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Optical Anisotropy of Anthracene Single Crystals for Photon Energies from 4.5 to 11.5 eV

by

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Optical Anisotropy of Anthracene Single Crystals for Photon Energies from 4.5 to 11.5 eV[+]

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Abstract

Reflection spectra between 4.5 and 11.5 eV were measured for near normal incidence (7.5°) with s-polarized light from the (001) and (010) plane of anthracene single crystals at room temperature. The strong molecular $^1B_{2u}$-transition causes a strong anisotropic reflection band from the (010) face. The Davydov splitting, unmasked by collective effects, is for this transition 0.15 eV ± 0.05 eV. There is evidence, that a transition starting at 7.05 eV is polarized perpendicular to the molecular plane.

Reflektionsspektren wurden zwischen 4.5 und 11.5 eV für nahezu senkrechten Einfall (7.5°) mit s-polarisiertem Licht von der (001) und (010)-Ebene von Anthrazen Einkristallen bei Zimmertemperatur gemessen. Die starke $^1B_{2u}$-Molekülanregung führt zu einem starken anisotropen Reflexionsband von der (010)-Ebene. Die durch kollektive Effekte nicht veränderte Davydov Aufspaltung beträgt für diesen Übergang 0.15 eV ± 0.05 eV. Ein bei 7.05 eV einsetzender Übergang ist wahrscheinlich senkrecht zur Molekülebene polarisiert.

1. Introduction

The investigation of the optical properties of organic molecular crystals gives information on the polarization direction of electronic transitions in the molecule and the shift and splitting of the transitions by intermolecular interactions. Because of the interaction of different electronic transitions, information on short wavelength transitions is needed for the theoretical interpretation of the observed splittings and polarization ratios of longer wavelength transitions. For anthracene, being the best studied molecular crystal, knowledge of the optical behaviour in the VUV-region is necessary for example to interpret the Davydov splitting[1] of the system at 3800 Å first studied by Obreimov and Prikhotko[2]. With the exception of the work by Clark and Philpott[3,4,5], optical investigations of anthracene have only been performed either in reflection from the easy cleavage plane of anthracene single crystals, which is the (001) plane (ab-plane), or in transmission through thin monocrystalline flakes with (001) surface[6].

The Davydov splitting of the transitions for the incident radiation propagating perpendicular to (001) with the electric vector parallel and perpendicular to the <u>b</u>-axis ⟨010⟩ was calculated as the energetic difference of the A_u (polarized ∥ <u>b</u>) and Bu (polarized ⊥ <u>b</u>) crystalline states (group C_{2h}) in the center of the Brillouin zone of crystalline anthracene (e.g. [1,7]). In this way one would have to expect the same excitation energy for a particular crystalline state for all directions of polarization perpendicular to <u>b</u> (e.g. for polarization direction perpendicular to <u>b</u> and propagation directions perpendicular to (001) or (010)). Fox and Yatsiv[8] were the first to point out that the direction of propagation cannot be neglected because of collective contributions to the interaction lattice sums, which do not disappear even in the limit of the wavevector being small compared to the extension of the Brillouin zone. These contributions may be considered as caused by the partially longitudinal character of electromagnetic waves in anisotropic crystals.

They have been taken into account in the dipole interaction calculations of Mahan[9] and Philpott[10]. Experimental evidence for these collective effects comes from characteristic electron energy loss work[11], where a shift was observed of the strong molecular $^1B_{2u}$-transition with the direction of momentum transfer of the scattered electrons (this direction is equivalent to the direction of the $\underline{E}$-vector in optical experiments) and from optical reflection measurements of Clark on crystal planes (001), $(20\bar{1})$ and $(\bar{1}10)$[3,4,5], showing more spectral details than the characteristic electron energy loss work.

It follows from the symmetry of the monoclinic crystal that these collective longitudinal effects are absent for normal incidence on the (001) plane and $\underline{E} \parallel \underline{b}$ and for normal incidence on (010) and all directions of $\underline{E}$. Therefore the Davydov splitting deduced from our measurements for these directions should provide a good check on the theory of intermolecular interactions[12]. Furthermore these spectra should well indicate the polarization directions of electronic transitions with respect ot the axes of the anthracene molecule, assuming that the polarization ratios as given by the oriented gas model are not reversed.

The polarization ratios may be taken from Fig. 1. It shows the projection of the two anthracene molecules on the planes (001) and (010). Furthermore the projections of the long (L) and short (M) molecular axes lying in the molecular plane and the normal axis (N) are given. The polarization ratios as given by the oriented gas model are $|\underline{A}_1 + \underline{A}_2|^2 / |\underline{A}_1 - \underline{A}_2|^2$ with $\underline{A} = \{L,M,N\}$.

2. Experiment

2.1 Crystals

The reflection spectra from the (001) plane were taken with solution grown crystals. The $\underline{b}$ direction was easily identified by the shape of the crystals and by a polarimetric method[13]. Reflection spectra from the (010) plane were taken from crystals grown by the Bridgman method (purchased from Princeton Organics). Their triplet life time was 22 to 24 msec. First the (001) plane was found by trial as an easy cleavage plane, then by cleaving off a thin flake, the b-axis of which was found in the same way as with the solution grown crystals. As the (010) plane is a distinct cleavage plane[14,15], it was found by cleaving perpendicular to b. However, since this plane was even more wavy than the (001) cleavage plane (we estimate the deviation from the main direction to be as large as up to ±3°), it was polished to a well reflecting plane on a xylol soaked tissue. Goniometric measurements showed the polished plane to be perpendicular within one degree to the (001) cleavage plane. The direction of the a-axis on the (010) plane to be studied is the cutting line with the (001) cleavage plane. It served as a reference for the polarization direction in our measurements.

There is no danger that the distortion of the crystalline structure by polishing affects the results of the reflection measurements: as the crystal was kept in the evacuated reflectometer during the measurements there was a slow evaporation from the crystal by which undisturbed crystalline structure was always exposed to the radiation.

2.2 Reflection Measurements

The measurements were taken using the polarized continuum of the synchrotron radiation from the 7.5 GeV Deutsches Elektronen-Synchrotron DESY[16]. The radiation was monochromatized by a near normal incidence monochromator in a modified Wadsworth mount, as described in Ref. [17]. For the present experiment an Al + MgF_2 coated 600 lines/mm grating, blazed at 1200 Å was used. The spectral resolution was 2.5 Å over the whole spectral range. The absolute energy positions given with our results are accurate within ± 0.025 eV. The monochromatic radiation of a high degree of polarization (better than 0.94) was reflected by a plane Al-coated mirror onto the sample, from where the light was reflected to the photomultiplier (Fig. 2). The angle of incidence onto the sample was 7.5°. The radiation was for all measurements s-polarized with respect to the plane of incidence. For an easy and quick check on the primary spectrum the Al-mirror could be turned into such a position that it was hit by the incoming radiation at the same spot and under the same angle of incidence. In this position the radiation was directly reflected onto the multiplier.

Three multipliers were used: one with a sapphire window and a CsTe photocathode (4.0 eV - 8.5 eV), one with a LiF-Window and CsTe photocathode (4.0 eV - 11.5 eV), and one with a LiF-window and a CsJ photocathode (6.5 eV - 11.5 eV). By the low energy cut off at 4.0 eV the influence of the well known fluorescence in the range of 2.7 to 3.2 eV [18] is excluded as an error in the reflectivity signal. Furthermore the good agreement of the photomultiplier signals in the overlapping energy range of the second and third multiplier shows, that the influence of a possible fluorescence between 4 and 6.5 eV can also be neglected.

Depending on the particular crystal, the reflectance from the (001) plane decreased exponentially with time to values as low as 50% of the value measured immediately after pumpdown. The relative spectral dependence, however, of the reflectance remained unchanged. The decrease of the reflectance is most probably due to increasing roughness of the surface because of the steady evaporation. Since the degree of the roughness induced Rayleigh scattering is not known, the reflectance is given in arbitrary units.

The reflectance spectra taken at room temperature were recorded for different fixed angles of polarization of the incident radiation with respect to the crystal axes. The angles were varied stepwise covering a full rotation of 360°. For excitation energies for which the spectra showed strong anisotropic reflectivity, the angular dependence of the reflectance was measured for a fixed wavelength by continuously changing the angle between the electric vector E of the incident light and the crystal axes. To this end the reflecting crystal plane was rotated around its normal.

The good twofold symmetry of these curves(Fig. 5), which is to be expected from crystal symmetry considerations, shows the good optical alignement and the relative small influcence of the wavy form of the reflecting surface.

3. Results

Fig. 3 shows the reflectivities from the ab-plane (001) for increasing angle γ between the b-axis <010> and the electric vector. For the directions $\underline{E} \parallel \underline{b}$ and $\underline{E} \parallel \underline{a}$ the agreement with the reflectivity spectra taken by Clark and Philpott below 7 eV is very good[4,19]. As the intensity for the different spectra of Fig. 3 is given in the same arbitrary units, they can be compared relative to each other.

From theoretical considerations it follows, that the reflectivity must vary continuously with γ as

$$R(\gamma) = \cos^2\gamma R_b + \sin^2\gamma R_a,$$

where R_b and R_a are the reflectivities for $\underline{E} \parallel \underline{b}$ and $\underline{E} \parallel \underline{a}$ respectively. This explains the steady change from the spectrum $\underline{E} \parallel \underline{b}$ to $\underline{E} \parallel \underline{a}$. Further the equation allows to compare the spectra to measurements with unpolarized light published recently by Cook and Le Comber[21]. In our experiments it was also confirmed that the reflectivity is the same for $+\gamma$ and $-\gamma$. As all this follows from simple crystal symmetry considerations, we consider the outcome of the variation of the reflectivity with γ as a positive check on the experimental setup.

Fig. 4 shows the reflectivities from the ac-plane (010) for photon energies from 4.5 eV to 8.5 eV for different directions of the electriv vector E of the incident radiation with respect to the crystalline directions a and c. There is a strong reflection band starting at 4.70 eV with vibrational structure and extending to a shoulder at 5.95 eV. This band has its maximum intensity for the electric vector E parallel to the projection of the long molecular axis L onto the (010) plane. For E⊥L it disappears nearly completely, except for a very weak and smooth structure at about 4.65 eV.

The angular rotation curves giving the reflectivity from the (010) plane at fixed photon energy versus the direction of E with respect to a and c (Fig. 5) show for the energy of 5 eV the change of the intensity of the above mentioned reflectivity band in a continous way.

The rotation curve for 2.75 eV has been taken with a conventional light source and a photomultiplier sensitive to visible radiation. The experiment confirms the data for the direction of the dielectric tensor axis in this spectral range as given by Winchell[15]. Preliminary experiments on the ac-face from 3.0 to 3.4 eV show three exciton bands at 3.13, 3.29 and 3.45 eV for E ∥ M. Within the errors of this preliminary experiment their position is the same as for E ∥ b on the ab-face [4]. For directions E nearly parallel L on the ac-face we observed without doubt the two first of these bands at approximately the same energy position. They appear on the slope of the intense L-polarized system between 4 and 6 eV[22].

Fig. 6 compiles the reflection data from the (001)-plane and E ∥ b and the (010)-plane and E ∥ L and E ∥ M. The two spectra from (010) are to be compared directly to each other, spectra from the two planes have been adjusted relatively to each other assuming the ratio for the maximal reflectivities to be 0.75 : 0.20. This ratio seems plausible by considering the absolute reflectivities given by Clark and Philpott[4] for the (001) and $(20\bar{1})$ planes. The reflectance at energies from 12 - 3o eV reported earlier by us[23] has not been confirmed yet. Meanwhile there is some doubt, whether the calibration factors, which were used to bring the relative reflection spectra to absolute values were correct.

4. Discussion

As mentioned in the introduction the Davydov splitting is usually given as the difference of peak positions of ε_2- or absorption spectra. However for the energy range investigated, absorption spectra are impossible to obtain, since the absorption is very high and specimens of (010)-orientation, which are thin enough, are impossible to obtain. Therefore ε_2-spectra can only be obtained by a Kramers-Kronig analysis from reflectivity measurements. As the Davydov splitting in most cases is of the order of 0.1 eV and smaller, the error in the ε_2-spectra introduced by the Kramers-Kronig analysis should be as small as possible.

We have performed a Kramers-Kronig analysis using different suitable extrapolations by taking into account data from the literature for energy ranges not covered by the present experiment. There is a general trend that the values for ε_2-peak positions are the same for different extrapolations within limits depending on the energy of the corresponding reflectivity peak (near 3 eV the limit is ± 0.01 eV increasing to ± 0.12 eV near 8 eV).

Since for peaks below 5 eV the difference in peak positions of reflectivity and ε_2-spectra does not exceed 0.02 eV we can give a value for the Davydov splitting of the $^1B_{2u}$-transition near 4.6 eV within ±0.05 eV. Values with similar reliability can not be given for peaks at higher energies, because of the above mentioned limits of the Kramers-Kronig analysis.

The strong reflection band starting at 4.70 eV seen on (010) for $\underline{E} \parallel \underline{L}$ is due to the molecular long axis polarized $\pi \rightarrow \pi^*$ transition $^1B_{2u} \leftarrow {}^1A_{1g}$, seen in the vapour phase at 5.24 - 5.25 eV[24,25] and in solution at 4.85 eV[26,27]. Theoretical work[4,10,28-31] agrees that the component polarized ‖b of this strong transition is the structure seen in the reflection spectra from (001) for E ‖ b between 4.55 and 4.90 eV. The Davydov splitting between the first vibronic peaks on (010) E ‖ L and on (001) E ‖ b which, as discussed in the introduction, is free of collective contributions, amounts to 0.15 ± 0.05 eV.

For E ‖ a on (001) (see Fig. 3) where collective effects are present this strong L-polarized excitation is shifted to higher energies: Clark and Philpott[4] calculate this transition to be shifted to about the position of the two reflectivity maxima seen near 6 eV. They point out that a definite value of the splitting of this molecular transition cannot be obtained from spectra for E ‖ b and E ‖ a on (001) because the structure for E ‖ a is due to the mixing of this shifted L-polarized transition with the M-polarized transitions seen near 5.5 eV and 6.4 eV for E ‖ b.

For E ‖ L on the ac-plane there appears a shoulder on the high energy side of the strong reflection band at 5.95 eV. Its crystalline b-polarized component may be the shoulder seen on (001) for E ‖ b at 5.90 eV. At low temperature this shoulder becomes a separate peak[27,32].

In the reflectivity spectra from (010) for directions of E approximately between the directions M and a a shoulder is seen at 7.05 eV (Fig. 4). As no such structure is seen on (001) for E ‖ b and since the direction for which this structure can be seen is the N-direction (see Fig. 1) the plausible molecular assignment of this transition is a $^1B_{3u} \leftarrow {}^1A_{1g}$ excitation polarized normal to the molecular plane. The corresponding structure on (001) for E ‖ a has already be seen by Clark[20] and assigned to the same transition.

The comparison of the three well defined structures near 5.5 eV, 6.4 eV and 7.65 eV on (010) for E ‖ M and on (001) for E ‖ B (Fig. 6) indicates their origin from M-polarized $^1B_{1u} \leftarrow {}^1A_{1g}$ molecular transitions. Corresponding absorption peaks for the first two reflectivity maxima are found in solution at 5.6 and 6.7 eV[26,27]. However there is no obvious correlation to vapour absorption data in this spectral range[24,33]. The rotation curves for the first two of these peaks, not displayed in Fig. 5, still show maximum reflectivities for $\underline{E} \parallel \underline{L}$, because the strong L-polarized reflection band extends up to these energies, so that the reflectivity for $\underline{E} \parallel \underline{L}$ is greater than the reflectivity for $\underline{E} \parallel \underline{M}$, caused by the ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition. (See also Fig. 4.) The angular dependence of the reflectance for the third peak at 7.75 eV is shown in Fig. 5. It indicates, that the maximum of the reflectivity lies rather in the direction perpendicular to $\underline{L}$ than in the direction of $\underline{M}$. A possible explanation may be, that the intensity underneath this peak has its maximum in N-direction. This N-polarized structure would then extend from the shoulder seen at 7.05 eV to higher energies.

Definite assignement of the 7.80 peak on (010) for $\underline{E} \parallel \underline{L}$ is not possible. It may be related to the $\underline{M}$-polarized maximum at 7.7 eV or be a separate $\underline{L}$-polarized transition. The later seems quite plausible since π-electron calculations of Pariser[34] show a weak L-polarized transition at 7.22 eV.

The interpretation of the structures above 9 eV is difficult. The rotation curve for $\hbar\omega = 9.63$ eV (Fig. 5) indicates some N-polarized contribution to the spectrum. A careful measurement of the reflectance from the ac-plane in this energy range for different closely spaced angular intervalls may possibly bring some conclusive information.

Acknowledgement

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Figure Captions

Fig. 1: Projection of the anthracene unit cell onto the (ac) and (ab) plane.

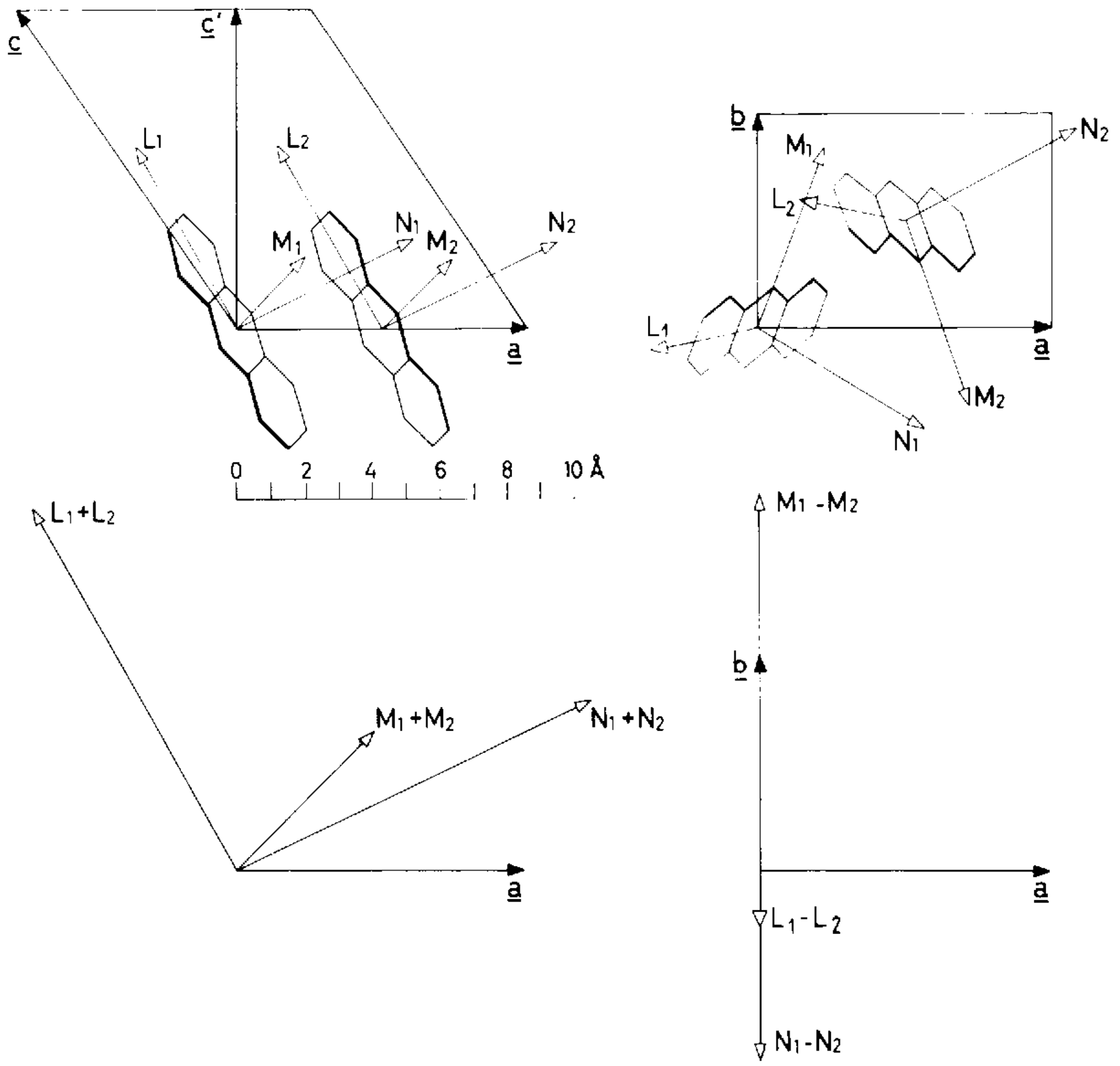
Fig. 2: Sketch of the experimental setup cut perpendicular to the synchrotron plane.

Fig. 3: Reflectance of anthracene single crystal from the (001)-plane at near normal incidence for various polarization directions.

Fig. 4: Reflectance of anthracene single crystal from the (010)-plane at near normal incidence for various polarization directions.

Fig. 5: Polar diagram of the reflectance of anthracene single crystal from the (010)-plane for different excitation energies. The curves represent the unnormalized, uncorrected experimental values.

Fig. 6: Reflectance of anthracene single crystal at near normal incidence from the (010)-plane for $\underline{E} \parallel \underline{L}$, $\underline{E} \parallel \underline{M}$ and from the (001)-plane for $\underline{E} \parallel \underline{b}$. Spectra from the two planes have been adjusted relatively to each other assuming a ratio for the maximal reflectivities of 0.75 : 0.20.



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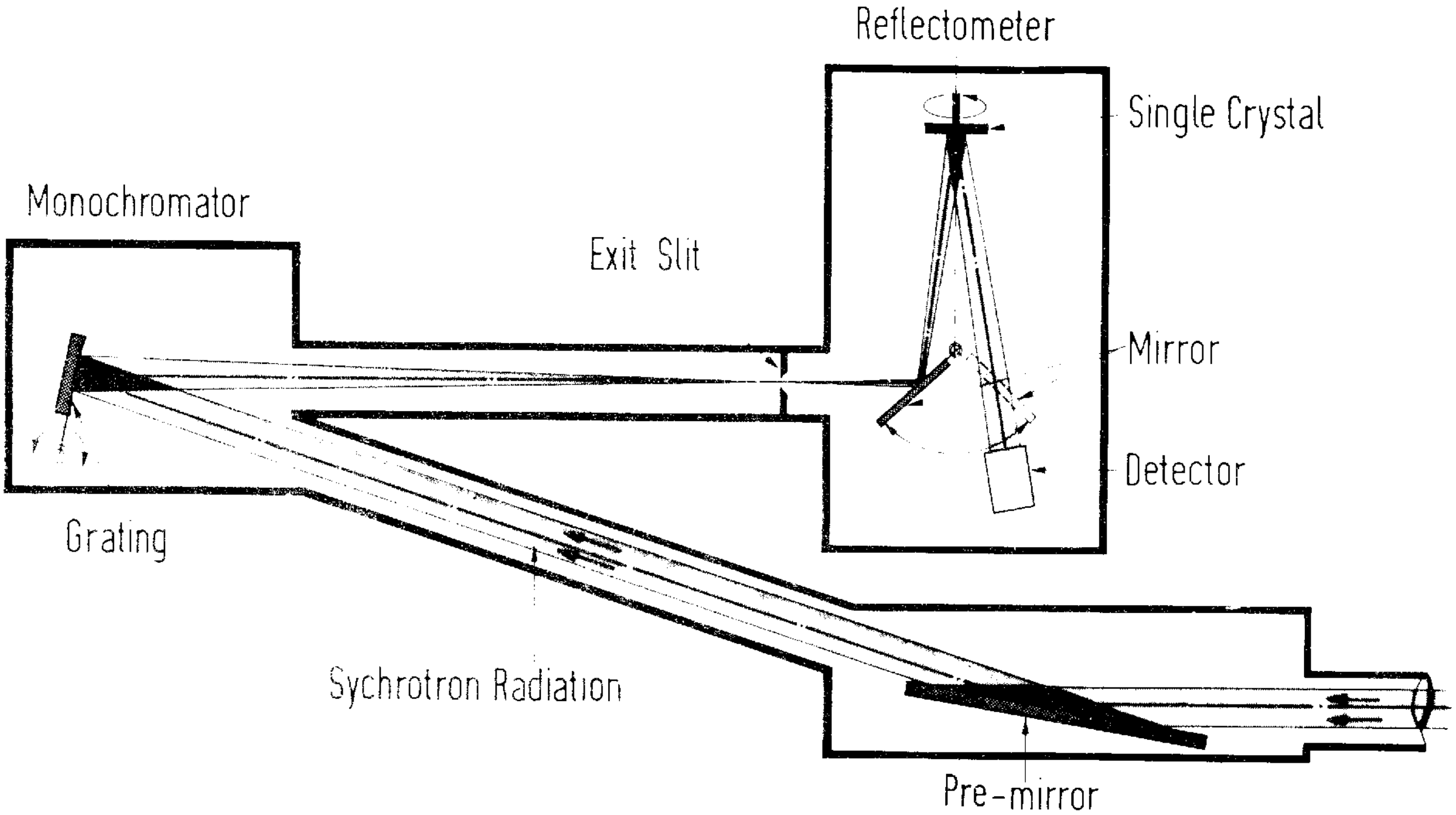
(0 0 1) PLANE

Fig. 1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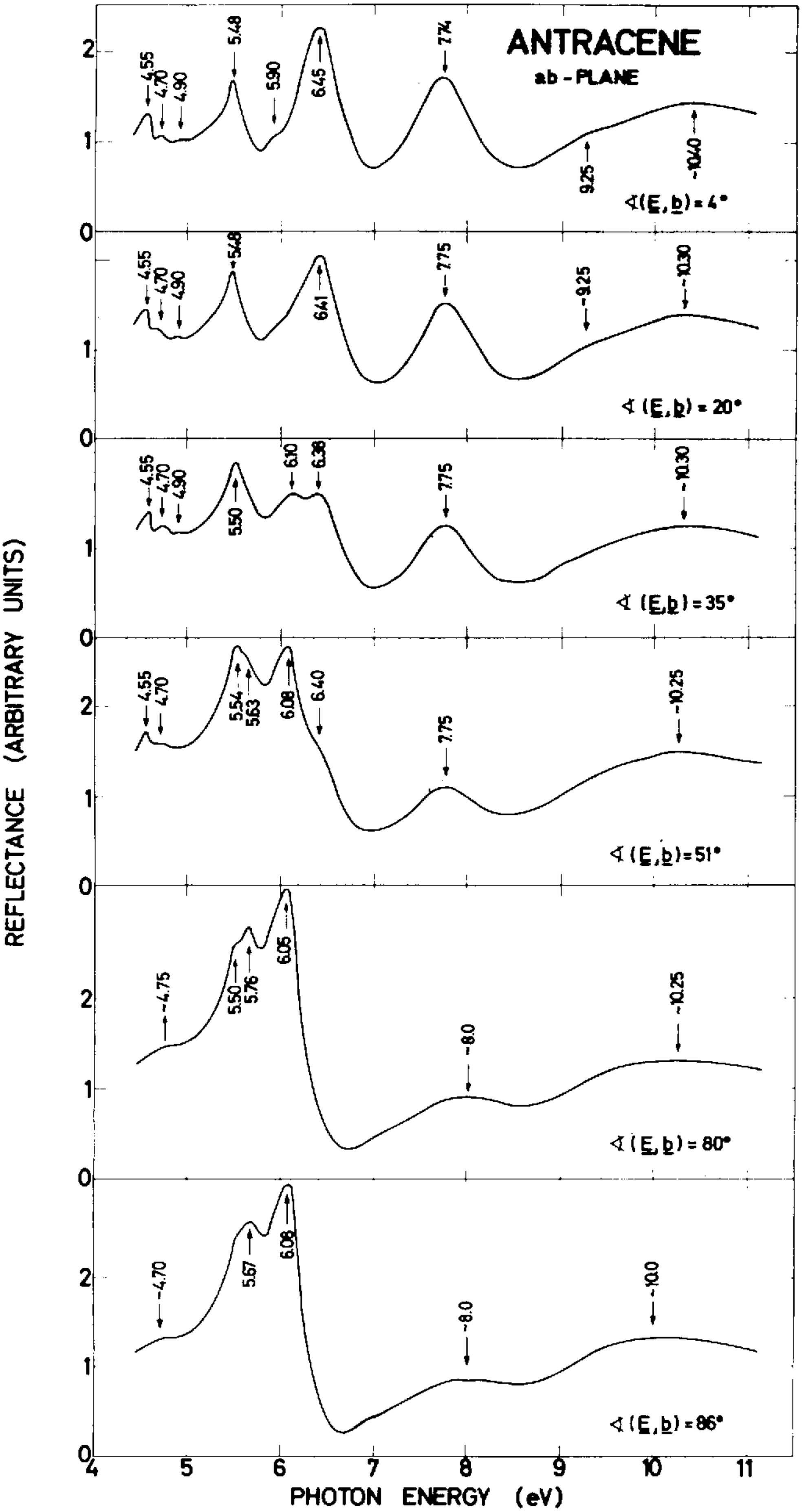
Monochromator
Exit Slit
Mirror
Detector
Grating
Sychrotron Radiation
Pre-mirror

Fig. 2


ANTRACENE
ab - PLANE
4.55
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∢(E, b) = 4°
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6.38
7.75
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4.70
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5.63
6.08
6.40
7.75
~10.25
∢ (E, b) = 51°
~4.75
5.50
5.76
6.05
~8.0
~10.25
∢ (E, b) = 80°
~4.70
5.67
6.08
~8.0
~10.0
∢ (E, b) = 86°
REFLECTANCE (ARBITRARY UNITS)
PHOTON ENERGY (eV)
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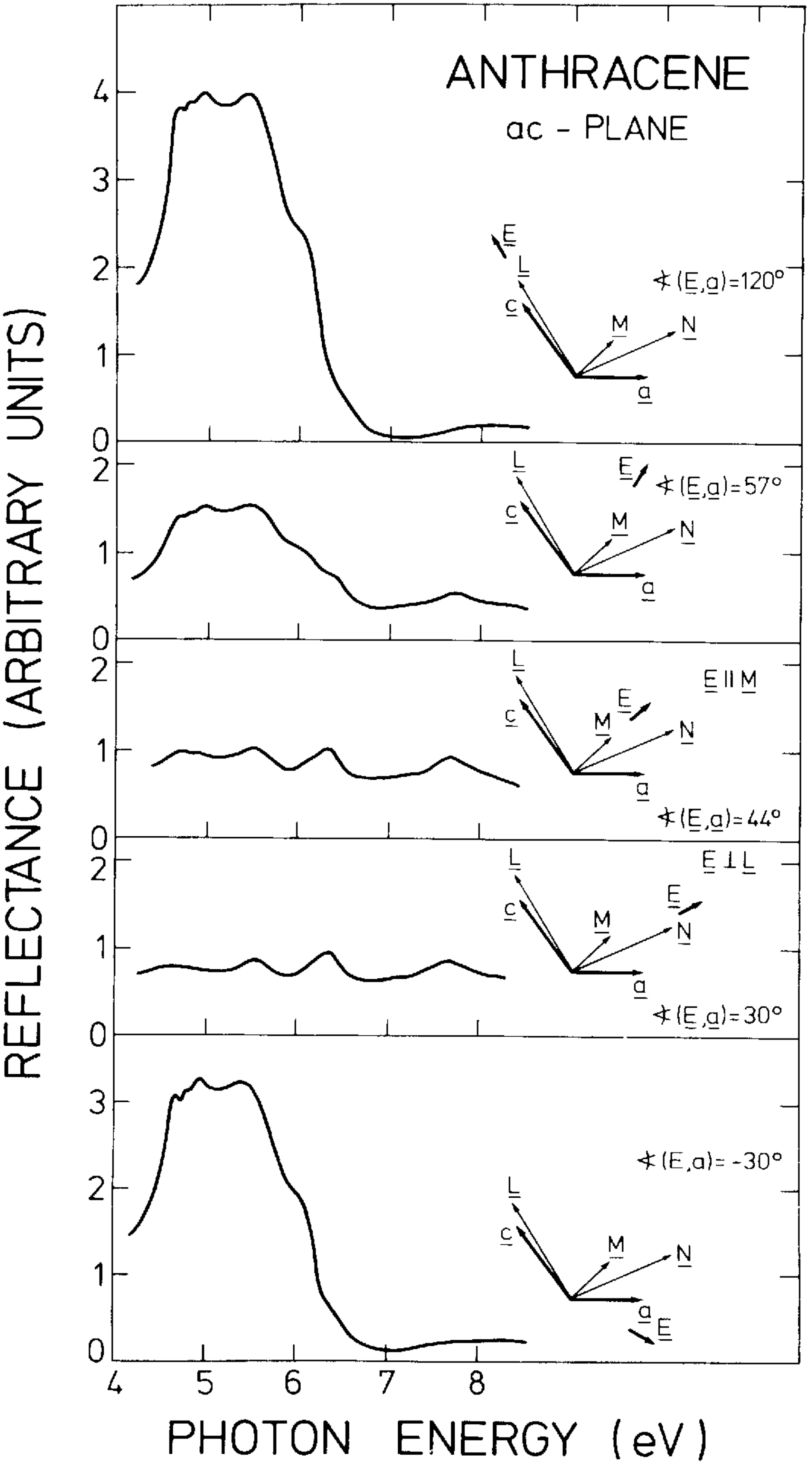
Fig. 3



ANTHRACENE
ac - PLANE
REFLECTANCE (ARBITRARY UNITS)
PHOTON ENERGY (eV)
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7
8
0
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4
∢(E,a)=120°
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M
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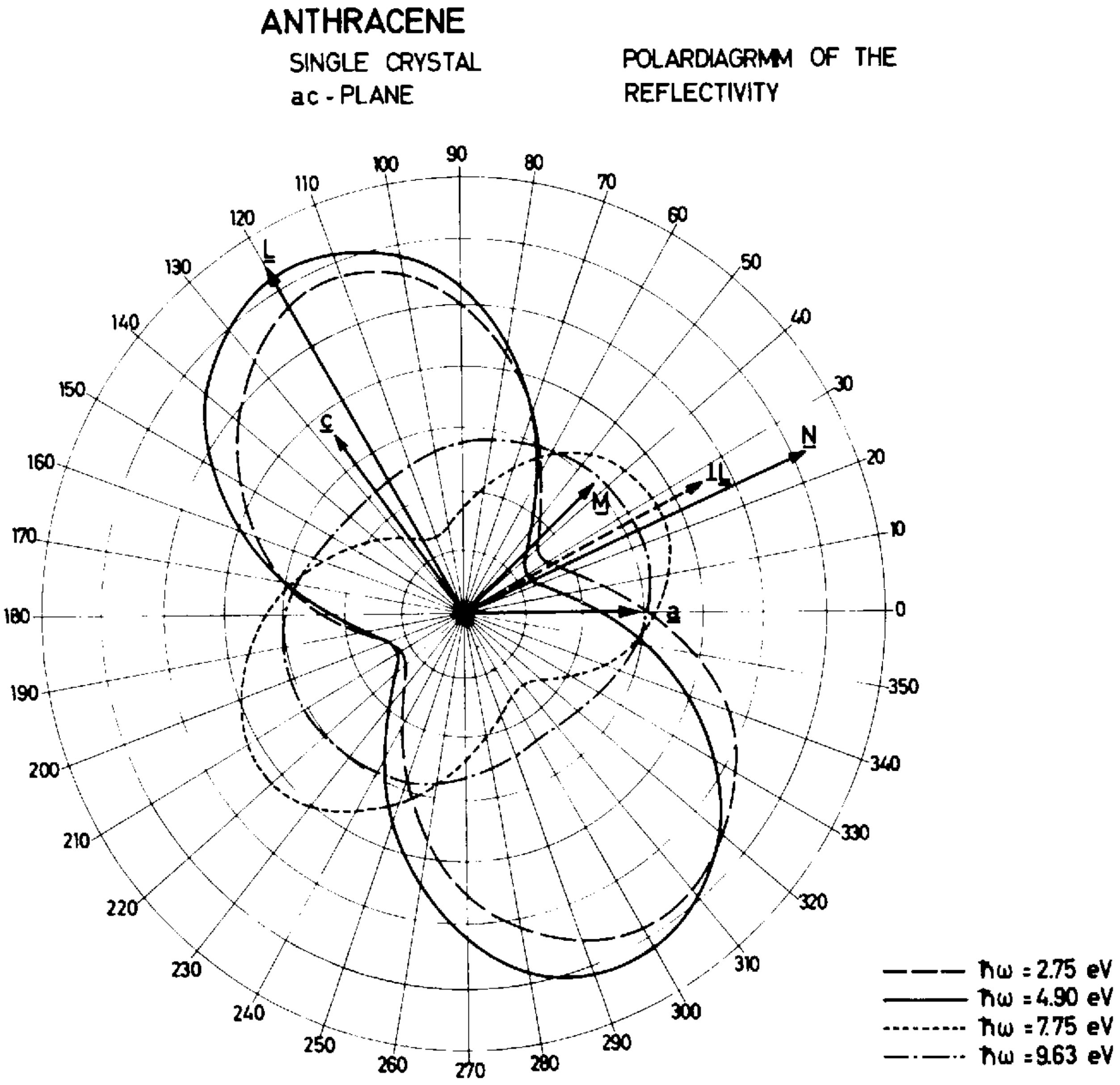
Fig. 4


ANTHRACENE
SINGLE CRYSTAL
ac - PLANE
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180
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200
210
220
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260
270
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330
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L
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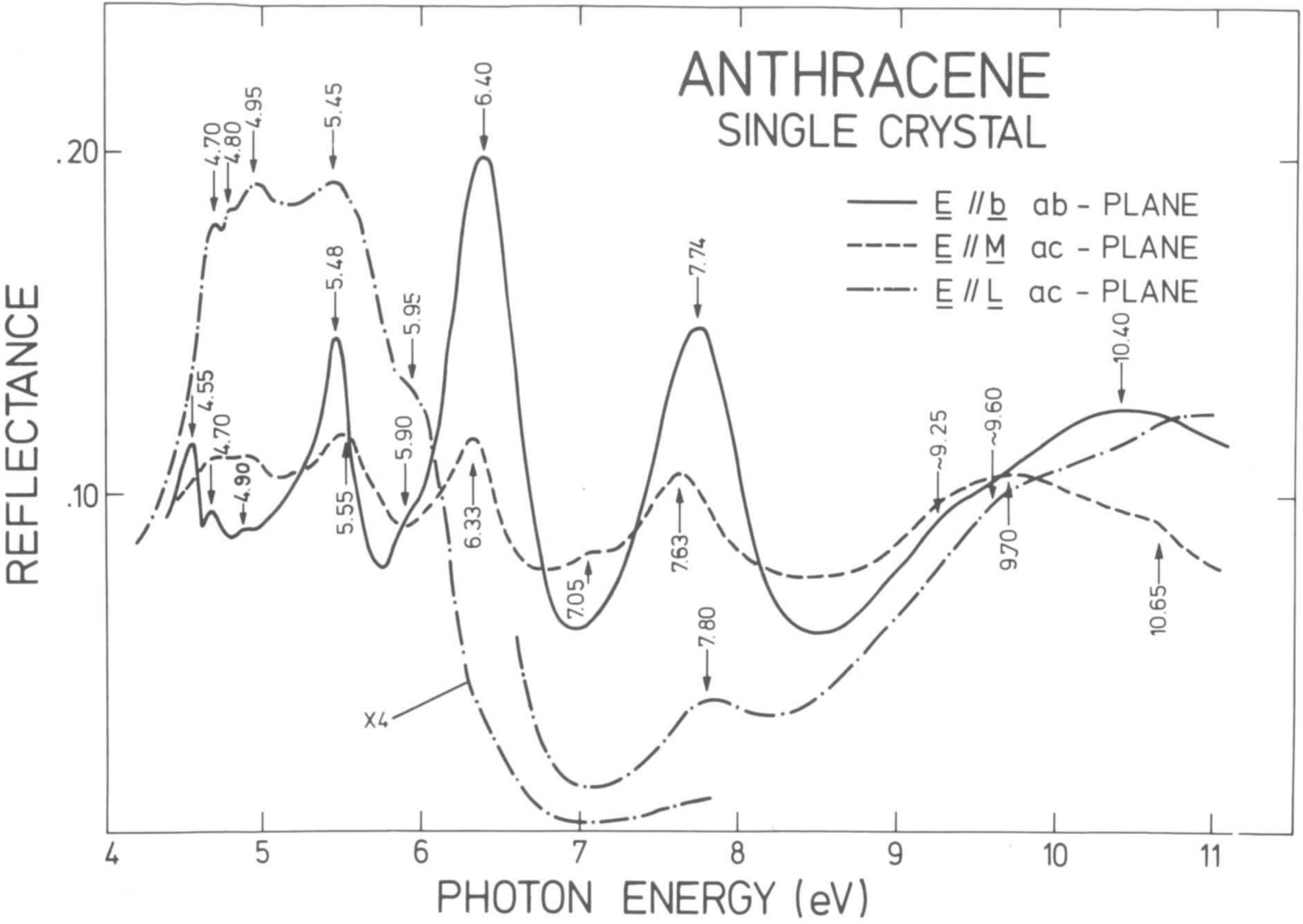
a
ħω = 2.75 eV
ħω = 4.90 eV
ħω = 7.75 eV
ħω = 9.63 eV

Fig. 5


ANTHRACENE
SINGLE CRYSTAL
E // b ab - PLANE
E // M ac - PLANE
E // L ac - PLANE
REFLECTANCE
.20
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PHOTON ENERGY (eV)
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4.70
4.80
4.95
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6.40
5.48
5.95
7.74
10.40
4.55
4.70
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5.90
5.55
6.33
7.05
7.63
~9.25
~9.60
9.70
10.65
7.80
X4

Fig. 6