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Photoemission from Polycyclic Aromatic Crystals in the Vacuum Ultraviolet Region. II

Masakatsu KOCHI, Yoshiya HARADA and Hiroo INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Azabu, Tokyo

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The external photoelectric effect of the molecular crystals in the vacuum ultraviolet region was observed. The ionization potential of tetrathiotetracene, indanthrone and perylene, as estimated by the threshold values of their spectral responses, were 4.55, 5.10 and 5.40 eV respectively. The band-gap energies, calculated on a band model, were 0.62, 0.68 and 1.72 eV respectively. These values were in fairly good agreement with those obtained from the temperature dependency measurements of their electrical resistivities. By analyzing the photocurrent-voltage relation for tetracene and pentacene, the kinetic energy distribution curves were obtained. From an analysis of those curves, it turned out that the one-electron process plays a dominant role in the emission processes and that illumination with a short-wavelength light (1200 Å—1500 Å) can excite electrons from the deeper levels of the valence band to a vacuum. The observed positions of the filled π-electron levels were almost consistent with the results obtained using the LCAO method; for tetracene the depths of lower levels in order from the uppermost one, were 1.52, 2.48, 2.96, 3.46 and 3.92 eV from the observations and 1.60, 2.34, 2.98, 3.32 and 3.89 eV from the calculations.

A threshold wavelength energy of the external photoeffect is a quantity relating directly to the work-function of solids. Further, some information can be obtained about the electronic states of the solids by analyzing the current-voltage characteristics and the incident photon energy dependency of the photoemissive current.

In the study of organic semisconductors, the measurement of the photoelectric emission is also a valid means of investigating the mechanism of the electric conduction.

However, precise measurements of the organic

compounds began rather recently. The work-functions from the spectral thresholds of the photoemission have been obtained for a series of dyes by Nelson;[1] for the phthalocyanines, polycyclic hydrocarbons and other heterocyclic aromatic compounds by Kearns and Calvin;[2] for a series of condensed aromatic hydrocarbons by Lyons and Morris,[3] and for a series of dyes and pigments by Terenin and Vilessov.[4] The latter authors have also succeeded in obtaining the photoelectron kinetic energy distribution for anthracene and tetracene.

We previously reported[5] our findings on such condensed aromatic hydrocarbons as quaterrylene, violanthrene, and so on. At that time, we also calculated the band-gap energy, $\Delta\varepsilon$, assuming the band model of the intrinsic semiconductor.

In this paper, we will present the results of the measurements of the work-functions of tetrathiotetracene, indanthrone, and perylene and of the calculations of the band-gap energies of these substances made in a way previously reported.[5] For tetracene and pentacene, the kinetic energy distribution curves will be shown in order to reveal the structure of the valence band.

Experimental Procedures

Figure 1 shows the materials—tetrathiotetracene, perylene, indanthrone, tetracene, and pentacene—used in the present study.

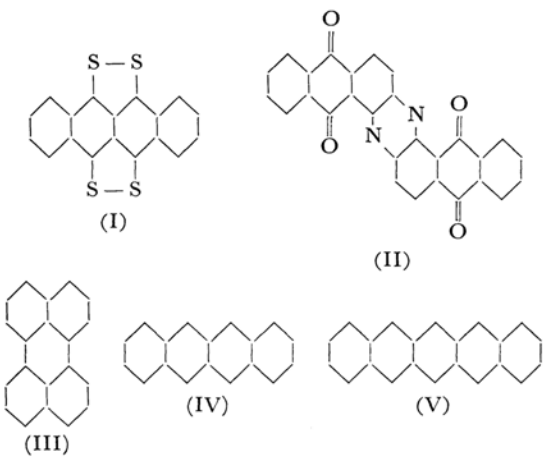

Fig. 1. Structural formula of materials.
(I) tetrathiotetracene (II) indanthrone
(III) perylene (IV) tetracene (V) pentacene

Tetrathiotetracene. This greenish-violet compound was synthesized by Yoshio Matsunaga. Pure tetrathiotetracene was obtained through vacuum sublimation and recrystallization.

Perylene. This hydrocarbon was provided by the Rütgerswerke-Aktiengesellschaft A. G., Germany. By repeated recrystallizations from xylene, flake-like crystallites of the hydrocarbon were obtained. When this compound was chromatographed under inert gas, it yielded yellow needles.

Indanthrone. This dyestuff, Indanthrene RSN, was first purified by a vatting method. The compound was then washed with chlorobenzene and with a sodium hydroxide solution, after which the compound was recrystallized from concentrated sulphuric acid. Further, by repeated sublimation in a vacuum, brown needle crystallites were obtained.

Tetracene and Pentacene. Both the hydrocarbons were furnished by the Rütgerswerke A. G., Germany. In order to purify the materials, tetracene and pentacene were sublimed *in vacuo* at about 200°C for the former and 250°C for the latter. Because of the instability of pentacene in reaction to ultraviolet light, the hydrocarbon had to be kept in a dark room.

All the purified samples mentioned above were deposited on a copper disk, 10 mm in diameter, by means of a sublimation method in a vacuum (10^{-6} mmHg), the thickness of the film being several microns.

The arrangement of the specimens in the photoemissive cell has already been reported.[5]

To observe the photoemission from the organic solids, a Seya-Namioka-type vacuum-ultraviolet monochromator was applied. In this apparatus, a Tanaka-type hydrogen discharge lamp[6] was used as a light source. With the lamp turned on, pure hydrogen, prepared by passing commercial hydrogen from a cylinder through a palladium thimble, was introduced into the instrument, which had been washed satisfactorily in advance with the above pure hydrogen. The temperature of the palladium tube and the opening of the reducing bulb were adjusted so that pure hydrogen flowed continuously through the monochromator chamber, including the discharge lamp, at an appropriate pressure. The normal operating pressure of hydrogen was around 4 mmHg. The details of the arrangement have also been described previously.

The photoemission current was amplified and observed by a Cary 31 vibrating-reed electrometer; its spectral response was found under an applied potential of 10 V.*1

The quantum yield, Y, of the photoemission against the incident light was found from the ratio between the number of the incident photons and that of the emissive electrons. The absolute measurement of the incident photons was made by means of an Eppley circular thermopile, the sensitivity of which was 0.30 $\mu V \cdot cm^2/\mu W$ *in vacuo*.

The relative value of light intensity was obtained by measuring the fluorescence intensity from a coronene film, evaporated onto a glass plate, with a RCA 5819 photomultiplier tube.

The characteristics of the photoemission current as

1) R. C. Nelson, *J. Opt. Soc. Am.*, **51**, 1186 (1961).
2) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).
3) L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1960**, 5192.
4) A. Terenin and F. Vilessov, "Advances in Photochemistry," Vol. 2, Interscience Publ., New York (1964), p. 407.
5) Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966).
6) R. G. Newburgh, L. Heroux and H. E. Hintereger, *Appl. Optics*, **1**, 773 (1962).
*1 This voltage is high enough for us to obtain the saturated photocurrent.

a function of the applied voltage were observed by a spherical retarding-field method and recorded with a Yokogawa x-y recorder, PRO-12.

The energy distribution curves were obtained by differentiating the current-voltage characteristics graphically.

Results and Discussion

The Spectral Distributions of the Yield. Figure 2 shows the spectral response curves of the photo emission of tetrathiotetracene. The quantum-yields of the photoemission increased with an increase in the photon energy, reaching the order of 10^{-2} electrons/quantum at an incident light of about 9 eV. Thus, the yield was about 10^4 times that of the internal photoconductive effect for the aromatic hydrocarbons.

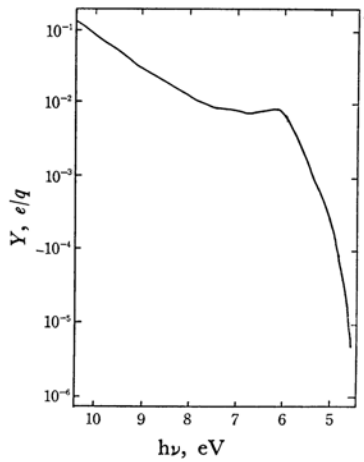

Fig. 2. Spectral distribution of the photoemission yield for tetrathiotetracene.

The threshold values of the photon energies required for photoemission are listed in Table 1. Since no appropriate extrapolation formula has yet been found, the numerical values of the threshold were determined temporarily by extrapolation to a quantum yield of 10^{-7} electrons per incident quantum. The threshold energy, E_{th}, corresponds to the ionization potential of the organic solids.

Matsunaga has reported that tetrathiotetracene forms stable molecular complexes with many electron acceptors and that the resulting complexes exhibit low resistivities.[7] We also found that

TABLE 1. THRESHOLD VALUES OF PHOTOEMISSION, E_{th}

Compound	E_{th}, eV
Tetrathiotetracene	4.55
Indanthrone	5.10
Perylene	5.40

7) Y. Matsunaga, *J. Chem. Phys.*, **42**, 2248 (1965).

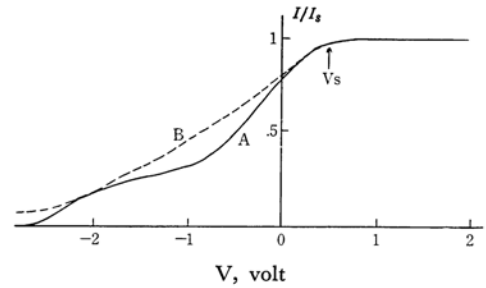

Fig. 3. Photoemission of tetrathiotetracene: the current-voltage relation.
hν: (A) 7.75 (B) 9.54 eV

tetrathiotetracene itself has a low resistivity, 10^6 Ωcm.[8] This behaviour may be explained by the fact that the threshold energy value of tetrathiotetracene crystal is fairly small, $E_{th}=4.55$ eV.

Current-voltage Characteristics. Figure 3 illustrates the current-voltage relation for tetrathiotetracene film, where the ordinate is normalized with the saturation current, $I_s=1.0$. The fact that the values of the saturation voltage, V_s, were less than one volt shows that the photocell used in the present study has a good spherical geometry. In the case of a thick film*2 of perylene, the value of the electrical resistivity is high enough to cause the potential drop within the film, so the thin film was employed for the measurement of the photoemission.

Calculation of the Band-gap Energy ($\Delta\varepsilon$). Following a band model of the intrinsic semiconductor, the energy of the band gap, $\Delta\varepsilon$, was calculated from the observed values of the threshold energy, E_{th}, and of the saturation potential, V_s.

If the organic molecular crystals studied are assumed to be intrinsic semiconductors, the schematic diagram illustrated in Fig. 4 can be introduced.

The energy difference, δ, between the top of the valence band and the Fermi level is a half of the band gap energy, $\Delta\varepsilon/2$, on the basis of findings concerning the temperature dependence of the semiconductivity. In the thermal equilibrium, the Fermi level of the emitter coincides with that of the collector. Hence,

$$\Delta\varepsilon = 2(E_{th} + eV_s) - \varphi_c \qquad (1)$$

where φ_c is the work function of a colloidal graphite, Aquadag.[9] Setting $\varphi_c=4.74$ eV, we can obtain the band gap energy from the observed values of V_s and E_{th}. In Table 2, the $\Delta\varepsilon$-values obtained from Eq. (1) are compared with those

8) M. Kochi and H. Inokuchi, Private communication.

*2 When the thick film was used to determine the V-I characteristics, the current was not saturated completely.

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

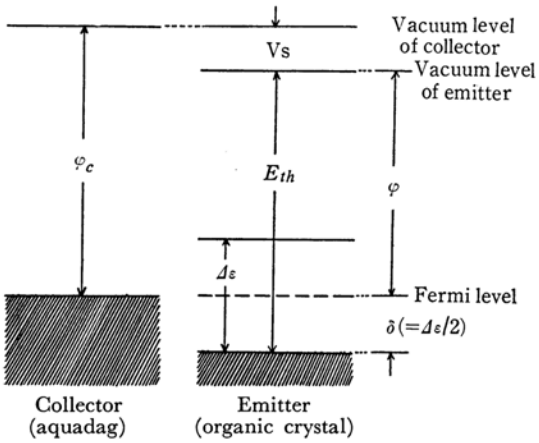

Fig. 4. Schematic diagram for the external photoelectric process of the organic molecular crystal.

found from the temperature dependence of the semiconductivity. The table indicates that the two values of the band-gap energy are in fairly good agreement.

Kinetic Energy Distribution of the Photoelectrons.—The differentiation*3 of the voltage-photocurrent curves on illumination by monochromatic light gives the electron kinetic energy distribution shown in Figs. 5 and 6. The relative

TABLE 2. SATURATION VOLTAGES OF THE CURRENT-VOLTAGE CHARACTERISTIC AND THE BAND GAP ENERGIES

Compound	V_s	$\Delta\varepsilon$, eV	$\Delta\varepsilon_f$, eV
Tetrathiotetracene	0.50	0.62	0.4—0.6
Indanthrone	−0.20	0.68	0.63[a]
Perylene	0.20	1.72	2.1[b]

a) H. Inokuchi, This Bulletin, **25**, 28 (1952).
b) M. Sano and H. Akamatu, *ibid.*, **34**, 1569 (1961).

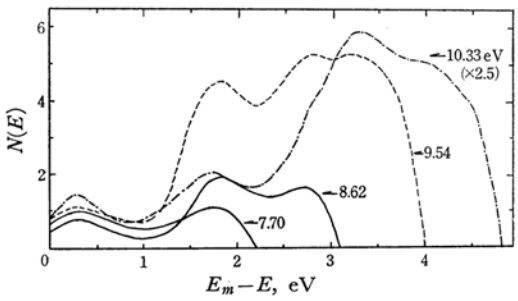

Fig. 5. Energy distribution curve of tetracene.

*3 The differentiation of the V-I characteristic curves was carried out graphically, because $I \propto \int_{E_0}^{E_{max}} N(\nu, E)\mathrm{d}E$. Here N is the energy distribution unction. In order to obtain more accurate differentiaon curves, an automatic differentiation instrumen istbeing pr epared.

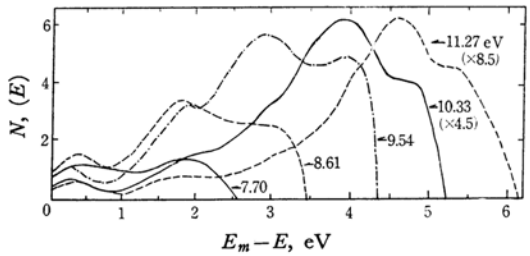

Fig. 6. Energy distribution curve of pentacene.

numbers of the emitted electrons were plotted on an ordinate axis (reduced to an equal number of incident photons). On the abscissa axis, the deficiency in kinetic energy relative to the maximum value, E_m, *i. e.*, the kinetic energy losses, were chosen.*4

As may be seen from Figs. 5 and 6, these distribution curves have the following characteristics; (a) each group of slow photoelectrons remains stationary independent of the incident photon energies, and (b) the number of slower electrons increases with an increase in the photon energy.

Generally, there are two alternatives for interpreting the appearance of some groups in the distribution curves: (1) the removal of an electron not from the uppermost occupied orbital but from a deeper one, a procedure which requires an additional energy expenditure in excess of E_{th}; (2) the photoemission by the ejection of an electron from the uppermost filled level, accompanied by a transfer of a second one to a vacant level. The latter alternative, requiring a two-electron transition, is less plausible, since such processes have smaller efficiency cross-sections than an one-electron processes. It will be seen from Figs. 5 and 6 that the maxima for the slow electrons are higher than the maxima for the fast electrons. The opposite should be expected for a two-electron process, which requires higher photon energies. Furthermore, the remark (a) above is consistent with the fact that the low energy levels of the valence band are considered to be kept constant relative to the uppermost filled level.

Hence, we concluded that the first alternative is more likely. However, a two-electron process which includes inelastic collisions between electrons or an electron and the lattice will be one of the factors deciding the shapes of the distribution curves.

For a tetracene polycrystalline film at a photon energy of 7.70 eV, the distribution curve consists of two maxima, at $E_m-E=0.28$ and 1.80 eV, meaning a loss in the photon energy of that amount. When the photon energy is increased to 8.62 eV, a third maximum appears at $E_m-E=2.76$ eV. Subsequent maxima appear at 3.24 and 3.90 eV at higher photon energies. The kinetic distribution curves for pentacene are qualitatively similar

*4 See Appendix.

to those of tetracene.

In Table 3 the discrete energy losses, $E_p=E_m-E$, are given relative to the position of the maximum of the fastest photo-electron for tetracene and pentacene.

In the column of "calcd." the depths of the filled π-electron levels are given, taking the uppermost one as zero, as calculated by Coulson using the LCAO method.[10] The resonance integral, β, was evaluated as -3.3 eV for tetracene and -3.5 eV for pentacene. It will be seen that the energy sequence of the molecular orbitals is well reproduced in the sequence of the discrete energy losses.

TABLE 3. ENERGY SEQUENCE OF THE VALENCE BAND

Tetracene		
calcd. $\beta=-3.3$ eV	Obs.	Y_{obs}*
1.60	1.52	1.31
2.34	2.48	2.51
2.98	2.96	3.06
3.32	3.64	—
3.89	3.92	—

Pentacene		
calcd. $\beta=-3.5$ eV	Obs.	Y_{obs}*
1.40	1.46	1.13
2.75	2.60	2.55
3.53	3.60	3.48
3.82	4.28	—
4.50	4.89	—

* Obtained from E_i-E_{th} E_{th} for tetracene is 5.24 eV and for pentacene 5.07 eV (see also Ref. 5). E_i is the energy at an inflection point, indicated by arrows in Figs. 8 and 9.

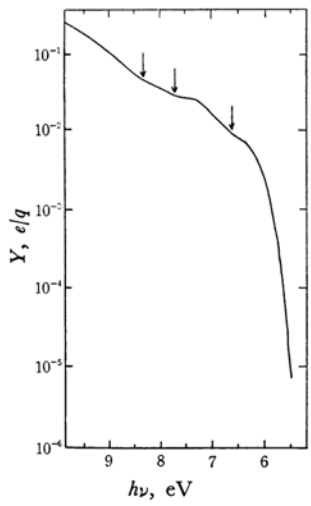

Fig. 7. Spectral distribution of the photoemission yield for tetracene. Arrows illustrate inflection points of the response curve.

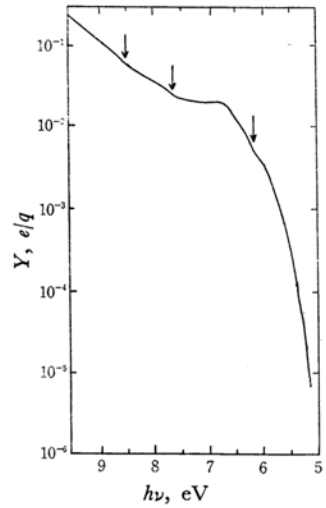

Fig. 8. Spectral distribution of the photoemission yield for pentacene. Arrows show inflection points of the response curve.

If the one-electron process is reasonable, the quantum yield may be expected to increase suddenly at the photon energies which can excite the electrons from low filled levels to the vacuum.

In Figs. 7 and 8, the spectral response curves of tetracene and pentacene are given. In both curves some inflection points are observed at which the quantum yield increases. For tetracene, they are situated at the higher energy values of 1.31, 2.51, and 3.06 eV, with the threshold energy value taken as 5.24 eV. For pentacne, they are at 1.13, 2.55, and 3.48 eV. In both cases these energy values of the inflection points correspond to the sequence of the observed values in Table 3.

The authors wish to thank Dr. Taiji Kitagawa for his helpful discussion. They also express thanks to Mr. Kiyoo Tsuji of our Institute for preparing the vacuum ultraviolet spectrometer.

Appendix

Theory of Retarding-potential Measurement.[9] In the photoelectric process, an electron with the energy ε absorbs a quantum and is excited to a state of total energy of $\varepsilon+h\nu$. When $\varepsilon+h\nu>\mu+\varphi$, where μ is the energy of the Fermi level and φ is the work-function, the electron can leave the crystal (see Fig. 5).

Just outside the surface barrier, it has a kinetic energy of E:

$$E=\varepsilon+h\nu-(\mu+\varphi) \quad (1)$$

Under an accelerating electromotive force, eV, a photoelectron originating in the ε state will just be collected by the collector when the following equation is satisfied:

10) C. A. Coluson, *J. Phys. Soc.*, **60**, 257 (1948).

$$\mu + \varphi_c - eV = \varepsilon + h\nu \tag{2}$$

Then the photoelectric current $I=0$ if $V<V_0$, where eV_0 is a stopping potential, thus satisfying Eq. (3):

$$eV_0 = \varphi_c + \delta - h\nu \tag{3}$$

where δ is a half of the band gap. From (1) and (2), the next relation is obtained:

$$E = \varphi_c - \varphi - eV \tag{4}$$

Setting $E=0$, the saturation point, V_s, of the current-voltage characteristic is obtained:

$$eV_s = \varphi_c - \varphi \tag{5}$$

For $V>V_s$, I is constant and equal to I_s if the Schottky effect is neglected. The Einstein relation is obtained by setting ε as equal to $\mu-\delta$ in Eq. (1):

$$E_m = h\nu - \varphi - \delta = h\nu - E_{th} = e(V_s - V_0) \tag{6}$$

Here E_m is the maximum energy of the photoelectrons from an ideal semiconductor.

From (4), (5) and (6), the kinetic energy losses, E_m-E, are equal to $h\nu-(E_{th}+eV_s)+eV$.