Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Photocurrent Induced by Detrapping of Charge Carriers Trapped by Radicals in Naphthalene and Anthracene Single Crystals

Takeyoshi Nakayama [a] & Noriaki Itoh [a]
[a] Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University, Nagoya, Japan

To cite this article: Takeyoshi Nakayama & Noriaki Itoh (1979): Photocurrent Induced by Detrapping of Charge Carriers Trapped by Radicals in Naphthalene and Anthracene Single Crystals, Molecular Crystals and Liquid Crystals, 51:3-4, 189-202

To link to this article: http://dx.doi.org/10.1080/00268947908084705

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 189–202

Printed in Holland

Photocurrent Induced by Detrapping of Charge Carriers Trapped by Radicals in Naphthalene and Anthracene Single Crystals

TAKEYOSHI NAKAYAMA and NORIAKI ITOH

Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University, Nagoya, Japan

(*Received August 30, 1978*)

Photocurrent spectra induced by detrapping of charge carriers trapped by neutral radicals in naphthalene and anthracene crystals have been studied. One broad band around 700 nm in naphthalene and two broad bands around 800 nm and 900 nm in anthracene were observed. It was shown that the broad bands in each crystal involve transitions of carriers trapped by a single trap. Studies of the effect of the polarity of injected carriers on detrapping photocurrent indicated that the broad band for naphthalene is induced by electrons and that for anthracene is by holes. A molecular orbital calculation of the positive and negative l-hydronaphthyl ions was made, The lowest transition energies of these ions were found to be larger than the photocurrent-band energy. This result together with the fact that the band is broad, leads us to a conclusion that the observed photocurrent band is due to the transfer of charge trapped at the neutral radical to the host molecules.

I INTRODUCTION

Mechanism of charge transport in aromatic hydrocarbon crystals has been a subject of several investigation during decades. Two types of studies have been carried out: (1) the studies of the transport of electrons and holes and (2) the studies of the action spectrum of the photogeneration of the charge carriers. In spite of the presence of a great deal of literatures, no definite conclusion has yet been drawn on the width of the conduction band nor the density of the states including the vibrational progression.

A measurement[1] of the hole effective mass through the cyclotron resonance of the photo-injected charge carriers in anthracene has been made recently, yielding the value of the hole effective mass to be 11 in the electron mass unit.

The measurements of the drift[2–7] and Hall[8,9] mobilities have been made by several authors and the values obtained for electrons and holes are of the order of 1 cm^2/Vs, except the value 40 cm^2/Vs obtained by Dresner[10,11] for anthracene. The low mobilities have been ascribed to that electrons and holes travel in a narrow conduction band and in a narrow valence band, respectively. The width of the conduction and valence bands derived from the mobility agrees with the result of the theoretical calculation.[12–16] Dresner[10] has suggested that the obtained mobility was the average of those in the narrow band and in the wide band which lies above the narrow conduction band and below the narrow valence band. He estimated the wide band mobility to be of the order of 200 cm^2/Vs. Burland[1] has also obtained the relaxation time for the scattering of holes in anthracene and obtained the value of 10^{-11} s. A combination of the values of the effective mass and the scattering time obtained by Burland should give a value of the hole mobility in anthracene as large as 200 cm^2/Vs. A measurement of the temperature dependence of the drift mobility has been made recently by Schein *et al.* and revealed the existence of the band motion at low temperatures.[7] In view of their result the mobility at high temperatures appears to be characterized by the hopping motion of the charge carriers. If so, the value of the mobility may yield an estimation of a lower bound of the width of the conduction band.

Charge carriers may be generated by photoexcitation of either valence electrons or trapped electrons or holes. The photoexitation of valence electrons creates pairs of electrons and holes which are under coulombic attraction. Application of electric field has been found to enhance the charge carrier generation.[17–22] The dependence of the quantum yield of the charge-carrier generation at the zero electric field on the exciting photon energy has been obtained.[21,22] The energy dependence of the yield of the carrier generation is not the same as the optical absorption spectrum and shows a broad peak near the band edge with a long tail to the higher energy side.

The photogeneration of charge carriers by two-photon excitation has been measured by Bergman and Jortner.[23] They observed a sharp peak at 4.04 eV with additional structures in anthracene and interpreted them as the transition of a valance electron to the narrow conduction band coupled with vibrational quanta. On the other hand, Strome[24] observed only a large broad peak in the photocurrent curve. Kepler[25] has also found a structureless photoresponse above the absorption edge by two-photon excitation and has shown that the photoresponse is proportional to $\sqrt{E - E_0}$, where E is the photon energy and E_0 is the width of the band gap. It is not yet clear whether the final states of the transition by one or two photon excitation of the valence electrons are the highly excited singlet exciton states or conductive states. If the former is the case, the autoionization should occur for the conductivity increase to be observed.

The photocurrent induced by detrapping of trapped charge carriers or injection of charge carriers from metals has been studied by several workers.[26–34] The photoexcitation spectrum of trapped holes into the valence band obtained by Burshtein and Many[26] shows a peak with a width of about 0.2 eV, followed by a broad band separated by 0.2 eV. Dresner[27] obtained a similar result by means of the photoemission of charge carriers from metal electrodes to the crystals, although quantitative values are slightly different. For the photoexcitation of trapped electrons into the conduction band, Many and coworkers[28] observed a series of sub-bands in the broad conduction band and ascribed them to the narrow conduction band separated by the vibronic interaction. Baessler and coworkers[29–31] have not observed the vibrational structures but deduced the presence of a narrow band and a broad band. Gaehrs and Willig[32] have observed only a broad photocurrent band with a width of about 1 eV induced by charge carrier injection and assumed that the broad band is due to the excitation into the surface states, not representing the density of the state in the conduction band. Karl and coworkers[33,34] have measured the photocurrent induced by detrapping of positive holes trapped by tetracene impurities in an anthracene crystal, and obtained a sharp peak, which was ascribed to an intramolecular transition in the tetracene monopositive ion. It is not yet clear whether the shallow peaks observed by Many and coworkers are originated from intramolecular transitions or from the narrow conduction band. It is also interesting to know whether a broad photocurrent band as observed by Gaehrs and Willig[32] is also observed by an internal photocurrent induced by detrapping.

One of the factors which should be considered in treating the detrapping is the charge state of the traps. If the traps are charged negatively or positively after detrapping occurs, resonant states may be created below, above or inside the continuum. Such resonant states may modify extremely the transition spectrum and therefore the transition spectrum may not represent the density of the states of the continuum. This is a well known fact for the *F* center in alkali halides, which is an electron trapped by a positively charged negative ion vacancy.[35] For the *F* center, the transitions to higher excited states consist of those from the ground state to hydrogenic excited states (*F* and *K* bands) and those to the resonant states in the continuum (L_1, L_2 and L_3 bands). On the other hand no resonant state may be formed in the detrapping processes which leave neutral species. The system employed by Karl and coworkers satisfies this requirement, even though only the intramolecular transition has been observed in this case. The transition from a localized state to a continuum state is a charge transfer transition by its nature. Absence of the resonant state may make it possible to deduce the density of the continuum states from the action spectrum of the charge-transfer-type photo-induced detrapping leaving neutral species. The optical absorption band due to the *F*′ center (two electrons trapped by a negative ion vacancy) in alkali halides has been interpreted to represent the product of the density of the states in the conduction band and the transition probability from the *s*-like state to the continuum state.[36]

The present authors have pointed out that the radical induced by irradiation in naphthalene acts as a trapping center for charge carriers.[37] They measured the photocurrent induced by detrapping of the charged radical ion and observed a broad photo-current band in naphthalene. This band has a bell-shaped curve with tails at both sides of the maximum but with little structures. It has been confirmed that a single kind of trapping centers is responsible to the photocurrent band. In the present paper the same technique as used before is extended to anthracene. Moreover, molecular orbital calculation was made of the species which can be the candidates of the source of the photocurrent band for naphthalene: 1-hydronaphthyl positive and negative ions. No intramolecular transitions cannot be expected in these species near infrared and it is concluded that the observed photocurrent band is due to the charge transfer transition of carriers trapped at the radical to the host molecules.

II EXPERIMENTAL

Naphthalene and anthracene single crystals were grown by the Bridgman technique after applying the zone-refinement to scintillation grade materials. Specimens with thickness between 0.5 and 2 mm were cleaved from large ingots. Radicals were introduced into the specimens by irradiation with 2 MeV electrons generated from a Van de Graaff accelerator or with X-rays generated from an X-ray tube operated at 50 kV 35 mA. The approximate dose rates of electron beam irradiation and X-ray irradiation were 1×10^6 rad/sec and 1×10^6 rad/hr, respectively. The optical density of the irradiated specimen around 700 nm was kept lower than 10^{-2} to obtain uniform light intensity within the specimen.

Although the specimen just after irradiation showed a strong photoresponse, the photoresponse is diminished after repeating measurements. Charge carriers were then injected into such specimens by irradiation with pulsed electron beams generated with a Febetron 707. The dose per pulse was approximately 1×10^5 rad. X-ray pulses with a dose of 10^3 rad were also generated by bombarding a tungsten target with the electron pulses and were used for the carrier injection. The dose for the charge carrier injection is usually smaller by 2 $\sim$ 4 orders of magnitude than the dose to create radicals. After injection of charge carriers, the specimens were placed between two 1 mol % NaCl electrodes. The light generated from a tungsten lamp was incident on the ac′-plane of the specimen through a Baush and Lomb grating monochromator. The electric field was applied to the electrodes, the direction of the field being in perpendicular to the incident light. The wavelength dependence of the intensity of the exciting light was determined with a thermopile. The photocurrent induced by the excitation with monochromatic light between 300 nm and 1600 nm was measured with a vibrating reed electrometer under an applied voltage of up to about 10^3 V.

A selective injection either of the holes or electrons was made using a semi-transparent electrode, kept either positive or negative, through which the specimen was irradiated with uv light. The semi-transparent electrode was either a quartz glass coated with SnO_2 (for anthracene) or a copper mesh (for naphthalene). The illumination was made in perpendicular to the ab crystallographic plane. The uv light was generated with a mercury lamp and was passed through filters: Toshiba UV-D25 for anthracene and 5 cm $NiSO_4$–$CoSO_4$ solution for naphthalene. All experiments were carried out at room temperature. The electron beam current was measured with a Faraday cup and the intensity of the X-ray pulse was measured with a calibrated plastic scintillater.

III EXPERIMENTAL RESULTS

Photocurrent of specimens irradiated with 2 MeV electron beams was measured under excitation with monochromatic light. The photocurrent was observed immediately after the irradiation but decreased by irradiation with infrared light generated from a tungsten lamp and transmitted through a filter which transmit above 650 nm. It decreased also by keeping the specimen at room temperature for about 10 days for both naphthalene and anthracene. The photocurrent, however, can be restored by ionizing radiation at a low dose such as irradiation with electron pulsed beams. The increase of the photocurrent by the low dose irradiation was observed to be saturated. This saturation value was found to increase with increasing the total radiation dose.

Wavelength dependence of the photocurrent near infrared is shown in Figure 1 for naphthalene and Figure 2 for anthracene. The ordinates of the figures are the photocurrent corrected with the wavelength dependence of the intensity of the exciting light and normalized to the largest value. One or two broad peaks in the region of near infrared were observed in each crystal. Figure 1 shows the photocurrent spectra for naphthalene obtained at two different radiation doses (A and B) and after prolonged infrared irradiation (C). The decrease of the photoresponse at a given wavelength in obtaining the spectrum was negligible. The curve A was obtained with a specimen irradiated at a dose of about 2 × 10^8 rad, and curve B at a dose of 2 × 10^6

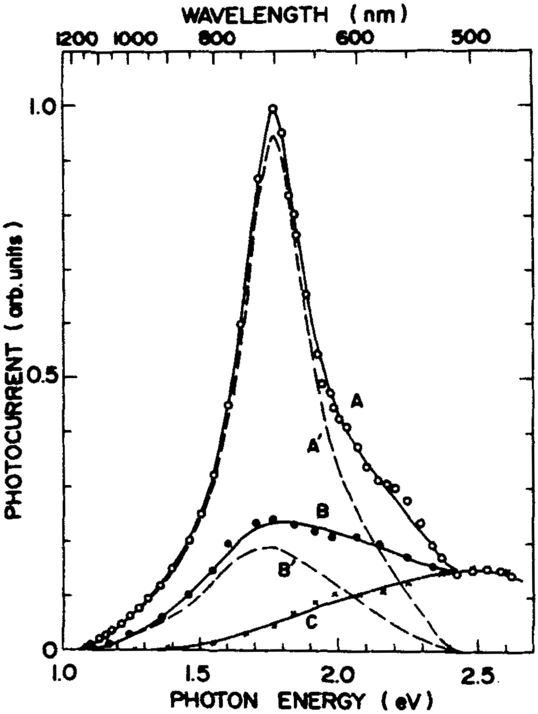

FIGURE 1 Photocurrent spectra of irradiated naphthalene single crystals measured after charge carrier injection and after prolonged infrared irradiation. Irradiation dose was about 2×10^8 rad for curve A and C and about 2×10^6 rad for curve B. Curve C was obtained after prolonged infrared irradiation. Dashed curves A′ and B′ show the difference between spectra A and C and spectra B and C, respectively.

rad. The curve C is the photocurrent spectrum after prolonged bleaching of the specimen giving the curve A. The dashed curves (A′ and B′) in Figure 1 were obtained by subtracting curve C from curves A and B and indicate the photocurrent spectra induced by charge carriers trapped by the radiation-induced radicals. The spectrum for anthracene shown in Figure 2 was obtained at an absorbed dose of 8×10^7 rad. Two peaks at 1.4 and 1.6 eV are observed and their relative height is not dependent on the radiation dose. Similar measurements were made for X-ray irradiation and the results were essentially the same.

On the basis of the experimental results that the band is optically bleached uniformly regardless with the wavelength of the bleaching light, it has been concluded already that the photo-current band for naphthalene is originated from a single kind of trapping center.[37] Similar experiments were performed for the photocurrent band for anthracene and the result is shown in Table I. The optical bleaching was carried out by using monochromatic light at an

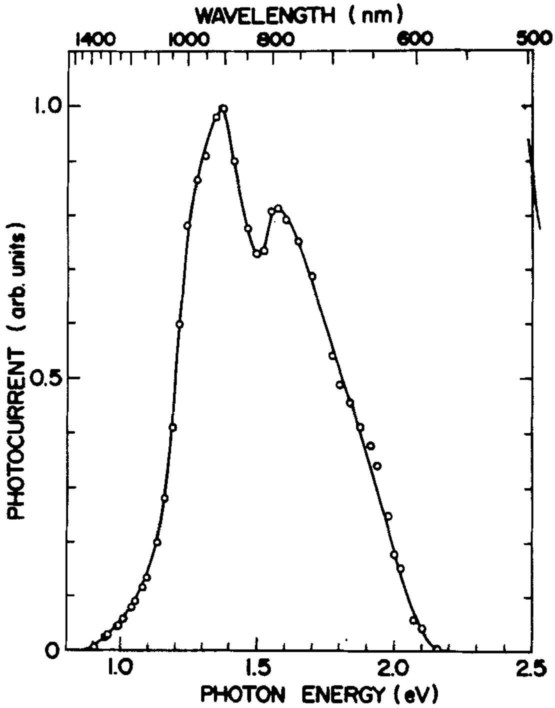

FIGURE 2 The increase of photocurrent of irradiated anthracene single crystal induced by charge carrier injection. The ordinate is normalized to the peak value at 1.4 eV.

interval of 100 nm from 1000 nm to 700 nm. The reduction of the photocurrent by optical bleaching was measured at various wavelengths. In the table, the reduction $\Delta I(\lambda)$ measured at a wavelength λ, divided by the reduction $\Delta I(900)$ of the peak value, are listed for the optical bleaching at 700, 800, 900 and 1000 nm. It turns out that $\Delta I(\lambda)/\Delta I(900)$ is independent of the wavelength of the bleaching light. The values of $\Delta I(\lambda)/\Delta I(900)$ in Table I

TABLE I

Optical bleaching behaviour of the photocurrent band for anthracene shown in Figure 2. $\Delta I(\lambda)$ represents the reduction of the photocurrent at a wavelength λ by optical bleaching

Bleaching light (nm)	$\Delta I(\lambda)/\Delta I(900)$			
	$\lambda = 700$ nm	$\lambda = 800$ nm	$\lambda = 900$ nm	$\lambda = 1000$ nm
700	0.54	0.85	1.0	0.81
800	0.50	0.80	1.0	0.80
900	0.55	0.84	1.0	0.82
1000	0.50	0.79	1.0	0.79

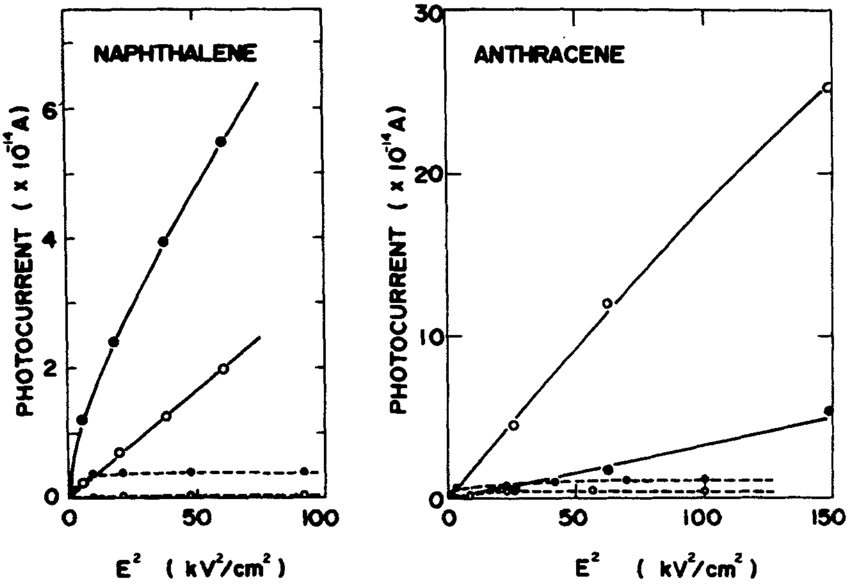

FIGURE 3 Polarity effect of the detrapping photocurrent of irradiated (solid line) and unirradiated (dashed line) naphthalene and anthracene crystals. Open and closed circles were obtained by irradiating with uv light under an applied electric field keeping the illuminated side positive and negative, respectively.

agree very well with those of the photocurrent spectrum shown in Figure 2. Thus it is clear that the photocurrent band shown in Figure 2 decreases uniformly independent of the wavelength of the bleaching light.

In order to clarify whether the photocurrent spectra shown in Figures 1 and 2 are attributed to hole or electron transport, charge carriers were produced by illuminating the specimen through an electrode which was polarized either positive or negative so that only one kind of carriers was injected. The dependence of the photocurrent at the peak on the applied electric field is shown by solid lines in Figure 3. The photocurrent is plotted against squared electric field since the same driving voltage was used for the carrier injection and for the photocurrent measurement. The photocurrent was more prominent for illumination through the negative electrode in naphthalene and circumstances were contrary for anthracene. The figure also includes the dependence of the photocurrent on the applied field in an unirradiated specimen induced by light of longer wavelength than 500 nm for naphthalene and than 650 nm for anthracene. Saturation characteristics were observed for both polarity of the illuminated electrode. It is seen that the Schubweg becomes much smaller by the presence of the radicals.

IV DISCUSSION

1 Origin of the photocurrent band

The photocurrent bands observed in irradiated naphthalene and anthracene have been shown to be reduced by thermal and optical bleaching at room temperature but to be restored by a low dose irradiation to a saturation value. These results show that the photocurrent band is caused by detrapping of the charge carriers trapped by the radiation-induced species, which are stable at room temperature against optical and thermal bleaching. The partial bleaching experiment for anthracene described in the last section indicates very clearly that the broad bands in anthracene are only associated with the optical transition in a single center and not a composite of many center transitions. Similar conclusion has been made for the 1.8 eV band for naphthalene as described in the previous paper.[37] Both the heights of the 1.8 eV band in naphthalene and 1.4 eV and 1.6 eV bands in anthracene obtained immediately after the irradiation were shown to increase with increasing the radiation dose. Thus it is concluded that these bands are induced by detrapping of charge carriers trapped by a single radiation-induced species.

It is well known that there are several kinds of radicals in naphthalene and anthracene crystals irradiated with ionizing radiation. Among them 1-hydronaphthyl radical in naphthalene and 9-dibenzo-cyclohexadienyl radical in anthracene are most numerous at room temperature, as indicated from EPR works.[38,39] Other radicals such as 2-hydronaphthyl radical in naphthalene have been known to be much smaller in concentration. It is also known that the naphthyl radical which is stable only at low temperature is converted to a diamagnetic species at room temperature. This diamagnetic species may have nearly the same concentration as 1-hydronaphthyl radical. Thus these two species may be the most probable cause of the photocurrent band.

The experimental results of the selective injection of charge carriers into specimens containing radicals show that the photocurrent with negative polarity is larger in naphthalene and that with positive polarity is larger in anthracene by a factor of 3 ~ 5. In the case of an unirradiated naphthalene, it is seen from the figure that the hole injection into specimen does not produce any photocurrent. On the other hand, the photocurrent is observed for both polarities in irradiated specimens. This may be caused by that the Schubweg has become much smaller and is comparable to the inverse of the absorption coefficient for the incident light owing to the presence of the radical. Since only one kind of traps contributes to the photocurrent band, in spite of the presence of photocurrent with the positive carrier injection, the polarity effect shown in Figure 3 for naphthalene is considered to be indicative that only the electrons are responsible for the photocurrent band. The electron current in the strongly absorbed layer is responsible for the current with the positive polarity. Similarly it is concluded that the photocurrent band for anthracene involves a transition of a positive hole.

2 Transition energy of the hydronaphthyl radical ion

In order to get into insight of the nature of the photocurrent band, it is of importance to know whether it is originated from the intramolecular transitions of the ions. Since the diamagnetic species created through photochemical reaction have been considered to be a complex alternant hydrocarbon molecule, it is unconceivable that such species have intramolecular optical transitions near or in infrared. Thus a molecular orbital calculation of the intramolecular optical transition of the positive and negative hydronaphthyl ions was made. The calculation was made using the self-consistent-field method developed by Pariser and Parr.[40,41] The configuration interaction (CI) was taken into account following the method developed by Pople[42] for the closed shell.

Two kinds of models for the hydronaphthyl radicals were used. The first model (model A) was the same as used by Shida and Hanazaki.[43] In the second model (model B) it was assumed that the radical is composed of nine carbon-$2p\pi$ orbitals: carbon orbitals at the position where hydrogen is attached was disregarded. This second model is justified since the occupation of unpaired electrons at the position where the additional hydrogen is attached is extremely low. Even though this model may not be accurate, this simple model is convenient since the pairing rule is still held.

The lowest transition energies for 1-hydronaphthyl ions are shown in Table II, where the experimental results[44–45] are also listed. The lowest transition for each ion is essentially from the highest filled level to the lowest vacant level, whereas the lowest transition for the radical is to the state

TABLE II

Transition energy to first excited state of 1-hydronaphthyl ions (eV)

	Calculation		
	Model A	Model B	Experiment
1-Hydronaphthyl			
Positive ion	2.92	3.08	3.17[a]
Negative ion	2.85	3.07	2.85[b]

[a] Ref. 44.
[b] Ref. 45.

TABLE III

Ionization potential of 1-hydronaphthyl ions

	Ionization potential (eV)		Electron affinity (eV)
	Model A	Model B	
1-Hydronaphthyl			
Positive ion	8.42	8.66	—
Negative ion	2.75	2.82	—
Naphthalene	8.12[a]		0.15[b]

[a] Experimental value: Ref. 46.
[b] Experimental value: Ref. 47.

resulting from the configuration interaction between the transitions to and from the half-filled level.[43] The agreement between the experimental and theoretical values is fairly good. Therefore it is clear that no intramolecular transition exists at the energy region where the photocurrent band appears.

The other point which is crucial for the assignment is whether the hydronaphthyl ion forms a stable localized state in a naphthalene crystal. Theoretically the decision could be made by comparing the ionization potential of the hydronaphthyl positive ion with that of the naphthalene molecule and that of the negative ion with the electron affinity of the napthalene molecule. Using the Koopman's theorem, the ionization potential of the positive and negative ions was obtained as shown in Table III, where the experimental values of the electron affinity[46] and ionization potential[47] of the naphthalene molecule is also shown. The result indicates that the hydronaphthyl negative ion has an ionization potential much larger than the electron affinity of the naphthalene molecule. Thus it is conceivable that the hydronaphthyl negative ion is stable in a naphthalene crystal.

3 Density of states above continuum edge

The photocurrent band obtained in the present work cannot be ascribed to an intramolecular transition in radiation-induced species by following two reasons: (1) the positive or negative ions of the most numerous radiation products at room temperature do not have the transition energy near infrared; and (2) the width of the photocurrent band is much broader than that usually observed for intramolecular transitions.[34] Thus we assigned the photocurrent band to be the charge transfer transition of electrons or holes trapped by the radiation-induced radical to the neighboring host molecules. Since the charge transfer state is composed of a neutral radical and electrons or holes attached to host molecules, the transition to such charge transfer states may be indicative of the density of the states in the continuum states, as described in Section I.

The broad photocurrent band observed in the present work is rather similar to that observed by Gaehrs and Willig[32] through photoemission from metal electrode. Even though they attributed it to the transition from metal to the energetic states near surface, the present photocurrent band was obtained for the transitions in the bulk. Moreover the neutral character of the species left after transition may exclude the possibility of forming resonant states. Thus it follows that the broad band represents the density of the states in the continuum. This conclusion is not in contradictory to the observation by Lyons and Milne[22] and by Kepler[25] that the final states of the one or two photon transition of the valence electrons are rather broad. The width of the conduction band calculated theoretically[14] is substantially smaller than the present experimental result. Besides the experimental values of Hall and drift mobilities, the theoretical result has been supported by another few experimental observations.[48,49] Thus it appears that the broad bands are the result of the overlap of vibrational progression of the narrow continua. Such overlaps of continuum states have been observed for the higher triplet exciton bands.[50] The present study indicates that there are no forbidden gaps between each vibrational band as suggested by Many and coworkers.[28] Instead of that the vibrationally progressive lines collapse into a single broad band. In this case the characters of each narrow band may be partly lost owing to the configurational interaction between each vibrational band.

It has been reported [23,26–31] that a narrow continuum exists beneath a broad continuum. According to the present investigation, only broad band for trapped electrons in naphthalene and for trapped holes in anthracene were observed. Both transitions of the charge carriers trapped by the radical to narrow broad continua are essentially those from localized discrete level to states described by plane waves and would have nearly the same transition cross section. If the narrow band exists, one should expect the presence of a narrow photocurrent band at lower energy side of the photocurrent band. Such a response was not observed. Unlike the present experiments, if the excitation is made from a neutral state (a charge carrier plus an oppositely charged trap), as may be often the case in the previous studies, a resonant state may be formed beneath the continuum. One may observe the photocurrent by the excitation to this localized state if the thermal ionization from the state is appreciable. The narrow band observed previously may be ascribed to transitions to such localized states. Optical absorption associated with the transition to such resonant states has been recently observed for the case of the neutral radical in naphthalene.[49]

The energy separations between the radical state and the lower and upper edges of the conduction band in naphthalene and the valence band in anthracene were tentatively taken as the lowest and highest energies of the broad photocurrent band due to the radical. Thus the lower and upper edges of the conduction band of the naphthalene measured from the trapped level was determined to be 1.1 eV and 2.4 eV. Similar results for the valence band of anthracene are 0.9 eV and 2.2 eV. Thus the overall width of the conduction band of naphthalene was determined to be 1.3 eV and that of the valence band in anthracene also to be 1.3 eV.

In conclusion, the optical transitions from the localized state to the conduction band in naphthalene and to the valence band in anthracene were found to show a broad band, possibly because of the overlap of the vibrational progression. The width of these bands was about 1.3 eV for both naphthalene and anthracene at room temperature. No indication of the existence of the narrow bands was obtained. This technique of exciting charge carriers trapped by neutral center to continuum appears to be one of the most appropriate way to obtain the structure of the continuum.

Acknowledgement

Authors are grateful to Drs. Chong and Nakagawa and Mr. Fujiwara for cooperation.

References

1. D. M. Burland, *Phys. Rev. Letters*, **33**, 833 (1974).
2. R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).
3. O. H. LeBlanc, Jr., *J. Chem. Phys.*, **33**, 626 (1960).
4. M. Silver, J. R. Rho, D. Olness, and R. C. Jarnagin, *J. Chem. Phys.*, **38**, 3030 (1963).
5. I. Nakada and Y. Ishihara, *J. Phys. Soc. Japan*, **19**, 695 (1964).
6. R. G. Kepler and D. C. Hoesterey, *Phys. Rev.*, **B9**, 2743 (1974).
7. L. B. Shein, C. B. Duke, and A. R. McGhie, *Phys. Rev. Letters*, **40**, 197 (1978).
8. A. I. Korn, R. A. Arndt, and A. C. Damask, *Phys. Rev.*, **186**, 938 (1969).
9. D. H. Spielberg, A. I. Korn, and A. C. Damask, *Phys. Rev.*, **B3**, 2012 (1971).
10. J. Dresner, *Phys. Rev.*, **143**, 558 (1966).
11. J. Dresner, *J. Chem. Phys.*, **52**, 6343 (1970).
12. O. H. LeBlanc, Jr., *J. Chem. Phys.*, **35**, 1275 (1961).
13. G. U. Thaxton, R. C. Jarnagin, and M. Silver, *J. Phys. Chem.*, **66**, 2461 (1962).
14. J. L. Katz, S. A. Rice, S. I. Choi, and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).
15. R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, Jr., *J. Chem. Phys.*, **42**, 733 (1965).
16. D. C. Singh and S. C. Marthur, *Mol. Cryst. Liq. Cryst.*, **27**, 55 (1974).
17. N. Geacintov and M. Pope, *J. Chem. Phys.*, **45**, 3884 (1966).
18. N. Geacintov and M. Pope, *J. Chem. Phys.*, **50**, 814 (1969).
19. R. H. Batt, C. L. Braun, and J. F. Hornig, *J. Chem. Phys.*, **49**, 1967 (1968).
20. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **59**, 2269 (1973).
21. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **64**, 3573 (1976).
22. L. E. Lyons and K. A. Milne, *J. Chem. Phys.*, **65**, 1474 (1976).
23. A. Bergman and J. Jortner, *Phys. Rev.*, **B9**, 4560 (1974).
24. F. C. Strome, *Phys. Rev. Letters*, **20**, 3 (1968).
25. R. G. Kepler, *Phys. Rev.*, **B9**, 4468 (1974).
26. Z. Burshtein and A. Many, *Mol. Cryst. Liq. Cryst.*, **25**, 31 (1974).
27. J. Dresner, *Phys. Rev. Letters*, **21**, 356 (1968).

28. A. Many, J. Levinson and I. Teucher, *Mol. Cryst.*, **5**, 273 (1969).
29. H. Baessler and G. Vaubel, *Solid State Commu.*, **6**, 97 (1968).
30. G. Vaubel and H. Baessler, *phys. stat. sol.*, **26**, 599 (1968).
31. H. Baessler, N. Riehl, and G. Vaubel, *phys. stat. sol.*, **26**, 607 (1968).
32. H. J. Gaehrs and F. Willig, *Chem. Phys. Letters*, **32**, 300 (1975).
33. H. Rohrbacher and N. Karl, *phys. stat. sol.*, (a) **29**, 517 (1975).
34. N. Karl and H. Feederle, *phys. stat. sol.*, **34**, 497 (1976).
35. W. B. Fowler, *The Physics of Color Centers* (ed. W. B. Fowler), (Academic Press, New York, 1968).
36. D. W. Lynch and D. A. Robinson, Phys Rev. *174*, 1050 (1968). See also A. M. Stoneham, *Theory of Defects in Solids* (Clarendon Press, Oxford, 1975) chap. 16.
37. T. Nakayama and N. Itoh, *Solid State Commu.*, **16**, 635 (1975).
38. T. Chong and N. Itoh, *J. Phys. Soc. Japan*, **35**, 518 (1973).
39. T. Chong and N. Itoh, *Mol. Cryst. Liq. Cryst.*, **36**, 99 (1976).
40. R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
41. J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).
42. R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
43. T. Shida and I. Harazaki, *Bull. Chem. Soc. Japan*, **43**, 646 (1970), I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Japan*, **38**, 1298 (1965).
44. C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).
45. W. Ij Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.* 3055 (1959).
46. R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).
47. M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).
48. L. B. Schein, *Phys. Rev.*, **B15**, 1024 (1977).
49. K. Nakagawa and N. Itoh, *Chem. Phys. Letters*, **47**, 367 (1977).
50. M. Higuchi, T. Nakayama and N. Itoh, *J. Phys. Soc. Japan*, **40**, 250 (1976).