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Photoemission from Polycyclic Aromatic Crystals in the Vacuum-Ultraviolet Region. V.[†] Photoelectron Spectroscopy by the Rare Gas Resonance Lines and Vacuum-Ultraviolet Absorption Spectra

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The photoelectron spectra (energy distribution curves, ECDs) of naphthacene, pentacene, perylene, coronene, and *p*-terphenyl by He(I), Ne(I), and Ar(I) resonance lines (photon energies, 11.62—21.22 eV**) and the absorption spectra of naphthacene, pentacene, perylene, and coronene at 4—9.5 eV are measured for evaporated polycrystal films. The absorption spectra are compared with the spectral dependence of the quantum yield (SDQY) of photoemission. A similar comparison is also made for *p*-terphenyl and anthracene. The origin of the structures in SDQY curves is discussed. The analysis reveals that: (1) the MOs of a molecule are preserved even in crystals; (2) the large peak at a low kinetic energy of the photoelectron spectra is due to secondary electrons, and (3) at least for naphthacene, pentacene, and coronene, autoionization takes place with a considerable efficiency.

Photoemission has now become a powerful tool for the study of the electronic properties of solids.[1)]

Polycyclic aromatic hydrocarbons form a major branch of organic semiconductors, and many studies have been made of their electronic properties.[2)] Experiments on photoemission from these compounds in the solid state have also been carried out since the beginning of the 1960s.[2,3)]

Usually two quantities are measured in photoemission experiments: the spectral dependence of its quantum yield (SDQY), and the energy distribution curves of photoelectrons (EDCs, photoelectron spectra) at each photon energy.

SDQY for photoemission from the aromatic hydrocarbons has been studied by many workers.[2,3)] Particular efforts have been made to explain the shape of SDQY around the threshold region in order to make an accurate extrapolation for determining the photoemission thresholds from SDQY.

The photoelectron spectroscopic study of organic solids was first made by Vilesov and his co-workers[4)] in the vacuum-ultraviolet (vacuum-UV) region. They measured the EDCs and discussed the energetics and mechanism of the photoemission. Related studies were also made by Kochi *et al.*,[5)] Hirooka *et al.*[6,7)] and Zagrubskii and Vilesov[8)] in the vacuum-UV region and by Belkind *et al.*[3)] in the region near to and below the threshold. Further, the introduction of the windowless monochromator[8a)] and the use of rare gas resonance lines[9,10)] extended the photon energies, and a high resolution was obtained by the use of a deflector-type analyzer.[10,11)]

These efforts clarified many points about the microscopic mechanism of the photoemission. However, the understanding of the mechanism for aromatic hydrocarbons seems still to be incomplete (for a review, see the article by Belkind *et al.*[3)]). This is partly due to the lack of experimental data. For example, almost all the optical studies of solid aromatics in the vacuum-UV region have been restricted to small molecules.[12)] On the other hand, Schechtman and Spicer[13)] made an extensive study of phthalocyanines and showed that the comparison of the optical spectra with the SDQYs of the photoemission is very useful for the analysis of SDQY. Although several electron energy-loss experiments have been carried out for large aromatics,[12,14)] Kramers-Kronig analysis must be carried out in order to obtain the absorption spectra. This was carried out only by Hinz and Venghaus[14)] for a few compounds. Due to the lack of experimental data on the optical spectra, no comparison between SDQY and the optical spectrum can be made for compounds such as naphthacene, which has been most frequently studied in photoemission work.

Further, almost all the investigations have been restricted to the photon energies of the LiF window cutoff (11.5 eV), with some recent exceptions. The extension of measurements to higher photon energies can be expected to give more useful information. For example, the effect of electron scattering will become clear with the increase in the photon energy. Further, deeper valence levels and upper conduction bands can be investigated by means of higher photon energies.

In this paper, we wish to report: (1) the photoelectron spectra of polycrystals of naphthacene, perylene, pentacene, coronene, and *p*-terphenyl by rare gas resonance lines with photon energies up to 21.22 eV, and (2) a comparison of SDQY with the optical spectra for these compounds and anthracene in the region of 5—11.5 eV. The results will be discussed in order to clarify the energy structures of these compounds and the nature and role of several processes in the photoemission. The results of the photoelectron spectra in the range of 5—11.5 eV have been reported elsewhere.[7)] Particular attention is paid to the characteristic properties of these compounds as molecular crystals; these properties distinguish them from other classes of substances. Information on these points will also be useful in other areas, such as the photoconduction and radiation physics of these substances. Some of the experimental results have already been

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** The electron volt is not coherent with the SI units. One electron volt≅1.6022×10^{-19} J.

reported in other periodicals.[9,15,16]

Experimental

Samples. The materials used in this study were purified by zone refining, recrystallization, and sublimation. X-Ray diffraction measurements revealed that the evaporated samples are oriented polycrystals, with their c-axes perpendicular to the substrates,[15,17] both for the photoemission and for the optical spectra measurements. The crystal structure of perylene is known to be the α-form, in which molecules form dimers.[18]

Photoelectron Spectra. The rare gas discharge lamp was of the π-type. He(I)(21.22 eV), Ne(I)(16.85 and and 16.67 eV), and Ar(I)(11.83 and 11.62 eV) resonance lines were used. For the He(I) discharge, 1—5×10^{-2} Pa of helium was supplied through a liquid nitrogen-cooled charcoal trap. For the Ne(I) and Ar(I) discharges, a small amount of neon and argon was added to the helium gas.[19] An a.c. voltage of 5—8 kV was applied from a neon-sign transformer. The photoelectron energy analyzer was of the retarding-potential type. A gold-plated collector 150 mm in diameter was used, with the emitter located at its center.

The samples were evaportaed onto a polished copper emitter substrate 12—20 mm in diameter in a separate evaporation vessel under a vacuum of 10^{-3}—10^{-4} Pa. Measurements were made under a vacuum of 1—3×10^{-4} Pa. The continuous slow sublimation of the organic specimen helped to maintain a clean surface and enabled satisfactory measurements to be made without the use of an ultrahigh vacuum. The sample thickness was monitored with a quartz crystal oscillator (Toyo Tsushinki TVF-1). Considering several factors (the charging of the sample, the effect of the substrate, and the loss of the sample due to sublimation), thin film specimens 30—200 nm thick were employed.

The photoelectron-energy distribution curves were measured by means of an a.c. modulation technique which has been reported previously.[6,7] A Cary-31 vibrating-reed electrometer and a PAR-128 lock-in amplifier were used, with an a.c. modulation of 200 $\mathrm{mV_{P-P}}$, 4 Hz. The total photocurrents were of the order of 10^{-10} to 10^{-11} A. The resolution of the spectrometer was estimated to be about 0.3 eV.

Optical Spectra. The method of the measurement of the absorption spectra of films evaporated onto LiF plates has already been reported.[15]

The measurement of the normal incidence reflection spectra of evaporated films was also attempted; it gave useful preliminary results for perylene and pentacene for $h\nu<7.7$ eV. The experimental details have been reported elsewhere.[20]

Results

Photoelectron Spectra. Figures 1—5 show the EDCs of naphthacene, perylene, pentacene, coronene, and *p*-terphenyl as functions of the retarding potential, *RP*. *RP* is related to the kinetic energy of the electron, *KE*, thus:

$$KE=e(RP+V_S), \tag{1}$$

where V_S is the saturation voltage defined as the negative of the value of *RP* at the right-hand cutoff point of the EDCs. If the electrical contact between the sample and substrate is good enough, the value of V_S is the contact potential difference between the sample and the collector. Further, the ionization

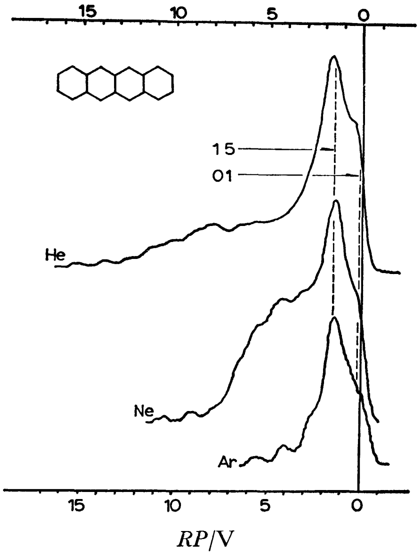

Fig. 1. EDCs of naphthacene in retarding potential scale.

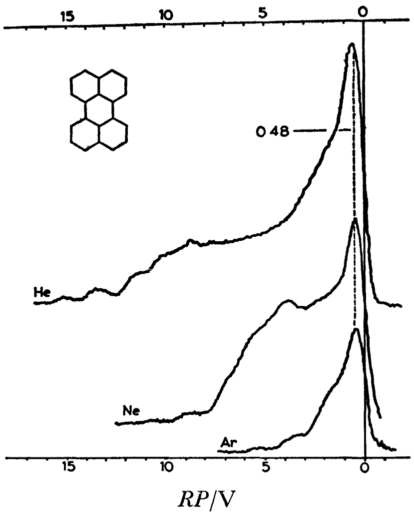

Fig. 2. EDCs of perylene in retarding potential scale.

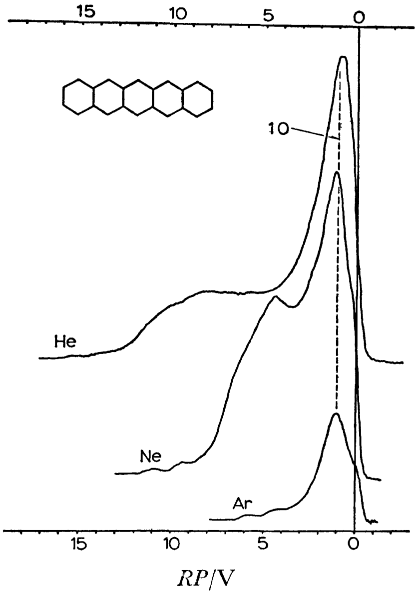

Fig. 3. EDCs of pentacene in retarding potential scale.

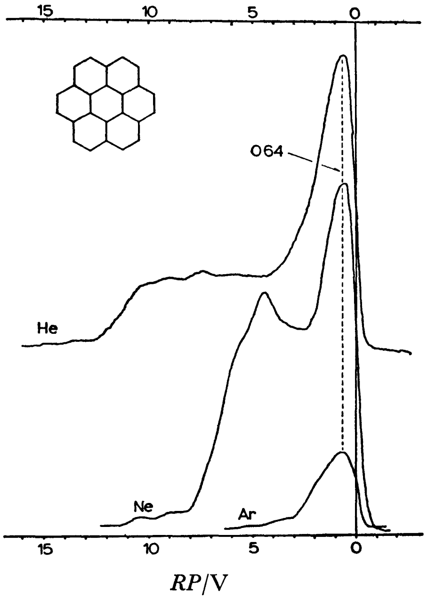

Fig. 4. EDCs of coronene in retarding potential scale.

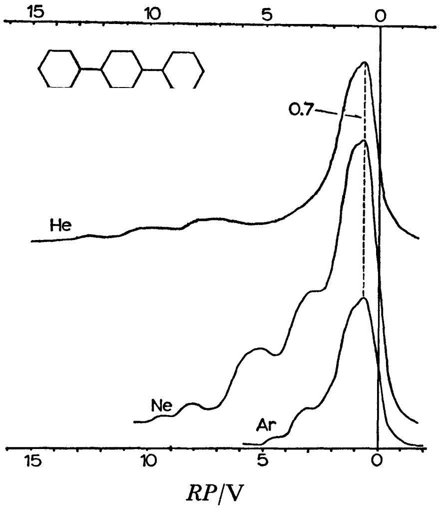

Fig. 5. EDCs of *p*-terphenyl in retarding potential scale.

potential, *IP* (binding energy measured from the vacuum level) is derived from the Einstein relation:

$$IP = h\nu - KE. \tag{2}$$

When $h\nu$ is changed, small moving structures in the higher *RP* region and large non-moving structures in the lower *RP* region were observed in all the spectra.

The non-moving structures can be classified into two groups: (1) the shoulders observed near zero *RP* for naphthacene and pentacene (whose spectral shapes and intensities were sensitive to the sample condition) and (2) the peaks observed in all compounds in the RP=0.5—1.5 V region (their peak intensities increased rapidly with the photon energy). These two groups of structures were also found by Hirooka[7] at lower photon energies. We shall refer to these structures as "lower energy non-moving structures" (LNMSs) and as "high energy non-moving peaks" (HNMPs) respectively. In Hirooka's work,[7] LNMSs were found for all the compounds, while HNMPs were found only for naphthacene, pentacene, and perylene. A recent report by Hino *et al.*[16] shows that LNMS does not appear in *p*-terphenyl, even at lower photon energies.

A weak charging effect was observed for some samples, due to fairly large photoemission currents. This caused a scatter of the observed values of V_S of 0.2 V. Therefore, the minimum value of V_S obtained was used to calculate the *IP*s. This gave a good agreement with the *IP*s obtained by Hirooka[7] and Hino *et al.*[16] The values of V_S and *KE* for the non-moving structures are listed in Table 1.

Figures 6—10 show the EDCs as functions of *IP*. It may be seen that the *IP*s of the moving structures have nearly constant values, independent of the photon energies. For comparison, the results of molecular photoelectron spectroscopy[21] are also shown in the figures. The *IP*s obtained are listed in Tables 2—6, together with the results of other photoemission studies[5—8,10] and of molecular photoelectron spectroscopy. In the tables, *P* is the polarization energy,[22] defined here as the difference in the *IP* values between the solid and gas phases.

Table 1. Saturation voltages and kinetic energies of non-moving structures

Compound	V_S/V	*KE*/eV
Naphthacene	0.4	0.5 1.9
Pentacene	0.3_5	1.4 0.6
Perylene	0.3	0.8
Coronene	0.4	1.0
p-Terphenyl	0.4	1.1

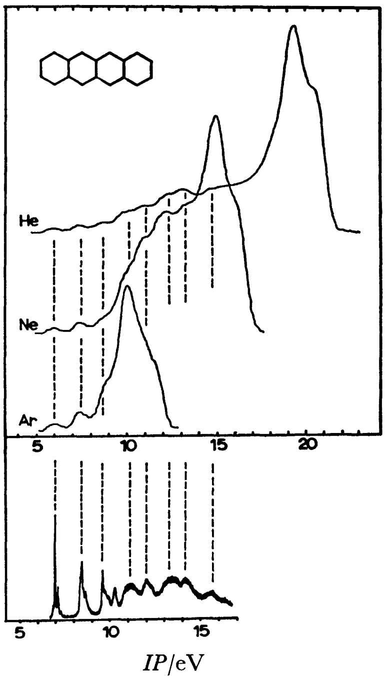

Fig. 6. EDCs of naphthacene in ionization potential scale (upper). Photoelectron spectrum of a free molecule is also shown (lower, Ref. 21a).

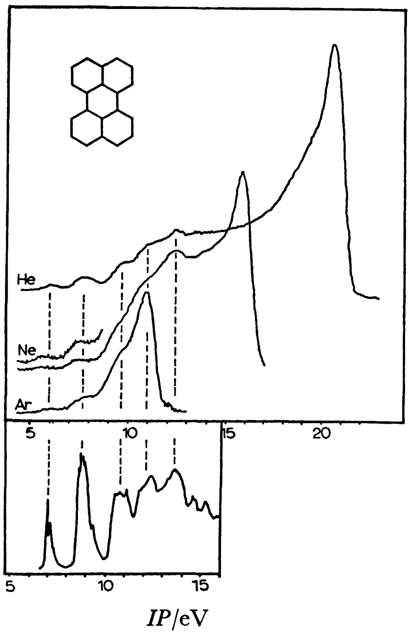

Fig. 7. EDCs of perylene in ionization potential scale (upper). Photoelectron spectrum of a free molecule is also shown (lower, Ref. 21c).

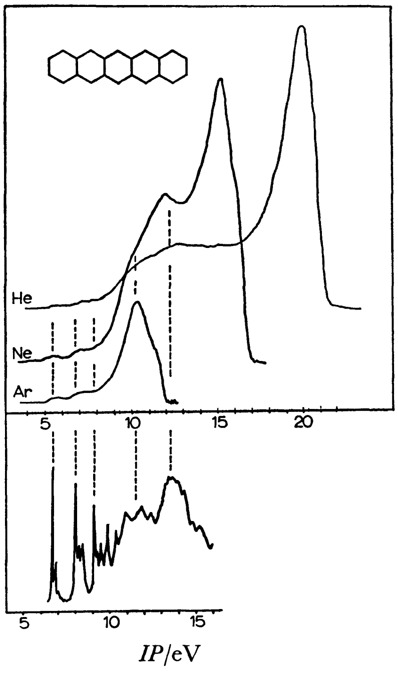

Fig. 8. EDCs of pentacene in ionization potential scale (upper). Photoelectron spectrum of a free molecule is also shown (lower, Ref. 21d).

On the whole, the agreement with the other photoemission studies and the correspondence with the gas-phase data are satisfactory. However, the *IP* values of 15.3 and 16.2 eV for naphthacene, which we reported in the preliminary communication,[9] seem dubious in the light of this work and the recent photoelectron spectrum obtained by Ueno *et al.*[10b] using a He(II) (40.8 eV) resonance line.

Recently, Shibata *et al.*[23] measured the Penning emission from naphthacene by means of rare gas metastable atoms. Their results for the location of valence levels agree with the present results very well.

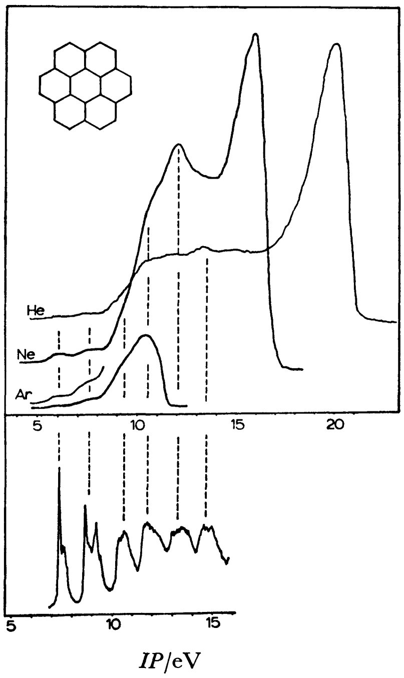

Fig. 9. EDCs of coronene in ionization potential scale (upper). Photoelectron spectrum of a free molecule is also shown (lower, Ref. 21d).

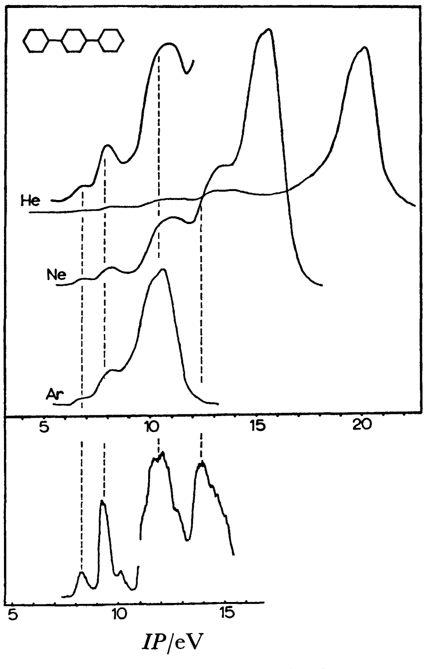

Fig. 10. EDCs of *p*-terphenyl in ionization potential scale (upper). Photoelectron spectrum of a free molecule is also shown (lower, Ref. 16).

The spectra for perylene are much clearer than the preliminary ones reported previously.[9] The sharpness of the structures of coronene depended on the sample preparation. A similar but weaker effect was also found for perylene; its origin is not understood. The structures of the spectra for pentacene are not very

TABLE 2. IONIZATION POTENTIALS/eV OF NAPHTHACENE IN SOLID AND GASEOUS STATES

Crystal		Gas[21a]		Polarization energy[b]	HTFIHK[6]		ZV[8]		KUH[10a]	
IP	ΔE[a]	*IP*	ΔE	(*P*)	*IP*	ΔE	*IP*	ΔE	*IP*	ΔE
5.3[c]					5.28[c]		5.2[c]			
5.9	0.0	7.01	0.0	1.1	5.83	0.0	5.76	0.0	5.75	0.0
7.3	1.4	8.41	1.41	1.1	7.28	1.45	7.15	1.39	7.27	1.52
		(8.6)	(1.5_9)							
8.7	2.8	9.56 (9.7)	2.55 (2.6_9)	1.0	8.29 8.70	2.46 2.87	8.25 8.6	2.49 2.8_4	8.64	2.89
(9.2)	3.2	10.25	3.24	1.1	9.40	3.57	9.5	3.7_4		
10.0	4.1	11.1	4.1	1.1					9.8	4.07
10.9	5.1	12.0	5.0	1.1	10.7		10.7	4.9_4	10.7	4.95
12.3	6.4	13.4	6.4	1.1			11.9	6.1_4	12.1	6.35
13.2	7.3	14.1	7.1	0.9					13.1	7.35
14.4	8.5	15.7	8.7	1.3					14.4	8.65
									15.0	9.25

a) Energy difference from the first peak. b) Defined as *IP*(gas) − *IP*(crystal). c) Photoemission threshold.

TABLE 3. IONIZATION POTENTIALS/eV OF PERYLENE IN SOLID AND GASEOUS STATES

Crystal		Gas[21c]		Polarization energy	Hirooka[7]		ZV[8]
IP	ΔE	*IP*	ΔE	(*P*)	*IP*	ΔE	ΔE
5.2[a]					5.37[a]		
5.8	0.0	7.00	0.0	1.1	5.88	0.0	0.0
		8.55	1.55		(7.15)	(1.27)	
7.7	1.9	8.68	1.68	1.0	7.48	1.60	1.75
		8.9	1.9		7.95	2.07	
		9.34	2.34				
9.7	3.9	10.4 11.1	3.4 4.1	(1.0_5)	9.10	3.22	
10.7	4.9	11.7 12.3	4.7 5.3	(1.3)			
12.3	6.5	13.6	6.6	1.3			
13.8	8.0	14.5 15.2	7.5 8.2				
(15.3)	(9.5)						

a) Photoemission threshold.

TABLE 4. IONIZATION POTENTIALS/eV OF PENTACENE IN SOLID AND GASEOUS STATES

Crystal		Gas[21c]		Polarization energy	Hirooka[7]	
IP	ΔE	*IP*	ΔE	(*P*)	*IP*	ΔE
4.9_5[a]					4.85[a]	
5.6	0.0	6.64	0.0	1.1	5.51	0.0
		7.93	1.29		6.61	1.10
7.2	1.6	8.35	1.71	1.1	7.13	1.62
		9.00	2.36		7.65	2.14
		9.39	2.75		(8.1)	(2.5_9)
		9.80	3.16			
9.7	4.1	10.26	3.62	0.6		
12.3	6.7					

a) Photoemission threshold.

clear. This might be partly due to the fact that the separations between the levels are rather small, as can be seen from the gas-phase photoelectron spectrum. For *p*-terphenyl, although the molecular structures in the solid and gaseous phases might differ a little, as a result of the rotation of phenyl groups, the correspondence seems to be good. Its details were reported elsewhere.[16]

Optical Spectra. The results of the absorption and reflection spectra for naphthacene, pentacene, perylene, and coronene are shown in Figs. 11—14(c). Further, the absorption spectra of anthracene and *p*-terphenyl obtained from the data by Clark[24] and Venghaus[14] are shown in Figs. 15 and 16(c).

The peaks observed in the absorption spectra are due to molecular excitons. Their interpretation has been discussed in another periodical.[15] The rising baselines may correspond to the direct ionization in solids. Some other workers have also suggested the occurrence of direct ionization.[20,24]

For comparison, the results of SDQY measurements of naphthacene, pentacene, perylene, coronene, and anthracene by Hirooka[7] are shown in Figs. 11—15(b). The result for *p*-terphenyl by Hino *et al.*[16] is also shown in Fig. 16(b). The quantum yield is defined here as

TABLE 5. IONIZATION POTENTIALS/eV OF CORONENE IN SOLID AND GASEOUS STATES

Crystal		Gas[21d]		Polarization energy	Hirooka[7]		ZV[8]
IP	Δ*E*	*IP*	Δ*E*	(*P*)	*IP*	Δ*E*	Δ*E*
5.3[a]					5.52[a]		−0.8
6.1	0.0	7.34	0.0	1.2	6.20	0.0	0.0
7.7	1.6	8.64 9.15	1.30 1.81	1.2	7.85	1.65	1.6
9.5	3.4	10.4 10.55	3.0_6 3.21	1.0	9.40	3.20	2.8
10.7	4.6	11.6	4.2_4	0.9			
12.0	5.9						
13.5_5	7.4_5						

a) Photoemission threshold.

TABLE 6. IONIZATION POTENTIALS/eV OF *p*-TERPHENYL IN SOLID AND GASEOUS STATES

Crystal		Gas[16]		Polarization energy	Hino[16]		ZV[8]
IP	Δ*E*	*IP*	Δ*E*	(*P*)	*IP*	Δ*E*	Δ*E*
6.2[a]					6.1[a]		−0.55
6.9	0.0	8.20	0.0	1.3	6.6	0.0	0.0
8.1	1.3	9.17	0.97	1.1	7.6 7.8_5	1.0 1.2_5	1.05 1.27
		10.10	1.90		8.7	2.1	2.09
		11.2 11.4 11.6	3.0 3.2 3.4		9.7	3.1	
11.0	4.1	12.1	3.9	1.1			
		12.7 13.1	4.5 4.9				
13.3	6.4	13.9	5.7	0.6			

a) Photoemission threshold.

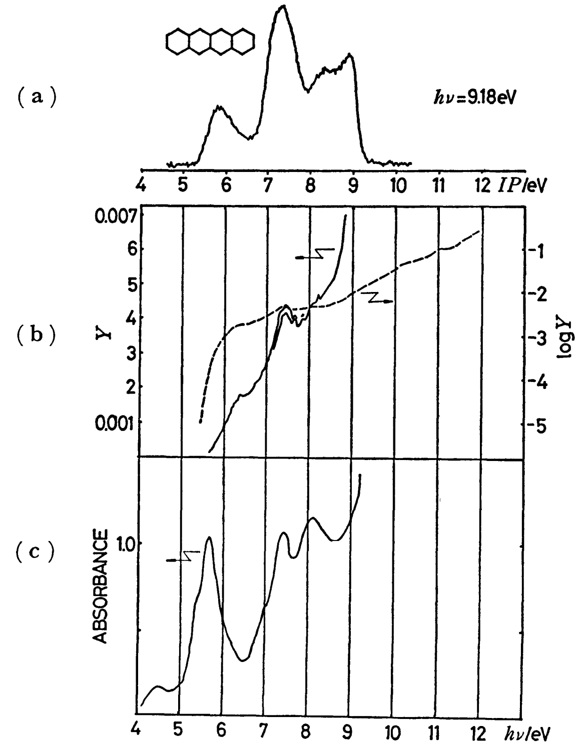

Fig. 11. Comparison of (c) the absorption spectrum of naphthacene with (a) EDC[7] and (b) SDQY[7] of photoemission.

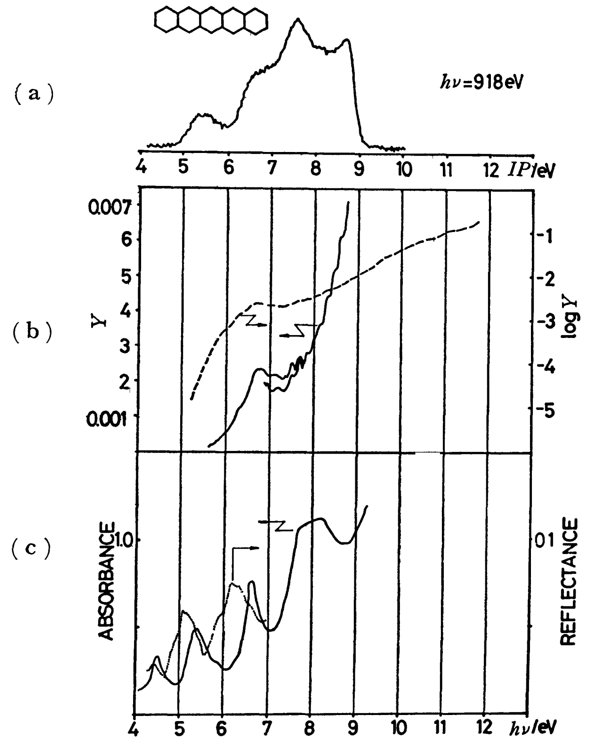

Fig. 12. Comparison of (c) the absorption and reflection spectra of pentacene with (a) EDC[7] and (b) SDQY[7] of photoemission.

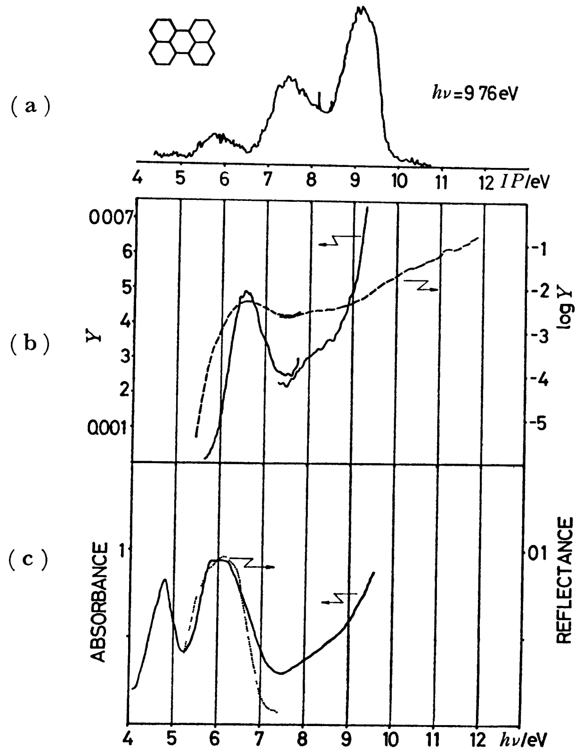

Fig. 13. Comparison of (c) the absorption and reflection spectra of perylene with (a) EDC7) and (b) SDQY7) of photoemission.

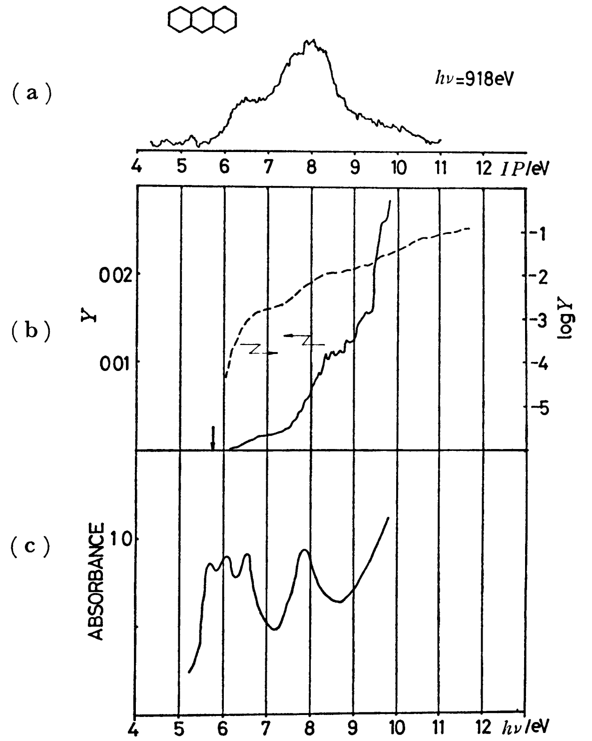

Fig. 15. Comparison of (c) the absorption spectrum of anthracene with (a) EDC7) and (b) SDQY7) of photoemission. Absorption spectrum is taken from Ref. 24, by averaging of the a- and b-axes components of ab-plane spectrum.

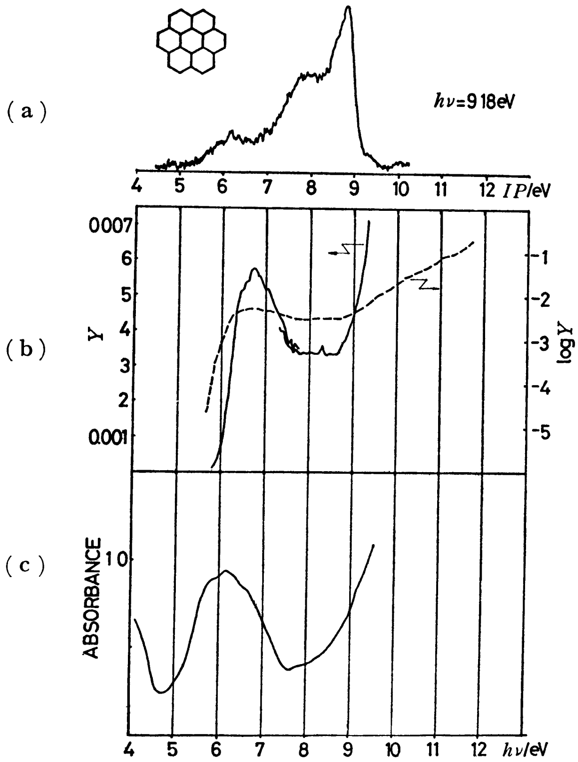

Fig. 14. Comparison of (c) the absorption spectrum of coronene with (a) EDC7) and SDQY7) of photoemission.

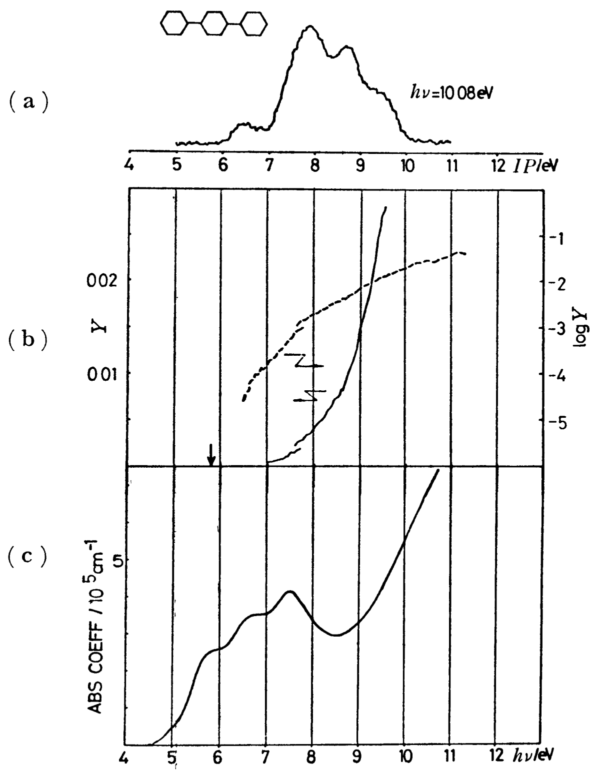

Fig. 16. Comparison of (c) the absorption spectrum of *p*-terphenyl with (a) EDC16) and (b) SDQY16) of photoemission. Absorption spectrum is obtained from the data of Ref. 14, by averaging the spectra for z and y axes of anisotropic dielectric tensor which roughly correspond to ab plane.

the number of photoelectrons per incident photon, and no correction of reflection is made. However, as will be seen later, the neglect of reflection has no significant effect. The discrepancies in the SDQY curves at 7—8 eV are due to the use of a quartz filter at low photon energies. The small ripples in the SDQYs are due to the experimental uncertainty caused by the use of a many-line hydrogen light source.

For perylene and pentacene, the results for SDQY agree well with those of other works.[5] For anthracene and naphthacene, however, some discrepancies from the findings of other works[5,25] were found. For the time being we shall rely on Hirooka's data,[7] although a more accurate measurement of SDQY should be attempted. For coronene and *p*-terphenyl, no other work is available on the vacuum-UV region.

Further, the EDCs at appropriate photon energies[7,16] are also shown in Figs. 11—16(a) to show the location of the valence-band levels.

Discussion

We adopted the phenomelogical three-step treatment.[1] The three steps are: (1) the formation of a quasi-free electron by photon absorption, (2) transport process to the surface, and (3) transmission through the surface. The characteristic aspects of these processes in molecular crystals are:[3,26] (a) not only direct ionization (DI) but also autoionization through a highly excited molecular exciton (AI) might take place; (b) on ionization, *k*-vector conservation is not an effective selection rule, because of the localization of the hole;[1] (c) quasi-free electrons must escape from geminate recombination in the Coulomb field formed by the hole, and (d) electrons can suffer energy loss due to the excitation of the exciton or the intramolecular vibration of other molecules, in addition to the other processes observed in inorganic solids.

The theory of photoemission for organic solids has already been discussed by several workers.[3,13,27]

I. Moving Structures of EDCs. The moving structures in EDCs are considered to be closely associated with the valence bands of the organic crystals. According to Koopmans' theorem, their *IP*s correspond to the energy of the valence levels. All the results show that the agreement of these levels between the gaseous and crystalline states is fairly good, if the polarization energy is assumed to be constant for a compound. This shows that the MOs of a molecule are preserved even in the solid because of the weak intermolecular interactions.

This result was predicted on the basis of a comparison with MO calculations[4,7] and was verified experimentally for π-levels.[7] Molecular photoelectron spectroscopy studies[21e] report that the onset of the ionization from σ levels is at about 10.6—11.0 eV for aromatic hydrocarbons. Assuming a polarization energy of about 1 eV, the emission from σ levels begins at the solid ionization potential of 9.5—10.0 eV. This should correspond to the observed sharp rise of EDCs at about 9 eV. Therefore, the good correspondence between the gas and solid phases extends into the σ electrons. This confirms the validity of the concept of polarization energy proposed by Lyons.[22]

The origin of the peak width of the photoelectron spectra for a solid was discussed previously.[11] We will not compare the peak intensities of the gaseous and solid phases because of the lack of information about the angular distributions of photoelectrons for gaseous samples. Further, the effect of scattering in the solid state makes comparison difficult for such high photon energies (see II).

II. Non-moving Structures in EDCs. Kochi *et al.*[5c] found the HNMPs for some compounds at $h\nu < 11.5$ eV and ascribed them to secondary electrons. The nature of the secondary electrons for organic crystals has been discussed by them and by Schechtman.[13] Their conclusions are: (1) the EDCs of secondary electrons show a peak at a small kinetic energy, and its position does not move significantly with the change in $h\nu$. (2) Secondary electrons contribute to photoemission only in the higher photon energy region, and their contribution grows rapidly with $h\nu$. Although the assumptions they used to derive these conclusions need some re-examination, these criteria are still valid for distinguishing the effect of secondary electrons (see Appendix).

Zagrubskii and Vilesov[8] also observed HNMP and LNMS for several compounds. However, they argued that they are not due to secondary electrons, for their quantum yields (for naphthacene) remain roughly constant at the photon energy of 12—13 eV before decreasing abruptly. They assigned this phenomenon to autoionization, with a preliminary energy loss (AIPL):

$$\begin{array}{l} M \xrightarrow{h\nu} M_i^{**} \\ M_i^{**} \longrightarrow M_j^{*} \\ M_j^{*} \longrightarrow M^+ + e^- \\ \qquad\quad \searrow M^{+*} + e^-, \end{array} \qquad (3)$$

where M is the ground state of a molecule, M_i^{**} is a high-energy exciton state, M_j^{*} is the autoionizing state, and M^+ and M^{+*} are the ground and excited states of an ion respectively. On the basis of this model, they attributed the structures of naphthacene at $KE = 0.4$ and 1.8 eV to autoionization to the M^+ state at 5.68 eV and the M^{+*} state at 7.15 eV. They also atrributed the HNMPs of EDCs for perylene and *p*-terphenyl to this mechanism.

They[8c] further attributed the peaks in the SDQY of naphthacene and perylene to the direct optical excitation of the autoionizing state, M^*_j. The energy values of M_j^* thus obtained are: 7.56 eV for naphthacene, 6.75 and 8.5 eV for perylene, and 7.13 eV for *p*-terphenyl. Further, they identified these autoionizing levels as plasma oscillations of π electrons on the basis of the coincidence of the reflection spectra of graphite, naphthacene, and *p*-terphenyl.

However, their conclusions are dubious for the following reasons; therefore, we assign HNMP to secondary electrons.

(1) The results obtained here for the high-photon-energy region satisfy the criteria described above. The HNMPs are not observed at lower photon energies. Hirooka[7] examined the ratio of the peak height to

the peak of the maximum KE and estimated that these peaks begin to appear at photon energies of 8.5—9.3 eV for naphthacene, pentacene, and perylene. In the present experiment also, this ratio increases monotonically with the photon energy. Further, their peak positions are roughly independent of the photon energy, as is shown in Table 1.

(2) The peak positions of HNMP agree with those of secondary electrons formed by slow electron impact.[10,32)]

(3) At least for naphthacene, pentacene, and coronene, the small values of the scattering length, L, of the order of 10 nm or less[28b)] suggest that scattering does occur in these crystals.

(4) The fact that the peak at $RP \cong 0$ V (LNMS) appears even at lower photon energies, while HNMP appears only at higher photon energies, cannot be explained by the AIPL model.

(5) The peak intervals between the LNMS and HNMP in pentacene do not agree with the interval between M^+ and M^{+*} (see Tables 1 and 4).

(6) At least for naphthacene, pentacene, and coronene, the structures of SDQY can be explained by ordinary autoionization, as will be described in III. Further, no structure is found in the SDQY of *p*-terphenyl at the predicted value, $h\nu = 7.13$ eV.

(7) According to Robin,[12)] it is useful for the identification of plasmon to compare the optical absorption and the electron energy-loss spectra. Plasma oscillation is intense in the energy-loss spectra, but it should be much weaker in the absorption spectra. For *p*-terphenyl and naphthacene, the absorption coefficient is fairly large at the predicted photon energies, 7.13 eV and 7.56 eV (Figs. 1 and 6). For perylene, there is a peak in the energy-loss spectrum (calculated from the data by Fuke *et al.*[20)]) at about 7 eV, but this can be attributed to the one-electron excitation at 6 eV in optical absorption. Therefore, the possibility of the existence of plasma oscillations at these energies is also dubious.

(8) Further confirmation is afforded by the recent experiment of Penning emission from naphthacene by rare gas metastable atoms.[23)] That experiment showed that two nonmoving structures also appear in the Penning-emission spectra at the positions of HNMP and the LNMSs. However, their relative intensities were reversed from those in the photoelectron spectra presented here. Considering the nature of the metastable atom, which cannot penetrate into the solid, the Penning-emitted electrons should be less affected than photoelectrons by bulk properties such as electronic scattering. Therefore, HNMP will become weaker in Penning emission, as was observed in the experiment. It is hard to explain this result by the AIPL model, although the detailed mechanism of Penning emission is not yet clear.

From these considerations, it seems certain that the HNMPs are due to secondary electrons. However, the abrupt decrease in the quantum yield for the HNMP of naphthacene above 13 eV reported by Zagrubskii and Vilesov[8)] remains unexplained. Furhter investigations are necessary for this point.

The small shoulders (LMNSs) observed in naphthacene and pentacene at $RP \cong 0$ V probably have a different cause from that of the HNMPs. The other compounds except *p*-terphenyl also show similar structures at lower photon energies, but they seem to be covered by the large peaks for perylene and coronene at the higher photon energies used here. The shapes and intensities of these structures are sensitive to the method of sample preparation. This fact was also found by Hirooka[7)] and by Schechtman.[13)] Therefore, it could be an effect due to some peculiarity of the transmission probability through the surface or to the effect of surface contamination.[7,13)]

III. Spectral Dependence of Quantum Yield (SDQY) and the Absorption spectra. As may be seen from Figs. 11—16(b), three regions can be distinguished in the SDQYs, except for the case of *p*-terphenyl: (a) near the threshold region (up to about 1 eV above the threshold): here a sharp increase in the quantum yield, Y, is observed; (b) the intermediate region (from 1 eV above the threshold to about 9.5 eV): here there is a rather gradual increase in Y, with several structures, and (c) far beyond the threshold region (above 9.5 eV): here there is a monotonic increase in Y.

In the region where the data of reflectance $R(h\nu)$ are available (anthracene,[29)] perylene,[20)] pentacene, *p*-terphenyl,[8)] and naphthacene[8)]), $R(h\nu)$ is smaller than 0.15 and the $1 - R(h\nu)$ factor does not correspond with SDQY. Therefore, the reflection of the incident light has no significant effect on SDQY.

As has been stated in II, the contributions of secondary electrons are small in the low-energy regions, (a) and (b).

(a) *Near the Threshold Region*: No correspondence is found between Y and the total absorption coeffecient, a_t, in this region. This has previously been noted by Lyons and his co-workers.[25,27)] Kochi *et al.*[5)] assumed that Y is determined by the energy distribution of photoelectrons arriving at the surface and by the transmission probability $T(E)$ through the surface. With this assumption, they could derive the cube root law which can explain the experimental results: $Y^{1/3} \sim a(h\nu - E_{th})$, where a is a constant and where E_{th} is the threshold of photoemission. This sharp increase in Y is sufficient to smear out the effect of the variation in a_t. Therefore, it is not surprising that no correspondence exists in this region.

(b) *Intermediate Region*: Vilesov *et al.*[4)] and Kochi *et al.*[5)] ascribed the structures of SDQY to the occurrence of the photoemission from deeper levels. As may be seen from the comparison of SDQY and EDC in Figs. 11—16(b) and (a), this theory can be applied to polyacenes. However, the distinct minima in SDQY for perylene and coronene (Figs. 13(b) and 14(b)) cannot be explained in this way. Kochi *et al.*[5c)] ascribed the decrease in Y in perylene to the abrupt decrease in the escape depth, $L(E)$, casued by the occurrence of pair-production, where E is the energy of the quasi-free electron measured from the top of the valence band. However, Zagrubskii and Vilesov[8c)] examined the EDC of perylene and concluded that $L(E)$ does not change so much with E. Further, it was shown that pair-production is not the main mechanism of the scattering of electrons (see Appendix).

On the other hand, there is another possible explanation, one based on the change in the absorption coefficient.[13,27] If $L(E)$ is much shorter than the extinction length of the incident light ($a_tL \ll 1$), only light absorbed in a thin layer, L, from the surface can contribute to photoemission. The number of photons absorbed in this layer is determined by the absorption coefficient. Then, if all the photons absorbed in this layer contribute to photoemission, and if the average escape depth does not change significantly with the photon energy, the quantym yield should be proportional to the absorption coefficient, a_t.

Of course, we must note that not all the absorbed photons might contribute to photoemission, unless autoionization occurs with a high probability. Batley[27] analyzed the expected behavior of Y under various conditions (whether scattering is severe and which, AI or DI, dominates ionization) in a way similar to that used by Pope[30a] for photoconduction. His results can be summarized as in Table 7. In Table 7, $a_{\mathrm{DI}}(h\nu, E)$ is the effective absorption coefficient to form quasi-free electrons with the E energy, a_{AI} is the absorption coefficient of the autoionizing exciton, $k(h\nu, E)$ is the autoionizing probability to form quasi-free electrons with the E energy, and A_t includes all factors other than the change in a_{DI}, a_{AI}, and a_t. In the last column of Table 7, it is assumed that $\int a_{\mathrm{DI}}\,\mathrm{d}E$ gradually increases with the photon energy.[13] Note that $a_t \sim a_{\mathrm{AI}}$ when autoionization dominates ionization. As may be seen from Table 7, a comparison of the absorption coefficient and SDQY will be useful in determining whether or not autoionization occurs with a high probability.

A comparison of the SDQY and a_t in Figs. 11—15(b) and (c) shows that a good symbatic correspondence exists between them for perylene and coronene and a fairly good one for polyacenes. *p*-Terphenyl seems to be an exception to this. However, as may be seen in Fig. 16(a), the intensity ratio of the first and other peaks of EDC is very large for this compound. Therefore this can be interpreted as ionization from deeper levels overwhelming other changes.

As may be seen from Table 7, the comparison of a_t and Y strongly suggests that $a_tL \ll 1$ and that autoionization takes place with considerable efficience.

TABLE 7. EXPECTED BEHAVIOR OF QUANTUM YIELD $Y(h\nu)$

Scattering condition	Dominant mechanism of ionization		Expected behavior of $Y(h\nu)$ when a_t decreases
$a_tL \gg 1$	DI	$Y \sim \mathrm{A}_1 \int \frac{a_{\mathrm{DI}}}{a_t} \mathrm{d}E$	increases
	AI	$Y \sim \mathrm{A}_2 \int \frac{a_{\mathrm{AI}}k}{a_t} \mathrm{d}E$	nearly constant
$a_tL \ll 1$	DI	$Y \sim \mathrm{A}_3 \int a_{\mathrm{DI}} L \mathrm{d}E$	gradully increases
	AI	$Y \sim \mathrm{A}_4 \cdot a_{\mathrm{AI}} kL$ $\sim \mathrm{A}_4 \cdot a_t kL$	decreases

The occurence of autoionization has also been suggested by other workers.[30] A similar correspondence between Y and a_t was found for phthalocyanines[13] and several inorganic materials.[31] In the case of polyacenes, the photoemission from deeper levels may also affect the shape of SDQY.

Recently several measurements of L have been made for organic solids.[28] Hino *et al.*[28b,c] showed that $a_tL < 1$ is satisfied for naphthacene, pentacene, and coronene. This confirms the present suggestion. For perylene, however, they reported that $a_tL = 1.3$ ($L = 80$ nm) for electrons injected from CuI by the illumination of light with a photon energy of 7.75 eV. When this is the case, the mechanism described above is not very effective for perylene. On the other hand, the other cases in Table 7 cannot explain the minimum of Y for perylene. One possible explanation involves a combination of the change in a_t and an abrupt decrease in $L(E)$. Such an abrupt decrease in $L(E)$ could occur when the probability of exciton formation increases sharply above a certain energy value, but Zagrubskii and Vilesov[8c] discounted such a possibility. We will not discuss this point in detail because no direct experimental data are available about the E dependence of $L(E)$. Further studies will be necessary for perylene.

Another mechanism to explain the shape of SDQY was proposed by Zagrubskii and Vilesov.[8] Their explanation, however, seems to be dubious, as has been described in II.

(c) *Far-beyond Threshold Region*: The sharp rise in Y in this region corresponds either to the photoemission from a deeper level or to the onset of the large peak in EDC (HNMP). The latter is due to secondary electrons, as has been described in II.

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PAPENDIX. Remarks on Electron Scattering

In their discussion of the effect of secondary electrons, Schechtman[13] and Kochi *et al.*[5] assumed that pair-production is the main electronic-energy-loss processes of electrons. However, recent results on the energy loss of slow electrons[10,28,33] show that exciton excitation (including triplet excitons) makes a greater contribution to scattering than does pair-production, partic-

Table 8. Energy parameters/eV of aromatic hydrocarbons

	I_g[a)]	E_{th}[b)]	E_c(calc) c)	E_T[d)]	E_S[e)]	E_T+E_c(calcd)	E_S+E_c(calcd)
Anthracene	7.47	5.70	3.93	1.85	3.11 3.16	5.8	7.1
Naphthacene	7.01	5.28	3.55	1.27	2.38 2.46	4.7	7.1
Pentacene	6.64	4.85	3.06	0.95	1.85	4.0	4.9
Perylene	7.00	5.37	3.74	1.56	2.65	5.2	6.4
Coronene	7.34	5.52	3.70	2.37	3.44	6.1	7.1
p-Terphenyl	8.20	6.1	4.0	2.55	4.48	6.6	8.5

a) The first ionization potential of a free molecule; from Refs. 16 and 21. b) Threshold energy of photoemission; from Refs. 7 and 16. c) The energy of the bottom of the broad conduction band calculated from Eq. 5. d) The energy of the lowest triplet state; from Refs. 2 and 34. e) The energy of the lowest singlet state; from Refs. 2 and 34.

ularly at a small energy loss. However, from a comparison of the results of Merkel and Hamill[33)] and that of Schechtman, it seems that the conclusion such as that (1) the scattering length $L(E)$ decreases monotonically with E, or that (2) secondary electrons tend to have only a small kinetic energy are also valid for the exciton-excitation process. Therefore, the conclusions described in the discussion should also be valid. The main change in going from pair-production to exciton excitation will be the change in the threshold for scattering: from $2E_g$ for pair-production to E_g+E_X for exciton excitation, where E_g is the band gap and where E_X is the energy of the lowest exciton.

It is somewhat difficult to determine the effective value of E_g for organic crystals. When energy loss occurs, the electron must fall into a lower conduction band. However, the lowest conduction band, at[2,26)]

$$E_c' = 2E_{th} - I_g - A_g \tag{4}$$

(where E_{th} is the threshold of photoemission and where I_g and A_g are the ionization potential and the electron affinity of a free molecule), is very narrow, and there may be band gaps between the conduction bands. Therefore, electrons cannot fall into this gap. There seems to be no definite experimental information about the threshold above which an electron with any given energy can undergo inelastic scattering. However, considering the breadth of the exciton bands and the fact that the intermolecular interaction increases with the electron energy, we may use the energy of the bottom of the 'broad conduction band', E_c, evaluated by[2,26)]

$$E_c = 2E_{th} - I_g \tag{5}$$

as a guide for the energy of the effective bottom of the continuous band, E_g. The quantities mentioned above are shown in Table 8 for both the lowest triplet and singlet excitons. The results shown in Table 8 demonstrate that almost all the electrons above the threshold can suffer inelastic scattering if triplet excitons are excited. However, no detailed information on the E dependence of $L(E)$ is available at present.

There are other mechanisms of energy loss in organic solids: the excitation and absorption of the phonon and intramolecular vibration, and the excitation of plasmon. The former two do not affect the quantum yield so much, and so we will not discuss them in detail. Plasmon was considered in the discussion of HNMP.

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