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Intramolecular Energy Band Dispersion of n-$C_{36}H_{74}$ observed by Angle-Resolved Photoemission with Synchrotron Radiation*

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Abstract

The energy band dispersion $E=E(\underline{k})$ is determined for the valence bands in a long-chain alkane n-$C_{36}H_{74}$ by angle-resolved photoemission from an oriented polycrystalline sample using synchrotron radiation. Comparison with theoretical calculations for a single chain shows good qualitative agreement for the position, width, and dispersion of the valence band. This is the first observation of energy band dispersion in an organic molecular solid.

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1. Introduction

Angle-resolved ultraviolet photoelectron spectroscopy combined with synchrotron radiation has been established as the most powerful tool for probing the energy band dispersion $E = E(\underline{k})$ of metals, semiconductors, and adsorbed layers [1, 2].

For organic molecular crystals a few $E(\underline{k})$ band structure calculations have been performed [3]. Due to the weak van der Waals interaction between the molecules in organic crystals, only small dispersions in the order of 0.1 eV can be expected. So far, experiments were not successful in observing these dispersions. Most of the compounds studied showed only changes in peak intensities related to the molecular orientation on the substrate [4].

Hexatriacontane n-$C_{36}H_{74}$ is a long saturated hydrocarbon with a structural formula n-$CH_3(CH_2)_{34}CH_3$, and thus a good model compound for simulating the electronic structure of polyethylene. Such a long molecule made up of regular repeating CH_2-units can be regarded as a one-dimensional crystal, and we can consider the formation of *intramolecular* bands. Actually, many theoretical calculations for a polyethylene chain [5] have indicated large intramolecular dispersion, in the order of 5 eV, due to the strong interatomic covalent bond within the chain. On the experimental side, UPS [6] and X-ray photoelectron spectroscopy (XPS) [7] have been applied to polyethylene and its model compounds in gaseous- and crystalline-states, but the intramolecular energy band dispersion has not yet been observed. A recent angle-resolved photoemission study of crystalline n-$C_{36}H_{74}$ using a HeII light source [6] showed a dependence on the angle of emission of the electrons, but its analysis was difficult.

Here we report an experimental determination of intramolecular energy band dispersion for crystalline n-$C_{36}H_{74}$ by means of angle-resolved UPS utilizing synchrotron radiation. This is the first observation of energy band dispersion in an organic molecular solid.

2. Experiment

The specimen was prepared as a film of $\sim$7 nm thickness by in situ evaporation of purified n-$C_{36}H_{74}$ on a Cu substrate. The sample preparation was done in a separate ultra-high-vacuum (UHV) preparation chamber at a pressure before and after evaporation of 5 x 10^{-10} Torr and subsequently transferred to the photoelectron spectrometer under UHV. Before evaporation the n-$C_{36}H_{74}$ was outgassed at elevated temperatures. Previous data from (i) X-ray diffraction of thicker films on Cu and (ii) vacuum-ultraviolet absorption spectra of films of comparable thickness on LiF showed that upon evaporation oriented polycrystalline films are formed with the molecular axis perpendicular to the substrate surface [6, 8] . This orientation was also confirmed in the present study by the dependence of the photoelectron spectra on the angle of incidence of the exciting light. The photoelectron spectra were measured with a setup described previously [9], consisting of a 1 m Seya-Namioka monochromator and a modified VG ADES 400 angle-resolving photoelectron spectrometer.

3. Results and Discussion

The study of the hν-dependence of the energy distribution curves of photoelectrons emitted normal to the surface is a well-established technique for band-mapping along the direction normal to the surface [1,2]. 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.

In Fig. 1 the photoelectron spectra for normal emission are shown. The upper part of the valence bands extending from 8 to 16 eV is formed by C 2p and H 1s electrons while the features at larger binding energies originate from C 2s electrons [5 - 7]. In the C 2p + H 1s bands two features A and C appear for photon energies $\lesssim$ 40 eV, while a new feature labelled B appears for hν $\gtrsim$ 40 eV. The initial state of peak B disperses towards higher binding energies with increasing photon energy. Peak C merges into it. In the C 2s range, a sharp peak labelled D of almost constant binding energy (18.0 eV) is observed.

The dispersion of an initial state $E_i = E_i(\underline{k}_i)$ can be deduced by assuming direct transitions and an appropriate final-state dispersion $E_f = E_f(\underline{k}_f)$ as [1,2]

$$E_i = E_f - h\nu \quad \text{and}$$
$$\underline{k}_i = \underline{k}_f$$

The photon-energy dependence of the intensity of peak D shows a maximum for hν = 36 eV [10] which determines the transition at the Γ point, i.e. the center of the Brillouin zone. By assuming a free-electron final state band fitted to that point, the experimental band structure was revealed. It is shown in Fig. 2.

In Fig. 2 we compare the experimental results with a recent ab-initio band structure calculation for polyethylene by Karpfen [5] . The symmetries of the bands were taken from Ref. [11]. In the original calculation the width of the valence bands is generally too large (e.g. about 25 % for the C 2p + H 1s bands). Therefore, we contracted the calculated band structure uniformly by a factor of 0.8 and shifted the resulting band structure to fit the experimental data. In this way a very good description of the experimental data is obtained. In particular, the dispersion of the upper B_1 band around the middle of the Brillouin-zone is clearly observed in the experiment. We note, however, that the uppermost band at $\underline{k}$ = 0 which, according to the calculation, forms the top of the valence bands, was not clearly observed separately from peak A.

The present experiment clearly shows the possibility of mapping intramolecular energy bands of oriented molecules by using angle-resolved photoemission and a tunable light source. A more detailed discussion, including the dependence of the photoelectron spectra on the angle of incidence of the photons and the polar angle of emission, as well as comparison with XPS spectra and other calculations, will be reported in a later publication [10] .

Acknowledgements

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Figure Captions

Fig. 1 Photon energy dependence of the energy distribution curves of electrons emitted normal to the surface for n-$C_{36}H_{74}$. The hatched part shows the intensity of peak D.

Fig. 2 Experimentally determined electronic band structure for n-$C_{36}H_{74}$ (circles). The calculated band structure for polyethylene (solid lines) is a modification of the results by Karpfen [5] (see text).
For comparison, reported peak positions in angle-integrated XPS [7] (rigidly shifted to fit the present results at the top of the lower B_1 band) and angle-resolved UPS by He II light source [6] are shown at the side of the frame.

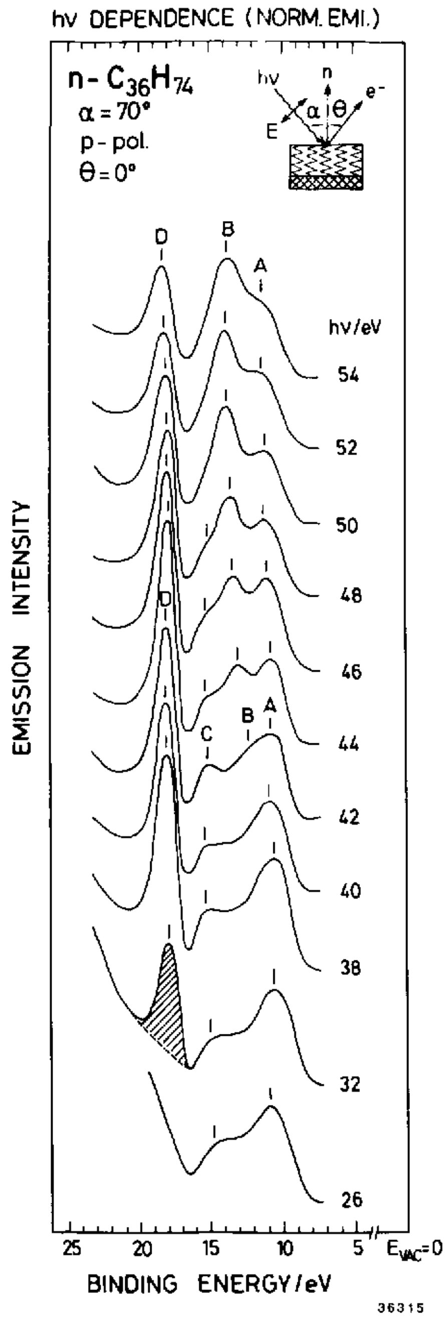
hν DEPENDENCE (NORM. EMI.)
n- $C_{36}H_{74}$
α = 70°
p - pol.
θ = 0°
hν
n
e⁻
E
α
θ
D
B
A
hν/eV
54
52
50
48
46
44
42
40
38
32
26
C
EMISSION INTENSITY
25
20
15
10
5
E_{VAC}=0
BINDING ENERGY / eV
36315

Fig. 1

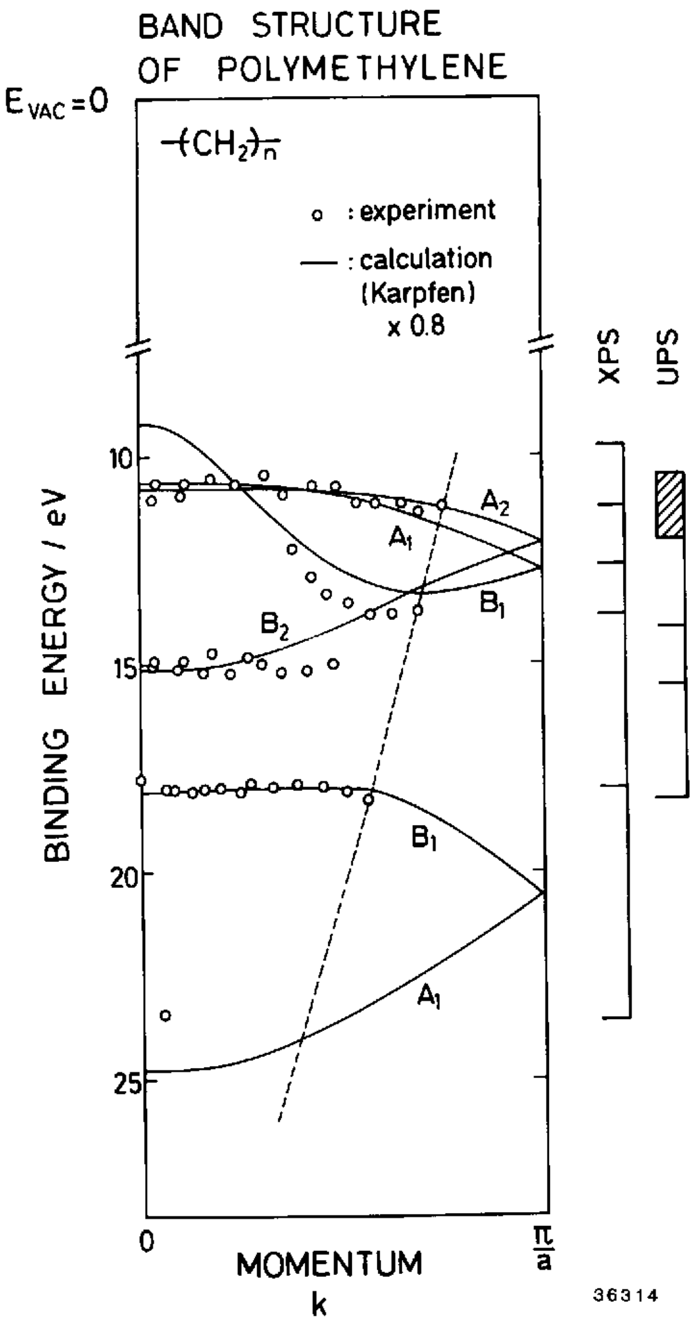
BAND STRUCTURE OF POLYMETHYLENE
E_{VAC} = 0
$-(CH_2)_n$
○ : experiment
— : calculation (Karpfen) x 0.8
XPS
UPS
BINDING ENERGY / eV
10
15
20
25
A_2
A_1
B_1
B_2
B_1
A_1
0
MOMENTUM k
π/a
36314

Fig. 2