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THE STRUCTURE AND BONDING OF HYDROCARBONS
ADSORBED ON METAL SURFACES

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Introduction

The molecular basis of many macroscopic surface phenomena that include adhesion, lubrication, wettability, and heterogeneous catalysis of organic reactants is the structure and bonding of monolayers of adsorbed hydrocarbons. The strength and orientation of the metal-hydrocarbon bond plays a very important role in determining the reactivity and the stability of adsorbed organic molecules. In an effort to gain a better fundamental understanding of their surface chemical bonds, several methods have recently been applied to study the structure of molecules adsorbed on metal surfaces. A listing of the more commonly used surface science techniques¹⁻³ for the determination of surface structure is given in Table 1.

Over the last few years, we have examined the structure and bonding of many organic molecules, mostly alkenes and alkynes, on the various crystal faces of platinum and rhodium metals; our findings point to the rich, diverse, and very exciting chemistry that exists in hydrocarbon monolayers adsorbed on metal surfaces. To study these hydrocarbon structures, we relied on two powerful structural probes, Low Energy Electron Diffraction (LEED)¹ and High Resolution Electron Energy Loss Spectroscopy (HREELS)². Both techniques utilize the surface sensitivity of low energy electrons. These electrons are strongly damped in the crystal lattice, so the backscattered fraction that emerges from the sample should carry only surface information to a depth of about 3 atomic layers.

LEED was employed to determine the bond distances and angles of the adsorbed hydrocarbons when they ordered into an overlayer lattice.

This method, like x-ray diffraction, provides the quantitative description of the molecular structure present on a surface; and thanks to the very high elastic cross-section of low energy electron scattering (about a million times larger than for x-rays), it is sensitive to less than 10% of a monolayer of adsorbates (10^{14} molecules/cm²). The LEED analysis is described in Figure 1. The backdiffracted electron intensity is measured as a function of the electron energy; a set of intensity vs. voltage (I-V) curves for possibly 40 diffraction beams are collected for any given structure determination. These experimental curves are then compared to calculated ones that assume particular model geometries; that geometry which gives best agreement between theory and experiment is considered to be the correct one.

HREELS, though not a quantitative method, is probably the most versatile surface structural tool available today; it measures the vibrational spectrum of an adsorbed molecule. The HREEL spectrum⁴ in Figure 2 obtained for CO on Rh(111) serves as an example. The stretching frequencies of the CO bond (1870 and 1990cm^{-1}) and the metal-carbon bond (480cm^{-1}) are measured, while the CO bending vibrations that occur parallel to the surface are not observed due to the "dipole selection rule" which governs the scattering process.⁵ From this spectrum we conclude that the CO molecule stands upright with its carbon end bound to the Rh surface; in addition, the observed frequencies of the CO stretch vibration indicate that the carbon atom bonds directly to only one metal atom, i.e. in an "atop" site (1990cm^{-1}) or to two metal atoms, i.e. in a "bridge" site (1870cm^{-1}). This technique can be

employed to study either disordered or ordered monolayers and, unlike most other surface methods, can detect hydrogen.

We shall now review what has been learned about the nature of hydrocarbon bonding to the Pt and Rh metal surfaces, the interesting contrast with hydrocarbon adsorption on other metals, the impact of these studies on our understanding of catalytic reactions, and finally the future directions that this rapidly growing field is likely to take.

Bonding of Alkenes (C_nH_{2n}) to the (111) Faces of Rh and Pt

The surface structures of ethylene (C_2H_4), propylene (C_3H_6), and the 2-butenes (C_4H_8) adsorbed on the (111) crystal faces of Pt and Rh have been studied in our laboratory. We shall first describe the results for the Pt (111) substrate and then turn to the Rh(111) substrate. The (111) surface of these face-centered cubic metals exposes a top layer of metal atoms arranged in an hexagonal mesh; and there are a number of different high-symmetry sites that an adsorbing molecule could possibly occupy: 3-fold symmetric hollow, bridge, and 3-fold top positions. Our LEED crystallography studies^{6,7} clearly show that the small alkenes choose the hollow sites of the Pt(111) surface at 300K. These alkenes undergo an interesting structural rearrangement upon adsorption; they form alkylidyne species ($\equiv C(CH_2)_nCH_3$) as illustrated in Figure 3. One hydrogen atom is released from the carbon skeleton of the alkene, while a terminal carbon atom forms three strong bonds with the surface metal atoms. The C-C bond closest to the metal is perpendicular to the surface plane and has a length (1.50Å) close to the single-bond distance in alkanes (1.54Å). The remainder of the hydrocarbon chain is structurally similar to that in the gas-phase alkanes (C_nH_{2n+2}). This structure is supported by recent HREELS^{8,9} and ARUPS¹⁰ studies (see Table 1) on the ethylidyne overlayer.

The alkylidyne species order into a (2x2) lattice on Pt; the (2x2) notation implies that the overlayer unit cell is parallel with the rhombic cell of the Pt surface and twice as large in each direction. LEED also determined which of the two different 3-fold hollow sites is occupied by the alkylidyne group. These two hollow sites are distin-

guished by the presence or absence of a second layer atom below them: we shall call them hcp hollow and fcc hollow sites, respectively. We find that the alkylidyne on Pt(111) prefer the fcc hollow site. The coverage of the hydrocarbon molecules in this lattice is designated as one-quarter of a monolayer which means that there is one molecule for every four top-layer Pt atoms.

The methyl group of propylidyne appears to rotate freely at room temperature; this was inferred from the near identity of the I-V curves due to propylene and ethylene. This strong similarity in the LEED I-V spectra can only come about by the random orientation of the freely rotating methyl group. Similarly, the ethyl group of butylidyne can rotate freely at low gas exposures (1-10L), but packs into a superlattice at higher exposures (~1000L). (The term exposure is used as a measure of the number of molecules that actually strike the surface, whether they stick or not; and a langmuir (L) corresponds to one monolayer of molecules striking the sample during the adsorption experiment.)

Figure 4 illustrates one model for the locked-in butylidyne structure that forms on Pt(111) at 300K. The γ -carbon atoms of neighboring butylidyne species ($\equiv\text{C}(\alpha)-\text{C}(\beta)\text{H}_e-\text{C}(\gamma)\text{H}_2-\text{C}(\delta)\text{H}_2$) rotate towards as far away from each other as possible. Another conformation of butylidyne is predicted by force-field calculations¹¹ that consider only the Van der Waals forces between neighboring hydrocarbon species; as we shall soon see, these calculations support our LEED result for the very comparable conformation of propylidyne adsorbed on Rh(111). In this structure, the γ -carbon atoms rotate towards each other by 30° and the δ -carbon atoms tilt away from each other by about 30° . To

confirm the predicted conformation of butylidyne on Pt, we have begun a LEED analysis of this structure as well. The packing of the ethyl groups in butylidyne thus appears to be controlled by intermolecular Van der Waals forces. The importance of these forces in understanding the structures of hydrocarbon crystals is already well-known¹² and it should really come as no surprise that they should also play an important role in determining the structure of adsorbed hydrocarbon monolayers.

The bonding of C_2H_4 ¹³, C_3H_6 ¹⁴, and C_4H_8 ¹⁴ on Rh(111) parallels the Pt(111) adsorption we just described. HREELS¹⁵ again found that an ethylidyne species forms on the surface after ethylene adsorption. Between 240 and 270K, the resulting alkylidynes again order into a (2x2) lattice on Rh(111). The Rh surface appears to be slightly more reactive than Pt, since the alkylidyne species form already at 240K. Our LEED studies indicate that the carbon-carbon bond which is closest to the Rh surface could be slightly shorter (1.45Å) than that found on Pt (1.50Å), while the metal-carbon bond is relatively longer on Rh than on Pt. The latter comparison is made with the carbon-covalent radii for the Rh-C (0.69Å) and Pt-C (0.61Å) bonds. The different bond lengths for alkylidynes on Rh and Pt is possibly due to the different hollow sites that are occupied on these two surfaces. We find that alkylidyne chooses an hcp hollow on Rh, while it prefers the fcc hollow on Pt. A detailed account of how the presence or absence of a second layer metal atom below the occupied hollow site could influence the bonding of alkylidyne can be found in reference 13.

Since the Rh lattice spacing is 4% smaller than that for Pt, a superlattice of methyl groups already develops for the propylidyne overlayer on Rh. The closer approach of the methyl groups to each other on the Rh surface probably restricts their rotation and favors their ordering to a greater extent than on Pt. Once again the methyl groups can rotate freely at low gas exposures, but lock into position at higher exposures. Figure 5 illustrates the structure we obtain by LEED for this overlayer and also indicates that an attractive Van der Waals interaction is driving the formation of the superlattice. The methyl groups are not positioned as far apart from each other as possible, but rather rotate towards each other by 30° . With this rotation, the Van der Waals spheres of neighboring methyl hydrogens just touch each other. This structure, as we mentioned earlier, corresponds closely to that predicted by force-field calculations¹¹ which consider only Van der Waals interactions and not the torsional energy for rotation about the $\text{CH}_2\text{-CH}_3$ and C-CH_2 bonds.

The 2-butenes can also form butylidyne on Rh(111) as indicated by another technique available to the surface scientist, Thermal Desorption Spectroscopy (TDS); this method will be described in the next section. Although butylidyne again occupies a (2x2) adsorption lattice, the LEED pattern suggests that the ethyl groups are disordered. This may occur because the activation barrier for rotation of the ethyl group is so high in this crowded overlayer (Rh has a 4% smaller packing than Pt) that the butylidyne superlattice can not order. Increasing the crystal temperature did not help overcome this rotational barrier,

but instead produced a new hydrocarbon structure. The nature of this temperature-dependent transition leads us into the next section.

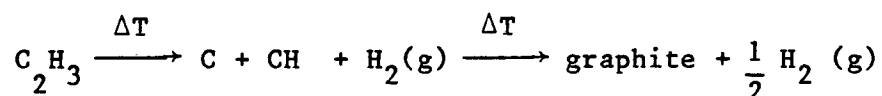
Temperature-Dependent Character of the
Surface Chemical Bonds of Hydrocarbons

The variety of different surface structures that form with increasing temperature is a unique and fascinating feature of surface chemistry. The hydrocarbon monolayers on Pt and Rh provide us with a good example of this diversity. A short summary of these temperature-dependent hydrocarbon structures that form on the Rh and Pt(111) surfaces is given in Table 2 and is intended as a guide for the following discussion. On heating the (2x2) lattice of alkylidyne that forms on Rh to above 270K, an irreversible transition to a c(4x2) lattice occurs. This transition has been followed with HREELS¹⁵ in the case of ethylidyne and this study indicates that the surface species itself is probably unchanged in the transition. Figure 6 illustrates that alternating rows of alkylidyne need only move by one metal atom spacing to change from a (2x2) to a c(4x2) lattice. The c(4x2) notation implies that an alkylidyne species is placed at the corners and in the center of a (4x2) cell, which is oriented parallel to the rhombic cell of the top layer Rh atoms.

Since the bonding of any alkylidyne molecule to the surface seems to be the same in the (2x2) and c(4x2) structures, intermolecular forces may be responsible for this transformation. As shown in Figure 6, ethylidyne molecules in neighboring rows are closer together in the c(4x2) than in the (2x2) lattice. Van der Waals or other through space interactions probably do not cause this transition. Force-field calculations for example give nearly identical Van der Waals energies for both alkylidyne lattices, when the effect of the

substrate is neglected. We believe that through-metal interactions may cause the intermolecular forces that drive this lattice transition.

Unlike on Rh, the alkylidyne overlayers on Pt do not produce a different ordered surface structure with increasing temperature; however, the alkylidyne species on both the Pt and Rh(111) surfaces will decompose in a similar fashion at still higher temperatures. The successive dehydrogenation of these alkylidyne layers with increasing temperature can be summarized by the following equation for ethylidyne:



As indicated by this equation, upon heating these ordered alkylidyne monolayers to above 400K, H₂ gas evolution can be detected by a mass spectrometer that is attached to the Ultra-High Vacuum (UHV) system.

Figure 7 shows the sequential loss of H₂ from the alkenes adsorbed on Pt(111) as a function of temperature¹⁶ in the form of Thermal Desorption Spectra. The similarity of the ethylene, propylene, and 2-butene curves suggests that very similar structural transitions occur for these adsorbed molecules with increasing temperature. The structural changes that happen during hydrogen desorption from both Rh and Pt(111) have already been monitored with HREELS^{15,17,18} and LEED.¹⁹ Peak A corresponds to alkylidyne conversion with a loss of one hydrogen from the adsorbed alkene; Peak B indicates carbon-carbon bond scission with the larger molecules being more sensitive to thermal decomposition. The set of peaks C arise from the final dehydrogenation of CH and CH₂ fragments on the surface to graphite. The last transi-

tion from C-H groups to graphite has serious consequences in many catalytic reactions and is therefore of great interest.²⁰ The graphite layer is quite stable and usually inert; it may effectively cover metal sites that would otherwise be active during catalytic reactions. On the other hand, the C-H groups are very reactive and are necessary intermediates in many catalytic processes.

Below the alkene to alkylidyne conversion temperature ($\sim 300\text{K}$ for Pt and $\sim 240\text{K}$ for Rh(111)), the alkenes probably all adsorb with each unsaturated carbon atom making one σ -bond to a metal atom on the surface. This changes the hybridization of the unsaturated carbon atoms from sp^2 to $\sim sp^3$. Only ethylene adsorbed on Pt(111)^{17,21} below 300K has been observed to di- σ bond in this fashion; however, the extreme similarity of the TDS spectra for all the alkenes adsorbed on Pt(111)¹⁶ and Rh(111)²² suggests that a similar bonding occurs in these overlayers as well. Unfortunately, the parallel-bonded alkenes do not order^{15,17,22} so LEED could not be used to determine their structure. The alkynes ($C_n H_{2n-2}$) however do order in this temperature range and also di- σ bond to two top layer metal atoms; this bonding arrangement is indicated from HREELS,^{15,17} UPS,²¹ and LEED^{7,22,23} studies carried out using alkyne overlayers. The unsaturated carbon atoms increase their hybridization from sp to $\sim sp^2$ when they each make one bond to neighboring metal atoms; the remaining p-orbitals of the unsaturated carbon atoms interact weakly with a third metal atom forming π -bonds. As the temperature is raised, these alkyne layers also convert to alkylidyne ($C_n H_{2n-1}$), but some coadsorbed hydrogen must be present for incorporation into the alkylidyne species.

Comparison With Hydrocarbon Adsorption on Other Metals

Hydrocarbon overlayers on Pt and Rh show a very different temperature dependence from those on Fe and W on the one hand, or Ag and Cu on the other. Fe and W are more reactive metals than Rh or Pt and can quickly dissociate the adsorbing hydrocarbon at room temperature.^{24,25} In fact, a UPS study^{24a} (see Table 1) reports the formation of CH or CH₂ species upon the adsorption of acetylene or ethylene, respectively, on the α -Fe(100) surface; these hydrocarbon fragments may then dehydrogenate at slightly higher temperatures to give iron carbide. Such a carbide has been inferred from HREELS^{25a,b} or Auger Electron Spectroscopy (AES)^{25c} studies on the (111), (110), and (100) faces of tungsten after a low acetylene exposure at room temperature. The adsorption of additional acetylene on the tungsten carbide^{25a-d} and iron carbide²⁴ surfaces resembles adsorption on Rh and Pt; ethylene probably di-bonds to these surfaces at low temperatures and dehydrogenates to acetylene near room temperature.^{24b,25e} This acetylene complex then desorbs or fragments at temperatures above 400K.^{24b,25e} The similarity between these carbides and the noble metals is not accidental; it has been known for some time that tungsten carbide, for example, has similar catalytic²⁶ and electronic properties²⁷ as Pt. It is very tempting to consider alkene or alkyne adsorption below 100K on the bare W or Fe surfaces where intact molecular adsorption may be possible but the sequence of structures that could form at these temperatures has yet to be explored.

Moving to the right in the periodic table, we find that the Ag²⁸ and Cu(111)²⁹ surfaces interact only weakly with adsorbed hydrocarbons.

At low temperatures (~200K for Ag and ~375K for Cu), ethylene and acetylene adsorb without any distortion from their gas-phase structure as seen by UPS. Upon heating, these C₂ hydrocarbons do not undergo successive dehydrogenation or structural rearrangements, but rather desorb. The adsorption is so weak on these surfaces (physisorption) that desorption occurs before the metal can chemically react with the adsorbate. To put it more precisely, the activation energy for reaction with the metal surface is significantly larger than the heat of adsorption for these hydrocarbons.

The reasons for these temperature-dependent processes are presently under intense investigation and some general principles are beginning to emerge. (1) The free energy of the reaction $C_2H_4 + 6M \rightarrow 2M-C + 4M-H$, where M represents adsorption sites on a metal surface, has large negative values. However, the process occurs in a few sequential steps with increasing temperature. It appears that each bond breaking step requires an activation energy, and the surface intermediates ($\equiv C(CH_2)_n CH_3$ or CH) that form are well-protected by these potential barriers in a finite temperature range. (2) Some temperature-dependent transitions (such as (2x2) \rightarrow c(4x2)) may be controlled solely by intermolecular forces including through-metal interactions rather than by any molecule-metal interaction; and hydrocarbons seem to be especially prone to such transformations. (3) The reactivity of a metal surface increases as we move toward the upper left hand corner of the transition metal series in the Periodic Table; this rule has been well-tested for diatomic molecules such as carbon monoxide and seems to hold for hydrocarbons as well. So Fe and W are more reactive than Rh and Pt which are in turn

more reactive than Ag and Cu. In fact, we even find that Rh is slightly more reactive than Pt in keeping with its position to the upper left of Pt in the Periodic Table. Not only does alkylidyne conversion occur at lower temperatures on Rh(111) (~240K) than Pt(111) (~300K), but ethylidyne is also seen to fragment at 420K for Rh and 450K for Pt. However, a word of caution should be inserted here; geometric effects may moderate the trend we see in metal reactivity. This question of structure sensitivity will be addressed in the next section.

The Structure Sensitivity of Hydrocarbon Bonding on Metals

Studies of structure sensitivity in catalysis have a distinguished history. It is well documented that the reactivity or selectivity of a catalyst may change dramatically as the dispersion of the particles is altered. A low dispersion will have large microcrystallites present on the catalyst surface; these microcrystallites have predominantly their hexagonal faces exposed to lower their surface free energy. At higher metal dispersions, however, a near random distribution of crystal faces appears on the catalyst surface. The structure of the metal atoms attached to the support material of a catalyst is found to be nearly as important as the electronic character of the metal in predicting the reactivity or selectivity of a catalyst. To better understand how the metal surface structure affects hydrocarbon bonding, the chemisorption of hydrocarbons on different faces of the same metal is now being investigated in a number of research laboratories.

We recall that the hexagonal array of metal atoms on the (111) face of Rh or Pt produce an ethylidyne layer after ethylene adsorption at room temperature. The more open (100) surface of these metals seems to be more reactive; the square mesh of metal atoms on this face will dehydrogenate ethylene to acetylene below room temperature and the ethylidyne layer appears to form at temperatures only below 200K.^{6,22,30,31} The different ethylene structures that occur on the (111) and (100) faces of Rh and Pt should be expected when we consider the very different arrangement of d-orbitals that the adsorbing ethylene molecule will bond with.

Low coordination number sites such as atomic steps or kinks that can occur on metal surfaces with high Miller indices show even stronger effects on bonding. Figure 8 illustrates two high Miller index surfaces of a face-centered cubic crystal like Rh or Pt. These surfaces are composed of terraces and step or kink edges. The terrace has a (111) packing of metal atoms with a coordination number of 9, while the instep or kink atoms have a higher coordination number of 10 or 11. A recent theoretical study³² suggests that these instep or inkink atoms are responsible for the frequently observed increased^{in the} reactivity of stepped and kinked crystal faces. The adsorption of acetylene on a stepped or flat Ni(111) surface serves as a good example of this enhanced reactivity. Using HREELS³³ and LEED,³⁴ acetylene is found to adsorb intact on the flat Ni(111) surface at room temperature yet it is clearly fragmented to a C₂ species on a stepped Ni(111) sample already at 150K.³⁵ This C₂ fragment probably bonds to both the step and terrace atoms simultaneously to increase the number of metal bonds that each carbon atom makes. As a result, the highly unsaturated C₂ species is stable to about 200K when it decomposes into a surface carbide.

In addition to these chemisorption studies, catalytic reaction experiments show major differences between flat and stepped surfaces. Hydrogenolysis and hydrogenation reactions on Ni catalysts are found to be structure sensitive³⁶ which is consistent with the change in C-H bond breaking ability we see for acetylene adsorption on the flat and stepped Ni(111) surfaces. On the other hand, hydrogenation or dehydrogenation reactions on Pt are not structure sensitive³⁶ and even the flat Pt surfaces are effective catalysts for these reactions. Why

Pt and Ni appear to show very different structure sensitivities in hydrogenation reactions is still an open question, yet an attractive explanation for this interesting effect has been proposed³⁵. This explanation assumes however that the less coordinated step or kink edge atoms are the most reactive and are responsible for the increased reactivity of stepped and kinked surfaces. The spatial extension of the d-orbitals compared to the nearest neighbor distance is smaller on Ni than on Pt. On the flat nickel surface then the d-orbitals contribute less to the bonding of adsorbates than on Pt; however, a step edge atom is depleted of sp-electrons which could expose the d-orbitals more, thus making them more available for adsorbate bonding.³⁷ Since the flat Pt surface already has protruding d-orbitals, the effect of the step edge atoms should be less dramatic. From this example, we see that the geometry of Ni atoms on the surface does moderate the inherent catalytic activity of the metal; yet we still do not fully understand the mechanism involved. Similar studies in this direction should prove very exciting and will certainly find considerable use in our chemical technology.

Conclusions and Summary

A rich variety of hydrocarbon structures is found on the Rh(111) and Pt(111) surfaces after alkene or alkyne adsorption. (See Table 2). These adsorbed hydrocarbons undergo successive dehydrogenation with increasing temperature. They rehybridize (di- σ bonding) at low temperatures, undergo a hydrogen rearrangement to produce an alkylidyne group near room temperature, have their carbon skeleton broken near 400K, and finally fully dehydrogenate to graphite above 700K. The alkylidyne overlayer has been the most extensively studied of these to date; this alkylidyne phase readily forms with a number of different gases (C_2 - C_4 unsaturated straight-chain hydrocarbons), with a few different metal substrates (Rh, Pt, and recently Pd(111)³⁸), and with two very different low Miller index faces ((100) and (111)). This stability of the alkylidyne group is paralleled in the Organometallic Chemistry³⁹ of trinuclear ethylidyne noncarbonyl clusters ($M_3(CCH_3)(CO)_9$). These clusters appear very resistant to thermal decomposition and oxidation reactions; and even more importantly, they can be easily synthesized by a large number of different pathways.

The importance of Van der Waals forces in determining the structures of hydrocarbon overlayers is clearly illustrated by the propylidyne and butylidyne superlattices that develop on the Rh and Pt(111) surfaces. The carbon-carbon bond in the alkylidyne species that is closest to the surface has a (2x2) periodicity; while the γ -carbon atom moves towards its neighbors and locks into a (2 3x2 3) $R30^\circ$ superlattice. The position of this γ -carbon allows an optimal Van der Waals interaction among the hydrogen atoms attached to neighboring

γ -carbon atoms. Force field calculations indicate that the superlattice packing potential energy is about 2-3 kcal/mole. Quite interestingly, a different intermolecular force may drive the $(2 \times 2) \rightarrow c(4 \times 2)$ lattice transition for alkylidyne on Rh(111). This force may not be due to a through-space, but rather a via-metal interaction.

In comparing the hydrocarbon adsorption on Rh or Pt(111) to other metal and high Miller index surfaces, we can study the influence of electronic and geometric effects on hydrocarbon bonding. The reactivity of a metal surface generally increases as we move to the upper left of the transition series. Fe and W surfaces are found to be more reactive than Rh and Pt that are in turn more reactive than Ag and Cu. For example, at 100K Fe or W(111) will decompose an adsorbed alkene, Rh or Pt(111) will rehybridize its unsaturated carbon atoms, and Ag or Cu(111) will not alter its gas phase structure significantly. We even find that Rh is slightly more reactive than Pt in keeping with its position to the upper left of Pt in the Periodic Table. Not only does alkylidyne conversion occur at lower temperatures on Rh(111) (~270K) than Pt(111) (~300K), but ethylidyne also fragments at 420K for Rh and 450K for Pt.

Geometric effects however can alter the chemical reactivity of a metal surface. Stepped and kinked surfaces tend to be more reactive than the corresponding flat surfaces. These geometric factors are in many cases nearly as important as the electronic character of the particular transition metal in determining the reactivity of a given surface. Acetylene for example adsorbs intact on the flat Ni(111)

face at room temperature yet already fragments to a C_2 species on a stepped Ni(111) sample at 150K.

A number of future research directions are suggested in our review of hydrocarbon adsorption on metals. (1) We find that only a few noble metals (Ni, Pt, Rh, and Pd) have been intensively studied in the past five years, while hydrocarbon bonding to other metals is still virtually unexplored. Low temperature experiments will probably be required to investigate the intact molecular adsorption of hydrocarbons on the more reactive metals that lie on the left side of the transition series. Our understanding of the hydrocarbon-metal bond should be significantly improved by such a systematic study, while many catalytically important surfaces (such as Fe or Ru in the Fischer-Tropsch synthesis) will come under closer scrutiny. (2) Due to the rapid progress of most surface structural techniques, we are no longer limited to the adsorption of C_2-C_4 alkenes or alkynes. Monolayers of the longer straight-chain hydrocarbons as well as some aromatics (benzene, naphthalene, and azulene) are beginning to be studied with LEED, HREELS, and UPS. (3) The influence of the metal surface geometry on hydrocarbon bonding should also be examined by determining the hydrocarbon structures that form on different crystallographic planes of the same metal. These future prospects alone should insure that the study of hydrocarbon monolayers will prove even more interesting to researchers and useful to our chemical industry as it matures over the next decade.

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FIGURE CAPTIONS

1. A comparison of an experimental electron diffraction beam intensity vs. energy curve (I-V spectrum) with a set of calculated curves. The experimental spectrum was obtained from an acetylene overlayer that formed on the Pt(111) surface at 300K. The calculated curves assume four different adsorption sites (atop, di- σ , triangular, and μ -bridging), but only the atop site geometry gives reasonably good agreement between theory and experiment.
2. ~~An~~ HREEL spectrum^a of the CO overlayer that forms above the Rh(111) surface at 300K. The CO stretching frequencies are seen near 1870cm^{-1} (bridge site) and 1990cm^{-1} (atop site), while a metal-carbon stretching frequency is observed at 480cm^{-1} .
3. Alkylidyne ($\text{C}_n\text{H}_{2n-1}$) species are produced on the Pt(111) face after alkene (C_nH_{2n}) adsorption at 300K. Large circles represent top-layer Pt atoms, dotted circles indicate carbon atoms, and slashed circles are hydrogen atoms.
4. A possible model for the butylidyne superlattice that forms on the Pt(111) surface is illustrated here. The γ -carbon atoms of neighboring butylidyne species are rotated as far away from each other as possible. A LEED crystallography study is presently underway to test this and other proposed models.

5. Propylidyne superlattice structure that occurs on the Rh(111) surface between 240 and 270K. This geometry is supported by a LEED analysis and force-field calculations. The γ -carbon atoms rotate 30° closer to one another to allow a more favorable Van der Waals interaction between neighboring hydrogen atoms.
6. The $(2 \times 2) \rightarrow c(4 \times 2)$ lattice transition for ethylidyne when the Rh(111) crystal is heated from 240 to 300K is illustrated here. The local geometry of any given ethylidyne group is probably the same in the (2×2) and $c(4 \times 2)$ phases; the $c(4 \times 2)$ phase may be favored due to stronger intermolecular interactions between neighboring rows of ethylidyne.
7. Thermal Desorption Spectra recorded for alkene ($C_2H_4, C_3H_6, 2-C_4H_8$) adsorption on the Pt(111) surface. Peak (A) represents H_2 desorption at the alkene \rightarrow alkylidyne conversion temperature; peak (B) indicates alkylidyne fragmentation and CH, CH_2 formation accompanied by some more H_2 desorption; and peaks (C) represent graphite formation with complete dehydrogenation of the hydrocarbon overlayer.
8. The flat (111), stepped (755), and kinked (10,8,7) surfaces of a face-centered cubic metal are illustrated. The step and kink edges usually form on high Miller index surfaces and they can alter the metal reactivity.

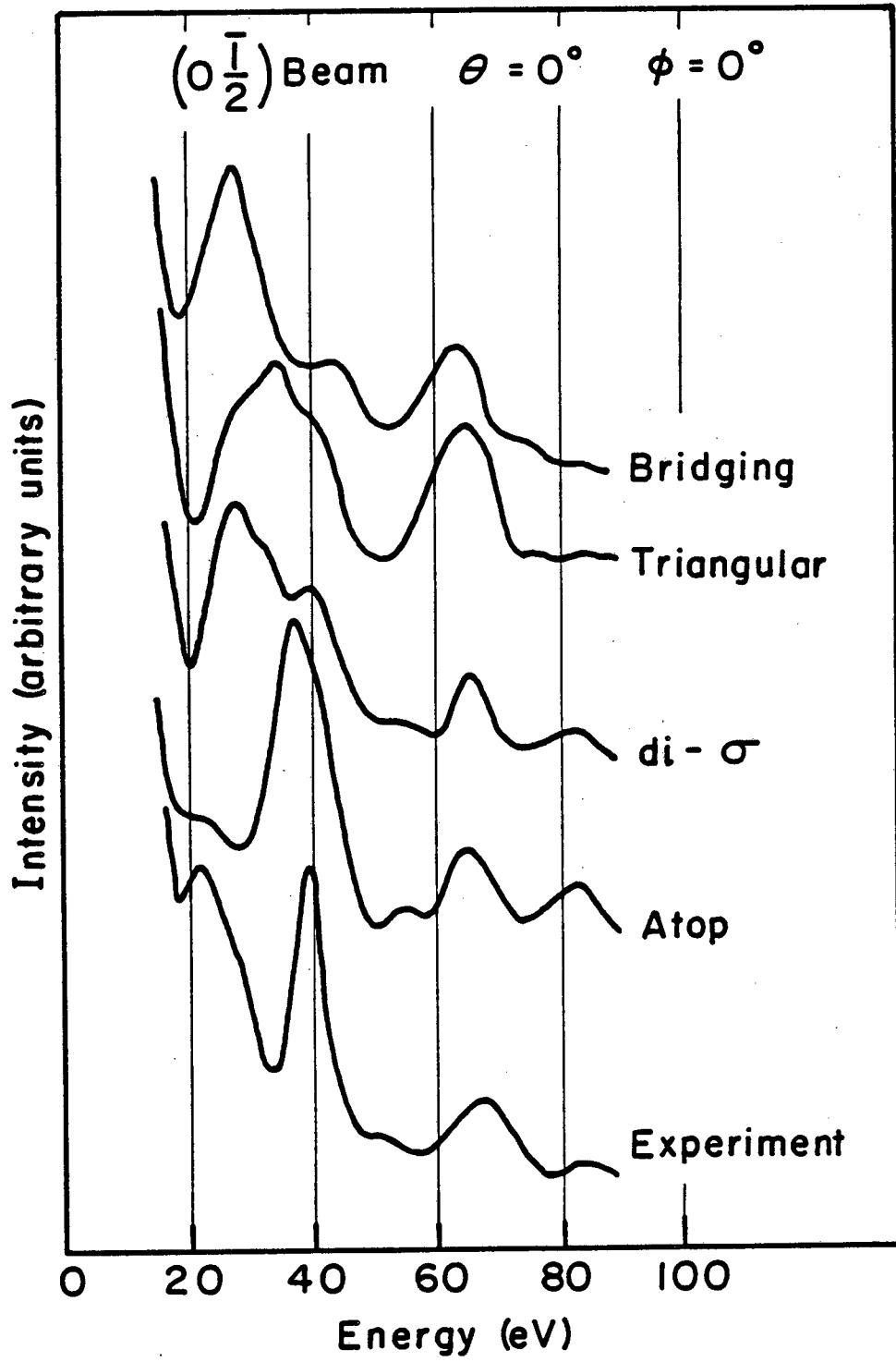
Table 1. Common structural methods in surface science

Acronym	LEED ¹	HREELS ²	SEXAFS ³	ARUPS ³	UPS ³
<u>Full Name:</u>	Low energy electron diffraction	High resolution electron energy loss spectroscopy	Surface extended X-ray absorption fine-structure spectroscopy	Angle-resolved ultraviolet photoemission spectroscopy	(Angle - integrated) Ultraviolet photoemission spectroscopy
<u>Sensitive to:</u>	Atomic positions	Molecular configuration	Atomic positions	Atomic positions	Electronic structure; Molecular configuration
<u>Underlying Principle:</u>	Electron diffracts from atomic cores	Electron energy gain or loss by interaction with the dynamic dipole moment or short-range forces of surface vibrations	Electron diffracts from atomic cores near emitting atoms	Photoelectron diffracts from atomic cores near emitting atoms	Photoelectron emission from molecular orbitals
<u>Advantages:</u>	Measures bond distances (+ 0.05-0.1Å) and bond angles (+10-15°)	Identifies molecular species present on surface and its adsorption site; detects hydrogen	Measures bond distances (+0.03Å)	Measures bond distances (+0.05-0.1Å) and bond angles (+10-15°); probes bond symmetry	Measures binding energy of molecular orbitals
<u>Disadvantages:</u>	Requires long range order; complicated multiple scattering occurs	Not quantitative; difficult to assign vibrational modes	Synchrotron radiation required	Synchrotron radiation required; complicated multiple scattering occurs	d-band emission and relaxation effects complicate interpretation of spectra

Table 2. Irreversible structural transitions for ethylene on Rh and Pt(111) that occur with increasing temperatures.

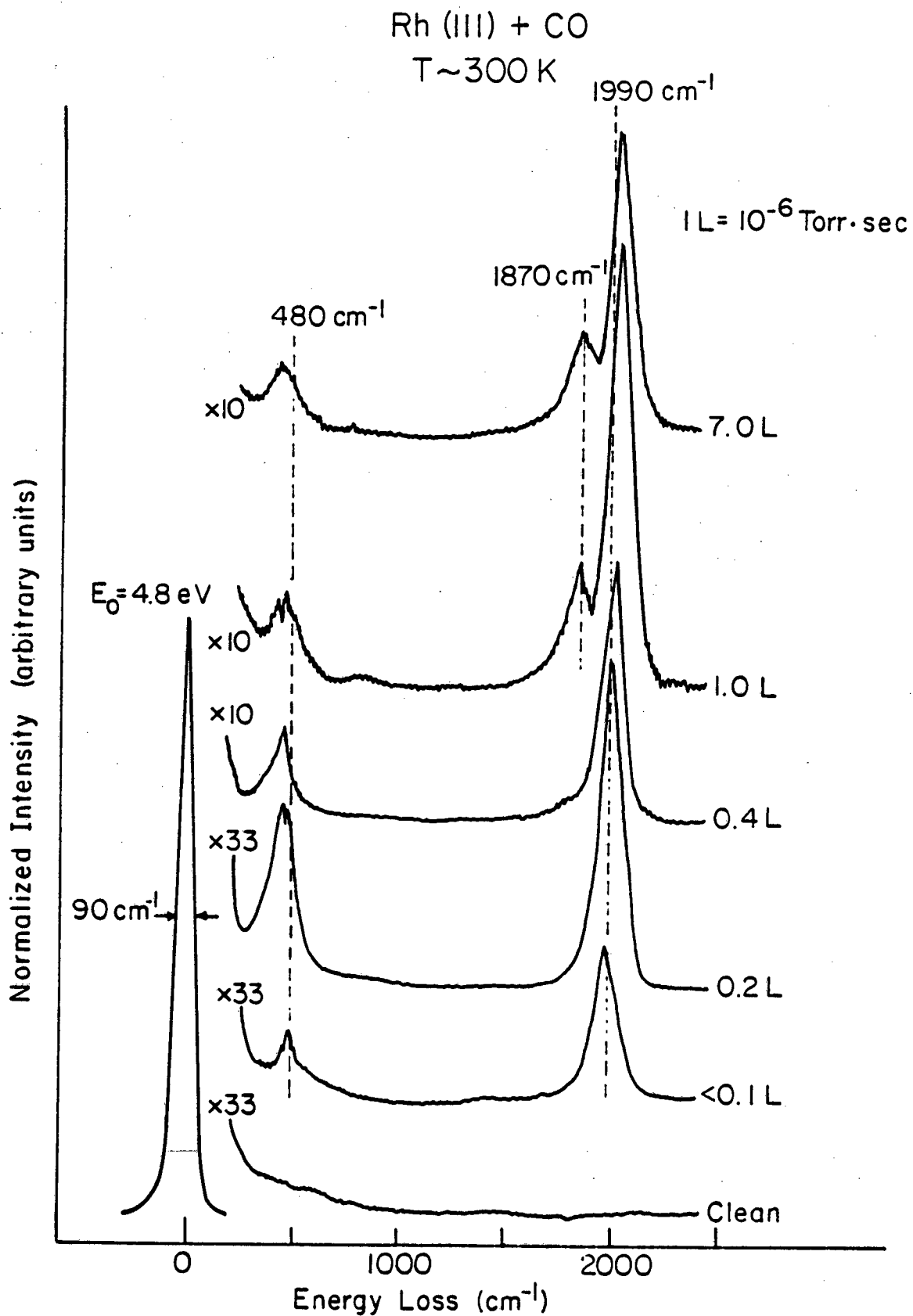
	Rh(111)		Pt(111)	
	<u>Alkene (C_nH_{2n})</u>	<u>Alkyne (C_nH_{2n-2})</u>	<u>Alkene</u>	<u>Alkyne</u>
<u>Low Temperature Species</u>				
structure	Ethynylidyne ($\equiv\text{CCH}_3$); (2x2)	di- σ , π acetylene (H-C \equiv C-H)	di- σ ethylene (H ₂ C-CH ₂)	di- σ , π acetylene (HC \equiv CH)
temperature range	230-270K	230-270K	140-290K	140-350K
<u>Room Temperature Species</u>				
structure	Ethynylidyne ($\equiv\text{CCH}_3$); c(4x2)	Ethynylidyne ($\equiv\text{CCH}_3$); c(4x2)	Ethynylidyne ($\equiv\text{CCH}_3$)	Ethynylidyne ($\equiv\text{CCH}_3$)
temperature range	270-420K	270-420K (H needed)	290-450K	350-450K (H needed)
<u>Carbon-Carbon Bond Scission</u>				
structure	CH species	CH species	CH species	CH species
temperature range	420-700K	420-700K	450-700K	450-700K
<u>Total Dehydrogenation</u>				
structure	graphite	graphite	graphite	graphite
temperature range	700K	700K	700K	700K

Acetylene on Pt(III)
Metastable Structure



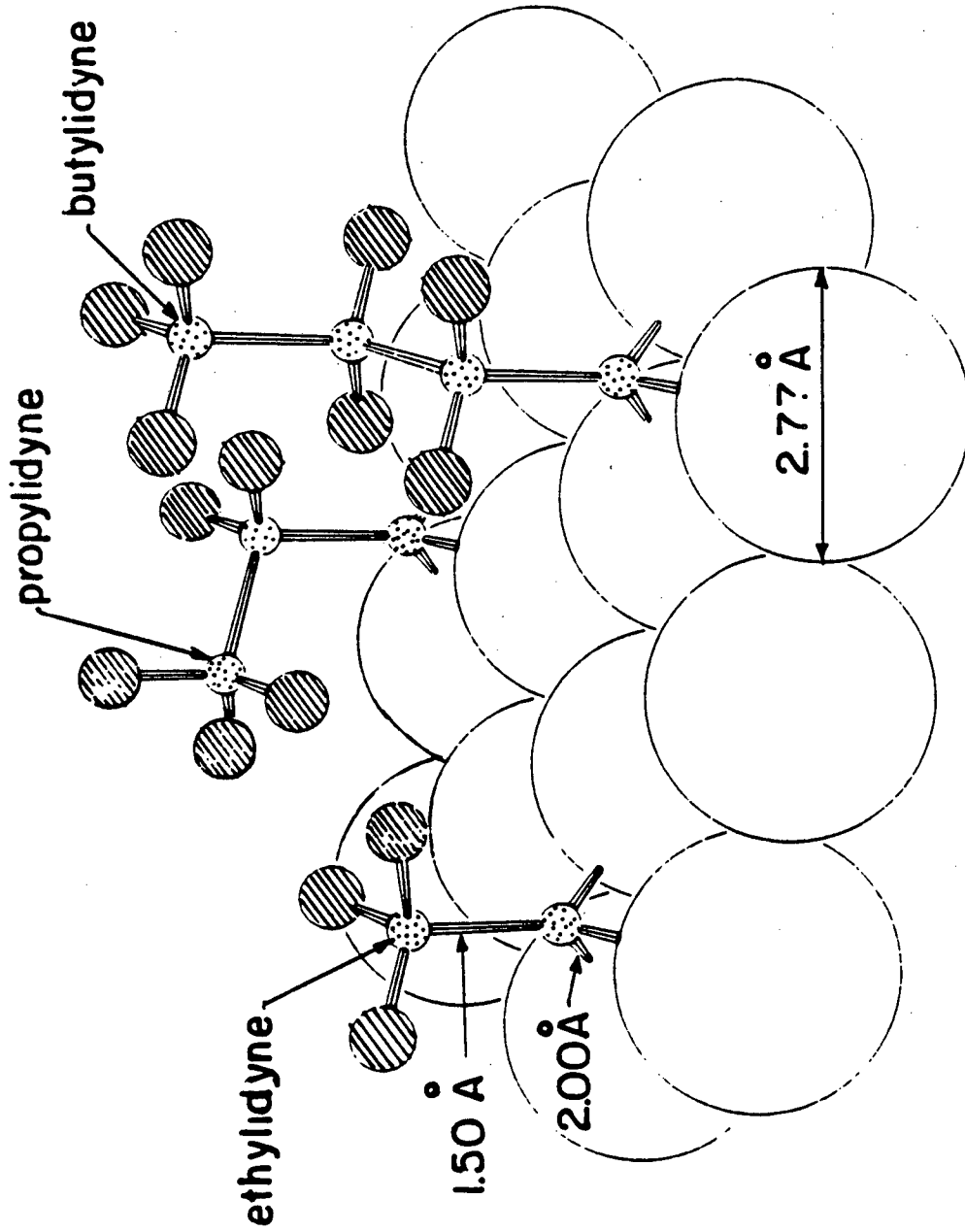
XBL 772-5068

Fig. 1



XBL 793-5880

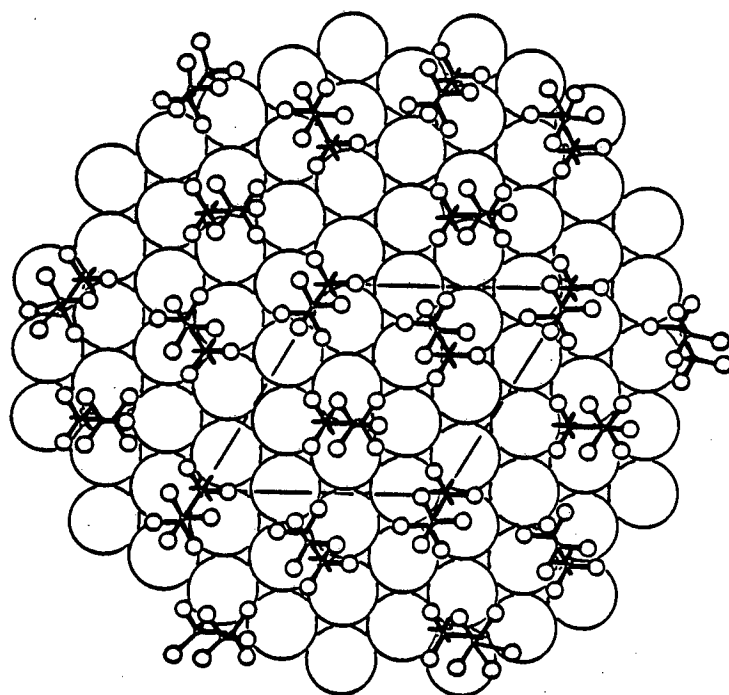
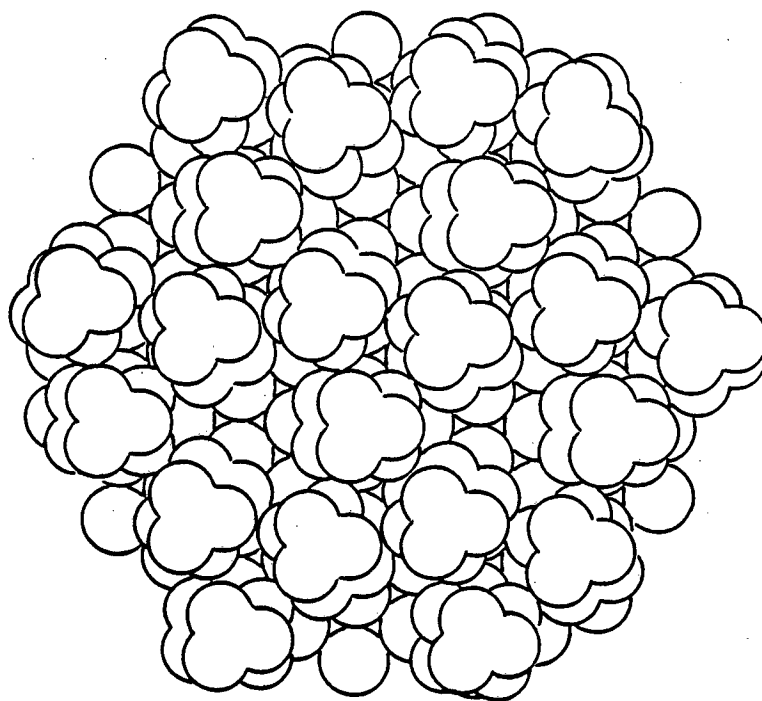
Fig. 2



Pt(III) + ethylidyne, propylidyne and butylidyne

Fig. 3

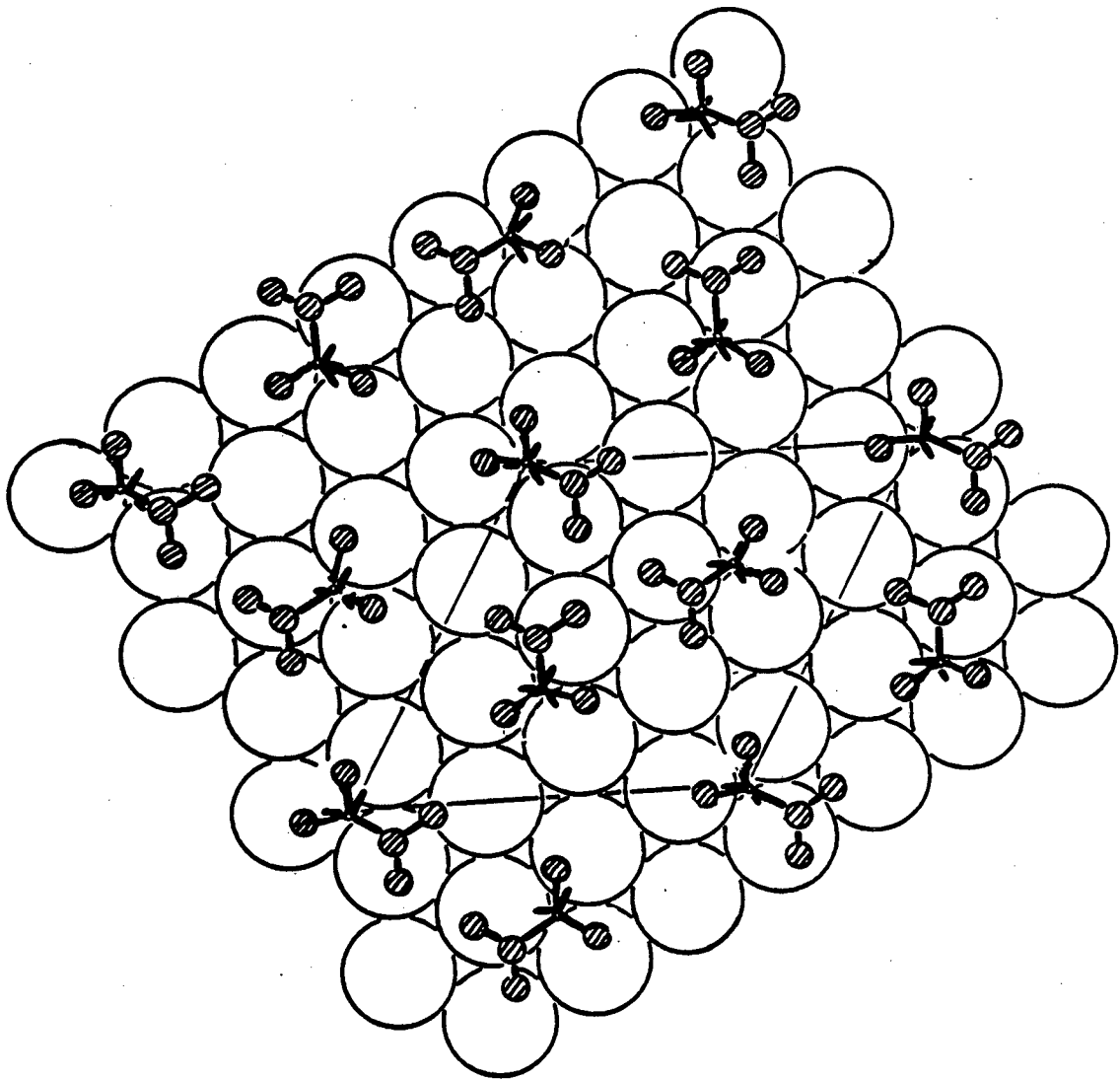
XBL 8110-6882



$\text{fcc(III)} + (2\sqrt{3} \times 2\sqrt{3}) R 30^\circ \text{C}_4\text{H}_7$ (butylidyne)

XBL 813-5411

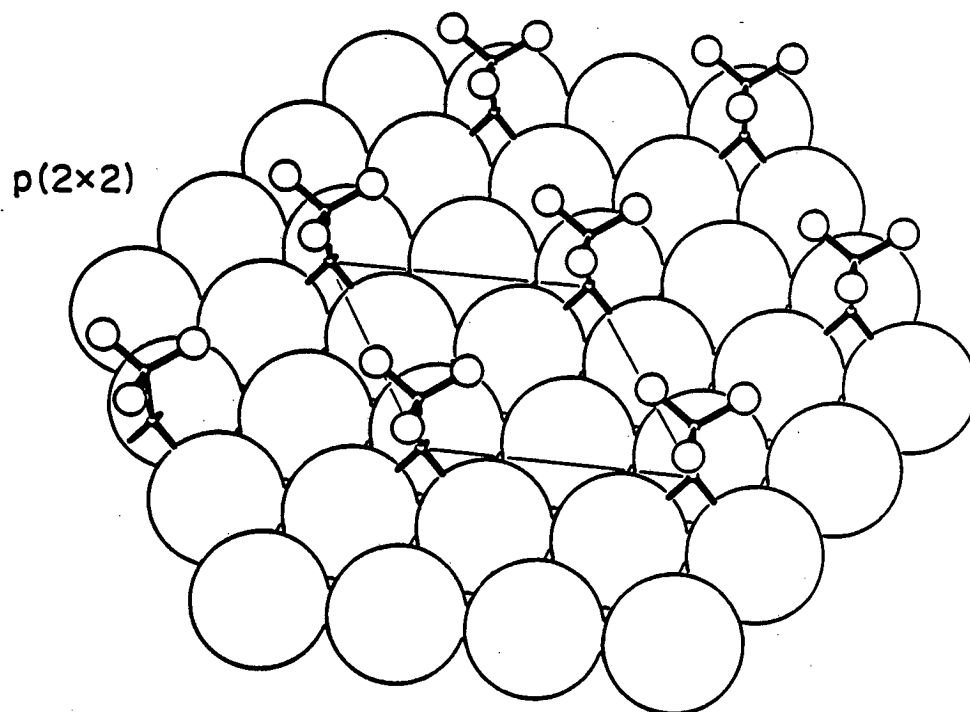
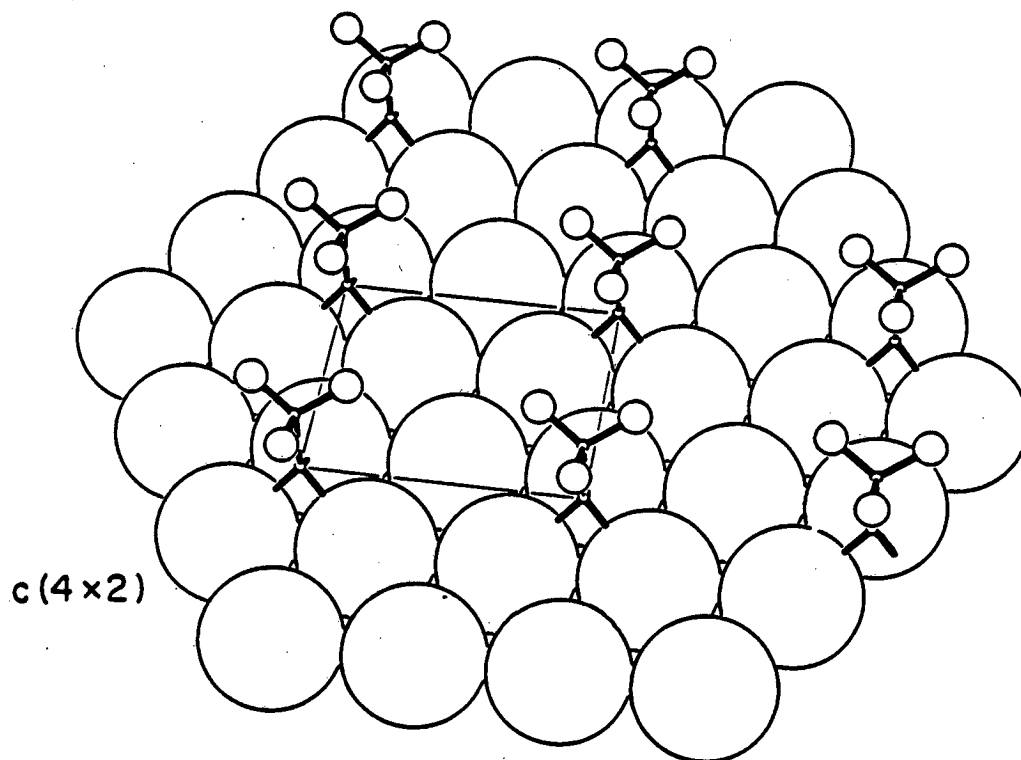
Fig. 4



$\text{Rh(III)} + (2\sqrt{3} \times 2\sqrt{3})\text{R}30^\circ$ (propylidyne)

XBL 82I-510I

Fig. 5



fcc (111) + C_2H_3 (ethynylidyne)

XBL813-5407

Fig. 6

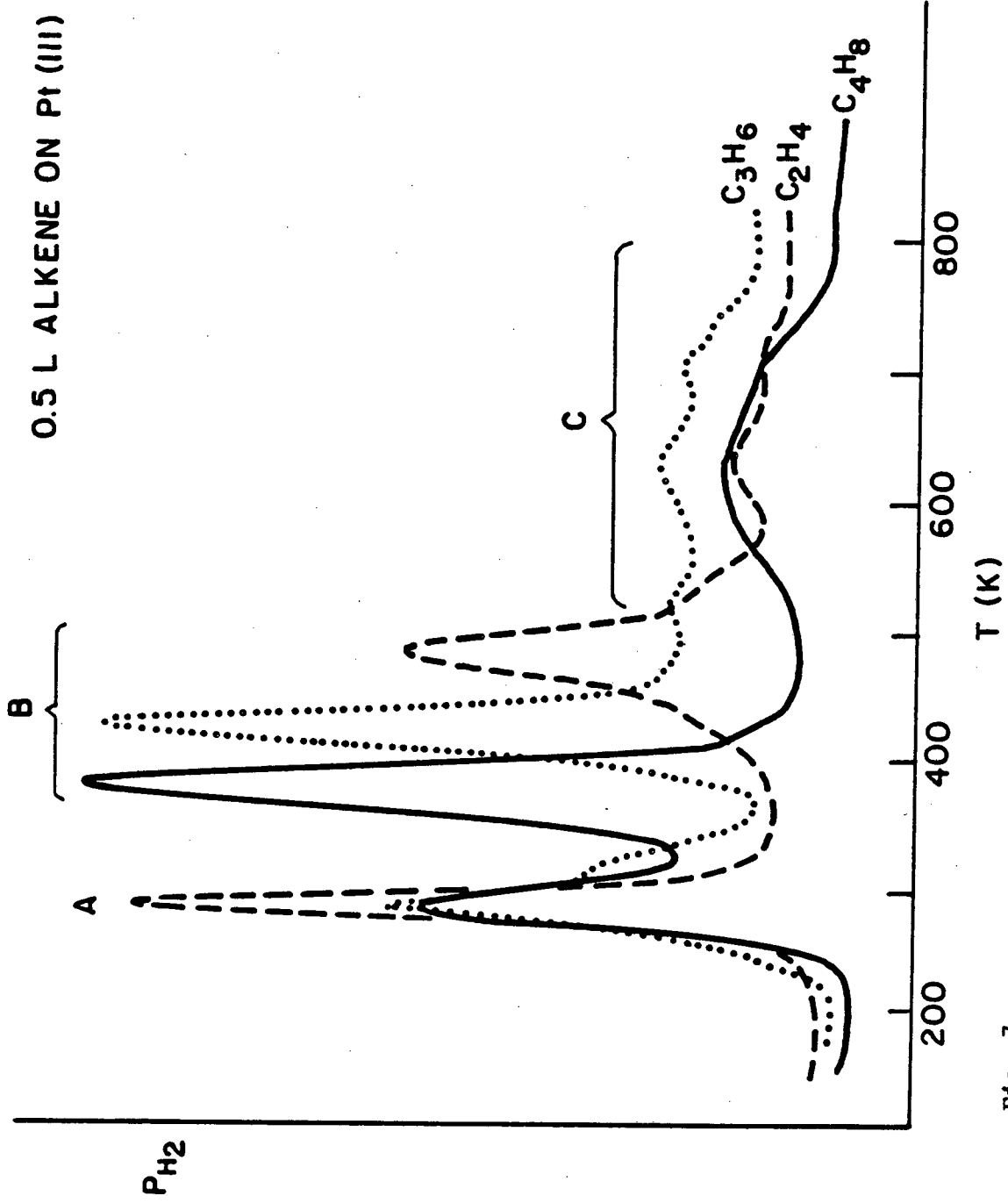
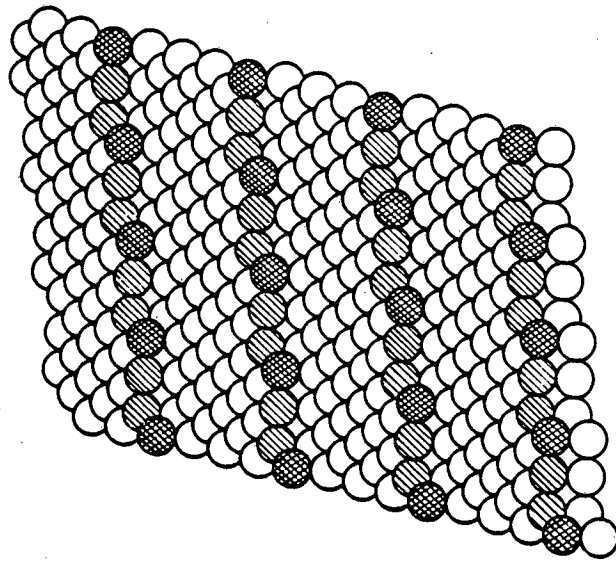


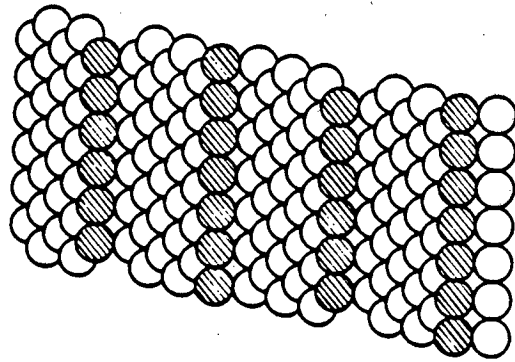
Fig. 7

XBL 814-5475

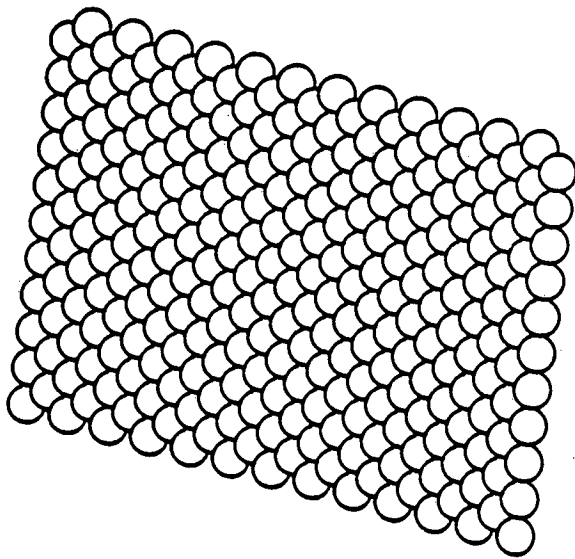


fcc (10, 8, 7)

XBL 806-10430



fcc (755)



fcc (111)

Fig. 8

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