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Near-IR Absorption Spectrum of Aromatic Excimers

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The absorption spectrum of excimers in fluid media has been measured with 1-methylnaphthalene, anthracene, pyrene, and perylene. In all compounds studied an absorption band characteristic of an excimer has been observed in the near-IR. It is shown that the IR band can be understood by assuming that an excimer is essentially a charge-transfer complex: The near-IR band is to be assigned to a transition from the lowest excimer state to a higher state which has an ion-pair character.

Introduction

It is well-known that an aromatic molecule in an excited-state M* interacts with another molecule M in the ground state and, as a result, an excimer (MM)* is formed. Aromatic excimers have been studied in fluid media and in crystals.[1,2] Formation of an aromatic excimer can be easily recognized by its characteristic fluorescence, which is red-shifted as compared to the monomer fluorescence and is broad and structureless.

In the case of an aromatic excimer the interaction is relatively weak, so that electronic states of a monomer are largely preserved in the excimer. This can be seen in the transient absorption spectrum in the visible range due to the excimers. The transient absorption spectrum due to the excimer in pyrene[3−5] and perylene[6] has been observed in the visible range. The positions of the absorption peaks are similar to those of monomers, and accordingly, the absorption bands can be assigned to transitions from the lowest excimer state to the locally excited states of the molecule in the excimer configuration. This, in turn, implies that this transient absorption in the visible is not very sensitive to the excimer formation. As a result, not much can be deduced regarding the formation of an excimer from the transient spectrum.

Recently Saigusa et al. observed, in a cluster-beam experiment, a near-IR absorption band of a naphthalene excimer in the gas phase[7] and pointed out the importance of the near-IR absorption for understanding the electronic structure of an excimer. In fluid media a near-IR absorption band has also been observed in anthracene[8] and pyrene.[5] Actually, the near-IR band seems to be a common feature of the aromatic excimers. Excited monomers do not show any absorption in the near-IR wavelength range. Therefore, it seems that the near-IR band is characteristic of an excimer and reflects sensitively the change in the electronic structure by excimer formation. Here we present the results of a systematic study of the near-IR absorption in aromatic excimers in fluid media and discuss its origin based on the concept of a charge-transfer complex. We assign the near-IR band as transition from the lowest excimer state to an excited state which is essentially an ion-pair state.

Experimental Section

The absorption spectrum of excimers was measured by using the pump−probe technique. A XeCl excimer laser (Lambda Physik, EMG 101 MSC, wavelength 308 nm) was used as the pumping light source. The pulse duration of the laser was 20 ns. In the case of the molten state of anthracene the absorption coefficient at 308 nm was high and, as a result, a thermal lens effect disturbed the measurement. This effect was efficiently reduced when excitation was made in the absorption edge. For this purpose 420 nm light pulses produced by a dye laser (Lambda Physik, FL-3002) pumped by the XeCl excimer laser were used. The pulse duration of the dye laser was 10 ns. A Xe flash lamp (EG&G, FX 279U) was used as the probe light source. The probe light transmitted through the sample was detected with a photodiode after being dispersed with a monochromator (Ritsu, MC10N). A Si-photodiode (Hamamatsu, S-1722) was used for detection in the visible range (300−950 nm) and an InGaAs-photodiode (Hamamatsu, G3476−10) for the near-IR range (900−1600 nm). Signals were amplified with a fast amplifier (Stanford, SR445), processed with a transient digitizer (Tektronix, 7612D), and accumulated with a computer.

Liquid 1-methylnaphthalene (Tokyo Kasei Ind., Ltd.) was used as received. Anthracene (Merck, scintillation grade), pyrene (Tokyo Kasei Ind., Ltd.), and perylene (Sigma) were purified by extensive zone refining. In the case of pyrene a prepurification (the Diels−Alder reaction) was made before zone refining.[9] Transient absorption measurements, except with anthracene, were made at room temperature. Pyrene solution in cyclohexane and perylene solution in benzene, both degassed, were used. Anthracene was measured in the molten state in a quartz tube sealed off with 200 Torr argon. The temperature was kept just above the melting point (489 K).

Results

Figure 1 shows transient absorption spectra of liquid 1-methylnaphthalene (A), the molten state of anthracene (B), pyrene solution in cyclohexane (2×10^{-3} mol L^{-1}), S−S and T−T spectra being subtracted (to be discussed later in detail) (C), and perylene solution in benzene (3.6×10^{-3} mol L^{-1}) (D).

A dilute cyclohexane solution of 1-methylnaphthalene exhibited fluorescence from a monomer excited state. In the same solution we observed around 400 nm transient absorption due to the monomer in an excited state, which resembles that of naphthalene solution.[10] When liquid 1-methylnaphthalene was irradiated with UV light, a broad and structureless fluorescence spectrum which was assigned to excimer fluorescence[11] was observed. In the same sample a broad absorption peak was observed around 900 nm (Figure 1A). The decay rate of the absorption band agreed with that of the excimer fluorescence.

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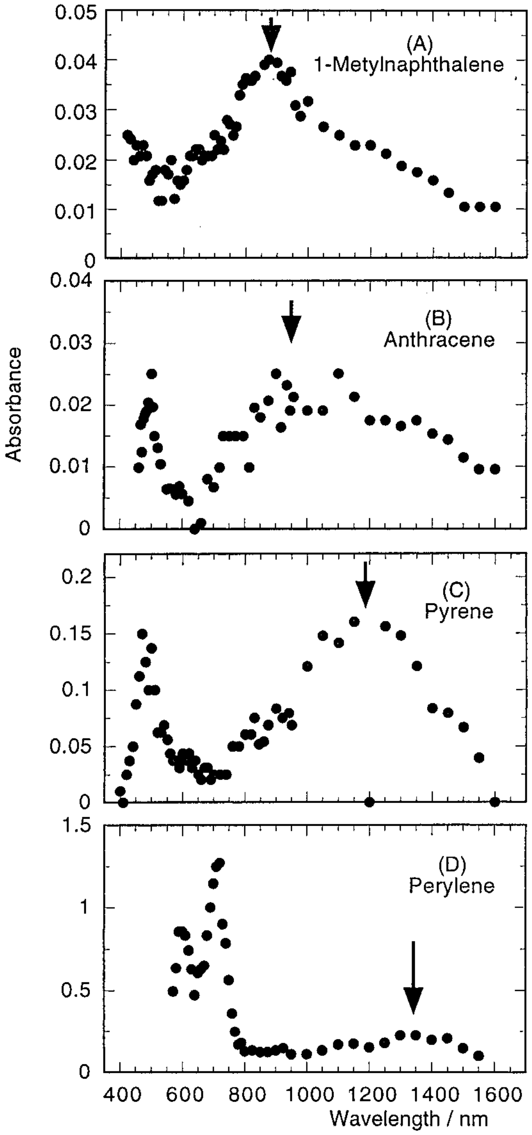


Figure 1. Transient absorption spectrum of aromatic excimer: liquid 1-methylnaphthalene (A), molten state of anthracene (B), pyrene solution in cyclohexane (2×10^{-3} mol L^{-1}) (C), perylene solution in benzene (3.6×10^{-3} mol L^{-1}) (a peak at 700 nm is S−S absorption of monomer) (D). Arrows indicate absorption peaks due to excimer in the near-IR range. Spectrum B has been obtained by subtracting from the observed spectrum S−S and T−T absorption due to the monomer, as shown in Figure 2. Other spectra are as observed experimeantally.

Hence, the absorption band is assigned to the absorption due to the excimer.

The transient absorption spectrum of anthracene in the molten state (Figure 1B) differs from that in dilute solution[12] and that in a single crystal[13] and is similar to the spectrum observed with concentrated benzene solution excited by a fast-electron pulse that shows a broad absorption extending beyond 1200 nm and having a peak around 1100 nm (1.1 eV) in addition to a smaller peak around 800 nm.[8] This shows that aggregation of anthracene molecules occurs in a singlet excited state, and therefore, both the absorption bands, one around 400 nm and the other around 950 nm, observed in the melt (liquid) can be assigned to the excimer. It is to be noted that the absorbance observed in the molten state is quite low. This reflects a short lifetime of the excimer in the molten state, which has been reported to be 0.2-0.3 ns through time-resolved fluorescence spectroscopy.[14] Such a short lifetime is most probably due to formation of dianthracene, which proceeds through excimer formation.[15]

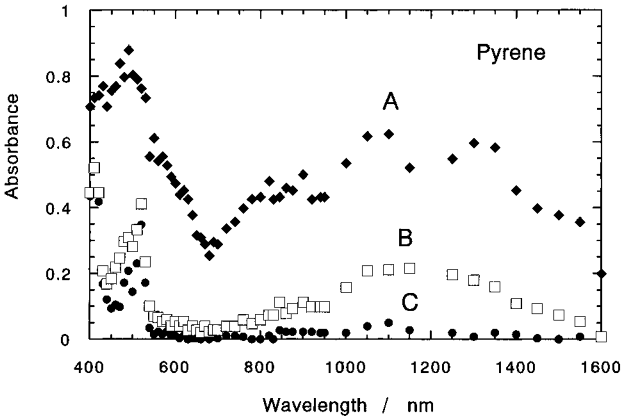
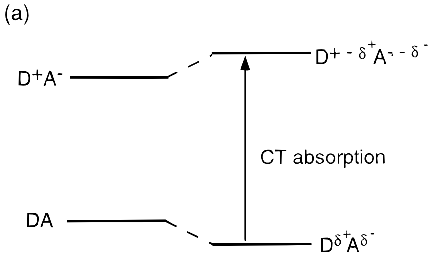


Figure 2. Transient absorption spectrum of pyrene in cyclohexane solution. At time $t = 50$ ns S−S, excimer, and T−T absorption coexist (A). At $t = 350$ ns fast S−S absorption has disappeared and absorptions due to excimer and triplet state are present (B). At $t = 800$ ns only T−T absorption remains (C). The absorption spectrum due to an excimer is obtained by comparing spectra B and C.

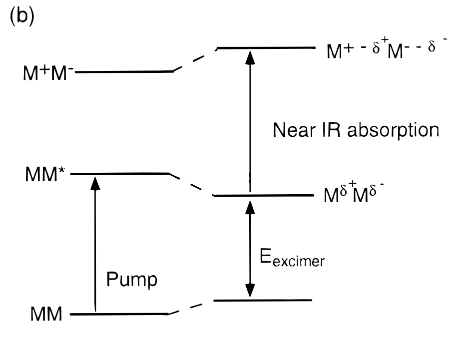
In the case of pyrene the situation was complicated by the presence of overlapping absorption bands of different origins. With a dilute solution both singlet−singlet (S−S) and triplet−triplet (T−T) absorptions of the monomer were observed in the visible, which agree well with the reported S−S[5] and T−T[16] absorptions, respectively. As the concentration of the solute increased, the spectral shape in the visible range changed and a new absorption band appeared in the near-IR range, which was due to excimer formation. In the visible range the S−S and the T−T absorptions of the monomer overlapped with the excimer absorption. To extract the absorption spectrum of the excimer, we analyzed the temporal change of the absorption spectrum. The excimer was generated with the same time constant as the decay of the singlet state of the monomer. At 350 ns delay time the singlet state of the monomer had almost completely disappeared, but the excimer remained. T−T absorption did not decay in the microsecond time range. Hence, the absorption spectrum of the excimer (Figure 1C) could be obtained by subtracting the spectrum at 800 ns delay from that at 350 ns delay. The spectrum of the excimer thus obtained (Figure 1C) agrees well with that observed by Post et al. (Figure 3 in ref 5).

A perylene solution in benzene (3.6×10^{-3} mol L^{-1}) exhibits three peaks: at 600, 700, and 1300 nm. The absorption peak at 700 nm is observed in dilute solution and has been assigned to S−S absorption of a monomer.[6] The peak at 600 nm becomes pronounced with increasing solute concentration and has been assigned accordingly to an excimer absorption.[6] We observed the same behavior with the peak at 1350 nm, as well as with the peak at 600 nm (Figure 1D). Hence, we assign both peaks as absorption bands due to the excimer.

Absorption bands due to excimers are observed in the visible and in the near-IR. Peak positions in the visible range $E_{\mathrm{VIS}}^{\mathrm{excimer}}$ in the transient spectrum are close to that in the monomer spectrum $E_{\mathrm{VIS}}^{\mathrm{monomer}}$ (Table 1). In the near-IR range absorption peaks $E_{\mathrm{IR}}^{\mathrm{obs}}$ due to an excimer are also observed (arrows in the Figure 1, summarized in Table 1). For benzene in a solution[17] and neat benzene liquid,[18] gas-phase naphthalene,[7] and anthracene solution[8] data reported by other authors are also included in Table 1. In this low-energy region excited monomers show no absorption bands. On the grounds of these data the origin of the near-IR absorption bands will be discussed below.



CT complex



Excimer

Figure 3. (a) Energy levels of a CT complex. CT transition is indicated by an arrow. (b) Energy level of an excimer. Transition from the lowest excimer state to an ion-pair state which correnponds to a CT transition is indicated as near-IR absorption.

TABLE 1: Peak Positions Observed in the Transient Absorption Measeurements

compound	solvent	$E_{\mathrm{vis}}^{\mathrm{monomer}\,h}$ (eV)	$E_{\mathrm{vis}}^{\mathrm{excimer}\,i}$ (eV)	$E_{\mathrm{IR}}^{\mathrm{obs}\,i}$ (eV)
benzene	(liquid)			2.38[a]
	cyclohexane	4.56		2.5[b]
naphthalene	(gas phase)			1.8[c]
1-methylnaphthalene	(liquid)			1.40
anthracene	(liquid)	2.07[d]	2.5	1.3
	benzene			1.14[e]
pyrene	cyclohexane	2.6[f]	2.6	1.05
perylene	benzene	1.74[g]	2.05	0.93

[a] Reference 15. [b] Reference 17. [c] Reference 7. [d] Reference 10. [e] Reference 8. [f] Reference 5. [g] Reference 6. $E_{\mathrm{vis}}^{\mathrm{monomer}}$ corresponds to the absorption peak due to a monomer. $E_{\mathrm{vis}}^{\mathrm{excimer}}$ and $\mathrm{E}_{\mathrm{IR}}^{\mathrm{obs}}$ are absorption due to an excimer.

Discussion

We propose a model for the electronic state of an excimer and discuss the origin of the near-IR bands observed. The model is based on the concept of charge-transfer (CT) complex. We explain briefly the energy diagram of a CT complex, which has been presented in many textbooks[19] (Figure 3a). When a donor molecule encounters an acceptor molecule, a CT complex forms. The stabilization energy for the ground state of the CT complex comes from the resonance interaction with the lowest excited state which has an ion-pair configuration. When the CT interaction is weak, the ground state of the CT complex is almost neutral. The excited state, on the other hand, is almost ionic due to the orthogonality of the two states. Accordingly, the transition to the lowest excited state, i.e., a CT absorption, can be considered as the transition from a neutral state to an ionic one.

According to the results of theoretical studies for the excimer,[1,20,21] two types of intermolecular interactions are important for excimer formation between M and M*. One is the exciton interaction (EX), i.e., resonance interaction between two configurations, M*M and MM*, of the excimer. The other is the charge resonance interaction (CR) between two ion-pair configurations, M^+M^- and M^-M^+. In fact, mixing of these interactions is important, and as a result, the lowest state of an excimer has a small, but finite, ion-pair character. In this sense the electronic structure of an excimer has a similarity to that of a CT complex. Namely, a pair composed of an excited molecule and another molecule in the ground state can be considered as a donor−acceptor pair. Therefore, an optical transition from the lowest excimer state should exist which corresponds to a CT absorption. An energy diagram with possible transitions is illustrated in Figure 3b.

The transition energy from the lowest excimer state to an ion-pair state $E_{\mathrm{IR}}^{\mathrm{IP}}$ can be expressed simply as

$$E_{\mathrm{IR}}^{\mathrm{IP}} = E_{\mathrm{IP}} - E_{\mathrm{excimer}} + 2E_{\mathrm{R}} \tag{1}$$

where E_{excimer} is the energy of the lowest state of an excimer with respect to that of molecular pair in the ground state with the excimer configuration and E_{R} is the resonance energy between the lowest excimer state and the ion-pair state. E_{excimer} can be estimated as the peak position of an excimer fluorescence. In the present model CT interaction in the excimer is considered to be weak, so that we assume that the resonance energy E_{R} is zero. The ion pair can be considered as a pair state of a cation and an anion which are positioned with a separation of r_{ip}. Accordingly, the energy of the ion-pair state E_{IP} with respect to the ground state with a dimer configuration can be expressed as

$$E_{\mathrm{IP}} = I_{\mathrm{g}} - E_{\mathrm{A}} + P_+ + P_- + C \tag{2}$$

where I_{g} is the ionization potential of a molecule in the gas phase, E_{A} is the electron affinity in the gas phase, P_+ and P_- are the polarization energies induced by a cation and an anion, respectively, and C is the Coulomb interaction. I_{g}'s and E_{A}'s of the compounds studied are available from literature, and the polarization energy P can be estimated by Born's formula,[22]

$$P = P_+ = P_- = -(e^2/8\pi\epsilon_0 R)[1 - (1/\epsilon)] \tag{3}$$

where e is the elementary charge, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of the vacuum, and R is the effective radius of the ion. It has been known that Born's formula gives reasonable values when the van der Waals radius R_{vdW}[23] is used as the effective radius R of the ion.[24] Therefore, we take R_{vdW} of molecules studied as the effective radius of the ion. We use the square of the refractive index n^2 as ϵ because solvents used are nonpolar. The magnitude of C can be estimated as

$$C = -e^2/(4\pi\epsilon\epsilon_0 r_{\mathrm{ip}}) \tag{4}$$

where r_{ip} stands for the intermolecular distance between the two molecules in excimer configuration. The distance was assumed to be $r_{\mathrm{ip}} = 0.33$ nm on the basis of a theoretical calculation of a naphthalene excimer.[25]

Finally, the transition energy $E_{\mathrm{IR}}^{\mathrm{IP}}$ can be expressed as

$$E_{\mathrm{IR}}^{\mathrm{IP}} = I_{\mathrm{g}} - E_{\mathrm{A}} + 2P + C - E_{\mathrm{excimer}} \tag{5}$$

Table 2 summarizes the results. Figure 4 shows the correlation between $E_{\mathrm{IR}}^{\mathrm{IP}}$ and $E_{\mathrm{IR}}^{\mathrm{obs}}$. It may be seen that a good linear relation exists. This correlation indicates that the near-IR band can be interpreted as due to the transition from the lowest

TABLE 2: Parameters for the Model

compound	solvent	I_g[a,j] (eV)	E_A[a,k] (eV)	P[l] (eV)	R_{vdW}[m] (nm)	n^2[n]	C[o] (eV)	$E_{excimer}$[p] (eV)	E_{IR}^{IP}[i,q] (eV)
benzene	(liquid)	9.2	−1.4	−1.51	0.268	2.28[c]	−1.91	3.94[e]	1.73
	cyclohexane	9.2	−1.4	−1.36	0.268	2.02	−2.16	3.75[f]	1.97
naphthalene	(gas phase)	8.2	−0.2	0.00	0.309	1.00	−4.36	3.13[e]	0.91
1-methylnaphthalene	(liquid)	8.2[b]	−0.2[b]	−1.38	0.323	2.62[c]	−1.67	3.14	0.83
anthracene	(liquid)	7.5	0.6	−1.44	0.341	3.12[d]	−1.40	(2.27)[g]	0.35
	benzene	7.5	0.6	−1.18	0.341	2.28	−1.92	2.27[h]	0.35
pyrene	cyclohexane	7.5	0.5	−1.03	0.352	2.02[c]	−2.16	2.59[e]	0.19
perylene	benzene	7.0	1.1	−1.07	0.378	2.28[c]	−1.92	2.14[e]	−0.30

[a] Reference 26. [b] The value for naphthalene. [c] Reference 27. [d] The value for crystal (ref 28). [e] Reference 29. [f] Reference 31. [g] The value for benzene solution (ref 30). [h] Reference 30. [i] Calculated using eq 5. [j] I_g: ionization potential in the gas phase. [k] E_A: electron affinity in the gas phase. [l] P: polarization energy. [m] R_{vdW}: van der Waals radius. [n] n: refractive index of solvent. [o] C: Coulomb energy. [p] $E_{excimer}$: peak energy of excimer fluorescence. [q] E_{IR}^{IP}: energy of near-IR transition calculated.

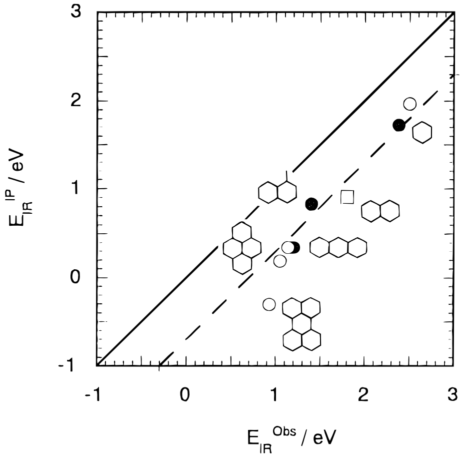


Figure 4. Correlation between the position of the near-IR bands observed E_{IR}^{obs} and the transition energy E_{IR}^{IP}, calculated on a model which assumes that the transition is from a state of weak CT character to an ion-pair state. Open circles: solution. Filled circles: neat liquid. Open square: gas phase (cluster beam).

excimer state to an ion-pair state, which corresponds to a CT absorption in a weak CT complex. It is noteworthy that, judging from the results of benzene and of anthracene, the effect of a medium is of minor importance in this plot.

As may be seen in Figure 4, there is a systematic deviation from the model: All transition energies calculated are smaller than the energies observed. This may be due to an oversimplification of the model. In the present model we neglect, at least, two effects. One is the overlap of solvation layers. Equation 2 implies that the polarization energies P_+ and P_- are independent and sum up. This is justified as long as the ions are far apart. When, however, they come close and form an ion-pair state, the polarization energy becomes smaller than the sum of the polarization energies of a cation and of an anion. The other is the neglect of the resonance energy E_R between the lowest exciton state and the ion-pair states. If we take these two effects into account, it has an effect of pushing up the values of E_{IR}^{IP}, and hence the discrepancy tends to become smaller.

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