VALENCE BANDS OF ORIENTED FINITE LINEAR CHAIN MOLECULAR SOLIDS

AS MODEL COMPOUNDS OF POLYETHYLENE STUDIED BY ANGLE-RESOLVED PHOTOEMISSION

by

K. Seki, N. Ueno, U.O. Karlsson, R. Engelhardt

Hamburger Synchrotronstrahlungslabor HASYLAB at DESY

E.E. Koch

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

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Model Compounds of Polyethylene Studied by Angle-Resolved
Photoemission [1]

K. Seki[2], N. Ueno[3], U.O. Karlsson[4], R. Engelhardt[5]

Hamburger Synchrotronstrahlungslabor HASYLAB at DESY

Notkestr. 85, D-2000 Hamburg 52, Germany

and

E.E. Koch

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

Faradayweg 4-6, D-1000 Berlin 33, Germany

permanent addresses:

[2] Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

[3] Dept. of Image Science and Technology, Faculty of Engineering, Chiba 260,
Japan

[4] Dept. of Physics, Linköping University, S-58183 Linköping, Sweden,
now at IBM Thomas J. Watson Research Center, Box 218, Yorktown Heights,
NY 10 598, USA

[5] II. Institut für Experimentalphysik, Universität Hamburg, D-2000 Hamburg 50,
Germany

ABSTRACT

Angle-resolved photoemission spectra were measured using
synchrotron radiation of two kinds of oriented model compounds of
polyethylene with their molecular axes perpendicular to the
substrate surface, i.e. evaporated films of hexatriacontane
$CH_3(CH_2)_{34}CH_3$ and Langmuir-Blodgett films of Cd arachidate
$(CH_3(CH_2)_{17}COO)_2Cd$. Both films show similar photoelectron
energy distribution curves determined by the long-alkyl chain.
The intramolecular energy-band dispersion of polyethylene was
determined from the photon-energy dependence of the normal-
emission spectra. This is the first direct observation of an
energy-band dispersions in organic solids. The upper bands
formed by C 2p and H 1s electrons extend from 8.8 to 15.5 eV
below the vacuum level, and the deeper-lying bands originating
from C 2s electrons lie from 17.5 eV to 24.7 eV. The band
structure obtained is compared to results from XPS and ESR
studies. Furthermore, the experimentally determined band
structure is discussed in detail in view of theoretical
calculations for polyethylene. Ab initio and extended Hückel
calculations give a good description of the experimental results.

2

1. Introduction

The electronic structure of polyethylene $+CH_2+_n$ has been studied extensively, since (i) it is one of the prototype polymers and also a typical quasi-one-dimensional compound, (ii) the elucidation of its electronic strucuture is the basis for understanding the electronic structure of many derivative polymers (e.g. vinyl polymers), and (iii) such studies may be helpful for clarifying the breakdown mechanism of polyethylene as a widely-used insulating material [1]. On the theoretical side, McCubbin and Gurney [2] first discussed the electronic structure of polyethylene, and virtually all existing versions of band calculations for the valence bands of a polymer chain have been applied to polyethylene as a test polymer to examine their validity [3-41].

On the experimental side, ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) have been used to elucidate the valence electronic structure. Fujihira and Inokuchi [42] first determined the photoemission threshold of polyethylene by UPS. Wood et al. [16] and Delhalle et al. [22] studied the whole valence band structure by a combination of XPS with theoretical calculations, and assessed that the valence bands consist of upper C_{2p} + H_{1s} bands and deeper-lying C_{2s} bands. Further, the formation of an intrachain band from C_{2s} orbitals and its insensitivity to the long-range order were clearly demonstrated by the XPS studies of linear alkanes [43,44]. Information on conduction bands and disordered states have also been obtained by UPS [45-47], secondary electron emission spectroscopy [46,48-50], absorption spectra [51,52], and photoconduction [53,54].

There are, however, still challenging questions related to the valence electronic structure of an isolated planar-zigzag extended chain. Firstly, the photoionization cross section of C_{2p} derived bands at XPS energies is small, and the decreased sensitivity hampered a detailed study of the upper C_{2p} + H_{1s} bands, which are more important than the deeper-lying C_{2s} bands in discussing the electronic conduction and fundamental photoabsorption. Since UPS is more sensitive to C_{2p} derived orbitals and generally yields higher resolution than XPS, a precise study of the valence bands by UPS is highly desirable.

Secondly, UPS and XPS experiments on organic polymers gave so far only information on the density of states (DOS), while theoretical calculations offer more detailed information, e.g. the wavevector, k, dependence of the electron energy, the intrachain energy band dispersion relation E = E(k). Such energy-band dispersions are now routinely determined for metals, semiconductors, or adsorbed layers by angle-resolved UPS (ARUPS) techniques [55]. In organic solids, the weak van der Waals intermolecular interaction causes only a small intermolecular energy band dispersion of the order of 0.1 eV [56]. This is negligible compared with the large intramolecular dispersion of the order of 5 eV, due to the strong interatomic covalent bond within the chain. So, the determination of an intrachain E = E(k) dispersion should be possible for an oriented sample. Up to now, however, this technique has not yet been successfully

applied to organic polymers, because of the difficulty in preparing well-oriented samples suitable for ARUPS measurements.

Fortunately, such oriented samples can be obtained for polyethylene by using model compounds with sufficiently long alkyl chains. Normal alkanes constitute one group of such compounds. XPS results [43] and our recent ab-initio MO calculations [57] indicate that a normal alkane $n-CH_3(CH_2)_{n-2}CH_3$ with $n \gtrsim 12$ is sufficiently long to simulate the whole valence electronic structure of polyethylene. Alkanes are also largely free from difficulties encountered with a real polyethylene solid, namely the coexistence of crystalline and amorphous regions, chain folding, branching, and incomplete purity [58]. Such factors hamper a meaningful comparison with theoretical calculations. Alkanes can be evaporated to form oriented polycrystalline films, in which fully extended planar zig-zag chains are packed with their molecular axes perpendicular to the substrate surface [45]. A significant angular-dependence of photoemission spectra was actually observed in our previous UPS study of an evaporated film of $n-CH_3(CH_2)_{34}CH_3$ with a rare-gas resonance line, and the possibility of studying intermolecular band using such an oriented film was suggested [47]. The elucidation of the $E = E(k)$ relation was hampered, however, since no tunable light source was available.

Another class of excellent model systems of oriented polyethylene are Langmuir-Blodgett films (LB films) consisting of fatty acids and their metal salts. They can be assembled layer by layer to form planar two-dimensional sheets, with the molecular axes perpendicular to the substrate. Since the compounds forming LB films consist of a hydrophobic long-alkyl chain and a hydrophillic group, they can be regarded as a model of polyethylene when the contribution of the hydrophyllic part can be neglected. An almost complete molecular orientation is realized in such films, which is ideal for angle-resolved studies. Furthermore, the elucidation of the electronic structure of such films is interesting in itself, since they have recently attracted interest for developing new types of electronic devices [59,60], two-dimensional magnets [61], and as good models of biological membranes.

In this paper we report on ARUPS studies of (i) oriented films of hexatriacontane $n-CH_3(CH_2)_{34}CH_3$ prepared by in-situ vacuum evaporation, and of (ii) LB films of a simple carboxylic acid salt Cd arachidate $(n-CH_3(CH_2)_{17}CH_2COO)_2Cd$, using synchrotron radiation as a tunable light source. Both samples showed remarkable spectral changes depending on the photon energy, the incidence angle of the photon beam (E-field vector dependence), and the emission angle of the electrons. In particular from the photon energy dependence we are able to determine the intramolecular $E = E(k)$ dispersion. These are the first experimental observation of an energy band dispersion in an organic solid, which we have already reported briefly elsewhere [62,63]. In the present paper we will present a more comprehensive study, including more detailed results and a complete comparison with previous XPS spectra and available theoretical band-structure calculations.

2. Experimental Procedure

2.1. Samples and Measurements

The sample of n-$C_{36}H_{74}$ was supplied by Tokyo Kasei Co. Ltd.,
and was purified in 3 cycles of recrystallization from benzene
solution. The specimen was prepared as a film of $\sim$7 nm thickness
on a polished Cu substrate by in-situ evaporation in an ultrahigh-
vacuum (UHV) preparation chamber (base pressure 5×10^{-10} Torr)
and subsequently transferred to the photoelectron spectrometer
under UHV. Previous data from (i) X-ray diffraction of thicker
evaporated films on Cu [45] and (ii) vacuum-uv absorption spectra
from films of comparable thickness on LiF [52] showed that
oriented polycrystalline films are formed by evaporation with the
molecular axis perpendicular to the substrate surface, as shown
in Fig. 1(a).

Three and two monomolecular cadmium salt layers of arachidic
acid of Y-type were prepared on aluminium- and gold-covered glass
plates, respectively, as shown in Fig. 1(b). The method for film
preparation is described in Ref. [64]. For both cases, the
sample surface was covered by the oriented hydrocarbon chains.
The subphase (Millipore water pH 5.5) contained 4×10^{-4} M $CdCl_2$.
Thus the Cd salt is deposited on the support giving the film a
good stability. These samples were prepared and kindly given to
us by H. Möhwald. We note that the conformation of the alkyl
chain in both hexatriacontane and Cd arachidate is essentially
the same as that of polyethylene crystals [65] shown in Fig. 1(c).

Photoelectron spectra were measured for various angles of
incidence α of the photon beam, polar emission angles θ of the electrons
and azimutal emission angles $\emptyset$ of the electrons (see Fig. 2(a)) with an

apparatus at the storage-ring DORIS II in the Synchrotron
Radiation Laboratory HASYLAB at DESY [66]. The setup consists of
a 1 m Seya-Namioka type monochromator and a modified VG ADES 400
angle-resolving photoelectron spectrometer. The light intensity
impinging on the sample was monitored by measuring the
photoemission from an Au-coated diode placed between the exit
slit of the monochromator and the sample. Prolonged illumination
with intense light caused a change of the spectra for both
compounds, which is probably due to radiation damage. In order
to avoid this, the intensity was kept low with narrow slit width.
Furthermore, the spectra were recorded with frequent changes of
the sampling position on the specimen. The absence of damage was
confirmed by remeasuring spectra for a fixed combination of $h\nu$,
α, θ, and $\emptyset$ after several runs. By such a careful procedure,
spectra amenable for subsequent analysis were obtained.

2.2. Band Structure Mapping by $h\nu$-dependent Normal Emission

In this section we will briefly describe the method of
energy-band mapping by ARUPS used in the analysis of our data.
For a detailed description, see Ref. [53].

Usually the photoemission process is treated in a three-step
(photoexcitation, transport, and emission through the surface)
model [67]. Further, we make the following two basic
assumptions:

PHOTOEXCITATION (energy and momentum conservation):

$$E_f = E_i + h\nu, \quad \mathbb{k}_f = \mathbb{k}_i + \mathbb{G} \qquad (1)$$

EMISSION (energy and momentum conservation for escape process):

$$E_{kin} = E_f, \quad \mathbb{K}^{\#} = \mathbb{k}_f^{\#} + \mathbb{G}^{\nu} \qquad (2)$$

where E_i, E_f, $\mathbb{k}_i$ and $\mathbb{k}_f$, are the energy and the wave vector of the electron before and after photoexcitation in the solid, E_{kin} and $\mathbb{K}$ are the energy and wavevector of the emitted free electron, and $\mathbb{G}$ is the reciprocal lattice vector. The component parallel to the surface is denoted by $/\!/$. All the energies are measured from the vacuum level.

Equation (1) shows that the transition is direct, i.e. both the energy and momentum of the excited electron must be conserved for the transition (see Fig. 2(b)). The conservation of $\mathbb{k}$ results from the negligible momentum of the exciting photon. Equation (2) indicates that the parallel component of the wavevector should be conserved on crossing a smooth surface, because of the absence of any abrupt change in the potential along the surface.

Using these equations and assuming a known final state dispersion $E_f = E_f(k)$ (see Fig. 2b and below), one can obtain the initial state dispersion $E_i = E_i(k)$ by tuning $h\nu$. Assuming a rather crude but successful approximation [55], we use a free-electron-like parabola as the final-state disperion curve at higher energies.

The relation between the kinetic energy and the wavevector of a free electron in the vacuum is expressed as

$$E_{kin} = \hbar^2 \mathbb{K}^2/2m = h^2 (\mathbb{K}^{\#2} + \mathbb{K}^{\perp 2})/2m. \qquad (3)$$

On the other hand, the corresponding relation in the solid is different due to the potential in the solid. For the final state, we assume the following relation for a nearly-free electron in a constant inner potential in the solid V_0:

$$E_f = \hbar^2 \mathbb{k}_f^2/2m + V_0 = h^2 (\mathbb{k}_f^{\#2} + \mathbb{k}_f^{\perp 2})/2m. \qquad (4)$$

For normal emission, $\mathbb{K}^{\#} = 0$, hence $\mathbb{k}_f^{\#} = \mathbb{k}_i^{\#} = 0$. Accordingly, the following relations can be derived:

$$\mathbb{k}_i^{\perp} = \mathbb{k}_f^{\perp} = \sqrt{2m(E_k - V_0)}/\hbar, \qquad (5)$$

$$E_i = E_{kin} - h\nu. \qquad (6)$$

These relations indicate that the values of E_i and $\mathbb{k}_i^{\perp}$ can be determined from the measured E_{kin} and $h\nu$, provided V_0 is known. Since $\mathbb{k}_i$ changes with the change of $h\nu$ to fulfill Eq. (1), we can probe the energy band dispersion $E_i = E_i(\mathbb{k}_i)$ by the $h\nu$-dependence of normal-emission spectra. In the present case, this direction is parallel to the molecular axis along which intramolecular interaction is expected to be strongest. Since the interaction between different chains is weak, the dispersion should be dominated by this intramolecular interaction.

3. Experimental Results, Wide Scan Spectra

In Fig. 3, examples of the photoelectron spectra of n-$CH_3(CH_2)_{34}CH_3$ for normal emission ($\hat{\theta} = 0^{\circ}$) and $h\nu = 22$ to 45 eV are shown on the kinetic energy (E_{kin}) scale. Similar spectra were obtained for LB films, indicating that the spectra are dominated by the contribution from the alkyl chains. Electrons emitted without inelastic scattering (primary electrons) form the peaks at large kinetic energies. They reflect the structure of the valence bands. The 2p electrons of C and 1s electrons of H

form the upper bands, and the C_{2s} orbitals form deeper-lying bands [16,22], as shown in the figure. They will be discussed in the following sections. The intense features observed in the photoelectron spectra at $E_{kin} \leq 8$ eV are due to secondary electrons produced by inelastic scattering.

The intensity ratio of the primary electrons (I_p) to secondaries (I_s) increases rapidly with $h\nu$. (Spectra at $h\nu \leq 20$ eV show smaller I_s/I_p ratios [45]). This change is due to strong inelastic scattering of primary electrons via electron-electron scattering. The threshold kinetic energy of this process can be estimated as $E_{kin} = E_x - E_A$, where E_x and E_A are the lowest electronic excitation energy and electon affinity, respectively. With reported values $E_x = 7.5$ eV [52] and $E_A \sim 0$ eV [68], we obtain a threshold of $E_{kin} = 7.5$ eV. This means that the primaries just start to be attenuated at $h\nu = 22$ eV, and the growing effect of scattering increases the I_s/I_p ratio rapidly.

In the region $E_{kin} \lesssim 8$ eV, the photoelectron spectra have structures at energies independent of $h\nu$, as already observed in angle-integrated UPS measurements [45,46] and secondary-electron emission measurements [46,50]. These features reflect the density of unoccupied states [45,46], and will be discussed in detail elsewhere [69]. In the following we will concentrate on discussing the primary electron emission reflecting the valence band structure.

4. Angular Dependence of Photoemission from the Valence-Bands and Molecular Orientation

Drastic changes in the energy distribution curves are observed by varying α and θ. For both compounds no ϕ-dependence of the spectra was found. The insensitivity to ϕ is reasonable when we consider that the sample films consist of microdomains with random azimutal orientation (for LB films, see Ref. [70]).

In Fig. 4(a), the α-dependence of the normal-emission spectra plotted on a binding energy scale for hexatriacontane at $h\nu = 38$ eV, is shown. In the C_{2p} +H_{1s} bands, two peaks A and C appear. In the C_{2s} range, a peak labelled D is observed. Assuming a fixed vertical orientation of the molecules with respect to the surface, a change of $\alpha = 15°$ to $\alpha = 70°$ corresponds to changing the angle between the electric vector of the polarized synchrotron radiation and the molecular axis. (see the insert in Fig. 4(a)). A drastic change of the relative emission intensity with α can be seen. The θ-dependence for $h\nu = 38$ eV and $\alpha = 70°$ is shown in Fig. 4(b). The small shift of the peak positions can be qualitatively understood by $E = E(k)$ dispersion. Similar α- and θ-depencences were also observed for the LB films.

Such large α- and θ-dependences reflect the good orientation of the molecules. Further support for high degree of orientation comes from thermally induced disorder. The heat-treated sample did not show such a clear α- and θ-dependence of the spectra as observed for ordered films (see Figs. 4(a) and (b)). For example, Fig. 5 clearly demonstrates the loss of angular dependence of the photoemission signal from heat-treated LB films, e.g. for $\theta = 0°$ the relatively intense peak D looses its intensity, and the intensity does not recover after cooling. A similar disappearance of anisotropy was also observed in the α-dependence of the

spectra. These observations concur with the results from X-ray
diffraction which show that the molecular orientation in the LB film
of Cd arachidate is destroyed by heating above 100 °C and that the
molecular orientation does not recover after cooling [71]. Thus
we conclude that the large angle (both α and β) dependence of the
spectrum is the result of the good orientation of the molecules.
We note here in passing that one can check the molecular orientation of sen-
sitive samples by in-situ ARUPS measurements as described above even for com-
pounds for which electron diffraction measurements produce severe radiation da-
mage followed by destruction of the molecular orientation.

From the above observation, we note that the intensity ratio of
peak D to peak A in normal emission can be used as an index of the degree
of orientation. Thus a 3-layer LB film showed better orientation
than a 2-layer LB film or even evaporated $n-C_{36}H_{74}$ as shown in
Fig. 4(c). This can be understood as follows: (1) an imperfect
surface of the substrate perturbs the orientation at the first
layer, (2) the second layer shows a better orientation since it
is deposited on the already oriented first layer, and (3) the
third layer shows a still better orientation owing to the well-
oriented 2nd layer, and so on. Our observation is supported by
recent results from Penning ionization electron spectroscopy on
LB films of anthraquinone derivatives [72].

For the moment we cannot analyze the intensity variation with α
and β in detail, but these experimental data will serve as a good
test for future theories of angular-dependent photoemission from
oriented molecules. For such theoretical studies, the C_{2s} peak
will be particularly suitable because of its simple character
discussed in section 7.

5. hν-Dependence of Normal Emission

The hν-dependence of the spectra of hexatriacontane for
photoelectrons emitted normal to the surface at 26 eV $\leq$ hν $\leq$ 54
eV is shown in Fig. 6. The spectra show changes both in peak
positions and peak intensities of the main features. In the C_{2p}
- H_{1s} bands, two peaks A and C appear for hν $\leq$ 40 eV, as
described above. For hν $\geq$ 40 eV, a new peak labelled B appears.
Peak B shifts toward higher binding energies with increasing
photon energy. Peak C merges into it. In the C_{2s} range, a sharp
peak labelled D, which was also mentioned above, is observed. Its
position changes slowly to higher binding energies with
increasing hν.

In Fig. 7, we show the corresponding data for a two-
monolayer Cd arachidate film. The results are essentially
similar to those in Fig. 7. This again indicates that the
spectra are dominated by the contribution from the alkyl chain
and not affected appreciably by the COO$^-$ or Cd^{2+} parts. This is most
probably due to the short electron mean free path ($\leq$ 10
A) [73] in the present energy range compared to the length of the alkyl
part ($\sim$ 23 A) in a Cd arachidate molecule and also due to the 214 to 42
ratio of valence electrons involved in the alkyl and the rest
parts of the molecule, respectively.

Furthermore, Fig. 7 clearly shows the hν-dependence of the
whole C_{2s} band. In addition to peak D, two features are visible
labeled D' and E. The peak energy of peak E in Fig. 7 shifts
towards lower binding energy by increasing hν. The weak shoulder

D' remains at an almost constant energy position independent of
hν. The intensity of feature D' depends on the position of the
sample monitored and on the history of the sample. After intense
VUV light irradiation it increases, while the intensity of
feature D decreases. We thus assume that the feature D'
originates from the photoemission of defects created in the film. This

could be emission from misaligned chains resulting from a
destruction of the polar head groups, which was observed in XPS
experiments [74]. This idea is also supported by the absence of
a corresponding feature in the spectra of irradiated
hexatriacontane.

In addition to peak positions also the intensities of spectral features
in Figs. 6 and 7 depend significantly on hν. This will be discussed in the
next section.

6. Intramolecular Energy-Band Mapping

For a determination of $E = E(k)$ energy band from the spectra
in Figs. 6 and 7, we follow the procedure as described in section
2.2. The value of V_0 can be determined from the hν-dependence of
the photoemission intensity of the upper C_{2s} band D shown in Fig.
8. The intensity shows a maximum when the energy matches the
energy separation between the C_{2s} valence band and the nearly-free
elecron parabola at the Γ point. In the lower part of Fig. 9, we
show the $E_i = E_i(k_i)$ relation by an ab-initio calculation [38],
which is a little modified as described below. We can easily
ascribe the peak D to the flat band around $E_i = -18$ eV. As shown

in Fig. 9, we assign the maximum at hν = 36 eV to a large joint
DOS for the transition at the Γ point [75] due to the flatness of
the nearly-free electron final-state bands at the Γ point [76].
From this, V_0 can be determined to be -5.5 eV, and we obtain an
$E_f = E_f(k_f)$ relation shown in the upper part of Fig. 9. Note
that the bottom part (indicated with broken lines) of the final
band cannot be approximated by a nearly-free-electron parabola
due to the effect of the potential in the solid. Thus only the
region above E_f ~10 eV was used for the subsequent analysis.

The experimental band structure obtained in this way is
shown in Fig. 10. As a guide for the eye, results of an ab-
initio calulation for a polyethylene chain by Karpfen [38] are
also shown. For a better fit with the experimental data, the
original calculated band structure was 0.8 times contracted and
shifted in energy scale. This dispersion relation of the occupied
states was also used for Fig. 9. ◄————————The symmetries of the
bands are taken from Ref [18a]. We note that the corresponding
figure for $n-CH_3(CH_2)_{34}CH_3$ in the rapid communication [62] was in
error for the width of the Brillouin zone by 7 %, but the main features of
the diagram and conclusions are not affected by this. The energy
band structure shown in Fig. 10 is the most detailed experimental information
on the valence electronic structure of a polymethylene chain.
Therefore, in the following sections we will compare the results
with other available from XPS, ESR, and with theoretical
calculations.

In passing we note that the hν-dependence of the
peak intensities in Figs. 6 and 7 can also be understood quantitatively
with the help of the electron band structure. For example, the

decrease of the intensity of peak D between 46 and 54 eV
is predicted by calculating the joint density of states using
values read from the figures in Karpfen's paper for the initial
However, for a more detailed comparison, the joint density of
states has to be calculated quantitatively.

7. Comparison with XPS results

Several XPS studies of the valence band of polyethylene and
its model compounds have been performed [22,42-44,77]. In these
studies, the C_{2s} band has been investigated in quite detail,
because of its large photoionization cross section. On the other
hand, the study of the $C_{2p} + H_{1s}$ band was much more difficult due
to the small cross section in XPS. Nonetheless, a detailed XPS
study of the whole valence band for highly crystalline
polyethylene [22] has served for the comparison with theoretical
calculations [18-24,28-31,33,35,38]. In Fig. 11 this spectrum
(solid line in (c)) is compared with the present UPS results ((a)
and (b)). Since the XPS spectrum reflects largely the density of
initial states, we have chosen several ARUPS spectra at different $h\nu$
for which the peak energies correspond to flat portions of the energy
bands giving large DOS. In (b), we also show an angle-
integrated spectrum of 2-layer LB film obtained with a He II light source
[78]. The XPS spectrum was shifted to align the upper C_{2s} peak
(D), since the original energy scale is relative to the Fermi
level. This corresponds to a work function of 4.8 eV, which is
close to the value of 4.5 eV determined in the previous UPS
experiments [42]. The peak positions are listed in Table 1, with

other relevant data.

There is a rough correspondence between the UPS and XPS
spectra. The large difference in relative peak intensities of
the $C_{2p} + H_{1s}$ and C_{2s} bands is due to the different $h\nu$-
dependences of the photoionization cross sections. As for the
C_{2s} band, the agreement of the peak energies is good.

However, we also note that there are several significant
differences: (i) binding energies for peak B and C do not agree.
(ii) The minimum between the $C_{2p} + H_{1s}$ and C_{2s} bands is far more
pronounced in our UPS data, furthermore its energetic separation
from the C_{2s} maximum is quite different. (iii) The shoulder
labelled X in the XPS spectrum is not observed in our UPS
spectra. As already mentioned, the difference in the carbon
number should not cause such significant differences [43,57].
For (i) and (ii), we believe that our results are more reliable.
Firstly, the signal-to-noise ratio in the present UPS study is
better than that in the XPS spectrum. Secondly, the present UPS
results agree with the XPS spectrum of $n-C_{36}H_{74}$ by Pireaux et al.
[43,77] (broken line in Fig. 11(c)), which was reported without
discussing the $C_{2p} + H_{1s}$ band. Point(iii), will be discussed in
section 8.1.

Finally we note that the simple nature of the C_{2s} band
allows us to compare the E = E(k) relation in Fig. 10 with the
previous XPS studies of the C_{2s} band formation by Pireaux et al.
[43,44]. The latter authors clearly demonstrated that the C_{2s}
level of methane is split into many levels in longer alkanes, a
result which agreed well with ab-initio calculations. By

assuming a tight-binding model for a 1-dimensional array with
nearest-neighbor interaction, we can assign a value of k to each
of such split levels as [79]

$$k = (2/a)m/(n+1), \qquad (7)$$

where n is the number of carbon atoms, and each m corresponds to
a pair in the upper and lower branch of split levels (m runs from
1 to the maximum integer not exceeding $(n + 1)/2$). Such a
treatment was successfully applied to a detailed analysis of the
valence electronic structure of poly-p-phenylene [80]. In Fig.
12 the results of Pireaux et al. for (a) n = 1 to 5 (gas) and (b)
n= 5 to 9 (solid) are plotted in this way. The absolute energy
scale was adjusted to give the best fit with our present UPS
data. We see a close agreement between the data from oligomers
with the present directly-measured results. This agreement
indicates that the simple assumption of the nearest-neighbor
interaction works reasonably well in the case of the C_{2s} band.

8. Comparison with theoretical calculations.

    Most methods for band structure calculations have been
applied to polyethylene as a standard polymer system. So it will
be useful to make an extensive comparison of the present results
with various calculations to examine their validity. A
comprehensive comparison of the numerical results is presented in
Table 2. In addition, in Fig. 13, representative calculated E =
E(k) diagrams are compared with the present experimental results
(points in Fig. 13(a) and(e)). Note that the energy scale of
the experimental data is shifted to show a better agreement with

calculations, as shown in the right ordinate of Fig. 13(a) and
(e). Finally the density of states obtained from these
calculations are compared with the UPS and XPS spectra in Fig.
14.

    Before we make a detailed comparison of the observed and
theoretical results, two remarks are in order. Firstly, there is
a difference due to the state of aggregation, between the
observed solid state photoelectron spectra and theoretical
calculations on an isolated chain. However, it is known that the
photoelectron spectrum of a molecular van der Waals solid agrees
well with that of the constituent molecule when we allow for a
rigid shift in the energy scale (solid state relaxation energy)
[81-84], which mainly arises from the electronic polarization of
the surrounding molecules in the solid (see e.g. Ref.
[56,84,85]). Fortunately, a detailed comparison with the
photoelectron spectra of $n-C_{36}H_{74}$ in the gas phase, which will be
reported separately [57], indicates that such a shift is of the
order of 0.5 eV or so in the present case, which is not
significant for our comparison. Hence we can directly compare
the observed and calculated results by adjusting the energy
scales.

    Secondly, many early calculations used a wrong molecular
geometry or failed in taking properly into account symmetry
requirements, such as the repulsion of the bands of the same
symmetry or the pairing of bands at the boundary of the
Brillouin-zone (X-point). We have indicated such problems in the
calculation in Table 2.

8. 1. Ab initio calculations

At first we will compare the observed results with the ab initio calculation by Karpfen [38], since (i) it was claimed to reach almost the Hartree-Fock limit, (ii) the correct exprimental geometry was used, (iii) the effects of choosing the optimum basis set was carefully assessed, and (iv) the degree of nearest neighbor—second nearest neighbor—etc.—interactions among $-CH_2CH_2-$ units is extrapola_ted to infinity. Figs. 10 and 13(a) are convenient for this comparison.

The calculated ionization potential (top of the valence band) 10.0 eV is in a fair agreement with the vertical ionization potential of 9.8 eV for the gas phase estimated from the experimental data [57]. The remaining difference may be ascribed to the assumption of Koopmans' theorem. We note, however, that the uppermost B_1 band at k = 0, which forms the top of the valence bands according to the calculation, was not observed separately from peak A, as already stated in section 6. Even around $h\nu$ = 27 eV, where $h\nu$ is expected to match the excitation energy from this band to the free-electron-like final state at the Γ point (see Fig. 9), we could not observe a separtate peak. Thus we are unable to confirm the observation of a weak shoulder labelled X in Ref. [22] (see Fig. 11(c)). One might speculate that the B_1 band actually does not form the top of the valence band. However, detailed ESR studies of long-alkane cation by Toriyama et. al. [86] clearly demonstrate that the ground state of a long-alkane cation is the B_1 state. So, we tentatively

ascribe this disappearance to the combination of three factors: (i) The solid-state broadening of each energy level ($\sim$0.6 eV FWHM) [84,87,88], (ii) the calculated energy separation between B_1 and A_1/A_2 bands at the Γ point is too large, and (iii) blurring of the peak in the DOS by electron-phonon coupling upon ionization, which is expected to be significant in quasi-1-dimensional systems [89]. Such a broadening will make it difficult to distinguish a weak feature at the top of the valence band from the closely-located intense feature A. In passing, we note that the highest occupied states of n-alkanes (except for methane) are not degenerate, in contradiction to the argument in Ref. [33] that a Jahn-Teller splitting of this degeneracy is a possible origin of the broadening of photoelectron spectra.

For deeper levels, the contracted-and-shifted ab initio results describe the experimental data very well. In particular, the dispersion of the upper B_1 band and the lower A_1 band around the middle of the Brillouin-zone is clearly observed in the experiment.

Karpfen pointed out that (i) the discrepancy due to Koopmans' theorem should become progressively larger when one goes to higher ionization energies and that (ii) the Hartree-Fock energy band will be too broad as a consequence of this effect. The present results clearly show that Karpfen's idea was correct. The apparent contradiction between this theoretical expectation [38] and previous bandwidth derived from XPS can be ascribed to an ambiguous determination of the bottom of the C_{2s} bands from experimental data.

As seen in Table 2, other ab-initio calculations also give

reasonable results. We note that the introduction of the equivalent-core-potential (ECP) approximation does not change the dispersion relation significantly [40].

8. 2. Semiempirical SCF-LCAO MO calculations

As seen in Fig. 13, original versions of semiempirical MO calculations such as CNDO (Complete Neglect of Differencial Overlap), CNDO/2, INDO (Intermediate Neglect of Differential Overlap), MNDO (Modified Neglect of Diatomic Overlap), MINDO (Modified INDO)/2, and MINDO/3 give too large total band widths due to the neglect of differential overlap of electrons. MNDO (Fig. 13(d)) [33] gives a reasonable description of the C_{2p} + H_{1s} band, except that the ionization potential is a little too large .

On the other hand, Fig. 13(b) and (c) indicate that the CNDO method can be modified to give a moderately good overall agreement with experiment concerning band widths (both C_{2p} + H_{1s} and C_{2s} bands) and the absolute energy scale. Based on this observation, we question the argument of Dewar et al. [33] that the too large C_{2s} band width of MNDO calculation is due to the neglect of 1s-2s interactions.

8. 3. Extended Hückel Method

It is noteworthy that this oldest band calculation on polyethylene [3], which is also quite simple, gives good results, as seen in Fig. 13(e), except that the binding energies are too large. Its calculated band widths and the E = E(k) dispersion are almost the same as those by ab initio calculation. These facts show the usefulness of this simple method for quantitative band calculations of saturated-hydrocarbon compounds and polymers.

8. 4. Other methods

The SAMO (Simulated Ab-initio Molecular Orbital), LCLO (Linear Combination of Localized Orbitals) and FSGO (Floating Spherical Gaussian Orbitals) methods are nonempirical methods, which were developed to simulate ab initio calculations and to save computer time, by using the transferability of the matrix elements of HF equations or localized orbitals from simple model molecules. As we can see from Fig. 13, the results of these methods indeed simulate the ab initio results and experimental results. The LCLO result is a little better in reproducing the dispersion in the C_{2p} + H_{1s} band. The FSGO method (Fig. 13(f)) gives too large binding energies, but the contraction of the energy scale by 0.7 time offers reasonable results [35].

In contrast to these, the techniques using local exchange, such as LCAO-MT (Muffin Tin), EMTO (Extended Muffin Tin Orbitals) and DV-X_α methods give rather poor agreement with experimental observations. The width of the C_{2p} + H_{1s} bands given by the LCAO-MT method (Fig. 13(g)) is too large. The EMTO and DV-X_α methods fail in placing the B_1 band at the top of the valence band at k = 0. Further, the bands in the reported EMTO calculation do not lie horizontally at k = 0.

These poor results are not surprising when we consider that

these calculations are still not yet well developed for dealing with organic molecular systems. Clearly some basic improvements are necessary for applying these techniques to organic solids.

9. Concluding Remarks

In this paper we have reported on a detailed study of angle-resolved photoelectron emission from oriented samples of hexatriacontane and Cd arachidate, which are good models of polyethylene in an extended-chain conformation. It was possible to determine intramolecular quasi-one-dimensional $E = E(k)$ energy band dispersion for the valence bands from the photon energy dependence of normal emission spectra. In fact, this is the first experimental observation of an $E = E(k)$ energy band dispersion in an organic solid. In particular, information concerning the upper $C_{2p} + H_{1s}$ valence band is much more precise than that from the previous XPS data. This allowed us a detailed comparison with theoretical band structure calculations.

Our experimental results in comparison with the many partly conflicting theoretical calculations stress the importance of polyethylene as a test material for the different methods of polymer-band calculations. It is encouraging that the most sophisticated ab-initio calculation [38] gives the best agreement. Semiempirical methods, some with proper modifications, give also reasonably good agreement. Among them we note the success of the simple extended-Hückel method.

The present study established the technique of intramolecular-band-mapping by angle-resolved photoelectron

spectroscopy via $h\nu$-dependence of normal emission. Furthermore, it clarified the electronic valence band structure of polyethylene. A determination of the intramolecular $E = E(k)$ dispersion is also possible by angle-resolved UPS from samples with the axes uniaxially oriented parallel to the surface [90], or by measuring the DOS of oligomers [80], a technique which was also applied here to the polyethylene C_{2s} band. Generally, angle-resolved UPS techniques can be applied to all polymers provided adequately oriented samples are available. Unfortunately this is not always the case, and we must stress the importance of obtaining such specimens. The "oligomer DOS" technique can be applied only to compounds with simple bands, but we can use non-oriented samples and a sophisticated angle-resolved instrument is not even necessary. We anticipate that the application of these complementary techniques will clarify the electronic structures of other organic compounds.

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Table 1. Binding Energies of Spectral Features for Linear Chain Molecular Solids Relative to the Vacuum Level (in eV).

Compound and Method	Upper Band ($C_2 + H_{1s}$)				Lower Band (C_{2s})			Ref.
	X	A	B	C	D′a)	D	E	
n-$C_{36}H_{74}$ and Cd arachidate Solid ARUPS		10.4 ±0.2	14.0 ±0.3	14.8 ±0.5	~17.1	18.1 ±0.2	24.1 ±0.3	this work
n-$C_{36}H_{74}$ Solid ARUPS		10.5b) to 12.0	14.0	15.5		18.3	24.6	[47]
Polyethylenec) Solid XPS	9.6	11.2	12.6	13.8		18.0	23.6	[22]
n-$C_{36}H_{74}$c)d) Solid XPS	9.8	11.1	13.7	15.4		18.0	23.8	[43,77]

a) Extrinsic feature observed for long-irradiated samples. See text.

b) Depends on the parameters of angle-resolved measurements.

c) Converted from the values relative to the Fermi level by using a value of 4.8 eV for the work function (see text).

d) Binding energies have been read from the spectrum.

Table 2. Comparison of the observed and calculated valence energy structure of polyethylene (in eV). All calculations are for an isolated extended planar-zigzag chain.

	Authors	Ref.	Upper band ($C_{2p} + H_{1s}$)					Lower Band (C_{2s})				Total Valence Band Width	Remark
			Top	Peaks	Bottom	Width	Gap	Top	Peaks	Bottom	Width		
Experiment	This Work		8.8	10.4 14.0 14.8	15.5	6.7	2.0	17.5	18.1 24.1	24.7	7.2	16.2	Solid state valuese)
Ab Initio	André, Leroy	[4]	16.88b)	10.4 14.0 14.8	20.41	3.53	6.53	26.94	—	33.47	6.53	—	wrong geometry
	André, Kapsomenos, Leroy	[8]	13.31	—	—	—	—	33.47	—	33.47	—	20.16	wrong geometry
	Clementi	[10]	12.84	—	(20.1)	(7.3)	(6.1)	—	—	(32.3)	(6.1)	19.5	wrong geometry
	André, Delhalle, Delhalle, Caudano, Pireaux, Verbist	[19]	—	13.46 15.53 17.61 20.19	—	—	—	—	26.81 33.37	—	—	—	same calculation
	Delhalle, André, Delhalle, Pireaux, Caudano, Verbist	[22]	13.2	—	[20.2]	7.0	6.0	[26.2]	—	[33.7]	7.5	[20.5]	same calculation
	Delhalle, Delhalle, André	[23]	—	—	—	—	—	—	—	—	—	—	same as Ref.[4]
	Armstrong, Jamieson, Perkins	[31]	10.45	—	(17.3)	(6.9)	(4.9)	(22.2)	—	(30.2)	(8.0)	—	
	Karpfen	[38]	10.0	—	[17.6]	7.6	3.0	[20.6]	[20.9] (29.3)	[29.3]	8.7	19.3	
Ab initio ECP	Weidman, Bedford, Kunz	[39]	—	—	(19.6)	(5.4)	(3.3)	(22.9)	—	(25.3)	(2.4)	(11.1)	(CH_2)6 (not an infinite chain)
	Teramae, Yamabe, Imamura	[40]	9.91	—	(18.9)	(9.0)c)	(2.8)c)	(21.7)	—	(30.3)	(8.6)	(20.4)	
ECP	Teramae, Yamabe, Imamura	[40]	11.05	—	(19.7)c)	(9.7)c)	(2.3)	(22.0)	—	(30.2)	(8.2)	(19.1)	

Table 2 (continued)

Method	Authors	Ref											Notes
CNDO	André, Kapsomenos, Leroy	[8]	11.70	—	—	—	—	—	—	[48.5]	—	36.84	
CNDO/2	Morokuma	[5]	(11.5)	—	(29.0)	(17.5)	—	—	—	(47.7)	—	(36.2)	crossing[d]
	Fujita, Imamura	[7]	(11.7)	—	(29.3)	(17.6)	—	—	—	(48.0)	—	(36.2)	crossing[d]
	Morokuma	[9]	(11.6)	—	(29.1)	(17.5)	—	—	—	(48.0)	—	(36.4)	crossing[d]
	André, Delhalle, Kapsomenos, Leroy	[14]	(11.1)	—	(29.3)	(18.2)	0	(25.6)	—	(48.5)	(22.9)	(37.4)	
	Delhalle, André, Delhalle, Pireaux, Caudano, Verbist	[22]	11.7	—	(30.0)	(18.3)	0	(26.2)	—	(48.8)	22.6	31.1	
Modified CNDO	Morosi, Simonetta	[11]	(13.1)	—	(26.4)	(13.3)	—	—	—	(40.8)	—	(27.7)	crossing[d] split at X point[e]
	McAloon, Perkins	[15]	(4.9)	—	(40.0)	(35.1)	0	(29.7)	—	(84.7)	(55.0)	(79.8)	split at X point[e]
	Wood, Barber, Hillier, Thomas	[16]	(11.0)	—	(20.2)	(9.2)	(1.3)	(21.5)	—	(33.7)	(12.2)	(22.7)	
	Delhalle, André, Delhalle, Pireaux, Caudano, Verbist	[22]	(9.6)	—	(20.1)	(10.5)	(1.0)	(21.1)	—	(32.6)	(11.5)	(23.0)	
	Perkins, Marwaha, Stewart	[34]	9.07	—	(16.4)	(7.3)	(2.9)	(19.3)	—	(29.3)	(10.0)	(20.2)	
INDO	Beveridge, Jano, Ladik	[13]	(9.6)	—	(29.2)	(19.6)	(6.2)	(25.8)	—	(48.8)	(23.0)	(39.2)	split at X point[e]
MINDO/2	Beveridge, Jano, Ladik	[13]	—	—	—	—	—	—	—	—	—	—	
	Beveridge, Wun	[20]	(7.0)	—	(18.4)	(11.4)	(0.8)	(19.2)	—	(41.0)	(21.8)	(34.0)	split at X point[e]
MINDO/3	Dewar, Suck, Weiner	[18]	(8.3)	—	(16.0)	(7.7)	(3.3)	(19.3)	—	(36.8)	(17.3)	(28.5)	peak energies are from Refs. [30] an[d] [33]
MNDO	Dewar, Yamaguchi, Suck	[30]	(11.0)	10.9 12.3 14.7 17.1	(17.2)	6.2	5.2	(22.4)	22.3 41.4	(41.4)	19.0	40.4	

continued

Table 2 (continued)

Method	Authors	Ref											Notes
	Dewar, Yamaguchi, Suck	[33]	(11.0)	11.0 12.1 12.4 17.2	(17.2)	6.2	5.5	(22.7)	22.7 41.5	(41.5)	18.8	30.5	
Extended Hückel	McCubbin, Manne	[3]	(12.4)	—	(17.0)	(4.6)	(2.9)	(19.9)	—	(28.7)	(8.8)	(16.3)	
	Imamura	[6]	12.05	—	16.94	[4.89]	[2.93]	[19.87]	—	[28.85]	[8.98]	[16.8]	
	André, Kapsomenos, Leroy	[8]	12.05	—	—	—	—	—	—	28.85	—	16.82	
	Delhalle, André, Delhalle, Pireaux, Caudano, Verbist	[22]	11.9	—	[17.4]	5.5	2.5	[19.9]	—	[29.4]	9.5	[17.5]	
	Delhalle, Delhalle, Damanet, André	[24]	12.05	—	16.94	[4.89]	[3.0]	[19.94]	—	[28.85]	[8.91]	[16.8]	
SAMO	Duke, O'Leary	[17]	12.76	—	(19.7)	(6.9)	(7.0)	(26.7)	—	33.28	(6.6)	20.52	
FSGO	Bredas, André, Delhalle	[35]	(8.7)	—	(15.1)	(6.4)	(6.4)	(17.1)	—	(23.7)	(6.6)	(15.0)	
LCLO	Dyachkov, Levin	[26]	10.2	—	—	—	—	—	—	(25.7)	—	(15.5)	split at X point[e]
	Dyachkov, Iosolovich, Levin	[27]	(10.6)	—	(16.9)	(6.3)	(2.1)	(19.0)	—	(25.8)	(6.8)	(15.2)	
	Armstrong, Jamieson, Perkins	[36]	7.81	—	[14.37]	6.56	(7.5)	(21.9)	—	(31.8)	(9.9)	(24.0)	
	Leroy, Peeters, Resoux-Clarisse	[28]	13.03	—	20.32	7.29	[1.84]	22.16	—	32.16	9.48	19.13	
	Delhalle, André, Delhalle, Pivont-Malherbe, Clarisse, Leroy, Peeters	[29]	13.17	—	[19.95]	6.78	[2.67]	[22.62]	—	[32.05]	9.44	18.88	
LCAO-MT	Falk, Fleming	[18]	11.3	—	(22.6)	11.3	1.0	(23.6)	—	(29.2)	(5.6)	17.9	
EMTO	Kasowski, Hsu, Caruthers	[37]	12.8	—	18.4	5.6	[2.2]	20.6	—	27.6	7.0	14.8	Bands are not flat at Γ Point
DV-Xα	Satoko	[41]	12.73	—	17.55	4.81	[2.56]	20.11	—	29.26	9.14	16.53	

Notes are in the following page.

Remarks to Table 2.

[ ]: derived from numerical values in the leterature.

( ): read from figures.

a) For comparison with calculations, a solid-state shift of ~ 0.5
   eV should be added. For details, see text.

b) This value listed by the authors is inconsistent with the
   figure in the same paper. A value of 13.31 eV in Ref. [8]
   seems more reasonable.

c) The value listed by the authors is inconsistent with the
   figures in the same paper.

d) There is a crossing of bands of the same symmetry, which
   should be split to avoid the crossing [12,25].

e) The rule of pairing at the edge of the Brillouin zone (X-
   point) is not fulfilled [18a].

Figure Captions

Fig. 1. Schematic structure of the evaporated film of
hexatriacontane (a), the Langemuir-Blodgett films of Cd
arachidate for two layers and three layers (b), and the
crystal of polyethylene [65](c). For both cases of (b),
the upper 20 $\overset{o}{A}$ layer consists of oriented hydrocarbon
chains. Due to the hydrophobic nature of Au and
hydrophillic character of Al, even or odd numbers of
monolayers can be deposited, respectivuely.

Fig. 2. (a) Parameters of angle-resolved UPS measurements: α,
incidence angle of photon, θ, polar emission angle of
electrons, and ϕ, azimutal emission angle of electrons.
(b) Schematic $E = E(k)$ bands. A direct transition
between an initial band E_i and a final band E_f
is depicted.

Fig. 3. Photoelectron energy distribution curves at normal
emission to the surface ($\theta = 0°$) of hexatriacontane
for photon energies ranging from 22 eV to 45 eV. In
this plot the same initial states follow inclined lines.

Fig. 4. (a) Normal-emission spectra of hexatriacontane for
$h\nu = 38$ eV for different angles of incidence of photons
α.
(b) Dependence of the hexatriacontane photoelectron
spectra for $h\nu = 38$ eV and $\alpha = 70°$ on the emission
angle of electrons θ.
(c) Comparison of the photoelectron energy distribution
curves of an evaporated film of n-$C_{36} H_{74}$ and 2- and
3-layer LB films of Cd arachidate for $\alpha = 70°$, $\theta = 0°$,

and hν = 38 eV. The ratio of the peak intensities A to

D is given for each spectrum.

Fig. 5. Change of the photoelectron spectra of Cd arachidate

for hν = 38 eV and two different emission angles θ (0°

and 60°) by heat treatment at 100 °C. Lower panel:

before heat treatment; upper panel: after heat treatment.

Note the disappearance of the -dependence after heat

treatment.

Fig. 6. Photon-energy dependence of the normal-emission spectra

of hexatriacontane for α = 70°. Arrows indicate

the location of the spectral features.

Fig. 7. Photon-energy dependence of the normal-emission spectra

of 2 layers LB film of Cd arachdate for α = 70°.

Arrows indicate the location of the spectral features.

Fig. 8. Photon-energy dependence of the intensity of the upper

C_{2s} derived band (D) for Cd arachidate.

Fig. 9. Illustration of the nearly-free-electron like final-state

energy dispersion (I - III) used for the analysis

and the transition corresponding to the intensity maximum

of   peak D in Fig. 8. The dispersion of the initial states

is taken from   Karpfen [38] with modifications described

in the text.

Fig. 10. Summary of the intramolecular energy band dispersion

data for the valence bands of hexatriacontane and Cd

arachidate.

  $\bullet$: from α = 70° measurements using evaporated n-$C_{36}H_{74}$

     film.

- 41 -

o: from α = 70° measurements uing 2 layers LB film of Cd

arachidate.

$\square$: from α = 70° measurements using 3 layers LB film.

$\triangle$: from α = 80° measurements using 3 layers LB film.

The calculated band structure for idealized

polyethylene (broken line) is a modification of the

results by Karpfen [38] (see text). The lack of the

experimental points near the X point (k = π/a) is only

due to the limitation of available photon energy by the

Seya-Namioka monochromator.

Fig. 11. Comparison of the UPS spectra of hexatriacontane (a) and

Cd arachidate (b) with the XPS spectra of polyethylene

[22] and hexatriacontane [43,77] (c). For details, see

text.

Fig. 12. Energy band dispersion of the C_{2s} band of polyethylene

derived from XPS results of alkane oligomers for (o)

from methane to pentane in the gas phase [43], and ($\bullet$)

from pentane to nonane in the solid state [44], using

Eq. (7). Bars indicate the direction of possible

error in separating multiple components in a single

observed spectral feature. The calculated energy-band

dispersion is the same as in Fig. 10.

Fig. 13. Comparison of the experimentally observed E = E(k)

relation ($\bullet$ in (a) and (e), this work) with theoretical

calculations.

(a) ab-initio method [38], (b) CNDO/2 method [22], (c)

Modified CNDO/2 method [34], (d) MNDO method [33], (e)

Extended Hückel method (Wolfsberg-Helmholtz parameter F

- 42 -

= 1.75) [3], (f) FSGO method [35], and (g) LCAO-MT
method [18]. The energy axis of (a) is not modified as
in Figs. 9 and 10. The energy scale of the experimental
data in the right ordinates of (a) and (e) are shifted
to show a good agreement with calculations.

Fig. 14. Comparison of the calculated density of states for
polyethylene ((a) - (g)) with UPS and XPS spectra of
hexatriacontane and Cd arachidate. For XPS, we
preferred the spectrum of hexatriacontane [77] to that
of polyethylene due to the reason described in the text.

(a)

$CH_3(CH_2)_{34}CH_3$

(b)

2 LAYERS   3 LAYERS

$CH_3(CH_2)_{18}COO^-$

(c)

O CARBON
° HYDROGEN

Fig. 1

(a)

n

hν(SR)

E

α θ e⁻

Φ

SOLID

(b)

SOLID   VACUUM

hν

E_f

ELECTRON ENERGY

$E_{kin} = E_f(\underline{k})$

$E_{VAC} = 0$

$h\nu = E_f(\underline{k}) - E_i(\underline{k})$

E_i

MOMENTUM $\underline{k}$

Fig. 2

$n - CH_3 (CH_2)_{34} CH_3$
ORIENTED FILM
NORMAL EMISSION

SECONDARIES

PRIMARIES

C_{2s} $C_{2p} + H_{1s}$

×6
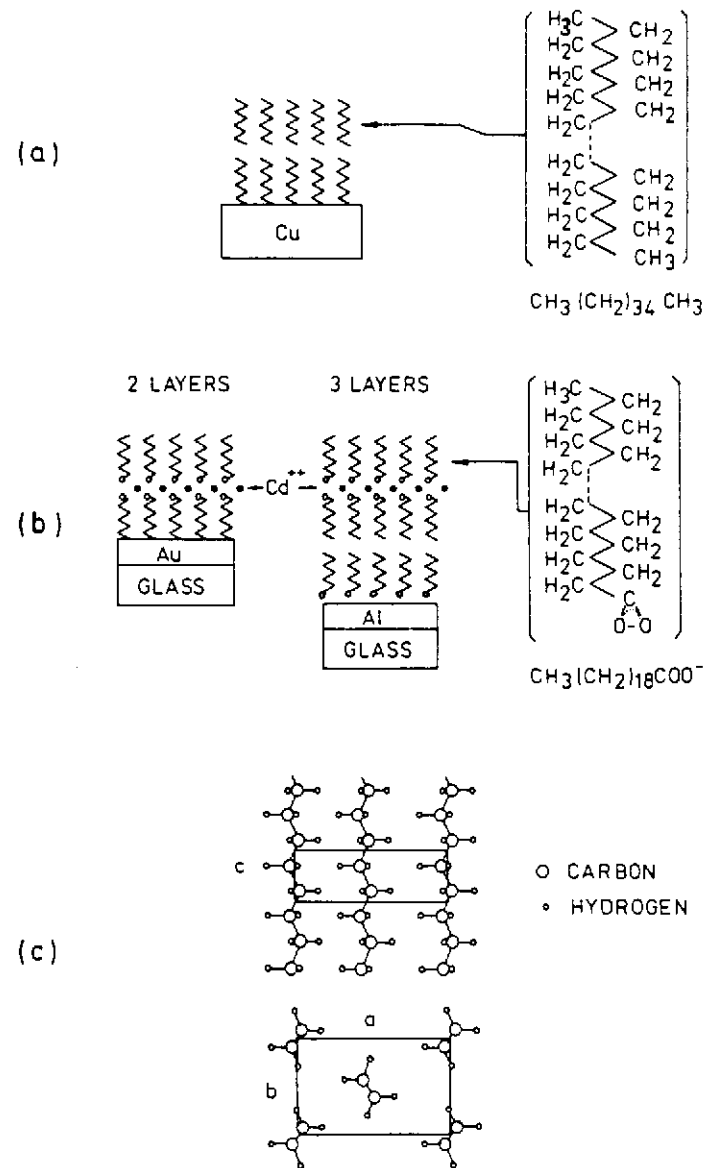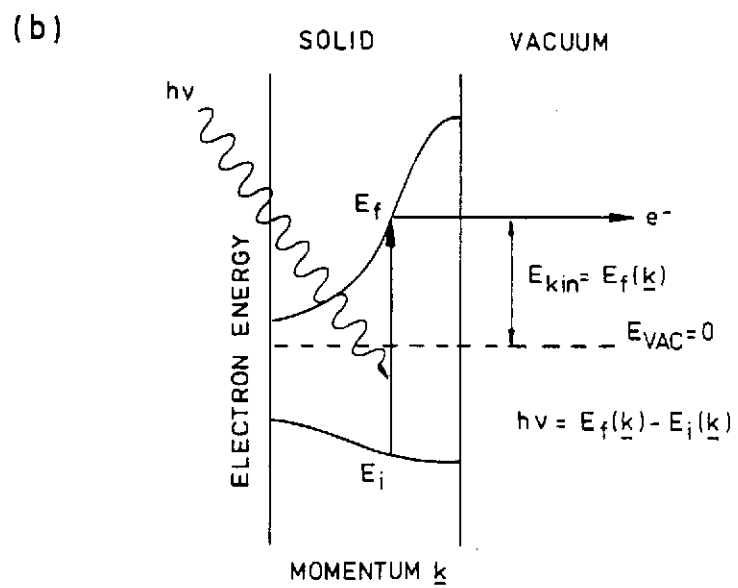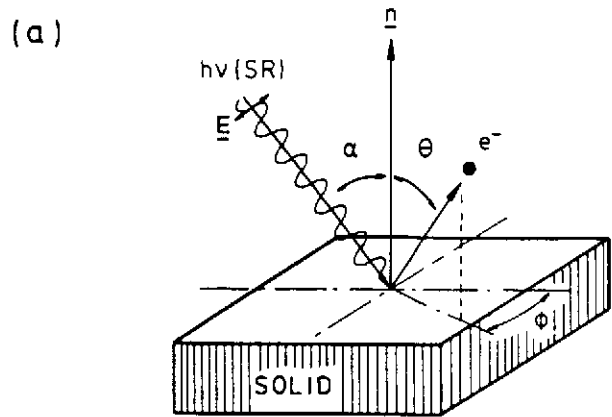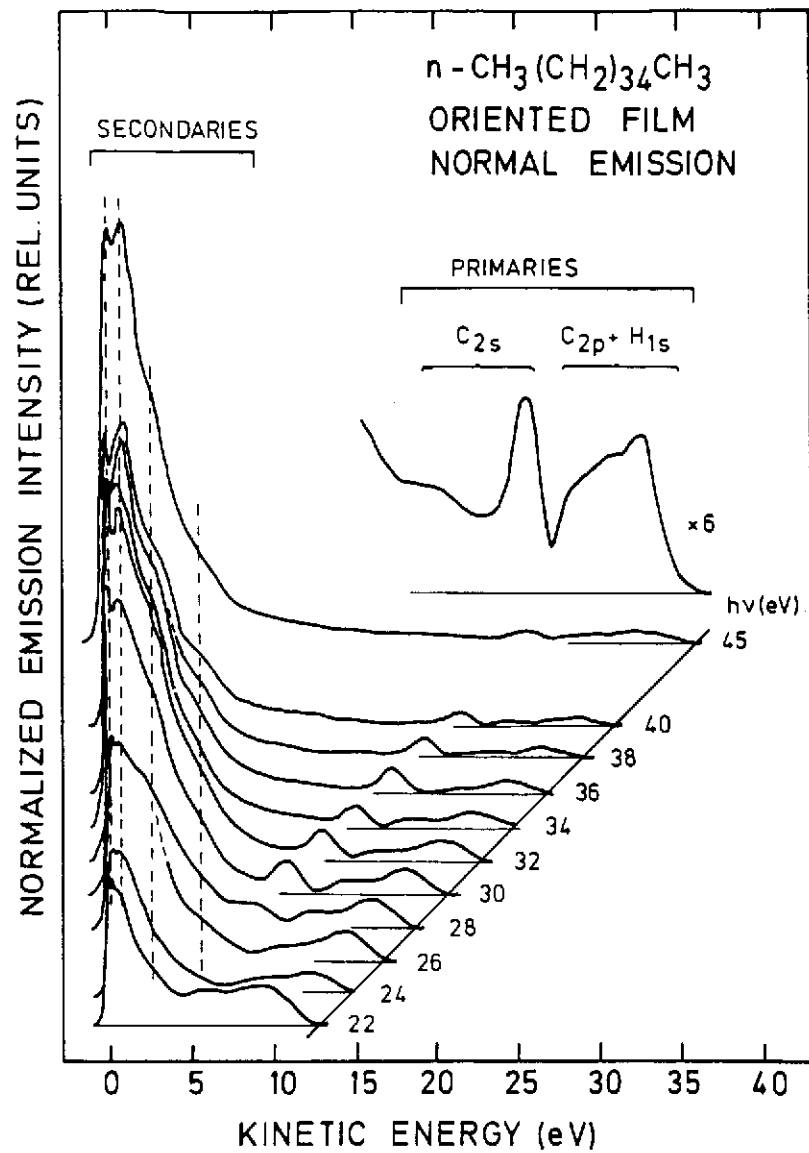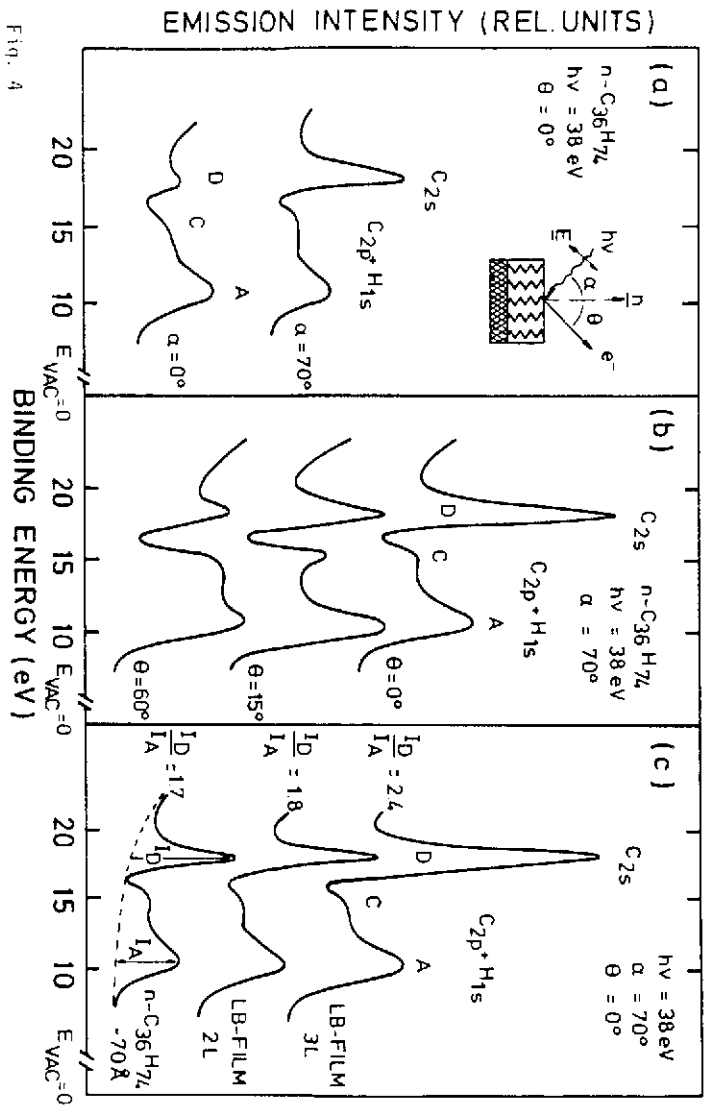
NORMALIZED EMISSION INTENSITY (REL. UNITS)

hν(eV)
45
40
38
36
34
32
30
28
26
24
22

0 5 10 15 20 25 30 35 40

KINETIC ENERGY (eV)

Fig. 3

Fig. 4
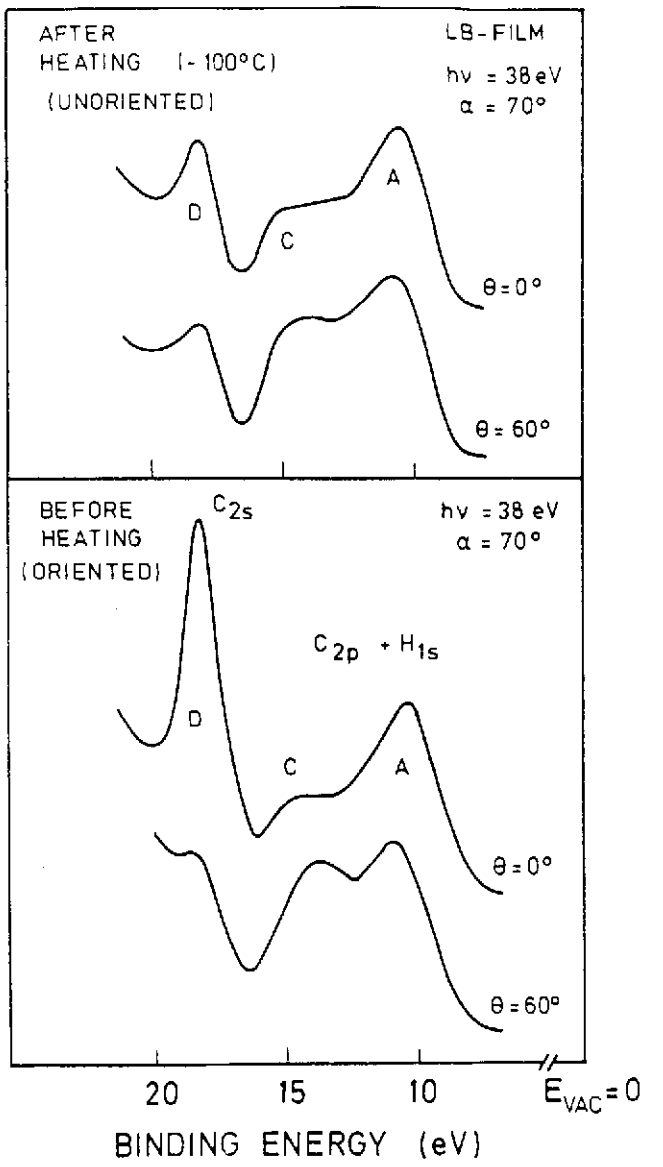
Fig. 5

Fig. 6

Fig. 7

Fig. 8

MOMENTUM k
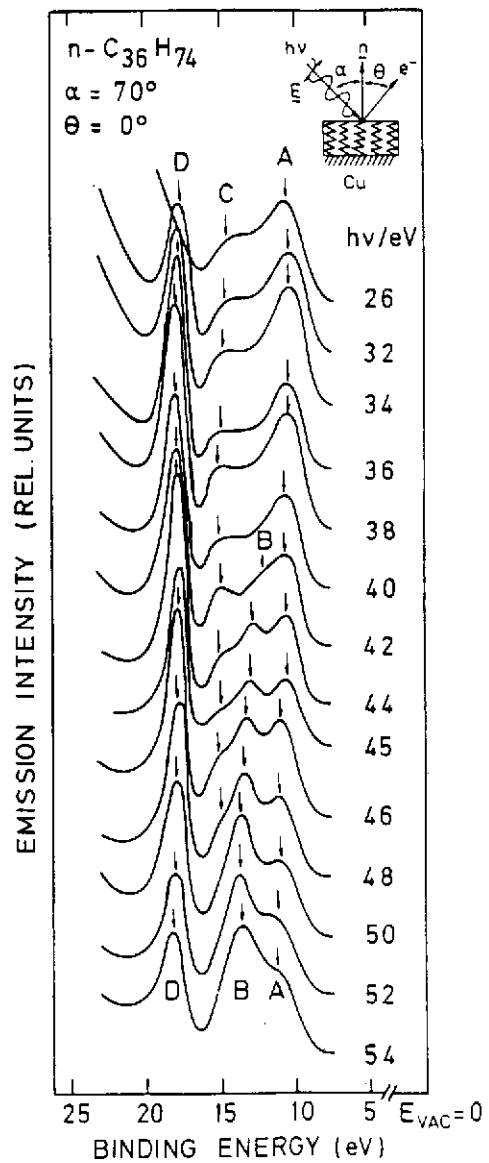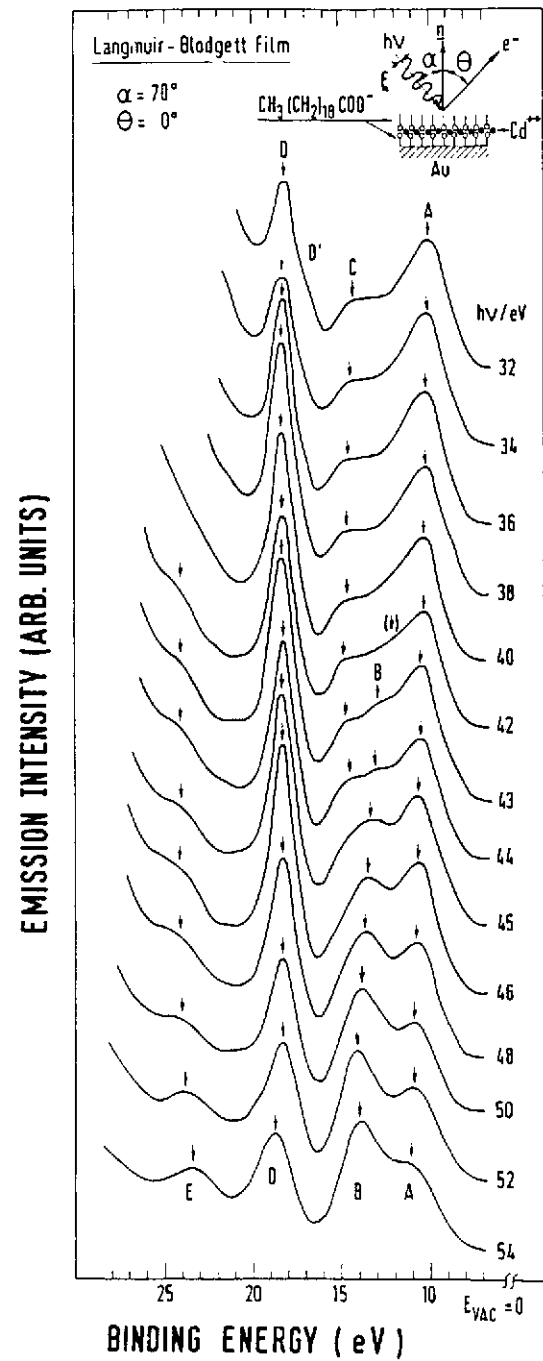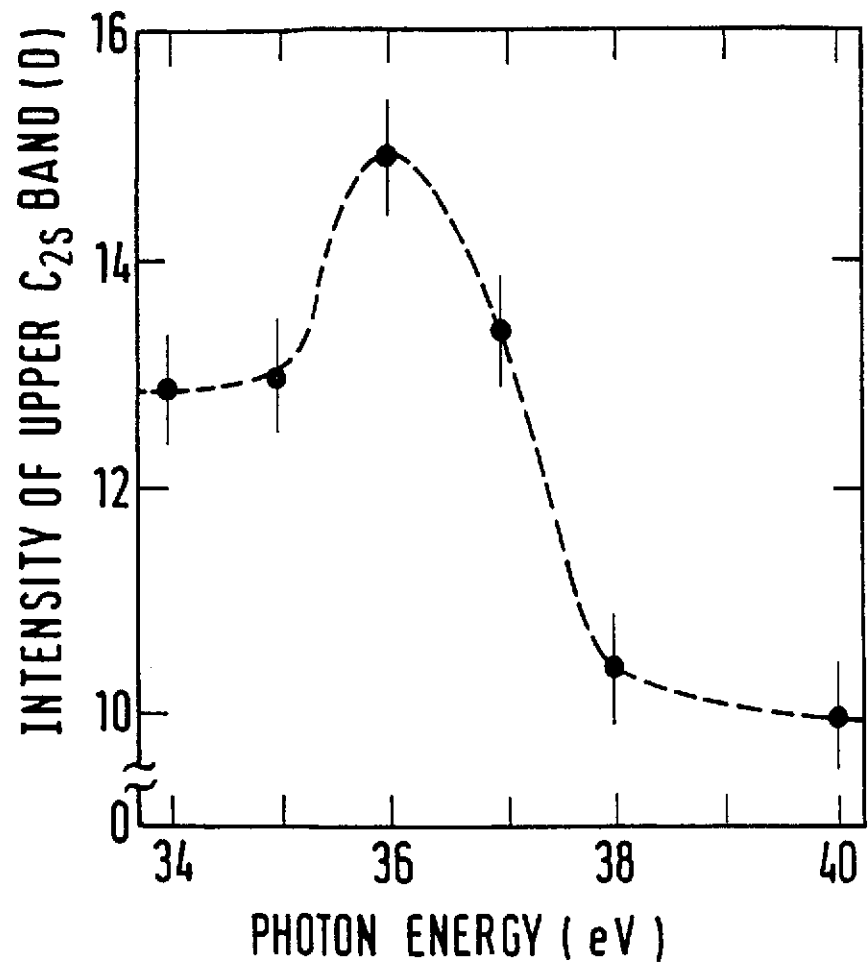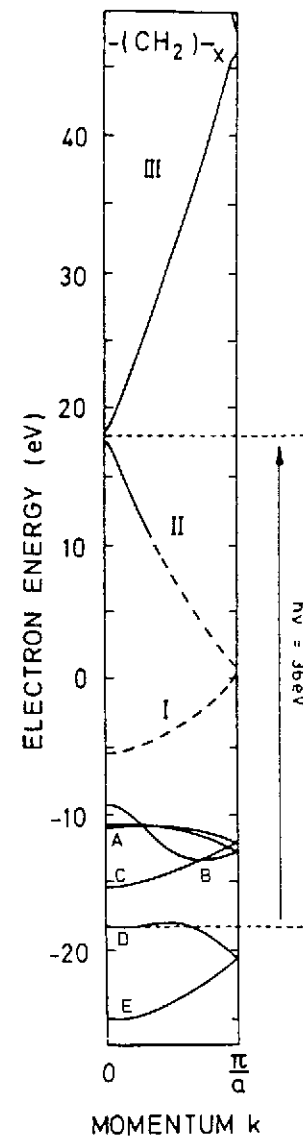
Fig. 9
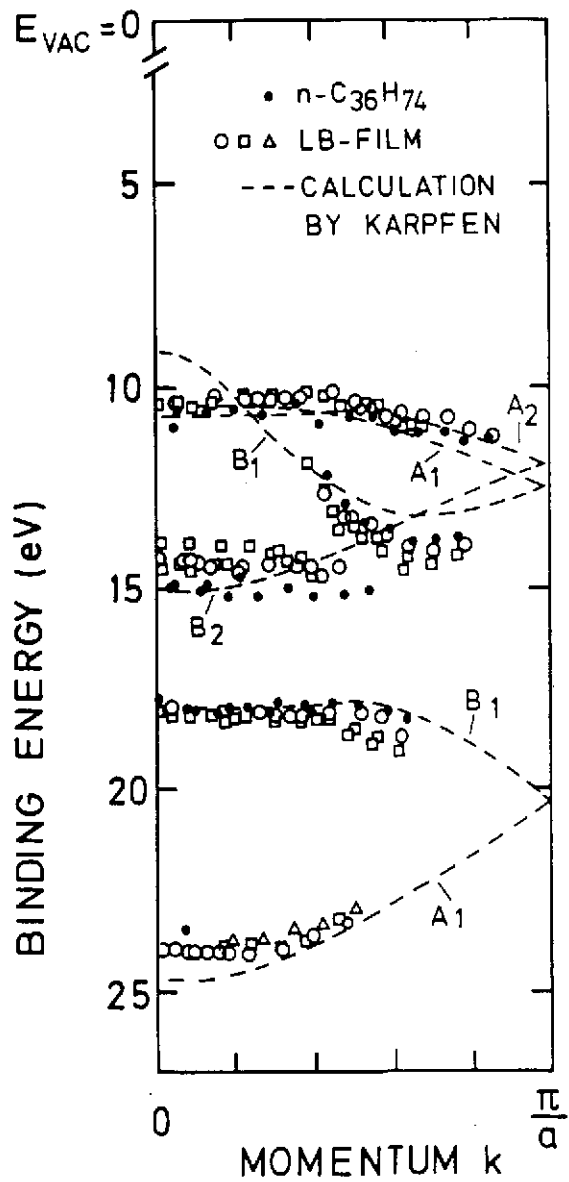
Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14