier in connection with electronic structure calculations with the SCF  $X\alpha$  scattered-wave method<sup>(18)</sup> and arises, for example, in organic molecules with  $\pi$ -electron systems.

In Table II we list the muffin-tin potential for carbon in  $C_2H_2$  obtained by the above method and compare this potential to that of atomic carbon.<sup>(19)</sup> We note that these two potentials are nearly identical for small radii (as expected) and that their difference at the sphere radius ( $r_C = 1.50$  au) is only 0.2 Rydberg. This similarity is obtained, of course, only because we have spherically averaged around each of the acetylenic carbon atoms. If one compares, for example, the electrostatic potential  $\phi(\underline{r})$  along the C-C bond direction with the potential at the same

radius perpendicular to the C-C bond, differences up to  $\sim 1$  Rydberg are found corresponding to the buildup of bonding charge between the carbon atoms. Given the similarity of the spherically-averaged acetylenic-carbon potentials to those derived from the corresponding atom we have accordingly employed atomic hydrogen potentials to approximate the hydrogen scattering in acetylene, as indicated in Table II.

Phase shifts ( $\delta_l$ ) derived from the muffin-tin potentials of carbon and hydrogen are shown in Figs. 2-3. Their behavior with energy is very similar to but they differ quantitatively from the corresponding free atom phase shifts<sup>(20)</sup> since the potentials are truncated at the sphere radii  $r_C$  and  $r_H$  given in Table II. We note that the s, p and d-waves are quite strong for carbon whereas the hydrogen scattering is weak with only the s-wave being relatively strong. We may also compare relative elastic scattering cross sections determined from the phase shifts. At 80 eV, for example, the platinum cross section is over 3 times larger than the carbon cross section and 25 times larger than the hydrogen cross section.

#### Intensity Averaging Over Equivalent Domains

The observed diffraction pattern for the acetylene overlayers may arise from domains of either (2x2) or (2x1) real space unit cells. In the case of (2x1) periodicity the presence of the three equivalent 120°-rotated domains of the molecule on the surface would be essential to produce the necessary spots that give a nominal (2x2) diffraction pattern. In the case of either (2x1) or (2x2) symmetry, however, the presence of equal numbers of the three domains is also necessary since unequal mixtures would not give the observed threefold symmetry of the spot intensities.

The small size, high intensity and good definition of the fractional-order diffraction spots indicates that order in the overlayer persists on a scale comparable to or larger than the coherence width of the electron beam ( $\sim 100 \text{ \AA}$ ). We make the assumption that only one of the three rotational orientations is present within a given coherence zone, i.e., we assume that boundary effects may be neglected. This assumption is valid providing either that the domains of a given orientation are much larger than the coherence zone or that no particular phase relation connects different domains. With this assumption it is only necessary to average together intensities (as opposed to adding amplitudes) calculated for the three orientations. For a general incident beam angle  $(\theta, \phi)$  this procedure then involves three independent intensity calculations. However, along high-symmetry azimuths ( $\phi$ ) only two calculations are necessary, and at normal incidence ( $\theta=0^\circ$ ) only one calculation is needed.

It has been noted that a  $(2 \times 1)$  overlayer is unlikely in the light of both helium scattering results as well as consideration of van der Waals radii.<sup>(8)</sup> However, in the absence of quantitative coverage data we carried out calculations for  $(2 \times 1)$  overlayer geometries at normal incidence. We did not find acceptable agreement for the  $(2 \times 1)$  acetylene lattice with the observed I-V profiles and in the following section, then, we consider only results for  $(2 \times 2)$  arrangements.

#### RESULTS AND DISCUSSION

In this section we present and discuss the I-V profiles calculated for the various model geometries shown schematically in Fig. 1. We believe a reliable structure determination for the stable acetylene  $(2 \times 2)$  overlayer has been made, but further study of the metastable acetylene system

is needed. We also indicate the influence of hydrogen scattering and suggest that it can be used to study hybridization of bonding orbitals upon chemisorption.

The I-V profiles were calculated for several fractional and integral-order beams at incident angles of  $\theta=0^\circ$ ,  $4^\circ$ ,  $8^\circ$  and  $16^\circ$ . Structural parameters which were varied in this study were: (i) the planar (x, y) position of the molecule (Fig. 1; Ref. 1, Fig. 1) to include high-symmetry sites with the C-C axis parallel to the surface, (ii) the z-distance of the molecule above the topmost plane of platinum atoms from  $1.3 \text{ \AA}$  -  $2.5 \text{ \AA}$ , (iii) the C-C distance from  $1.20 \text{ \AA}$  (triple bond) to  $1.54 \text{ \AA}$  (single bond) for a restricted set of geometries, (iv) the CCH angle for a restricted set of geometries. The upper layer z-spacing of the platinum substrate was held fixed at the bulk value determined previously from clean surface studies.<sup>(14)</sup> Thus we assume that the surface platinum atom positions remain invariant during the chemisorption of  $C_2H_2$ . The lack of platinum relaxation during adsorption is supported by our experimental observation that the higher energy ( $E \gtrsim 100 \text{ eV}$ ) I-V peak positions of the integral-order beams, which are dominated by platinum scattering, do not change with acetylene adsorption.

No attempt at refinement of the calculations by variation of non-structural parameters such as the overlayer muffin-tin potential or its level relative to the substrate potential has been made, and as noted earlier, we have also neglected reflection due to the vacuum-solid barrier. Whereas these refinements would almost certainly result in improvement in the agreement between theory and experiment in the low-energy region  $E \lesssim 40 \text{ eV}$  their omission should not affect our general conclusions which

are based on a comparative study of various structures over a rather wide data base. Over 25 diffraction beam profiles in the energy range 15-95 eV were analyzed in terms of relative intensities, peak positions and line shapes.

Before comparing the various profiles, we first note that (for reasons of computational savings) hydrogen scattering was not included in most of the results to be presented; this procedure will be justified below. Secondly, reasonable variation in the C-C distance was found in trial calculations to be a small perturbation on the I-V profiles, and for this reason the C-C distance was held at the 1.20 Å value. In particular we find a C-C expansion to the double bond distance of 1.34 Å to be below the practical detection limit of the method. However, a major expansion to the single bond distance of 1.54 Å (although not anticipated based on the data for complexes in Table I) causes significant relative intensity changes and peak energy shifts in selected diffraction beams and selected energy ranges. A careful study, then, could be expected to detect changes in intramolecular bond distances down to 0.3 Å but this is, of course, poor resolution for chemical applications. Part of this insensitivity is due to the special case we have considered, namely variations of the C-C distance parallel to the surface plane. We expect greater sensitivity to out-of-plane (z) variations since most of the momentum-transfer in conventional LEED experiments is in the direction perpendicular to the surface.

#### Analysis of the Stable Acetylene (2x2) Surface Structure

Comparisons of calculated and experimental I-V profiles (stable structure) for both fractional and integral-order beams are shown in

Figs. 4-5. Several additional comparisons have been reported previously.<sup>(1)</sup> The one-coordinate  $\pi$ -complex was readily ruled out (cf. Ref. 1, Fig. 2). In Figs. 4-5 we compare selected results for di- $\sigma$ , bridging and triangular structures. On the (111) surface of f.c.c. crystals (ABC stacking) there are two inequivalent triangular sites distinguished by the presence or absence (hole-site) of a second-layer substrate atom located beneath the center of the triangle formed by substrate atoms in the topmost layer. The hole-site corresponds to the site that would be filled in the formation of an additional substrate layer and this is also found in the calculations to be the particular triangular site giving the optimum agreement for the location of  $C_2H_2$  molecules in the acetylene overlayer. The z-distance of 1.9 Å employed in these comparisons was optimum for all three structures and all diffraction angles to within  $\pm 0.1$  Å.

Analysis of Figs. 4-5 shows that the triangular geometry gives consistently better agreement than either the bridging or di- $\sigma$  geometries. The di- $\sigma$  geometry is most readily ruled out; we note, for example, in Fig. 5 that whereas both triangular and bridging structures give similar good agreement for substrate beams, the di- $\sigma$  geometry exhibits several discrepancies. In Fig. 4 for the fractional-order beams the di- $\sigma$  geometry also does poorly, and we also see marked differences between the bridging and triangular structures. Note, for example, the structure in the  $(1/2\ 0)$

beam profile in the region 40-70 eV which is adequately described only by the triangular-site profile. Similarly, the two-peak structure at 60-80 eV in the  $(\frac{1}{2}\ \frac{1}{2})$  beam is reproduced by the triangular but not the bridging-site calculation. Since the triangular and bridging-site calculations show similar agreement at normal incidence<sup>(1)</sup> we have thus found

a close comparison of several fractional-order beams at non-normal incidence to be essential to the analysis and to favor the triangular geometry.

In addition to visual evaluations we have also carried out a computerized analysis of the I-V profiles in which comparison is made of relative intensities and percentage of matching peaks between theory and experiment. (21) Both of these comparisons were consistent with the visual evaluation. For example, at  $z=1.9 \text{ \AA}$  the triangular structure reproduces 63% of the peaks in the fractional-order experimental I-V profiles (within a 7 eV window), the bridging structure 54% and the di- $\sigma$  structure 46%. However, these overall statistical comparisons tend to average over important discrepancies occurring in selected beams and selected energy ranges. Accordingly, we feel that visual comparison is quite essential in LEED analyses particularly at the crucial stage of discerning differences between two favorable candidate structures.

Finally, we note the effect of scattering by the hydrogen atoms in a trial calculation for the bridging structure at normal incidence in Fig. 6. These results show that above  $\sim 40$  eV there is little sensitivity to hydrogen even at a  $60^\circ$  cis-bending of the hydrogens away from the surface (CCH angle= $120^\circ$ ). However, we have noted in Fig. 6 two low-energy peaks whose ratio does change significantly with CCH angle. These peaks also appear for the triangular structure which exhibits very similar I-V profiles at normal incidence. (1) Comparing in a literal fashion the calculated curves to experiment we may conservatively estimate the CCH angle  $\alpha$  to be greater than  $\sim 150^\circ$  for acetylene in the adsorbed state. Analogous behavior for the  $(\frac{1}{2} \frac{1}{2})$  beam is also consistent with this result. Although we must view these considerations as preliminary, since the very low-energy

region of the I-V profiles is the least reliable, we certainly have evidence that a major  $sp \rightarrow sp^2$  rehybridization of acetylene does not occur. We fully expect that refined calculations in the very low-energy region of the spectrum will lead to a more precise measure of the degree of CCH angle bending.

Analysis of the Metastable Acetylene (2x2) Surface Structure

A satisfactory structure for the metastable acetylene overlayer<sup>(3)</sup> (which forms upon the initial room-temperature exposure of acetylene to the Pt(111) surface) has not been forthcoming in the course of the present intensity calculations, but some preliminary remarks are appropriate here. It appears that the metastable structure involves significantly different C-Pt bond distances and very possibly a different planar bonding site on the platinum surface. In fact, the most consistent agreement between the experimental and calculated intensity curves found thus far for the metastable layer is when the acetylene molecule is placed in the bridging or triangular positions at the z-distance of  $2.4 \pm .1 \text{ \AA}$  above the Pt substrate. This length is  $0.5 \text{ \AA}$  longer than for the stable acetylene structure, consistent with the formation of a stronger C-Pt bond (and probable reduction in C-C bond order) in the course of the metastable-stable transition. However, the degree of agreement achieved for this model structure between calculated and experimental I-V profiles is not of sufficient quality to permit a reliable structure determination. A major reason for this may be our neglect of inner potential differences between the substrate and overlayer, an approximation whose accuracy decreases for increasing z distance of the overlayer from the substrate.

Evidence Against the Dissociative Adsorption of Acetylene

Although we have heretofore implicitly assumed acetylene to adsorb associatively at the low temperatures ( $\lesssim 400$  K) relevant to this study we may also consider dissociative adsorption models in which C-C bond scission occurs, and the apparent (2x2) diffraction pattern is then due to either (2x2) or (2x1) arrays of chemisorbed C or CH fragments. We have accordingly performed calculations at  $\theta=0^\circ$  and  $8^\circ$  for these "carbonaceous" overlayer models, again at z-distances of 1.3-2.5 Å. For a given bonding site and z-distance, the calculated I-V profiles for the fragmented species are very similar to those reported earlier for (associative) molecular adsorption; comparatively small differences in relative intensities and line shapes are generally found.

Importantly, the distance of  $z=1.9 \pm 0.1$  Å is found to be optimum for models involving either associatively held  $C_2H_2$  or fragmented (C;CH) species at the triangular bonding site. Previous LEED studies of atomic adsorption on a variety of metal surfaces have shown that the metal-atom bond distance is given by the sum of the metallic radius of the substrate atom and the covalent radius of the adsorbed atom.<sup>(22)</sup> For covalently bonded systems this rule has consistently held with an accuracy of 0.1-0.2 Å. If we now consider a carbon atom bonded to platinum (111) in the 3-fold hollow (triangular site) this rule then implies a z-distance of 1.45 Å (C-Pt bond distances of 2.16 Å). Since this distance is 0.5 Å less than that found in the present LEED analysis it seems that a carbonaceous layer is very improbable. On the other hand, the associative model appears quite reasonable since at  $z=1.9$  Å, C-Pt distances of 2.2 Å are found for  $C_2H_2$  centered on the triangular site (see Fig. 1d). This value is very close to the predicted covalent bond distance of 2.16 Å.

CONCLUSION

We have been able to distinguish amongst various proposed bonding models for acetylene adsorption on the Pt (111) surface using dynamical (multiple-scattering) analysis of low-energy electron diffraction intensity profiles. We have found that bonding of acetylene in a triangular site on the Pt (111) surface is the stable and preferred configuration. It is interesting to note (cf. Table I) that this same bonding geometry is exhibited in trinuclear metal-alkyne clusters; moreover, the average C-Pt distance we find ( $2.42 \pm 0.1 \text{ \AA}$ ) is similar to that ( $2.22 \text{ \AA}$ ) determined for the  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$  cluster (Table I), the osmium covalent radius being only  $0.04 \text{ \AA}$  shorter than that of platinum. Although we cannot detect a small C-C bond length change we do anticipate a C-C bond stretch of about  $0.1 \text{ \AA}$  to occur for acetylene adsorption judging from the C-C lengths found in x-ray crystal structure determinations of the metal-alkyne clusters.

We have also found encouraging evidence that CCH angle bending may be studied by the dynamical technique in spite of the fact that electron scattering by hydrogen is relatively weak.

Finally, it is important to note that since sensitivity to the acetylene overlayer<sup>(3)</sup> is found only in the low-energy range of 10-100eV it is very doubtful that alternative data reduction techniques<sup>(23)</sup> (which rely on single-scattering diffraction features over a wide energy range) can be used to advantage on low-coverage hydrocarbon-transition metal surfaces. Indeed, the complexity introduced by the strong multiple-scattering of electrons provides the essential sensitivity needed to extract the metal-ligand bonding in these heterogeneous systems.

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Table I. Examples of bonding structures and bond lengths for acetylenic ligands ( $RC\equiv CR$ ) in various transition-metal complexes.

<u>Compound</u>	<u>Bonding Geometry</u>	<u>Average M-C</u> <u>(Å)</u>	<u>C≡C</u> <u>(Å)</u>
$(Ph_3P)_2Pt(C_2Ph_2)^a$	one-coordinate $\pi$	2.04	1.32
$(CO)_6Co_2(C_2Ph_2)^b$	bridging ( $\mu$ )	1.97	1.46
$(\eta^5-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)^c$	di- $\sigma$	2.04	1.29
$Os_3(CO)_{10}(C_2Ph_2)^d$	triangular	2.22	1.29

<sup>a</sup> J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.* 7, P9 (1967).

<sup>b</sup> W. G. Sly, *J. Am. Chem. Soc.* 81, 18 (1959).

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Table II. Muffin-tin potentials for carbon and hydrogen<sup>†</sup>  
[-rV(r)(au)]

<u>r</u>	<u>Carbon in C<sub>2</sub>H<sub>2</sub></u>	<u>Atomic Carbon</u>	<u>Atomic Hydrogen</u>
0.00	12.00	12.00	2.00
0.25	8.46	8.45	1.94
0.50	6.26	6.27	1.82
0.75	5.06	5.05	1.70
1.00	4.32	4.21	1.58
1.20	3.92	3.67	1.48
1.50	3.36	3.05	1.36

<sup>†</sup> C-C distance = 2.28 au

C-H distance = 2.00 au

$r_C$  = 1.50 au (muffin-tin radius)

$r_H$  = 0.86 au (muffin-tin radius)

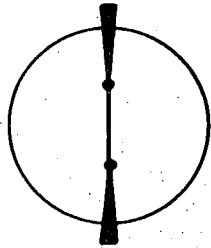
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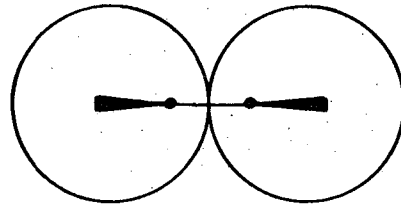
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FIGURE CAPTIONS

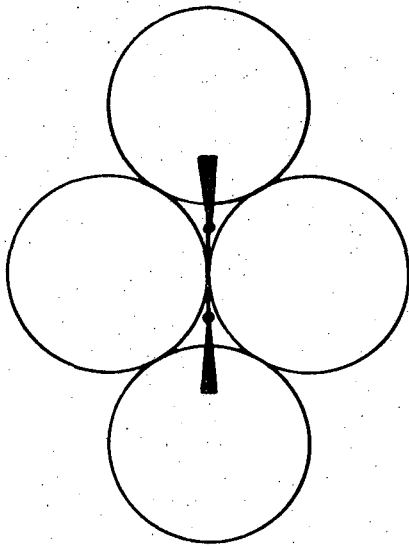
- Fig. 1: Schematic indicating various high-symmetry local bonding sites for acetylene on the (111) face of an f. c. c. crystal: (a) one-coordinate  $\pi$ , (b) di- $\sigma$ , (c) bridging, (d) triangular.
- Fig. 2: Phase shifts in radians for carbon based on the muffin-tin potential appropriate for acetylene used in this work. Energies are referred to the muffin-tin zero.
- Fig. 3: Phase shifts in radians for hydrogen based on an atomic hydrogen potential with the muffin-tin radius ( $r_H = 0.86$  au) used in this work. Energies are referred to the muffin-tin zero.
- Fig. 4: Comparison of calculated I-V profiles for various model geometries ( $z = 1.9 \text{ \AA}$ ) to experiment (stable acetylene overlayer) for two fractional-order beams.
- Fig. 5: Comparison of calculated I-V profiles for various model geometries ( $z = 1.9 \text{ \AA}$ ) to experiment (stable acetylene overlayer) for two integral-order beams.
- Fig. 6: Dependence of the calculated I-V profiles on CCH angle and comparison to experiment (stable acetylene overlayer) for the bridging geometry ( $z = 1.9 \text{ \AA}$ ). Also shown is a profile for which hydrogen scattering is neglected. The ratio of low-energy peaks labeled 1 and 2 is sensitive to CCH angle.



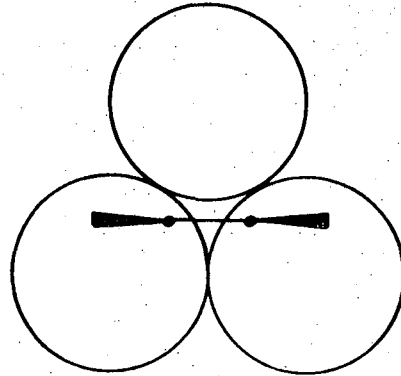
(a)



(b)



(c)

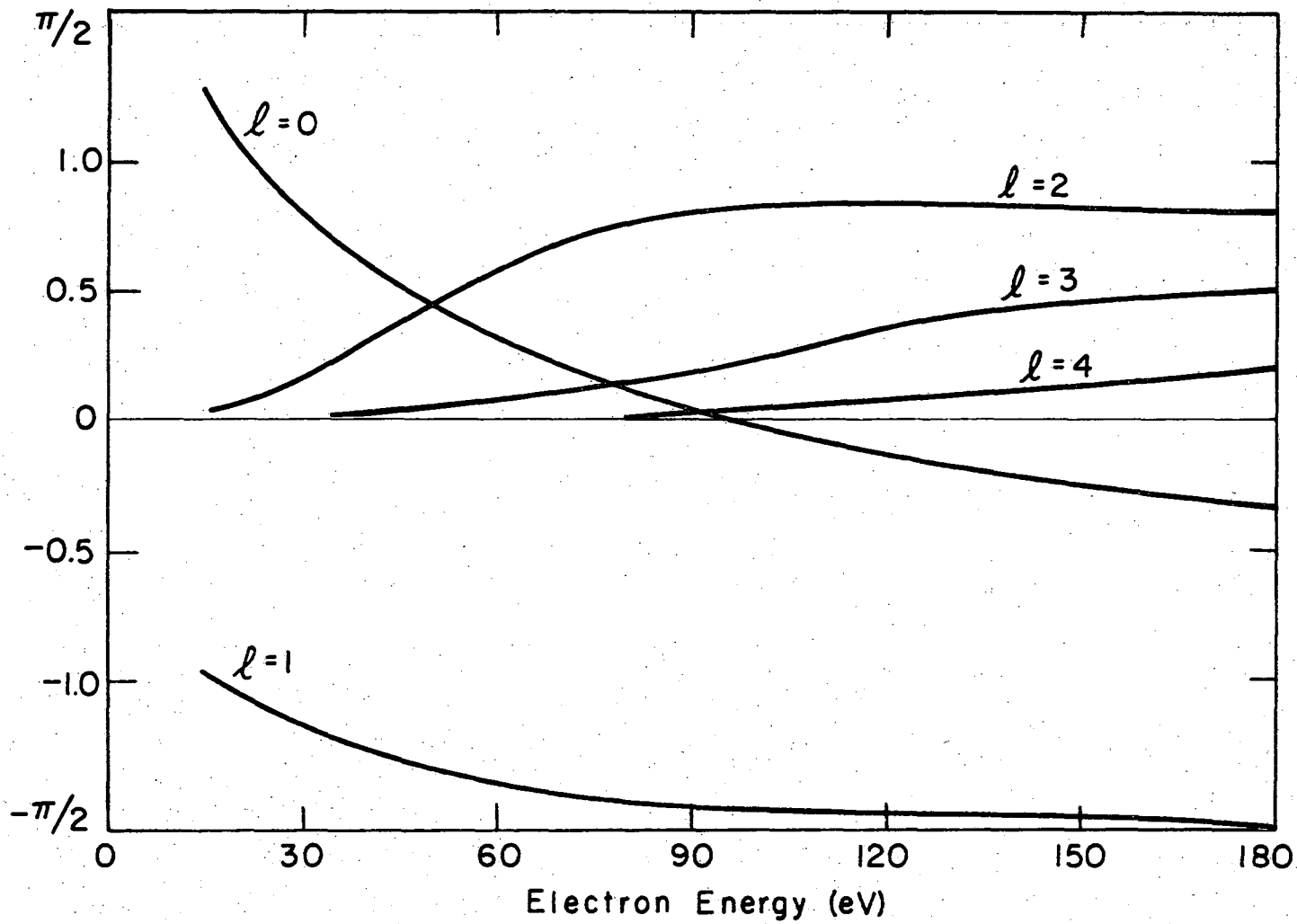


(d)

XBL 767-7141

Fig. 1

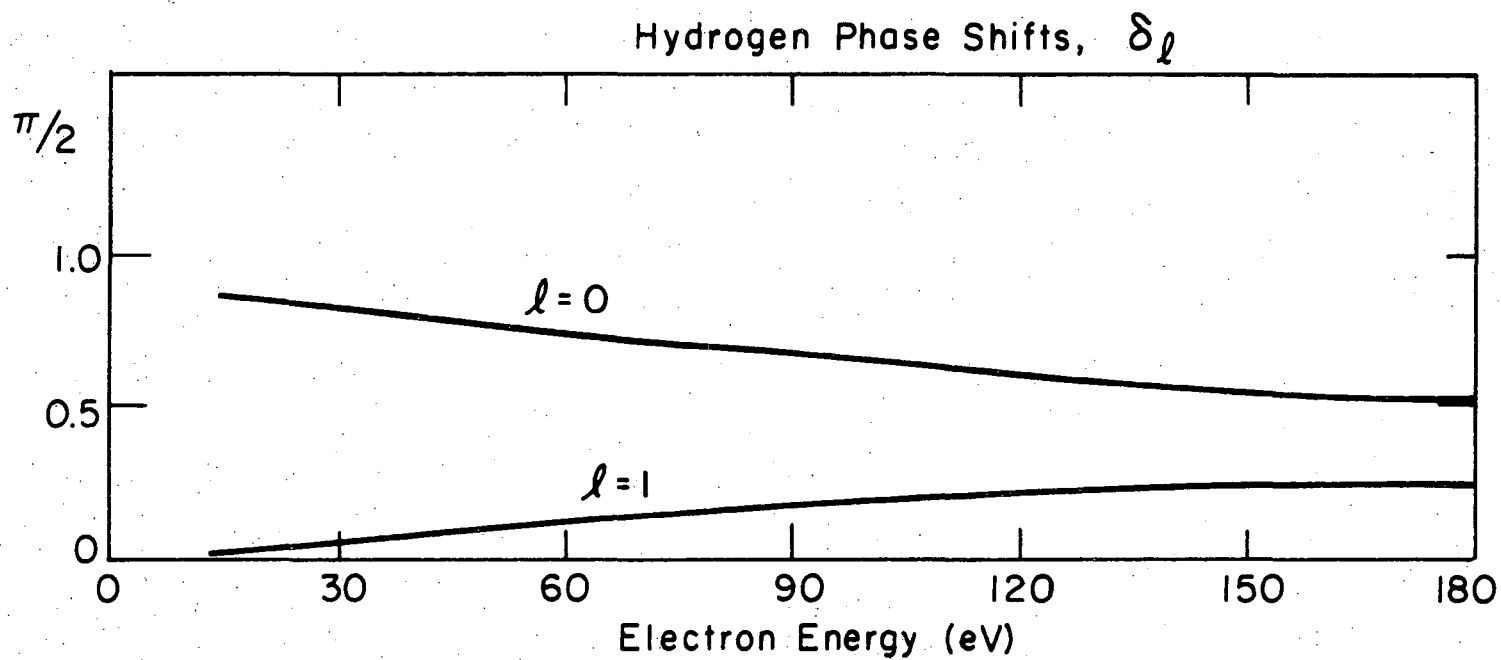
Carbon Phase Shifts,  $\delta_l$



XBL767-7143

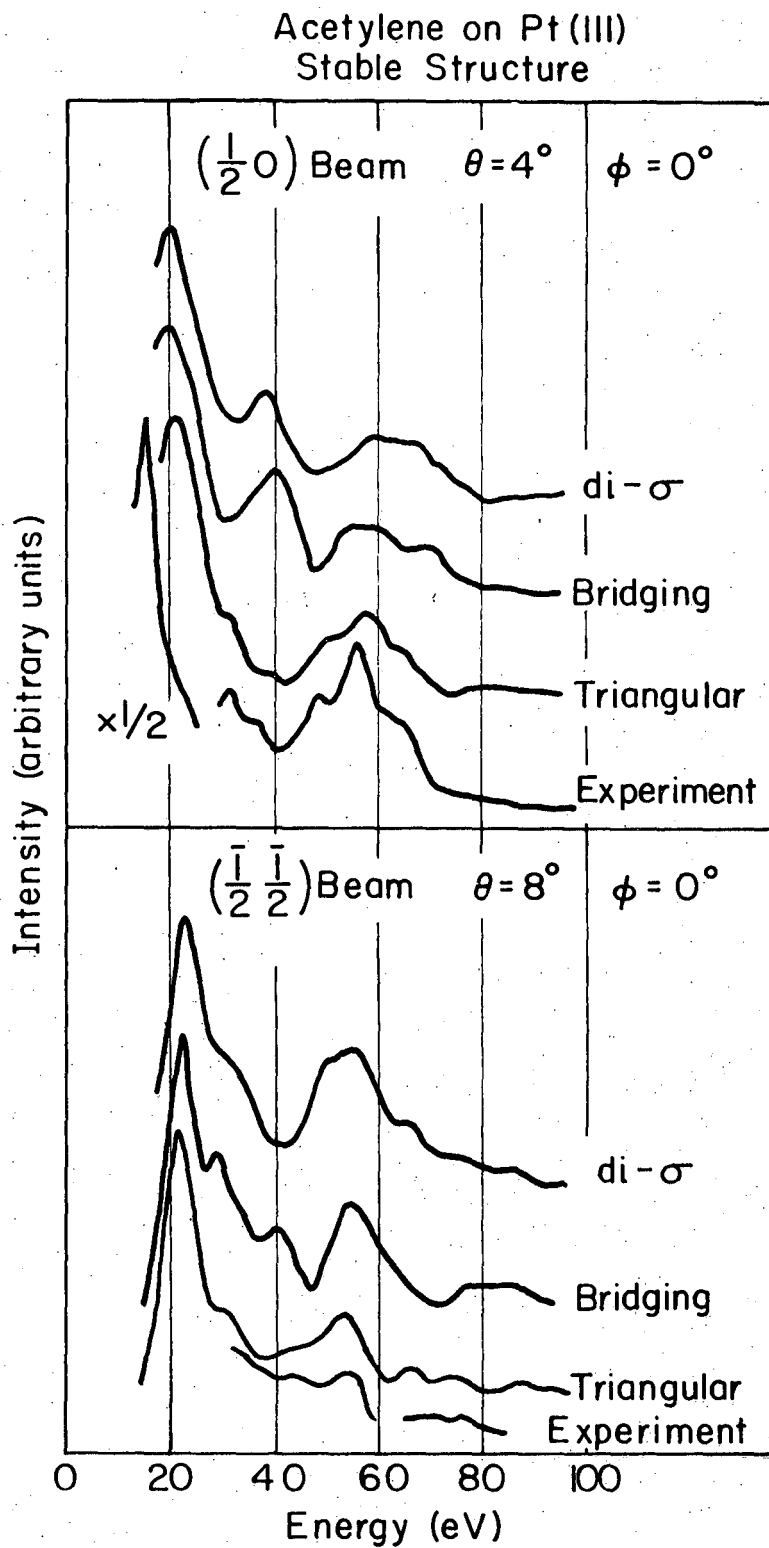
Fig. 2

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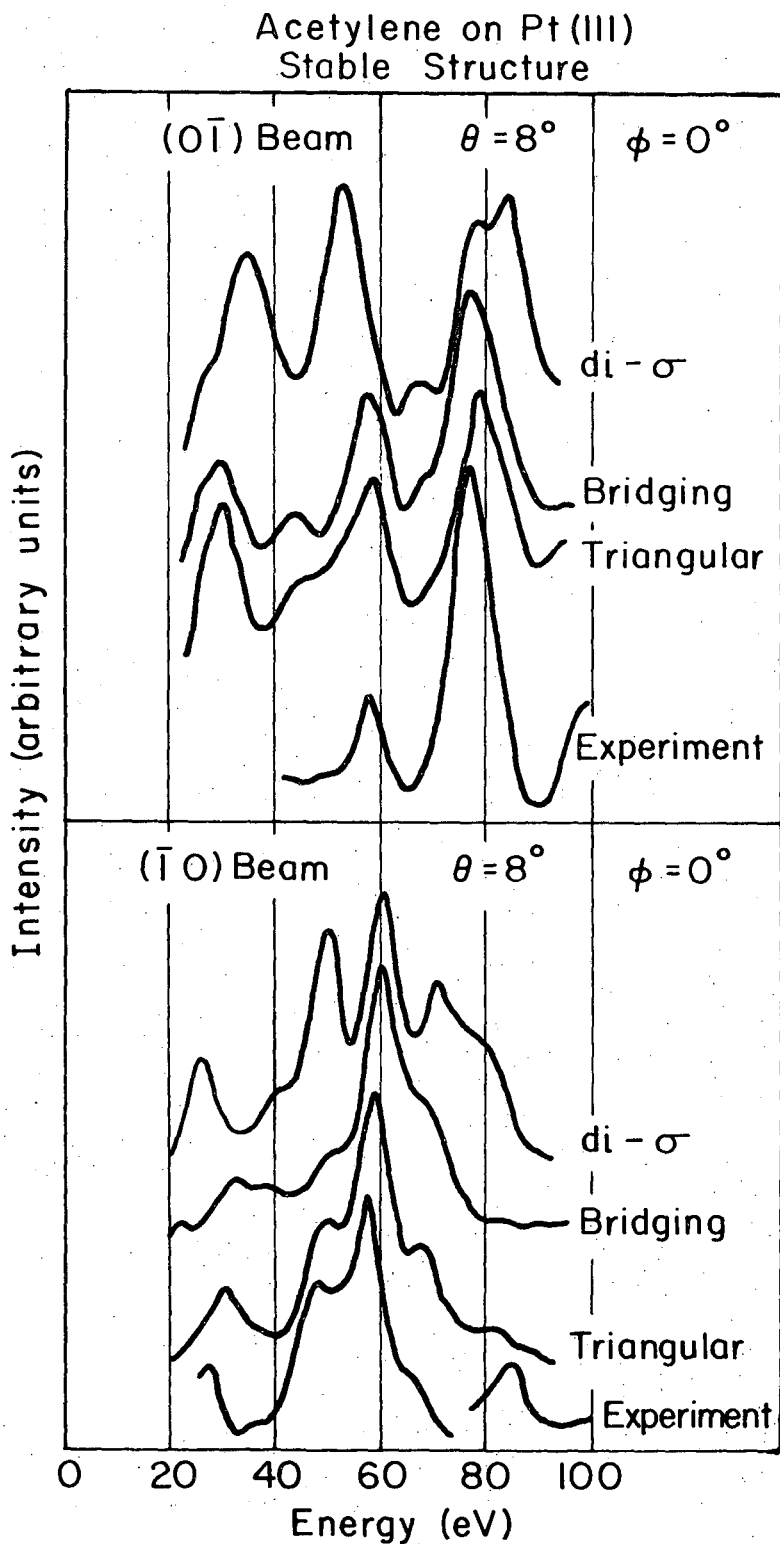
XBL 767-7142

Fig. 3



XBL 767-7145

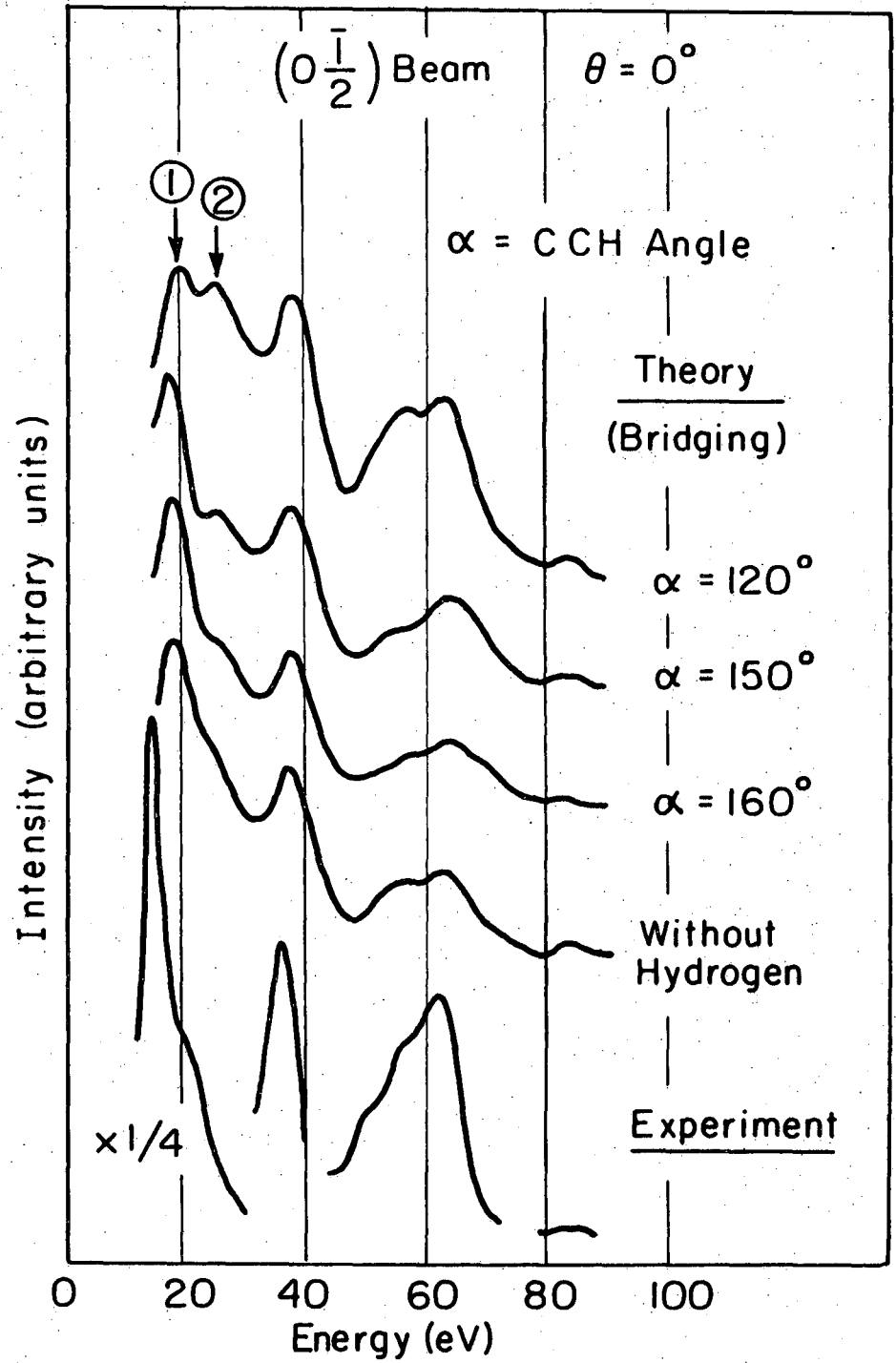
Fig. 4



XBL 767-7146

Fig. 5

Acetylene on Pt(III)  
Stable Structure



XBL 767-7144

Fig. 6

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