DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

QUASI-MOLECULAR ANGLE DEPENDENCE OF PHOTOEMISSION

FROM THIN FILMS OF POLYSTYRENE

by

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NOTKESTRASSE 85 · 2 HAMBURG 52

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Abstract

Angle resolved photoelectron spectra from thin films of randomly oriented
polystyrene show a pronounced angular dependence of the emission for several
peaks derived from benzene molecular orbitals in the valence band region.
The analysis yields a clear molecular behaviour for the angular distribution
of the uppermost π-band ($1e_{1g}$) which can be described by a β-parameter of
$\beta = 0.6$ for $h\nu = 31$ eV. These results support for polystyrene the notion
of weak intermolecular interaction in a randomly oriented "condensed gas".

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Introduction

Angle resolved ultraviolet photoemission spectroscopy (ARUPS) combined with
synchrotron radiation has been established as a very powerful tool for in-
vestigating the electronic structure, in particular the valence bands of
metals and semiconductors [1]. A number of ARUPS studies have been carried
out for adsorbed organic molecules; for organic solids, however, this technique
has been used   to investigate oriented thin films thus giving important
information about the origin of photoemission bands [2,3], molecular orienta-
tions [2] and intramolecular dispersion relations [4,5]. These investigations
have been carried out on the basis that the angular dependence of photo-
emission is produced predominantly by directional asymmetries of electronic
states in the oriented sample. It is generally difficult, however, to prepare
oriented films of organic molecular solids. Due to this difficulty the angle
resolved photoemission technique has been applied only to a limited number
of molecular solids for which we can prepare thin oriented films.

For a dipole process in a free atom or molecule, on the other hand, the
angular distribution of photoelectrons is given by the well known relation [6,7]

$$\frac{d\sigma(\omega)}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \frac{1}{2} \beta(\omega) \left(3 \cos^2\alpha' - 1 \right) \right] \tag{1}$$

where $\sigma(\omega)$ is the energy-dependent total cross section and α' is the angle
between the directions of the vector potential $\underline{A}$ associated with the incident
photon field and the photoelectron momentum $\underline{p}$. In this case, the angular
pattern of the photoelectron intensities is only dependent on the angle
α' for a given β value at fixed $h\nu$. The value of the asymmetry parameter
β is determined by the relative amplitudes of the $1 \to 1 + 1$ and $1 \to 1 - 1$
channels in the matrix element and can take on values anywhere between $- 1$
and $+ 2$. The intermolecular interaction in a molecular solid is so weak
that the valence electron states of the free molecule largely determine
the valence band structure of the solid. This view has now been supported
by a large number of photoemission experiments for organic solids [8]. Further-
more, the final states in the photoemission process can in first approxi-
mation also be described by the final states of the free molecule for many
molecular solids so, that $\sigma(\omega)$ of molecular solids shows good agreement
with that of free molecules (see e.g. Ref. [9].)Thus we can expect that
a solid made up from randomly oriented non or weakly interacting molecules
shows the same angular emission pattern as a condensed gas, although for
photoemission from oriented solids and adsorbates the angular dependence

is mainly dominated by the crystallographic or molecular axes and scattering effects [10]. This expectation holds, as long as the transport process does not introduce asymmetries, and as long as anisotropic scattering effects can be neglected, that is at medium kinetic energies ($E_{kin} \approx$ 5-50 eV) [11]. Thus, it is of great interest to test the applicability and validity of eq. (1) to photoemission from weakly interacting organic molecules.

We mention in this context that Dilks discussed the importance of the angular distribution of photoelectrons, determined by the asymmetry parameter, for XPS of randomly oriented polyatomic molecular solids [12] and Davis et al. reported recently a large angle dependence in intermediate-energy photo-emission spectra from core and valence levels in metals and adsorbates showing an atomic behaviour [13].

The purpose of our present experiment is to clarify the applicability of eq. (1) to unoriented organic solids. We have choosen thin films of poly-styrene (PS) as a sample for this investigation because (i) PS can be con-sidered as a model of randomly oriented benzene in the solid state [14,15] (ii) various experimental data are available for PS [15-18], and (iii) the β parameters for gaseous benzene have been already measured [19].

Our results give clear experimental evidence that the photoemission spectra from PS excited by synchrotron radiation in the range $h\nu$ = 20-35 eV show a strong angular dependence which can be described by eq. (1). Furthermore the angular dependence of the intensities of different valence bands are different depending on the origin of these bands.

Experimental details

The experiments were performed with our previously described apparatus at the DORIS II storage ring in the synchrotron radiation laboratory HASYLAB at DESY [20]. The system consists of a 1m Seya-Namioka monochromator and a modified VG-ADES 400 angle resolving photoelectron spectrometer.

The thin films of PS were prepared on a well-polished Cu substrate from toluene solution of PS by spin-coating technique [21]. The thickness of the samples was estimated to be $\approx$ 100 Å. After the preparation of the thin films of PS, the sample was immediately introduced into the spectrometer chamber. The base pressure during the measurements was 2 x 10^{-10} Torr.

The photoelectron spectra were measured with an angular resolution of $\sim 2°$ and an energy resolution less than 0.3 eV by changing Θ, the angle between $\underline{p}$ and sample normal $\underline{n}$, at α = 0 and by changing α at Θ = 15°. Here α is the angle between the incident photon direction and $\underline{n}$ (see Fig. 2). The vectors $\underline{A}$, $\underline{p}$, and $\underline{n}$ were in the same plane perpendicular to the sample sur-face The surface area irradiated by the incident photon beam was smaller than the sampling area of the energy analyzer for all combinations of α and Θ used in the present experiments.

Results and Discussion

In fig. 1, two sets of angle-resolved energy distribution curves are shown for a PS film at $h\nu$ = 31 eV, measured by varying Θ or α. The spectra in fig. 1 have been normalized to the intensity of the second band B. In this way it is easy to compare the relative intensity variations of different peaks. Six features labeled A to F can be distinguished. The energy positions of these features show no angle dependence and excellent agreement with those in angle integrated spectra for PS [15] and condensed benzene [8]. They show a one-to-one correspondence to the gas phase spectrum of benzene [22] (see fig. 1 and table 1). From this correspondence we can easily assign these spectral bands A, B, C, D, E, and F to $1e_{1g}$, $3e_{2g}$ + $1a_{2u}$, $3e_{1u}$ + $1b_{2u}$, $2b_{1u}$, $3a_{1g}$, and $2e_{2g}$ of benzene molecular orbitals, respectively. These comparisons are summarized in Table 1.

We note that the uppermost valence band A, which corresponds to the π-type $1e_{1g}$ state of benzene, shows a prominent increase in intensity relative to band B ($3e_{2g}(\sigma)$ + $1a_{2u}(\pi)$) with increasing angle of incidence α and also with increasing Θ. Thus for example the intensity ratio I_A/I_B changes from 0.36 to 0.57 when Θ is increased from 15° to 75°. An increase of intensities with increasing Θ is also seen for features D and E in fig. 1. These changes with different take-off angle Θ are displayed in the difference spectrum $(N(E)^{\alpha=0}_{\Theta=75} - N(E)^{\alpha=0}_{\Theta=15})$ between the two spectra with Θ = 75 and Θ = 15 both taken at normal incidence (α = 0). In this way the relative increase of the intensities of features A, D and E with respect to peak B becomes obvious. For lower photon energies we have observed a qualitative similar angular dependence. At these photon energies a straight forward analysis is hampered however by the large underlying background of scattered slow secondary electrons.

From the spectra in fig. 1 the intensity of peak A was determined as a function of α', that is the angle between the direction of $\underline{A}$ and the excited photoelectron. We note that peak A is free from overlapping photoemission bands from the back-bone of PS [23]. However, unlike in the gas phase the analysis is not straight forward because in general the angles determining the experimental geometry (α, θ, and $90-\alpha-\theta$, see insert in fig. 2) are not identical with the angles γ, ϑ and α', describing the geometry at the point of photoexcitation within the sample. Furthermore we have to consider the absorption and scattering of the incident photons and the excited electrons, respectively. For the analysis we took the refraction and attenuation (absorption) of both the incident photons and the primary photoelectrons into account by using the three step model for the photoemission process [24,25] and assuming isotropic properties for randomly oriented PS-films. The optical constants were taken from Refs. [17,18]. The electron affinity of 0.4 eV, which was determined by comparing low-energy electron transmission and low-energy electron loss spectra of PS [14], was used to evaluate the refraction of electrons at the surface. Thus the refraction coefficients for PS were 0.97 for 31 eV photons and 0.99 for electrons of peak A (E_{kin} = 23.3 eV). The Fresnel's equations were used to estimate the change of the intensity of reflected light at the surface. The contribution of the reflected light was small enough for incident light of $h\nu$ = 31 eV and the incident angle $0 \leq \alpha \leq 45°$. We neglected the reflection of the photoelectron at the sample-vacuum interface, because the refraction coefficient of the photoelectron is approximately unity.

Under the conditions described above, the observed intensity I_θ^α at angles α and θ can be approximated by

$$I_\theta^\alpha \propto I_\vartheta^{\gamma'} \; \Lambda \; \cos\vartheta / (\mu \Lambda \cos\vartheta + \cos\gamma), \tag{2}$$

where $I_\vartheta^{\gamma'}$ is the intensity of photoelectrons at the point of excitation, and Λ and μ are the electron attenuation length and the absorption coefficient for the incident photons, respectively [25]. An electron attenuation length of 1×10^{-7} cm was used as an approximate value for electrons of peak A by using the "universal curve" for the electron mean free path [26]. We found that the product of the absorption coefficient μ and Λ is much smaller than 1, so that $\mu \Lambda \cos \vartheta \approx 0$. Thus the important correction factors in deducing the α' dependence ($90°-\gamma-\vartheta$) of the excitation probability from the observed intensities of peak A at the present conditions were $\cos\gamma$ for the incident light and $1/\cos\vartheta$ for the photoelectrons. The results are shown

in fig. 2. Inspection of fig. 2 shows that the two sets of data, the α-dependence and the θ-dependence, display the same angular variation when we plot the intensities as a function of α'. The quantitative agreement in the two sets of angular variation of the intensity of peak A was also obtained when I_A/I_B was plotted against α', further supporting the validity of our analysis for PS. The applicability of the simple relation (2) to UPS from PS rests on the fact that the refraction coefficient of PS is almost unity for both the incident photon and for the photoelectrons for the given energies. Our analysis leads us to the conclusion that the observed angular dependence is satisfactorily explained by eq. (1). The best fit between the observed points and eq. (1) was obtained for β = 0.6 as shown in fig. 2. Mehaffy et al. determined the β parameter for various orbitals of free benzene up to the photon energy of 27 eV [19]. By extrapolating their data to higher photon energies we expect a larger β value (≈ 1.4) for the $1e_{1g}$ state than that obtained here for PS. This difference may be partly due to the difference of the electronic final states between free benzene and benzene bound to a PS chain and to the non perfect sample surface.

In fig. 1 we also give for comparison the EDC's of gaseous benzene with $h\nu$ = 21 eV measured at two extreme angles, α' = 0° and 90°, by Mehaffy et al. [19]. A comparison to our data seems justified since the photon energy dependence of β parameters for benzene is not so large above $h\nu$ = 20 eV [19]. For molecular benzene the $1e_{1g}$, $2b_{1u}$, and $3a_{1g}$ orbitals show a large angular dependence in the molecular case and these intensity variations agree well with those observed for PS. The small angular variation in band C of PS compared to that of the $3e_{1u}$ band of molecular benzene can be understood by considering the overlapping $1b_{2u}$ state, which shows a smaller β value [19].

The main conclusion from our experiments is the observation that there are pronounced angular dependences in the photoemission intensities from unoriented condensed molecular systems. Moreover, the angular dependences can be well explained by the asymmetry parameter β characterizing different electronic states. We point out that this type of experiment will be useful in characterizing and distinguishing the origins of photoemission bands from organic solids for which one cannot prepare oriented films.

Acknowledgement

Table I Ionization energies (eV) of ultraviolet-photoemission bands for benzene and polystyrene. Values in parenthesis indicate energy differences from peak A ($1e_{1g}$)

	Polystyrene (a)	Polystyrene (b)	Benzene (solid) (c)	Benzene (d)	Benzene (gas) (e)	Assignment
A	7.7 (0)	7.6 (0)	8.1 (0)	9.3 (0)	9.25 (0)	$1e_{1g}$
B	10.4 (2.7)	10.2 (2.6)	10.7 (2.6)	11.45 (2.15)	11.53 (2.28)	$3e_{2g}$
				12.15 (2.85)	12.38 (3.13)	$1a_{2u}$
C	12.9 (5.2)	12.8 (5.2)	13.1 (5.0)	13.85 (4.55)	13.98 (4.73)	$3e_{1u}$
				14.65 (5.35)	14.86 (5.61)	$1b_{2u}$
D	13.8 (6.1)		14.1 (6.0)	15.40 (6.10)	15.46 (6.21)	$2b_{1u}$
E	15.0 (7.3)	15.0 (7.4)	15.4 (7.3)	16.85 (7.55)	16.84 (7.59)	$3a_{1g}$
F	17.5 (9.8)	17.4 (9.8)	17.6 (9.5)	18.6 19.2-(9.3 9.9)		$2e_{2g}$
	20.9 (13.3)			22.0-22.8 (12.7-13.5)		$2e_{1u}$
				28.7 (19.4)		$2a_{1g}$

a: Present results
b: Angle integrated measurements with HeII (hν = 40.8 eV). From ref. 16.
c: From ref. 8
d: From ref. 22a
e: From ref. 22b

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BENZENE (GAS)

$3a_{1g}$ $3e_{2u}$ $1e_{2u}$ $1a_{2u}$ $3e_{2g}$ $1e_{1g}$

$2b_{1u}$

$\alpha' = 0°$

$\alpha' = 90°$

$N(E)^{\alpha=0}_{\theta=75} - N(E)^{\alpha=0}_{\theta=15}$

POLYSTYRENE

A B C D E F

$\theta=75$
$\theta=60$
$\theta=45$
$\theta=30$
$\theta=15$

$\alpha=0$

$\alpha=45$
$\alpha=30$
$\alpha=15$
$\alpha=0$

$\theta=15$

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INTENSITY (RELATIVE UNITS)   PHOTOEMISSION

BINDING ENERGY (eV) $E_{VAC}=0$

Fig. 1

Figure captions

Fig. 1   Angle-resolved photoemission spectra of polystyrene at a photon energy of 31 eV. In the lower part of the figure spectra are shown which were measured for different angles of incidence ranging from 0° to 45° at a fixed angle of emission $\theta = 15°$. In the middle part data are shown for θ ranging from 15° to 75° with α fixed at $\alpha = 0°$. These spectra were normalized to the intensity of band B. $N(E)^{\alpha=0}_{\theta=75} - N(E)^{\alpha=0}_{\theta=15}$ shows the difference spectrum between spectra at normal incidence $\alpha = 0°$ with $\theta = 75°$ and $\alpha = 0°$ and $\theta = 15°$. The angle resolved photoemission spectra from gaseous benzene measured at $h\nu = 21$ eV by Mehaffy et al. [19] are also shown for comparison (top part of the figure). The gaseous spectra were shifted to lower binding energies ($\Delta E \simeq 1.5$ eV) to fit the energy position of the uppermost π-level to the peak A of PS.

Fig. 2   Angular dependence of the intensity of band A ($1e_{1g}$) of polystyrene. The intensities were normalized to the number of incident photons, and the effects of the attenuation and refraction of both incident photons and excited photoelectrons were taken into account. The relevant geometry is depicted in the inset. o: calculated from θ-scan data, : calculated from α-scan data. α' is the angle between the electric field vector $\underline{A}$ and the momentum $\underline{p}$ of the excited photoelectrons. The dashed curve was calculated with eq. (1) for $\beta = 0.6$.
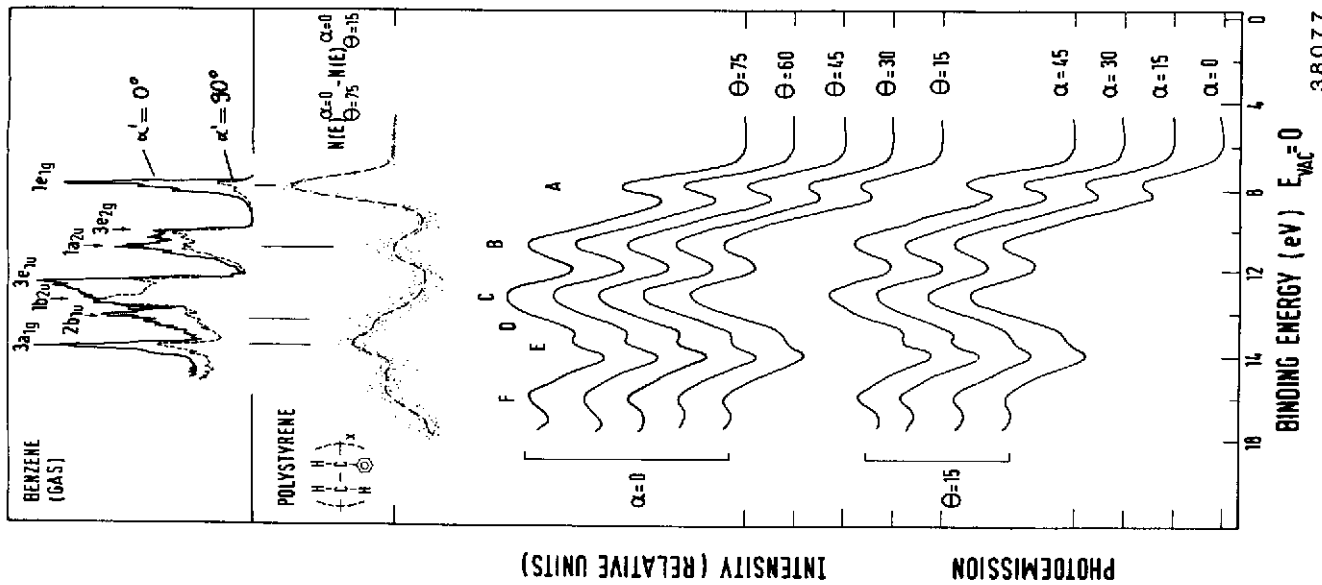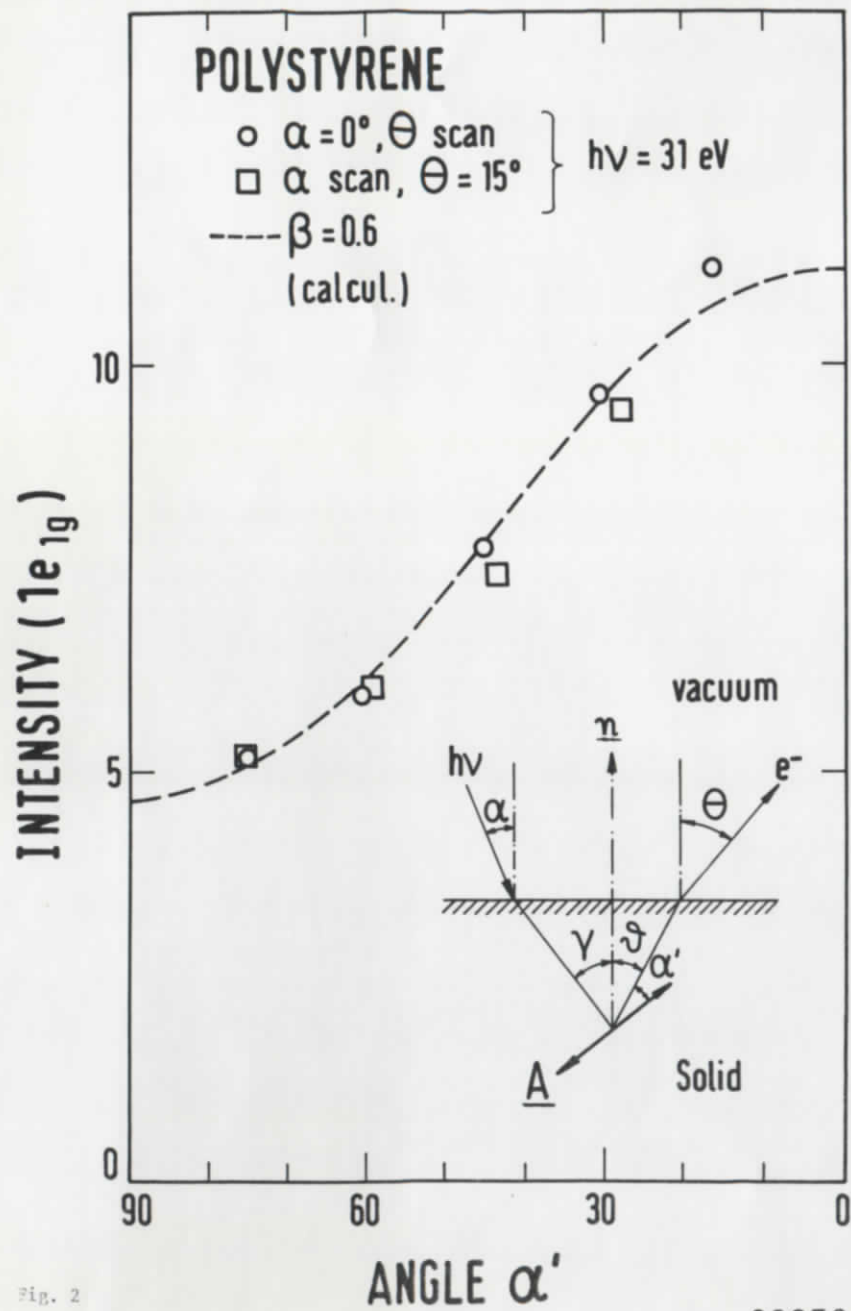
Fig.

Fig. 2

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