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PRESSURE EFFECT ON INTERSYSTEM CROSSING FROM THE FIRST EXCITED SINGLET STATE OF ANTHRACENE AND ITS DERIVATIVES IN SOLUTION

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The fluorescence yields of anthracene and its derivatives have been measured in several solvents at room temperature up to 3000kg/cm^2. The solvent and pressure effects on the intersystem crossing rates (k_{is}) have been interpreted in view of changes in the Franck-Condon factors due to variations in the S_1–T_2 energy gap. The previously presented idea that k_{is} varies with the changes in the S_1–T_2 energy gap in correspondence to a vibrational structure of the Franck-Condon factor between S_1 and T_2 has been supported by the present results though somewhat qualitatively. The deuteration effects on k_{is} have also been investigated from similar standpoints.

Introduction

It is well known that the intersystem crossing from the first excited singlet state S_1 in anthracene and its derivatives[1,2] takes place dominantly to a nearby triplet state T_2[3~5]. Several interesting phenomena associated with this transition have been observed, for instance, substitution[2,4~6], temperature[2,4~8], solvent,[2,9,10] pressure[11~13] and deuteration effects[14,15]. Experimental and theoretical[16] approaches have been made to clarify a complicated nature of this transition. In previous papers[12,13], Tanaka and Osugi reported the distinct effects of pressure on the fluorescence yields of anthracene and

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2) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959)
3) R. E. Kellogg. *J. Chem. Phys.*, **44**, 411 (1966)
4) E. C. Lim, J. D. Laposa and J. M. H. Yu, *J. Mol. Spectry*, **19**, 412 (1965)
5) R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966)
6) W. R. Ware and B. A. Baldwin, *ibid.*, **43**, 1194 (1965)
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8) E. R. Pantke and H. Labhart, *ibid.*, **16**, 255 (1972)
9) E. J. Bowen and K. West, *J. Chem.Soc.*, **1956**, 4394
10) E. J. Bowen and D. M. Stebbens, *ibid.*, **1957**, 360
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12) F. Tanaka and J. Osugi, *Rev. Phys. Chem. Japan*, **42**, 85 (1972)
13) F. Tanaka and J. Osugi, *Chem. Lett.*, 1279 (1973)
14) E. C. Lim and H. R. Bhattacharjee, *Chem. Phys. Letters*, **9**, 249 (1971)
15) E. C. Lim and H. R. Bhattacharjee, *J. Chem. Phys.*, **55**, 5126 (1971)
16) B. Sharf and R. Silbey, *ibid.*, **53**, 2626 (1970)

some derivatives in *n*-hexane. And it was suggested that the pressure dependences of intersystem crossing rates corresponded to changes in the Franck-Condon factors caused by changes in the S_1-T_2 gaps. Further, by estimating a relation between the Franck-Condon factor and the S_1-T_2 energy gap17), it has been shown that the intersystem crossing rate depends rather strongly on the S_1-T_2 gap and that some phenomena associated with this transition may be explained by this relation. To ascertain the idea presented, the effects of substitution, deuteration, solvent and, in particular, pressure on the intersystem crossing rate have been investigated by measuring fluorescence yields in the pressure range up to 3000 kg/cm^2 at room temperature.

Experimental

Materials

Anthracene-h_{10} and 9, 10-diphenylanthracene are reagents for scintillation (NAKARAI CHEMICALS, LTD.) and anthracene-d_{10} is a Merck reagent (min. 99%). The other compounds were prepared according to the well known methods and purified by recrystallization, column chromatography and sublimation. *n*-Pentane, *n*-hexane, *n*-heptane, tetraline (NAKARAI) and toluene (Merck) are of spectroscopic grade. Methylcyclohexane of guaranteed grade (NAKARAI) was purified by distillation.

Determination of fluorescence yields at normal pressure

The concentrations of sample solutions were adjusted so that the optical densities at the exciting wavelength became the same value for all the compounds; the concentrations were in a range of $(1-5)\times 10^{-4}$M. For these degassed solutions the relative fluorescence yields were measured by using an ethylene glycol solution of rhodamine B as a photocounter. Although in the previous paper13) the absolute value of the fluorescence yield of 9, 10-diphenylanthracene in *n*-hexane was taken as 0.8318), Berlman has asserted that its value is unity in his recent note19). The consistence between the values measured in this work and those in literatures was examined for some compounds, and Berlman's comment was found to be reasonable. Here the fluorescence yield of 9, 10-diphenylanthracene was assumed to be unity in all the solvents studied.

Determination of fluorescence yields at high pressures

The fluorescence yields at high pressures were determined in the same way as described previously12, 13). The concentrations of sample solutions ranged from 7×10^{-5} to 3×10^{-4} M. The solutions were degassed and put into a cell under a stream of nitrogen gas. Although the elimination of oxygen was not complete, fluorescence quenching by oxygen was practically negligible because of the short life times of the S_1 states of the studied compounds.

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17) F. Tanaka and J. Osugi, *Chem. Phys. Letters*, **27**, 133 (1974)
18) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961)
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Theoretical Background

Since an internal conversion for anthracene has been verified to be negligible[4,20], the intersystem crossing rate (k_{is}) can be expressed by the radiative rate (k_f) and the fluorescence yield (ϕ_f)

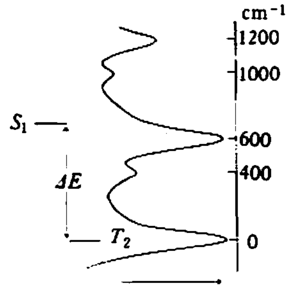
$$k_{is}=k_f(\phi_f^{-1}-1). \qquad (1)$$

Variations of the magnitude of k_{is} have been explained on the basis of the relative energies in S_1 and T_2. For example, the fluorescence yields of 9-substituted anthracenes in which S_1 lies below T_2 show strong temperature dependences, while the effect of temperature is not so strong in anthracene and side-substituted anthracences in which S_1 lies above T_2[2,4~6]. Also, the fact that the fluorescence yield of anthracene is much larger in crystal than in solution has been attributed to an inversion of energy levels between S_1 and T_2[3]. For anthracene in solution, S_1 has been estimated to be located at *ca.* 400 cm^{-1}[21] or *ca.* 650 cm^{-1}[3] above T_2.

A nonradiative transition rate in the statistical limit is expressed as follows[22].

$$k_{is}=\frac{2\pi}{\hbar}V^2F\rho$$

where V, F and ρ are the electronic matrix element, the Franck-Condon factor and the density of final states, respectively. As previously shown[17], for anthracene the Franck-Condon factor between S_1 and T_2 possesses the progressions of *ca.* 400 cm^{-1} and *ca.* 600 cm^{-1}, which are considered to be vibrationally resolved in the range of small S_1-T_2 energy gaps. In such a case the Franck-Condon factor changes significantly even by small changes in the S_1-T_2 gap. This circumstance is described schematically in Fig. 1. Probably, similar relations between F and $\Delta E=S_1-T_2$ can also be postulated for the deriva-



Franck-Condon factor

Fig. 1. Relation between the Franck-Condon factor and the S_1-T_2 gap for anthracene.
This scheme shows more probable one of the two relations estimated in ref. 17. See ref. 17 for the details of the estimation.

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20) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965)

21) L. M. Logan, I. H. Munro, D. F. Williams and F. R. Lipsett, "Molecular Luminescence", ed. by E. C. Lim, Benjamin, New York (1969) p. 775

22) For the theories of nonradiative transitions, for instance see (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963) (b) J. Jortner, S. A. Rice and R. M. Hochstrasser, "Advances in Photochemistry", Vol. 7, p. 149 (1969) (c) E. W. Schlag, S. Schneider and S. F. Fischer, "Annual Review of Physical Chemistry", Vol. 22, p. 465 (1971). In particular, for Franck-Condon factor, W. Siebrand, *J. Chem. Phys.*, **46**, 440 (1967), *ibid.*, **47**, 2411 (1967)

tives of anthracene though the quantitative feature may change. Owing to the difference in the electronic nature of S_1 and T_2, the S_1-T_2 gap depends on the condition of the system, such as solvent and pressure. Thus the effects of solvent and pressure on k_{is} are considered to arise mainly from the changes in the Franck-Condon factors due to the changes in the S_1-T_2 energy gap. According to Fig. 1, when S_1 is lowered relative to T_2 by solvent or pressure, k_{is} shows increases and decreases under the condition of $S_1>T_2$, while k_{is} decreases monotonically under $S_1<T_2$.

Results and Discussion

Changes in the S_1-T_2 gap by solvent and pressure

In general the energy of S_1 can be used as a measure of the sign and magnitude of the S_1-T_2 energy gap under the viewpoint that S_1 is more sensitive to environment and substitution than T_2[3~5,11]. The energies of S_1 at normal pressure are given in Table 1. In the present work, the fluorescence spectra shifted to the red with increasing pressure in all of the studied cases. These red shifts of S_1 suggest related changes in the S_1-T_2 gaps. Although the magnitudes of the red shifts could not be measured accurately, they were roughly 200–300 cm^{-1} at 3000 kg/cm^2 for all the compounds and solvents. According to Robertson *et al.*'s precise measurements of absorption spectra[23], the energy of S_1 of anthra-

Table 1. The energies (cm^{-1}) of S_1 at normal pressure[a]

	Hex.	MCH	Hex.+Tol.[c]	Tol.	Tet.[b]
anthracene-h$_{10}$ (A)	26,670	26,600	26,520	26,400	26,330
anthracene-d$_{10}$	26,730	26,660	26,580	26,470	26,390
2-methyl (2-mA)	26,520	26,460	26,380	26,270	26,190
1-methyl (1-mA)	26,430	26,360	26,290	26,170	26,110
9-methyl (9-mA)	25,930	25,860	25,790	25,680	25,630
2-chloro (2-cA)	26,330			26,110	
1-chloro (1-cA)	26,210			25,970	
9-chloro (9-cA)	25,770			25,530	
9-deutero (9-dA)	26,670				
9-ethyl (9-eA)	25,920				
9-*n*-propyl (9-pA)	25,880				
9-*n*-butyl (9-bA)	25,860				
2, 3-dimethyl (2, 3-mA)	26,480			26,230	
1, 3-dimethyl (1, 3-mA)	26,290			26,040	
1, 4-dimethyl (1, 4-mA)	26,110			25,880	
1, 4-chloromethyl (1, 4-c,mA)	26,020			25,740	

a) Values obtained from the 0–0 band of absorption.

b) The notations express *n*-hexane, methylcyclohexane, a mixture of *n*-hexane and toluene, toluene and tetraline, respectively.

c) 1 : 1 in volume at normal pressure.

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23) W. W. Robertson, O. E. Weigang, Jr. and F. A. Matson, *J. Mol. Spectry*, **1**, 1 (1957)

cene in *n*-pentane at room temperature is lowered by *ca.* $300\,\mathrm{cm}^{-1}$ at $3000\,\mathrm{kg/cm}^2$. There is no information on the pressure shift of T_2. However, from the following facts it is predicted that pressure lowers the energy of S_1 relative to that of T_2; (i) In the optical transitions between singlet states for polycyclic aromatic hydrocarbons the pressure-induced shift depends on the oscillator strength and hence the red shifts of ^1L_a states are three or four times larger than those of ^1L_b states[23]. (ii) In naphthalene, where S_1 is ^1L_b and T_1 is ^3L_a, the pressure-induced red shifts of fluorescence and phosphorescence are nearly equal[24]. Considering this fact and (i) collectively, in anthracene where both S_1 and T_1 are L_a the lowering of S_1 by pressure is probably larger than that of T_1. (iii) The pressure shift of T_2 relative to T_1 is considered to be fairly small owing to a small absorption coefficient in the T_1-T_2 absorption[3].

If this is the case, when S_1 is lowered by the changes in solvent and the increase in pressure, the S_1-T_2 energy gap decreases under the condition of $S_1 > T_2$ and increases under $S_1 < T_2$.

Pressure dependences of k_{is} for anthracene and its methyl- and chloro-derivatives in *n*-hexane and toluene

For anthracene (A), methylanthracene (mA) and chloroanthracene (cA), the pressure dependences of fluorescence yields in *n*-hexane and toluene are shown in Figs. 2 and 3. Assuming that k_f does not depend on pressure, the pressure dependences of k_{is} are obtained from the equation 1. As Figs. 4 and

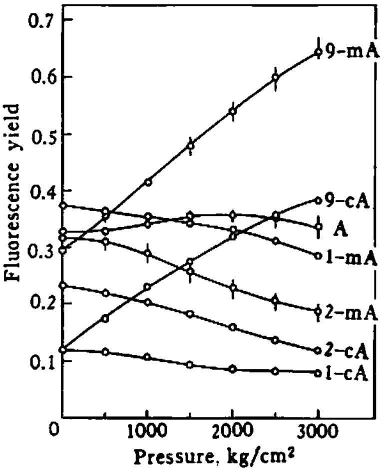

Fig. 2. Pressure dependences of fluorescence yields of anthracene, methylanthracenes and chloroanthracenes in *n*-hexane at room temperature.
The notations in Figs. 2–10 are given in Table 1.

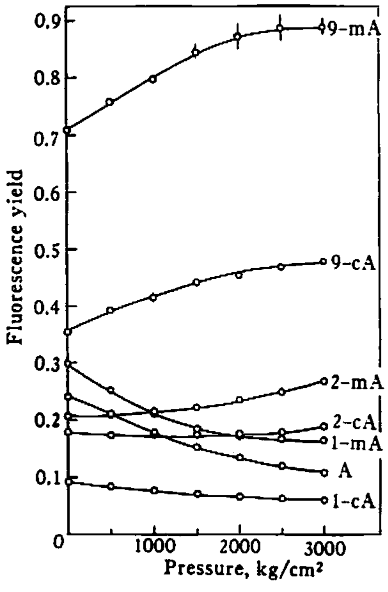

Fig. 3. Pressure dependences of fluorescence yields of anthracene, methylanthracenes and chloroanthracenes in toluene at room temperature.

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24) M. F. Nicol, *J. Chem. Phys.*, 45, 4753 (1966)

5 show, the pressure dependence of k_{is} is markedly affected by the substituted position in both methyl- and chloro-derivatives, and it is also very different between two solvents. These results can now be explained by the above-mentioned relation between the Franck-Condon factor and the S_1-T_2 energy gap. The energies of S_1 shown in Table 1 change in the following order in all the solvents; anthracene $>$2-$>$1-$>$9-derivatives. It has been considered that S_1 lies below T_2 in 9-derivatives and S_1 lies above T_2 in other compounds[1~6]. As to the solvent shift of S_1, Table 1 shows that a change from n-hexane to toluene lowers S_1 relative to T_2 for all the compounds. Regardless of the difference in the S_1-T_2 gap between two solvents, k_{is} for 9-derivatives decreases monotonically with increasing pressure in both solvents as expected in the case of $S_1 < T_2$. On the other hand, the pressure dependences of k_{is} for anthracene and its 1- and 2-derivatives are much complicated as seen in Figs. 4 and 5. In the case of $S_1 > T_2$, the ways in which k_{is} changes with increasing pressure depend strongly on the situation of the S_1-T_2 gap at normal pressure in the pattern of fluctuation of the Franck-Condon factor, and therefore the pressure dependence of k_{is} is considered to vary with compounds and solvents even under the same condition of $S_1 > T_2$. k_{is} of anthracene scarcely depends on pressure in n-hexane and increases steeply with increasing pressure in toluene where the S_1-T_2 gap is already diminished to a certain degree at normal pressure. k_{is} of 2-derivatives increases in n-hexane and decreases in toluene when pressure increases. This inversion in the pressure dependence of k_{is} is considered to be caused by a certain peak of the Franck-Condon factor as predicted under $S_1 > T_2$. k_{is} of 1-derivatives increases gradually in n-

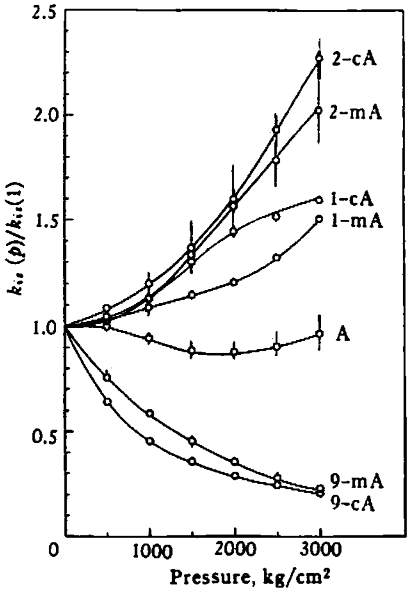

Fig. 4. Pressure dependences of intersystem crossing rates of anthracene, methylanthracenes and chloroanthracenes in n-hexane at room temperature.

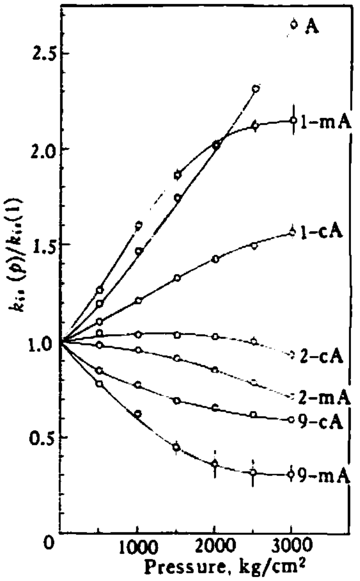

Fig. 5. Pressure dependences of intersystem crossing rates of anthracene, methylanthracenes and chloroanthracenes in toluene at room temperature.

hexane and steeply in toluene with increasing pressure. In addition, the effect of solvent on the fluorescence yields at normal pressure accords qualitatively with the tendency expected by the results of the pressure effect, *i. e.*, the fluorescence yields are higher in toluene for 9-derivatives and lower in toluene for other compounds than in *n*-hexane.

Substituent effect at 9-position

In addition to the relative energies in S_1 and T_2, Lim *et al.* have pointed out steric or vibrational effects localized at 9-position as factors responsible for the strong temperature dependences of the fluorescence yields of 9-derivatives[4]. The influence of changes in substituent at the 9-position was investigated by the pressure effects on the fluorescence yields in *n*-hexane. As seen in Table 1, the deuteration at the 9-position or the changes in alkyl substituent from methyl to *n*-butyl affect the energies of S_1 only slightly; therefore it is considered that the S_1-T_2 gap scarcely changes by the differences in substituent. As evident in Fig. 6, the effects of bulkiness of substituents or the vibrational

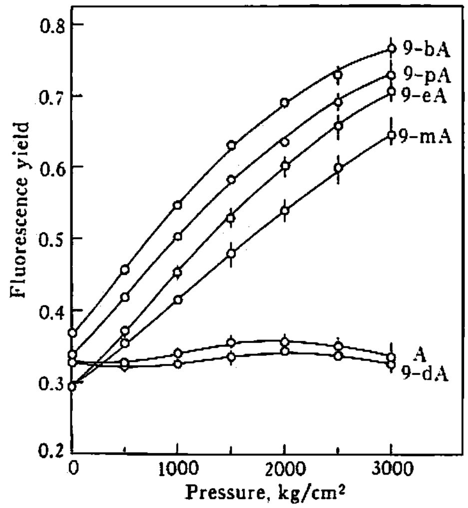

Fig. 6. Pressure dependences of fluorescence yields of 9-substituted anthracenes in *n*-hexane at room temperature.

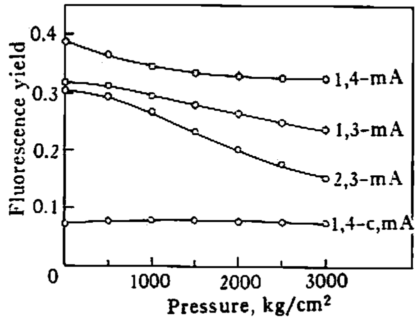

Fig. 7. Pressure dependences of fluorescence yields of disubstituted anthracenes in *n*-hexane at room temperature.

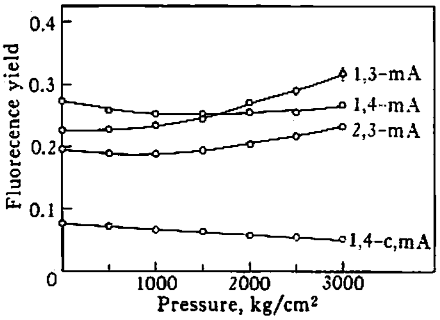

Fig. 8. Pressure dependences of fluorescence yields of disubstituted anthracenes in toluene at room temperature.

effects at the 9-position were not observed in the pressure effect.

Pressure dependences of k_{is} for disubstituted anthracenes in *n*-hexane and toluene

The results of similar measurements in *n*-hexane and toluene for anthracenes disubstituted at a side ring are shown in Figs. 7–10. For these compounds, in which S_1 probably lies above T_2, the distinct differences in the pressure dependences of k_{is} between *n*-hexane and toluene are still seen.

Changes in k_{is} during systematic variations in the S_1-T_2 gap by solvent and pressure

The feature of pressure dependences of k_{is} in different solvents may be qualitatively explained by Fig. 11. It shows how k_{is} changes with a systematic lowering of S_1 caused by solvent and pressure in the region where there is a peak in the Franck-Condon factors (see Fig. 1). The original points in arrows express the situations at normal pressure in each solvent. The motion of an arrow shows the pressure dependence of k_{is} in the solvent. To ascertain the changes in k_{is} predicted by this figure, similar measurements in other several solvents were made for anthracene and 1-, 2- and 9-methylanthracene. The results are shown in Figs. 12–19. As seen in Table 1, the energies of S_1 change in the order of *n*-hexane>methylcyclohexane>a mixture of *n*-hexane and toluene (1 : 1 in volume at normal pressure)>toluene>tetraline. *Anthracene:* As S_1 is lowered by solvent and pressure, at first k_{is} scarcely changes and then begins to increase rapidly and thereafter the rate of the increase becomes

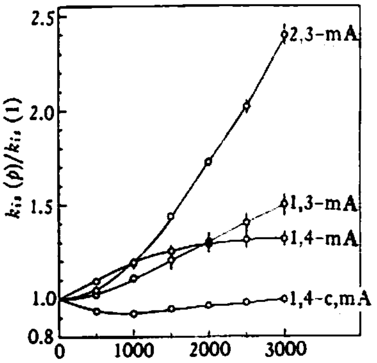

Fig. 9. Pressure dependences of intersystem crossing rates of disubstituted anthracenes in *n*-hexane at room temperature.

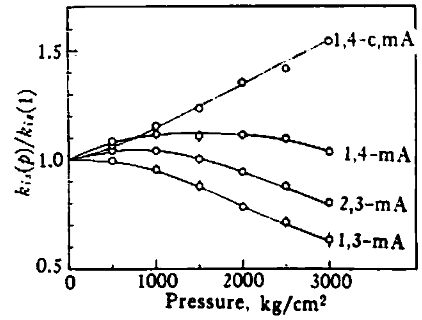

Fig. 10. Pressure dependences intersystem crossing rates of disubstituted anthracenes in toluene at room temperature.

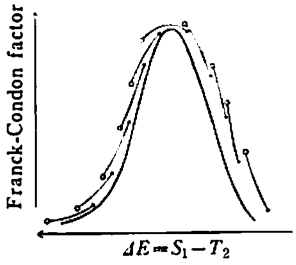

Fig. 11. Scheme showing the effects of solvent and pressure on k_{is}. See the text.

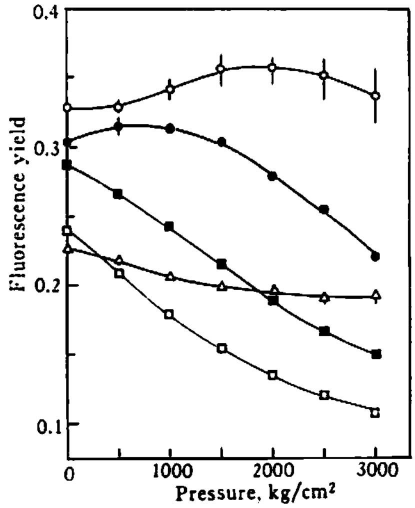

Fig. 12. Pressure dependences of fluorescence yields of anthracene in various solvents at room tempera ture.

○ n-hexane,
● methylcyclohexane,
■ n-hexane+toluene (1 : 1 in volume at normal pressure),
□ toluene, △ tetraline.
The symboles are common in Figs. 12–21.

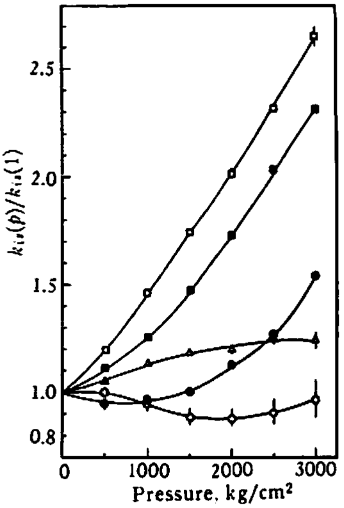

Fig. 13. Pressure dependences of intersystem crossing rates of anthracene in various solvents at room temperature.

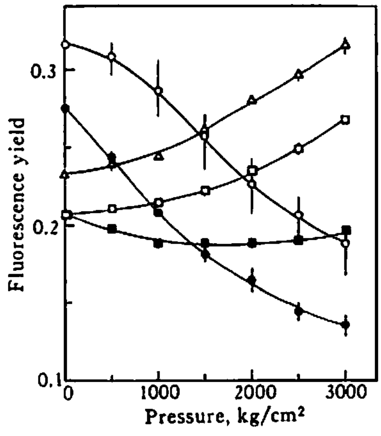

Fig. 14. Pressure dependences of fluorescence yields of 2-methylanthracene in various solvents at room temperature.

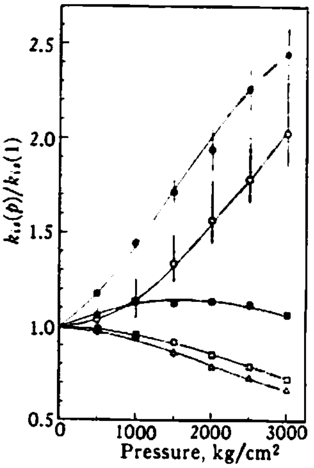

Fig. 15. Pressure dependences of intersystem crossing rates of 2-methylanthracene in various solvents at room temperature.

slow. This suggests that the Franck-Condon factor gets near to a peak with an decreasing S_1-T_2 gap. *2-Methylanthracene:* k_{it} shows continuous changes from the increases to the decreases with lowering of S_1 as seen in Figs. 14 and 15. This behavior of k_{it} is considered to be an evidence for the existence of the structure of the Franck-Condon factor. *1-Methylanthracene:* As in Figs. 16 and 17, this compound also shows the rapid increases and inversion of k_{it} with increasing pressure. In accordance with the results

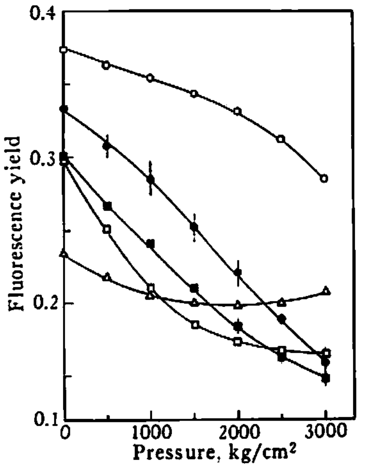

Fig. 16. Pressure dependences of fluorescence yields of 1-methylanthracene in various solvents at room temperature.

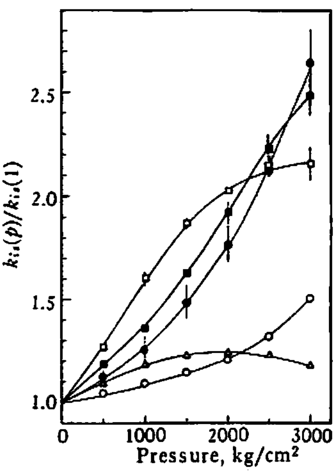

Fig. 17. Pressure dependences of intersystem crossing rates of 1-methylanthracene in various solvents at room temperature.

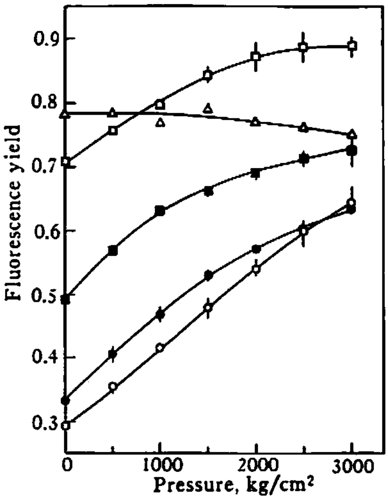

Fig. 18. Pressure dependences of fluorescence yields of 9-methylanthracene in various solvents at room temperature.

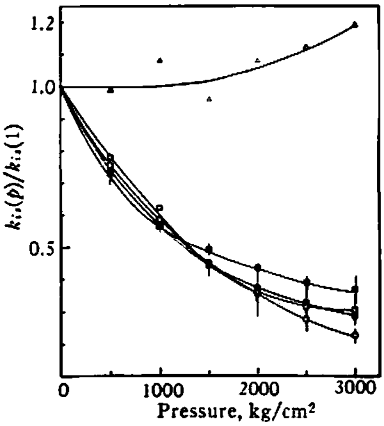

Fig. 19. Pressure dependences of intersystem crossing rates of 9-methyl anthracene in various solvents at room temperature.

of pressure effects, the fluorescence yield at normal pressure is diminished in solvents where the energy of S_1 is lower. *9-Methylanthracene:* Contrary to the three other compounds, in this case where S_1 lies below T_2 the fluorescence yield at normal pressure is higher in solvents where the energy of S_1 is lower. And k_{is} decreases monotonically with increasing pressure in the solvents from *n*-hexane to toluene, though this tendency becomes obscure in tetraline. The determination of changes in k_{is} is accompanied by large errors in the case of high fluorescence yields. Therefore, although the result of 9-methylanthracence in tetraline is fairly uncertain, at least it shows that k_{is} does not decrease with an increasing S_1-T_2 gap so rapidly as predicted only by the intersystem crossing from S_1 to T_2, and the same tendency is also seen for 9-chloroanthracene in toluene in Fig. 5. There may be another nonradiative process. A similar observation has been made in the solvent effect on the fluorescence yield of 9-methylanthroate25).

Deuteration effect

The deuteration effect in this transition has also received a considerable interest. An inverse deuteration effect, *i. e.*, an increase in k_{is} due to deuteration, has been observed14, 15) and it has presented a theoretical problem in nonradiative transitions26, 27). Deuteration is considered to have two effects on the Franck-Condon factor: (i) a change in the difference of the zero-point energy between S_1 and T_2, which causes a change in the S_1-T_2 energy gap; (ii) changes in the frequencies of the vibrational modes17, 28)

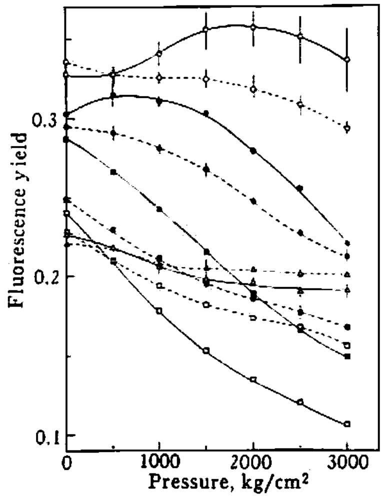

Fig. 20. Effects of deuteration on the fluorescence yield of anthracene in various solvents.
full line: anthracene-h_{10},
broken line: anthracene-d_{10}

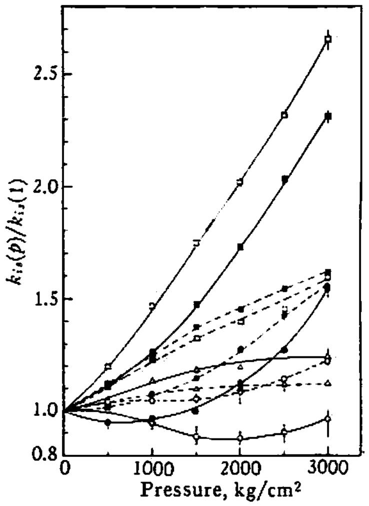

Fig. 21. Effects of deuteration on the intersystem crossing rates of anthracene in various solvents.
full line: anthracene-h_{10},
broken line: anthracene-d_{10}

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25) T. C. Werner and R. M. Hoffman, *J. Phys. Chem*, 77, 1611 (1973)

26) B. Sharf and R. Silbey, *Chem. Phys. Letters*, 5, 314 (1970)

27) B. Sharf, *J. Chem. Phys.* 55, 320 (1971)

28) A. Bree, S. Katagiri and S. R. Suart, *ibid.*, 44, 1788 (1966)

responsible for the progressions of the Franck-Condon factor, which modify the relation between F and ΔE in Fig. 1.

In view of these effects, the ways in which deuteration affects k_{is} depend on the condition of system, that is, in one case an increase in k_{is} and in the other case a decrease will be observed. For anthracene-h_{10} and -d_{10} the effects of pressure on the fluorescence yields in several different solvents were compared. As shown in Fig. 20, deuteration scarcely affects the fluorescence yield in the region where the energy of S_1 is high (such as in n-hexane at lower pressures). As S_1 becomes lower the fluorescence yield is diminished by deuteration, and with further lowering of S_1 deuteration enhances the fluorescence yield as observed in toluene and tetraline at higher pressures. The vibrational structure of the Franck-Condon factors, which is suggested by the pressure dependences of k_{is} in Fig. 21, seems to be fairly different between anthracene-h_{10} and -d_{10}. However, because of insufficiency of available data on the energy gaps and the vibrational feature and because of thermal perturbation at room temperature, it is considered to be difficult to understand the results more quantitatively.

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