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Author

Kesmodel, L.L.

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

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LEED AND ELS ANALYSIS OF ACETYLENE AND ETHYLENE CHEMISORPTION ON THE PT(111) SURFACE: EVIDENCE FOR ETHYLIDYNE FORMATION

by

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

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California,
Berkeley, California 94720

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* Permanent Address: Department of Physics, Indiana University, Bloomington, Indiana 47401

Abstract

The stable surface species formed from the chemisorption of acetylene (C_2H_2) or ethylene (C_2H_4) on the Pt(111) surface (T∿300-350K) has been studied by a low-energy electron diffraction intensity analysis. High resolution electron energy loss spectra reported by Ibach _et al_. have been interpreted by comparison to infrared data on relevant model compounds. The surface species most consistent with these studies is ethylidyne ($\gg$C-CH_3). The species is coordinated to a threefold surface site with the C-C axis normal to the surface within an uncertainty of $\sim 15^{o}$. A saturated C-C bond length of 1.50Å ± 0.05Å and three equivalent Pt-C bond lengths of 2.00Å ± 0.05Å are determined by the LEED analysis and are consistent with the reported structures of ethylidyne in organometallic clusters. The ethylidyne group forms readily upon exposure of C_2H_4 to the Pt(111) surface at T∿300K with the transfer of one hydrogen atom to the surface per ethylene. The complete conversion of C_2H_2 to ethylidyne requires the presence of surface hydrogen atoms and proceeds rapidly at T∿350K. By comparison to reported reaction mechanisms on related transition metal clusters it seems likely that vinylidene (>C=CH_2) is an intermediate in both reactions.

1. Introduction

The chemisorption of simple hydrocarbons and subsequent surface reactions on well-characterized transition metal surfaces has become a topic of considerable interest in surface science. The aim of such studies is to provide fundamental information on the initial stages of hydrocarbon catalysis and to establish a framework for the interpretation of results on more complex catalysts. One of the few systems to be studied by several complimentary surface analysis techniques is the chemisorption of acetylene (C_2H_2) and ethylene (C_2H_4) on the platinum (111) surface. These systems have been most recently studied by ultraviolet photoelectron spectroscopy (UPS),[1-3] low-energy electron diffraction (LEED),[4-6] high resolution electron energy loss spectroscopy (ELS)[7,8] and thermal desorption spectroscopy (TDS)[2]. The authors have all reported the presence of at least two binding states and conversion from one state to the other as a function of temperature. However, the bonding and the nature of the adsorbed species is not completely characterized. Demuth has interpreted UPS studies of C_2H_2 chemisorption as indicating formation of olefinic C_2H_2[1]. More recently he has proposed vinylidene ($>C{=}CH_2$) and a vinyl species ($-CH{=}CH_2$) as the stable species resulting from the chemisorption of C_2H_2 and C_2H_4, respectively[2]. He has also reported TDS experiments for C_2H_4 on Pt(111) which are indicative of a species with C_2H_3 stoichiometry[2]. Both Ibach *et al*. and the present authors have proposed that C_2H_2 and C_2H_4 form a *single* stable species but do not agree as to the nature of this surface phase. Ibach, Hopster and Sexton[7], and Ibach and Lehwald[8] have reported ELS data which they have interpreted in terms of the formation of an ethylidene ($>CH-CH_3$) surface species. We have briefly discussed a LEED intensity analysis which provides evidence for the ethylidyne ($>C-CH_3$) group and have given a new vibrational mode assignment to the ELS data in further support of this model[6]. This recent work supersedes an earlier LEED analysis in which we considered only structural models having the carbon-carbon axis parallel to the surface plane[5].

Since LEED intensity analysis has been applied to only a few molecular chemisorption systems (the present system, CO on Ni(100)[9] and CO on Ti(0001)[10])it is important to document the structural analysis in considerable detail. In this paper we present extensive results from the analysis of hydrocarbon species on Pt(111) having the C-C axis inclined at large angles to the surface. We have analyzed models in a range of surface bonding sites and with varying C-C and C-Pt bond lengths. Variation in the angle of the C-C axis with respect to the surface has been considered in selected cases although emphasis is placed on near-perpendicular orientations. Results for a range of model geometries having the C-C axis parallel to the surface were reported earlier[5]. We also discuss in detail the ELS data of Ibach[7,8] which we believe is most supportive of a $>C-CH_3$ species.

The principal results of this work which are discussed in detail in subsequent sections are: (i) The LEED intensity analysis of the most stable surface structure favors a hydrocarbon species coordinated to a threefold Pt surface site with structural parameters characteristic of an ethylidyne group, i.e., a C-C bond length of 1.50Å ± 0.05Å, three equivalent Pt-C bond lengths of 2.00Å ± 0.05Å with the C-C axis normal to the surface within an estimated uncertainty of ∿15°. (ii) High-index diffraction beams having large components of momentum transfer parallel to the surface have proven to be critical in resolving closely related structural models which exhibit very similar low-index beam intensity profiles. (iii) The vibrational frequencies observed by high-resolution ELS are in rather good agreement with infrared data reported for ethylidyne bonded to the trinuclear organometallic cluster $Co_3(C\text{-}CH_3)(CO)_9$[11].

2. Experimental Procedure

Both the apparatus and the experimental procedure used to obtain LEED intensity-voltage (I-V) profiles of diffraction beams have been described previously[4]. The measurements were carried out in an ultra-high vacuum chamber (background pressure $\sim 10^{-9}$ torr) equipped with four-grid 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 under conditions of relatively low gas exposure (∿1 Langmuir) as discussed by Stair and Somorjai[4]. The I-V data was obtained by a rapid photographic method[12] which minimized possible electron beam damage to the hydrocarbon overlayer and permitted simultaneous recording of all diffraction beams.

In this paper we report new I-V data obtained at an incident electron beam angle of $\theta=30^{\circ}$ from the surface normal. This angle of incidence allows the recording of intensity data on relatively high-index diffraction beams. These beams are quite sensitive to lateral movements of surface atoms and have proven essential in discriminating between certain competing structural models as discussed below[13]. We also make extensive comparison to data previously reported by Stair and Somorjai[4] at $\theta=4^{o}$ and 8^{o}. This data pertains to relatively low-index diffraction beams which have large components of momemtum transfer normal to the surface and are therefore sensitive to the perpendicular displacement of surface atoms. Analysis of these low-index beams has provided a measure of the C-C bond length for the stable surface species.

The formation of a more stable surface hydrocarbon species from the adsorption of either C_2H_2 or C_2H_4 on Pt(111) was first reported by Stair and Somorjai using LEED[4]. These authors found that C_2H_2 initially chemisorbed at T∿300K underwent a change in I-V profiles upon heating to T∿350K while preserving the (2x2) LEED pattern. The I-V data for converted C_2H_2 was found to be identical to that for C_2H_4 chemisorbed at T∿300K. This indicated that the same surface species was formed under the conditions of the LEED experiments. This transformation has also been studied with UPS[1-3] and high resolution ELS[7,8]. The ELS experiments have further indicated that the presence of surface hydrogen atoms are required for the complete conversion of C_2H_2 to the stable species[8]. Under the conditions of the LEED experiments such surface hydrogen adsorbed from the ambient in levels of ∿0.2 monolayers is probable.

3. Dynamical LEED Calculations

The basic approach to surface crystallography by means of a dynamical (multiple-scattering) LEED calculation of reflected beam intensities is by now a rather well-established methodology which has yielded reliable structural data for a wide variety of metals, semiconductors and atomic overlayer systems[14]. Similar results for chemisorbed molecules are very recent and few, and their validity is perhaps best judged by consistency with other data and by comparison with model systems, where appropriate.

The procedure employed to calculate the reflected beam intensities for ordered hydrocarbon overlayers has been given in some detail previously[5]. Scattering parameters relevant to carbon, hydrogen and platinum have been discussed, and the same values for all such non-structural parameters are used in the present work. The method used in this work involves a separate calculation of the reflection coefficients (in a plane-wave representation) for individual layers of platinum, carbon and hydrogen atoms. Platinum layers are then combined by the "layer doubling" method[15] to yield a converged substrate reflectivity matrix representing the reflectivity of 8 Pt layers. Then, given a model overlayer structure, the C and H reflectivity matrices are combined with appropriate phase factors. Such an approach has the advantage that each additional model geometry for the overlayer represents a small (typically 3%) increase in computation time. The computer program used for this analysis is capable of treating a substrate system and two independently moveable overlayers, each with a maximum of 4 different basis atoms per unit cell[16].

4. LEED Analysis Results

4.1 Model Structures

In this work we have evaluated a large (but not exhaustive) set of model geometries representing a range of probable structures for the rather stable hydrocarbon species formed from C_2H_2 or C_2H_4 chemisorption on Pt(111). For the local site geometry on the surface we have restricted the analysis to the high symmetry sites shown in Figure 1 as atop (A), bridge (B) and threefold (T). The threefold sites labeled T_b and T_c are distinguished by the respective presence or absence of a Pt atom in the second layer, along the threefold axis. For the C-C bond length we have examined structures ranging from 1.20Å (triple bond) to 1.54Å (single bond). The C-Pt distance is allowed to vary from 1.94Å to 2.30Å. The diffracted beam intensities are very insensitive to hydrogen (see below) so that the C-H bond length was fixed at 1.06Å.

Consideration of all possible C-C axis orientations and surface sites is beyond our computational resources. Hence our general approach has been to consider likely structures (and variations of these) which have been found in related organometallic compounds. In Ref. 5 we considered a variety of bonding structures for geometries having the C-C axis parallel to the surface as would be expected for π or di-σ bonding of C_2H_2. The optimum structure found in the analysis of parallel-bonded C_2H_2 is shown schematically in Figure 2d and corresponds to an approximately olefinic molecular configuration, the C-C bond length in related clusters[17] being intermediate between that of a single and double bond.

However, such a C_2H_2 species is not consistent with the ELS vibrational mode analysis[7], and we must consider other surface species.

The structures shown in Figure 2a, c and d have been reported for organometallic compounds and serve as the focal point of the present analysis. The ethylidyne group ($>C-CH_3$) (Figure 2a) and vinylidene ($>C=CH_2$) (Figure 2c) have been observed in the reaction of ethylene with certain trinuclear organometallic compounds[18]. We note that the vinyl species $-CH=CH_2$ and $>C=CH_2$ have been recently proposed on the basis of UPS studies[2]. The ethylidene group ($>CH-CH_3$) has not, to our knowledge, been reported for trinuclear compounds but has been advocated on the basis of ELS data[7,8]. A probable geometry for ethylidene is shown in Figure 2b. Note that considerable ($\gtrsim 20^{o}$) tilt of the C-C axis from the surface normal is expected for this species on the basis of both steric and bond angle considerations. Ibach has proposed a similar angle by analyzing the intensity of certain vibrational modes[8].

We should emphasize here that the optimum structure discussed below corresponding to ethylidyne (Figure 2a) was discovered in the course of a geometry search, prior to the authors' knowledge of this species in organometallic chemistry. Hence, the "model compound" approach taken here is after the fact and is employed primarily to point to the possible utility of relating organometallic and surface chemistry.

4.2 Analysis of Structures with the C-C Axis Normal to the Surface

In this section we consider model structures having the C-C bond normal to the surface for various surface sites, C-C bond lengths and C-Pt bond lengths. We find that electron scattering by hydrogen is weak as expected, and we neglect it in the analysis. That such an approach is valid is illustrated in Figure 3 in which I-V profiles calculated with and without H scattering are compared. We note that there are few distinctions between the two methods and that, importantly, the same behavior in peak positions and relative intensities with changing surface geometry is found.

In Figure 4 we show a comparison of theory and experiment for I-V profiles as a function of site geometry. The calculations have been done with the C-C axis normal to the surface while the local surface site geometry is varied. In Figure 4 the C-C and C-Pt bond lengths are held fixed; however, these parameters were also varied and good agreement is found only for the threefold site T_c for C-C=1.50Å and Pt-C=2.00Å within an uncertainty of ±0.05Å (see below). This site symmetry and the saturated C-C bond length is characteristic of the ethylidyne group[19,20]. In Figure 5 we show comparisons of theory and experiment for this optimum structure at two different incident beam angles for several fractional order beams. Consistently good agreement in terms of peak positions, relative intensities and lineshapes is found. Failure to accurately match the positions of the very low energy peaks (∿15eV) in Figure 5b is most likely due to an inadequacy in the theoretical model at energies below ∿30eV rather than an error in structure. This calculational method does not account for reflection at the vacuum-solid potential barrier nor for differences in overlayer and substrate inner potentials, effects which may result in substantial peak shifts and relative intensity changes for very low beam energies[21].

In Figures 6-13 we consider the optimization of the model structures having the C-C axis oriented normal to the surface at the T_c site. Our intent here is to demonstrate the marked sensitivity to the C-C and C-Pt bond lengths and the consistency of the results for a large number of diffraction beams. The results for $\theta=8^o$ (Figures 6-10) and $\theta=4^o$ (Figures 11-13) were calculated for slightly different bond length meshes, but it is readily seen that the best agreement occurs for C-C=1.50Å and C-Pt=2.00Å, with an uncertainty of ±0.05Å. Note, for example, the strong dependence on C-C length of the calculated I-V profiles for the $(\frac{1}{2}\ 0)$ and $(\frac{1}{2}\ \bar{\frac{1}{2}})$ beams (Figures 6-7) whereas the $(0\ \bar{\frac{1}{2}})$ beam in Figure 13 exhibits a marked dependence on the value of the Pt-C distance. Figure 14 shows the ethylidyne structure proposed on the basis of these LEED results.

4.3 Effect of C-C Axis Orientation

We have seen above that a rather consistent fit to the I-V data is found for a species having the C-C axis normal to the surface at the surface site T_c with C-C=1.50Å. The question arises as to whether or not other model structures could provide better or equally good agreement with experiment. Let us consider a tilt of the C-C axis away from the surface normal while maintaining the C-Pt_3 nature of the molecule-surface bond. Such a class of geometries includes the vinylidene structure found in organometallic compounds (Figure 2c) and may also approximate the bonding of ethylidene (Figure 2b). In Figures 15 and 16 we show results for such a class of tilted structures at angles (θ_t) ranging from 0^o to 55^o from the surface normal for two different C-C bond lengths of 1.34Å (olefinic) and 1.54Å (saturated). We note that the structure having $\theta_t=45^o$, C-C=1.34Å is representative of vinylidene[19] whereas $\theta_t=25^o$, C-C=1.54Å corresponds to the ethylidene structure suggested by Ibach <u>et al</u>.[8] It is clear that only the ethylidyne geometry with $\theta_t=0^o$ and C-C=1.50Å±0.05Å gives satisfactory agreement with experiment. In Figures 15 and 16 we have also indicated the <u>projection</u> of the C-C bond length on the surface normal for each value of θ_t. We have done this to emphasize that structures having similar projected bond lengths exhibit similar profiles, especially with regards to the positions of the main intensity maxima. This projection rule, which was discussed previously[6], applies to low-index beams for which the parallel component of the momentum transfer is a small fraction of the perpendicular component. We may use this rule to estimate that $\theta_t \lesssim 15^o$.

We should emphasize here that the LEED analysis cannot distinguish between ethylidyne and ethylidene if each species is oriented normal to the surface at a T_c site, since the difference due to hydrogen scattering would be negligible. However, we suggest that such a configuration is unlikely for ethylidene (cf. Figure 2b) since the lone H atom would have Pt-H $\sim$ 1.6Å-1.8Å for the optimum geometry given by LEED. This would imply a strong Pt-H interaction (which is inconsistent with the ELS analysis (see below)) and it is improbable that such an arrangement would be stable on the surface.

Of course we have only considered a very restricted class of structures having a tilted C-C axis at the T_c site. These results are useful, however, in illustrating the marked changes in the I-V profiles which result from small changes in the orientation of the C-C axis.

4.4 The Use of High-Index Diffraction Beams

In this work we have shown that an ethylidyne species oriented normal to the surface at site T_c provides rather good agreement with a large body of LEED data at incident beam angles of $\theta=4^o$ and 8^o for low-index diffraction beams. However, in a previous work a parallel-bonded species was also found to give satisfactory agreement[5]. In Figure 17 we show these two optimum structures, and we note that they are closely related in that the center of the C-C bond is directly over the three-fold (T_c) site at a z-distance of 1.95Å from the plane of the Pt atoms in each case. It is evident that a phase averaging of waves scattered from the two carbon atoms has resulted in the similar I-V profiles for these two structures. This effect is compounded by a domain averaging over the three degenerate azimuthal orientations of the parallel-bonded model[5].

We have found, however, that the high-index beams having large components of momentum transfer parallel to the surface easily resolve these two structures. In Figure 18 a comparison is given for high-index beams for the two model structures shown in Figure 17. There are major differences between the results for the two models in terms of both peak positions and relative intensities even though close similarities are found for the low-index beams[6]. The ethylidyne model reproduces the major features in the experimental data at $\theta=30^0$ although the relative intensity fit is not as good as for the low-index beam data obtained at $\theta=4^0$ and 8^0. Calculations for large angles of incidence are more sensitive to differences in the inner potential of the overlayer and substrate, and this may partially account for the relative intensity problem. We suggest that these high-index beams, which have heretofore been neglected in LEED analyses, will prove very useful in the future and will certainly enhance sensitivity to lateral displacements of surface atoms[13].

5. High Resolution ELS Analysis

During the past year several groups have offered an interpretation of the high resolution electron energy loss spectra of the stable species formed when either C_2H_2 or C_2H_4 is chemisorbed on Pt(111). This data, originally published by Ibach et al.[7,8], has led researchers to consider the following three models: ethylidene ($>CH-CH_3$)[7,8], ethylidyne ($>C-CH_3$)[6] and a vinyl species ($-CH=CH_2$)[2]. A comparison of these models with the observed spectrum will now be undertaken. Currently the best method for analyzing vibrational spectra of adsorbed species is by comparison with model compounds. The model proposed by Ibach for ethylidene is Cl_2CH-CH_3.[8] We have recently compared the ELS spectra of the surface complex with the infrared spectra of both $Co_3(C\text{-}CH_3)(CO)_9$ and $Br_3C\text{-}CH_3$.[6] No model compounds have been presented for the vinyl species.

Table I shows a comparison of the observed vibrational frequencies of the various suggested surface species with those of the model compounds. It is clear that the ethylidyne species shows the best agreement. Not only do the number of vibrational modes match, but their frequencies are quite close as well. Problems occur with the other two models: for the case of ethylidene, at least one mode is missing. More importantly, for a species oriented at an angle of about 20° to the surface normal[8] there should be a strong interaction between the lone hydrogen and the nearest platinum atom (see Figure 2b). Such a weakening of the C-H bond has been clearly seen for C_2H_4 chemisorbed on Ni(111)[24], but is not visible here. Demuth assigns the 900 cm^{-1} peak to a C=C double bond stretch in a vinyl species[2], but this is far too low in energy for this type of vibration (typical values are between 1500 and 1700 cm^{-1})[25]. Also, a C-H stretch at 2900-3000 cm^{-1} is not representative of an olefinic species[25].

A question arises as to which of the above modes should be "ELS active."[26] Sokcevic <u>et al.</u> have shown that the "perpendicular dipole selection rule," which should rigorously hold for infrared spectroscopy, does not necessarily apply to high resolution ELS[27]. In the IR the photon wavelengths are such that $\lambda >> z_o$ where z_o is the height of the oscillating dipole above the surface. Therefore, both the molecule and its "image" interact with the incident radiation together, giving cancellation of all parallel vibrations. However, this is not the case for

ELS since the incident electrons have wavelengths on the order of angstroms. Furthermore the cross section for the excitation of parallel vibrations is a strong function of z_o and in the above models z_o is quite large for modes which involve primarily hydrogen. The results of Sokcevic et al.[27] would suggest that it is for this reason that the methyl rocking (1130 cm^{-1}), the antisymmetric methyl deformation (1420 cm^{-1}) and the antisymmetric methyl stretching (3025-3105 cm^{-1}) modes in ethylidyne are observed. This apparent breakdown in the surface selection rule also implies that more modes should be visible for both ethylidene and the vinyl species.

Further evidence for the ethylidyne group comes from a study of the deuterated species. This is shown in Table II. Again, the agreement between the observed vibrational frequencies and those found in the model compounds is quite good. A question that should also be answered at this time is why the ELS spectrum of "stable C_2H_4" shows two intense features while that of C_2D_4 displays only one. The answer to this comes from vibrational mode mixing. The extent of this mode mixing can only be determined from a normal coordinate analysis. Such analyses have been carried out for the model compounds[22,23], and they do show extensive mode mixing upon deuteration. Therefore this phenomenon should also be present on the surface.

Definitive interpretation of high resolution ELS spectra is quite difficult at this time since the theory is not well-established. Originally, long-range dipole interactions between the incident electrons and the vibrating adsorbate molecules were thought to account for all of the observed modes[28]. Recent results have indicated that possible negative ion resonances and/or short-range interactions are present[29].

6. Analogies with Organometallic Chemistry

A natural extension of the discussion of two (a metastable and a stable) surface species is the development of a mechanism for this conversion. Here again a study of related organometallic compounds is of some use. Acetylene reacts with $H_2Os_3(CO)_{10}$ (I)[30] under very mild conditions to give $HOs_3(CHCH_2)(CO)_{10}$, (II)[31] and upon heating yields $H_2Os_3(C{=}CH_2)(CO)_9$ (III)[31]. We have recently proposed vinylidene ($>C{=}CH_2$) as an intermediate in the formation of ethylidyne[6]. This species has also been proposed by Demuth on the basis of some UPS and ELS results[2]. Ethylene reacts with $Os_3(CO)_{12}$ to give the identical compound[18]. Furthermore, (II) has been proposed as a very short lived intermediate for this transformation as well[31]. Finally, the more stable ethylidyne complex, $H_3Os_3(C\text{-}CH_3)(CO)_9$ (IV), can be formed by bubbling H_2 through a refluxing n-heptane solution of (III)[18]. This is analogous to the surface phase transformation undergone by C_2H_2 upon heating and the addition of hydrogen. The surface mechanism can then be written as follows:

$$CH{\equiv}CH \xrightarrow{Pt(111)} (HC{\equiv}CH)^* \longrightarrow {}^*C{=}CH_2 \xrightarrow[\substack{\text{or}\\ H^*}]{H} {}^*C\text{-}CH_3$$

$$H_2C{=}CH_2 \xrightarrow{Pt(111)} (H_2C{=}CH_2)^* \longrightarrow {}^*CH{=}CH_2 + H^* \longrightarrow {}^*C{=}CH_2 + 2H^* \longrightarrow {}^*C\text{-}CH_3 + H^*$$

where * indicates adsorbed species. This is only one possible reaction scheme and the lifetimes of the intermediates are not known, but it does seem likely that vinylidene is an intermediate in the formation of ethylidyne on Pt(111) since it must be present in the cluster analogs. Strongly bound olefinic species such as $Os_3(HC{=}CH)(CO)_{10}$ cannot be hydrogenated to (IV) nor can they be converted to (III)[32].

The structural parameters of the surface ethylidyne species and several trinuclear organometallic compounds [19,20] are also quite similar. A table of these values has been published previously[6]. Bond lengths agree to better than 0.05Å after correcting for metal-metal bond lengths. Furthermore, the infrared data of $Co_3(C{-}CH_3)(CO)_9$[11] and the high resolution ELS spectra of the proposed ethylidyne surface species agree remarkably well.

Finally, it has been shown that the metal triangle in $Co_3(C{-}CH_3)(CO)_9$ is electron withdrawing with respect to the apical substituent[33] and this is precisely what is seen on the surface: upon adsorption of either acetylene or ethylene, the work function of Pt(111) decreases by 1.5eV[34]. A delocalized carbyne type bonding between the lower carbon atom and the three cobalt atoms has been proposed for the cluster analog[33]. This is consistent with the short metal-carbon bond distance measured here.

7. Summary and Conclusions

We have found consistent evidence from LEED, high resolution ELS and thermal desorption spectroscopy to indicate the formation of a stable ethylidyne species on the Pt(111) surface. A structure with the C-C axis approximately normal to the surface and a C-C bond length of

1.50Å±0.05Å has been determined by the LEED intensity analysis of Section 4. This is characteristic of a carbon-carbon single bond and is consistent with a C-C stretching vibration at 900 cm^{-1} [25] found in the ELS spectrum of the stable species. The presence of methyl stretching (2900-3100 cm^{-1}), deformation (1360, 1420 cm^{-1}) and rocking (1130 cm^{-1}) modes confirms the existence of a saturated carbon species. The TDS experiments of Demuth[2] indicating a surface stoichiometry of C_2H_3 clearly rule out the presence of additional hydrogen. The LEED analysis further shows a rather short Pt-C bond length of 2.00Å±0.05Å, suggestive of strong carbyne type bonding.

It is interesting that the ethylidyne species has only recently been proposed to form on metal surfaces[6] in spite of the large number of classical studies of ethylene and acetylene chemisorption on metal catalysts. Nevertheless, this species has been known to organometallic chemists for a number of years. We have found that both the LEED structure and the vibrational modes of the surface species compare very favorably with the related organometallic compounds containing ethylidyne[11,19,20]. Certainly many more definitive studies, employing a combination of surface analysis techniques, are needed to further explore the surface-cluster analogy.

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TABLE 1

Vibrational Assignments for "Stable Species" on the Pt(111) Surface

(all vibrational frequencies are in cm^{-1})

Surface Species[8]	CH_3CHCl_2[22]	Ethylidene[8]	$CH_3CCo_3(CO)_9$[11]	CH_3-CBr_3[23]	Ethylidyne	Vinyl Species[2]
3025-3105 W	3015 M	CH stretch	2924 M	2993 M	CH_3 stretch (a)	[CH and/or CH_2 stretch]*
---	3001 W	CH_3 stretch (a)				
2900-2940 M	2946 M	CH_3 stretch (s)	2882 M	2938 M	CH_3 stretch (s)	CH & CH_2 stretch
1420 M	1446 M	CH_3 deform (a)	1420 M	1432 M	CH_3 deform (a)	[CH_2 scission]
1350-1360 S	1381 M	CH_3 deform (s)	1359 M	1373 M	CH_3 deform (s)	CH_2 scission or wag
1130 S	1280 M	CH bend	1161 M	1064 S	CH_3 rock	CH bend
---	1091 W	CH_3 rock				
900 M	982 M	C-C stretch	1006 S	1045 M	C-C stretch	C-C 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

* The frequencies enclosed in brackets are proposed to correspond to CH or CH_2 species present on the surface[2].

** Can equally well be assigned to CH and CH_2 out of plane deformation modes[2].

TABLE 2

Vibrational Assignments for "Stable C_2D_4" on the Pt(111) Surface*

(all vibrational frequencies are in cm^{-1})

Surface Species[8]	CD_3-$CDCl_2$[22]	Ethylidene (d_4)[8]	CD_3-CBr_3[23]	Ethylidyne (d_3)
broad	2165 W	CD stretch		
unresolved	2248 M	CD_3 stretch (a)	2241	CD_3 stretch (a)
band	2125 W	CD_3 stretch (s)	2116	CD_3 stretch (s)
not resolved	1047 M	CD_3 deform (a)	953 W	C-C stretch
1010 W	1014 M	CD_3 deform (s)	1038 W	CD_3 deform (a)
850 W	775 M	CD bend	883 M	CD_3 rock
---	932	CD_3 rock		
1150 S	1151 S	CC stretch	1110 W	CD_3 deform (s)
430 M	600 M	C-Pt stretch	388 S	C-Pt stretch

* An assignment for the deuterated vinyl species was not presented in Ref. 2.

Figure Captions

Figure 1. Schematic diagram of an f.c.c. (111) surface indicating various high-symmetry adsorption sites: atop (A), bridge (B), threefold (T_b, T_c). The dashed line defines the surface unit cell.

Figure 2. Models for the stable chemisorption state discussed in the text: (a) ethylidyne, (b) ethylidene, (c) vinylidene and (d) distorted acetylene.

Figure 3. Comparison of calculated LEED I-V profiles for the $\geqslant C-CH_3$ species on Pt(111) with the C-C axis oriented normal to the surface at the T_c site (see Figure 1 and Figure 2a). The experimental data is for the stable species formed from C_2H_2 or C_2H_4 chemisorption[4]. The calculations are made with (solid line) and without (dotted line) electron scattering by the hydrogen atoms. The curves are labeled with the value of the C-C bond length. The Pt-C bond length is fixed at 2.00Å.

Figure 4. (a) Local bonding models for a species oriented with the C-C axis normal to the surface (see also Figure 1). (b) Comparison of theory and experiment for LEED I-V profiles as a function of site geometry for the stable species (C-C= 1.50Å, Pt-C=2.00Å).

Figure 5. Comparison of theory and experiment for the optimum ethylidyne model of the stable surface species (in (a) C-C=1.50Å, Pt-C=2.00Å and in (b) C-C=1.44Å, Pt-C=2.00Å) for several fractional-order beam I-V profiles.

Figure 6. Dependence of calculated I-V profiles on (a) C-C bond length and (b) Pt-C bond length and comparison to experiment for the stable surface species. The results are shown for incidence angle $\theta=8^{\circ}$ for the $(\frac{1}{2}\ 0)$ beam. The C-C axis is oriented normal to the surface at the T_c site (in (a) Pt-C=2.00Å and in (b) C-C=1.50Å).

Figure 7. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(\frac{1}{2}\ \bar{\frac{1}{2}})$ beam, $\theta=8^{\circ}$.

Figure 8. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(0\ \bar{\frac{1}{2}})$ beam, $\theta=8^{\circ}$.

Figure 9. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(\bar{\frac{1}{2}}\ \bar{\frac{1}{2}})$ beam, $\theta=8^{\circ}$.

Figure 10. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(\bar{1}\ 0)$ beam, $\theta=8^{\circ}$.

Figure 11. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(\frac{1}{2}\ 0)$ beam, $\theta=4^{\circ}$. In (a) Pt-C=2.00Å, in (b) C-C=1.44Å.

Figure 12. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(\frac{1}{2}\ \bar{\frac{1}{2}})$ beam, $\theta=4^{\circ}$. In (a) Pt-C=2.00Å, in (b) C-C=1.54Å.

Figure 13. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 6 for the $(0\ \bar{\tfrac{1}{2}})$ beam, $\theta=4^{\circ}$. In (a) Pt-C=2.00Å, in (b) C-C=1.54Å.

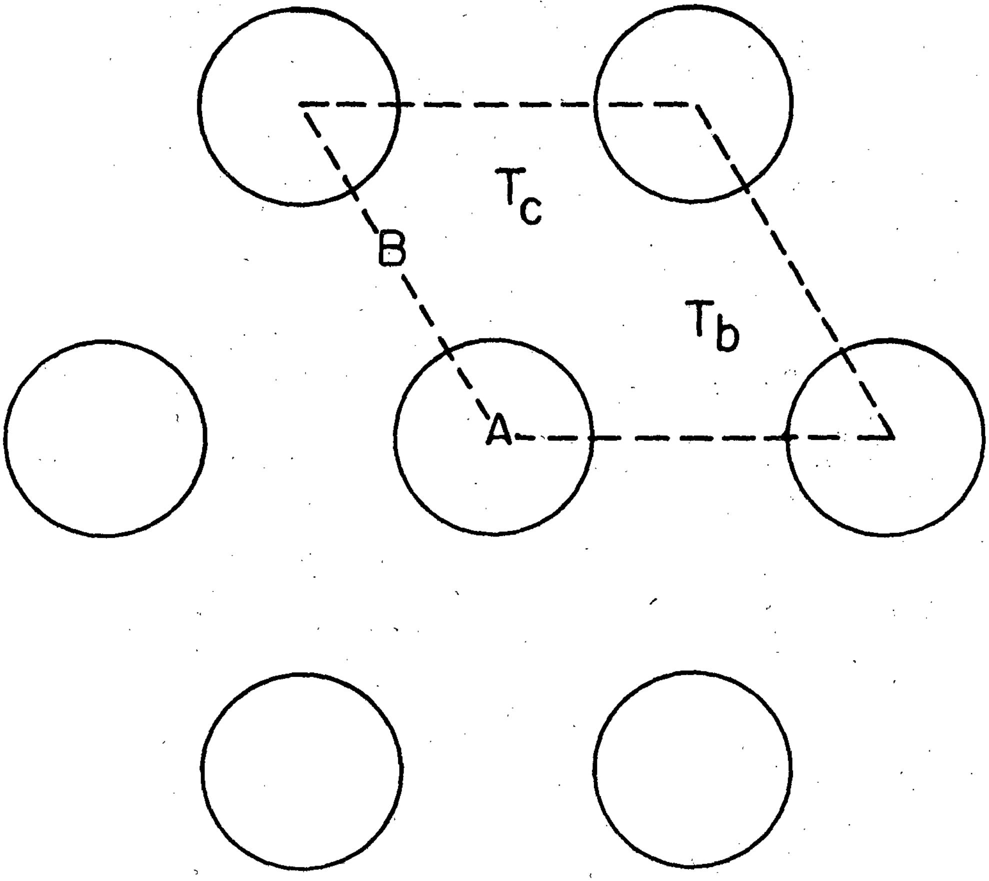
Figure 14. Optimum structure for the ethylidyne species on the Pt(111) surface indicated by the LEED analysis. The C-C and Pt-C bond lengths have uncertainties of ±0.05Å. The H atoms are not located in the LEED analysis.

Figure 15. Dependence of calculated I-V profiles on the tilt angle (θ_t) of the C-C axis from the surface normal and comparison to experiment for the stable surface species. The lower carbon is coordinated at the threefold site T_c with Pt-C= 2.00Å. Numbers in parentheses refer to the projection of the C-C bond length on the surface normal. The results shown are for the $(\tfrac{1}{2}\ 0)$ beam at incidence angle $\theta=8^{\circ}$.

Figure 16. Comparison of calculated and experimental I-V profiles for the conditions given in Figure 15 for the $(\tfrac{1}{2}\ \bar{\tfrac{1}{2}})$ beam, $\theta=8^{\circ}$.

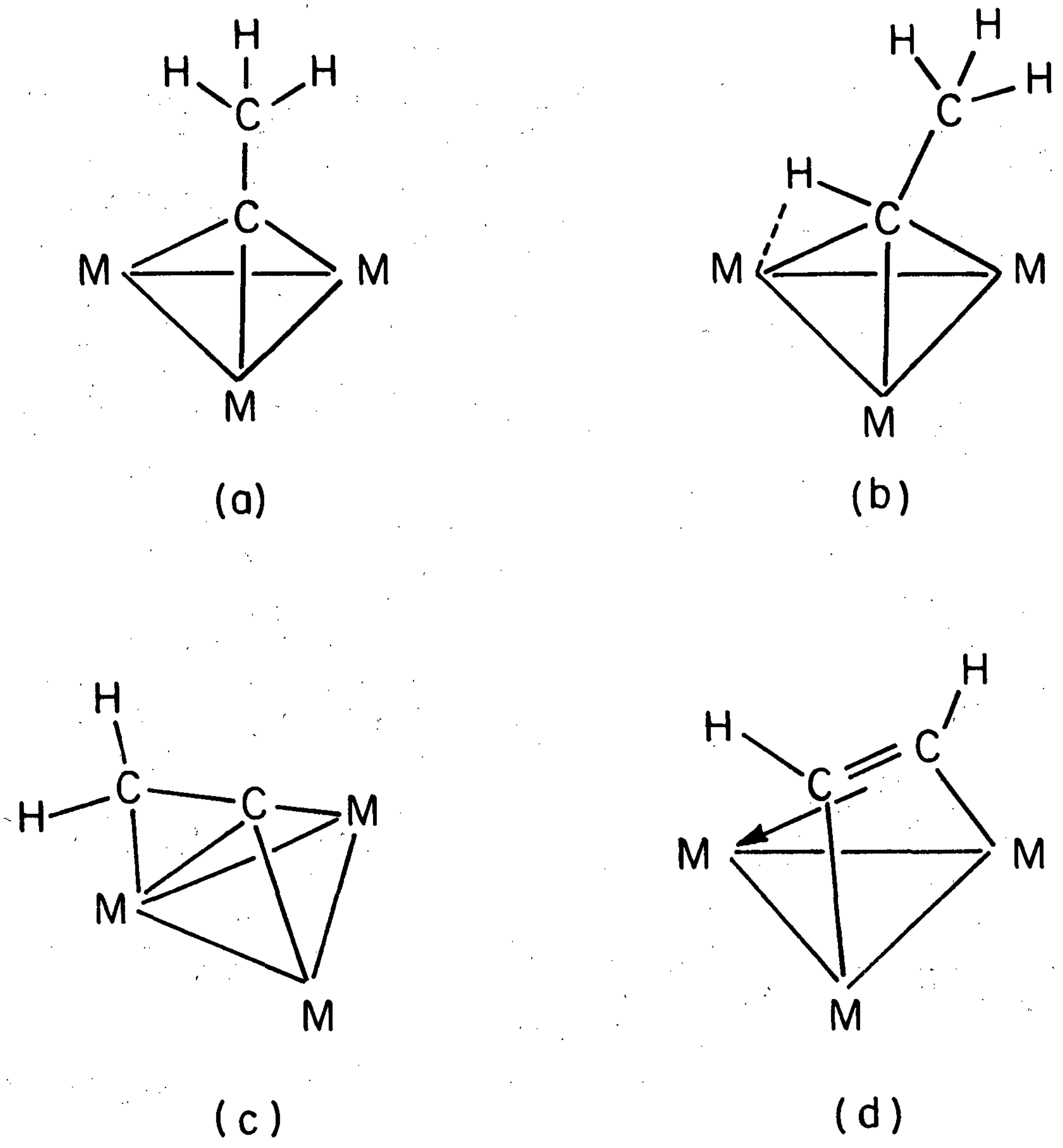
Figure 17. Schematic diagram showing the relationship of the optimum structures found in the LEED analysis for models having the C-C axis normal and parallel to the surface. Each structure has the midpoint of the C-C axis at the threefold site (T_c) at an elevation of 1.95Å from the Pt surface layer.

Figure 18. Comparison of calculated I-V profiles for the two optimum structures shown in Figure 17 corresponding to $>C-CH_3$ and parallel-bonded C_2H_2 at the threefold site T_c. The comparison is made to experimental data for the stable surface species on high-index diffraction beams measured at incident beam angle $\theta=30^{\circ}$.



XBL 786-5142

Figure 1



(a)

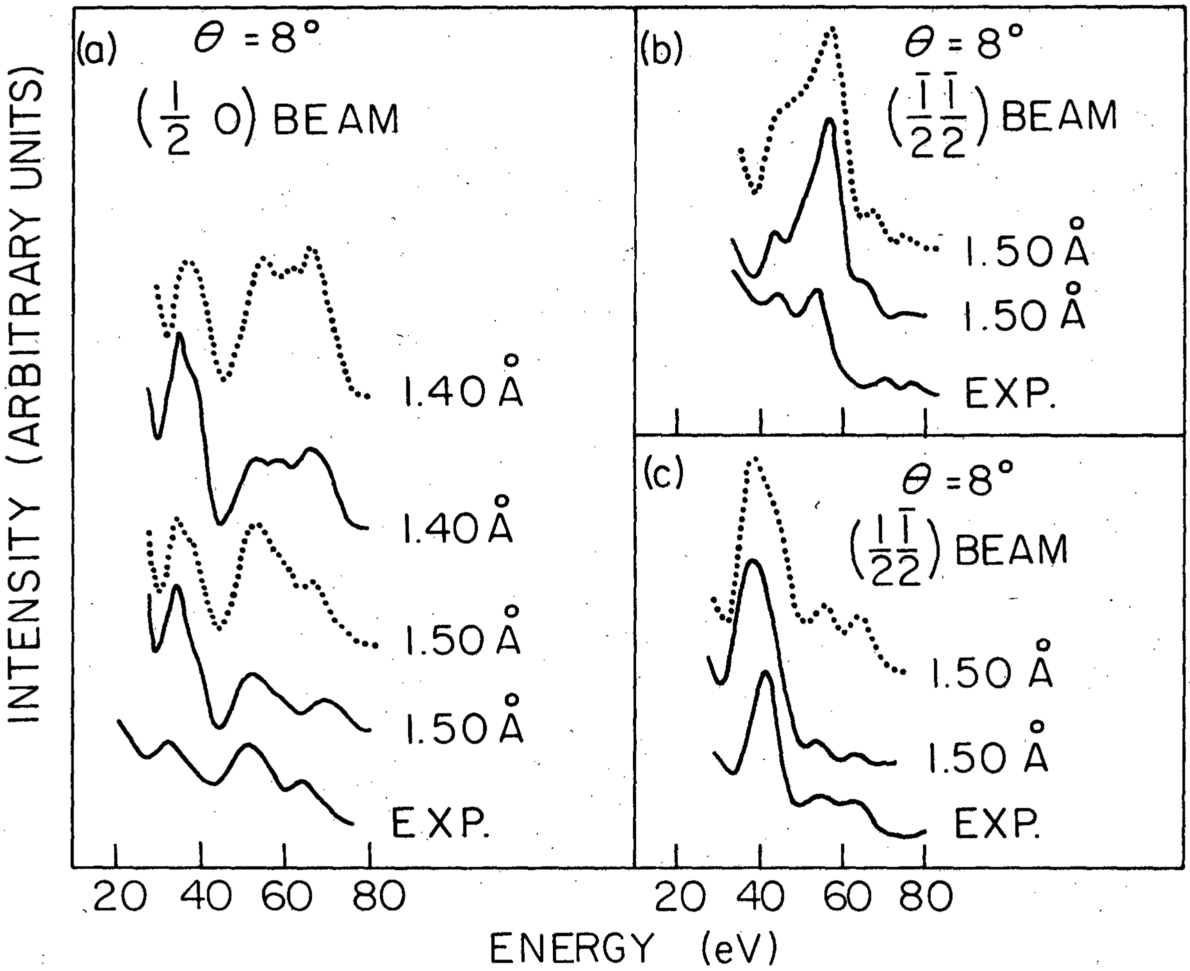
(b)

(c)

(d)

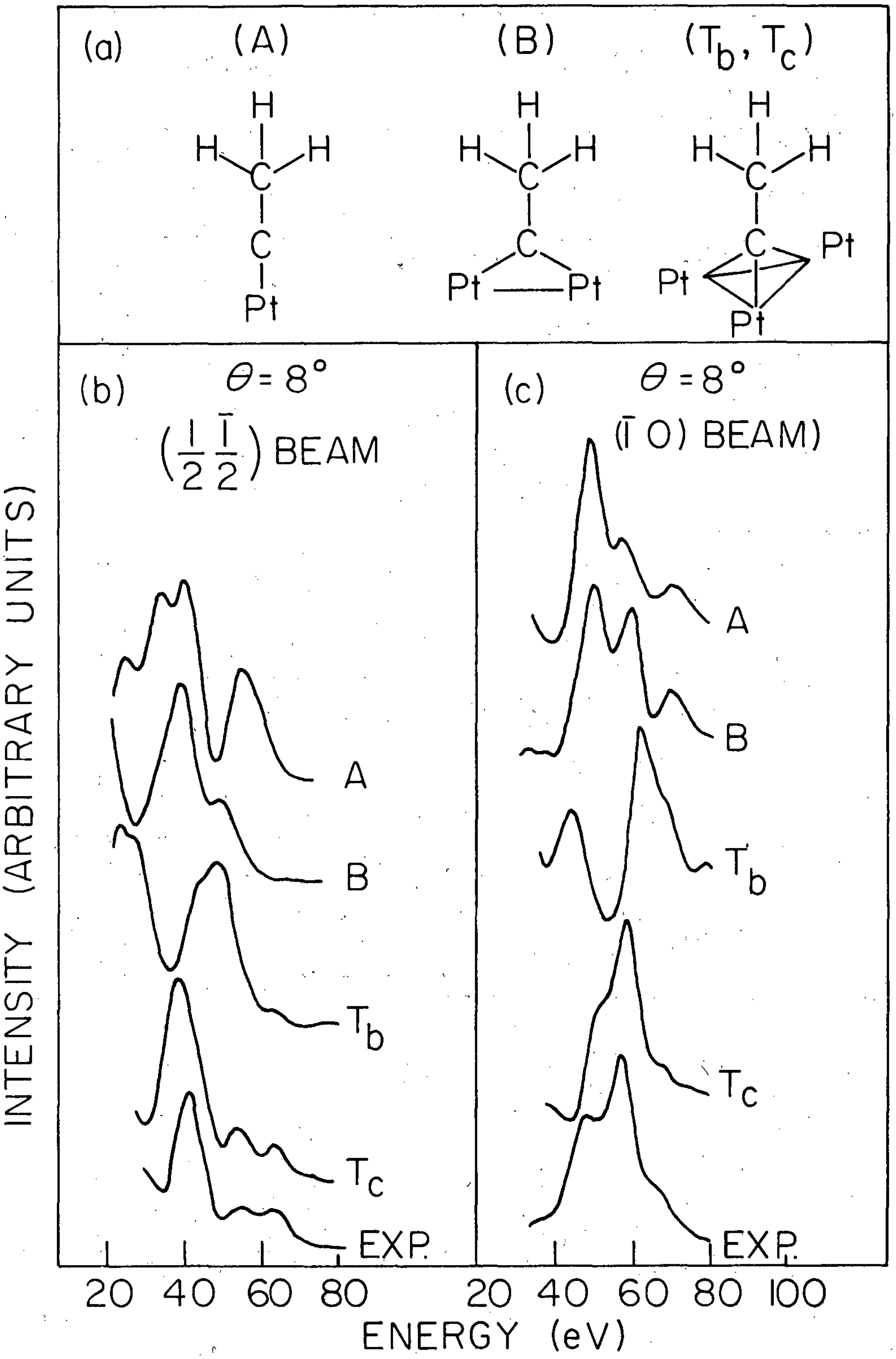
XBL 786-5141

Figure 2



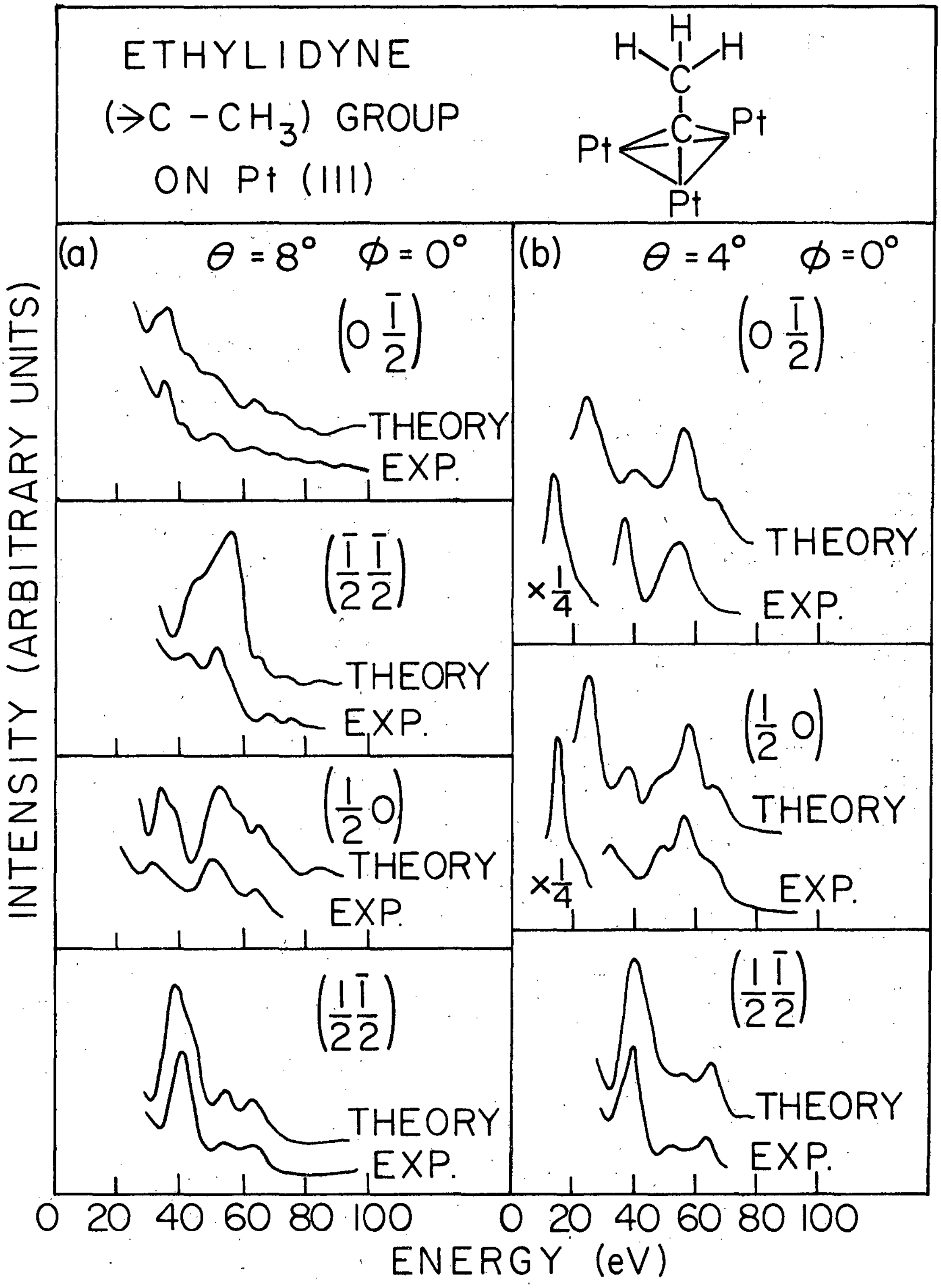
XBL 786-5152

Figure 3



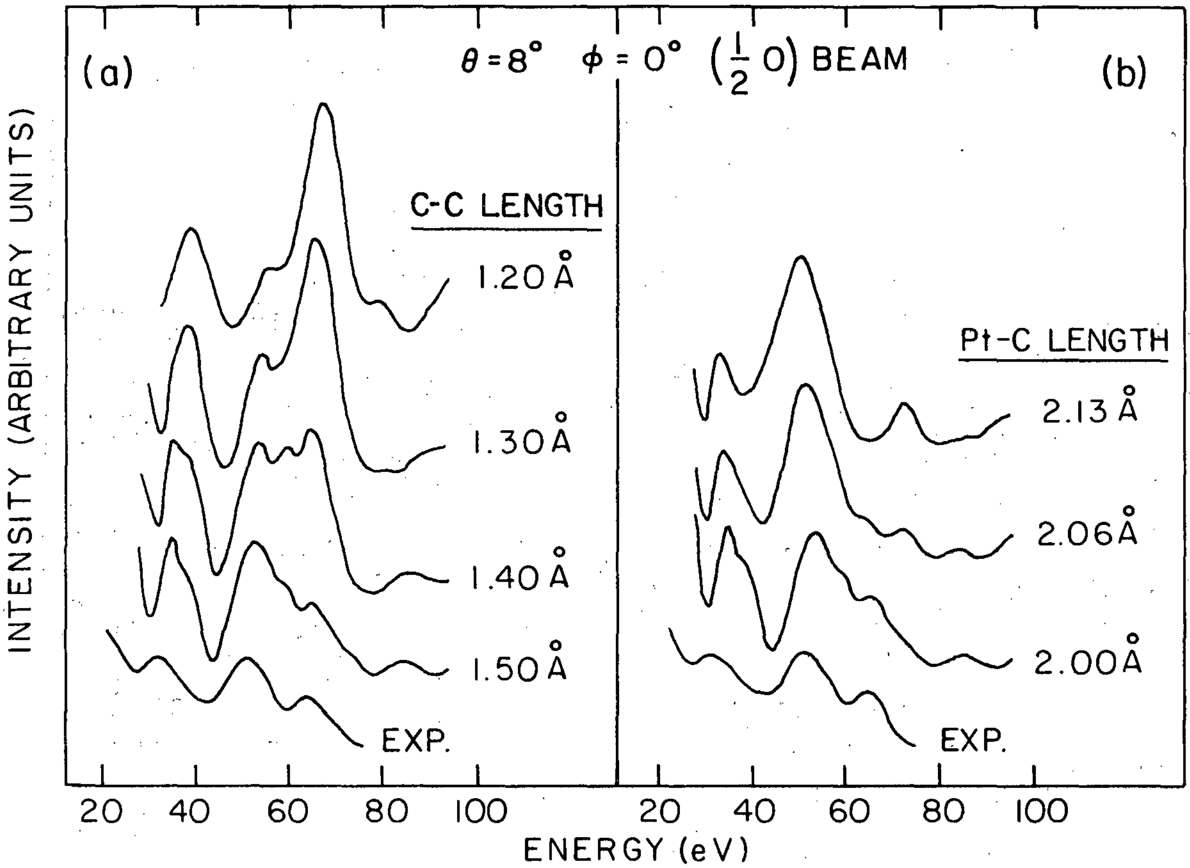
XBL 786-5151

Figure 4



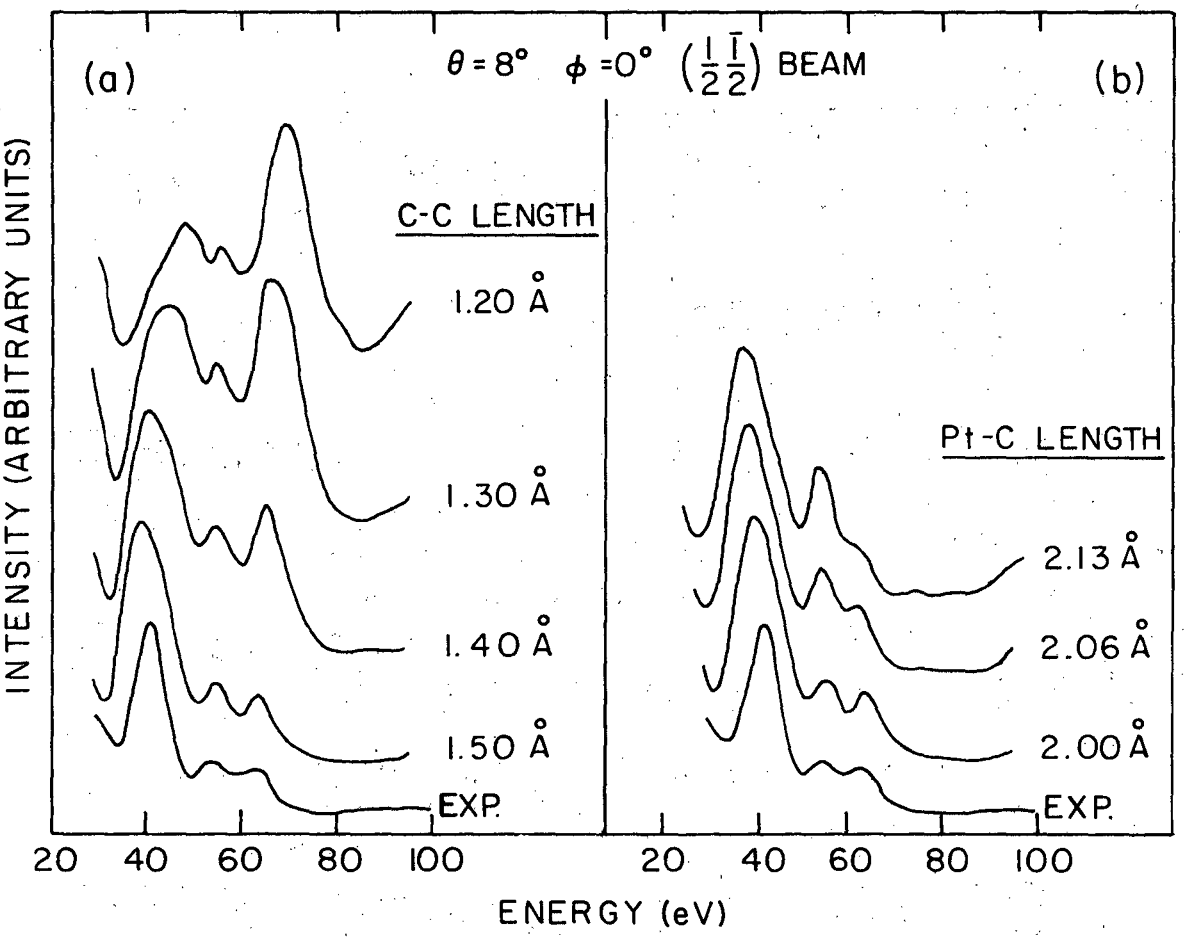
XBL786-5156

Figure 5



XBL 786-5148

Figure 6



XBL 786-5150

Figure 7

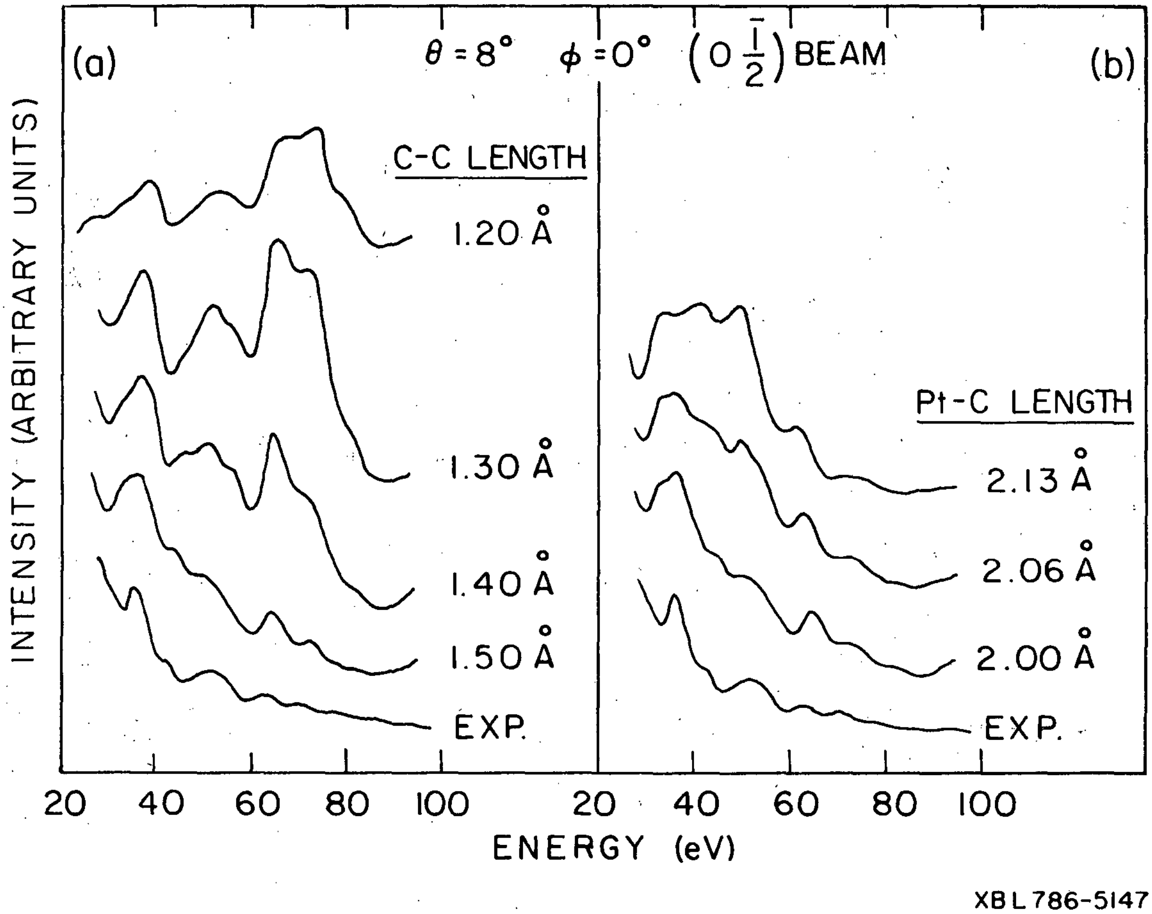
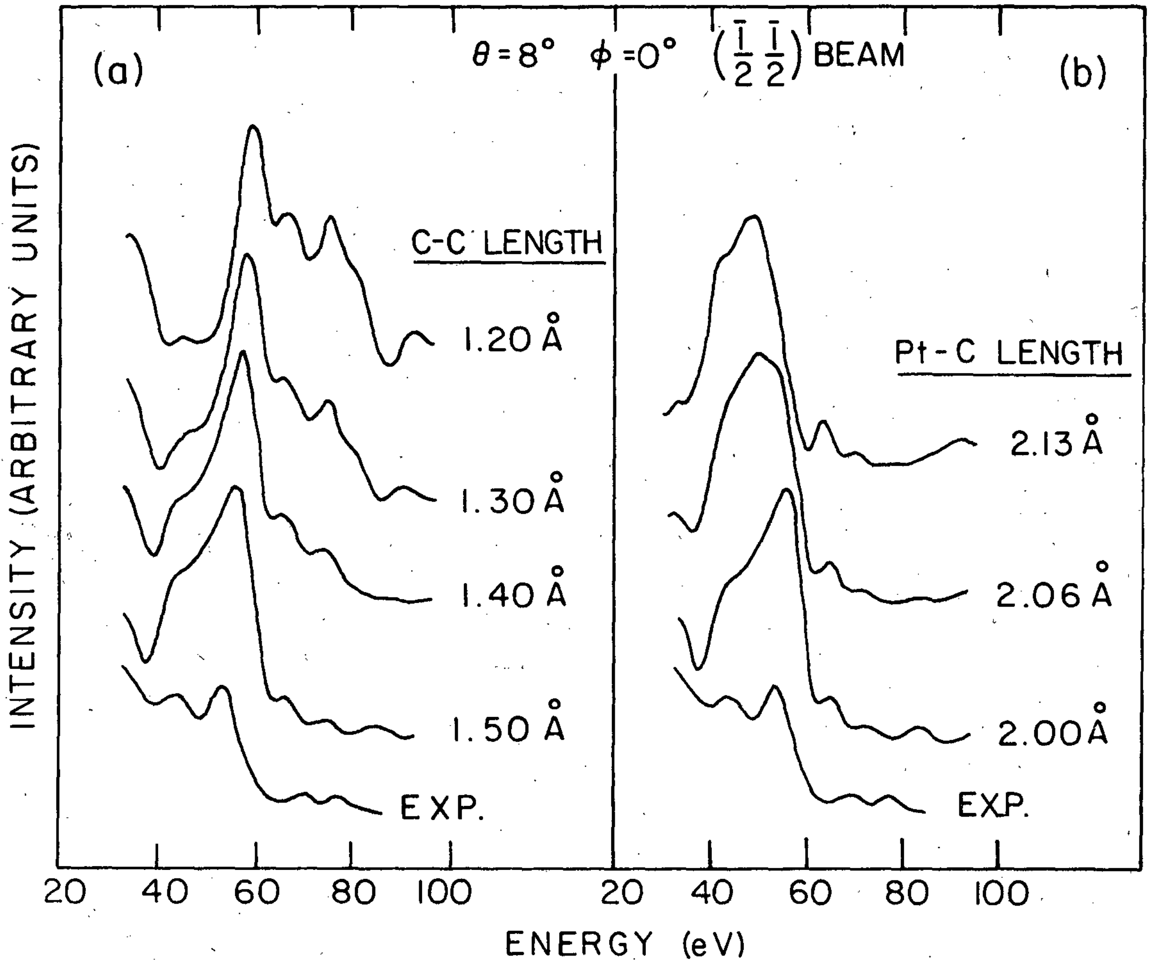
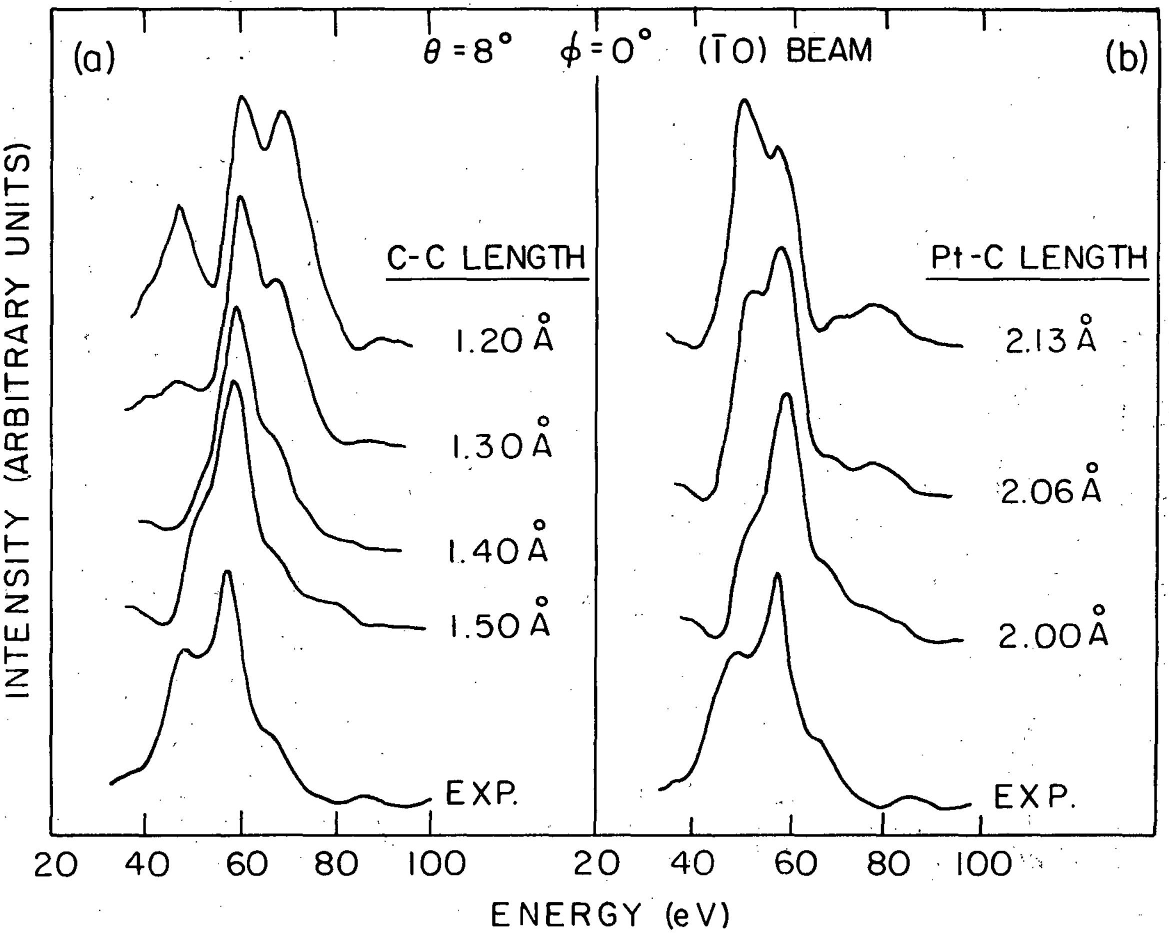

(a)
θ = 8° φ = 0° (0 $\bar{1}$/2) BEAM
(b)
INTENSITY (ARBITRARY UNITS)
C-C LENGTH
1.20 Å
1.30 Å
1.40 Å
1.50 Å
EXP.
Pt-C LENGTH
2.13 Å
2.06 Å
2.00 Å
EXP.
20
40
60
80
100
20
40
60
80
100
ENERGY (eV)
XBL 786-5147

Figure 8



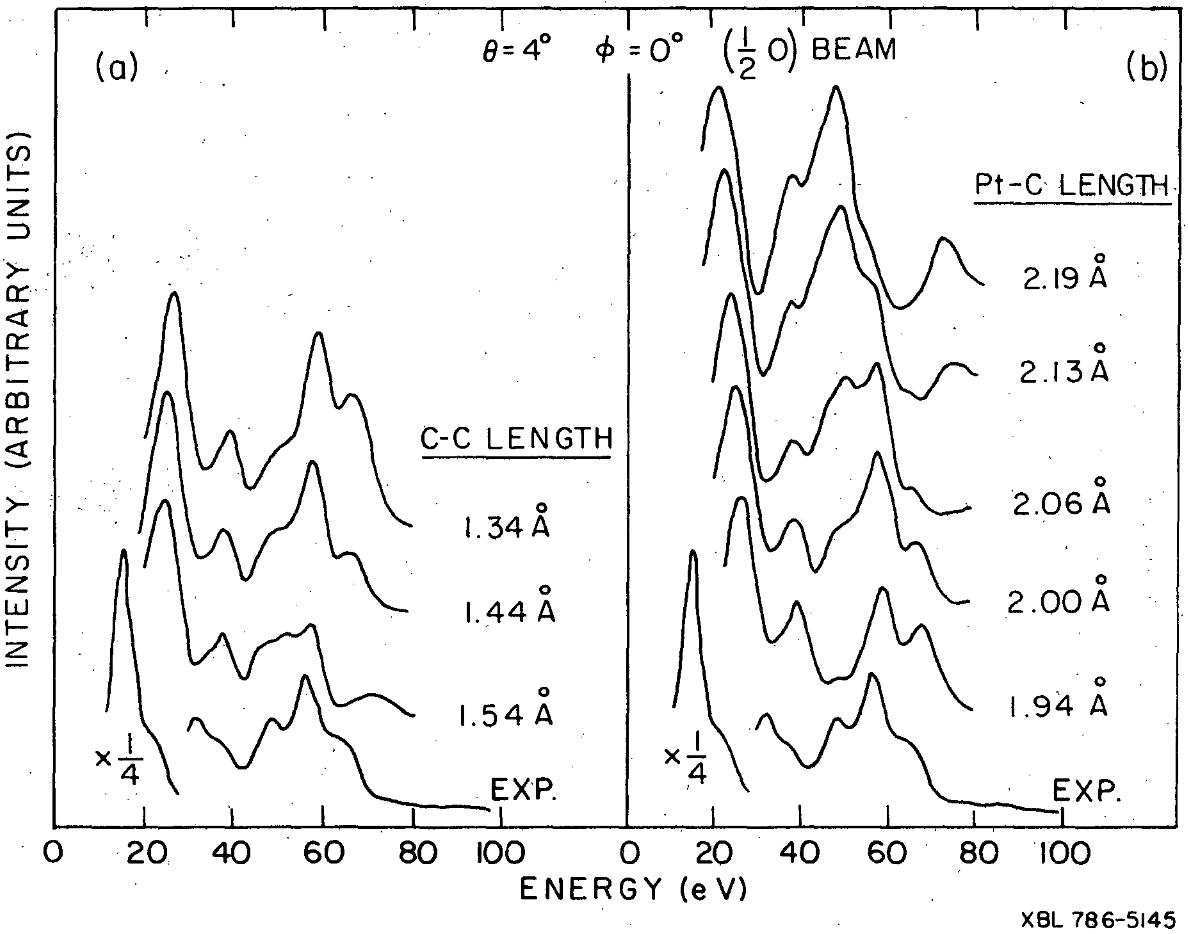
XBL786-5149

Figure 9



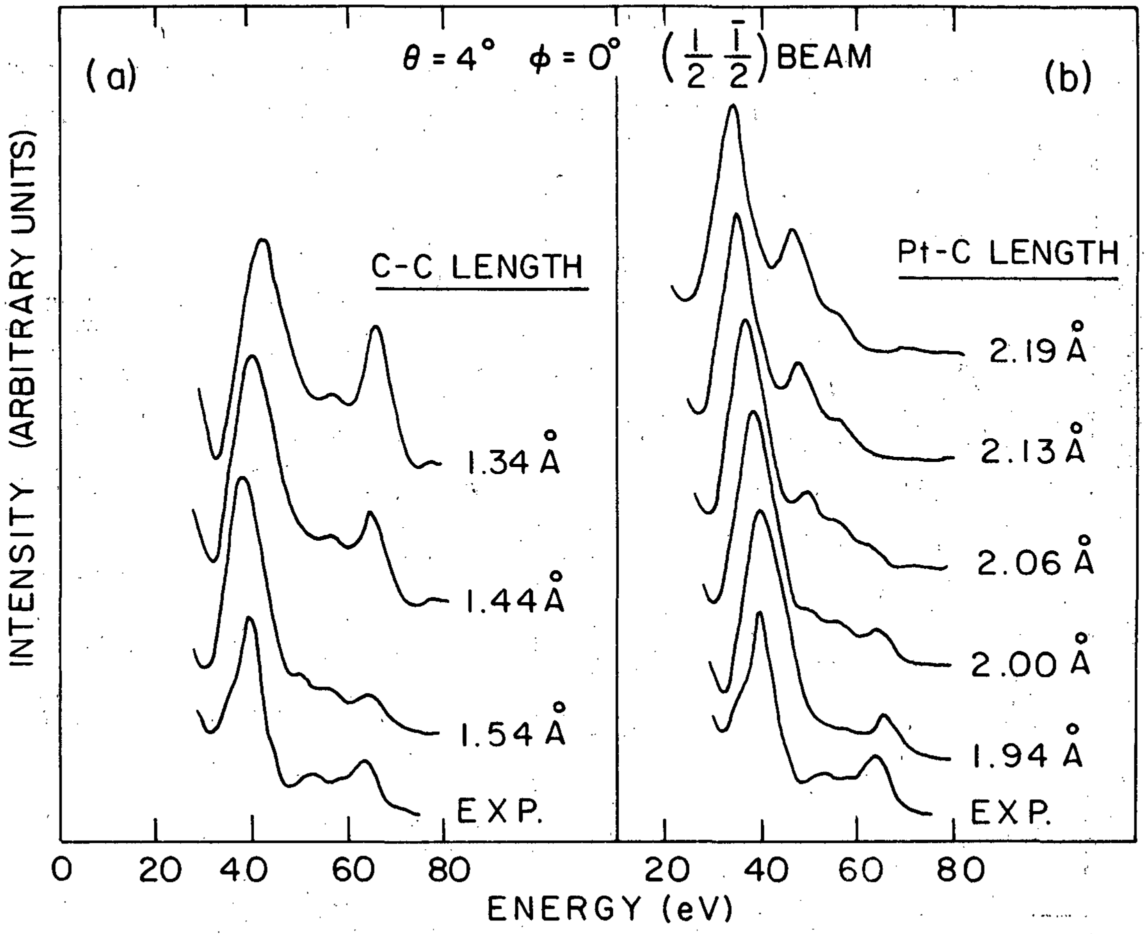
XBL 786-5146

Figure 10



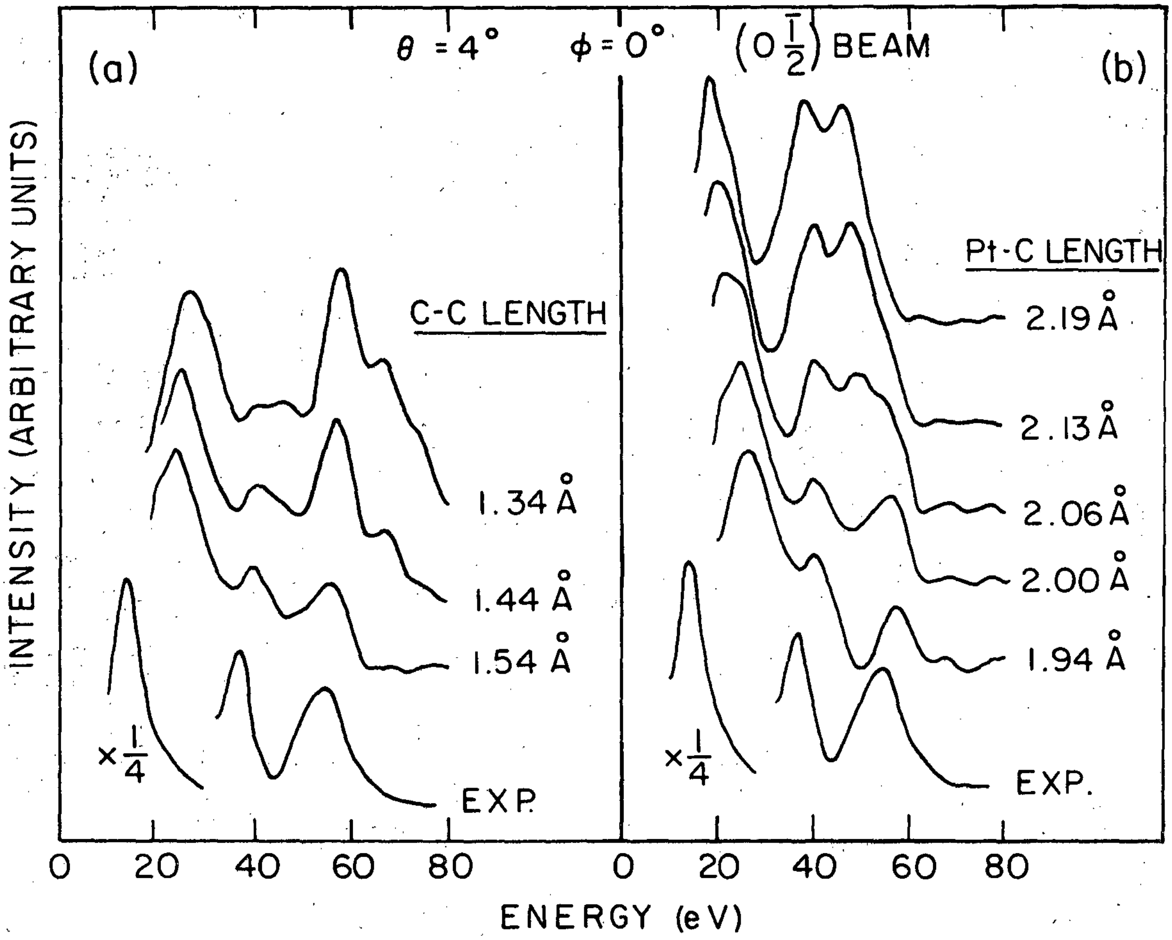
(a)
θ=4°
φ=0°
(½ 0) BEAM
(b)
INTENSITY (ARBITRARY UNITS)
C-C LENGTH
1.34 Å
1.44 Å
1.54 Å
×¼
EXP.
Pt-C LENGTH
2.19 Å
2.13 Å
2.06 Å
2.00 Å
1.94 Å
×¼
EXP.
0
20
40
60
80
100
0
20
40
60
80
100
ENERGY (e V)
XBL 786-5145

Figure 11



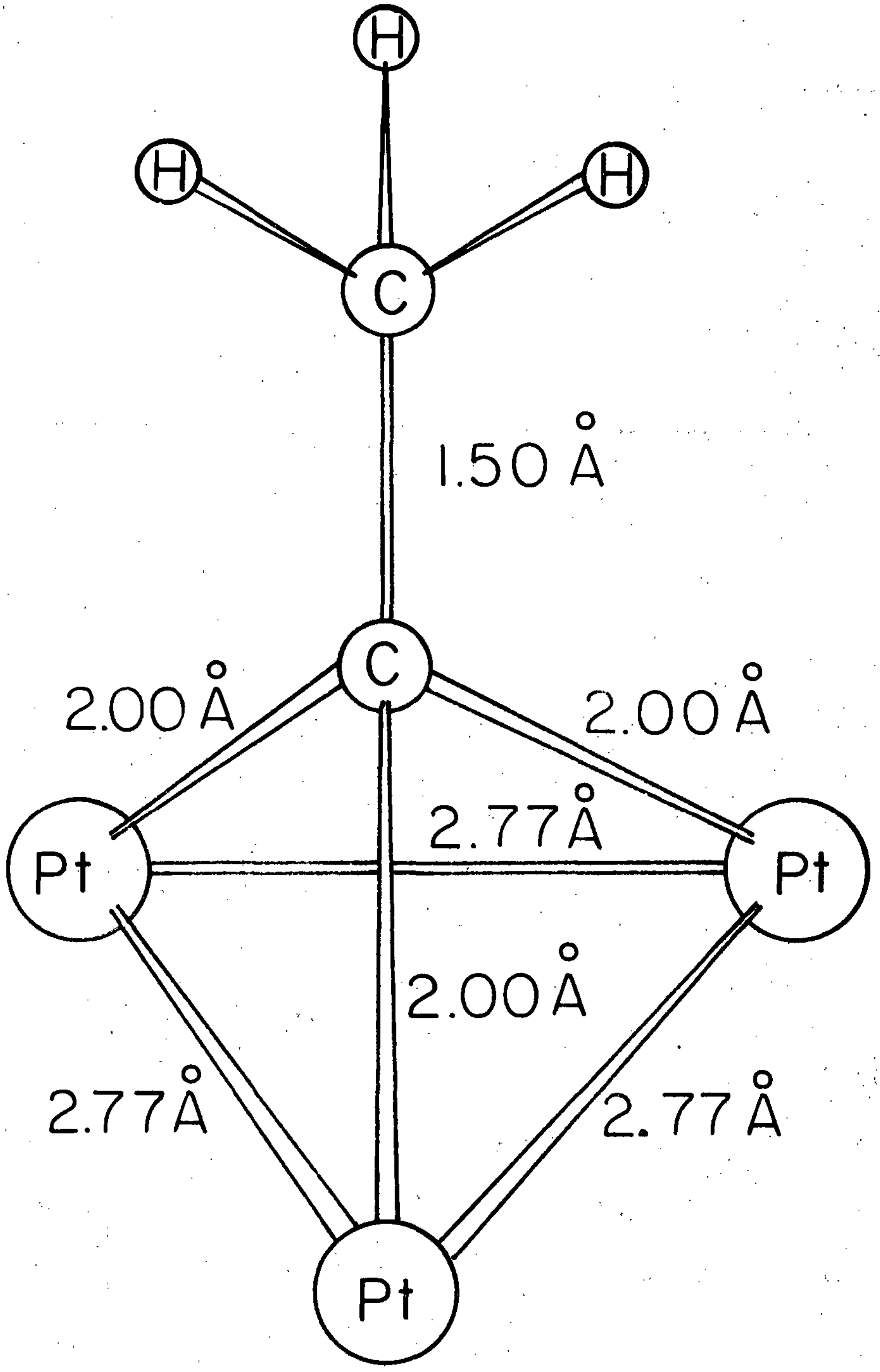
XBL 786-5143

Figure 12



XBL 786-5144

Figure 13



XBL 7712-6591

Figure 14

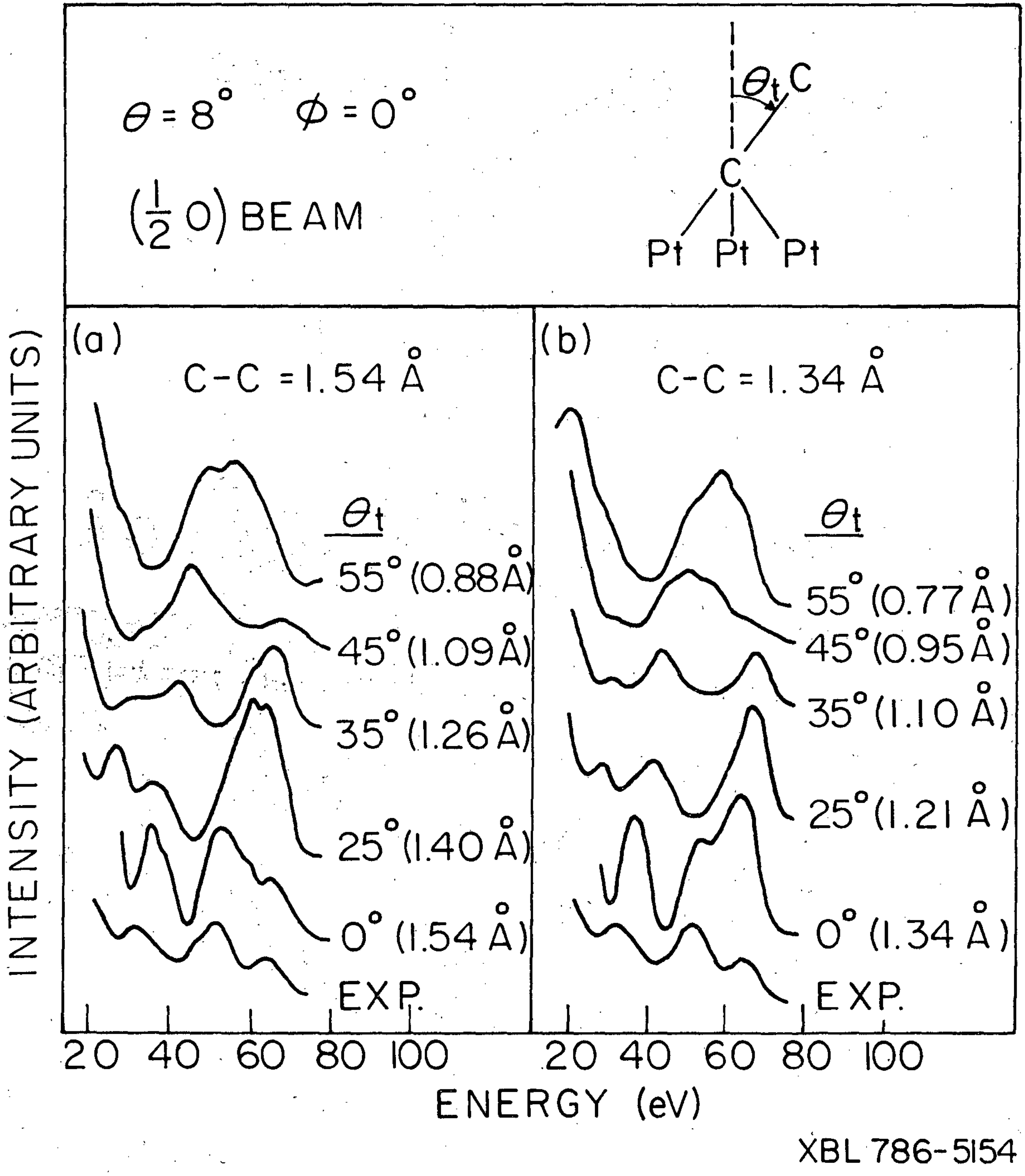
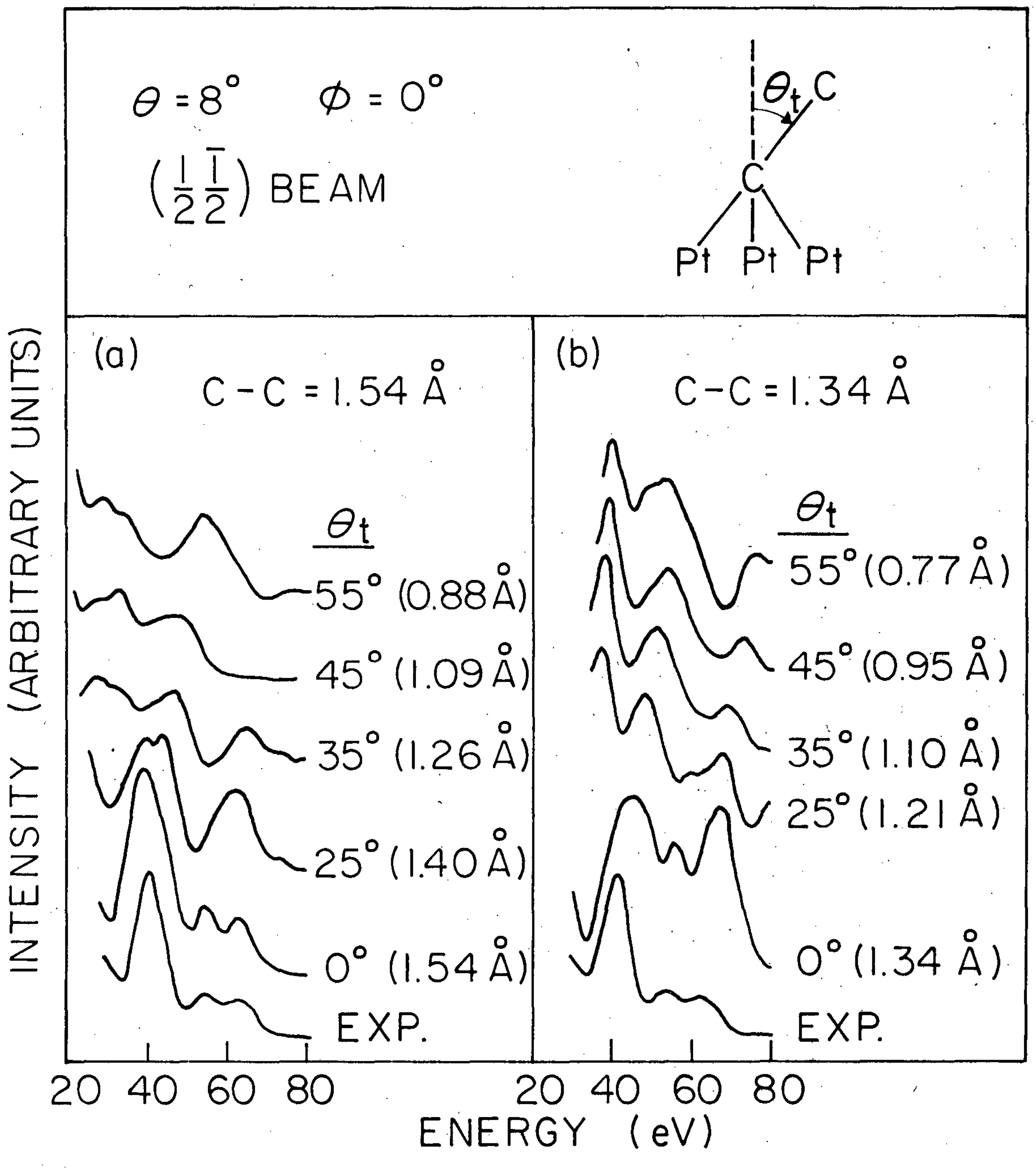

θ = 8°   φ = 0°
(½ 0) BEAM
θt
C
C
Pt Pt Pt
(a)
C-C = 1.54 Å
θt
55° (0.88 Å)
45° (1.09 Å)
35° (1.26 Å)
25° (1.40 Å)
0° (1.54 Å)
EXP.
(b)
C-C = 1.34 Å
θt
55° (0.77 Å)
45° (0.95 Å)
35° (1.10 Å)
25° (1.21 Å)
0° (1.34 Å)
EXP.
INTENSITY (ARBITRARY UNITS)
20 40 60 80 100
20 40 60 80 100
ENERGY (eV)
XBL 786-5154

Figure 15



XBL 786-5153

Figure 16

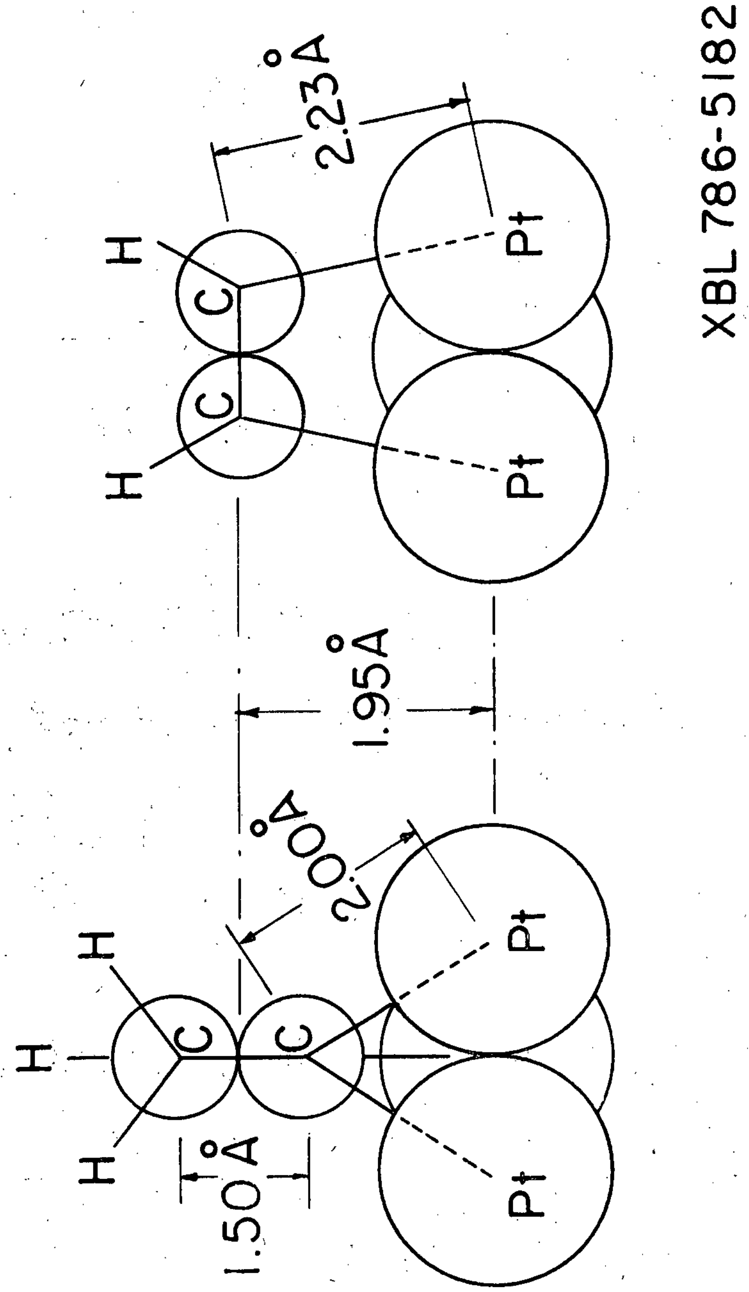


Figure 17

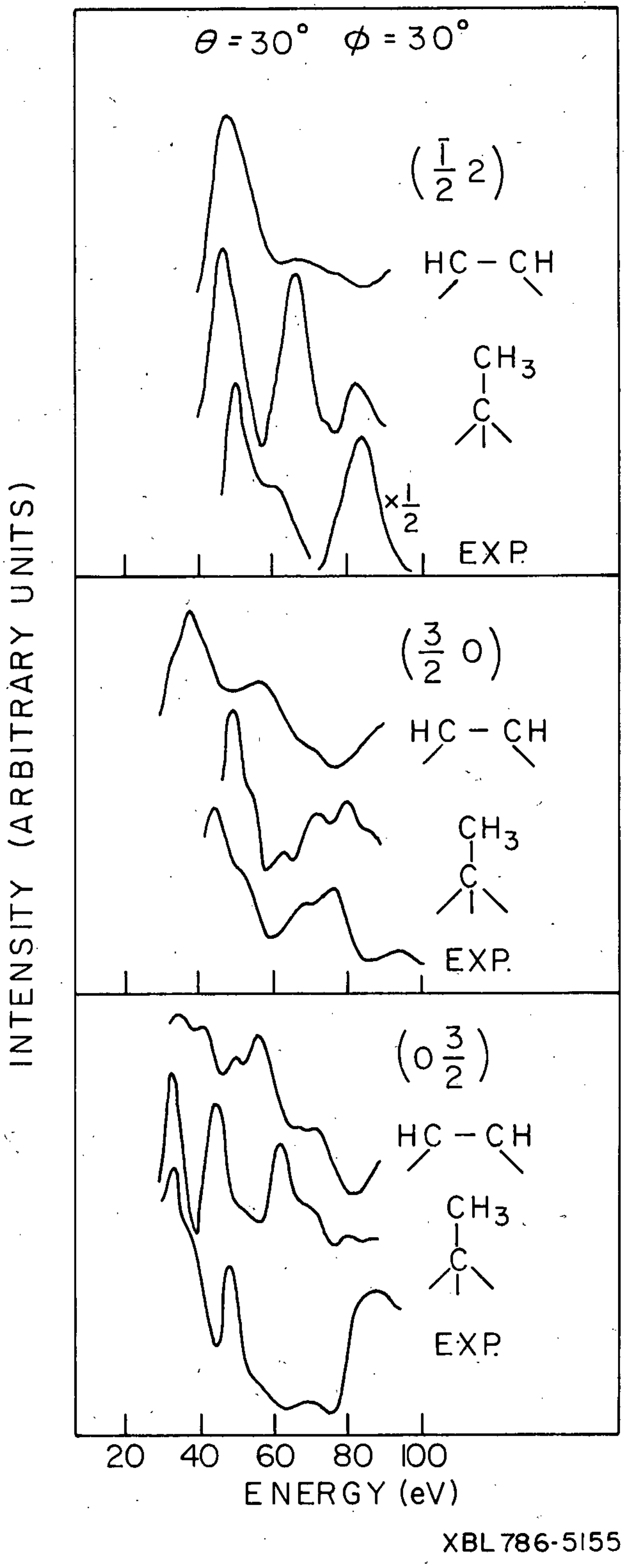

θ = 30° φ = 30°
$(\frac{\bar{1}}{2}\,2)$
HC — CH
CH3
C
×1/2
EXP.
$(\frac{3}{2}\,0)$
HC — CH
CH3
C
EXP.
$(0\,\frac{3}{2})$
HC — CH
CH3
C
EXP.
INTENSITY (ARBITRARY UNITS)
20
40
60
80
100
ENERGY (eV)
XBL 786-5155

Figure 18

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720