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Photoemission from Polycyclic Aromatic Crystals in the Vacuum Ultraviolet Region

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The external photoelectric effect of thin films of tetracene, pentacene, violanthrene, quaterrylene and tetrathiotetracene was studied in the vacuum ultraviolet region. The contact potential differences between the emitters, organic crystals, and the collector (Aquadaq) were determined from the saturation points of the current-voltage characteristics. It was observed that the quantum yields of photoemission increase markedly with an increase in the photon energy, reaching the order of 10^{-2} electrons/quantum at $h\nu=10$ eV. The threshold energies were lower by 1—2 eV. than the molecular ionization potentials. An energy diagram for the external photoelectric process of organic molecular crystals was introduced on the basis of the intrinsic band model. With the aid of this diagram, the band gap energies, $\Delta\varepsilon$, were obtained from the observed values of photoemission. The values of $\Delta\varepsilon$ thus obtained were in fairly good agreement with those based on the results of the temperature dependence of semiconduction.

The external photoelectric effect is valuable in investigating the electrical properties of organic molecular crystals, because the current-voltage characteristics and the spectral distribution of the yield offer knowledge concerning the electronic structure of the crystal.

At the beginning of this century the external photoelectric effect of a polycyclic aromatic hydrocarbon, anthracene, was observed by Pochettino.¹⁾ Subsequently Hughes²⁾ and Volmer³⁾ measured the threshold of photoemission from anthracene and reported the values of 5.6—6.2 eV. and 5.5 eV. respectively. After these works, there was no observation of photoemission from polycyclic aromatic hydrocarbons until the 1950's. In 1953, Carswell and Iredale⁴⁾ investigated the photoelectric emission from anthracene and phenanthrene. Later the external photoelectric effect of aromatic hydrocarbons was studied by Kearns and Calvin,⁵⁾ Lyons and Morris,⁶⁾ and Vilessov, Sagrubsky, and Grabusov.⁷⁾ In the latter two articles observations of the emission extending to the vacuum ultraviolet region were reported.

In this paper, we will present the external photoelectric effect of some polycyclic aromatic hydrocarbons and tetrathiotetracene in the vacuum ultraviolet region. Further, an energy diagram for the photoelectric process will be introduced in order to correlate the observed values of photoemission with the activation energy of the electrical conduction.

Experimental

The materials used in the present study are shown in Fig. 1. Violanthrene (III) and tetrathiotetracene (V) were kindly furnished by Junji Aoki and Yoshio Matsunaga respectively. The other compounds were

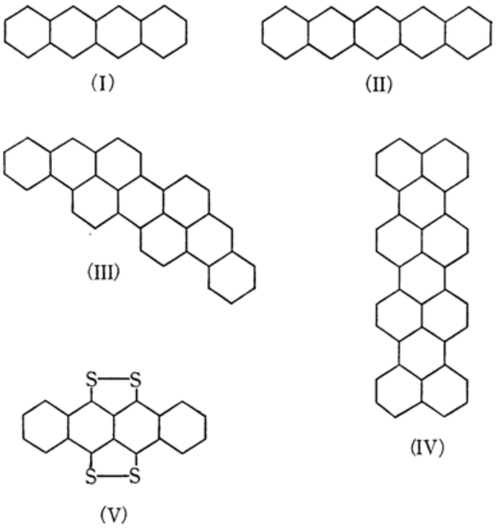

Fig. 1. Structural formulae of materials.
(I) Tetracene
(II) Pentacene
(III) Violanthrene
(IV) Quaterrylene
(V) Tetrathiotetracene

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1) A Pochettino, *Atti reale Accad. Lincei*, **1**, 355 (1906); **2**, 17 (1906).

2) A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

3) M. Volmer, *Ann. Phys.*, **40**, 775 (1913).

4) Carswell and Iredale, *Aust. J. Appl. Sci.*, **4**, 329 (1953).

5) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).

6) L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1960**, 5192.

7) F. I. Vilessov, A. A. Sagrubsky and D. S. Garbusov, *Physika Tverdogo Tela*, **5**, 2000 (1963).

provided by the Rütgeswerke-Aktiengeselshaft A. G., Germany. All of the materials were carefully purified by the recrystallization and vacuum sublimation method.

The photoemission was measured with a 0.5 meter Seya-Namioka-type[8] vacuum ultraviolet monochromator.* The monochromator, with its associated equipment, is shown schematically in Fig. 2. The grating was made by Bausch and Lomb Optical Company and had 1200 lines per mm. The wavelength calibration was made using the central image of the grating (0 Å) and also the line spectra of mercury (3650.2, 3654.8 and 3663.3 Å). Further, in the vicinity of the 1800 Å peak the wavelengths of the Schumann-Runge absorption band system of oxygen were compared with those described in the literature.[9]

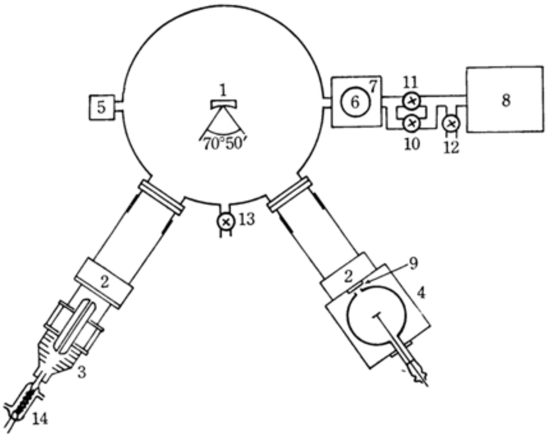

Fig. 2. Vacuum spectrometer.
1 Grating, 2 slit, 3 light source, 4 photoemission attachment, 5 Phillipps gauge, 6 oil diffusion pump, 7 cold trap, 8 rotary pump, 9 lithium fluoride window, 10 reducing valve, gate valve, 12 loak valve, 13 chamber leak valve and 14 palladium tube.

As a light source a Hinteregger-type hydrogen discharge lamp[10] was used. With the lamp turned on, pure hydrogen, prepared by passing commercial hydrogen from a cylinder through a palladium thimble (14 in Fig. 2), was introduced into the instrument. In order to control the velocity of the passage through the thimble, the Pd thimble was heated electrically by a coil wound on a Pyrex envelope. The temperature of the palladium tube and also of the opening of the reducing valve (10 in Fig. 2) were adjusted so that pure hydrogen flowed continuously through the monochromator chamber at an appropriate pressure. The normal operating pressure of hydrogen was around 4 mmHg.

In order to measure the photoemission the attachment illustrated in Fig. 3 was mounted onto the exit slit of the monochromator by iron fittings (6) and sealed vacuum-tight by means of an 0-ring (4). A photoemission cell (1) was mounted in a cylindrical chamber made of brass. A collector lead of the cell was taken out of the chamber through a glass-fused seal (3). When the vacuum spectrometer was used in the near-ultraviolet or visible region, the use of a set of filters became necessary in order to separate the higher-order spectra. From 2100 Å to 3500 Å, a potassium bromide plate was provided as a filter. Further, a glass filter was used in the wavelength region longer than 3500 Å. The filters (5) were mounted on a holder and were made exchangeable by sliding the holder shaft from the outside of the chamber.

In Fig. 4 the photocell is shown in detail. It is basically similar to that designed by Apker et al.[11] The collector is a glass sphere about 13 cm. in diameter. On the inside it is coated with a conducting layer of Aquadag (3), which was baked at 500°C in an electric furnace. After the heat treatment the work function

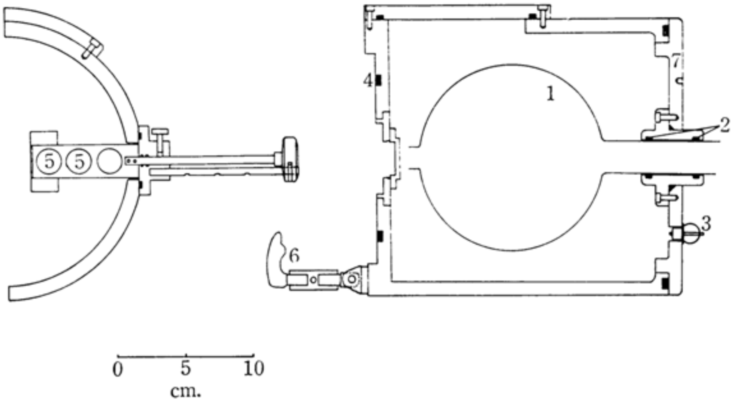

Fig. 3. Photoemission attachment.
1 Photoemission cell, 2 0-ring, 3 glass fused seal, 4 0-ring, 5 filter, 6 iron fitting, 7 flange.

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* The monochromator used in this experiment was a considerable improvement over the instrument produced by Jarrell-Ash Co.

[8] M. Seya, *Science of Light*, **2**, 8 (1952); T. Namioka, *J. Otp. Soc. Am.*, **49**, 951 (1959).

[9] K. Watanabe, E. Edward, C. Y. Inn and M. Zelikoff, *J. Chem. Phys.*, **21**, 1026 (1953); R. W. Ditschburn and D. W. O. Heddle, *Proc. Roy. Soc.*, **A226**, 509 (1954); A. M. Bass and H. P. Broida, *J. Mol. Spect.*, **12**, 221 (1964).

[10] R. G. Newburgh, L. Heroux and H. E. Hinteregger, *App. Optics*, **1**, 733 (1962).

[11] L. Apker, E. Taft and J. Dickey, *Phys. Rev.*, **74**, 1462 (1948).

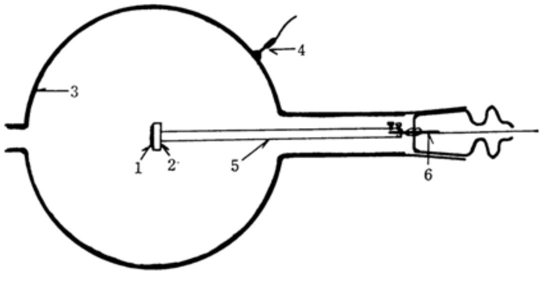

Fig. 4. Photocell.
1 Sample, 2 copper substrate, 3 graphite coating, 4 collector lead (tungsten rod), 5 brass rod, 6 tungsten rod.

of the Aquadag layer was practically always 4.74 ± 0.05 eV.11) A polycyclic organic compound (1) deposited onto a copper disk (2) (12 mm. in diameter) was fixed at the centre of the glass bulb as an emitter. The sublimation of the compound was carried out in vacuo (10^{-6} mmHg), the thickness of a film being several microns. Since the cell had no window, the pressure in it was equal to that in the attachment chamber (10^{-6} mmHg).

The absolute measurement of the light intensity was made by means of an Eppley circular thermopile, the sensitivity of which was $0.30\ \mu$V./μW. in vacuo. The output potential was amplified by a Keithley model 149 milli-micro voltmeter. The relative light intensity was obtained by measuring the fluorescence intensity from a coronene film evaporated onto a glass plate.12) In this case the flange of the attachment chamber (7 in Fig. 3) is changed for another one which can be fitted with an end-on-type photomultiplier tube, RCA 5819. The intensity of the light source was examined in relative units after each series of photoemission measurements.

The emission current was amplified by a Cary 31 vibrating-reed electrometer.

Results

Current - voltage Characteristics. — Monochromatic lights were used to observe the current-voltage characteristics of photoemission. The experimental results for tetracene and quaterrylene films are given in Figs. 5 and 6, where the ordinates are normalized with the saturation current, $I_s=1.0$. The values of the saturation voltage, V_s, of the current-voltage curves (the contact-potential differences between the emitters and the collector) are given in Table I for all of the compounds studied.*

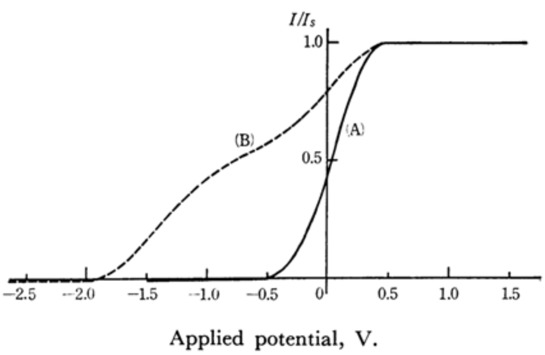

Fig. 5. Current-voltage relation of tetracene.
hν: (A) 6.20, (B) 7.75 eV.

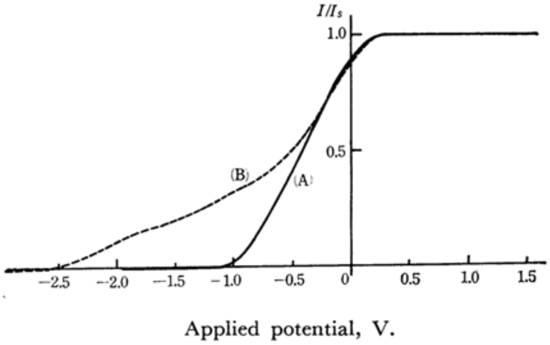

Fig. 6. Current-voltage relation of quaterrylene.
hν: (A) 6.20, (B) 7.75 eV.

TABLE I. SATURATION VOLTAGES OF THE CURRENT-VOLTAGE CHARACTERISTIC

Compound	V_s, volt
Tetracene	0.44
Pentacene	0.41
Violanthrene	0.21
Quaterrylene	0.28
Tetrathiotetracene	0.42

In order to determine the saturation point, the data of the current-voltage relation are plotted in the form:

$$1-(1-I/I_s)^{1/2} \quad \text{vs. V.} \qquad (1)$$

The intersection of two straight lines, one in the retarding potential region, and the other in the saturation region, obtained by the plot gives the value V_s.13)

In the case of tetracene, since the value of the electrical resistivity is high enough ($\rho_{15}=10^{15}\Omega$cm.), the potential drop within a thick film becomes comparable to that between its surface and the collector. Hence, a thin film ($<1\ \mu$) should be examined if we are to observe the correct current-voltage characteristics. The current-voltage relations of the other compounds were successfully obtained for films with thicknesses of several microns.

Spectral Distributions of the Yield.—The spectral responses of photoemissive currents were

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12) H. Inokuchi, Y. Harada and T. Kondow, *J. Opt. Soc. Am.*, **54**, 849 (1964).

* The V_s values obtained from I-V curves observed at different photon energies were in good agreement with each other.

13) L. Apker, E. Taft and J. Dickey, *Phys. Rev.*, **73**, 46 (1948).

observed under an applied potential of 10 V. In Figs. 7—9 the results for tetracene, pentacene and violanthrene are given. In each figure the ordinate shows the quantum yield, *Y*, derived from the ratio between the number of the incident photons and that of the emissive electrons.

The threshold values of the photon energies required for photoemission are compared in Table II with those obtained by other investigators. The table also includes the molecular ionization potentials. Since no appropriate extraporation formula has yet been found, the numerical value of the threshold was determined by extraporation to a quantum yield of 10^{-8} electrons per incident quantum.

Discussion

As may be seen from Table I, photocurrents saturate at low applied potentials (potentials of less than one volt). This phenomenon shows that the photocell used in the present study has a good

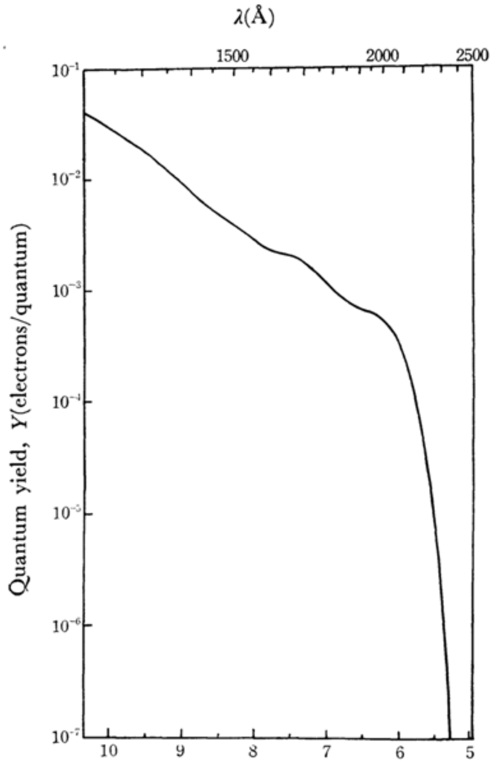

Fig. 7. Spectral distribution of the photoemission yield for tetracene.

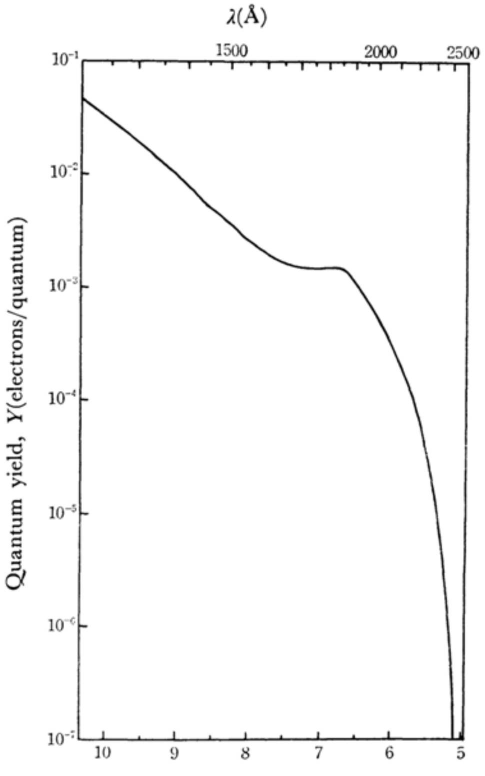

Fig. 8. Spectral distribution of the photoemission yield for pentacene.

TABLE II. THRESHOLD VALUES OF PHOTOEMISSION, E_{th} IN ADDITION TO MOLECULAR IONIZATION POTENTIALS, I_g

Compound	I_g, eV.	E_{th}, eV.			
		Present work			
Tetracene	6.88[a]	5.24	5.26[e]	5.38[f]	5.25[g]
Pentacene	6.73[b]	5.07	5.08[f]	5.1[g]	
Violanthrene	6.55[c]	4.96	5.20[f]		
Quaterrylene	5.98[d]	4.76	—		
Tetrathiotetracene	—	4.56	—		

a) F. I. Vilessov, *Dokl. Akad. Nauk SSSR*, **132**, 632 (1960).
b) R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).
c) F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1955).
d) Estimated from the energy of the longest absorption band (cf. Ref. c).
e) Ref. 6.
f) Ref. 5.
g) Ref. 7.

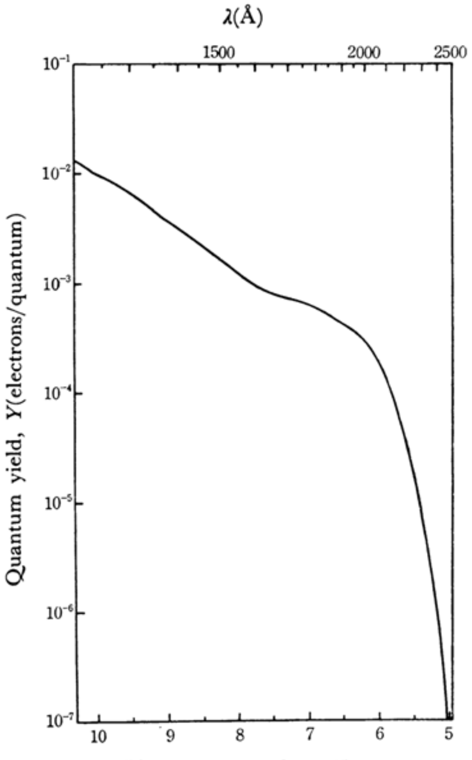

Fig. 9. Spectral distribution of the photoemission yield for violanthrene.

spherical geometry.

In the region of low applied potentials, the current-voltage curves are not parabolic (Figs. 5 and 6); especially, the curves for the incident light of 7.75 eV. have inflections. Hence, it can be pointed out that the kinetic energy distributions of the emitted electrons have several maxima. This behaviour of the emitted electrons will be discussed in a subsequent article.

Figures 7—9 show that the quantum yields of photoemission from tetracene, pentacene and violanthrene increase with an increase in the photon energy and reach the order of 10^{-2} electrons/quantum at $h\nu = 10$ eV. The other compounds give similar results. Thus, at large photon energies the yield of aromatic hydrocarbons is relatively large, comparable to those observed in such metals as palladium, tungsten and molybdenum.[14]

Table II shows that the threshold of photoemission (solid state ionization potential) occurs at an energy lower than by 1—2 eV. than the molecular ionization potential. As was suggested by Lyons,[15] this difference may be due to the polarization energy of the crystals by a positive centre.

Finally, let us consider the external photoelectric process of the organic molecular crystal quantitatively using the observed threshold values of the photoemission and the saturation potential of the current-voltage curve. In the case of the intrinsic semiconductor, the energy difference, δ, between the top of the valence band and the Fermi level is a half of the band gap energy, $\varDelta\varepsilon/2$, based on the results of the temperature dependence of the semiconduction. Generally, in the external photoelectric process, the Fermi level of the emitter coincides with that of the collector in thermal equilibrium. Thus, if we assume that the organic molecular crystals studied are intrinsic semiconductors, the schematic diagram in Fig. 10 can be introduced. In the diagram, the threshold energy, E_{th}, is determined by the energy difference between the vacuum level and the top of the valence band. On the other hand, the work function, φ, is the energy difference between the vacuum level and the Fermi level. Hence;

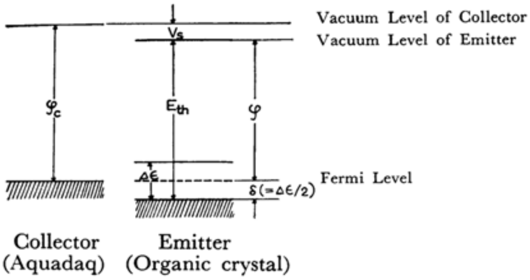

Fig. 10. Shematic diagram for the external photoelectric process of the organic molecular crystal.

$$E_{th} = \varphi + \delta = \varphi_c - eV_s + \varDelta\varepsilon/2 \qquad (2)$$

TABLE III. COMPARISON OF BAND GAP ENERGIES

Componud	$\varDelta\varepsilon$, eV.[a]	$\varDelta\varepsilon$, eV.[b]
Tetracene	1.88	1.70[c]
Pentacene	1.48	1.50[d]
Violanthrene	0.86	0.85[e]
Quaterrylene	0.60	0.60[f]
Tetrathiotetracene	0.48	0.41—0.57[g]

a) Present work; obtained from Eq. 3.

b) Obtained from the results of the temperature dependence of semiconduction.

c) D. C. Northrop and O. Simpson, *Proc. Roy. Soc.*, **A234**, 124 (1956). This value of $\varDelta\varepsilon$ seems to be too low as compared with those of other hydrocarbons of polyacene series (anthracene, $\varDelta\varepsilon = 2.7$ eV.; pentacene, $\varDelta\varepsilon = 1.50$ eV.). The correct value may be near 2 eV.

d) Ref. c.

e) H. Inokuchi, This Bulletin, **24**, 222 (1951).

f) Y. Maruyama, H. Inokuchi and Y. Harada, ibid, **36**, 1193 (1963).

g) M. Kochi, private communication.

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[14] W. C. Walker, N. Wainfan and G. L. Weisser, *J. Appl. Phys.*, **24**, 1318 (1953); **26**, 1366 (1955).

[15] L. E. Lyons, *J. Chem. Soc.*, **1957**, 5001; L. E. Lyons and J. C. Mackie, *Proc. Chem. Soc.*, **1962**, 71.

where φ_c is the work function of a colloidal graphite, Aquadag. Setting $\varphi_c=4.74$ eV.,[11] we can obtain the band gap energy from the observed values of V_s and E_{th}:

$$\Delta\varepsilon = 2(E_{th} + eV_s) - 9.48\,\text{eV.} \tag{3}$$

In Table III the $\Delta\varepsilon$ values obtained from Eq. 3 are compared with those found from the temperature dependence of the semiconduction. The table indicates that the two values of the band gap energy are in fairly good agreement. It has thus been established that the present diagram can explain the external photoelectric process of the organic molecular crystals studied.*

Future experiments on the photoemission of these crystals will be devoted to a study of the spectral dependence of the quantum yield at low temperatures and also to a detailed analysis of the current-voltage relation.

It is a great honour to dedicate this paper to Professor Masao Kotani in celebration of his sixtieth birthday.

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* Recently, Maruyama and Inokuchi (This Bulletin, **39**, 1418 (1966)) studied the effect of oxygen on the semiconductivity of a quaterrylene film and found that the intrinsic semiconductor model is applicable only when there is a high vacuum ($\sim10^{-8}$mmHg), the band gap being 1.7 eV. in this case. According to their results, the band gap of 0.6 eV. which is observed for a film exposed to air is due to an acceptor level formed by an oxygen impurity. Thus, the present results for quaterrylene should be interpreted in terms of the extrinsic band model. Since, in this case, the Fermi level is located halfway between the acceptor level and the top of the valence band, and since also, the emitted electrons from the acceptor level can be neglected, the energy diagram shown in Fig. A (instead of Fig. 10) may be considered to hold for photoemission from quaterrlene.

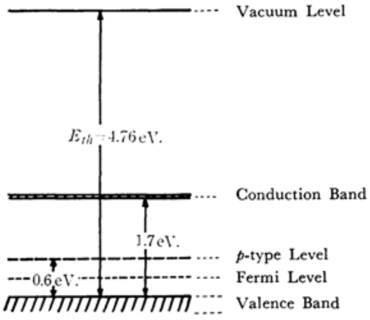

Fig. A