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A Development in Polarization Experiments; Emission Spectra of Anthracene, Dibenzothiophene, and Xanthone in Stretched Polyethylene Films1)

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The polarized emission spectra of anthracene, dibenzothiophene, and xanthone have been studied in stretched polyethylene films at 77 and 4.2 K. Applicability and advantage of this method are examined by virtue of conventional polarization technique and modulation technique. The latter leads us to finding of an important role of a nontotally symmetric vibration, the b_{3g} ring vibration at 1655 cm^{-1}, in the fluorescence spectrum of anthracene. An assignment for several prominent vibrational bands in the phosphorescence spectrum of dibenzothiophene is proposed from detailed analysis of the modulation polarization spectrum at 77 K. The phosphorescence properties of xanthone are also investigated.

A number of polarization measurements of electronic transitions of molecules have been carried out mainly in crystal systems2—5) and in glasses6—10) using the single crystal technique and the photoselection technique, respectively. During the present decade another polarization technique has been developed through the measurements of the absorption11—15) and emission16,17) spectra of oblate or prolate organic molecules oriented in stretched polymer films.

Main advantages of the emission polarization measurements in the stretched polyethylene film over conventional photoselection and mixed-crystal methods are in wider range of the degree of polarization and less ambiguous environmental effects. In the present work a modulation polarization technique is applied to these film systems and its applicability and advantage are shown in several examples of emission spectra. An application of the similar techniques to the single crystal systems has been reported elsewhere.18,19)

Experimental

Materials. Commercial extra-pure-grade heptane and zone refined anthracene, both obtained from Tokyo Kasei Co. Ltd., were used without further purification. Dibenzothiophene and xanthone, products of the same company, were purified by zone-refining after several vacuum sublimations. Commercial polyethylene films of 0.15 mm in thickness were swollen in heptane for a few days before measurements. The films treated in this way showed no background emission at 77 K.

Apparatus. The optical arrangement employed in this work is schematically shown in Fig. 1. Light from a 500 W xenon arc lamp (**1**) passed through a condensing lens (**2**) and a combination filter system (**3**), *i.e.*, a Corning glass of type 7—54 of 3 mm in thickness and a 30% NiSO$_4$ aqueous solution of 30 mm in pathlength. The sample film (**4**) was set in a Dewar (**5**) with an aluminum cell holder. The direction of the stretching axis of the film was then inclined by 45° from the vertical axis of the Dewar for possible diminution of the systematic error of polarization coming from the curvature of the Dewar wall. The emission from the sample film passed through a lens (**6**), a standing polarizer (**7**) (and, if necessary, a rotating polarizer system (**8**) according to two different methods of polarization measurements as mentioned below), and a slit of a 3/4 m Czerny-Turner Nalumi grating spectrometer (**9**) in order. The polarization emission spectra were recorded on the spectrometer in the first order with an HTV R-375 photomultiplier tube (**10**). An HN 22 polaroid sheet employed in the polarizer systems (**7** and **8**) showed transmittance of about 8% at 375 nm and 28% at 500 nm.

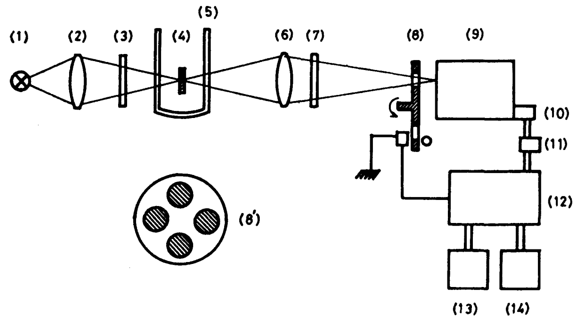

Fig. 1. Optical arrangement. For the notations (**1**)—(**10**) see descriptions in the Experimental section of this paper. Other notations are: (**11**), preamplifier; (**12**), lock-in-amplifier; (**13**), Iwatsu Dual beam oscilloscope type DS-5016; and (**14**), Hitachi recorder type 056. The drawing (**8'**) shows the front view of (**8**).

Measurements. Two kinds of techniques were employed for polarization measurements. One is the same as given by Dekkers *et al.*:16) Two intensities $I_{//}$ and $I_{\perp}$ are measured independently and compared each other against wavelength. Here $I_{//}$ and $I_{\perp}$, respectively, refer to the intensity of an emission with the electric vector parallel to the direction of the stretching axis of the sample film and that perpendicular to it. We shall call this type of experiment *the DP method* and the spectrum *the DP spectrum* hereafter. The other method is an application of the modulation technique to the polarization experiments. The rotating-polarizer system (**8**) consists of a 120 mmϕ aluminum chopper with four holes (20 mmϕ) to which one each HN 22 polarizer sheet was fixed in such a way that the axis of the analyzing polarizer appears alternatively either parallel to or perpendicular to the stretching axis of the film. The emission signals were thus modulated at 100 Hz and fed to a lock-in-amplifier type NF model-LI-572B. If an appropriate phase relation is selected between the sample and reference signals, the output voltage of the lock-in-amplifier will be proportional to the difference between two intensities of interest, *i.e.*, $I_{//}-I_{\perp}$. This method will be called *the MP method* after its modulation polarization technique. The spectrum obtained by this method will also be *the MP spectrum.*

There is a problem in the case of analysis of the MP spectrum. The extremum of the MP spectrum does not always signify the existence of a band ! An apparent maximum is

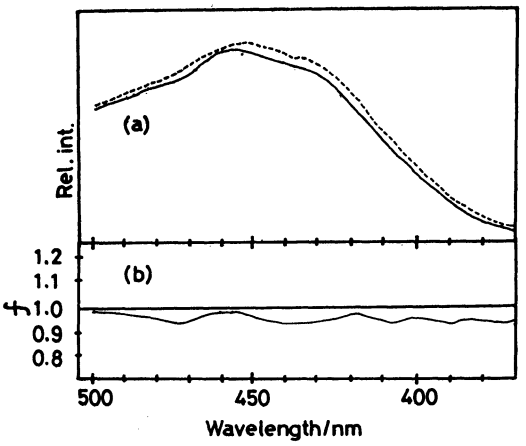

Fig. 2. (a) The self-polarization of the optical system employed. The solid curve denotes the polarization parallel to the stretching direction of polyethylene films and the dotted one that perpendicular to the film direction. (b) The dispersion curve of the correction factor f $(=I_{//}/I_{\perp})_{\rm system}$ against wavelength.

formed among overlapping bands on rare occasions. A maximum appears sometimes near a minimum position between two emission bands, while another occurs in a region where the $I_{//}-I_{\perp}$ signal of a certain band competes with those of neighboring bands. Therefore, it is very meaningful to compare the MP spectrum with a well-resolved spectrum such as that in a Shpolskii matrix.[20)]

Correction. In polarization experiments we sometimes encounter a problem of instrumental self-polarizations; in this work these come largely from a Dewar, lenses, and a spectrometer. The correction for the self-polarizations was carried out according to a conventional method.[21)] As shown in Fig. 2, the correction factor in our system was found to vary little over a wide range of wavelength and to be nearly equal to 0.95 on an average. The correction factor of 0.95 was thus adopted for the DP experiments.

In principle, of course, the MP spectrum should also be corrected through 5% attenuation of $I_{\perp}$-component intensity. However, the actual correction of the MP spectrum leads to only a little increase in intensity toward the (+) parity direction and, accordingly, a little change in the band feature. Consequently, no correction was applied for the MP spectra in this work.

Sample Preparation. Swollen in heptane for a few days, a polyethylene film of 3×6 cm^2 was immersed in a solution of sample of 10^{-3} M in heptane. After natural evaporation of the solvent in the atmosphere, it was fixed on a stretching machine and extended by 500% in length at room temperature. Then the stretched sample film was set on an aluminum cell-holder.

Results and Discussion

Anthracene. The fluorescence and its polarization spectra of anthracene in polyethylene film systems are shown in Fig. 3, together with the fluorescence spectrum in heptane matrix. The spectroscopic data are also given in Table 1. The DP spectra shown in Fig. 3a are in good agreement with those reported by Dekkers *et al.*[16)] It should be noted that the minima of bands shown in Fig. 3c just correspond to the band locations of the short-molecular-axis polarized spectrum (see also the dotted curve in Fig. 3a); and that the MP spectral line crosses the base line at the same wavelength position as the $I_{//}$ curve does the $I_{\perp}$ one in the DP spectra. This means that there is a one-to-one correspondence between the DP and MP spectra. The MP spectrum shows several extrema at 386.4 (α in Fig. 3c), 406.4 (γ),

TABLE 1. VIBRATIONAL ANALYSIS OF THE FLUORESCENCE SPECTRUM OF ANTHRACENE AT 77 K

Stretched polyethylene[a)]			Heptane		Assignment[c)]	
ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Sign[b)]	ν/cm^{-1}	$\Delta\nu$/cm^{-1}		
26265	0	− (*o*)	26212	0	0−0 of $^1B_{1u}$-^1A_g	
25870	395	− (α)	25819	393	0−393	a_g
25505	765	−	25458	754	0−754	a_g
			25425	787	0−2×393(−1)	A_g
			25201	1011	0−1011	
			25056	1156	0−1156	
			24956	1256	0−1256	
24855	1410	− (β)	24807	1405	0−1405	a_g
			24648	1564	0−1564	a_g?
24610	1655	+ (γ)	24575	1637	0−1637	b_{3g}
24445	1820	− (δ)	24413	1799	0−1405−393(−1)	A_g
			24253	1959	0−1564−393(−2)	A_g?
24220	2045	+ (ε)	24183	2029	0−1637−393(+1)	B_{3g}
24020	2245	−	24020	2192	0−1405−787(0)	A_g
			23792	2420	0−1405−1011(−4)	
			23643	2569	0−1405−1156(−8)	
			23545	2667	0−1405−1256(−6)	
23470	2795	− (θ)	23402	2810	0−2×1405(0)	A_g
			23244	2968	0−1405−1564(+1)	
23180	3085	+ (η)	23171	3041	0−1637−1405(+1)	B_{3g}

a) Results obtained with the MP method. b) The sign "+" means a maximum peak of $I_{//}-I_{\perp}$ signal in the MP spectrum and the "−" a minimum one. Band designations to the figures are given in parenthesis by greek letters. c) Deviation in cm^{-1} units from the first fundamental combinations is given in parenthesis.

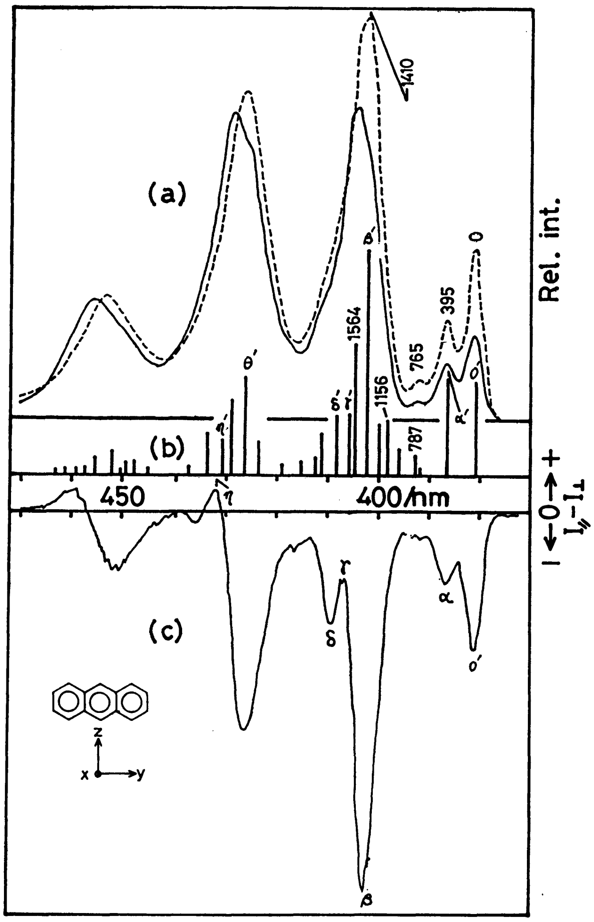

Fig. 3. The fluorescence and its polarization spectra of anthracene at 77 K. (a) The DP spectra in stretched polyethylene film systems; the solid curve denotes the polarization parallel to the stretching direction of polyethylene films and the dotted one that perpendicular to the film direction. (b) The fluorescence spectrum in heptane matrix (schematic). (c) The MP spectrum. Band notations are defined in Table 1.

and 409.0 nm (δ). These extrema are difficult to be identified in the DP spectra because of the band broadness. Among them the first two extrema in the MP spectrum are attributed to several vibrational bands in comparison with the spectrum in a Shpolskii solvent, heptane (see Fig. 3b). In view of concentrations employed a considerable weakness of the origin band in intensity is ascribed to the reabsorption effect of the 0—0 band.[22,23]

The DP and MP spectra show that the origin band of the fluorescence spectrum of anthracene is polarized along the short axis of the molecule under an assumption of *nice* molecular orientations in stretched polymer systems. This result is in good agreement with those from other experimental[24–26] and theoretical[27–29] works.

The band at 386.4 nm in the DP spectra, *i.e.*, the 0—395 cm^{-1} (±15 cm^{-1}) band in Table 1 and Fig. 3a, is assigned to be of an a$_g$-vibration, based on the band behavior in the MP spectrum. Dekkers *et al.* reported $P=-0.39$ for the 0—0 band and $P=-0.30$ for the 0—395 cm^{-1} band from their DP spectra and inferred that the latter came from accidental overlapping of a totally symmetric a$_g$-mode and a nontotally symmetric b$_{3g}$-mode. The MP spectrum also supports such an assignment from the intensity consideration.

The weak band at 392.0 nm, *i.e.*, the 0—765 cm^{-1} band in Fig. 3a, is ascribed to an a$_g$-fundamental vibration or an overtone of the a$_g$-vibration at 394 cm^{-1}.[25] Although the corresponding band also appears in the MP spectrum, it is too weak to discriminate between these assignments.

The strong band at 402.2 nm in the DP spectrum, *i.e.*, the 0—1410 cm^{-1} band, consists of several overlapping bands as can be seen from the broad band feature. Therefore, detailed discussion for the "band" is not possible with the DP spectra. However, it is an experimental fact that $I_{//}$ (max) appears at a longer wavelength than $I_\perp$ (max) does. Through the vibrational analysis of the fluorescence spectrum in heptane matrix (see Table 1), $I_\perp$ (max) is attributed mainly due to the band of 0—1405 cm^{-1} (±5 cm^{-1}) and $I_{//}$ (max) due to those of 0—1564 cm^{-1} (±5 cm^{-1}), 0—1637 cm^{-1} (±5 cm^{-1}), and 0—1799 cm^{-1} (±5 cm^{-1}) as Dekkers *et al.* suggested.[16]

On the other hand, the MP spectrum clearly discriminates among three bands of 0—1410 cm^{-1} (±15 cm^{-1}), 0—1655 cm^{-1} (±15 cm^{-1}), and 0—1820 cm^{-1} (±15 cm^{-1}) which are designated as β, γ, and δ in Fig. 3c and correspond to those of 0—1405 cm^{-1}, 0—1637 cm^{-1}, and 0—1799 cm^{-1} in the fluorescence spectrum in heptane matrix, respectively. From their polarization behaviors we attribute these bands to a$_g$, b$_{3g}$, and a$_g$ fundamentals, respectively, in good correspondence with suggestions inferred from the experiments in the crystal systems.[30] The band of 0—1564 cm^{-1} in heptane matrix does not correspond to any maximum or minimum position in the MP spectrum. However, it is suggested that this band would be based on an a$_g$ fundamental mode from viewpoints of the band shape of the MP spectrum.

Although the fluorescence polarization spectrum of anthracene has been studied in naphthalene crystals at 4.2 K, no positive evidence has been found for the existence of long-molecular-axis polarized bands, possibly due to strong crystal effects.[24] We also confirmed this in our mixed crystal systems at 4.2 K. Only one report has been given for observation of the long-molecular-axis polarized fluorescence spectrum of anthracene in fluorene at 20 K.[25] However, the band system is complicated reflecting site emissions and no precise data concerning polarization intensities is available. Thus it should be noted that the present work gives a clear-cut evidence for a participation of the b$_{3g}$ vibration in the $S_1 \rightarrow S_0$ fluorescence process. This observation is in good agreement with finding of the band intensification observed in the pre-resonance Raman effect of anthracene by Ohta and Ito.[31]

Dibenzothiophene. The phosphorescence spectrum of dibenzothiophene (DBTH in abbreviated form) in heptane at 77 K is shown in Fig. 4, together with the DP spectra in stretched polyethylene film systems. A considerable polarization of the origin band observed in the DP spectra establishes that DBTH molecules are sufficiently oriented in the systems in such a way that

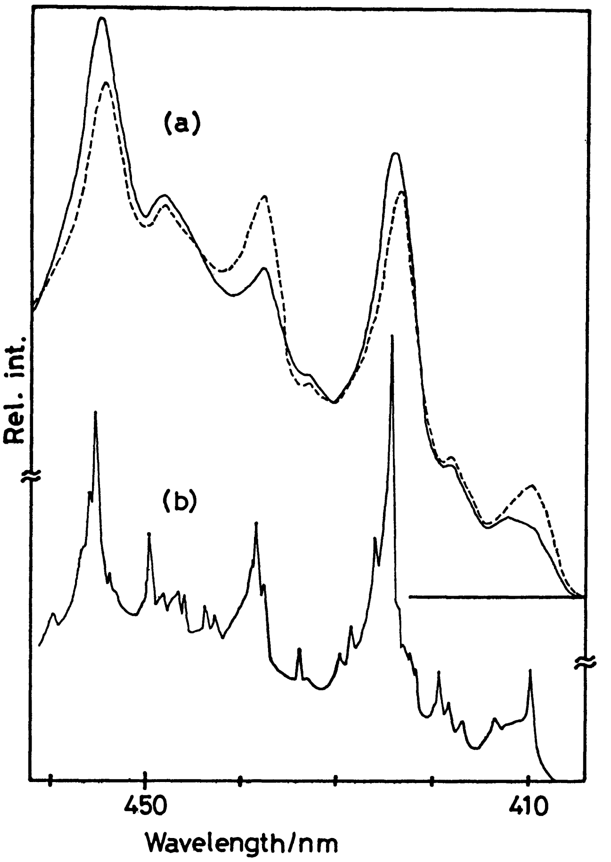

Fig. 4. (a) The phosphorescence polarization spectrum of DBTH in stretched polyethylene film systems at 77 K with the DP method; the solid curve represents the spectrum polarized parallel to the stretching direction of the films and the dotted one that perpendicular to the film direction. (b) The phosphorescence spectrum of DBTH in heptane at 77 K.

the long-molecular-axis is parallel to the stretching axis of the film.

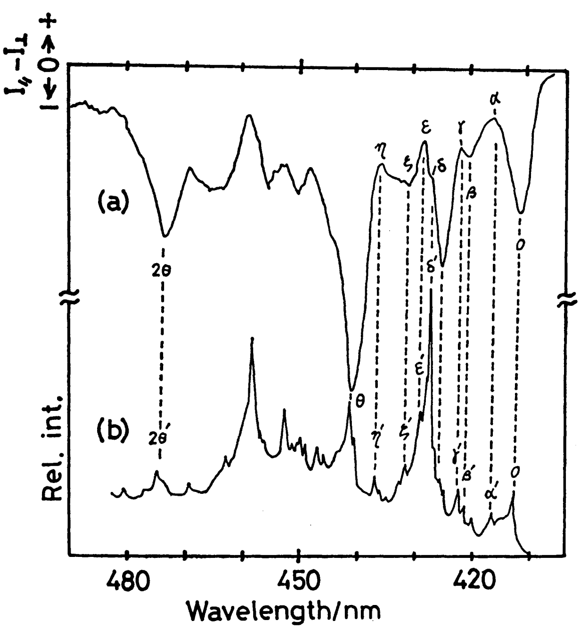

Fig. 5. (a) The MP phosphorescence spectrum of DBTH in polyethylene film systems at 77 K and (b) the phosphorescence spectrum of DBTH in heptane at 77 K. Band notations are given in Table 2.

The MP spectrum is compared with the phosphorescence spectrum in heptane matrix in Fig. 5, where the positions of the origin bands are adjusted to be identical. A tentative vibrational assignment for the first main bands is also given in Table 2. As shown in Fig. 5a, the origin band (designated as *o* in the figure) is polarized normal to the long axis of the molecule, *i.e.*, along the x- or z-axis in the molecular coordinates shown in Fig. 6. Since the emission is certainly ascribed to be of $\pi\pi^*$ in the nature from the long lifetime of 0.5 s, the origin band is assumed to be polarized along the out-of-plane axis of the molecule, *i.e.*, the x-axis, on the basis of the predominant first-order spin-orbit coupling mechanism illustrated schematically in Fig. 6a.

As shown in Fig. 5a, the 0—240 cm^{-1} (±15 cm^{-1}) band (α) in the MP spectrum is polarized along the

TABLE 2. VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF DBTH AT 77 K[a)]

Streched polyethylene[b)]			Heptane		Assignment		
ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Sign[c)]	ν/cm^{-1}	$\Delta\nu$/cm^{-1}	Present work		Bree and Zwarich[d)]
24260	0	− (*o*)	24413	0	0—0 of $^3A_1$-$^1A_1$		0—0 of $^3A_1$-$^1A_1$
24020	240	+ (α)	24184	229	0—229	b_1	a_1(0—210/221)
			23991	422	0—422	?	b_1
23760	500	− (β)	23911	502	0—502	a_1	a_1
23690	570	+ (γ)	23848	565	0—565	a_2	b_2
			23701	712	0—712	a_1?	a_1
			23668	745	0—745	?	b_1
23490	770	−	23640	773	0—773	a_1	a_1
23410	850	+ (δ)	23562	851	0—851	b_1	b_2
23325	935	+ (ε)	23479	934	0—934	b_1	b_1
23185	1075	− (ζ)	23347	1066	0—1066	a_1	a_1
23120	1140	−	23282	1131	0—1131	a_1	a_1
22910	1350	+ (η)	23062	1351	0—851—502(+2)	B_1	B_2
22655	1605	− (θ)	22806	1607	0—1607	a_1	a_1

a) For brevity we list only the assignment of bands sufficient enough to show the vibronic pattern. b) See Table 1, footnote a. c) See Table 1, footnote b. d) Data taken from Ref. 32.

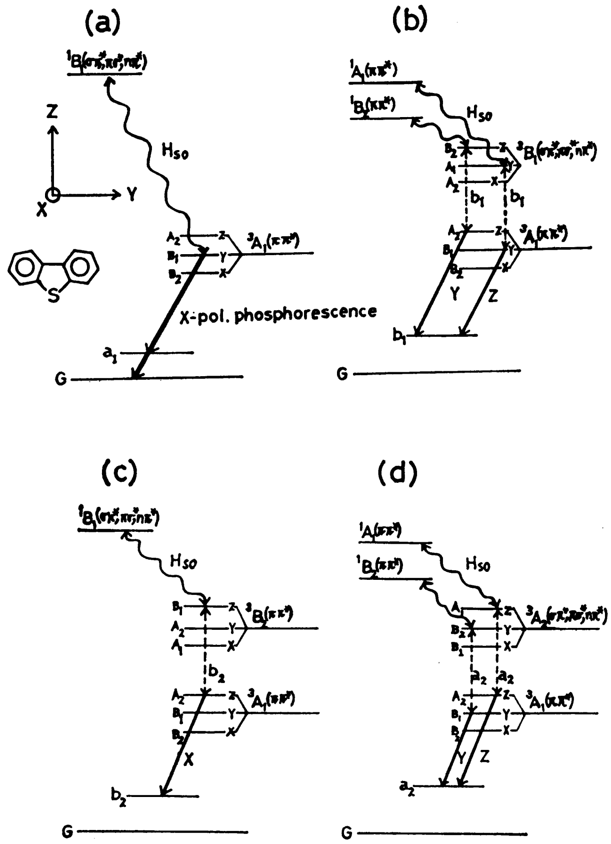

Fig. 6. Main coupling mechanisms in the phosphorescence process of DBTH. (a): 1st-order spin-orbit coupling. (b), (c), and (d): 2nd-order spin-orbit-vibronic couplings due to b_1, b_2, and a_2 vibrations, respectively. Here are described only vibronic couplings between triplet manifold for the saving of the space. Similar schemes, of course, hold for singlet manifold.

y-axis. It is evident from the coupling schemes given for triplet manifold (see Figs. 6b and 6d) and from the similar ones for singlet manifold that the y-axis polarized transition is caused by nontotally symmetric b_1 and/or a_2 vibrations through the second-order spin-orbit-vibronic coupling mechanisms under the assumption that the first-order spin-orbit-vibronic couplings are negligibly small.[32] The spacing of 0−240 cm^{-1} observed in the MP spectrum is found to correspond to a b_1-fundamental vibration of 226 cm^{-1} assigned from the observed IR and Raman spectra.[33]

The 0−500 cm^{-1} ($\pm$15 cm^{-1}) band (β) in the MP spectrum is polarized perpendicular to the long axis of the molecule. This band is close in wavenumber to the 0−502 cm^{-1} ($\pm$5 cm^{-1}) band in the phosphorescence in heptane matrix (see also Table 2). Several coupling schemes are possible for such transitions that are polarized perpendicular to the long axis, as shown in Fig. 6. According to the vibrational analysis, a band at 498 cm^{-1} in the IR spectrum of crystalline DBTH has been assigned as an a_1 fundamental.[33] If this vibration is employed, the 0−500 cm^{-1} band in the MP spectrum is to be polarized along the x-axis. Similarly, many other bands are assigned on the basis of the IR and Raman data.

The vibrational assignment for most of the bands are in accord with that given by Bree and Zwarich (hereafter referred to BZ).[32] However, several prominent bands are assigned here in a different way: They are the bands of 0−229 cm^{-1} (α' in Fig. 5b), 0−565 cm^{-1} (γ'), 0−851 cm^{-1} (δ'), and 0−1351 cm^{-1} (η') in the phosphorescence spectrum in heptane matrix at 77 K, as designated by greek symbols in Fig. 5b. In an energy region of 200—300 cm^{-1} from the origin band of the phosphorescence of DBTH in heptane at 15 K, BZ observed two main bands at 210 cm^{-1} and 221 cm^{-1} and assigned as (a_1) and (a_1+phonon) modes, respectively, in comparison with the assignment to the X-trap emission of DBTH in the crystal at the same temperature. We also studied the phosphorescence spectrum in heptane at 4.2 K and obtained a similar band pattern to that reported by BZ. We find that the band system contains several site emissions and that the 0−210 cm^{-1} band reported by BZ is ascribed to an emission from a different site. On the other hand, the phosphorescence of DBTH in heptane at 77 K is found to be mainly due to one site as shown in Fig. 5b, although it is not clear at present what is the origin of those sites in heptane matrix at low temperatures. The 0−229 cm^{-1} band (α') in heptane matrix at 77 K, *i.e.*, the main band between 200 and 300 cm^{-1} from the origin band (o') should thus correspond to a maximum position in the MP spectrum (α in Fig. 5a) which is here ascribed to a b_1 fundamental vibration as mentioned above.

The 0−565 cm^{-1} band (γ') in heptane matrix was attributed to a b_2 symmetry mode by BZ. However, the corresponding MP band is found at 570 cm^{-1} from the origin peak (o) and has a nature of the (+) parity polarization. This property is in contrast with the predicted (−) polarization if the BZ's b_2-assignment would be accepted for the band (*e.g.*, see Fig. 6c). The coupling schemes (**b**) and/or (**d**), however, suggest such (+) polarization behaviors. Thus we assign this band as due to an a_2 mode which is only out-of-plane fundamental vibration predicted in a wavelength region of 500—650 cm^{-1}.[33]

The 0−851 cm^{-1} band (δ') is the strongest one in the phosphorescence system of DBTH. Observing an IR active b_2 vibrational band at 868 cm^{-1}, BZ attributed this phosphorescence band to the b_2 mode. However, the result of the MP spectrum indicates that the band should be out-of-plane vibration from the same reason as mentioned in the case of the 0−565 cm^{-1} band. In a wavenumber region of 800—900 cm^{-1} only one out-of-plane vibration was observed at 859 cm^{-1} (b_1) by BZ. The b_1 assignment is thus preferable. This revised assignment leads us to another prediction that the 0−1351 cm^{-1} band (η'), which can be assigned here as a combination band of 851+502 cm^{-1} ($b_1 \times a_1 = B_1$) in accord with the assignment by BZ, might manifest a similar polarization behavior to that of the 0−851 cm^{-1} band. The MP spectrum shown in Fig. 5a endorses this prediction.

Xanthone. The phosphorescence spectrum of xanthone (hereafter XTH) in 3-methylpentane and EPA has been reported to be very sensitive to temperature.[34,35] This is also confirmed to be the case

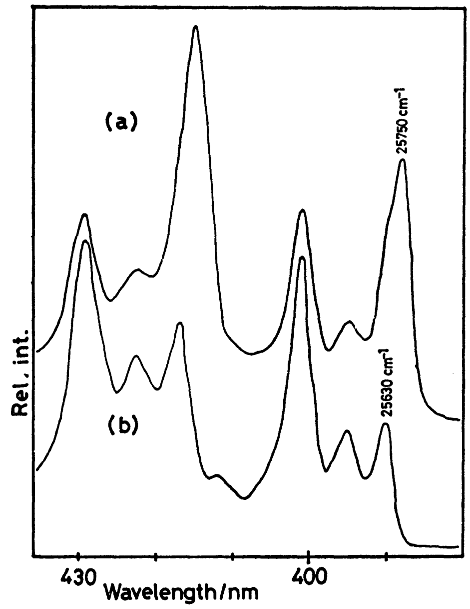

Fig. 7. The phosphorescence spectrum of XTH in polyethylene polymer systems (a) at 77 K and (b) at 4.2 K.

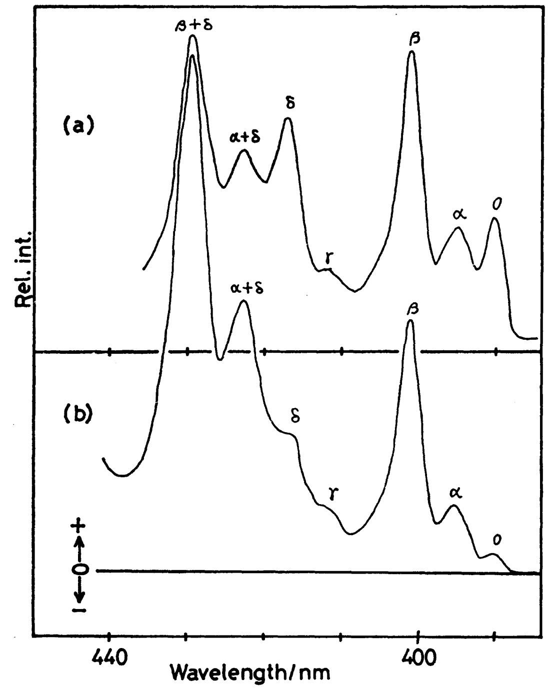

Fig. 8. (a) The phosphorescence spectrum of XTH in polyethylene polymer systems at 4.2 K. (b) The phosphorescence polarization spectrum of XTH with the MP method at 4.2 K. Band notations are given in the Text.

in polyethylene matrix; *e.g.*, the spectra at 4.2 and 77 K as illustrated in Fig. 7. On account of a small energy separation between $^3\pi\pi^*$ and $^3n\pi^*$ levels and a general existence of molecules at different sites the phosphorescence spectrum of XTH in aliphatic hydrocarbons has generally been found to manifest complicated band-patterns.[34–36] Especially, a statistical distribution of emission sites in polyethylene film systems seems to increase the complication of the spectrum, as can be seen in too much deviation from an exponential decay relationship of the phosphorescence lifetime at 77 K.

On the other hand, the phosphorescence at 4.2 K is observed to decay nearly exponentially and to show little change in intensity with a decrease in temperature to 1.5 K. The strong activeness of several out-of-plane vibronic bands and the rather long lifetime of the order of $\approx 10^{-1}$ s are manifestations that the lowest excited triplet state of almost all the emission sites in polyethylene matrix is of $\pi\pi^*$ type. These features resemble those reported in the spectra of XTH in the crystal and in diphenylmethane matrix at 1.5 K by Chakrabarti and Hirota,[37] although there is a big difference in the T_1-T_2 energy separation between their systems and ours, possibly based on environmental difference (*e.g.*, $\Delta E(T_2\text{-}T_1) \approx 1680$ cm⁻¹ in their diphenylmethane matrix and $\Delta E(T_2\text{-}T_1) \approx 140$ cm⁻¹ in the present work). Thus, we confine ourselves to the spectrum at 4.2 K in this paper. The phosphorescence spectrum of XTH in polyethylene film systems and its MP spectrum are shown in Fig. 8. Except for some combination bands, the band system consists mainly of the origin band (band notation *o* in Fig. 8) and several fundamental bands such as $0-320$ cm^{-1} (± 20 cm^{-1}) (α), $0-700$ cm^{-1} (± 20 cm^{-1}) (β), $0-1320$ cm^{-1} (± 20 cm^{-1}) (γ), and $0-1670$ cm^{-1} (± 20 cm^{-1}) (δ). It is found that the bands α, β, γ, $\alpha+\delta$, and $\beta+\delta$ are strongly polarized along the long axis of the molecule (P: 0.40—0.50). The origin band itself and the $0-\nu(\text{C=O})$ band (δ) are also polarized along the long-molecular-axis, but their degrees of polarization are considerably small ($P=0.10$). The great degrees of polarization along the long-molecular-axis observed in the bands α, β, γ, $\alpha+\delta$, and $\beta+\delta$ support a large contribution to the overall phosphorescence system through the second-order spin-orbit-vibronic mixings *via* the magnetic z-sublevel.[37] However, it is difficult to mention from only the present work which coupling scheme plays a predominant role in the phosphorescence process for such a close-energy-system *via* singlet manifold or *via* triplet manifold. As has been suggested in the case of the phosphorescence spectrum of *p*-methoxybenzaldehyde in *p*-dimethoxybenzene,[19] remarkable degrees of the depolarization of the bands *o* and δ may be attributed to the existence of the competitive processes of the environmental direct coupling between $^3\pi\pi^*$ and $^3n\pi^*$ and the first-order spin-orbit coupling between $^3\pi\pi^*$ and $^1\sigma\pi^*$.

Concluding Remarks

The DP method in stretched polymer film systems has extensively been employed for absorption and emission polarization measurements. The method is attractive certainly in simplicity of the experiment, but it is unfortunately subject to a limitation in its applicability. In general the wide band-width originating from a statistical distribution of emission sites in those polymer film systems prevents us from finding out a weak band near a strong band and from discriminating a band from the overlapping bands. Despite the unavoidable problem of the band broadness in stretched polyethylene film systems, the MP method is found to improve the band resolution remarkably. The high S/N ratio in the MP method promises a future development in the application to other molecules.

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References

1) A preliminary report of this work was presented at the 26th IUPAC congress, Tokyo, 1977.

2) D. S. McClure, *Solid State Phys.*, **8**, 1 (1959); *ibid.*, **9**, 399 (1959).

3) H. C. Wolf, *Solid State Phys.*, **9**, 1 (1959).

4) D. P. Craig and S. H. Walmsley, "Excitons in Molecular Crystals," Benjamin Inc., New York (1968).

5) R. M. Hochstrasser, *Rev. Mod. Phys.*, **34**, 531 (1962).

6) A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).

7) A. H. Kalantar and A. C. Albrecht, *Ber. Bunsenges. Phys. Chem.*, **68**, 361 (1964).

8) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

9) E. C. Lim and J. M. H. Yu, *J. Chem. Phys.*, **49**, 3878 (1968).

10) F. Dörr, *Angew. Chem.*, **78**, 457 (1966).

11) P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **48**, 851 (1968).

12) Y. Tanizaki, H. Inoue, and N. Ando, *J. Mol. Spectrosc.*, **17**, 156 (1965); H. Hiratsuka, Y. Tanizaki, and T. Hoshi, *Spectrochim. Acta, Part A*, **28**, 2375 (1972).

13) E. W. Thulstrup and J. H. Eggers, *Chem. Phys. Lett.*, **1**, 690 (1968); E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3868 (1970).

14) Å. Davidsson and B. Nordén, *Chem. Phys. Lett.*, **28**, 221 (1974).

15) Y. Tanizaki and H. Hiratsuka, *J. Spectrosc. Soc. Jpn.*, **25**, 205 (1976) and references cited therein.

16) J. J. Dekkers, G. Ph. Hoornweg, C. MacLean, and N. H. Velthorst, *Chem. Phys.*, **5**, 393 (1974); *Chem. Phys. Lett.*, **19**, 517 (1973).

17) J. J. Dekkers, G. Ph. Hoornweg, K. J. Terpstra, C. MacLean, and N. H. Velthorst, *Chem. Phys.*, **34**, 253 (1978).

18) K. Ohno and H. Inokuchi, *Chem. Phys.*, **33**, 585 (1975).

19) M. Koyanagi, K. Higashi, and Y. Kanda, *Chem. Phys. Lett.*, **52**, 184 (1977).

20) E. V. Shpolskii, *Usp. Fiz. Nauk.*, **80**, 255 (1963) [*Sov. Phys. Usp.*, **6**, 411 (1963)].

21) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

22) W. H. Wright, *Chem. Rev.*, **67**, 581 (1967).

23) M. Nakamizo and Y. Kanda, *Spectrochim. Acta*, **19**, 1235 (1963).

24) J. W. Sidman, *J. Chem. Phys.*, **25**, 115 (1956).

25) A. V. Bree and S. Katagiri, *J. Mol. Spectrosc.*, **17**, 24 (1965).

26) C. D. Akon and D. P. Craig, *Trans. Faraday Soc.*, **62**, 1673 (1966).

27) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

28) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

29) J. A. Pople, *Proc. Phys. Soc. (London), Ser. A*, **68**, 81 (1955).

30) R. M. Macnab and K. Sauer, *J. Chem. Phys.*, **53**, 2805 (1970).

31) N. Ohta and M. Ito, *Chem. Phys.*, **20**, 71 (1977).

32) A. V. Bree and R. J. Zwarich, *Spectrochim. Acta, Part A*, **27**, 621 (1971).

33) A. V. Bree and R. J. Zwarich, *Spectrochim. Acta, Part A*, **27**, 599 (1971).

34) H. J. Pownall, R. E. Connors, and J. R. Huber, *Chem. Phys. Lett.*, **22**, 403 (1973).

35) H. J. Pownall and W. W. Mantulin, *Mol. Phys.*, **31**, 1393 (1976).

36) H. J. Pownall and J. R. Huber, *J. Am. Chem. Soc.*, **93**, 6429 (1971).

37) A. Chakrabarti and N. Hirota, *J. Phys. Chem.*, **80**, 2966 (1976).