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Solvent Effect on the Vibrational Structures of the Fluorescence and Absorption Spectra of Pyrene

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The anomalously large Ham effect observed in pyrene has been studied in various solvents at room temperature by measuring the fluorescence and absorption spectra. As in the case of benzene, the Ham bands of pyrene were assigned to the 0–0 and a_g-vibration bands. This was confirmed by fluorescence polarization measurement. The correlation of the intensities of the fluorescence and absorption bands to solvent polarities is discussed.

Despite much work on the solvent shifts[1–8] of electronic spectra, comparatively few studies of the solvent effect on their vibrational structures have been carried out. In general the vibrational components in the fine structure of a weak electronic transition are expected to show different intensity behaviors under the action of solvent perturbation.[9] Such a structural change in an electronic band system can be observed remarkably in an electronically forbidden transition containing both vibrationally-induced and forbidden components. However, the phenomenon can rarely be observed in the spectrum of an electronically allowed transition.[9]

Recently the author noticed that the vibrational structures of the fluorescence and absorption spectra of pyrene are markedly altered in various fluid solvents and this effect can be ascribed to the same phenomenon as that known as the Ham effect[10–15] well investigated on benzene. Extensive studies[9,13–18] of the Ham bands in the 2600 Å region of the benzene absorption revealed that the effect is taken to be the appearance of the symmetry forbidden 0–0 progression in the $^1B_{2u}$—$^1A_{1g}$ band system[19,20] affected by dispersion forces between benzene and solvent molecules. As has been demonstrated by Durocher and Sandorfy,[9] and also by Koyanagi,[18] this phenomenon is not restricted to benzene, but can be observed with many benzene derivatives,[9,16,17] naphthalene,[9,16] phenanthrene,[9] *p*-benzoquinone,[18] and perhaps a number of other aromatic molecules.

Most studies on the Ham effect have been performed mainly by the measurements of absorption spectra by adding some amount of highly polarizable substances at relatively low temperatures.[9,10,13,14,16,17] This work was carried out by observing both the fluorescence and the absorption spectra of pyrene in pure solvents at room temperature. When the first absorption band under consideration overlaps the neighboring strong band as in the case of pyrene, the studies by means of fluorescence spectra are advantageous, unless the solvent quenching of fluorescence occurs appreciably.

How the observed effect is to be associated with the solvent properties is a difficult problem of the work.

Experimental

Pyrene was purified by recrystallization, chromatography, zone-refining, and sublimation.

Spectroscopic grade (Dotite Spectrosol) *n*-hexane, cyclohexane, benzene, carbon tetrachloride, acetonitrile, *N,N*-dimethylformamide, and dimethylsulfoxide were obtained from Wako Pure Chemical Industries, Ltd. Spectroscopic grade ethyl ether and tetrahydrofuran were obtained from Kishida Kagaku Co., Ltd. GR grade methanol, ethanol, chloroform, 1,2-dichloroethane, toluene, *p*-dioxane, acetone, and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. All these solvents were used without further purification. Isopentane and methylcyclohexane were purified by chromatographic adsorption on silica gel and subsequent fractional distillation. Chlorobenzene of Wako EP grade was dried and fractionally distilled.

The absorption spectra were measured with a Hitachi EPS-3 recording spectrophotometer. The fluorescence spectra were obtained using a Hitachi MPF-2A spectrofluorimeter with sensitivity corrections.[21] The fluorescence polarization spectrum was measured at 77°K in a mixture of methylcyclohexane and isopentane (1 : 1) by use of an apparatus constructed with a Hitachi G-3 grating monochromator and

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1) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 549(1954).

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11) J. R. Platt, *J. Mol. Spectry.*, **9**, 288 (1962).

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14) S. Leach and R. Lopez-Delgado, "Advances in Molecular Spectroscopy," Vol. 1, ed. by A. Mangini, Pergamon Press, Oxford (1962), p. 419.

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18) M. Koyanagi, *J. Mol. Spectry.*, **25**, 273(1968).

19) A. Kronenberger, *Z. Physik*, **63**, 494(1930).

20) H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.*, **7**, 207(1939).

21) E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger, and W. Voss, *Z. Anal. Chem.*, **170**, 1(1959).

a Hitachi EPU-2A prism monochromator.

All the solvents used were confirmed to emit no luminescence having any essential influence on the fluorescence spectra with excitation at about 330 mμ. The concentration of pyrene for fluorescence measurements were of the order of 10^{-5} mol/*l*. The gas-phase fluorescence was measured with a non-fluorescent square quartz cell containing a small amount of pyrene, evacuated and sealed, in a regulated electric furnace.

Results and Discussion

The spectral changes of pyrene fluorescence in various solvents at room temperature are shown in Figs. 1 and 2. The characteristic bands are named *a*, *b*, *c*, *d*, *e* in the decreasing order of wave number. All the fluorescence spectra were normalized for convenience at 26200 cm^{-1} (band *c*). The vapor-phase spectrum is somewhat diffuse because of the high temperature (180°C) at which it was measured. The bands are observed as shoulders. The relative intensities of the bands *a*, *b*, and *e* increase markedly with the increase of the apparent solvent polarity in going from the gaseous state or a nonpolar solvent such as *n*-hexane to a highly polar solvent such as acetonitrile, while the frequency shifts of these bands are very small and nearly comparable to the experimental error. The slight solvent shifts are in striking contrast to the pronounced solvent enhancement.

The absorption spectra in the region of the first singlet-singlet transition are also shown in Fig. 2. Since no spectral change can be expected to occur, the absorption spectra were not measured in the regions of higher strongly allowed transitions. We see that the fluorescence spectra bear a general mirror-image relationship to the absorption spectra, taking account of the absorption tail of the second intense transition. The first and second absorption bands (corresponding to the fluorescence bands *a* and *b*, respectively) also increase similarly with increasing solvent polarity. It can therefore be accepted that the Ham effect for pyrene takes place

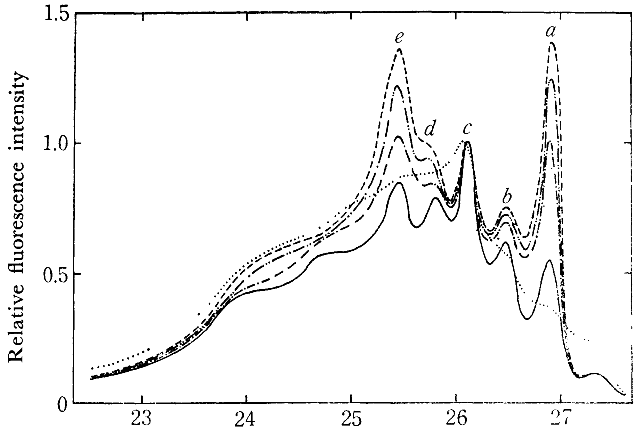

Fig. 1. Fluorescence spectra of pyrene in various solvents. ……: gaseous state, ——: *n*-hexane, —·—·—: benzene, —··—··—: methanol, -----: acetone.

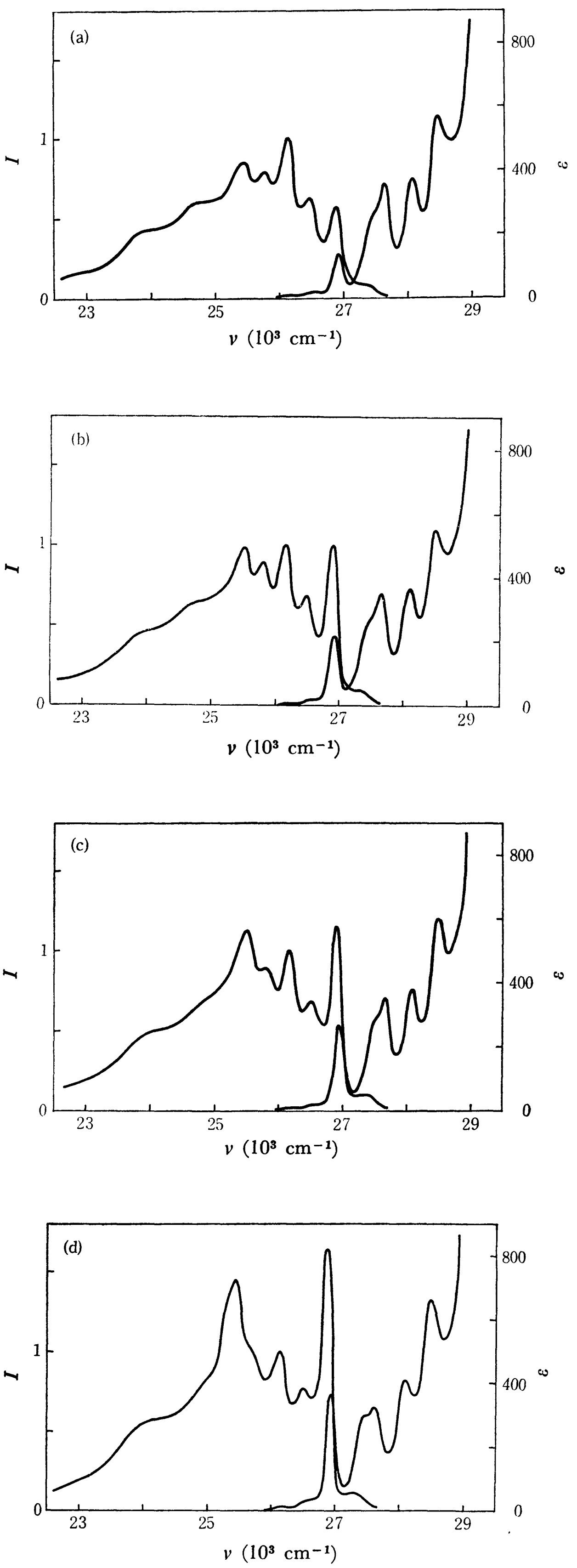

Fig. 2. Fluorescence and absorption spectra in various solvents at room temperature.
(a) cyclohexane, (b) ethyl ether, (c) ethanol, (d) acetonitrile.

TABLE 1. OBSERVED WAVE NUMBERS AND ASSIGNMENT OF VIBRATION BANDS OF FLUORESCENCE

Band	Present work			Klimova[22]	Assignment	
	n-hexane, 25°C (cm^{-1})	methylcyclohexane + isopentane, 77°K (cm^{-1})	Polarization	n-hexane, 4°K (cm^{-1})		
a	26880	26880	−0.18	26837	0	0-0
b	26450	26460	+0.01	26431	406	a_g
c	26110	26100	+0.02	26100, 26034	736, 802	?
d	25770	25780	+0.24	25730	1107	b_{1g}
e	25450	25460	+0.03	25432	1405	a_g
		25300		25207, 25201		
(g)		25050	+0.16	25027	406+1405	a_g
		24850		24863, 24797		
(i)	24690	24670	+0.16	24697, 24630		
(j)		24380	+0.27	24326	1107+1405	a_g+b_{1g}
		24210		24200, 24192		
(l)		24040	+0.15	24028	1405×2	a_g
(m)	23870	23850	+0.20	23801	1405+1631	a_g

to almost the same extent in the absorption and the fluorescence spectra.[22]

As has been suggested,[9] the Ham effect proves to be a helpful tool in vibrational analysis. In analogy with benzene, the solvent-enhanced components can be assigned to the 0–0 band, the a_g-vibration bands and their progressions.[9,14,17,20] From the other vibrationally-induced bands much less influenced by the solvent, information on the mechanism of intensity borrowing due to vibronic coupling[20,23] can be deduced. As given in Table 1, the assignment of the vibrational bands of the fluorescence spectrum was made in reference to the reliable work by Klimova.[24] The band c, though strong, could not be assigned.

Based on the presence of the b_{1g}-vibration bands and other evidences,[25–27] Klimova concluded that the first excited singlet electronic state of pyrene (belonging to the point group D_{2h}) has B_{3u} symmetry and the second, B_{2u}.[24] The first singlet transition $^1B_{3u}\leftarrow{}^1A_{1g}$ is, like that of naphthalene,[9] not symmetry forbidden[25] but the contributions to the transition moment cancel each other in a good approximation.

For the sake of confirmation the fluorescence polarization of pyrene[27–29] was measured by the usual photoselection technique.[30] The polarization spectrum together with the low-temperature fluorescence spectrum is illustrated in Fig. 3. It is seen that the weak components are intensified with the increased solvent polarity by cooling and by the additional crystal forces in the rigid matrix.[17,31] The polarization of the main part of the band system is shown to be weakly parallel to the direction of the moment of the second electronic transition. At the wave numbers for the b_{1g}-vibration bands (the d band and some bands at lower energies) the polarizations are positive, indicating that the intensity is derived from the neighboring second electronic state with B_{2u} symmetry through coupling with the b_{1g} vibrations.[27] On the other hand, the 0–0 band (a) and a_g-vibration bands (b, e) are negatively polarized against

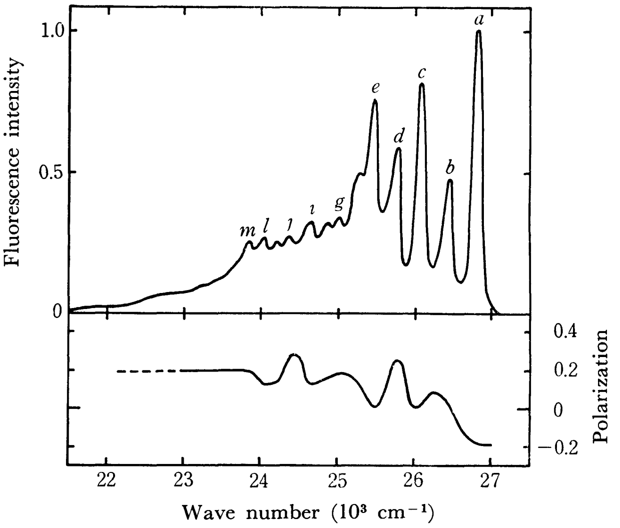

Fig. 3. Polarization and fluorescence spectra of pyrene at 77°K in a methylcyclohexane-isopentane (1 : 1) mixture.
Above: Fluorescence spectrum,
Below: Polarization as a function of wave number with excitation at 30300 cm^{-1}.

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[22] Since the relative intensities of the fluorescence bands I are given as the ratios of their observed intensity to that of the c band, the intensity variation of the c band in various solvents may be disregarded. However, it can be regarded as small, because the intensity of the third absorption band being a mirror image of the c band changes within 20% in the solvents used and most part of this change is affected by the solvent-broadened absorption tail of the second strong transition.

[23] D. P. Craig, *J. Chem. Soc.*, **1950**, 59.

[24] L. A. Klimova, *Opt. Spectry.*, **15**, 185 (1963).

[25] N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **25**, 1, 13 (1956).

[26] J. Tanaka, *Suppl. Progr. Theoret. Phys.*, No. 12, 183 (1959).

[27] H. Zimmerman and N. Joop, *Z. Elektrochem.*, **65**, 138 (1961).

[28] R. W. Williams, *J. Chem. Phys.*, **26**, 1186 (1957).

[29] R. M. Hochstrasser, *ibid.*, **33**, 459 (1960).

[30] A. C. Albrecht, *J. Mol. Spectry.*, **6**, 84 (1961).

[31] Y. Kanda, Y. Gondo, and R. Shimada, *Spectrochim. Acta*, **17**, 424 (1961).

the background of positive polarization, in harmony with the assignment of the first excited singlet π state to B_{3u} symmetry.[24,27]

Care should be taken to make a correct symmetry assignment of an electronic state with several different vibrational components by polarization measurements.[27,29] In this sense the solvent-enhanced 0–0 band can play a very significant role.

Considering the relation between the intensities of the Ham bands and the properties of the solvent molecules, the Ham effect might be due to the reduction of molecular symmetry in the field of surrounding solvent molecules or to the distortion of the π electron cloud by the environmental perturbation.[9,12,14,17,18] Confirmation of the cause of the effect is, however, very difficult.

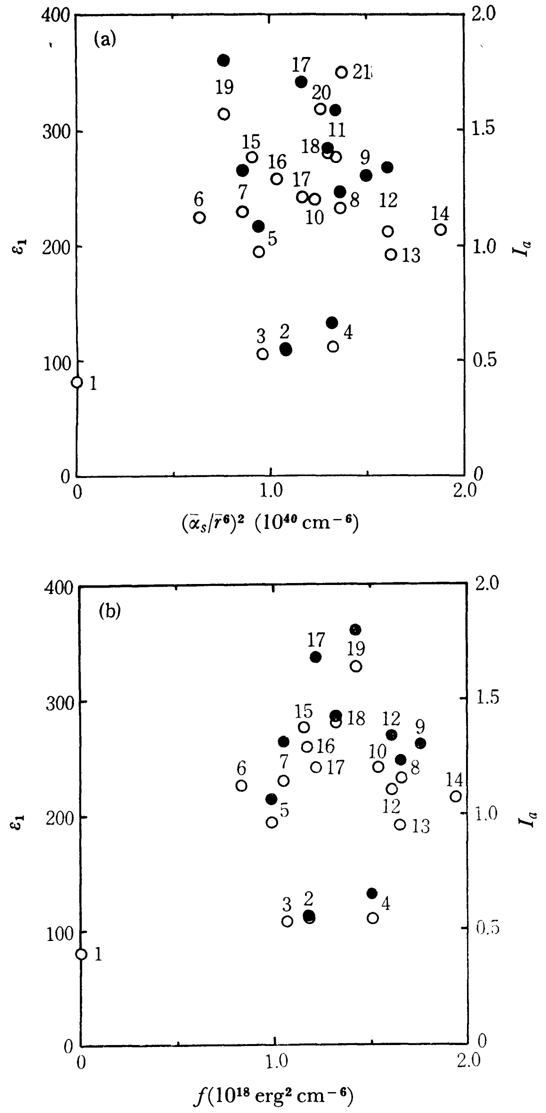

Fig. 4. Plots of the molar extinction coefficient ε_1 of the 0-0 absorption band and the intensity I_a of the *a* fluorescence band *vs*.

(a) the square of relative dispersion energy and (b) the square of dispersion *plus* induction terms.

1: gas, 2: *n*-hexane, 3: isopentane, 4: cyclohexane, 5: ethyl ether, 6: methanol, 7: ethanol, 8: chloroform, 9: carbon tetrachloride, 10: dichloromethane, 11: dichloroethane, 12: benzene, 13: toluene, 14: chlorobenzene, 15: acetone, 16: ethyl acetate, 17: tetrahydrofuran, 18: dioxane, 19: acetonitrile, 20: *N,N*-dimethylformamide, 21: dimethylsulfoxide. ○: fluorescence, ●: absorption.

In the study of the Ham bands of benzene, Koyanagi[17,18] showed a correlation between the apparent molar extinction coefficient of the origin band and the square of the relative quantity relating to dispersion energy $(\bar{\alpha}_s/\bar{r}^6)^2$, where $\bar{\alpha}$ denotes the mean polarizability of the solvent[32] and $\bar{r}$ the mean intermolecular distance between the solute and the solvent molecules.[33,34] Following his theory,[18] the effect of dispersion forces[35] was examined by a similar plot of the molar extinction coefficient ε_1 of the 0–0 band for absorption or the relative intensity I_a of the *a* band for fluorescence against $(\bar{\alpha}_s/\bar{r}^6)^2$ shown in Fig. 4(a). No perceptible trend can be found among these scattered points. Taking further into account not only the dispersion term[35] including the ionization potentials of the solute and the solvent but also the induction term arising from the interaction between the solvent permanent dipole and the solute induced dipole, the following factor[17,18] was introduced in Fig. 4(b).

$$f = \left\{\left(\frac{3}{2}\cdot\frac{I_p\cdot I_s}{I_p+I_s}\cdot\bar{\alpha}_s + \bar{\mu}^2\right)\Big/\bar{r}^6\right\}^2$$

where I_p and I_s are the ionization potentials[36] of pyrene and the solvent, respectively, and $\bar{\mu}^2$ is the mean square of the solvent dipole moment.[34] The situation, however, is not as improved as might be expected. The errors inherent in the evaluation of the inverse twelfth power of $\bar{r}$ might become serious, but it should be kept in mind that $\bar{r}$ is the proper quantity to be uniquely determined from the molar volumes of the solute and solvent.[37] One possible explanation is that the molecular size of pyrene is several times larger than that of benzene, implying some local interaction between pyrene and the solvent molecules. It is likely that the approximation[18] of a polarizable rigid sphere to a solvent molecule would not be justified in the present system.

Some other attempts have been made to find a correlation. Since it appears that the dielectric constant D of the solvent is of major importance in the enhancement of the bands, it is instructive to plot ε_1 or I_a *vs.* the dielectric factor $(D-1)/(2D+1)$ for the

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32) $\bar{\alpha}_s$ was calculated from the refractive index and the molar volume of the solvent.[33,34]

33) The Chemical Society of Japan, ed., "Kagaku Binran," (Handbook of Chemistry), Maruzen, Tokyo (1958).

34) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Troops, Jr., ed., "Organic Solvents," Technique of Organic Chemistry, Vol. VII, Interscience, New York (1955).

35) F. London, *Z. Physik*, **63**, 245 (1930); *Z. Phys. Chem.*, **B11**, 222 (1930).

36) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold, London (1966).

37) $\bar{r}$ is a sum of the molecular radii of the solute and the solvent estimated from the respective molecular weight and density.[33] The molecular radius s of a solvent molecule assumed as spherical was calculated by the formula

$$4\pi s^3/3=0.7405\ V/\boldsymbol{N}$$

V: molar volume, $\boldsymbol{N}$: Avogadro number.

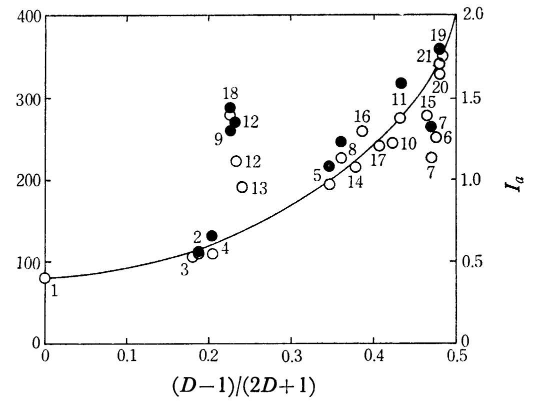

Fig. 5. Plots of ε_1 or I_a *vs.* $(D-1)/(2D+1)$.
See Fig. 4 for the numbering of the points. ○: fluorescence, ●: absorption.

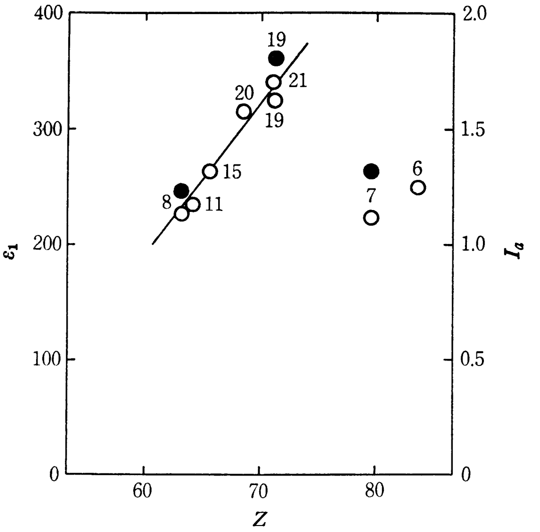

Fig. 6. Relationship between I_a (or ε_1) and the *Z*-value.
See Fig. 4 for the numbering of the points. ○: fluorescence, ●: absorption.

solvent as shown in Fig. 5. This reveals that there is an appreciably clear relation between them.[38] Moreover, an explicit relationship between the relative fluorescence intensities I_a and Kosower's *Z*-values[39] can be seen from Fig. 6 for the non-alcoholic polar solvents.

Recently, W. Liptay *et al.*[40] studied the solvent effects on the wave numbers and intensities of the absorption bands of fluorenone and showed the validity of their theoretical relation expressed by means of the ground- and excited-state dipole moments of the solute.[41] In the present case, however, their relation cannot be employed,[42] since pyrene has no dipole in either the excited or ground state.

Accordingly, in view of the appreciable dependence on the solvent dielectric constant, the following quantity was tentatively defined with an adjustable parameter χ:

$$f' = \left(\frac{D-1}{2D+1} - \chi\cdot\frac{n^2-1}{2n^2+1}\right),$$

where n denotes the refractive index of the solvent.[33,34] The case where $\chi=0$ was examined previously. As shown in Fig. 7, assuming that $\chi=0.5$, a rather good correlation was obtained between ε_1 or I_a and f', except for benzene and dioxane which are also known to give an anomalous effect on the frequency shifts of electronic spectra.[40] Other χ-values (*e.g.*, $\chi=1$) and other similar factors appearing in the ordinary solvent shift theories[1-8] have been found to give no better results. Applicability of the quantity given above in the original sense[1-3,8] to the molecule without dipole may, of course, be doubtful. The dielectric nature of solute-solvent interaction in the present system seems to be of significance. No correlation could be found with the energy parameters $\gamma\varepsilon^{*}$[43] employed in the solution theory[44] based on the cell method.[43] It is only inferred at present that both the dispersive and the inductive interactions involving more complex or microscopic solution structures might be of considerable importance.

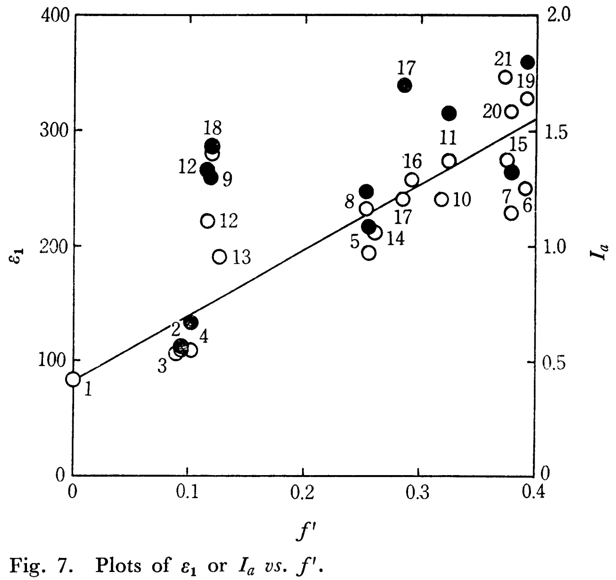

Fig. 7. Plots of ε_1 or I_a *vs.* f'.
See Fig. 4 for the numbering of the points. ○: fluorescence, ●: absorption.

It has been reported by Robinson[45] and Bayliss[46] that the Ham bands of benzene in carbon tetrachloride arise from the intensity borrowed from the solvent. Though the intensities of the Ham bands (and the shifts and broadenings of the spectra) of

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[38] The relation obtained by plotting ε_1 or I_a against the dielectric constant D itself is less clear.

[39] E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253, 3261 (1958).

[40] W. Liptay, H. Weisenberger, F. Tiemann, W. Eberlein, and G. Konopka, *Z. Naturforsch.*, **23a**, 377 (1968).

[41] W. Liptay, *ibid.*, **21a**, 1605 (1966).

[42] According to the formula obtained by W. Liptay,[41] the small remaining term when the ground- and excited-state dipole moments are zero is dependent only on the solvent refractive index.

[43] K. Arakawa and O. Kiyohara, This Bulletin, **43**, 975 (1970).

[44] J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths, London (1969).

[45] G. W. Robinson, *J. Chem. Phys.*, **46**, 572 (1967).

[46] N. S. Bayliss, *J. Mol. Spectry.*, **31**, 406 (1969).

pyrene in carbon tetrachloride[47] are observed to be relatively large, the contribution by Robinson's mechanism[45] seems to be a smaller fraction of the observed effect.

Extention of this fluorescence study to aromatic molecules other than pyrene is of interest. Experiments in various mixed solvents provide some useful information regarding solvent-solute and, in certain cases, solvent-solvent interactions, in which connection, knowledge of the recent solution theory[44] is helpful. It might be interesting to investigate from similar viewpoints the vibrational structures of phosphorescence spectra[14,48] as well for a variety of compounds in different media.

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[47] Pyrene fluorescence was considerably quenched and a chemical reaction was observed in carbon tetrachloride. A specific interaction seems to take place.

[48] Y. Kanda and R. Shimada, *Spectrochim. Acta*, **17**, 7 (1961).