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DYNAMICAL LEED STUDY OF C₂H₂ AND C₂H₄ CHEMISORPTION ON PT(111): EVIDENCE FOR THE(->C -(H₃) ETHYLIDYNE (-> C-CH₃) GROUP

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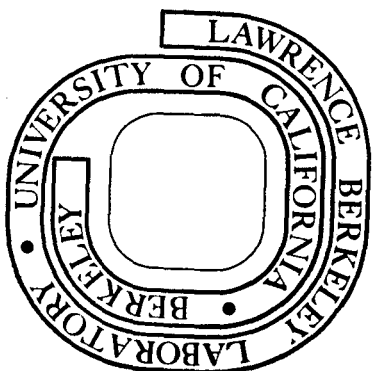
L. L. Kesmodel, L. H. Dubois, and
G. A. Somorjai

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DYNAMICAL LEED STUDY OF C_2H_2 and C_2H_4 CHEMISORPTION
ON PT(111): EVIDENCE FOR THE ETHYLIDYNE ($\geq C-CH_3$) GROUP

by

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Abstract

We propose ethylidyne ($\geq C-CH_3$) as the stable species formed from C_2H_2 and C_2H_4 chemisorption on the Pt(111) surface ($T \sim 300-350$ K). Consistent evidence to support this proposal is given by LEED intensity analysis and high resolution ELS studies of this species.

1. Introduction

In this Letter we report the first structural evidence for the formation of the ethynidyne ($\geq \text{C}-\text{CH}_3$) group on the Pt(111) surface, a surface species which arises from either acetylene (C_2H_2) or ethylene (C_2H_4) chemisorption. We note that in recent high resolution electron energy loss spectroscopy (ELS) studies of this system, Ibach *et al.*¹ have identified the surface species as ethynylene ($>\text{CH}-\text{CH}_3$) on the basis of vibrational mode assignments. However, using a dynamical analysis of low-energy electron diffraction (LEED) intensity data and a reassignment of the ELS modes, we find convincing evidence for the presence of the ethynidyne group.

The purpose of this Letter is to present the main evidence for our proposal from both LEED and ELS analysis. A more detailed presentation will be given elsewhere.² Here we report (i) new LEED data to discriminate between hydrocarbon species having the C-C axis near parallel vs. near perpendicular to the surface, (ii) determination of the surface bonding site for chemisorbed ethynidyne, (iii) determination of the C-C and C-Pt bond lengths for this species, and (iv) new vibrational assignments for $\geq \text{C}-\text{CH}_3$ which are in close agreement with the ELS data reported by Ibach. We also briefly discuss the energetics involved in the formation of ethynidyne, a probable surface intermediate, and the close analogy of the surface chemistry with known reactions of organometallic clusters.

2. Previous Work

The chemisorption of C_2H_2 and C_2H_4 on the Pt(111) surface has been studied by several investigators in recent years, principally with LEED,^{3, 4}

ultraviolet photoelectron spectroscopy (UPS),^{5, 6} and ELS.¹ There is general agreement that C_2H_2 chemisorbed on Pt(111) at $T \sim 300$ K undergoes an irreversible transition to a more stable surface species (referred to here as the "stable species") upon gentle heating to $T \sim 350$ K. Stair and Somorjai³ observed this transition with LEED and found that the chemisorption of C_2H_4 at $T \sim 300$ K also resulted in the same stable species. This lent apparent support to the model proposed by Merrill et al.⁷ that C_2H_4 dehydrogenates to C_2H_2 and chemisorbed hydrogen. This transition has also been observed with UPS by Demuth⁵ and by Lo et al.⁶ Demuth identified the stable species as an olefinic surface complex of C_2H_2 .

We reported a dynamical LEED analysis of the stable species⁴ in which we examined structural models representative of π and di- σ bonded C_2H_2 (and hence restricted the analysis to geometries having the C-C axis parallel to the surface). We found a rather satisfactory fit to the data of Stair and Somorjai³ for a parallel bonded C_2H_2 at a threefold symmetric site on the Pt(111) surface. In more recent work, Ibach et al.¹ have employed high resolution ELS to obtain the vibrational spectra of C_2H_2 and C_2H_4 chemisorbed below $T \sim 300$ K as well as the species formed at $T \sim 350$ K. These authors have shown that residual surface H atoms are necessary to effect the complete conversion of C_2H_2 to the stable species, which they identified as ethylidene ($>CH-CH_3$). This new ELS data has led us to reexamine and expand the LEED analysis to include species bonded with the C-C axis inclined at large angles to the surface.

3. Experimental Procedure

Both the apparatus and the experimental procedure employed for obtaining LEED intensity-voltage (I-V) profiles for surface structure analysis have been described elsewhere.³ We mention here only the salient features. The measurements were carried out in a Varian ultra-high vacuum chamber (background pressure $\sim 1 \times 10^{-9}$ Torr) equipped with LEED/Auger optics, a sputter ion gun and a quadrupole mass spectrometer. The adsorption of either C_2H_2 or C_2H_4 resulted in well-ordered (2x2) LEED patterns. The I-V data was obtained by photographing the LEED patterns at 2 eV intervals and was reproduced several times.

In this paper we compare to I-V data previously obtained at incident electron beam angles of $\theta = 0^\circ$ and 8° from the surface normal.³ We have also obtained new data at $\theta = 30^\circ$ on high-index fractional order beams. This new data has proven essential in discriminating between various orientations of the C-C axis. We compare only to data obtained for the stable species. As noted before, the resulting I-V profiles of this species are the same for C_2H_2 heated to $T \sim 350$ K as for C_2H_4 adsorbed at $T \sim 300$ K.

4. Dynamical LEED Analysis

The geometry of the stable species formed from C_2H_2 and C_2H_4 chemisorption has been analyzed by the comparison of I-V profiles calculated for various model structures to the experimental data. We have previously given an analysis of possible configurations having the C-C axis parallel to the surface.⁴ Details of the multiple scattering method and the nonstructural parameters are given in Ref. 4. Here we consider chemisorption geometries having the C-C axis at large angles to the surface as would be expected for $\geq C-CH_3$ or $>CH-CH_3$ groups.

We have examined various bonding sites for ethynidyne on the Pt(111) surface. As illustrated in Fig. 1, the threefold symmetric site was found to be optimum for all beams analyzed. This site was found to be best for the parallel species as well.⁴ In Fig. 2, we compare I-V profiles for parallel bonded C₂H₂ and perpendicularly bonded >C-CH_3 . We find as shown in Fig. 2b for the (1/2 0) beam that the general structure of the I-V profiles for the two different configurations of the C-C axis is quite similar. This is a general result found for other low-index beams and may be explained² by the fact that coincidentally each configuration has the same elevation of the C-C bond midpoint above the surface. However, high index beams are more sensitive to the different axial orientations as shown for the (3/2 0) beam in Fig. 2a. We find that the >C-CH_3 species gives a much better fit to the experimental data as compared to parallel bonded C₂H₂ both in terms of peak positions and lineshapes.

In Fig. 3a, we present an analysis of the C-C bond length for perpendicularly oriented ethynidyne. A C-C bond length of 1.5 Å yields optimum agreement between the experimental and calculated I-V curves. This is consistently found for the other beams analyzed.² This result is indicative of a C-C single bond and is in agreement with the ELS observations (vide infra) which show an aliphatic C-C stretching frequency. Fig. 3b illustrates the analysis of the C-Pt bond length which is found to be 2.0 Å.

The question arises as to how to possibly distinguish between >C-CH_3 and >CH-CH_3 with LEED. Since LEED is very insensitive to the

additional H atom on ethylidene we must consider probable differences in C-C axis orientation. We may reasonably expect ethylidyne to be perpendicular to the surface^{8, 9} whereas the extra H atom will cause ethylidene to tilt $\geq 30^\circ$ by both steric and bonding considerations. Furthermore, this is the angle predicted by Ibach's interpretation of the ELS results.¹ An ethylidene species at this angle would have a component of the C-C bond length normal to the surface of $\leq 1.3 \text{ \AA}$, which gives poor agreement with the results illustrated in Fig. 3a. This projection argument is valid in LEED analysis providing that the parallel component of momentum transfer is a small fraction of the perpendicular component; this is true for the $(1/2 \ 1/2)$ beam.

In summary, the optimum geometry found in the LEED analysis corresponds to a species having a C-C axis normal to the surface with a C-C bond length of $1.5 \text{ \AA}$ and three equivalent C-Pt distances of $2.0 \text{ \AA}$. Further support for this model comes from comparison to X-ray structure determinations for the organometallic compounds $\text{CH}_3\text{CCo}_3(\text{CO})_9$ ⁸ and $\text{CH}_3\text{CRu}_3(\text{CO})_9\text{H}_3$,⁹ as shown in Table 1. There is a remarkable agreement between the bond lengths and bond angles for the Pt(111) surface ethylidyne complex and those found in the trinuclear metal cluster compounds.

4. ELS Vibrational Analysis

Ibach et al.¹ have obtained identical vibrational spectra for both the stable acetylene and ethylene molecules adsorbed on a Pt(111) surface using high resolution ELS. They have assigned the spectrum to that of an ethylidene group. At first glance, it is not obvious that

C_2H_2 and C_2H_4 should yield identical vibrational spectra when adsorbed on Pt(111) since acetylene needs to gain two hydrogen atoms and a hydrogen in ethylene must transfer from one carbon atom to the other. However, Ibach conclusively showed that in order for C_2H_2 to make a transition from the metastable to the stable state, hydrogen atoms must be present. Ethylene rapidly undergoes this transition at room temperature.

Table 2 lists the bond vibrational frequencies observed by Ibach et al. The band between 2900 and 3000 cm^{-1} is indicative of a C-H stretching vibration for an aliphatic carbon. The existence of a carbon-carbon single bond is confirmed by the peak at 900 cm^{-1} , the characteristic stretching frequency for a C-C single bond. This agrees quite well with a C-C bond length of $1.5\text{ \AA}$ determined from the LEED intensity analysis. The presence of methyl deformation ($1420, 1360\text{ cm}^{-1}$) and methyl rocking (1130 cm^{-1}) modes confirms the existence of a methyl group. The intensity of the antisymmetric stretching and deformation bands is relatively weak, in keeping with the perpendicular dipole selection rule.¹³ Ibach has incorrectly assigned this spectrum to an ethylidene species by analogy with 1, 1-dichloroethane.¹⁰ It is clear from Table 2 that the agreement between this model compound and the surface species is not very satisfactory. Their vibrational analysis ignores the methyl rocking mode which should be ELS active since movement of the hydrogen atoms has a large component normal to the surface.

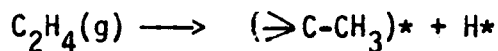
The vibrational frequencies for the ethynylidyne species proposed herein are in much better agreement with the observed spectra. This

becomes clear if one considers $\text{CH}_3\text{CCO}_3(\text{CO})_9$ ¹¹ and CH_3CBr_3 ¹² as model compounds (see Table 2). Due to the high symmetry of the ethylidyne radical (C_3v) only seven vibrational modes should be present and all of these are observed. A study of the deuterated molecules lends further credence to this new assignment.²

6. Conclusion

We have found very consistent evidence from LEED structural analysis and from high resolution ELS for the formation of the ethylidyne group on the Pt(111) surface. We have reported the most probable surface geometry for this species based on a LEED analysis of a wide (but not exhaustive) set of model configurations.

The overall reactions of C_2H_2 and C_2H_4 on Pt(111) may be written as follows:



where (*) indicates a surface species. The extra hydrogen necessary for the acetylene reaction comes from background hydrogen in the ultrahigh vacuum chamber. Simple energetic considerations of the above reactions indicate that the binding energy of the ethylidyne species with the Pt(111) surface must be greater than 100 kcal/mole.²

Ethylidyne species are quite well known to organometallic chemists. Clusters containing this radical $(\text{CH}_3\text{CCO}_3(\text{CO})_9)$ ¹¹, $\text{CH}_3\text{CRu}_3(\text{CO})_9\text{H}_3$,⁹ and $\text{CH}_3\text{COs}_3(\text{CO})_9\text{H}_3$ ¹⁴ have been studied for almost 20 years. All of these species have proven to be quite stable, although bond strengths are not

yet known. Quite possibly, there is a close analogy between the reactions of small hydrocarbons with metal surfaces and those found with metal cluster compounds.¹⁵ For example, $M_3(CO)_9$ ($M=Ru, Os$) reacts with ethylene to yield $H_2M_3(CO)_9CCH_2$,¹⁶ a vinylidene species. This cluster can be converted to the more stable ethylidyne complex by bubbling H_2 through a refluxing n-heptane solution of $H_2M_3(CO)_9CCH_2$.¹⁴ By analogy with these observations we propose vinylidene as a possible intermediate in the formation of ethylidyne on a Pt(111) surface. More work needs to be done before any conclusive statements about the mechanism can be made.

Acknowledgement

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TABLE 1

Structural Comparison Between Pt(111)
Surface and Organometallic Clusters

Compound	C-C (Å)	C-M (Å)	M-M (Å)	< M-C-M °
Pt(111) - Ethynylidyne Surface Complex	1.5	2.0	2.77	88
CH ₃ CCo ₃ (CO) ₉ ⁸	1.53	1.90	2.47	81
CH ₃ CRu ₃ (CO) ₉ H ₃ ⁹	1.51	2.08	2.84	86

Table 2

Vibrational Assignments for "Stable Species" on Pt(111)
(all vibrational frequencies are in cm^{-1})

1 Surface Species	10 CH_3CHCl_2	1 Ethylidene	11 $\text{CH}_3\text{CCo}_3(\text{CO})_9$	12 $\text{CH}_3\text{-CBr}_3$	Ethylidyne
3025-3105 W	3015 M	CH stretch	2924 M	2993 M	CH_3 stretch (a)
---	3001 W	CH_3 stretch (a)			
2900-2940 M	2946 M	CH_3 stretch (s)	2882 M	2938 M	CH_3 stretch (s)
1420 M	1446 M	CH_3 deform (a)	1420 M	1432 M	CH_3 deform (a)
1350-1360 S	1381 M	CH_3 deform (s)	1359 M	1373 M	CH_3 deform (s)
1130 S	1280 M	CH bend	1161 M	1064 S	CH_3 rock
----	1091 W	CH_3 rock			
900 M	982	CC stretch	1006 S	1045 M	CC stretch
435 M	650 M	C-Pt stretch	650-600 var	408 M	C-Pt stretch

S = strong, M = medium, W = weak, (a) = assymmetric, (s) = symmetric

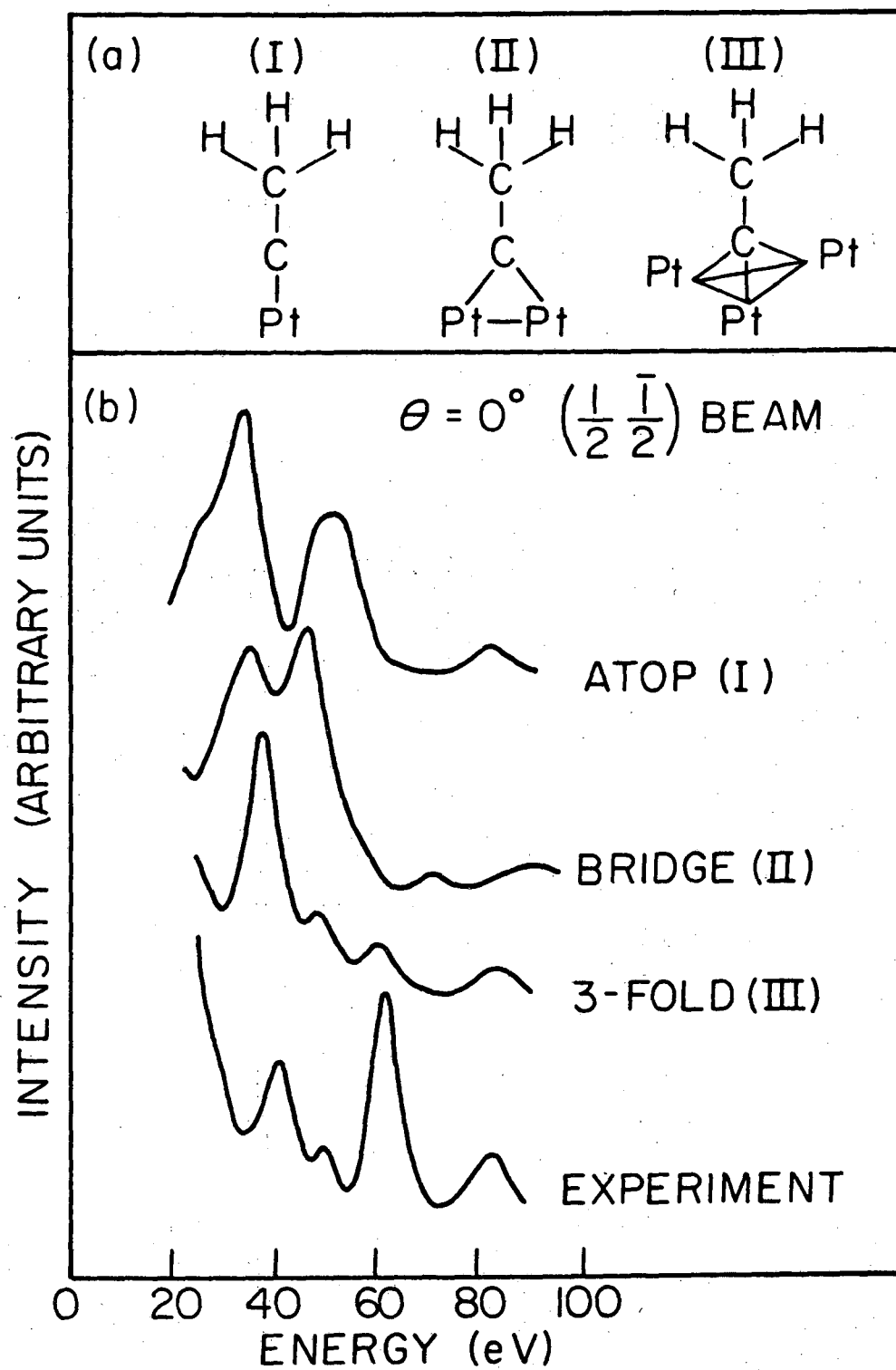
Figure Captions

Fig. 1a Model geometries for high-symmetry bond sites for ethylidyne chemisorption on Pt(111);

1b Comparison of calculated and experimental I-V profiles as a function of site geometry ($C-C = 1.5 \text{ \AA}$, $C-Pt = 2.0 \text{ \AA}$).

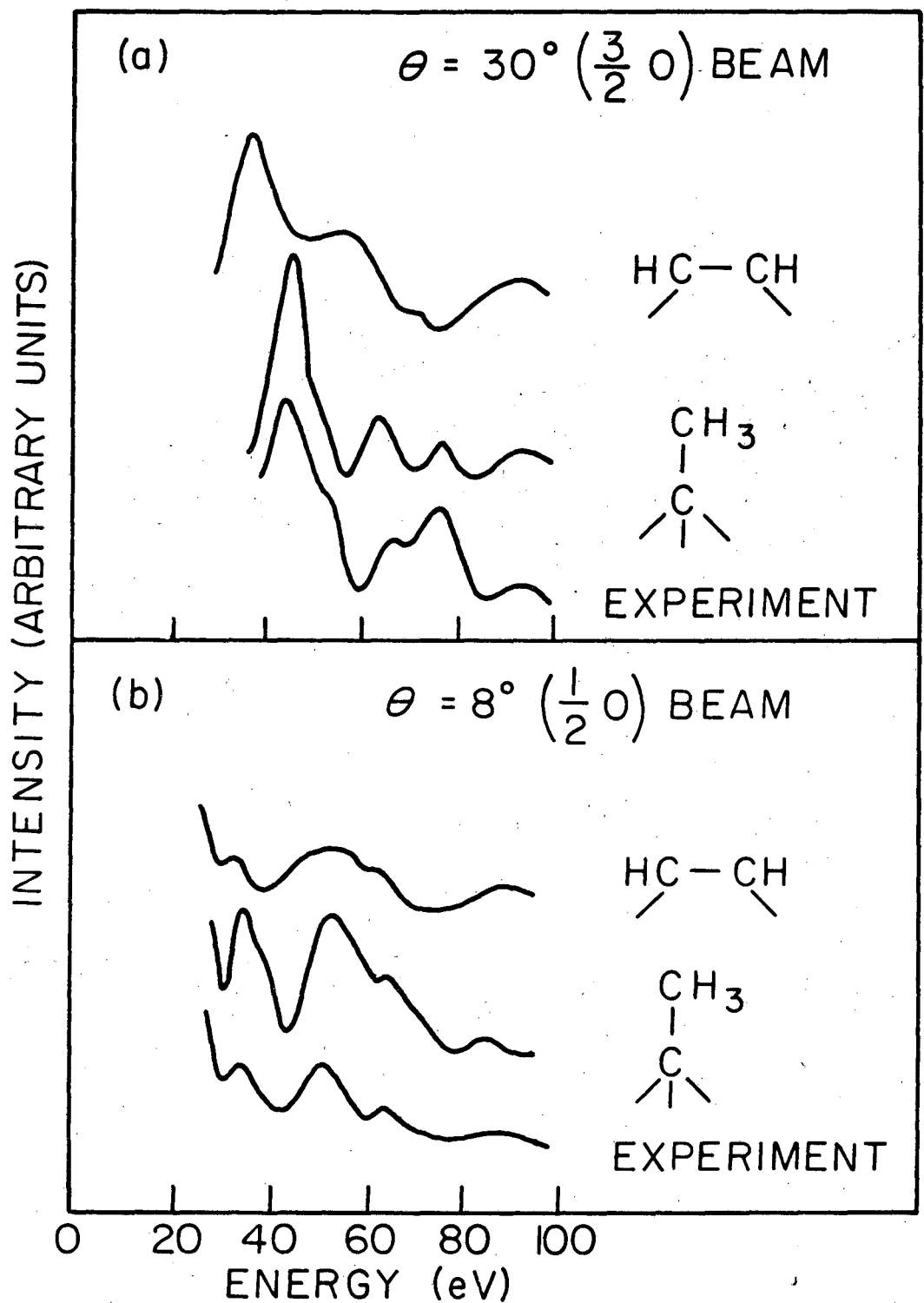
Fig. 2 Comparison of calculated I-V profiles for the optimum geometries found for models of parallel bonded C_2H_2 and perpendicularly bonded $\geq C-CH_3$ for (a) high-index diffraction beam and (b) low-index beam on the Pt(111) surface. The experimental data is for the stable chemisorption state (see text). The model geometries correspond to adsorption at a threefold site.

Fig. 3 LEED I-V analysis of bond lengths for chemisorbed ethylidyne on Pt(111): (a) C-C bond length variation for $Pt-C = 2.0 \text{ \AA}$, (b) Pt-C bond length variation for $C-C = 1.5 \text{ \AA}$. The C-C axis is oriented perpendicular to the surface at a threefold site as shown in the inset.



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Fig.1



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Fig.2

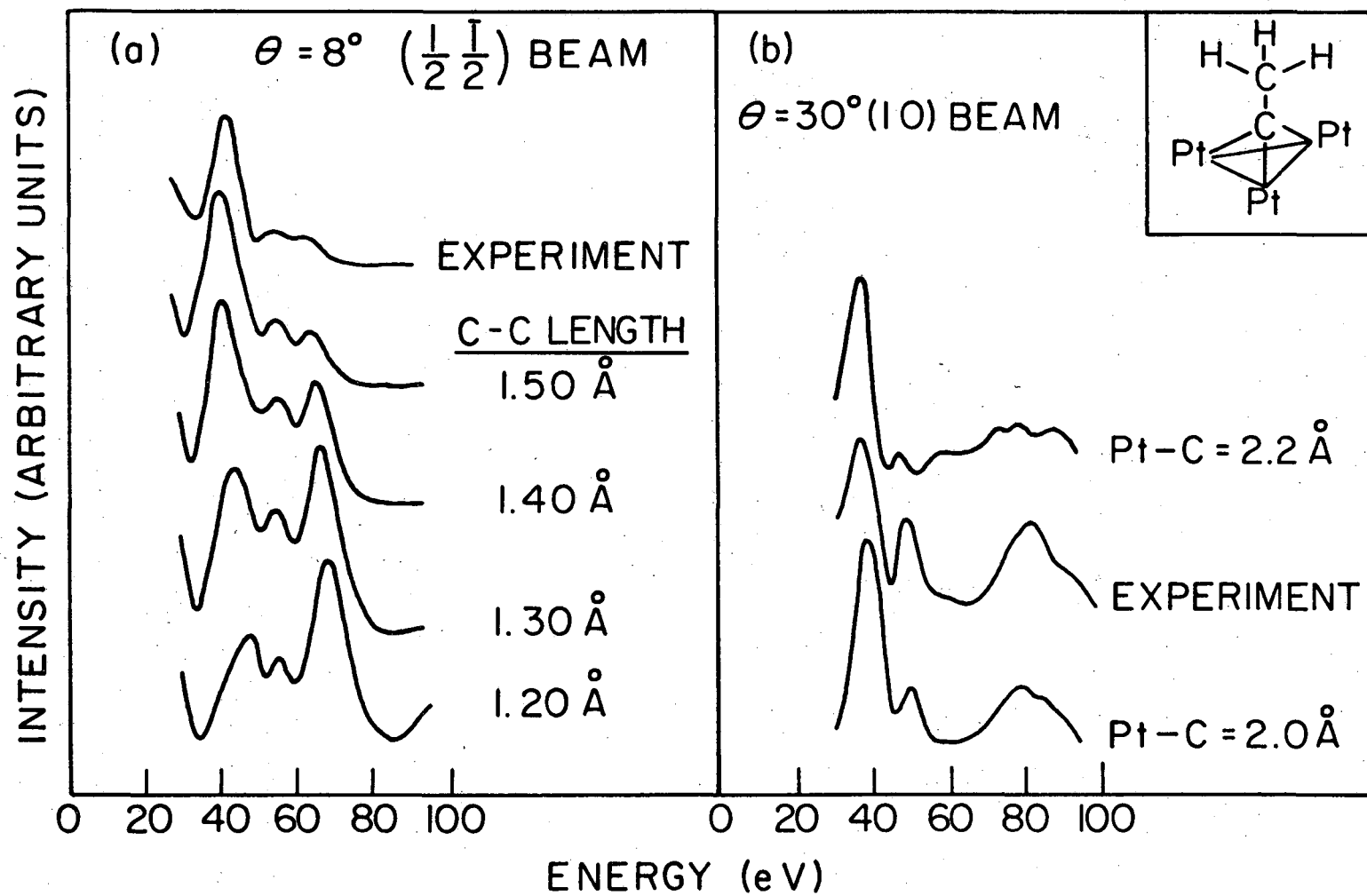


Fig.3

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