

 Open access • Journal Article • DOI:10.1063/1.434162

The adsorption of hydrocarbons on platinum studied by low-energy electron diffraction intensities. The ordered (2×2) overlayers of acetylene and ethylene on the (111) crystal face of platinum — [Source link](#)

Peter C. Stair, Gabor A. Somorjai

Institutions: University of California, Berkeley, Lawrence Berkeley National Laboratory

Published on: 01 Mar 1977 - Journal of Chemical Physics (American Institute of Physics Publishing LLC)

Topics: Platinum, Electron diffraction, Low-energy electron diffraction, Acetylene and Bond length

Related papers:

- [LEED analysis of acetylene and ethylene chemisorption on the Pt\(111\) surface: Evidence for ethylidyne formation](#)
- [Identification of surface radicals by vibration spectroscopy: Reactions of C₂H₂, C₂H₄, and H₂ on Pt \(111\)](#)
- [Dynamical LEED study of C₂H₂ and C₂H₄ chemisorption on Pt\(111\): evidence for the ethylidyne group](#)
- [Desorption, decomposition, and deuterium exchange reactions of unsaturated hydrocarbons \(ethylene, acetylene, propylene, and butenes\) on the platinum\(111\) crystal face](#)
- [The surface structure and bonding of \(2 × 2\) acetylene overlayers on platinum \(111\): LEED intensity analysis](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/the-adsorption-of-hydrocarbons-on-platinum-studied-by-low-e4jzphixgd>

Lawrence Berkeley National Laboratory

Recent Work

Title

THE ADSORPTION OF HYDROCARBONS ON PLATINUM STUDIED BY LOW-ENERGY ELECTRON DIFFRACTION INTENSITIES. THE ORDERED (2x2) OVERLAYERS OF ACETYLENE AND ETHYLENE ON THE (111) CRYSTAL FACE OF PLATINUM

Permalink

<https://escholarship.org/uc/item/2gh281x9>

Author

Stair, P.C.

Publication Date

1976-07-01

0 0 0 0 4 6 0 2 7 9 0

Submitted to Journal of Chemical Physics

LBL-5421
Preprint c.1

THE ADSORPTION OF HYDROCARBONS ON PLATINUM
STUDIED BY LOW-ENERGY ELECTRON DIFFRACTION
INTENSITIES. THE ORDERED (2x2) OVERLAYERS OF
ACETYLENE AND ETHYLENE ON THE (111) CRYSTAL
FACE OF PLATINUM

P. C. Stair and G. A. Somorjai

July 28, 1976

RECEIVED
LIBRARY
BERKELEY LABORATORY

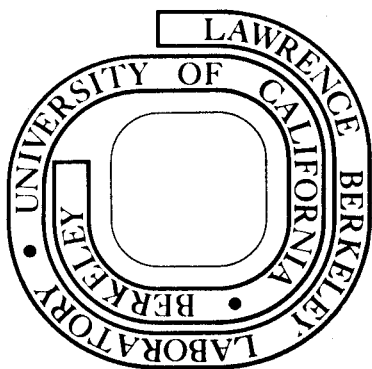
SEP 28 1976

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-5421

c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

The Adsorption of Hydrocarbons on Platinum Studied by Low-Energy Electron Diffraction Intensities. The Ordered (2x2) Overlayers of Acetylene and Ethylene on the (111) Crystal Face of Platinum

by

P. C. Stair and G. A. Somorjai

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

ABSTRACT

The intensities of the low-energy electron diffraction beams back-scattered from the ordered (2x2) overlayers of acetylene and ethylene on the platinum (111) crystal face are measured by a photographic technique. The intensities are presented in an appendix in the form of normalized-diffraction beam-intensity vs. incident-electron-energy (I-V curves). Acetylene spontaneously forms the ordered (2x2) adsorbate on platinum at 300 K and low exposure under ultra-high vacuum conditions. The intensity profiles reveal that this structure is metastable and upon heating to 350-400 K for 1 hr undergoes a transformation to a stable structure with the same (2x2) unit cell size. The acetylene transformation is thought to involve an expansion of the carbon-carbon bond length with an activation energy determined by the reduction in the carbon-carbon bond order. Ethylene adsorbs on the platinum (111) surface with dehydrogenation to form an acetylenic species whose structure is identical to the stable acetylene structure as shown by the intensity profiles.

INTRODUCTION

In order to understand the details of platinum catalysis in a variety of hydrocarbon reactions, an understanding of the structure and chemical bonding of the adsorbed hydrocarbon is necessary. Low-Energy Electron Diffraction (LEED) intensity analysis has been shown to be useful for determining the structure of clean, single crystal metal surfaces as well as simple monatomic overlayers adsorbed on metal surfaces.⁽¹⁾ Several years ago Morgan and Somorjai showed that a number of simple hydrocarbons would form ordered monolayer structures when adsorbed on the platinum (111) and (100) crystal faces and thus were suitable for LEED structure analysis.⁽²⁾ Subsequently, a variety of more complex hydrocarbons such as naphthalene and the normal paraffins up to octane were shown to have ordered surface structures both as monolayers on metal substrates and as molecular crystals grown under low temperature, ultra-high vacuum conditions.^(3,4) However, until recently the experimental difficulties involved in measuring Low-Energy Electron Diffraction intensities have prevented the application of this technique to the surface crystallography of adsorbed hydrocarbons. In particular, the time-dependent destruction of these ordered overlayers by the incident electron beam makes the traditional intensity measurement techniques using either a Faraday cup or a spot photometer inadequate. The need for a solution to this problem led to the development of a photographic intensity measurement technique which lowered the total electron beam exposure to an acceptable level by significantly reducing the measurement time.⁽⁵⁾ As a result the structure analysis of acetylene adsorbed into an ordered (2x2) overlayer on the (111) crystal face of

platinum was recently completed.^(6,7) This work was important not only as the first hydrocarbon surface structural determination but also as the first molecular adsorbate of any kind to be so analyzed.

Recently acetylene was found to adsorb into two ordered adsorbate structures on the Pt(111) surface.⁽⁸⁾ The two structures have the same (2x2) diffraction pattern (see Fig. 2), but have substantially different intensities. This implies that acetylene undergoes a significant structural and therefore chemical change from one structure to another as a function of time and/or temperature, so that even a simple molecule adsorbed on a close-packed surface can display complex chemical behavior. The exact chemical nature of these two structures has not been completely determined as yet even by dynamical LEED structure calculations.⁽⁷⁾ The present paper gives a detailed description of how each acetylene structure on Pt(111) is obtained and characterized using LEED intensities. We shall also provide some conjecture concerning the chemical state of the two acetylene species as well as information regarding the nature of the transformation.

Merrill et al.^(9,10) have proposed that ethylene dehydrogenates to form an acetylene species plus surface hydrogen atoms when adsorbed on the Pt(111) surface. LEED intensity measurements reported in the present paper confirm this proposition by indicating that the structure of the ethylene on Pt(111) overlayer is identical to one and only one of the two possible acetylene structures. From the adsorption and ordering behavior of ethylene as compared to acetylene combined with our notions of

the chemical change which takes place with adsorbed acetylene we shall present a model of ethylene adsorption on platinum.

The present paper is also the first reporting of the complete Low-Energy Electron Diffraction intensity data from ordered hydrocarbon surface adsorbates. The data is presented as an appendix in the usual form of Intensity vs. Incident Electron Energy (I-V) curves. In order to facilitate future work in this area, the experimental techniques for hydrocarbon adsorption and intensity measurement will be discussed in some detail. Finally, we hope that by publishing this data we will promote further investigation of the molecular structure and chemical bonding of hydrocarbons on metal surfaces.

EXPERIMENTAL

(a) Apparatus and samples

Since the present paper is the first complete reporting of intensity measurements from ordered organic overlayers, we shall describe the experimental procedure in some detail. A Varian ultra-high vacuum LEED/Auger apparatus modified for intensity measurements was used in these experiments. The platinum single crystal sample was cut from an X-ray oriented 99.999% pure platinum single crystal rod. The sample was polished and the surface cleaned using techniques developed in this laboratory. (11,12) Further details on the apparatus and platinum sample handling are available elsewhere. (5,12) The acetylene and ethylene were obtained from the Matheson Company. The purity of both gases was checked using gas chromatography. The ethylene was found to contain only 10 ppm ethane as the major contaminant and so was used without further purification. The acetylene contained ~1% acetone since acetylene is commonly stored in an acetone solution to prevent the formation of explosive acetylides. The acetone was found to interfere with the adsorption of acetylene on the Pt(111) surface by preventing the spontaneous ordering of the acetylene adsorbate into the (2x2) structure. Only by exposure to the electron beam was it possible to order the contaminated acetylene. The acetone was easily removed from the acetylene, however, by passing the gas through a molecular sieve trap cooled to dry ice temperature (-78°C). This treatment reduced the acetone concentration to below the 1 ppm level and permitted the spontaneous ordering of acetylene on the Pt(111) surface.

(b) Adsorption and ordering

Following a standard cleaning procedure⁽¹²⁾ but before the hydrocarbon adsorption the platinum sample was flashed to 900°C for 2 mins to remove any adsorbed ambient CO or O₂. The sample was allowed to cool for 25 mins in a background pressure of less than 1×10^{-9} Torr so that the hydrocarbon adsorption was carried out at or near 300 K. During the cooling period, the (111) surface was accurately positioned normal to the incident electron beam by using the threefold symmetry of the first-order diffraction beams. The azimuthal angle, $\phi = 0$, as defined by Jona⁽¹³⁾ was used for all measurements because the diffraction beam intensities have reflection symmetry through the line labelled k_x in Fig. 1 for all polar angles θ . This provides a more accurate azimuthal determination than by means of a mechanical or photographic position measurement.

After the cooling period the hydrocarbon of interest was leaked into the vicinity of the sample via a stainless steel needle pointed at the crystal and 4 cm from the surface. The vacuum chamber was pumped continuously at all times by a 240 ℓ /sec sputter ion pump and by freshly sublimed titanium. After a pressure rise of 0.8×10^{-9} Torr above the background, the leak was stopped. The total exposure was estimated to be about $1L = 10^{-6}$ Torr-sec. Although we could not measure the exposure accurately, a given pressure rise from the leak resulted in an overlayer diffraction pattern of reproducible quality and intensity. All the adsorptions were performed without the electron beam striking the surface.

The adsorption of purified acetylene on Pt(111) at 300 K as described above resulted in an ordered (2x2) acetylene structure which we refer to as

metastable acetylene. Upon heating the Pt(111) sample with the metastable acetylene overlayer for one hour at 350-400 K, then allowing the sample to cool to 300 K or letting it stand for 24 hrs at 300 K, there was no change in the (2×2) diffraction pattern. However, the LEED intensity profiles showed marked changes from the intensities measured for the metastable acetylene (see Fig. 3) indicating that a structural transformation had occurred. We shall refer to this latter structure as stable acetylene. The two acetylene structures will be discussed in more detail later in this paper.

The adsorption of ethylene was carried out under the same conditions of exposure and temperature as for acetylene. However, ethylene adsorption did not immediately give an ordered structure but required some electron beam exposure before a (2×2) diffraction pattern was obtained which was identical to the acetylene diffraction pattern. The electron beam exposure necessary for the appearance of the (2×2) diffraction pattern was $\sim 50 \mu \text{ amp-sec-mm}^{-2}$ for 60 eV electrons.

(c) Intensity measurement

After the vacuum chamber pressure had returned to the background level ($\sim 1 \times 10^{-9}$ Torr), the crystal was rotated to the desired polar angle as measured by the angular scale engraved on the sample manipulator. Photographs were taken from 10 eV to 200 eV in 2 eV intervals using the camera and film described before⁽⁵⁾ with an aperture set at f 1.8 and a shutter speed of 1/2 sec. This is 1/2 the exposure time reported before.⁽⁵⁾ The reproducibility was checked only up to 100 eV for reasons which will be discussed later.

The influence of electron beam exposure on the diffraction pattern resulting from both acetylene structures as well as the ethylene adsorbate was investigated in order to determine the extent to which this might affect the intensity measurement. For 60 eV electrons, an exposure of $\sim 700 \mu \text{ amp-sec-mm}^{-2}$ was necessary for all three hydrocarbon structures to reduce the intensity of the $(\frac{11}{22})$ beam (see Fig. 1) to one-half its initial value.

By means of a modification in the LEED power supply we were able to deflect the electron beam in such a way that the electrons could not escape the electron gun. This allowed us to limit the overlayer electron beam exposure to the time when the camera was actually taking a picture without disturbing the stability of the electron gun filament or focussing electrodes. The total electron beam exposure was approximately $60 \mu \text{ amp-sec-mm}^{-2}$ for a complete set of pictures up to 200 eV. Based on the electron beam sensitivity measured above, the intensities should not change by more than $\sim 5\%$ during the measurement.

Finally, the incident electron beam current was measured at each energy where pictures were taken to permit the normalization of the intensity profiles to a constant beam current of $1 \mu \text{ amp}$. The film developing, film scanning and the computer analysis of the scans necessary for reducing the photographs to I-V curves have been described elsewhere. (5)

RESULTS

(a) Acetylene adsorption

Acetylene adsorbs on the Pt(111) crystal face at room temperature spontaneously forming an ordered (2x2) structure at exposures of $1L = 10^{-6}$ Torr-sec or less. Because of the low exposure and the weak acetylene intermolecular interactions the adsorbed gas is believed to form only a single layer over the clean metal. The diffraction pattern characteristic of the (2x2) structures is shown in Fig. 2. The background is very low and the spot size of the fractional order beams is the same as for the clean platinum integral order beams implying that the ordered domains are larger than the coherence width of the incident electron beam, $\sim 100 \text{ \AA}$. The diffraction pattern intensities are threefold symmetric at normal incidence indicating that the surface must contain equal amounts of domains where the acetylene is rotated by 120° between domains. This follows since the acetylene molecule itself would not have threefold symmetry if it is lying parallel to the surface as proposed in the companion paper.⁽⁷⁾

As mentioned above, by heating the sample gently to 350-400K followed by cooling to 300 K, no change in the diffraction pattern can be observed, but the intensity profiles change with respect to the metastable acetylene first adsorbed at 300 K. An example of the kinds of changes observed are shown in Fig. 3. Note that the structure of the intensity curves is quite different in the number of peaks and their position in energy as well as in the relative intensity of the peaks that occur at the same energy in both curves. Changes such as these can be observed between the two acetylene structures

throughout the data in the appendix and are the basis for distinguishing the two structures. It is also important to note that for the diffraction beams which show significant modulation of their intensity above 100 eV, there are no significant differences between the intensity profiles for the two acetylenic states in this energy range. We were never able to reconvert the stable acetylene structure to the metastable acetylene, and the metastable to stable transformation was not enhanced by exposure to the electron beam. Heating either the metastable or stable acetylene overlayer much above 400 K caused the destruction of the ordered (2x2) diffraction pattern. This indicates that further chemical-structural changes are taking place. The changes cannot be well-characterized by Low-Energy Electron Diffraction, but may involve some sort of decomposition of the molecular structure in the overlayer.

Both acetylene structures were extremely sensitive to further exposure to fluxes of either acetylene or ethylene. An additional hydrocarbon dose corresponding to a pressure rise of 0.1×10^{-9} Torr was sufficient to completely disrupt the ordered (2x2) structure, or if the initial dosing was too large the ordered structure would form, reach a maximum brightness and then begin to fade. This is in agreement with previous results and has been interpreted as a disordering of the first layer by adsorption of the excess acetylene into first layer interstitial sites. (10)

If acetone-contaminated acetylene is adsorbed on the (111) surface, the ordering is severely impaired. Only very faint, diffuse fractional order diffraction beams are observed. Upon exposure to the incident electron beam, however, the fractional order beams are observed to sharpen

and brighten with prolonged exposure, but this ordering takes place only at those areas on the crystal where the electron beam has been impinging. If the acetone-contaminated sample is heated in the usual way to produce the stable acetylene structure, the stable structure is observed on the ordered region of the sample. Following the heat treatment, areas of the crystal surface which have not been exposed to the electron beam still show only the diffuse fractional order diffraction beams. Under electron beam exposure the unexposed surface again orders into the sharp (2x2) diffraction pattern, but this time the overlayer is stable acetylene as determined from the intensities. Apparently the acetone prevents the acetylene surface diffusion which is necessary to spontaneously form the ordered (2x2) structure. However, under the electron beam the acetone and/or acetylene is mobilized enough for surface diffusion to occur. Also, the transformation from metastable acetylene to stable acetylene is independent of whether the overlayer is well-ordered or not, and the molecules in both of the structures are mobile under the electron beam.

(b) Ethylene adsorption

Ethylene adsorbs on the Pt(111) surface under conditions identical to the acetylene adsorption and is thought to form only a single layer under these conditions. Unlike acetylene, ethylene does not form an ordered (2x2) structure spontaneously upon adsorption. As mentioned above, some exposure to the electron beam is necessary for the ordered (2x2) structure to appear, and the ordering takes place only at the locations on the sample which have been exposed to the electron beam. The diffraction pattern which is formed is the equal of acetylene for brightness and sharpness, but

it is not nearly so sensitive to further exposure to either acetylene or ethylene in agreement with prior work.⁽¹⁰⁾

Merrill et al.^(9,10) have proposed that ethylene dehydrogenates upon adsorption on the Pt(111) surface to form an acetylenic species and adsorbed hydrogen atoms. The intensity profiles from ordered ethylene confirm this proposal. As can be seen by perusal of the appendix, the ethylene I-V curves are virtually identical to the stable acetylene I-V curves, indicating the formation of the acetylenic species. The surface hydrogen formed with the acetylenic species apparently acts to prevent adsorption of additional acetylene or ethylene into first layer interstitial sites lowering the ordered overlayer sensitivity to hydrocarbon exposure. The hydrogen may also prevent spontaneous ordering of the acetylenic species in perhaps the same way as acetone does with unpurified acetylene.

(c) Intensity measurements

The diffraction intensities from both acetylene structures and from ethylene were measured at normal incidence and at polar angles, θ , of 4° , 10° and 16° to provide an extensive data base for structure analysis. The acetylene intensities were also measured at one additional polar angle, $\theta=8^\circ$. The intensities are presented in the appendix in the usual form of normalized intensity vs. incident electron beam energy.

While as many as twenty-seven diffraction beams are within the camera field of view at one time, most of these are either too dim to be detected by the film, or they have intensity curves without any structure. Therefore, only the brightest diffraction beams with an abundance of intensity structure

are reported. The diffraction beam labelling follows Jona's convention⁽¹³⁾ as shown in Fig. 1. The intensity scales are in arbitrary units; however, the same units are used for all curves and each curve has been normalized to an incident electron current of 1μ amp. Gaps in the curves occur whenever the spot intensity falls below the threshold of the film. Since at lower energies the incident electron current is reduced, the threshold occurs at higher normalized intensity. There are also gaps in the profiles whenever the diffraction beam is obscured from the camera's view by the sample holder. This happens with the $(\bar{1}0)$ beam at 76 eV for $\theta = 10^\circ$ and between 46 eV and 120 eV for $\theta = 16^\circ$.

The energy range below 100 eV is the most sensitive to the presence of the hydrocarbon overlayer. At higher energies as the ratio of carbon to platinum scattering cross-sections decreases⁽¹⁴⁾ one might expect the platinum substrate to dominate and obscure the scattering due to the overlayer. An increase in the penetration depth of the incident electrons may also contribute to the predominance of Pt scattering. An inspection of the intensity curves above 100 eV for the two acetylene structures shows them to be nearly identical with regard to peak position and shape even in the fractional order beams. The profiles of the integral order beams at these higher energies are identical to those from clean platinum. Only differences in absolute intensity are evident. Below 100 eV, however, we can observe substantial changes which distinguish the two structures. Because of the long times necessary to scan the film for each angle (~ 30 hrs), as well as the similarity between structures above 100 eV, checks on the reproducibility of the intensity curves were restricted

to the lower energies. The dotted curves on the intensity profile Figures indicate the results of repeat measurements. We feel that the reproducibility, while not perfect, is certainly sufficient to permit a structural determination within the accuracy which the present theories are capable. In addition, these checks permit an evaluation of which structural differences in the I-V profiles can be attributed to experimental error and which are due to a bonafide physical change in the surface. This is an important consideration which has not been included in previous reportings of intensity measurements.

DISCUSSION

Acetylene

A discussion of the important differences between the intensity profiles from the two acetylene structures was given previously.⁽⁸⁾ Briefly, the dramatic changes we observe, the disappearance and appearance of major peaks in the intensity profiles from one structure to another, indicate a major change in the chemical state of acetylene bound to the platinum surface. This is yet another example of the richness and diversity exhibited by the hydrocarbon chemistry at the vapor-solid interface.

Since the Low-Energy Electron Diffraction intensities are sensitive primarily to the inter-planar spacing normal to the surface,⁽⁷⁾ the metastable to stable acetylene transformation probably involves a change in the distance from the carbon overlayer to the first platinum layer. Changes in the spacings of the topmost platinum layers are ruled out since none of the intensity profiles show changes above 100 eV where the platinum scattering is dominant (see above). This implies a change in the carbon-platinum bonding, and therefore, a concomitant change in the carbon-carbon bond. An attractive model is that the metastable to stable transformation involves an increase in carbon-platinum bonding and a decrease in the carbon-carbon bonding in the acetylene molecule. From the temperature dependence of the rate of metastable to stable transformation, the process is seen to be activated. According to the above model, the activation barrier may be due to the energy required to reduce the carbon-carbon bond order. There may also be a contribution to the barrier from some reduction in a platinum-platinum bond order. However, the results from ethylene adsorption favor the carbon-carbon bond reduction as the major cause of the activation energy.

The structure and chemical bonding of these states are being studied by a dynamical structure calculation⁽⁷⁾ but have not yet been completely resolved. However, it appears that neither structure involves completely dehydrogenated species such as isolated carbon atoms or carbon dimers. This results comes from the following argument: At high temperature (~1100 K) the hydrocarbon overlayers are not desorbed but form rotationally disordered domains of the graphite which is then stable at lower temperatures. If the stable acetylene structure was composed of either carbon dimers or single carbon atoms, the high temperature would then serve only to break the carbon-platinum bonds allowing surface diffusion of the carbon and consolidation into graphite. However, from the results obtained on adsorbing acetylene contaminated with acetone, we see that when either of the acetylene structures is mobilized by the electron beam, inducing surface diffusion, only the ordered (2x2) overlayer is formed and not graphite. We propose that the acetylene structures must have carbon species which are at least partially hydrogenated.

Ethylene

As mentioned above, in comparing the intensities from the ethylene ordered overlayer to those from acetylene we see that ethylene and the stable acetylene structure are virtually identical. This supports the model proposed by Merrill et al. that ethylene dehydrogenates on the Pt(111) surface to form an acetylenic species and chemisorbed hydrogen atoms.^(9,10) Assuming that we actually have acetylene and hydrogen on the surface the

question arises as to why the acetylene that forms from dehydrogenation of ethylene takes the form of the stable species and never the metastable species. If the activation barrier to formation of the stable acetylene structure is due to a required reduction in the carbon-carbon bond order as proposed above, then the activation barrier for ethylene would be reduced or even eliminated because the carbon-carbon bond order is already reduced or even eliminated because the carbon-carbon bond order is already reduced as compared to acetylene. The ethylene then dehydrogenates directly into the stable acetylenic structure at 300K, and the carbon-carbon bond order reduction is seen to be the major factor in the activation barrier for the acetylene metastable to stable transformation.

ACKNOWLEDGMENT

We would like to thank L. L. Kesmodel for many useful discussions. This work was done under the auspices of the U. S. Energy Research and Development Administration.

REFERENCES

- (1) J. A. Strozier, D. W. Jepsen, F. Jona, Surf. Phys. of Mat. 1, 1-77 (1975).
- (2) A. E. Morgan and G. A. Somorjai, J. Chem. Phys. 51, 3309(1969).
- (3) J. L. Gland, Ph.D. Thesis, Department of Chemistry, University of California, Berkeley (1973).
- (4) L. E. Firment, Ph.D. Thesis, Department of Chemistry, University of California, Berkeley (1976).
- (5) P. C. Stair, T. J. Kaminska, L. L. Kesmodel and G. A. Somorjai, Phys. Rev. B 11, 623 (1975).
- (6) L. L. Kesmodel, P. C. Stair, R. C. Baetzold and G. A. Somorjai, Phys. Rev. Lett. 36, 1316 (1976).
- (7) L. L. Kesmodel, R. C. Baetzold and G. A. Somorjai, LBL-5407, companion paper.
- (8) P. C. Stair and G. A. Somorjai, to be published in Chem. Phys. Lett.
- (9) O. S. Smith and R. P. Merrill, J. Chem. Phys. 52, 5861 (1970).
- (10) W. H. Weinberg, H. A. Deans and R. P. Merrill, Surf. Sci. 41, 312 (1974).
- (11) J. J. Wasilczyk, M. S. Thesis, Department of Chemistry, University of California, Berkeley (1973).
- (12) R. W. Joyner, J. S. Gland and G. A. Somorjai, Lawrence Berkeley Laboratory, Report LBL-414 (1971).
- (13) F. Jona, I. B. M. J. Res. Develop. 14, 444 (1970).
- (14) L. L. Kesmodel, Private communication.

FIGURE CAPTIONS

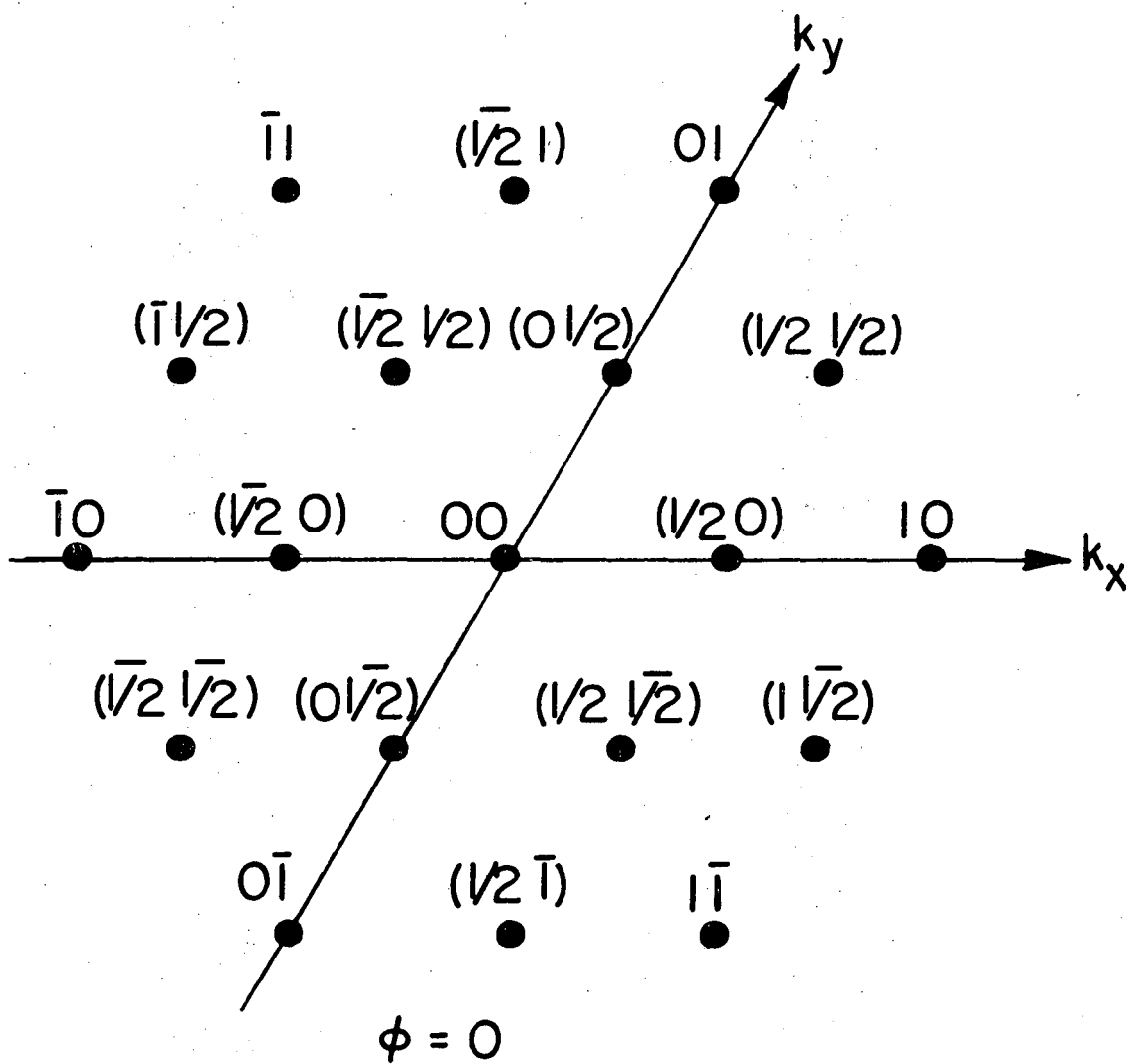
- Fig. 1. Diffraction beam labelling for the (2×2) -Pt(111) diffraction pattern following the convention of Jona (Ref. 13).
- Fig. 2. Low-Energy Electron Diffraction patterns from the clean platinum (111) crystal face (above) and the acetylene on platinum overlayer (below). Both pictures are for normal incidence and 68 volts.
- Fig. 3. I-V profiles of the $(\frac{1}{2} 0)$ beam at $\theta = 4^\circ$, $\phi = 0^\circ$ from the metastable acetylene structure (—) and the stable acetylene structure (•••••). The large dot indicates the point of scaling factor change.

APPENDIX

The appendix contains the complete set of intensity vs. incident electron energy, (I-V), curves from metastable acetylene, stable acetylene and ethylene adsorbed on the platinum (111) crystal face. The intensity scales are all the same, and all the curves have been normalized to a constant incident electron current of 1μ amp. The dotted lines indicate the reproducibility of the data. The large dots indicate the points of scaling factor changes.

A-Figure Captions

- Fig. A1. I-V profiles from the metastable acetylene structure at normal incidence.
- Fig. A2. I-V profiles from the metastable acetylene structure at $\theta = 4^\circ$.
- Fig. A3. I-V profiles from the metastable acetylene structure at $\theta = 8^\circ$.
- Fig. A4. I-V profiles from the metastable acetylene structure at $\theta = 10^\circ$.
- Fig. A5. I-V profiles from the metastable acetylene structure at $\theta = 16^\circ$.
- Fig. A6. I-V profiles from the stable acetylene structure at normal incidence.
- Fig. A7. I-V profiles from the stable acetylene structure at $\theta = 4^\circ$.
- Fig. A8. I-V profiles from the stable acetylene structure at $\theta = 8^\circ$.
- Fig. A9. I-V profiles from the stable acetylene structure at $\theta = 10^\circ$.
- Fig. A10. I-V profiles from the stable acetylene structure at $\theta = 16^\circ$.
- Fig. A11. I-V profiles from the ordered ethylene structure at normal incidence.
- Fig. A12. I-V profiles from the ordered ethylene structure at $\theta = 4^\circ$.
- Fig. A13. I-V profiles from the ordered ethylene structure at $\theta = 10^\circ$.
- Fig. A14. I-V profiles from the ordered ethylene structure at $\theta = 16^\circ$.



XBL 767-7147

Fig. 1

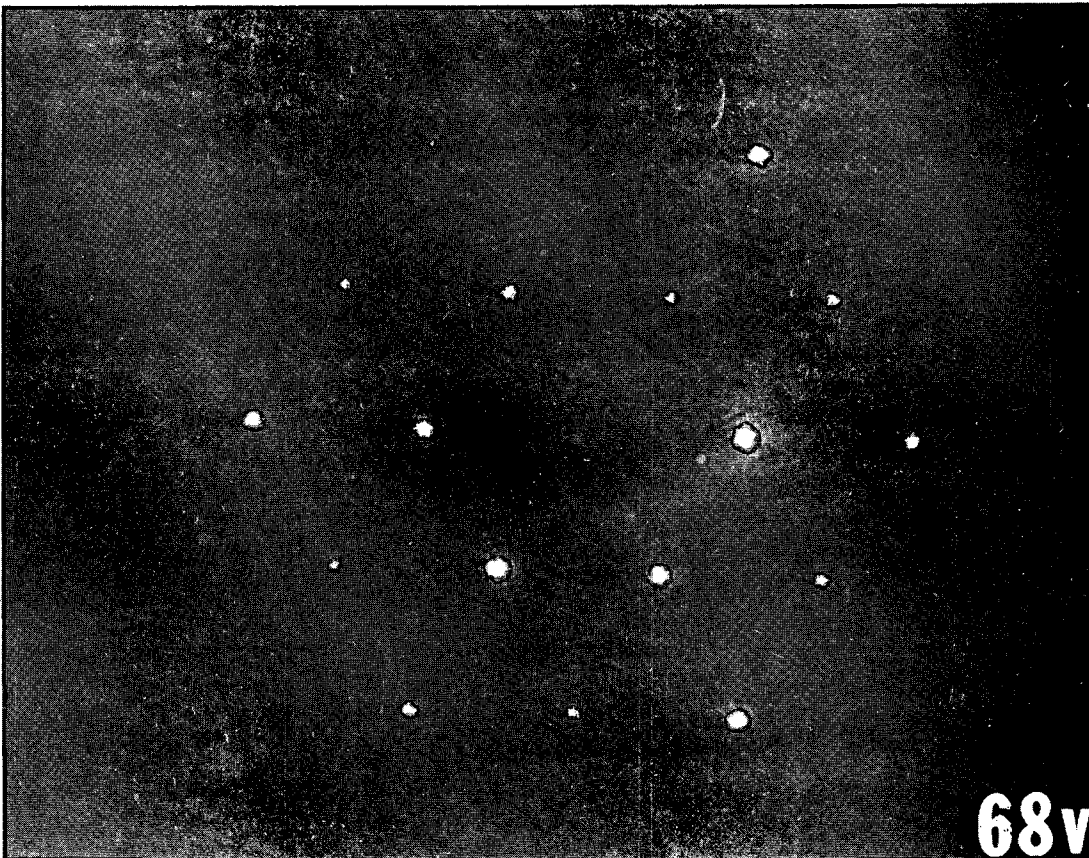
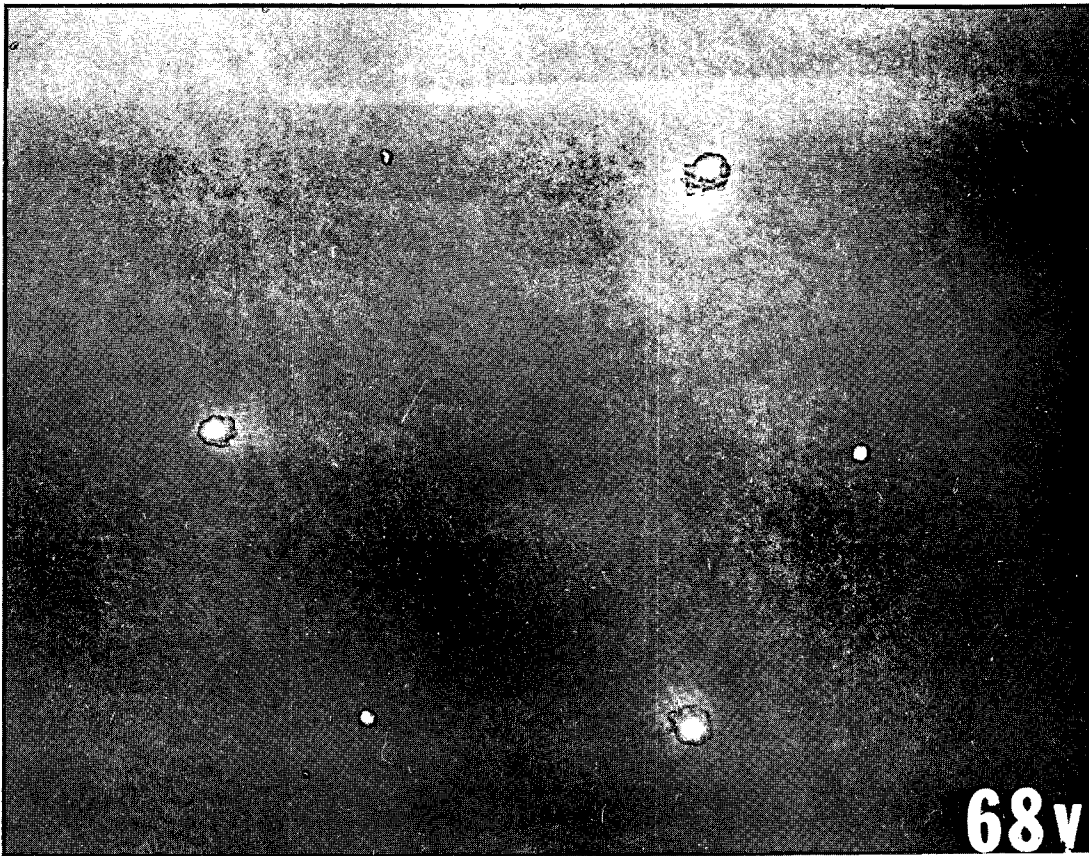
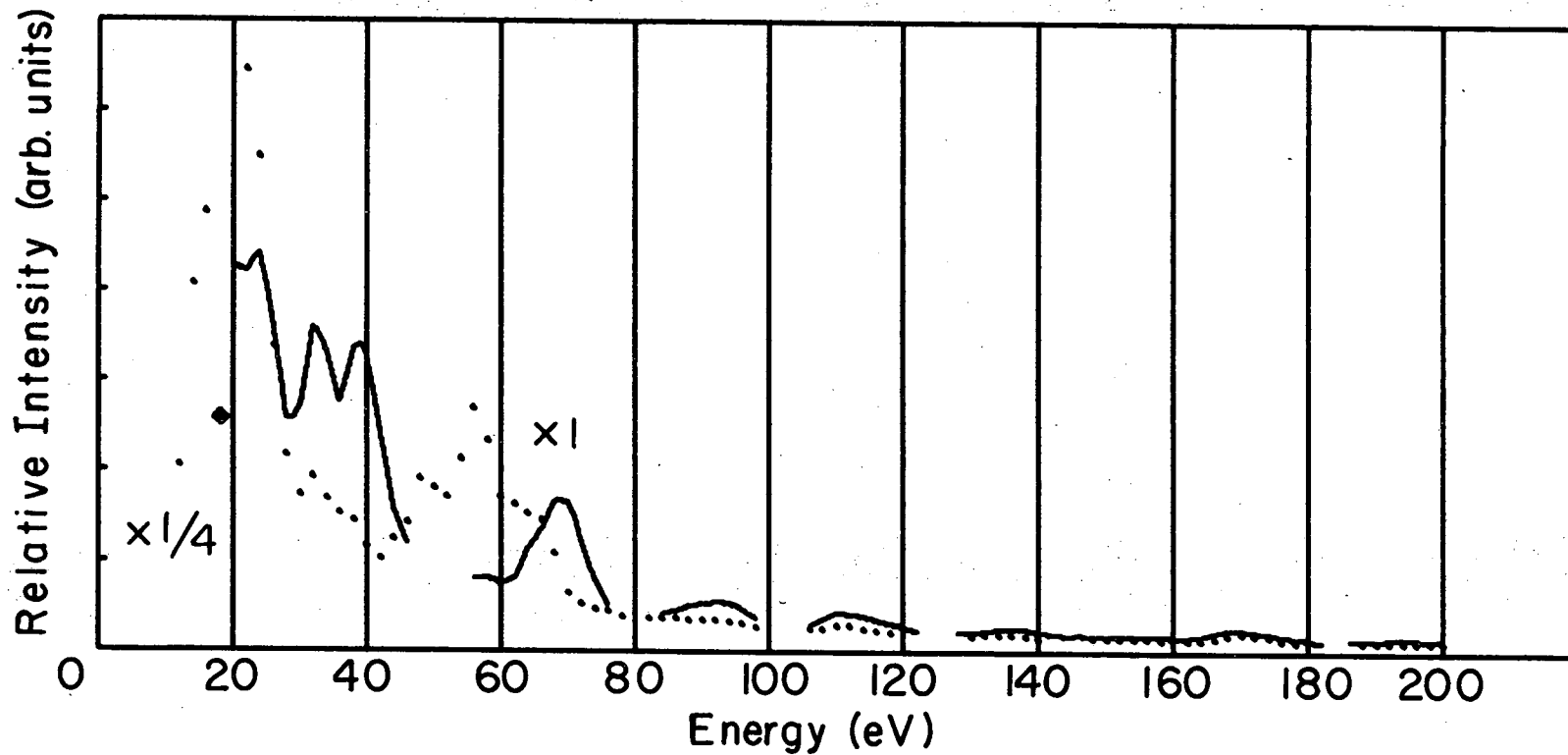


Fig. 2

XBB 763-2777

ACETYLENE ON Pt(III) - (1/2 0) BEAM

$\theta = 4$ $\phi = 0$ $T = 300$ K

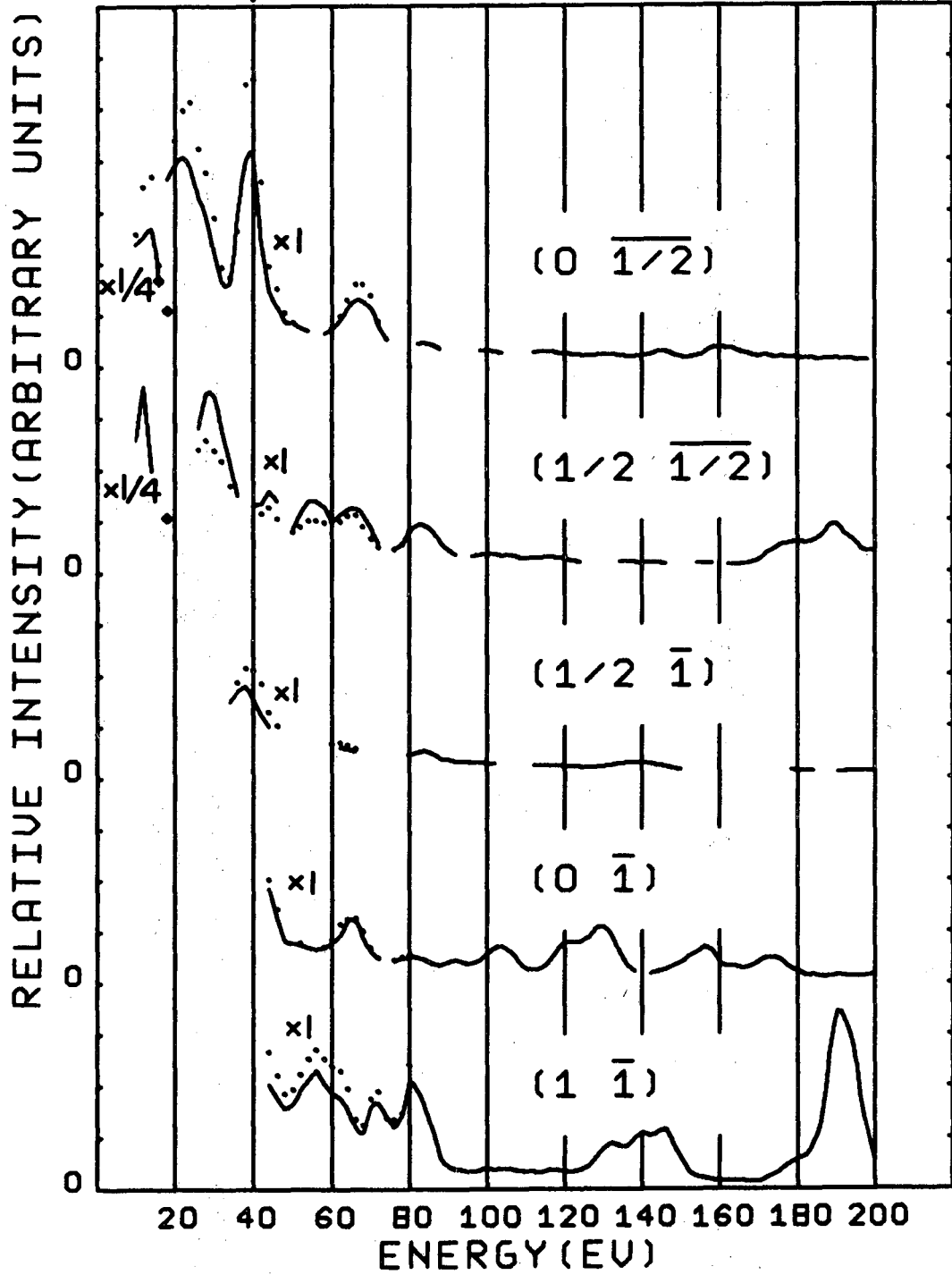


XBL 767-7207

Fig. 3

METASTABLE ACETYLENE-PT(111)

$\theta=0$ $\phi=0$ T=300K

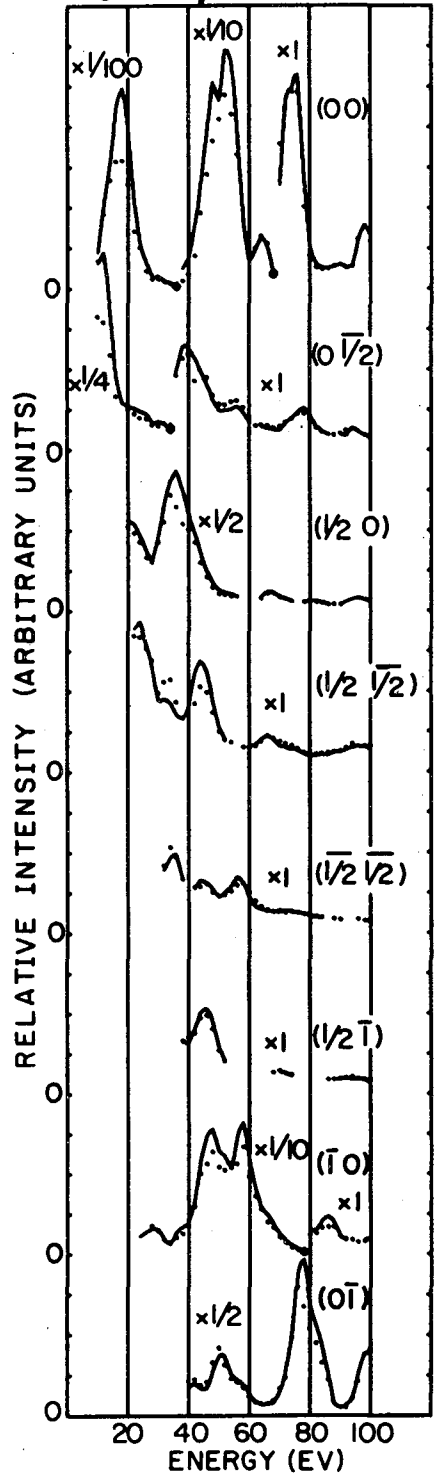


XBL 767-7148

Fig. A1

METASTABLE ACETYLENE - PT (III)

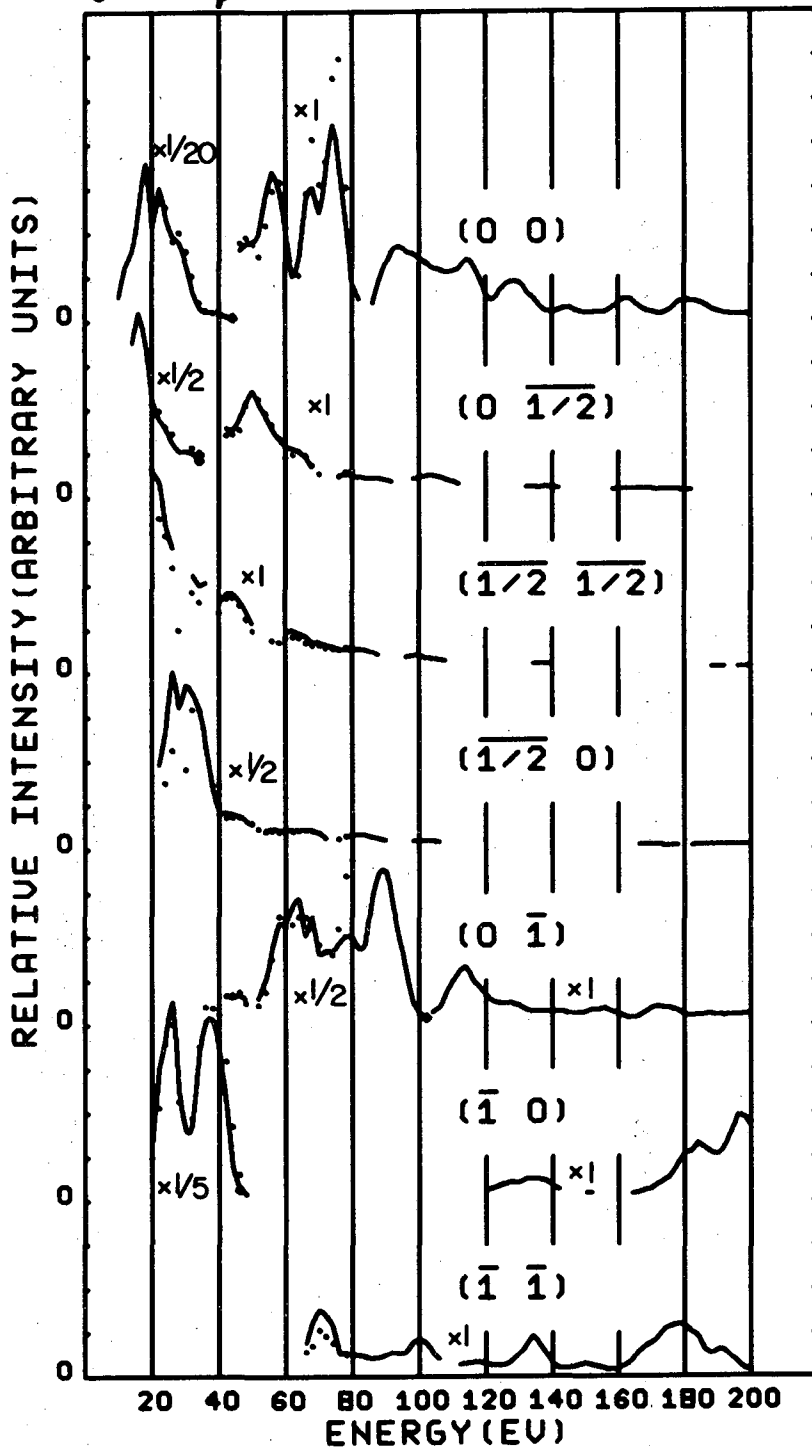
$\theta = 8$ $\phi = 0$ $T = 300K$



XBL 767-7150

Fig. A3

METASTABLE ACETYLENE-PT(111)
 $\theta=16$ $\phi=0$ $T=300K$

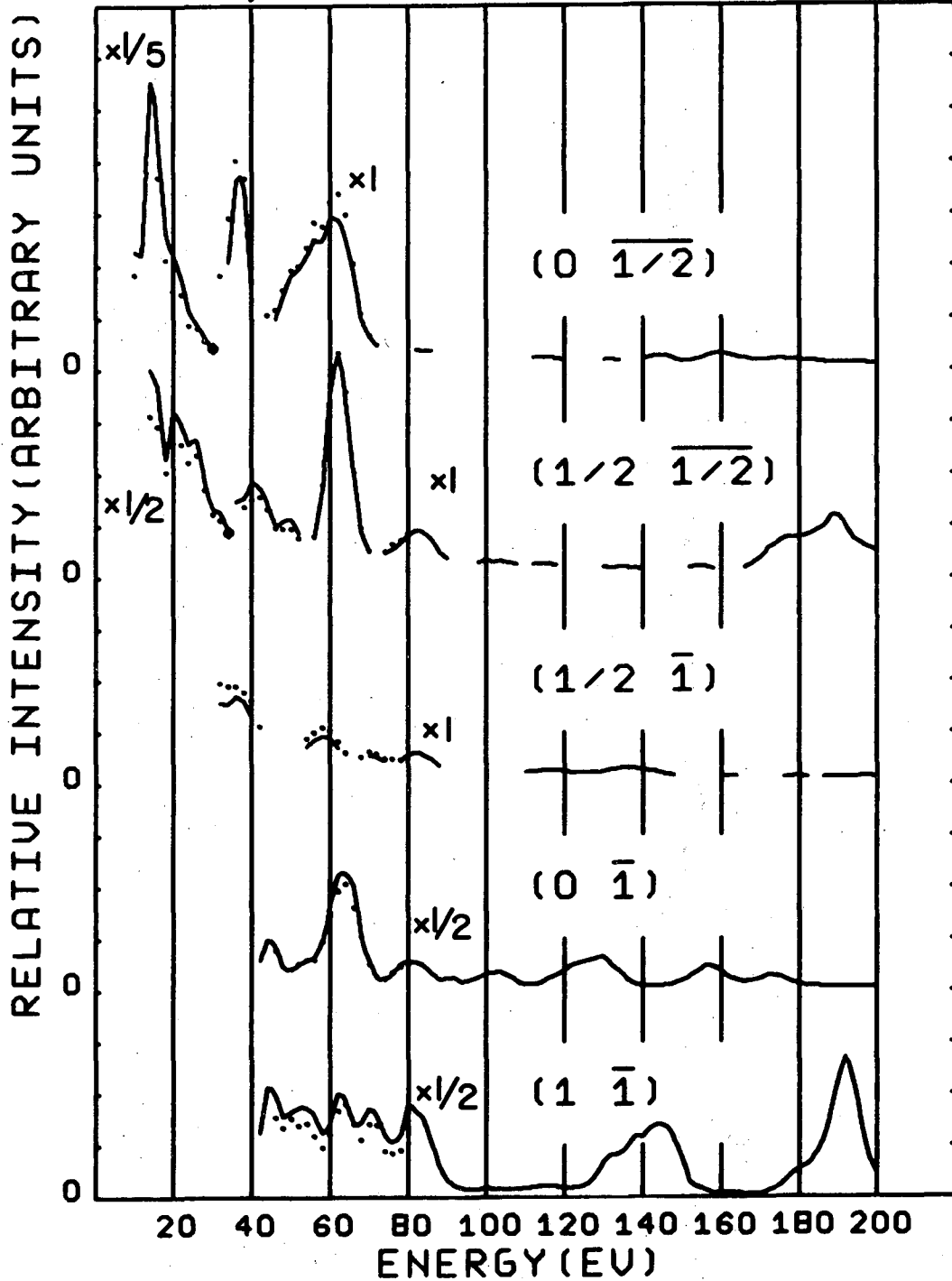


XBL 767-7152

Fig. A5

STABLE ACETYLENE-PT(111)

$\theta=0$ $\phi=0$ T=300K

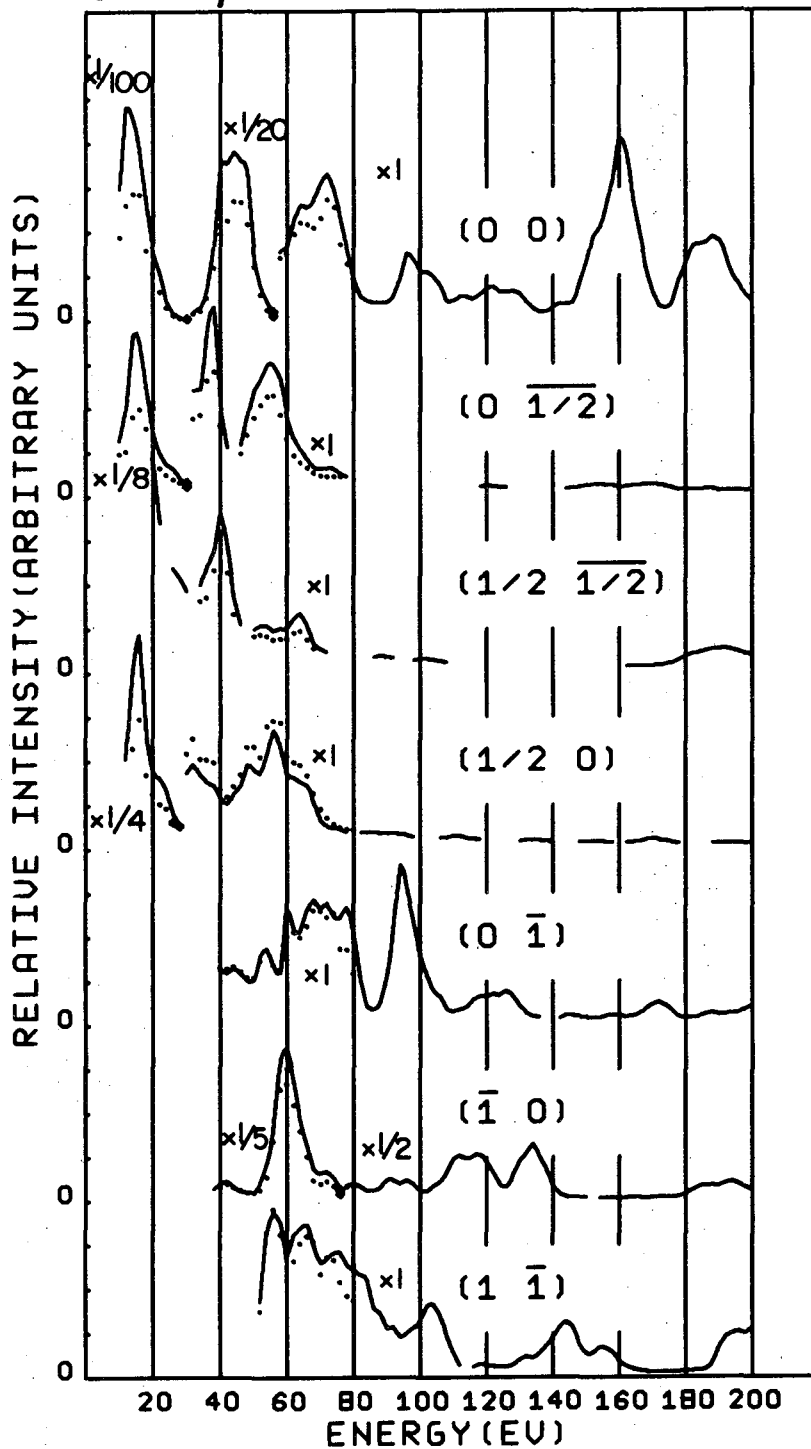


XBL 767-7153

Fig. A6

STABLE ACETYLENE-PT(111)

$\theta=4$ $\phi=0$ T=300K



XBL 767-7154

Fig. A7

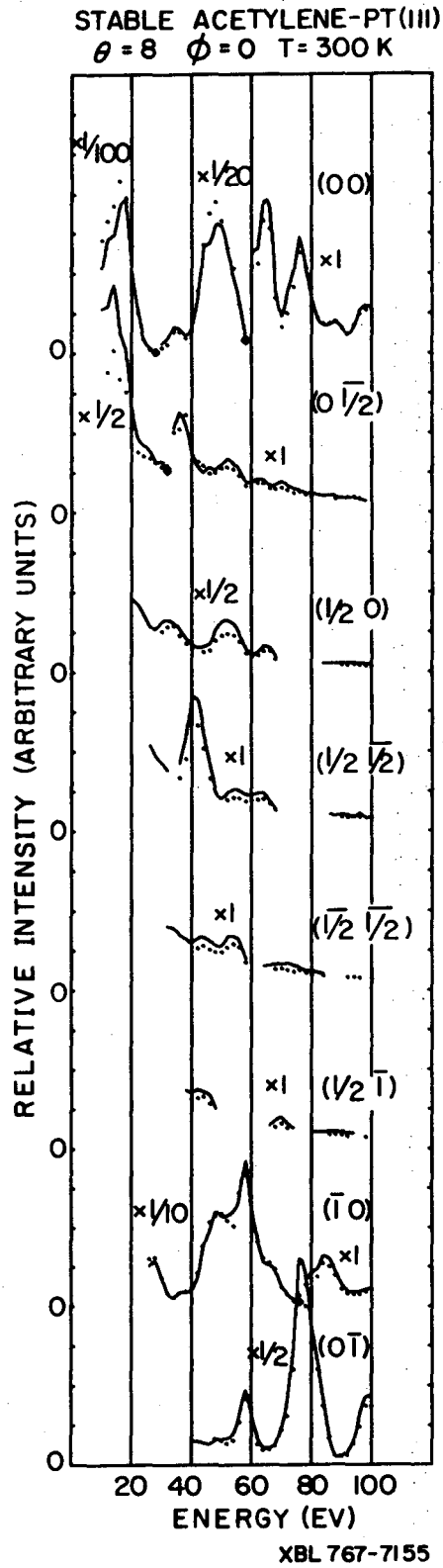
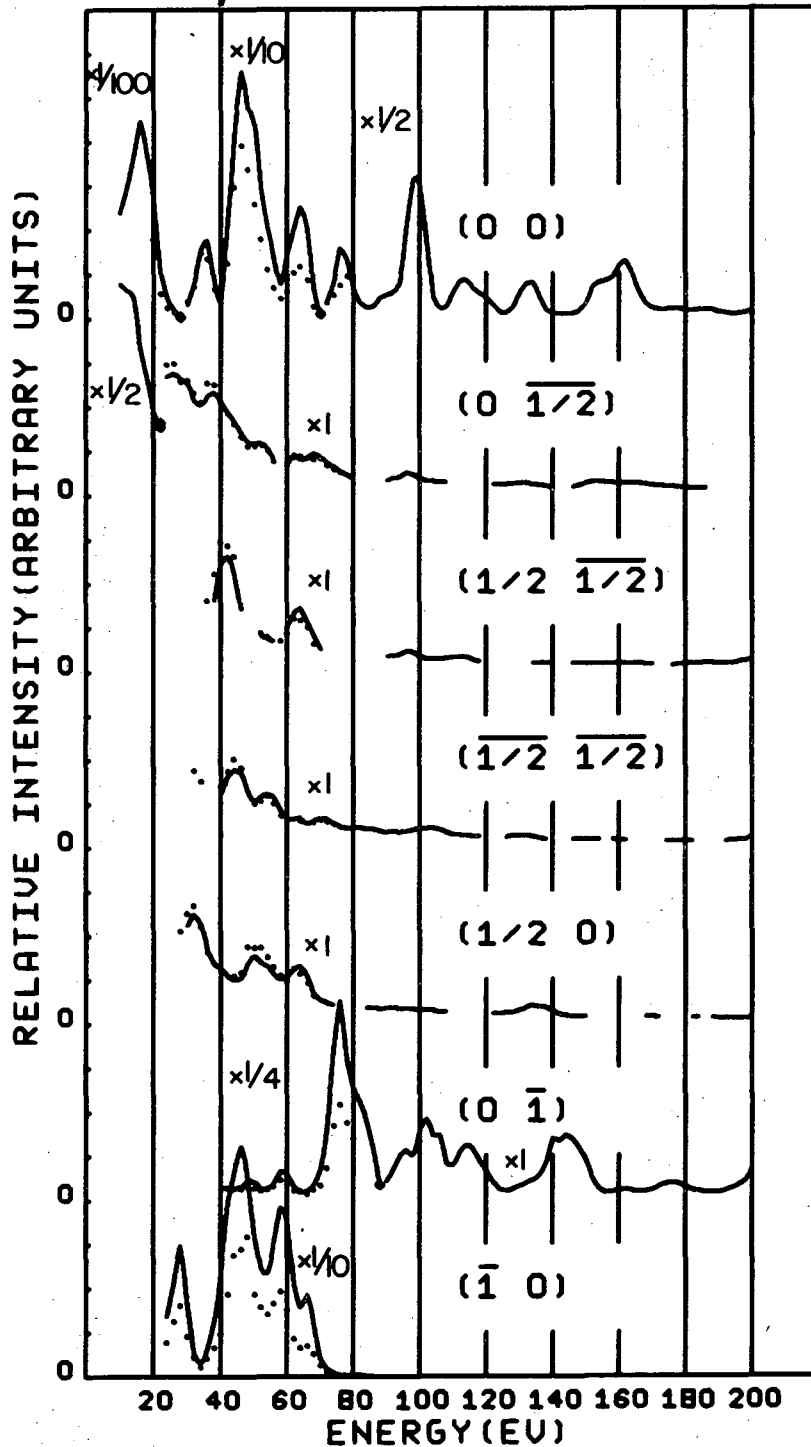


Fig. A8

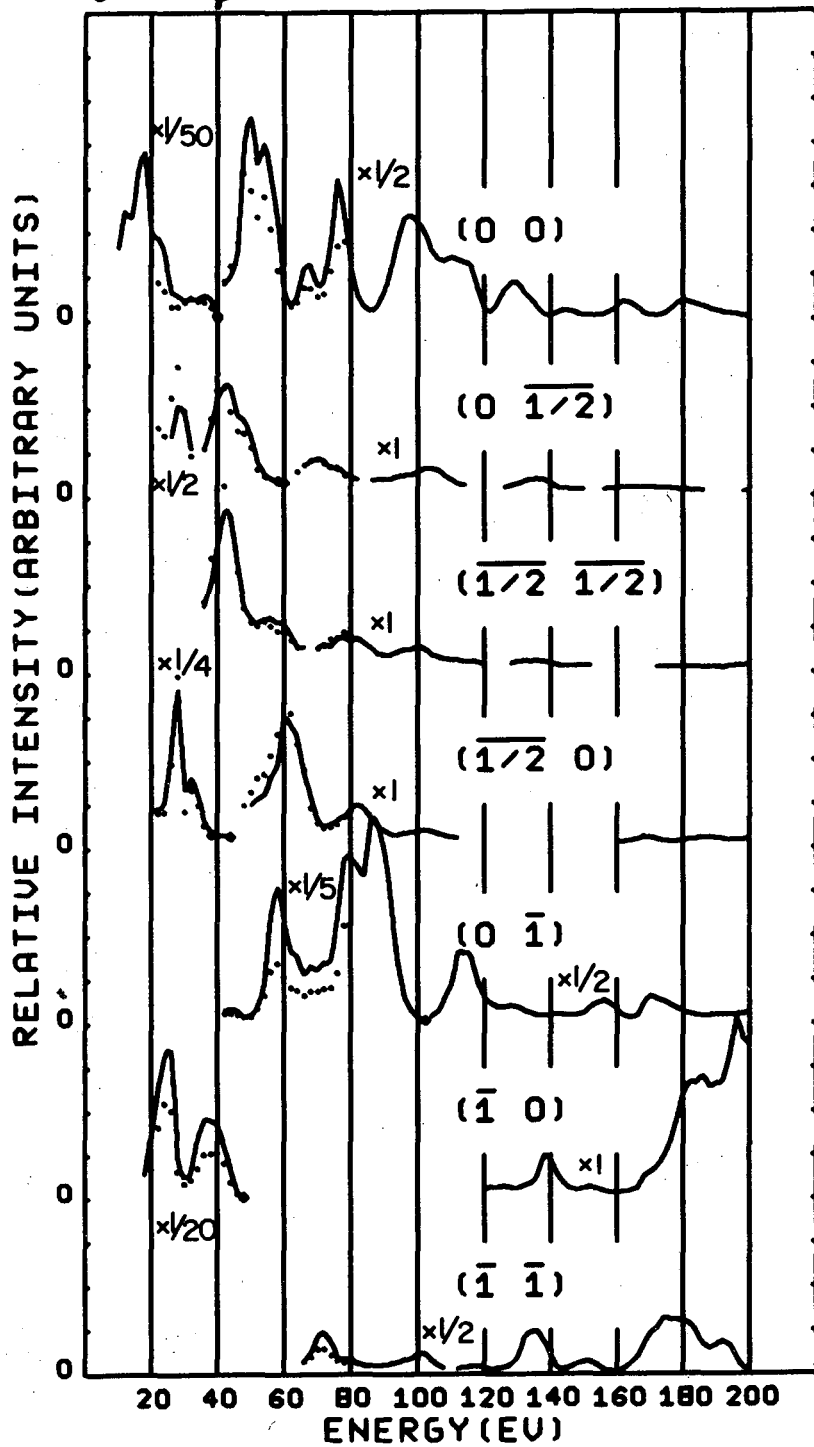
STABLE ACETYLENE-PT(111)
 $\theta=10$ $\phi=0$ $T=300K$



XBL 767-7156

Fig. A9

STABLE ACETYLENE-PT(111)

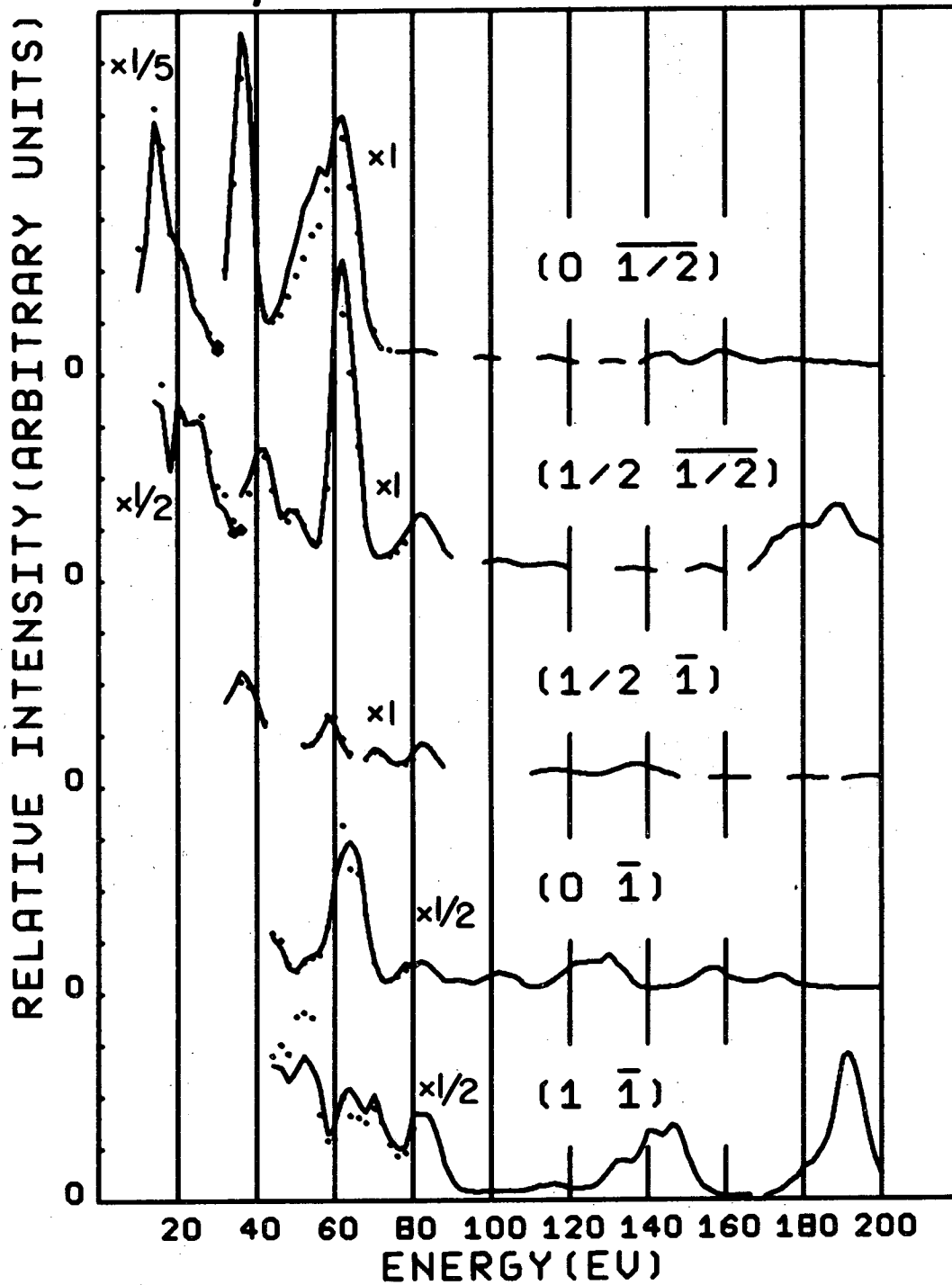
 $\theta=16^\circ \phi=0^\circ T=300\text{K}$ 

XBL767-7157

Fig. A10

ETHYLENE ON PT(111)

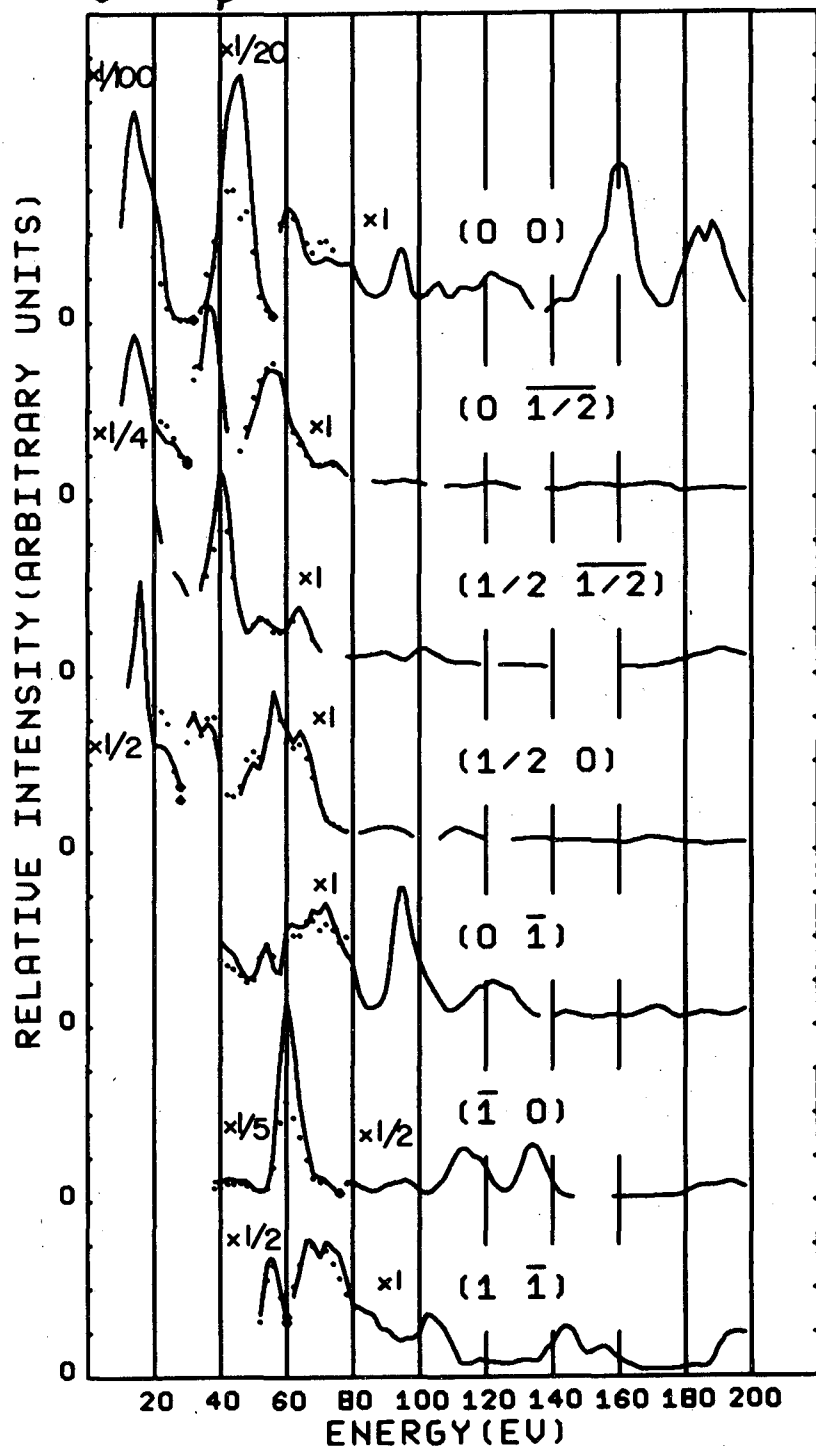
$\theta=0$ $\phi=0$ T=300K



XBL 767-7158

Fig. All

ETHYLENE ON PT(111)

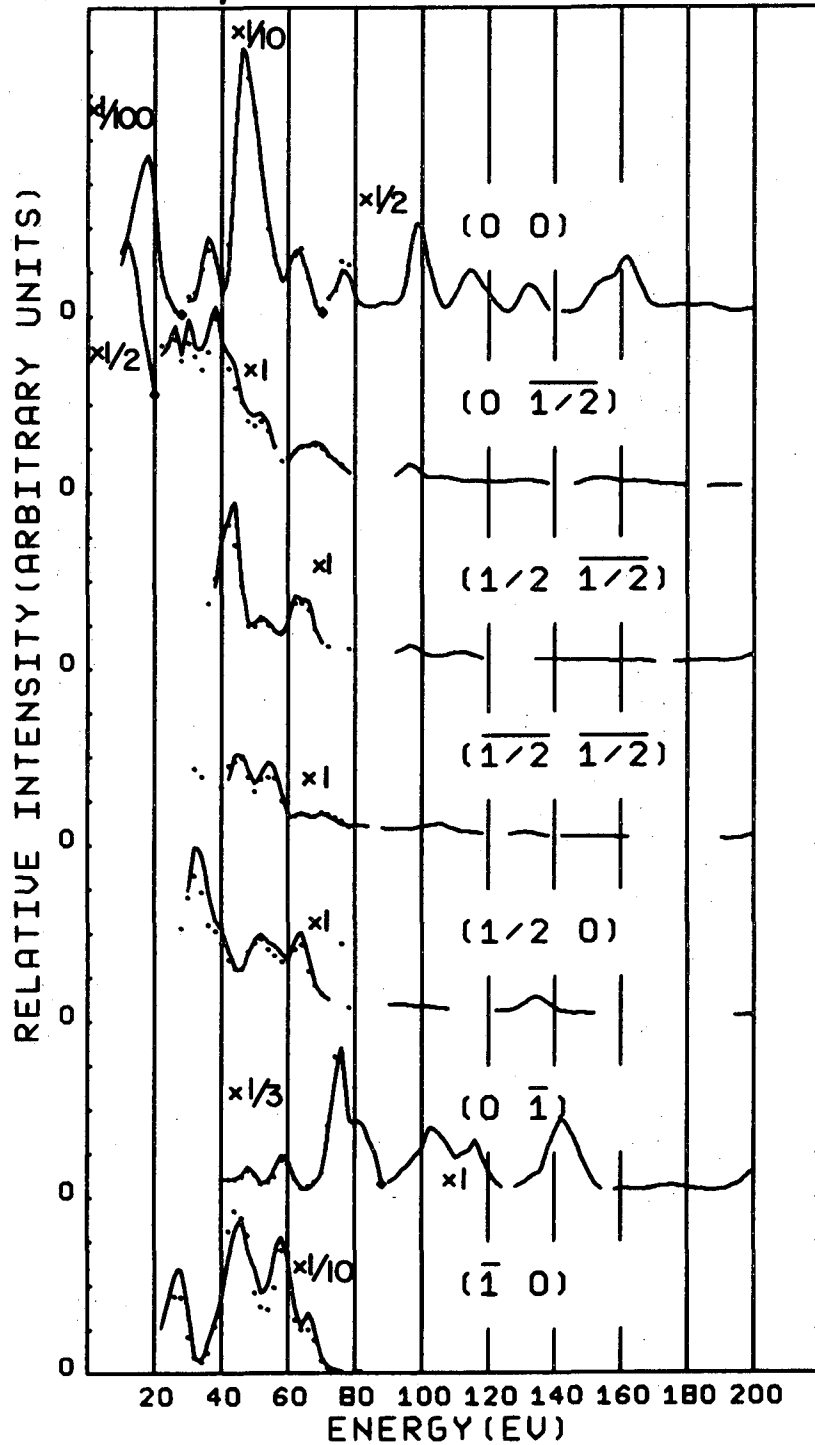
 $\theta=4$ $\phi=0$ $T=300\text{K}$ 

XBL 767-7159

Fig. A12

ETHYLENE ON PT(111)

$\theta=10$ $\phi=0$ $T=300K$



XBL 767-7160

Fig. A13

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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