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One-dimensional energy band dispersion in Langmuir-Blodgett films determined by angle-resolved photoemission with synchrotron radiation*

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Abstract

The intramolecular energy band dispersion E = E(k) has been determined for the valence bands of the $(CH_2)_{18}$ chain in Langmuir-Blodgett (LB) films of cadmium arachidate by angle-resolved photoemission using synchrotron radiation. Comparison with similar results for long-chain alkane n-$C_{36}H_{74}$-films and theoretical calculations for polyethylene confirm the existence of one-dimensional energy bands along the individual molecules. Due to the high chain order the use of LB films allows a better resolution of the band structure compared to previous experiments.

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Introduction

Langmuir-Blodgett films (LB-films) are interesting ordered organic systems. They can be assembled monolayer by monolayer to form a planar two-dimensional sheet of controlled thickness. They are interesting models of biological membranes [1,2,3]. Due to almost complete molecular orientation and weak intermolecular interaction, these films have recently attracted interest for developing new types of electronic devices [4,5] and low-dimensional magnets [6,7]. Comparatively little, however, is known about the electronic band structure of such films which is essential for the description of fundamental electronic properties such as the electrical conductivity, optical properties and substrate-interface properties. In this letter we describe the application of angle resolved photoemission spectroscopy combined with tunable synchrotron radiation [8] to characterize the electronic energy bands of Langmuir-Blodgett films and in particular to study the energy vs. momentum E(k) dispersion.

Due to the weak van der Waals interaction between the constituting molecules for a large number of organic systems the electronic band structure is largely determined by the electronic structure of the individual molecules forming the solid [9]. For systems build up by long chain molecules a particularly interesting situation arises, since the energy band should show quasi-one-dimensional properties determined by intramolecular interaction along the long molecular axis [10]. Although there are many kinds of organic crystals which consist of long chain molecules such as n-alkanes and fatty acids etc., the experiments using single crystals have not yet been successful due to experimental difficulties, e.g. severe charging effects during photoemission. In Langmuir-Blodgett films the situation is much more favourable, as the insulator is ultrathin and as the molecules constituting the films are well oriented with their long axis perpendicular to the film surface [12]. Therefore we can use LB films which consist of long chain fatty acids as excellent model compounds for angle-resolved photoemission to study intramolecular dispersion associated with the valence electrons localized in the $(CH_2)_x$ zig-zag chain. We have measured photoelectron energy distribution curves (EDC's) from LB films consisting of the cadmium salt of arachidic acid $CH_3(CH_2)_{18}COOH$ using synchrotron radiation as a tunable light source. In this paper we present the experimental determination of the one-dimensional energy band dispersion for the whole valence band region in a binding energy range from 5 to 25 eV derived from the $(CH_2)_{18}$ chain in arachidic acid.

Experiment

Three and two monomolecular cadmium salt layers of arachidic acid of Y-type were prepared on aluminium and gold coated glass plates, respectively, as shown in Fig. 1. The method for film preparation is described in Ref. [2,11]. For both cases, the sample surface was covered by the oriented hydrocarbon chains. The subphase (Millipore water pH 5.5) contained 4 x 10^{-4} M $CdCl_2$. Thus the Cd salt is deposited on the support giving the film a good stability.

The experiments were performed at a pressure of 10^{-10} torr and at room temperature using an apparatus at the DORIS II storage ring in the Synchrotron Radiation Laboratory HASYLAB at DESY. The apparatus consists of a 1 m Seya-Namioka monochromator and a modified VG ADES-400 angle resolving photoelectron spectrometer [12]. The emission spectra were measured at normal emission with photon energies ranging from 21 eV to 54 eV.

Results and Discussion

Figure 2 shows an example of EDC's measured for different photon energies at normal emission with an incident angle $\alpha = 70°$ from the two-monolayer LB film. The upper part of the valence band extending from 8 eV to 16 eV is derived from C 2p and H 1s orbitals, and the lower part below 17 eV originates from C 2s orbitals [13]. In the C 2p and H 1s bands three features (A, B, and C) depending on the photon energy can be observed. Feature C does not show a clear energy shift while A and B disperse towards lower binding energies with decreasing photon energy. The intensity of feature A decreases monotonically with photon energy, whereas that of feature B increases in the photon energy range covered in our experiments. In the C 2s derived bands, three features are visible labeled D, D', and E. The position peak D changes slowly to lower binding energies with decreasing photon energy, whereas feature E shows an opposite shift. The intensities of these C 2s bands show also opposite photon energy dependence. That of peak D has obviously a maximum at $h\nu \approx 36$ eV (see Fig. 3). The weak shoulder D' remains at an almost constant energy position independent of the photon energy. 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 whereas the intensity of feature D decreases. We thus assume that feature D' originates from the photoemission of defects created in the film. This could be emission from misaligned chains

that might result from a destruction of the polar head groups. The latter was observed in XPS experiments [14].

From the photon energy dependence of the EDC's one can deduce the bandstructure using common methods for band structure mapping [8,15]. If EDC's are measured only at normal emission one has $k_{\parallel} = 0$ (parallel to the surface) and only states along one line in $\underline{k}$-space with $k_\perp$ (perpendicular to the surface) are sampled. Furthermore we assume direct interband transitions and use as the simplest approximation for the final state a parabolic free-electron-like band in a constant inner potential V_o: $E^f(k_\perp) = (\hbar^2 k_\perp^2/2m) + V_o$. In the present situation this dispersion perpendicular to the surface corresponds to the one-dimensional $E(\underline{k})$-dispersion along the molecular chains. The inner potential V_o was determined to be − 5.5 eV (averaged value) by adjusting the free-electronlike parabola at k = 0 with the help of the photon energy dependence [16] of the intensity of the upper C 2s band D, as shown in Fig. 3.

The experimentally determined valence band dispersions for the LB film thus obtained are summarized in Fig. 4. We also show in Fig. 4 the result of the recent ab initio band calculation for an infinite polyethylene chain by Karpfen [17] and the experimental results for n-$C_{36}H_{74}$ films obtained by Seki et al. [18] Here we contracted the calculated results uniformly by a factor 0.8 and shifted the resulting bands to fit the experimental $E(\underline{k})$ curves in accordance with Seki et al. [18]. As can be seen from Fig. 4, good agreement was obtained between the present data, those of n-$C_{36}H_{74}$, and theoretical calculations for idealized one-dimensional chains. In particular, the highly dispersive band (upper B band) and the lower C 2s band (lower A band) which were not observed for n-$C_{36}H_{74}$ are clearly visible. This demonstrates that due to the good chain orientation more features in the spectra can be resolved. The photon energy dependence of the intensities of features can be simply understood by changes in the joint density of states between valence bands and final free electron band.

The agreement between the present data and theoretical calculations over the whole valence band region confirms the existence of a one-dimensional energy band along the $(CH_2)_x$ chain in the long chain molecular crystal. It also points to the reliability of band structure calculations for aliphatic chains. This may be interesting in view of the discussion on electron transfer through membranes or within proteins where virtual states of hydrocarbon chains may play an important role. A more detailed description of this study will be presented in a subsequent paper.

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Figure Captions

Fig. 1 Schematic picture of the Langmuir-Blodgett films for two layers and three layers. For both cases, the upper 20 Å layer exists of oriented hydrocarbon chains. Due to the hydrophobic nature of Au and the hydrophilic character of Al even or uneven numbers of monolayers can be deposited, respectively.

Fig. 2 Photoelectron spectra in normal emission from the Langmuir-Blogett film consisting of two monolayers for various photon energies hν.

Fig. 3 Photon energy dependence of the intensity of the upper C 2s derived band (D).

Fig. 4 Summary of energy band dispersion data for the valence bands of the Langmuir-Blodgett film.

o : from α = 70° measurements using 2 layers LB film

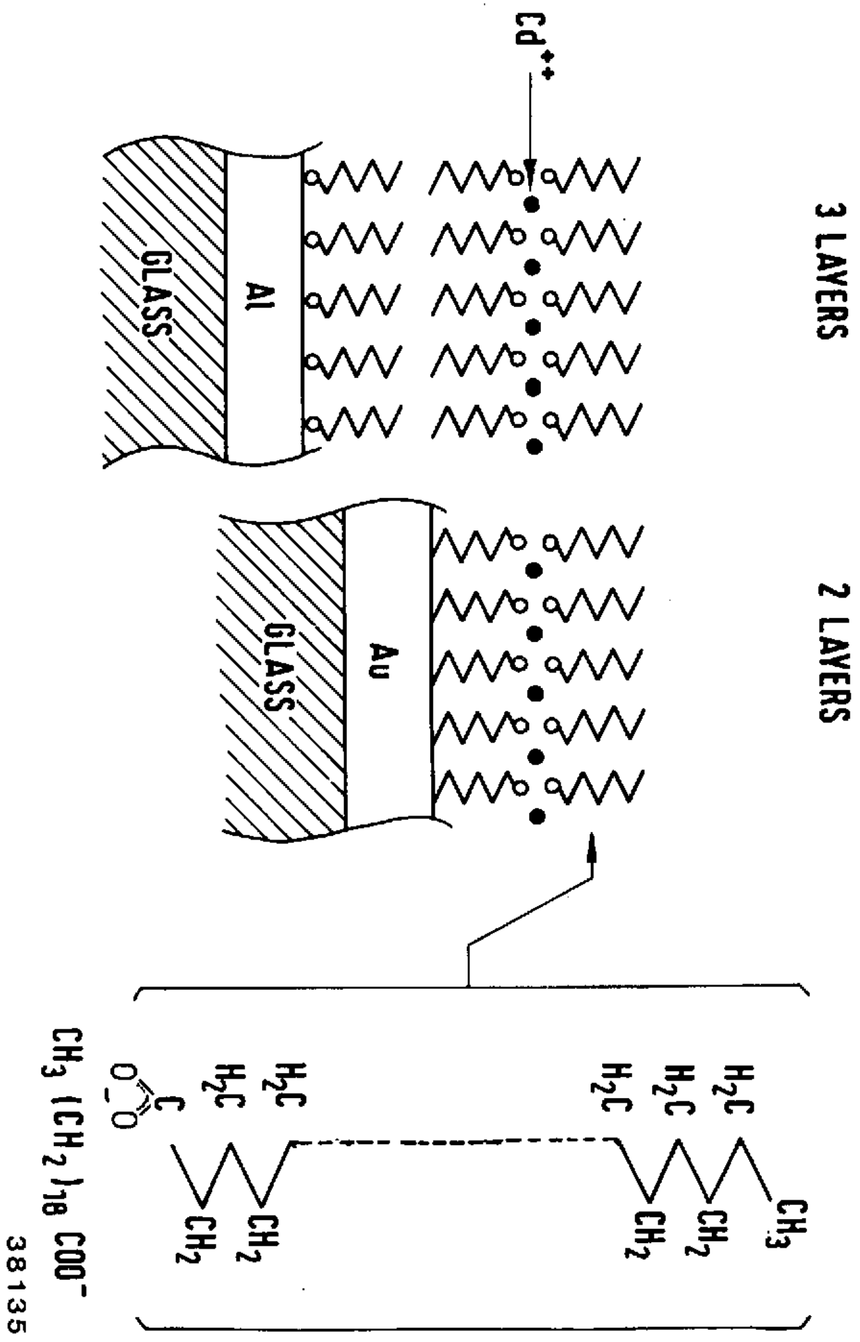
■ : from α = 70° measurements using 3 layers LB film

Δ : from α = 80° measurements using 3 layers LB film

-- : The calculated band structure for idealized polyethylene is a modification of the results by Karpfen [17] (see text).

● : Experimental results for n-$C_{36}H_{74}$ measured by Seki et al. [18].

Fig. 1



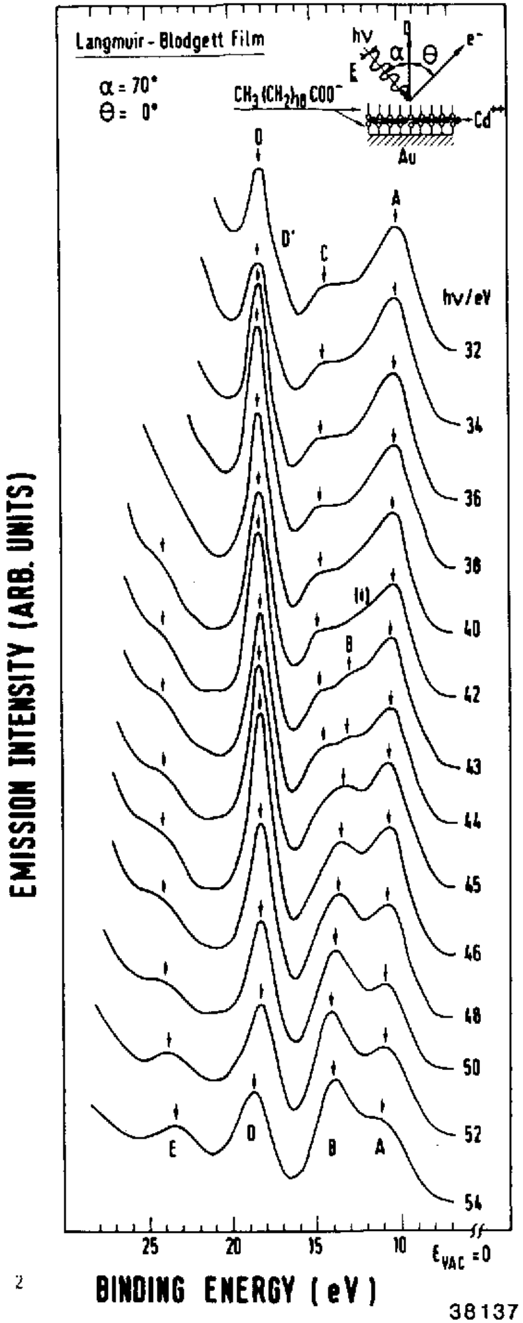


Fig. 2

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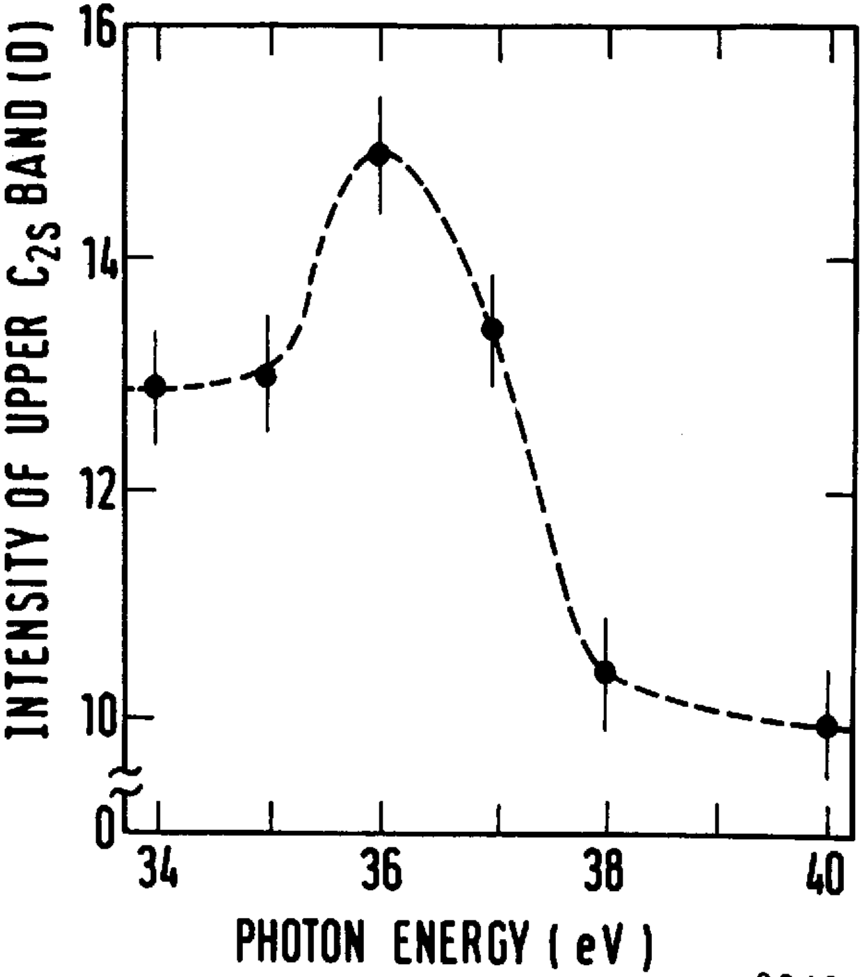

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Fig. 3

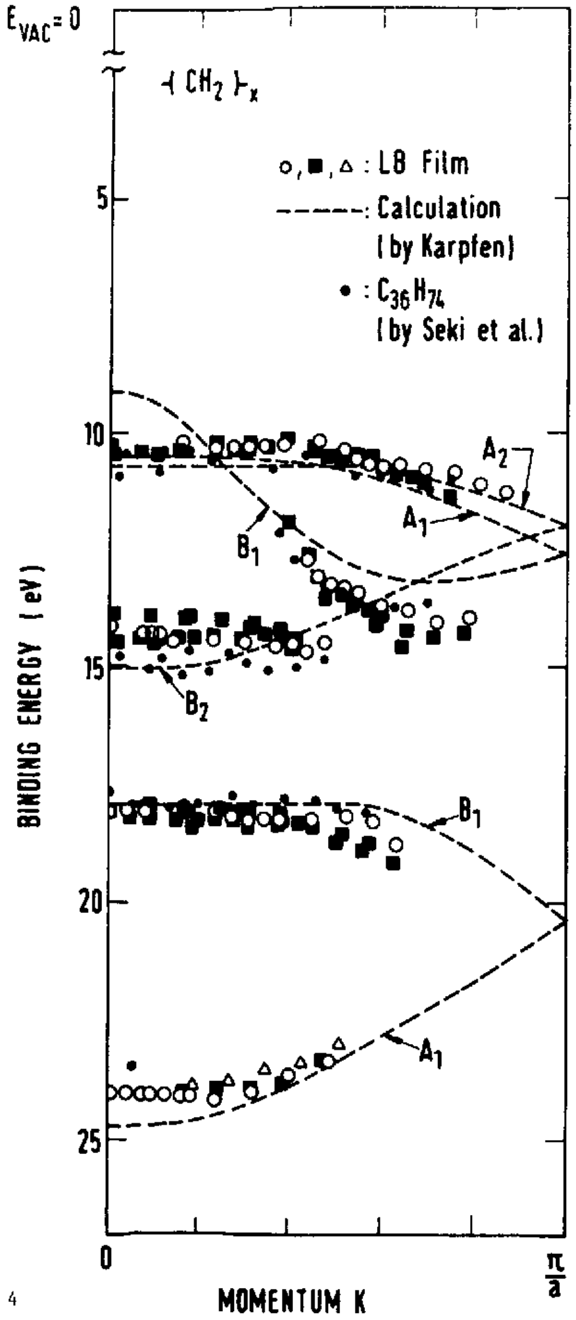
$E_{VAC}=0$
$-(CH_2)-_x$
○, ■, △ : LB Film
------: Calculation (by Karpfen)
● : $C_{36}H_{74}$ (by Seki et al.)
A_2
A_1
B_1
B_2
B_1
A_1
5
10
15
20
25
BINDING ENERGY (eV)
0
$\frac{\pi}{a}$
MOMENTUM K

Fig. 4

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