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journal or publication title	Journal of Chemical Physics
volume	82
number	4
page range	1651-1660
year	1985
URL	http://hdl.handle.net/10097/52456

doi: 10.1063/1.448397

Mechanisms of external heavy atom effects on the lowest excited triplet states: Naphthalene and biphenyl X traps

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(Received 6 August 1984; accepted 14 September 1984)

An external heavy atom effect was investigated on the phosphorescent states of naphthalene X traps and biphenyl X traps using a variety of heavy atom perturbers at liquid helium temperatures. Phosphorescence spectra, triplet lifetimes, sublevel properties, and detrapping rates were measured. The well-resolved phosphorescence spectra were obtained in almost all cases. The intensities of the vibronic bands were extremely weak in the heavy atom systems compared with those of the light atom systems. The triplet lifetimes range from 10 to 2300 ms in the naphthalene X traps and from 240 to 4200 ms in the biphenyl X traps. Selective enhancements were observed in the radiative decay rate constants of the triplet sublevels. Correlation between the intensities of phonon bands and the magnitudes of detrapping rates was found in the naphthalene X traps. From these results we conclude that: (i) The shortening of the triplet lifetimes is mostly due to the radiative enhancements of the $T_1 \rightarrow S_0$ transitions; (ii) the molecular states of the perturber, especially the lowest excited triplet states, are the most important perturbing states among the three possible states (atomic states, CT states, and molecular states); and (iii) the magnitudes of the intermolecular interactions are also enhanced in the heavy atom systems, which is partly due to those of electron-phonon interactions.

I. INTRODUCTION

The external heavy atom effect on phosphorescent states of aromatic molecules has been investigated by utilizing a variety of heavy-atom-containing perturbers (heavy atom perturbers).¹⁻¹³ The magnitude of the effect varies depending on the nature of the heavy atom perturber. One of the most important problems associated with this effect is identification of the main perturbing states of the heavy atom perturbers. There have been many investigations to answer this problem,^{1-5,14-17} but there still remain unsolved questions. In this work we have made a systematic study by changing heavy atom perturbers in a common environment in order to identify the main perturbing states and to establish the mechanisms of the external heavy atom effect.

Three kinds of states have been considered as candidates of the main perturbing states¹; states mainly localized on heavy atoms (hereafter we abbreviate as atomic states), intermolecular charge transfer (CT) states, and delocalized molecular states including heavy atoms. Heavy atom perturbers may be classified into three groups. The first group consists of atoms, inorganic molecules, and alkyl halides such as inert gases (Xe, Kr),^{4,5} C_2H_5I ,⁶ and CH_3Hg .^{7,8} Perturbers of the second group involve the lowest excited CT states which are remarkably red shifted from the unperturbed states.¹¹⁻¹³ Tetrachlorophthalic anhydride (TCPA) and tetrabromophthalic anhydride (TBPA) are examples in this group. It has been concluded that the atomic states and the intermolecular CT states are the main perturbing states for the first and the second groups, respectively. The third group consists of aromatic halides such as halobenzenes and halonaphthalenes. For this group we must consider delocalized $^3\pi\pi^*$ states in addition to the atomic states and CT states, since they are rather close to the lowest excited triplet (T_1) states of the perturbed molecules. Despite many investi-

gations, however, there have been different views about the main perturbing states of this group of molecules.¹⁻³ This is mainly due to the fact that in most cases experiments were performed in different environments (heavy atom host systems) and the results could not be compared each other on the same ground.

X -trap systems induced by heavy atom containing dopants are convenient systems to study the effect of different heavy atom perturbers in common environments. Weinzierl and Friedrich studied the properties of the naphthalene X traps induced by halonaphthalenes paying attention to external heavy atom effect.³ They considered that the atomic states are the main perturbing states. On the other hand, in our preliminary report¹⁸ we have suggested that the molecular states are likely to be the main perturbing states in the naphthalene X traps induced by aromatic halides. Here we extend our study including different types of perturbers and biphenyl X traps to examine relative importance of the three perturbing states and to obtain further information about molecular interactions in the X traps induced by the heavy atom perturbers.

We examined many perturbers with different energy separations, $\Delta E_{TT} [\equiv E_{T_1}(\text{perturber}) - E_{T_1}(\text{exciton})]$ including those having CT characters. Phosphorescence spectra, triplet lifetimes and triplet sublevel properties were obtained at liquid helium temperatures. Detrapping rates were also measured for naphthalene X traps at 1.4–20 K. From the obtained results we first determine the most important perturbing state among the three possible states. We then estimate contributions from the other less important perturbing states. Finally we evaluate magnitudes of intermolecular interactions for these heavy atom systems and discuss the obtained values in relation to the electron-phonon couplings and the exciton-trap interactions.

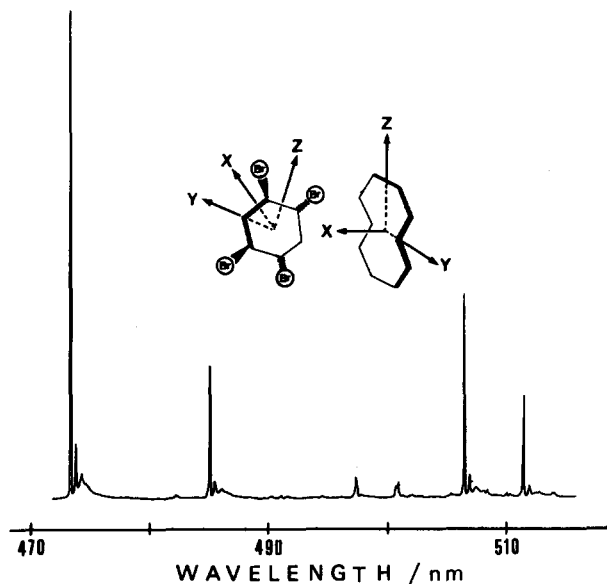


FIG. 1. Phosphorescence spectrum of the naphthalene X trap induced by s -tetrabromobenzene at 4.2 K. The insert is the structure of the X trap.

II. EXPERIMENTAL

Naphthalene and biphenyl were purified by zone melting after recrystallization from ethanol. Solid dopants were purified by zone melting or vacuum sublimation after recrystallization. Liquid dopants were purified by distillation under a reduced pressure. Mixed crystals ($\sim 10^{-3}$ mol/mol)

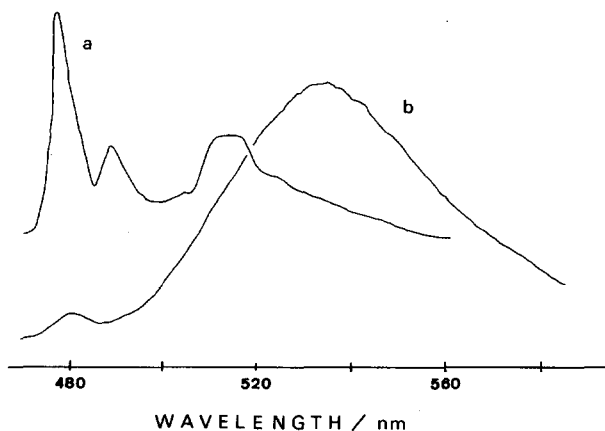


FIG. 2. Phosphorescence spectra of the naphthalene X traps induced by TBPA (a) at 4.2 K and (b) at 77 K.

were prepared by the Bridgman method. The experimental setups for optical, ODMR, and MIDP experiments were similar to those described previously.¹⁹ Phosphorescence spectra were observed at 4.2 K. Sublevel properties, total decay rate constants k_i ($i = x, y,$ and z), relative radiative decay rate constants k_i^r and zero-field splitting constants (ZFS) were measured at 1.4 K by the ZFODMR, MIDP, and fast passage techniques.²⁰⁻²⁴ Detrapping rate constants were measured at various temperatures following the procedure by Weinzierl and Friedrich²⁵; the naphthalene X traps were prepared by doping heavy atom perturbers (shallow traps)

TABLE I. Phosphorescence properties of the naphthalene X traps and the heavy atom perturbers.

Perturber	Naphthalene X -trap		Perturber	
	$k(X)/s^{-1}$	$\Delta\epsilon/cm^{-1}$ ^a	$k(p)/s^{-1}$	$\Delta E_{TT}/cm^{-1}$ ^b
β -bromonaphthalene (β -BN)	24.1	266	64.5	110
3-bromoquinoline (3-BQ)	20.9	253	70.9	360
1,2,3,4-tetrabromophthalic anhydride (TBPA)	11.5	~ 240	465	2 100
1,2,3,4-tetrachlorophthalic anhydride (TCPA)	0.98	~ 0	147.6	2 400
5-bromoindole (5-BIN)	13.3	181	31.3	3 350
5-chloroindole (5-CIN)	0.57	136	1.18	3 350
hexabromobenzene (HBB)	8.4	~ 290	...	~ 4 300
s -tetrabromobenzene (TBB)	3.2	76	1820 ^c	5 250
p -dibromobenzene (DBB)	4.1	70	3330 ^c	6 110
p -dichlorobenzene (DCB)	0.43	52	62.5	6 200
p -diiodobenzene (DIB)	96.0	203	...	~ 6 000
s -tribromobenzene (TRBB)	2.5	76	1350 ^a	6 410
α, α' -dibromo- p -xylene	0.43	231	...	~ 7 000
1,4-dibromocyclohexane	0.56	74	...	~ 20 000
bromocyclohexane	0.68	119	...	~ 20 000
ethyl iodide	7.9	52

^a $\Delta\epsilon$: trap depth = E_T (exciton) - E_{T_i} (X trap).

^b $\Delta E_{TT} = E_{T_i}$ (perturber) - E_T (exciton).

^c D. S. McClure, J. Chem. Phys. 17, 905 (1949).

TABLE II. Relative intensities of the vibronic bands in the phosphorescence spectra of the various naphthalene X traps.

Perturber		Indole					
Bands ^a		(IN)	DCB	DBB	TBB	5-BIN	3-BQ
0-0	a_{1g}	1.0	1.0	1.0	1.0	1.0	1.0
393 cm^{-1}	b_{1g}	4.8×10^{-2}	5.0×10^{-2}	6.0×10^{-3}	7.6×10^{-3}	2.9×10^{-4}	2.0×10^{-5}
902	b_{2g}	2.0×10^{-2}	1.5×10^{-2}	8.2×10^{-4}	2.2×10^{-3}	2.9×10^{-4}	2.0×10^{-5}
904	b_{1g}	2.0×10^{-2}	2.5×10^{-2}	6.6×10^{-4}	4.0×10^{-4}	2.3×10^{-4}	2.0×10^{-4}
951	b_{1g}	2.0×10^{-2}	2.5×10^{-2}	6.6×10^{-4}	4.0×10^{-4}	2.3×10^{-4}	2.0×10^{-4}
980	b_{1g}	2.0×10^{-2}	2.5×10^{-2}	6.6×10^{-4}	4.0×10^{-4}	2.3×10^{-4}	2.0×10^{-4}
982	b_{2g}	3.6×10^{-2}	4.3×10^{-2}	9.9×10^{-4}	8.0×10^{-4}	1.8×10^{-4}	2.9×10^{-4}
983	b_{2g}	3.6×10^{-2}	4.3×10^{-2}	9.9×10^{-4}	8.0×10^{-4}	1.8×10^{-4}	2.9×10^{-4}

^aD. M. Hanson, J. Chem. Phys. 51, 5063 (1969).

and 4-bromoisoquinoline (deep trap) into naphthalene crystals. We measured temperature dependence of the phosphorescence intensities of the shallow traps relative to that of the deep trap from 1.4 to 20 K and calculated detrapping rate constants from these relative intensities using the Fayer and Harris's model.²⁶ A calibrated carbon resistor was used as a thermometer in this temperature range.

III. RESULTS

A. Naphthalene X traps

1. Phosphorescence spectra and lifetimes

We observed the phosphorescence spectra of the naphthalene X traps induced by a variety of heavy atom perturbors at 4.2 K. The spectra of the crystals doped with *s*-tetrabromobenzene and TBPA are shown as typical examples in Figs. 1 and 2 (a), respectively. Moderately strong phosphorescence was observed for all X traps in contrast to very weak phosphorescence from the neat crystal of naphthalene. In many systems the spectra were sharp and well resolved as shown in Fig. 1. Only in two systems, hexabromobenzene and TBPA, the spectra were broader as shown in Fig. 2(a). Although spectra due to several X traps were detected by increasing concentration of dopants, phosphorescence from only one X trap was observed at lower concentrations ($\sim 10^{-3}$ mol/mol) in most cases. We measured phosphorescence properties of the X traps at these low concentrations.

Locations of the 0-0 bands of the phosphorescence spectra are summarized in Table I together with trap depths $\Delta\epsilon[\equiv E_{T_1}(\text{exciton}) - E_{T_1}(X \text{ trap})]$, which shows that larger molecules provide deeper traps. Vibrational structures of the spectra similar to that observed for naphthalene- h_8 in naphthalene- d_8 ²⁷ except that the intensities of nontotally symmetric bands are much weaker in the heavy atom systems as shown in Table II.

Structures and intensities of phonon bands in the phosphorescence spectra were very different depending on the perturber. Some of the phonon structures are shown in Fig. 3 together with the relative intensities of the phonon bands, $I_{\text{phonon}}/I_{0-0}$. These values are increased by heavy atom substitution as seen in the figure. The phonon bands of 16-22 cm^{-1} and their overtones are resolved in the spectra. Since the phosphorescence decays of the shallow traps at 4.2 K are

affected by detrapping and/or spin lattice relaxation processes, accurate measurements of the intrinsic decay rate constants are difficult. Therefore, we have determined the total decay rate constant as the average decay rate constants $k(X)$ [$\equiv 1/3(k_x + k_y + k_z)$] from the sublevel decay rate constants measured at 1.4 K. The decay rate constants of the deeper traps ($\Delta\epsilon \gtrsim 65 \text{ cm}^{-1}$) could be obtained directly from the phosphorescence decays at 4.2 K. The results are summarized in the second column of Table I. The total decay rate constants $k(X)$ studied here range from 0.4 to 96 s^{-1} . The effect on $k(X)$ becomes larger by changing perturbors from chloro-, bromo- to iodo-derivatives. Aromatic halides give rise to larger effects than the corresponding aliphatic halides.

In the experiments at 77 K we found another trap for the TBPA system as shown in Fig. 2(b). In this case the phosphorescence spectrum was broad and structureless with its peak located at $\sim 535 \text{ nm}$ and the triplet lifetime of 26 ms. These properties are very similar to those reported by Czekała and Mager¹¹ for the TBPA-naphthalene crystalline system.

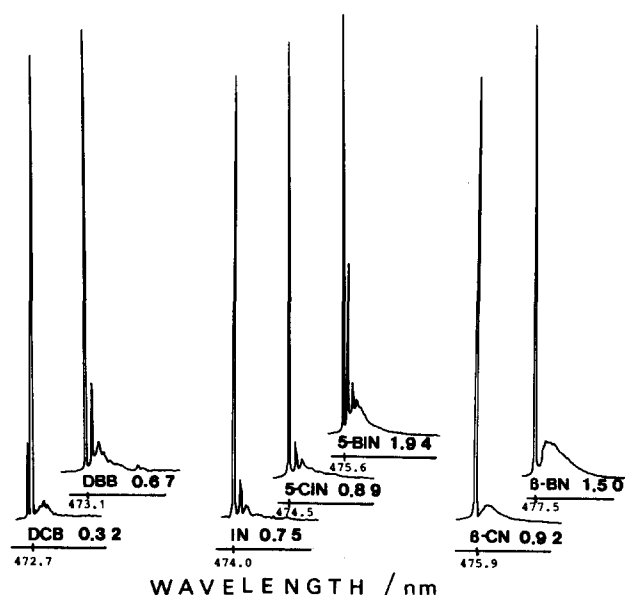


FIG. 3. Phonon structures around the 0-0 bands in the phosphorescence spectra of the various naphthalene X traps. The relative intensities of the phonon bands $I_{\text{phonon}}/I_{0-0}$ are shown.

TABLE III. Sublevel properties of the naphthalene X traps.

Perturber		k_i/s^{-1}	$k_i'(0-0)$	D/MHz	E/MHz^a
β -bromonaphthalene	T_z	37.5	1.0	2965	- 455
	T_y	21.4	0.56		
	T_x	13.5	0.20		
3-bromoquinoline	T_z	34.0	1.0	2955	- 455
	T_y	11.3	0.30		
	T_x	17.5	0.10		
1,2,3,4-tetrabromophthalic anhydride	T_z	11.5	0.59	2775	- 385
	T_y	20.1	1.0		
	T_x	2.8	0.20		
5-bromoindole	T_z	19.0	1.0	2945	- 465
	T_y	10.0	0.53		
	T_x	10.8	0.58		
hexabromobenzene	T_z	6.3	0.68	3005	- 485
	T_y	4.9	0.74		
	T_x	14.0	1.0		
<i>s</i> -tetrabromobenzene	T_z	5.0	1.0	2970	- 460
	T_y	2.7	≤ 0.50		
	T_x	1.9	≤ 0.30		
<i>p</i> -dibromobenzene	T_z	2.2	≤ 0.15	2965	- 455
	T_y	2.5	≤ 0.25		
	T_x	7.5	1.0		
<i>p</i> -diiodobenzene	T_z	130	1.0	2925	- 495
	T_y	80	0.51		
	T_x	78	0.34		
ethyl iodide	T_z	0.83	0.12	2960	- 460
	T_y	3.2	0.27		
	T_x	19.8	1.0		

^a D and E are zero-field splitting parameters. $2E = E(T_y) - E(T_z)$, $D = -(3/2) \cdot E(T_x)$.

2. Sublevel properties

Zero field splitting (ZFS) parameters, D and E , were obtained for some of the X traps and are shown in Table III. The values are almost the same as those observed for naphthalene in the mixed crystals.²⁸ But in the case of TBPA the

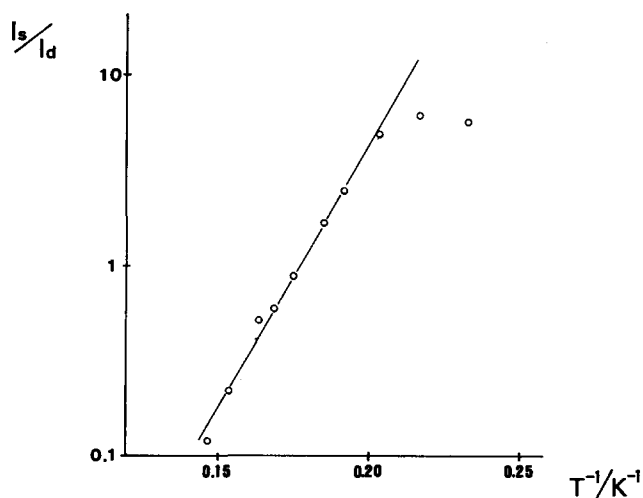


FIG. 4. Typical temperature dependence of the phosphorescence intensity of the naphthalene X trap I_s (*p*-dibromobenzene) relative to that of the deep trap I_d (4-bromoisoquinoline).

values decrease by 70–200 MHz. The total decay rate constants and the relative radiative decay rate constants were obtained at the 0–0 bands as shown in Table III. From the table we find that the heavy atom perturbers exert selective influences on the triplet sublevels. Even in the case of ethyl iodide remarkable sublevel dependence was observed for the heavy atom effect. In almost all cases the decay rate constants of the T_z or T_x sublevels are enhanced most by the perturbers. The T_y sublevel is affected most only in the case of TBPA.

3. Detrapping rate constants

Using the method by Fayer and Harris²⁶ we measured detrapping rate constants k_d of the X traps from the ratios of

TABLE IV. Detrapping rate constants k_d^0 of the naphthalene X traps.

Perturber	k_d^0/s^{-1}
β -bromonaphthalene ^a	$3.5 \pm 1.0 \times 10^{11}$
β -chloronaphthalene ^a	$1.0 \pm 0.5 \times 10^{11}$
5-bromoindole	$1.2 \pm 0.5 \times 10^{12}$
5-chloroindole	$2.0 \pm 1.0 \times 10^9$
<i>p</i> -dibromobenzene	$1.0 \pm 0.5 \times 10^9$

^a Reference 25.

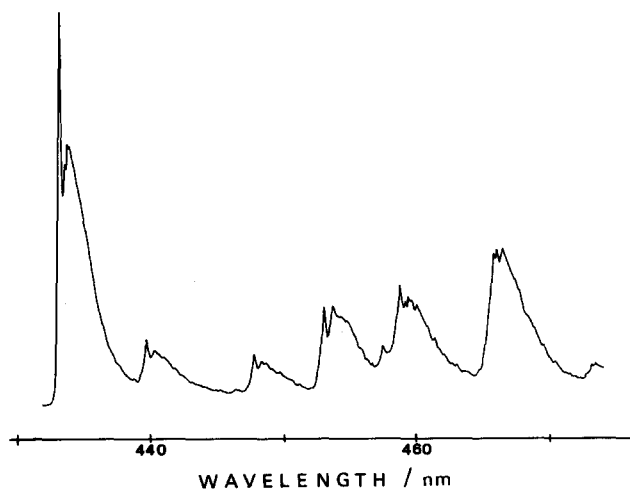


FIG. 5. Phosphorescence spectrum of the biphenyl X trap induced by 2-bromofluorene at 4.2 K.

the phosphorescence intensities of the shallow traps (naphthalene X traps) and the deep trap (4-bromoisoquinoline). The intensity of the deep trap is used as the reference for the temperature-independent process. These ratios, and therefore k_d , vary with temperature as shown in Fig. 4. As k_d is obtained by the equation $k_d = k_d^0 \exp(-\Delta\epsilon/kT)$ a preexponential factor k_d^0 is obtained from the slope of the curve. The obtained k_d^0 are listed in Table IV. From the table we surely recognize that there exists a heavy atom effect on the detrapping process. In the case of 5-bromoindole k_d^0 is remarkably larger than others.

B. Biphenyl X traps

We examined the biphenyl X traps induced by similar heavy atom containing dopants. In the biphenyl hosts phosphorescence spectra usually consist of two spectra; one very sharp and the other broader. A typical spectrum of the biphenyl X trap is shown in Fig. 5 for the case of 2-bromofluorene. All properties were measured at the origins of the sharper spectra. The vibronic structures of the spectra are very similar to that observed for biphenyl- h_{10} in biphenyl- d_{10} .²⁹ The phosphorescence from the neat crystal is moderately strong and the triplet lifetime is 3.65 s.

The trap depths are summarized in Table V. The phosphorescence decay curves were measured at 4.2 K and were analyzed by single exponentials. The heavy atom effect is

again clearly seen in these cases, although magnitudes of the effects in the biphenyl X traps are much smaller than those in the naphthalene X traps. The total decay rate constants range from 0.24 to 4.2 s⁻¹. Indole and fluorene derivatives provide larger effects.

IV. DISCUSSION

A. Systems and mechanisms

As mentioned in the previous section sharp phosphorescence spectra due to only one kind of X traps are observed at low concentration in the naphthalene X traps. This means that phosphorescence comes from a well defined trap. Based on the EPR and ENDOR experiments Wolf and Schmid^{30,31} suggested that β -halonaphthalene induces a X trap at the nearest nonequivalent sites in a unit cell as shown in Fig. 1. The directions of the fine structure tensors of the X traps coincide with those of normal naphthalene with 10° in the cases of halobenzenes¹⁸ and halonaphthalenes.^{30,31} Since all the naphthalene X traps give well resolved phosphorescence spectra, we assume that well defined X traps are produced by similar substitutions at the nearest nonequivalent sites even in other systems. The notable features of the present systems are the following: The perturbed naphthalene and the heavy atom perturbers have well defined configurations. The decay and spectroscopic data can be obtained for many different kinds of perturbers, still maintaining similar trap configurations. Therefore, the effect of the different perturbers can be compared directly under similar conditions. These features were not realized in the previous experiments using heavy atom solvents and heavy atom hosts. We now compare the results obtained for different perturbers in view of the mechanisms.

We briefly summarize the mechanisms of the external heavy atom effect on the $T_1 \rightarrow S_0$ radiative decay processes, originally proposed by Robinson.¹⁷ When we consider a weakly interacting pair composed of X trap naphthalene X and a heavy atom perturber p , the mechanism of the external heavy atom effect is represented by the following scheme

$$\begin{aligned} & |T_1(X)S_0(p)\rangle \xrightarrow{H_{\text{int}}} |S_0(X)T_1(p)\rangle \xrightarrow{H_{\text{so}}(p)} \\ & |S_0(X)S_0(p)\rangle \xrightarrow{eF} |S_0(X)S_0(p)\rangle, \end{aligned} \quad (1)$$

where H_{int} and $H_{\text{so}}(p)$ are Hamiltonians for intermolecular interactions and for spin-orbit couplings in perturber mole-

TABLE V. Phosphorescence properties of the biphenyl X traps and the heavy atom perturbers.

Perturber	Biphenyl X trap $k(X)/s^{-1}$	Perturber $k(p)/s^{-1}$	$\Delta E_{TT}/\text{cm}^{-1}$ ^a
2-bromofluorene	4.2	52.6	200
9-bromofluorene	0.48	1.54	400
5-bromoindole	0.86	31.3	1540
5-chloroindole	0.24	1.18	1540
<i>p</i> -dibromobenzene	0.42	3330	4300
bromocyclohexane	0.30

^a $\Delta E_{TT} = E_{T_1}(\text{perturber}) - E_{T_1}(\text{exciton})$.

cules, respectively. This scheme shows that naphthalene X traps borrow their phosphorescence intensities from those of heavy atom perturbers. A crucial point about this mechanism is to identify the perturber triplet states $T_i(p)$. In the

$$\Delta k^r(X) = \frac{64\pi^4\nu^3(X)}{3hc} \sum_i \sum_j \left| \frac{\langle T_i(X) | H_{\text{int}} | T_i(p) \rangle}{E_{T_i(p)} - E_{T_i(X)}} \frac{\langle T_i(p) | H_{\text{so}} | S_j(p) \rangle \langle S_j(p) | \text{er} | S_0(p) \rangle}{E_{S_j(p)} - E_{T_i(X)}} \right|^2, \quad (2)$$

where $|T_i(X)S_0(p)\rangle$ and $|S_0(X)T_i(p)\rangle$ are abbreviated by $|T_i(X)\rangle$ and $|T_i(p)\rangle$, respectively. If we assume that only one triplet state m is important as the main perturbing state, Eq. (2) is rewritten by a simple equation

$$\Delta k^r(X) = \frac{\nu^3(X)}{\nu^3(p)} k^r(p_m) \left| \frac{\langle T_i(X) | H_{\text{int}} | T_m(p) \rangle}{E_{T_m(p)} - E_{T_i(X)}} \right|^2. \quad (3)$$

Here the radiative decay rate constant $k^r(p_m)$ of the m state of the perturber is given by

$$k^r(p_m) = \frac{64\pi^4\nu^3(p)}{3hc} \sum_j \left| \frac{\langle T_m(p) | H_{\text{so}} | S_j(p) \rangle}{E_{S_j(p)} - E_{T_m(p)}} \times \langle S_j(p) | \text{er} | S_0(p) \rangle \right|^2, \quad (4)$$

$k^r(p_m)$ is related to the total decay rate constant $k(p_m)$ by the equation $k^r(p_m) = f \cdot k(p_m)$.

We further extend this theory to include the effect on the triplet sublevels. When we use Eq. (3) and the fact that intermolecular interaction H_{int} does not include an electron spin part, we obtain enhancements for the radiative decay rate constants of the triplet sublevels as

$$\Delta k_i^r(X) = C \sum_j \cos^2 \theta_{ij} k_j^r(p_m) \quad (i, j = x, y, \text{ and } z). \quad (5)$$

Here θ_{ij} is the angle between the fine structure (fs) i axes of the ${}^3\pi\pi^*$ X trap naphthalene and the fs j axes of the triplet state perturbers. C is a constant which depends on the magnitude of intermolecular interaction.

B. Estimation of radiative enhancement

The result that the phosphorescence intensities are still strong despite shortening of the triplet lifetimes suggests that the $T_1 \rightarrow S_0$ radiative decay rate constants $k^r(X)$ are surely enhanced by heavy atom perturbers. These values, however, cannot be obtained by the usual method, because quantum yields of phosphorescence Φ_p cannot be obtained in the single crystalline systems. Here we estimate $k^r(X)$ by comparing the phosphorescence spectra in the light atom systems (indole and p -dichlorobenzene) and those in the heavy atom systems as the following.

We notice that the intensities of the nontotally symmetric bands are extremely weakened by the heavy atom perturbers; the 0-0 and a_{1g} bands increase their phosphorescence intensities much more than the nontotally symmetric bands. This result is consistent with the previous works^{1,2} and is interpreted by the fact that the heavy atom effect on the vibronic bands of nontotally symmetric vibrations involves higher order terms than that for the 0-0 and totally symmetric bands. If we assume that the nontotally symmetric (nt) band is not affected at all by the heavy atom per-

later section we consider three possible states, atomic states, CT states, and molecular states. Using second order perturbation theory and the mechanism (1) we obtain enhancements of radiative decay rate constants $\Delta k^r(X)$ by

turbars, we can estimate a lower limit for the enhancement of the radiative decay rate constant $k^r(X)_{\text{min}}$ by the equation

$$k^r(X)_{\text{min}} = k^r_{\text{naph}} \times \frac{I_{\text{nt}}(\text{naph})/I_{0-0}(\text{naph})}{I_{\text{nt}}(X)/I_{0-0}(X)}. \quad (6)$$

Since the 0-0 and totally symmetric (ts) bands are dominant both in the light and heavy atom systems, we replace $k^r(X)$ by $\sum_{\text{ts}} k^r_{\text{ts}}(X)$. Using Eq. (6), $k^r_{\text{naph}} = 0.028 \text{ s}^{-1}$,³² and the values of I_{nt}/I_{0-0} (Table II), we obtain 1.4, 6.6, and 13.8 s^{-1} for $k^r(X)_{\text{min}}$ of the s -tetrabromobenzene, 5-bromoindole, and 3-bromoquinoline systems, respectively. These values are nearly one half of the total decay rate constants of these systems. Furthermore, as the enhancements of the nontotally symmetric bands are also expected by an amount of 1%–3% of those for totally symmetric bands, actual $k^r(X)$ are larger than $k^r(X)_{\text{min}}$ estimated above. Therefore, we conclude that enhancements in the total decay rate constants of the heavy atom systems are mostly due to radiative enhancements; $k(X) \approx k^r(X)$. This result is consistent with the previous reports that only radiative decay rate constants are enhanced by the perturbers of the third group,^{1,2} contrast to the cases of the first and second groups.^{13,33} For the latter two groups the external heavy atom effect on both the radiative and nonradiative $T_1 \rightarrow S_0$ decay processes have been observed as in the case of an internal heavy atom effect.

C. Main perturbing state

1. Naphthalene X traps

In this section we try to determine the main perturbing states of heavy atom perturbers and discuss the magnitudes of the enhancements in terms of Eqs. (2), (3), and (5). We have classified perturbers into three groups in Sec. I. We first compare the external heavy atom effects among these three groups. We examine bromocyclohexane and ethyl iodide, and many aromatic halides as representatives of the first and third groups, respectively. TBPA is classified into the second (CT) group because the ZFS of this case was obviously smaller ($D \sim 2775$, $E \sim 385$ MHz) than those of the other cases ($D \sim 2950$, $E \sim 470$ MHz).

From Table I we easily notice that the perturbers of the first group (bromocyclohexane and ethyl iodide) are less effective as heavy atom perturbers than those of the corresponding perturbers of the third group (bromobenzenes and p -diiodobenzene). The magnitudes of the enhancements in the former are about one tenth of those of the latter. In this group only molecular states of higher energies ($\sigma\sigma^*$ type) or/and atomic states of heavy atoms are involved and these states are less effective. We also find that TBPA (second group) behaves normally as one of the aromatic halides; the enhancement in $k(X)$ is not much larger or smaller than those

TABLE VI. Sublevel properties of the heavy atom perturbers.

Perturber	Host		k_i/s^{-1}	$k'_i(0-0)$	D/MHz	E/MHz
β -bromonaphthalene	durene	T_z	70.8	1.0	3320	- 380
		T_y	147.8	0.08		
		T_x	4.2	0.05		
3-bromoquinoline	durene	T_z	78.7	1.0	3505	- 455
		T_y	129.5	0.13		
		T_x	3.3	0.05		
p -dibromobenzene ^a	p -xylene	T_z	264	1.0	8049	- 1799
		T_y	2560	4.3		
		T_x	118	1.0		
s -tetrabromobenzene ^b	durene	T_z	820	2	10141	- 3039
		T_y	1053	0		
		T_x	76.3	0.1		
5-bromoindole	durene	T_z	44.0	1.0	3200	- 1400
		T_y	64.0	0.93		
		T_x	1.7	0.02		

^aG. Kothandaraman and D. S. Tinti, Chem. Phys. Lett. **19**, 225 (1973).

^bA. H. Francis and C. B. Harris, J. Chem. Phys. **57**, 1050 (1972).

of similar aromatic halides of the third group. This fact indicates that an introduction of a CT character does not cause an additional enhancement. Therefore, we conclude that the molecular states of lower energies ($\pi\pi^*$ type) are much more important as perturbing states than the atomic states, $\sigma\sigma^*$ states and CT states for aromatic halides.

Next we discuss the validity of this conclusion in terms of the energy differences, radiative activities, and sublevel properties. From Eqs. (2) and (3) we expect a correlation between the magnitudes of the effect and the energy differences $\Delta E_{T_m T_1} [=E_{T_m}(p) - E_{T_1}(X)]$. This expectation is qualitatively realized in the result that perturbers of the naphthalene skeleton (naphthalene and quinoline) provide greater effects than those of benzene skeleton. When we take $T_m(p)$ as the lowest triplet state of the perturber $T_1(p)$, we find a very nice correlation between $\Delta k(X) [=k(X) - k(\text{naph})]$ and $\Delta E_{T_m T_1}$. This seems to indicate that the T_1 states of the perturbers are most effective in this effect.

Another factor which influences heavy atom enhancements is the radiative activities of the triplet perturbers $k'(p_m)$. This correlation is also seen in the result that the heavier the heavy atoms (I > Br > Cl) the more effective is the enhancement. A difference in the effects between bromobenzenes and α, α' -dibromo- p -xylene is also attributed to that in the radiative activity; the formers are more radiative because of a larger internal heavy atom effect. When we attend to the decay rate constants of the X traps induced by different bromobenzenes $\Delta k(\text{DBB}) > \Delta k(\text{TBB}) > \Delta k(\text{TRBB})$. We find a nice correlation between $\Delta k(X)$ and the decay rate constants of the T_1 perturbers $k(p_{T_1})$; $k(\text{DBB}) > k(\text{TBB}) > k(\text{TRBB})$. These results again support the importance of the lowest excited triplet state.

The above conclusion is further supported by the results of the sublevel properties as the following. We derived Eq. (5) for the heavy atom effects on the sublevel decay rate constants. If we know the values of $k'_j(p_m)$ ($j = x, y, \text{ and } z$) and θ_{ij} , we can estimate the values of $k'_i(X)$ ($i = x, y, \text{ and } z$). If

the T_1 state is the main perturbing state, $k'_j(p_m)$ is obtained as $k'_j(p_{T_1})$ of the triplet states of the perturbers determined by the MIDP technique (Table VI). θ_{ij} are estimated from the crystallographic data of naphthalene³⁴ with the assumption that the fine structure axes of the perturber and those of the X -trap naphthalene are parallel to each molecular axis. From these data of $k'_j(p_{T_1})$ and θ_{ij} we estimated the relative values of $k'_i(X)$ as shown in Table VII. Agreements between the experimental and predicted $k'_i(X)$ are satisfactory, although we completely neglected deviations of the axes of the X -trap molecules and perturbers from those of naphthalene in the single crystal and the contributions due to the higher triplet states of the perturbers.

The observations described above show the importance of the lower excited states, especially the T_1 states of the perturber molecules in the external heavy atom effect.

TABLE VII. Observed and calculated relative radiative decay rate constants of the sublevels in the naphthalene X traps.

Perturber		$k'_i(0-0)_{\text{obs}}$	$k'_i(X)_{\text{cal}}$
β -bromonaphthalene	T_z	1.0	1.0
	T_y	0.56	0.23
	T_x	0.20	0.13
3-bromoquinoline	T_z	1.0	1.0
	T_y	0.30	0.25
	T_x	0.10	0.17
5-bromoindole ^a	T_z	1.0	1.0
	T_y	0.53	0.53
	T_x	0.58	0.70
p -dibromobenzene	T_z	≤ 0.15	0.49
	T_y	≤ 0.25	0.63
	T_x	1.0	1.0
s -tetrabromobenzene	T_z	1.0	1.0
	T_y	≤ 0.50	0.21
	T_x	≤ 0.30	0.07

^aThe fine structure axes were presumed to be the same as those of indole.

2. Biphenyl X traps

In the biphenyl X -traps heavy atom effects are also observed as shown in Table V, though magnitudes are not so large compared with those of the naphthalene X traps. Aliphatic halides (bromocyclohexane) and chloroderivatives (5-chloroindole) are not effective heavy atom perturbers just as in the cases of the naphthalene X traps. A qualitative correlation between $\Delta k(X)$ and ΔE_{TT} is nicely seen in the results of p -dibromobenzene, 5-bromoindole, and 2-bromofluorene; the values of $\Delta k(X)$ and $1/\Delta E_{TT}$ increase in this order. A correlation between $\Delta k(X)$ and $k(p_T)$ is also observed in the results of 2-bromofluorene (240 ms) and 9-bromofluorene (2030 ms); the T_1 state of the former ($\tau_p \sim 19$ ms) is more radiative than that of the latter ($\tau_p \sim 650$ ms) because of the larger intramolecular heavy atom enhancement.

These results are very similar to those found for the naphthalene X traps. Therefore, the phenomena observed in the naphthalene X traps are considered to be general in the X -trap systems. We have again concluded that the T_1 states of perturbers are the most important perturbing states for the aromatic halide perturbers.

D. Contributions of other perturbing states

1. Atomic states

We have concluded that the atomic states are less effective perturbing states for aromatic halides. But for aliphatic halides they might play important roles as perturbing states. If the atomic states are the main perturbing states in these cases we can estimate their magnitudes of enhancements from the results of $k(X)$ (Table I). The total decay rate constants of the bromocyclohexanes and ethyl iodide systems are about one tenth of those of the bromobenzenes and p -diiodobenzene systems, respectively. Therefore, we estimate that the atomic states are less effective by a factor of ~ 10 than the molecular states of lower energies of the halobenzene perturbers. As contributions from atomic states do not vary so much from molecule to molecule, they become much less effective for the halonaphthalene perturbers.

We found that ethyl iodide exerted a remarkably selective influence on the triplet sublevels of naphthalene ($k_z^r:k_y^r:k_x^r = 0.12:0.27:1.0$). This selective enhancement could be caused by the preferable configuration for the naphthalene

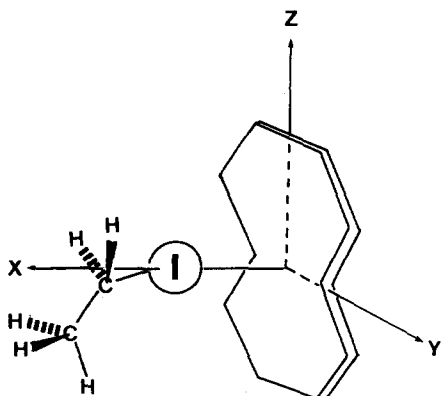


FIG. 6. Proposed structure of the naphthalene X trap induced by ethyl iodide. See the text in Sec. IV D 1 in detail.

and ethyl iodide pair in the crystal. Weinzierl and Freidrich³ have discussed the external heavy atom effects on aromatic molecules, where they derived equations for matrix elements of spin-orbit couplings, paying attention to overlaps between atomic orbitals of heavy atoms and π orbitals of aromatic molecules. They obtained a symmetry rule for each sublevel; T_x is always affected by heavy atoms regardless of the configurations of pairs. T_z and T_y are affected only when heavy atoms are located in the ZX and YX planes of aromatic molecules, respectively, but both are not affected when heavy atoms are located at the center of molecules. Following this result our observation that k_x is dominantly enhanced seems to indicate that the iodine atom of ethyl iodide locates very close to the center position of the naphthalene molecule as shown in Fig. 6.

2. CT states

In the case of TBPA we observed two kinds of traps which involve different CT characters. One (trap I) is just similar to the other X traps, showing a phosphorescence spectrum of naphthalene with a triplet lifetime of 79 ms. The other (trap II) is different from others, showing a broad and structureless phosphorescence spectrum with a large red shift ($\lambda_{\max} \sim 535$ nm) and a triplet lifetime of 26 ms, which are characteristics of a pronounced CT character. The difference between the two traps must be due to that in magnitudes of intermolecular (CT) interactions. In the latter case a pair of the molecules take a more preferable (probably parallel) configuration and larger intermolecular interactions are expected. However, in the former case intermolecular interactions are not so large. Therefore, CT states are considered to be important in the external heavy atom effect only when intermolecular (CT) interactions are large.

We found an interesting result for the radiative decay rate constants $k_i^r(X)$ of the triplet sublevels of the trap I system, where the T_y sublevel was most affected by TBPA. Using Eq. (5) and the values of $k_i^r(X)$ and θ_{ij} the radiative ratio of triplet TBPA is predicted to be as $k_z^r:k_y^r:k_x^r = 0.4:0:1$. This result that T_x is most radiative in TBPA is not expected unless triplet TBPA is very distorted towards the out of plane vibrational mode. Since this possibility is highly unlikely, we prefer another possibility that the configuration of the trap I is different from those of the other traps and θ_{ij} used here are not appropriate. The pair of trap I might take a more parallel configuration to obtain a larger CT character.

E. Detrapping process

The external heavy atom effect on the detrapping process was examined in the naphthalene X trap systems. As shown in Table IV the temperature independent parts k_d^0 of the detrapping rate constants vary from 10^9 to 10^{12} s⁻¹ depending on the heavy atom perturber. By comparing chloro and bromo derivatives we find that k_d^0 are surely enhanced by heavy atom perturbers. In this section we discuss the mechanisms of this phenomenon in terms of trap-phonon and trap-exciton interactions.

According to Fayer and Harris²⁶ k_d^0 is expressed by the equations

$$k_d^0 = \sum_{\kappa} \sum_{E_0 > E_{\alpha}} L_{E_0 \kappa}, \quad (7)$$

$$L_{E_0 \kappa} = (2\pi/\hbar) |\langle \tau P(E_0) | H_{TP} | \tau_{\alpha} P(E_0 - E_{\alpha}) \rangle \times \langle \tau_{\alpha} P(E_0 - E_{\alpha}) | H_{TE} | \kappa P(E_0 - E_{\alpha}) \rangle|^2 \rho(E_{\alpha}), \quad (8)$$

H_{TP} and H_{TE} are Hamiltonians for trap-phonon and trap-exciton interactions, respectively. $|P(E_0)\rangle$ is a wave function of phonon with energy E_0 and $\rho(E_{\alpha})$ denotes an exciton density-of-state function evaluated at E_{α} , an energy difference between a trap τ and a band state. Equations (7) and (8) show that detrapping processes proceed with two steps; a trap τ interacts with its phonon band τ_{α} through the trap-phonon interactions and then detraps into a specific band state κ through the trap-exciton interactions.

Therefore, the observed heavy atom effect on k_d^0 must be due to the enhancements in the trap-phonon and/or trap-exciton interactions. Although we do not know exactly which is more effective in these processes, we know that the trap-phonon interactions are apparently increased by heavy atom perturbors from the phosphorescence spectra. The relative intensities of the phonon bands $I_{\text{phonon}}/I_{0-0}$ are enhanced in the heavy atom systems as shown in Fig. 3. A nice correlation between k_d^0 and $I_{\text{phonon}}/I_{0-0}$ is seen in these results where both values are larger in the 5-bromoindole and β -bromonaphthalene systems. From these results we can conclude that the intermolecular interactions including the trap-phonon interactions are surely enhanced in the heavy atom systems.

F. Magnitudes of intermolecular interactions

When we use Eq. (3) with the optical data measured for the T_1 states of the perturbors and put $f = 0.2$ (benzene; 0.22, indole; 0.19, quinoline; 0.19, naphthalene; 0.064³²) we can estimate the matrix elements of the intermolecular interactions. The results are shown in Tables VIII and IX for the naphthalene and biphenyl X traps, respectively. The magnitudes of $\langle H_{\text{int}} \rangle$ are smaller in the biphenyl systems being consistent with the result that the external heavy atom effect is less effective in these systems. We also find that magnitudes obtained here are much larger than those ($\leq 100 \text{ cm}^{-1}$) obtained from measurements of factor groups or Davydov splittings, although the latter values have been obtained for light atom hosts such as naphthalene and benzene.^{35,36} The value of $\langle H_{\text{int}} \rangle$ for the 5-bromoindole-naphthalene system is especially large. We discuss possible sources for large $\langle H_{\text{int}} \rangle$ estimated here.

TABLE VIII. Magnitudes of the intermolecular interactions in the naphthalene X traps.

Perturber	$\langle H_{\text{int}} \rangle / \text{cm}^{-1}$
β -bromonaphthalene	150
3-bromoquinoline	440
5-bromoindole	6000
<i>p</i> -dibromobenzene	660
<i>s</i> -tetrabromobenzene	780
<i>s</i> -tribromobenzene	680

TABLE IX. Magnitudes of the intermolecular interactions in the biphenyl X traps.

Perturber	$\langle H_{\text{int}} \rangle / \text{cm}^{-1}$
2-bromofluorene	45
9-bromofluorene	210
5-bromoindole	470
<i>p</i> -dibromobenzene	95

We first note a relation between the heavy atom effect on the $T_1 \rightarrow S_0$ decay and that on the detrapping rate. It was concluded that the intermolecular interactions including trap-phonon interactions were enhanced in the heavy atom effect on the detrapping rate. A similar enhancement is considered to be important in the $T_1 \rightarrow S_0$ decay process. The large detrapping rate and large $\langle H_{\text{int}} \rangle$ found for the 5-bromoindole system is indicative of a connection between the detrapping rate and the external heavy atom effect on the $T_1 \rightarrow S_0$ decay process.

The importance of the trap-phonon interactions in the external heavy atom effect has been discussed by Law and Prasad.³⁷ They obtained an equation for the heavy atom enhancement of the radiative decay rate constant $\Delta k^r(X)$ as

$$\Delta k^r(X) = \sum_m \frac{\nu^3(X)}{\nu^3(p)} \left| \frac{\langle T_1(X) | H_{\text{int}} | T_1(p) \rangle}{E_{T_1}(p) - E_{T_1}(X)} \right|^2 \times k^r(p) \exp(-\gamma_{T_1}) \left(\frac{\gamma_{T_1}^m}{m!} \right), \quad (9)$$

where γ and m denote coefficients for magnitudes of electron-phonon couplings and a distribution of phonons, respectively. Comparing Eq. (9) with Eq. (3) we find that Eq. (3) gives rise to enhancements in zero phonon lines of phosphorescence. As shown in Fig. 3 we notice that the intensities of the zero phonon bands are rather weaker than those of the phonon bands in the heavy atom systems. Therefore, the values observed for $k^r(X)$ are much larger than those expected from Eq. (3), and H_{int} estimated from this equation are expected to be larger. From the experimental results, however, it is not possible to separate the enhancement due to the trap-phonon interaction from that due to the purely electronic interactions between the perturber and X trap naphthalene. The latter may also be enhanced significantly in the heavy atom systems.

We consider other possible sources of large $\langle H_{\text{int}} \rangle$. Contributions from interactions with higher triplet states of perturbors are also considered to be a possible source of larger $\langle H_{\text{int}} \rangle$. Particularly, in halobenzenes where $^3\sigma\pi^*$ states are considered to be close to the $T_1(\pi\pi^*)$ states,³⁸ they may make significant contributions. However, we do not think that these higher triplet states contribute heavily to these effects because the sublevel data clearly support the importance of the T_1 states. Furthermore for the perturbors of small $\Delta E_{T_1, T_2}$ (naphthalenes, indoles, and quinolines) the $\Delta E_{T_m, T_1} [\equiv E_{T_m}(p) - E_{T_1}(X) (m \neq 1)]$ are much larger than $\Delta E_{T_1, T_2}$ and the contribution from the higher triplet state is likely to be small.

CT interactions may contribute to larger $\langle H_{\text{int}} \rangle$. The value of $\langle H_{\text{int}} \rangle$ is calculated as $\sim 1100 \text{ cm}^{-1}$ for the TBPA-

naphthalene system (trap II) where the CT interactions were really observed. This value is a little bit larger than those of others (Table VIII) except the case of 5-bromoindole. The difference in $\langle H_{int} \rangle$ between the TBPA (trap II) and the other systems may be due to that in CT character. Therefore, we can conclude that CT interactions are important for TBPA, but are less important in almost all other systems where the phosphorescence and ZFS show no measurable CT character.

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