Spectral Response of Photoconductivity in Polycyclic Aromatic Compounds

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The photoconductive behaviors of polycyclic aromatic hydrocarbons have been investigated in the previous paper$^{1)}$. Concerning the nature of conducting electrons in these organic solids, it is interesting to investigate the spectral response of photoconductivity. In the previous reports$^{2,3)}$ from our laboratory, it was noted

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1) M. Sano, This Bulletin, 34, 1668 (1961).

2) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, 20, 1481 (1952).

3) H. Inokuchi, This Bulletin, 27, 22 (1954).

that the optical threshold energies for photoconduction were nearly in accord with the long-wavelength edges of the optical absorption spectra of crystals, and also in agreement with the values of the energy gaps which were estimated from the temperature dependence for electrical resistivity. From these observations, it was concluded that the semiconductive properties of polycyclic aromatic compounds are intrinsic.

Meanwhile, a number of investigations have been reported on photoconduction in organic solids. Most of them have been concerned with simple compounds, especially with anthracene crystal. Carswell and Lyons[4) found, by employing a surface-type photocell, that the spectral response curve of photoconduction reproduced quite well the absorption spectrum of anthracene crystal. A similar result was observed by Rosenberg[5), who employed a sandwich-type photocell with conducting glass electrodes. Kommandeur and Schneider[6) have found a more complex behavior by employing a sandwich cell with silver electrodes; e. g., the peaks on the response curve of the photocurrent correspond to the minima of the absorption spectrum.

On the other hand, Kallmann and Pope[7) and Moore and Silver[8) have indicated the extrinsic nature of photoconduction in anthracene; i. e., the injection of holes or electrons from metal electrodes, rather than the generation of charge carriers in the bulk of the crystal, is predominant. This might be due to the high-insulating nature of the materials. At any rate, both effects concerning the carrier generation make the photoconductive behaviors complicated.

Thus, it might be anticipated that polycyclic aromatic compounds, poor insulators or semiconductive materials, would show much simpler behaviors in photoconduction. In this paper, the spectral response of the photoconductivity of polycyclic aromatic compounds is investigated in relation to the optical absorption spectra and the thermal energy gaps.

Experimental

Procedures in the photoconductivity measurements are similar to those described in the previous report[1). For the investigation of the spectral response of the photocurrent, a single monochromator with the normal Wadsworth arrangement was used, associated with a 1000-watt tungsten lamp as the light source. The calibration for the monochromator was made by referring to emission lines from mercury (435.8 mμ, 546.1 mμ, 579.1 mμ), sodium (589 mμ), lithium (670.8 mμ) and potassium (770 mμ) vapors, and to absorption lines of liquid chloroform (1411 mμ, 1694 mμ, 1861 mμ) and of liquid 1, 2, 4-trichlorobenzene (1660 mμ). All of these spectra were detected by a thermopile or a PbS photocell, which was placed in front of the output slit. The spectrum from the monochromator extends from about 370 mμ to 2500 mμ, with the maximum intensity of 2×10^{16} photons/sec. cm^2 at 1415 mμ.

The surface-type photocell was employed; hence the image of the output slit of the monochromator was directed onto the cell perpendicularly to the direction of the electric field. Aromatic films were about 0.5 μ in thickness.

Absorption spectra, in ultraviolet and visible regions, of aromatics, both in thin films and dissolved in benzene, were recorded at room temperature using a Cary Model 14 spectrophotometer. The films, of a suitable thickness, about one micron or less, were prepared on pyrex plates by the sublimation method. The concentration of the solution was adjusted into the order of 10^{-5} mol./l. Measurements of the absorption spectra of solid phases were not easy because their surfaces were not completely flat. It was necessary, consequently, to take account of the light loss due to scattering at the surface and in the bulk, as well as the reflection loss at the surface. Confusion was avoided by inserting a "diffuser" (a pair of opal glass plates) in front of the photoreceiver of the spectrometer.

Fluorescence spectra excited by 365 mμ ultraviolet irradiation from a mercury discharge lamp were determined with the aid of the spectrophotometer. The irradiation was applied to the surface of film which faced the input slit of the spectrophotometer.

Measurement of the electrical resistivity as a function of temperature was made similarly to that method described by Inokuchi[9).

Results

Absorption Spectra.—The optical absorption spectrum of polycrystalline film was noted to resemble closely that of the solution of the same compound, excepting some broadening and shift of peaks. In consequence, assignments of the bands were made easily, according to Clar's notation[10), to the p-, α- and β-bands. The values of the shift for each transition induced by the phase change from solution to polycrystalline film are given in Table I. The red-shifts of the p-bands are in the order of from 1050 cm^{-1} (0.13 eV.) to 2260 cm^{-1} (0.28 eV.) throughout the series of compounds; the larger molecules show greater shifts. On the

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4) D. J. Carswell and L. E. Lyons, *J. Chem. Soc.*, **1955**, 1734.

5) B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).

6) J. Kommandeur and W. G. Schneider, ibid., **28**, 582 (1958).

7) H. Kallmann and M. Pope, ibid., **32**, 300 (1960).

8) W. Moore and M. Silver, ibid., **33**, 1671 (1960).

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

10) E. Clar, "Aromatische Kohlenwasserstoffe", Springer Verlag, Berlin (1952).

TABLE I. THE RED-SHIFT OF THE ABSORPTION PEAK INDUCED BY THE CHANGE OF PHASE FROM SOLUTION TO POLYCRYSTALLINE FILM

	Peak on the spectrum of solution		Peak on the spectrum of film		Red-shift	
	p-Band	α-Band	p-Band	α-Band	p-Band	α-Band
Anthracene	3.32 eV.	eV.	3.16 eV.	eV.	0.16 eV.	eV.
Chrysene	3.89	3.46	3.73	3.39	0.16	0.07
Pyrene	3.72	3.35	3.56	3.31	0.16	0.04
Perylene	2.87	3.68	2.67	3.61	0.20	0.07
Anthanthrene	2.87		2.71		0.16	
1, 12-Benzperylene	3.21		3.02		0.19	
2, 3, 7, 8-Dibenzpyrene	2.76		2.63		0.13	
Coronene	3.64		3.44		0.20	
Pyranthrene	2.69		2.41		0.28	
Violanthrene	2.53		2.29		0.24	
Ovalene	2.68		2.44		0.24	

other hand, the shift of the α-band remains nearly constant at a magnitude of about 400 cm^{-1} (0.05 eV.). However, there is the possibility that the weak α-band underlies the intense p-band; therefore, it is difficult to detect the α-band from the spectrum, especially when it is a broad one. The vibrational structure was seen in the p-band, which possessed a spacing of about 1450 cm^{-1} (0.18 eV.). This value was noted to be nearly constant for the series of compounds studied in polycrystalline film as well as in solution. This mode of vibration which couples with the electronic excitation might be the stretching of the aromatic skeleton.

No variation was found in the spectra by pumping out the ambient air of the film specimen. In general, the absorption curve of film possesses a considerably long tail extending to long-wavelength range. For instance, the absorption spectrum of pyranthrene film extends its tail as long as to 2.6 μ, the long-wavelength limit of the spectrophotometer. This leads to difficulty in specifying a unique absorption edge. In relation to the spectral response of photoconductivity which will be discussed in the later section, careful observation was made on the absorption in the long-wavelength region outside the main absorption region.

In some cases, a band, weak but comparable in sharpness with p-band, was observed on the tail of the film spectrum. Pyranthrene exhibited the maximum at 1.53 μ, and violanthrene at 1.40 μ. These bands possess no vibrational structure. When a thicker film was employed, the band was quite well developed without any change in the position of the maximum. This is shown in Fig. 1 for violanthrene film. Concerning the origin of these weak absorption bands, it is unlikely that the absorption is caused by an inclusion of impure molecules, for an incorporated impurity usually exhibits a much sharper absorption band. It is also unlikely that the absorption is due to a transition between vibrational levels. Polycyclic aromatic hydrocarbons exhibit specific infrared absorption bands in the wavelength region longer than 3.33 μ11). All these absorption bands appear out of the wavelength region concerned. However, there remains the possibility that overtone or combination bands of these fundamental vibrations would appear in the region which is

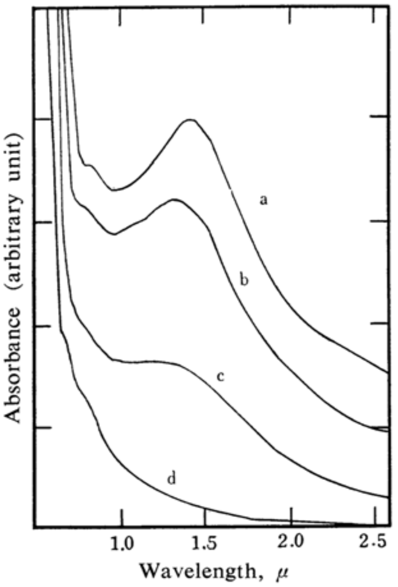

Fig. 1. The optical absorption spectrum of violanthrene film of various thickness in the near infrared region. The thickness of film: a>b>c>d.

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11) H. W. Thompson, E. E. Vago, M. C. Cornfield and S. F. D. Orr, *J. Chem. Soc.*, **1950**, 214.

concerned. It was attempted to record the absorption spectra in thick single crystals of pyrene and perylene. Seventeen narrow bands were separated in the region from 2.05 to 2.60 μ (0.13 eV. in interval), of which the most intense band showed a band-width of the order of 0.005 eV. In addition, pyrene exhibited another narrow absorption band at 1.68 μ, 0.01 eV. in width, which was accompanied by a less pronounced peak with the maximum at 1.64 μ. (Fig. 2). In comparison with the bands concerned, these vibrational bands are much sharper in band-width. Other possibilities such as the molecular exciton band or the intermolecular charge transfer band must be kept in mind; however, these have not been clarified at present.

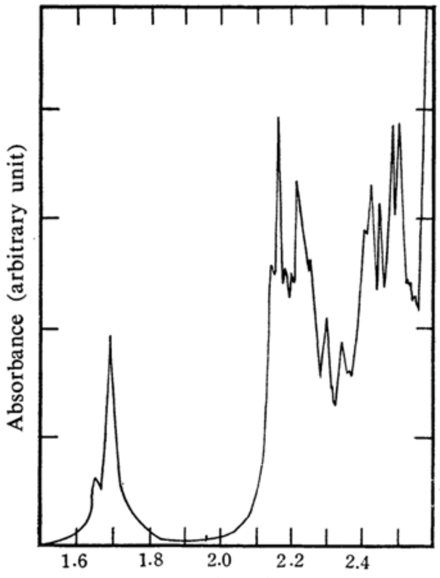

Fig. 2. The optical absorption spectrum of pyrene single crystal in the near infrared region.

Spectral Response of Photoconductivity.—Photocurrent arises whenever light falls in an electronic absorption region of a compound. The magnitudes of the photocurrents were usually in the range of $10^{-9} \sim 10^{-14}$ amp. in vacuo (10^{-3} mmHg). A preliminary experiment showed, however, that exposure to air enhanced the photocurrent for most of the specimens. To preclude the oxygen effect, the spectral response of photoconductivity was observed in vacuo, with surface-type cells. The measurements of photocurrent with varying intensity of the incident light indicated that the current observed was almost proportional to the light intensity in the region lower than 10^{16} photons/sec. cm². This was true with the different wavelengths[1]. Therefore, in order to normalize the photocurrent to the same input intensity of illumination, the observed photocurrent was divided by the incident light intensity for each wavelength.

The photoconduction spectra of pyranthrene, violanthrene, perylene, violanthrone, anthanthrone and indanthrazine are illustrated in Figs. 3—8. The optical absorption spectra of these films are also shown in the same figures. The photoconduction spectrum resembles the

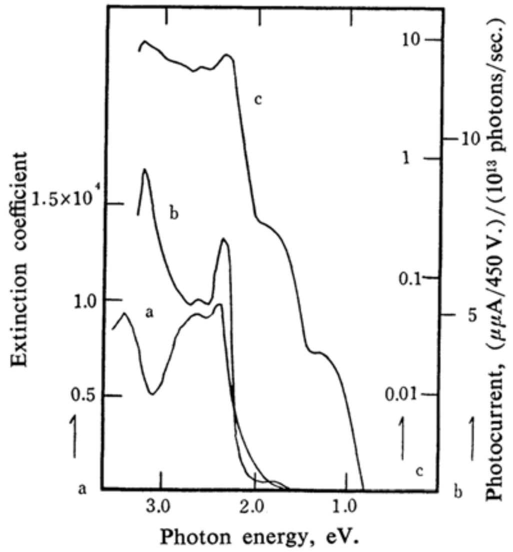

Fig. 3. The spectral responses of (a) extinction coefficient and (b), (c) photocurrent for pyranthrene film.

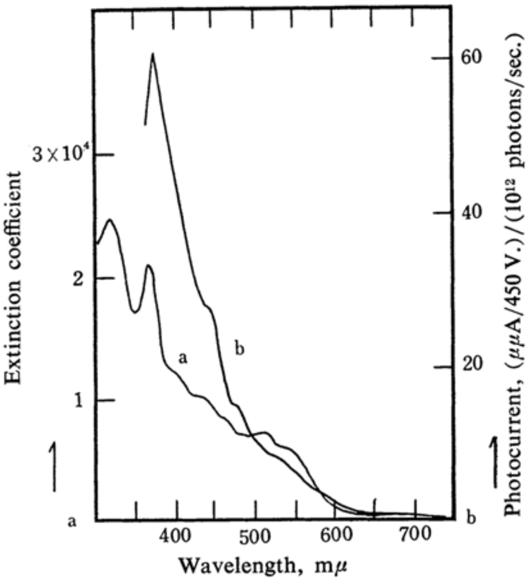

Fig. 4. The spectral responses of (a) extinction coefficient and (b) photocurrent for violanthrene film.

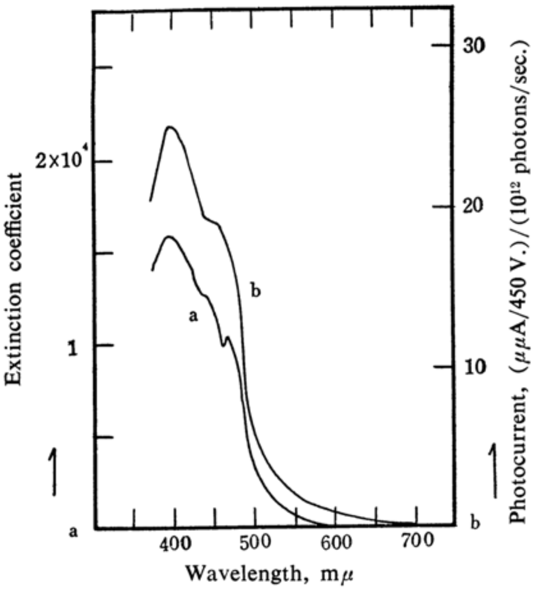

Fig. 5. The spectral responses of (a) extinction coefficient and (b) photocurrent for perylene film.

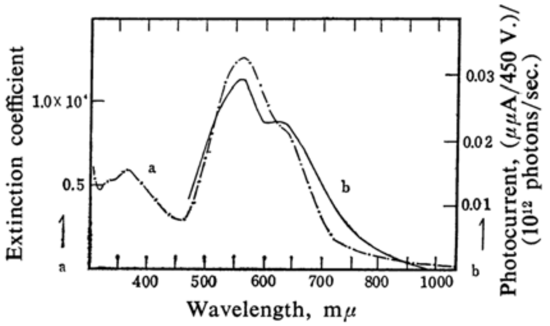

Fig. 6. The spectral responses of (a) extinction coefficient and (b) photocurrent for violanthrone film.

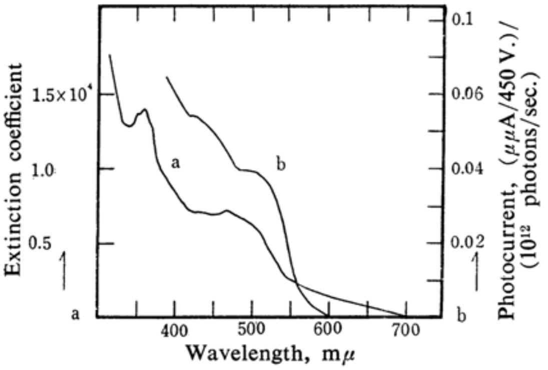

Fig. 7. The spectral responses of (a) extinction coefficient and (b) photocurrent for anthanthrone film.

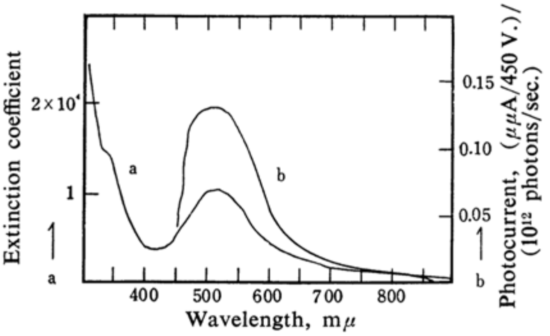

Fig. 8. The spectral responses of (a) extinction coefficient and (b) photocurrent for indanthrazine film.

TABLE II. THE PEAK ON THE SPECTRAL RESPONSE CURVE OF PHOTOCONDUCTION

	Peak of photoconduction spectrum	Peak of absorption spectrum	Assignment
Perylene	25300 cm^{-1}	25700 cm^{-1}	p
		24300	p
		22900	p
	21200	21500	p
Pyranthrene	25800	28000	β
		23400	p
	21300	21400	p
	19000	19400	p
Violanthrene	26400	27100	β
		24300	
	22700	22900	p
		21600	p
	20900	20700	p
		19600	p
	18000	18500	p
Indanthrazine	19400	19550	
Anthanthrone		27700	
	23300	23150	
	19600	21200	
Violanthrone		22750	
	18000	17900	
	15900	15800	

absorption spectrum of the same film, and a good correspondency was found between peaks on the response curve and peaks on the absorption curve, concerning both position and intensity. (Table II). Consequently, assignments could be made for peaks on the response curve by referring to the p- or β-band on the absorption spectrum.

It is concluded that the photoconduction spectrum reproduces the absorption spectrum essentially and, in consequence, that the photocurrent is produced by the light energy which is absorbed into the bulk of the organic solid.

Out of the region of the principal absorption band, the sensitivity of photoconduction

TABLE III. THE THRESHOLD OF THE PHOTOCONDUCTION

	Practical threshold value	$\lambda_{1/2}$ point of the longest wavelength p-band on the photoconduction spectrum	Thermal energy gap ε
Violanthrene	0.70 eV.	2.11 eV.	0.89 eV.
Violanthrone	0.99	1.75	0.78*
Pyranthrene	0.64	2.24	1.11
Indanthrazine	0.80	2.11	0.66**
Anthanthrone	1.91	2.27	1.70*
Perylene	0.94	2.52	2.2***
Anthracene	2.2	3.10	2.7****

* Ref. 9.
** H. Inokuchi, This Bulletin, **25**, 28 (1952).
*** M. Sano and H. Akamatu, **34**, 1569 (1961).
**** H. Inokuchi, ibid., **29**, 131 (1956).

TABLE IV. THE X-BAND IN THE PHOTOCONDUCTION SPECTRUM

	Pyranthrene	Violanthrene	Perylene
X-Band	1.28 eV.	1.09 eV.	2.05 eV.
$\lambda_{1/2}$ point of X-band	1.05	0.87	1.95
Thermal energy gap (ε)	1.11	0.89	2.2
Triplet level presumed	1.29	1.12	1.57*

* G. G. Hall, *Proc. Roy. Soc.*, **A213**, 113 (1952).

decreased more or less exponentially with the increasing wavelength and continued to extend over the infrared region. This makes it difficult to specify the threshold value. The attempt was made, nevertheless, to find a threshold beyond which the photocurrent could not be detected practically. The practical threshold values are compared with the thermal energy gaps for semiconduction for a series of compounds in Table III. It is to be noted that these values are not coincident with each other and that in some cases a rather large discrepancy was found. In the same table, the photon energies at the $\lambda_{1/2}$ point, where the photoconductive sensitivity falls to half its maximum value (the peak of the p-band), are also shown.

In the cases of pyranthrene, violanthrene and perylene, weak maxima were observed on the response curve in the wavelength region longer than the main peaks. These maxima, which are named here as the X-band and the Y-band respectively, were found at 10300 cm^{-1} and 13900 cm^{-1} for pyranthrene (Fig. 3), at 8800 cm^{-1} and 13400 cm^{-1} for violanthrene, and at 16500 cm^{-1} for perylene. These weak bands (X and Y) were detected by a sandwich-type cell as well as by a surface-type cell. Variation in applied electric field and in temperature (from room temperature to $-100°$C), or opening the film to the air, did not change the shape of these extra bands, in spite of the variation in their magnitudes.

An attempt was made to measure photoconduction under an ambient illumination. The pyranthrene surface-type cell was placed under the illumination (ambient) of a monochromatized light, and the same surface was irradiated with a second monochromatized light. The spectral response curve (of the second irradiation) was found to be unchanged from the response curve which was observed in the absence of the ambient light, independently of its wavelength. This was the case for the extra weak bands also; such a behavior as the infrared quenching of the photocurrent could not be observed. The result implied that the X- and Y- bands could not be distinguished in their natures from the main bands and were not produced by trapped electrons.

Discussion

From comparing our results with those of others$^{4-6)}$, it can be concluded that the photoconduction spectra of aromatic crystals reproduce the optical absorption spectra. With the surface-type cell, when the irradiation is made normally on the film surface, the greatest variation in electrical conductivity (i. e., photocurrent) will be produced in the uppermost layer of the film, because the photons are absorbed most prominently according to Lambert's law; furthermore, the flux of the electric field is concentrated along the uppermost layer to which the electrodes are attached. If it is assumed that the photoconductivity is of the intrinsic nature of the compound and that the charge carriers are produced in the bulk of the compound, then the number of carriers will be proportional to the number of photons absorbed into the bulk, with a definite coefficient of quantum yield.

The number of photons (L) absorbed by the film with the thickness d is given by the formula

$$L=L_0(1-10^{-Kd})$$

where L_0 is the incident light intensity and K is the extinction coefficient. As K is the order of $10^4\,\mathrm{cm}^{-1}$ for the principal bands, a film 0.5 μ in thickness absorbs nearly 70 per cent of the incident light. When Kd is small enough for its higher powers, L will be proportional to Kd. Thus the photocurrent can be anticipated to be proportional to K when the film thickness is slight. Furthermore, when it is assumed that the quantum yield of photoconduction is constant independently of the wavelength of the illumination, the response curve will reproduce the absorption curve. This is the case we have observed. The principal bands of the absorption spectra consist of the singlet-singlet transitions; thus, all of these excited states are equally responsible for the electronic conduction, but with a probability depending on each transition moment.

Outside the principal bands, a long tail is generally observed on the response curve. No reliable interpretation has been offered for the photosensitivity in the long wavelength region. This makes it difficult to specify the threshold of photoconductivity. The practical threshold value is dependent on the sensitivity of the equipment; thus, the concept becomes rather a vague one. For the intrinsic photoconductors, Moss[12] has proposed a convenient characteristic wavelength at which the photosensitivity falls to half its maximum value (the $\lambda_{1/2}$ point). In the cases of perylene and anthracene, the coincidence of the energy values between the thermal energy gap and the $\lambda_{1/2}$ point is not so bad, but in other cases large discrepancies are noted. (Table III). Similar discrepancies were pointed out by Vartanyan and Karpovich[13] for violanthrone and pyranthrone.

In connection with this, the extra peaks which were found on the tail of the main bands of photoconduction spectra are of interest. Similar extra peaks were found for anthracene by Rosenberg[5], and for pyrene by Kommandeur, Korinek and Schneider[14]. In the latter case, it was reported that the extra bands were observable in crystal possessing a rather considerable thickness. In the present case, however, the film was as thin as 0.5 μ in thickness, and the bands are of the same nature as the main bands, as was mentioned in the previous section. The most characteristic fact for the extra bands is that one of them (the X-band) is located at the energy which corresponds to the thermal energy gap. Thus, the $\lambda_{1/2}$ point of the X-band is in fairly good agreement with the value of the thermal energy gap. This is shown in Table IV.

A number of possible explanations for the extra bands are conceivable; some of them were pointed out by Kommandeur et al.[14], while Rosenberg[5] assumed the electron transfer through the triplet state for anthracene.

The location of the X-band is far below the singlet-singlet transition. Concerning the lowest excited singlet state, the fluorescence spectrum is suggestive. For instance, the p-band of the pyranthrene film ranged from around 400 mμ to 650 mμ, with the maximum at 516 mμ, while the fluorescence band ranged from 496 mμ to 734 mμ, with the maximum at 648 mμ (1.92 eV.) (Fig. 9). The peak-peak separation between the absorption and the fluorescence bands is generally found to be in the order of a few thousands cm^{-1} for polycyclic aromatic compounds in a crystalline state. This might be due to the molecular interaction in the excited state. However, it is clear that the lowest excited singlet level lies above 1.92 eV. for pyranthrene film, while the X-band is located at 1.28 eV. It is known[15] that the lowest triplet state (^3L) is 2.32 eV. below the p-band (^1L_a) in benzene and 1.71 eV. below in naphthalene, while the $^1L_a-{}^3L$ separation is around 1.4 eV. in the larger aromatic

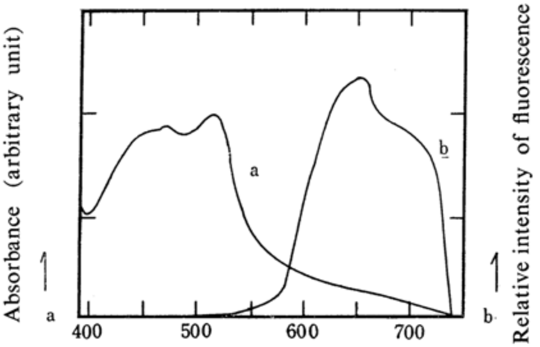

Fig. 9. (a) Absorption and (b) fluorescence spectra of pyranthrene film.

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12) T. S. Moss, "Photoconductivity in the Elements", Butterworths Publ., London (1952).

13) A. T. Vartanyan and I. A. Karpovich, *Doklady Akad. Nauk. S. S. S. R.*, **113**, 1020 (1957).

14) J. Kommandeur, G. J. Korinek and W. G. Schneider, *Can. J. Chem.*, **36**, 607 (1958).

molecules. If it is true for pyranthrene and violanthrene and if the triplet level in the crystalline state is not far from the molecular level, it follows that the bands concerned may be assigned to the lowest triplet state (Table IV).

The weak absorption band which was found at 1.40 μ (0.89 eV.) for violanthrene is not far from its X-band, but 1.53 μ (0.81 eV.) for pyranthrene is not in coincidence with the X-band.

From the above discussion, it may be concluded that the photoconduction takes place by associating with the lowest excited state of molecules in the aromatic crystals. The semiconduction also occurs in the same excited state, or even with smaller energy. It has been frequently presumed[16] that the photoconduction band should be located near the ionization level of the molecule, but that the lowest excited state could not be responsible for the electrical conduction, even though the dipole-dipole interaction between excited states results in developing the molecular exciton band. But this is not coincident with observed results. Recently, Lyons and Morris[17] have attempted ultraviolet irradiation in the vacuum region onto anthracene crystal; however, no photoconductivity distinguishable from the usual one could be found.

Concerning the mechanism for photoconduction in the lowest excited state, there are three possible schemes at least. (1) There might be a sufficient intermolecular orbital overlap which results in developing the true conduction band even in the lowest excited state. (2) If it is not the case, the electrons or the positive holes might be exchangeable between neighboring molecules through the vibrational levels in the lowest excited state during the life time of the excited state ($\sim 10^{-8}$ sec.), which is long enough compared with the vibrational period ($\sim 10^{14}$ sec.). This would result in the hopping conduction. (3) The electron transfer may take place via the triplet state much more easily than via the excited singlet state, because of its long life time; the singlet-triplet transition through the intersystem crossing is well known.

Lyons and Morris[18] have found that the photo-emission of electrons from aromatic crystals can occur at a potential which is lower by 1∼2 eV. than the ionization potential of the molecules. However, the ionization continuum in the crystal is still much higher than the energy level of the lowest excited state.

With regard to the second and the third scheme, the temperature dependence for photoconductivity is of interest. As reported in the previous paper[1], the activation energy of photoconduction is 0.18 eV. for pyranthrene; nearly the same value was found for anthracene (0.17 eV.) by Rosenberg[5], and for pyranthrone (0.2 eV.) and for violanthrone (0.2 eV.) by Vartanyan[13]. Thus, this value is apparently quite general for polycyclic aromatics and is coincident with the vibrational energy of the skeletal stretching of aromatics. Some reason might be expected for the fact that such a mode of vibration is the most favorable for the coupling with the electronic excitation as well as for the intersystem crossing.

The photosensitivity which was found in the region of the triplet state supports the possibility of the third scheme. Moreover, it has been confirmed[19] that the electron spin resonance absorption in aromatic crystals under irradiation is due to the triplet state. Thus, the scheme for electron transfer via the triplet state is an attractive one.

Summary

The spectral responses of the photoconductivity of perylene, pyranthrene, violanthrene, anthanthrone, violanthrone and indanthrazine, as well as the optical absorption spectra of these aromatic solids, have been investigated. Associated with the surface-type cells, when the aromatic films are thin enough, the response curves reproduce the absorption spectra. It has been concluded from this that the photoconductivity is the intrinsic property of the compound and that the lowest excited states are responsible for the electrical conduction.

The thresholds for photoconductivity are rather vague. In some cases, however, extra bands are found in the photoconduction spectra outside the main bands. These extra bands locate in the energy regions which correspond to the triplet states of the molecules and are coincident with the thermal energy gaps for the semiconduction.

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