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Relations between Intramolecular Energy Transfer Efficiencies and Triplet State Energies in Rare Earth β-diketone Chelates

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The fluorescence yield of europium chelates in several solutions varies, through its maximum value, with the increase in the energy difference between the triplet state of a ligand and the emitting level of an europium ion. The time-resolved spectroscopic measurements show that the excitation energy is transferred from the triplet state to the lower and nearest resonance level of the europium ion. The intramolecular energy transfer mechanisms for europium chelates and terbium chelates are proposed, taking the resonance exchange interaction and the thermal deactivation processes from the emitting levels of rare earth ions into consideration. Steady-state rate equations are made, and the equation of the fluorescence yield is obtained. Thus, the relations between the fluorescence yield and the triplet state energy are estimated and the fluorescence properties of rare earth β-diketone chelates may be qualitatively described.

A number of europium and terbium β-diketone chelates give a narrow-band emission from the rare earth ion under near UV excitation, and some of these chelates exhibit laser action when dissolved in organic solvents.[1-3] The absorbed pump energy is transferred to a triplet state (by the intersystem crossing), and is then intramolecularly transferred to the rare earth ion.[4] Since this intramolecular energy transfer from the triplet state to the resonance level of the rare earth ion is of a spin-forbidden type, the energy is transferred by the resonant exchange interaction[5] and the role of the triplet state is very important. There have been some reports discussing the role of the triplet state, and it has been concluded that the excitation energy could not be transferred from the ligand to the rare earth ion if the triplet state of the ligand was below the resonance level of the rare earth ion.[4] However, few experimental

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[1] A. Lempicki and H. Samelson, *Phys. Lett.*, **4**, 133 (1963).

[2] M. L. Bhaumik, P. C. Fletcher, L. J. Nugent, S. M. Lee, S. Higa and C. L. Telk, *J. Phys. Chem.*, **68**, 1490 (1964).

[3] E. J. Schimitschek and R. B. Nehrich Jr., *J. Appl. Phys.*, **35**, 2786 (1964).

[4] G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).

[5] V. L. Ermolaev, V. G. Aleshin and E. A. Saenko, *Sov. Phys. Doklady (English Transl.)*, **10**, 1186 (1966).

studies have been done on the dependence of the energy transfer efficiency upon the triplet state energy. The fluorescence yield of rare earth *β*-diketone chelates varies widely depending on the temperatures, the solvents, the ligands, the central ions and bases, and, further, whether they are of a tris or a tetrakis form. Therefore, the dependence of the fluorescence yield upon the triplet state energy must be measured by changing only the energy level of the triplet state, maintaining the other conditions as constant as possible.

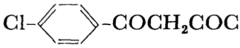
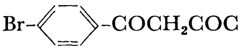
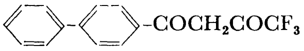
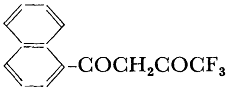
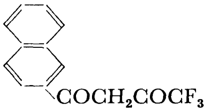
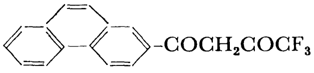
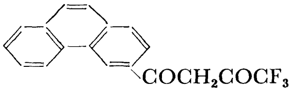
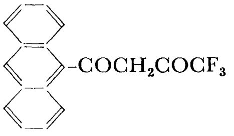
The europium *β*-diketone chelate derived from BTFA (benzoyltrifluoroacetone), which contains a benzene ring and a trifluoromethyl group, shows a high fluorescence yield of an europium-ion emission at room temperature. Many other *β*-diketone compounds similar to BTFA have been prepared in which the benzene ring was replaced by other aromatics, such as naphthalene, phenanthrene, and anthracene. The optical and fluorescent properties of europium chelates derived from substituted *β*-diketone compounds were measured.⁶⁾ The triplet state energy of these substituted *β*-diketone compounds is expected to be changed. In this paper, using europium and terbium chelates prepared from these substituted *β*-diketone compounds, the effects of the triplet state energy upon the energy transfer mechanism will be investigated and discussed.

Sample Preparation

The compounds discussed in the present article are listed, along with their abbreviation codes, in Table 1. In these *β*-diketone compounds, BTFA and TTA were obtained from Dotite reagents. All the other compounds were synthesized from the proper monoketone and ethyltrifluoroacetate by a manner reported previously.⁶⁾

The europium, terbium, and gadolinium *β*-diketone chelates were synthesized by ordinary piperidine methods. The analytical data of the rare-earth-metal contents for these chelates are shown in Table 2. It can be seen that all of the

TABLE 1. *β*-DIKETONE COMPOUNDS

Name	Code	Formula
Benzoyltrifluoroacetone	BTFA	
p-Chlorobenzoyltrifluoroacetone	PCBTFA	
p-Bromobenzoyltrifluoroacetone	PBBTFA	
p-Phenylbenzoyltrifluoroacetone	PPBTFA	
1-Naphthoyltrifluoroacetone	1NTFA	
2-Naphthoyltrifluoroacetone	2NTFA	
2-Phenanthoyltrifluoroacetone	2PTFA	
3-Phenanthoyltrifluoroacetone	3PTFA	
9-Anthroyltrifluoroacetone	9ATFA	
Cinnamoyltrifluoroacetone	CTFA*	
2-Thenoyltrifluoroacetone	TTA	

* This compound was derived from benzylideneacetone and had been named to BZDTFA previously.⁶⁾

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6) S. Sato, M. Wada and T. Seki, *Japan. J. Appl. Phys.*, **7**, 7 (1968).

TABLE 2. RARE EARTH β-DIKETONE CHELATES

Ligand	Eu-chelate %Eu_2O_3		Tb-chelate %Tb_4O_7		Gd-chelate %Gd_2O_3	
	Calcd*	Found	Calcd*	Found	Calcd*	Found
BTFA	16.2	14.5	17.1	17.2	16.4	16.2
TTA	15.9	16.4	16.8	14.6	16.1	17.6
PCBTFA	14.4	13.9	15.2	15.5	20.0**	23.2
PBBTFA	12.6	11.3	13.3	13.7	17.4**	15.3
PPBTFA	12.7	12.4	13.4	14.8	12.9	13.2
1NTFA	13.7	14.2	19.6**	18.2	19.0**	17.0
2NTFA	13.7	14.7	14.5	15.0	13.9	14.1
2PTFA	11.9	11.0	12.5	13.2	16.4**	20.9
3PTFA	11.9	11.0	16.9**	16.3	16.4**	15.4
9ATFA	11.9	11.3	12.5	12.3	12.1	12.7
CTFA	14.8	14.3	15.6	16.7	20.6**	21.6

* Calculated as the tetrakis form, (HQ) R.E. (β-diketone)$_4$ R.E.=rare earth ion, Q=pyrrolidine for europium and terbium chelates, piperidine for gadolinium chelates

** Calculated as the tris form, R.E.(β-diketone)$_3$

europium chelates and most of the terbium chelates are of the tetrakis form, (HQ)R.E.(β-diketone)$_4$ (Q=pyrrolidine, R.E.=Eu or Tb), but the gadolinium chelates are of the tetrakis form or the tris form, R.E.(β-diketone)$_3$ (R.E.=Gd), or a mixture of these two forms.

Results and Discussion

Triplet State Energy of β-Diketones. The phosphorescence spectra of gadolinium chelates were measured at 77°K in an EPA solution (5 parts diethylether, 5 parts isopentane, and 2 parts ethanol by volume). The exciting light source was a combination of a high-pressure Hg lamp and a UV-DIB bandpass filter (300—400 mμ transmission range). The phosphorescence band emission of gadolinium chelates was strong, and two or three clearly-defined bands were observed for most of the chelates investigated. The shortest-wavelength phosphorescence band was assumed to be the 0–0 transition7), and the triplet state energy was determined. The results are summarized in Table 3. However, the phosphorescence of $Gd(CTFA)_3$ was so weak that it was very difficult to determine the triplet state energy exactly. The resonance levels of europium and terbium ions and the triplet state of each β-diketone compound listed in Table 3 are shown in Fig. 1.

TABLE 3. TRIPLET STATE ENERGY OF GADOLINIUM β-DIKETONATES

Compound	Triplet state (cm^{-1})
BTFA	21400
PCBTFA	21300
PBBTFA	21200
2PTFA	20600
PPBTFA	20400
TTA	20300
3PTFA	19800
2NTFA	19600
1NTFA	19400
CTFA	~17500
9ATFA	13600

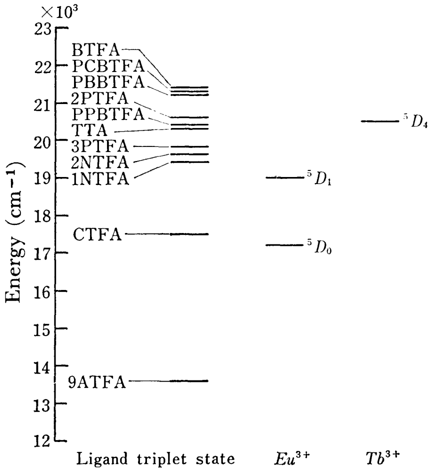

Fig. 1. Triplet states of β-diketonates and related levels of europium and terbium ions.

Europium chelates prepared from the β-diketone compounds, the triplets state of which is above the $^5D_0$ level of the Eu^{3+} ion, emit the intense fluorescence of the Eu^{3+} ion at room temperature, but $Eu(CTFA)_4^-$ fluoresces only at relatively low temperatures. $Eu(9ATFA)_4^-$ does not fluoresce even at the temperature of liquid nitrogen. On the other hand, terbium β-diketone chelates derived from the β-diketone with a triplet state higher than that of TTA emit the fluorescence of the Tb^{3+} ion at low temperatures, but no other terbium

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7) W. F. Sager, N. Filipescu and F. A. Serafin, *J. Phys. Chem.*, **69**, 1092 (1965).

chelates fluoresce.

Relation between the Fluorescence Yield and the Triplet State Energy. Measurements of the fluorescence quantum yields were made at room temperature by a method similar to one reported previously.[6] The relations between the fluorescence quantum yields at room temperature and the energy difference between the ligand triplet state and $^5D_1$ level of the Eu^{3+} ion are plotted for several solutions in Fig. 2. It can be seen that the fluorescence yield varies through its maximum value as the energy difference becomes larger. In terbium chelates, the fluorescence was nearly quenched at room temperature; therefore, a relation such as that shown in Fig. 2 could not be obtained. These results will be discussed in detail later.

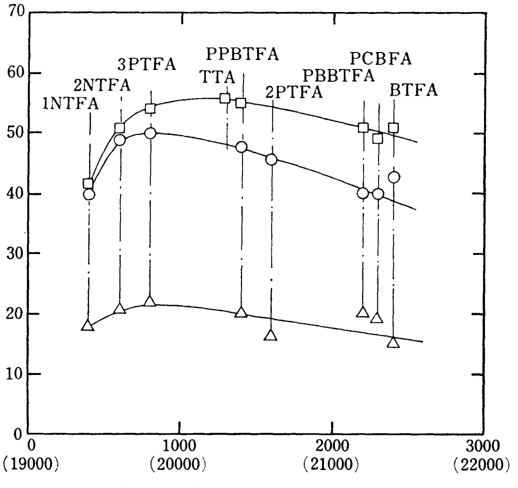

Fig. 2. Relations between fluorescence yields of europium β-diketone chelates and the energy difference between the ligand triplet state and the $^5D_1$ level of the Eu^{3+} ion.
□: acetonitrile solution
△: alcohol solution
○: dimethylformamide solution

Temperature Dependences of Fluorescence Lifetimes. The fluorescence lifetimes of the europium and terbium chelates were obtained by a stroboscopic method[6]; their values were of the order of 10^{-3}—10^{-4} sec. The normalized temperature dependences of the fluorescence lifetimes of europium and terbium β-diketone chelates are shown in Fig. 3. It can be seen that the quenching temperature moves toward the higher-temperature region as the energy difference between the triplet state of the ligand and the emitting level of the rare earth ion becomes larger. The temperature dependence of the fluorescence intensities showed thermal quenching properties quite similar to those of the temperature dependence of the fluorescence lifetimes.

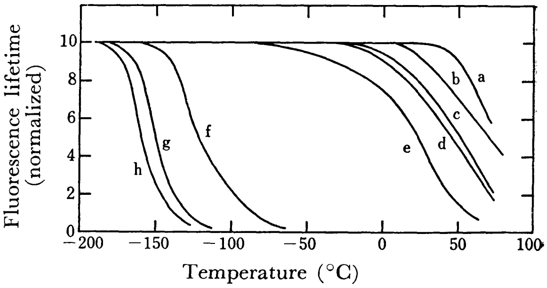

Fig. 3. Temperature dependences of fluorescence life-times. (europium chelates (a)~(e): powders, terbium chelates (f)~(h): EPA solutions)

(a): $(HQ)Eu(BTFA)_4$	(f): $Tb(BTFA)_4^-$
(b): $(HQ)Eu(PPBTFA)_4$	(g): $Tb(PPBTFA)_4^-$
(c): $(HQ)Eu(TTA)_4$	(h): $Tb(TTA)_4^-$
(d): $(HQ)Eu(2NTFA)_4$	
(e): $(HQ)Eu(1NTFA)_4$	

Q = pyrrolidine

Time-resolved Spectroscopy. Time-resolved spectroscopy was carried out by a stroboscopic technique similar to that described by Bhaumik *et al.*[8] The resolution time of our apparatus was about 0.3 μsec. Figures 4 (a) and (b) show the time-resolved spectra of $Eu(BTFA)_4^-$ in an acetonitrile solution at room temperature and of $Eu(CTFA)_4^-$ in an EPA solution at 77°K. For most europium chelates with the same properties as that of $Eu(BTFA)_4^-$, the emission due to the $^5D_0\rightarrow{}^7F$ transition begins to build up as the emission due to the $^5D_1\rightarrow{}^7F$ transition begins to decrease. On the other hand, the emission from the $^5D_1$ level of

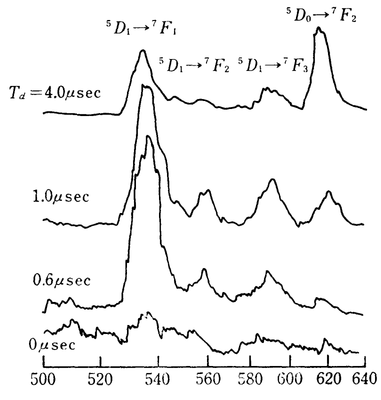

Fig. 4(a). Time-resolved spectra for (HQ)Eu(BTFA)$_4$ Q = pyrrolidine in acetonitrile solution at room temperature.
The delay time after the flash of exciting light is given by T_d.

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8) M. L. Bhaumik, G. L. Clark, J. Snell, and L. Ferder, *Rev. Sci. Instr.*, **36**, 37 (1965).

[*1] The same phenomenon was observed in $Eu(1NTFA)_4^-$ at room temperature; this will be discussed elsewhere.

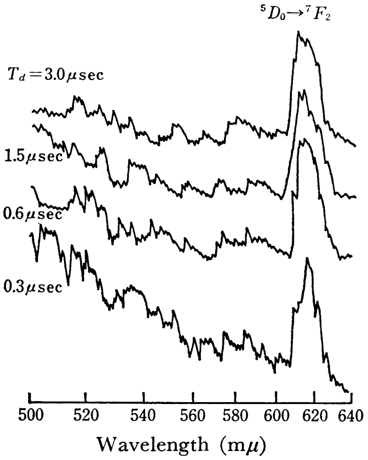

Fig. 4(b). Time-resolved spectra for (HQ)Eu-(CTFA)$_4$ (Q=pyrrolidine) in EPA solution at 77°K.
The delay time after the flash of exciting light is given by T_d.

Eu(CTFA)$_4^-$ can not be detected, and the rise time of the emission originating from the $^5D_0$ level is very short and is beyond the resolution time of the apparatus.*1 As can be seen in Fig. 1, the triplet state of CTFA exists between the $^5D_1$ level and the $^5D_0$ level of the Eu^{3+} ion, but the triplet states of all the other β-diketone compounds except 9ATFA are above the $^5D_1$ level. Therefore, in the europium chelates other than Eu(CTFA)$_4^-$, it may be concluded that the excitation energy is transferred from the ligand's triplet state to the $^5D_0$ level *via* the $^5D_1$ level of the europium ion. In Eu(CTFA)$_4^-$, it may be transferred directly from the triplet state to the $^5D_0$ level.

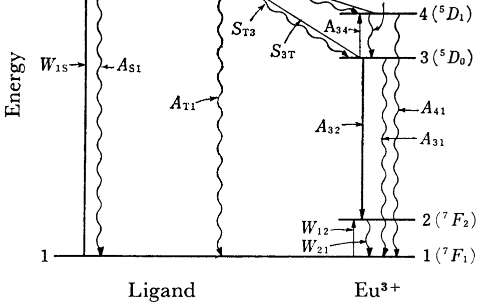

Fig. 5. Energy transfer diagram for europium chelates.

Intramolecular Energy Transfer Mechanism. The energy-level scheme to be used in describing the intramolecular energy transfer mechanism for europium chelates, is similar to that given by Samelson *et al.*[9]; it is shown in Fig. 5, where the wavy lines represent the energy transfer or the loss due to the radiative or nonradiative transition to the ground state, while the straight lines represent the absorption or the radiative transition due to $^5D_0\to{}^7F_2$ or thermal-deactivation processes. In this figure, the singlet state is denoted by S, the triplet state of a ligand is denoted by T, and the $^5D_1$, $^5D_0$, $^7F_2$, and $^7F_0$ levels of the Eu^{3+} ion are shown as 4, 3, 2, and 1 respectively. The transitions associated with the other levels have not been considered. The steady-state rate equations are:

$$\mathrm{d}N_S/\mathrm{d}t = W_{1S}N_1-(A_{S1}+S_{ST})N_S = 0 \tag{1}$$

$$\mathrm{d}N_T/\mathrm{d}t = S_{ST}N_S-(A_{T1}+S_{T4}+S_{T3})N_T+S_{4T}N_4 +S_{3T}N_3 = 0 \tag{2}$$

$$\mathrm{d}N_4/\mathrm{d}t = S_{T4}N_T-(A_{43}+A_{41}+S_{4T})N_4+A_{34}N_3 = 0 \tag{3}$$

$$\mathrm{d}N_3/\mathrm{d}t = S_{T3}N_T+A_{43}N_4 -(A_{32}+A_{31}+A_{34}+A_{3T})N_3 = 0 \tag{4}$$

$$\mathrm{d}N_2/\mathrm{d}t = A_{32}N_3+W_{12}N_1-W_{21}N_2 = 0 \tag{5}$$

$$N_0 = N_1+N_2+N_3+N_4+N_T+N_S \tag{6}$$

where W_{1S} is the transition probability for the absorption; where A_{S1}, A_{T1}, A_{41}, and A_{31} are loss probabilities due to the transitions from the excited states to the ground state; where S_{ST}, S_{T4}, and S_{T3} are the transition probabilities for radiationless processes; where A_{32} is the radiative transition probability for the europium fluorescence, and A_{43}, the transition probability for the decay from the $^5D_1$ level to the $^5D_0$ level; where W_{12} and W_{21} are the transition probabilities for the thermal and relaxation processes between the ground state and the terminal states, and where S_{T3}, S_{T4}, and A_{34} are the probabilities for the thermal-deactivation processes and are the inverse processes of S_{T3}, S_{T4}, and A_{43} respectively. The population of the jth state is denoted by N_j, and the total concentration of molecules, by N_0. Degenerations should be considered for each level; the thermal deactivation probabilities are, then, given by:

$$S_{4T} = S_{T4}\exp(-E_{T3}/\boldsymbol{k}T) \tag{7}$$

$$S_{3T} = 3S_{T3}\exp(-E_{T3}/\boldsymbol{k}T) \tag{8}$$

$$A_{34} = 3A_{43}\exp(-E_{43}/\boldsymbol{k}T) \tag{9}$$

where E_{T4}, E_{T3}, and E_{43} are the energy differences between the corresponding respective two levels. The fluorescence yield for the $^5D_0\to{}^7F_2$ transition is defined as follows:

$$\eta_{Eu} = A_{32}N_3/W_{1S}N_1 \tag{10}$$

Under the steady-state condition, the fluorescence yield, η_{Eu}, is obtained from Eqs. (1) to (10) as follows:

$$\eta_{Eu} = [1+(S_{T3}/S_{T4})(1+A_{41}/A_{43})+(S_{T3}/A_{43}) \times \exp(-E_{T4}/\boldsymbol{k}T)]/(1+A_{S1}/S_{ST})[(1+S_{T3}/S_{T4}$$

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[9] H. Samelson, A. Lempicki and C. Brecher, *J. Chem. Phys.*, **40**, 2553 (1964).

$$+ A_{T1}/S_{T4})(1+A_{41}/A_{43})(1+A_{31}/A_{32})$$
$$+ (1+A_{31}/A_{32})\{(A_{T1}+S_{T3})/A_{43}\} \exp(-E_{T4}/\boldsymbol{k}T)$$
$$+ (3S_{T3}/A_{32})\{(A_{41}/A_{43}+A_{T1}/S_{T4}+A_{T1}A_{41}/S_{T4}A_{43})$$
$$+ 3A_{T1}/A_{32}\} \exp(-E_{T3}/\boldsymbol{k}T)$$
$$+ (1+S_{T3}/S_{T4}+A_{T1}/S_{T4})(3A_{41}/A_{32})$$
$$\times \exp(-E_{43}/\boldsymbol{k}T)+(3A_{T1}S_{T3}/A_{32}A_{43})$$
$$\times \exp\{-(E_{T3}+E_{T4})/\boldsymbol{k}T\}] \tag{11}$$

Assuming that $A_{S1}/S_{ST} \ll 1$, $A_{41}/A_{43} \ll 1$, and $S_{T3}/S_{T4} \ll 1$ for the sake of simplicity, we have:

$$\eta_{Eu} = 1/[1+A_{T1}/S_{T4}+(A_{T1}/A_{43})\exp(-E_{T4}/\boldsymbol{k}T)$$
$$+ (3A_{T1}/A_{32})\exp(-E_{T3}/\boldsymbol{k}T)] \tag{12}$$

Equation (12) shows that when the temperature is low or the energy difference is large (provided that A_{T1} is constant), the exponential terms may be negligible and the fluorescence yield depends only upon S_{T4}. On the other hand, when the temperature is high or the energy difference is small, the exponential terms become large and the term of S_{T4} may be negligible.

In the case of terbium chelates, the situation is somewhat simpler; the energy transfer diagram is shown in Fig. 6.

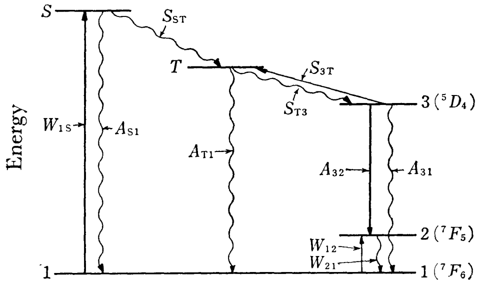


Fig. 6. Energy transfer diagram for terbium chelates.

The fluorescence yield, given by a similar way, is:

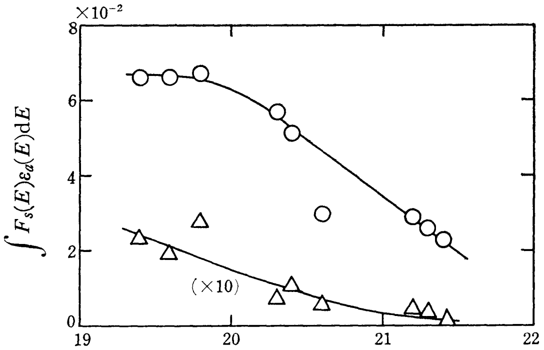
$$\eta_{Tb} = 1/[(1+A_{S1}/S_{ST})\{(1+A_{T1}/S_{T3})(1+A_{31}/A_{32})$$
$$+(A_{T1}/3A_{32})\exp(-E_{T3}/\boldsymbol{k}T)\}] \tag{13}$$

Therefore, the fluorescence yield also depends upon S_{T3} when the temperature is low or the energy difference is large, and *vice versa.*

In Eqs. (11), (12), and (13), which represent the fluorescence yields of europium and terbium chelates, the transition probability for the nonradiative energy transfer, S_{T3} or S_{T4}, is important. This transition probability was taken into consideration by Ermolaev *et al.*[5] and by Matsuda *et al.*,[10] along with the exchange-interaction theory described by Dexter.[11] The transition probability for the exchange interaction, P_{sa}, is given as follows:

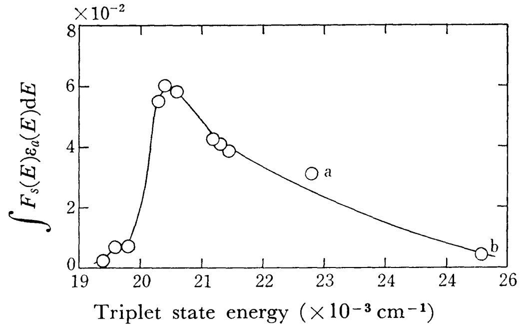
$$P_{sa} = (2\pi Z^2/\hbar)\int F_s(E)\varepsilon_a(E)\mathrm{d}E \tag{14}$$

where F_s is the emission spectrum of the sensitizer (donor) and corresponds to the phosphorescence spectrum of a ligand in this case, where ε_a is the absorption spectrum of the activator (acceptor) and corresponds to the absorption spectrum for the $^7F \rightarrow {}^5D$ transition in the Eu^{3+} ion or the Tb^{3+} ion, where E is an energy (and now we use the unit of a wave number), and where Z^2 is the term of the overlap of electron clouds and cannot be determined by optical experiments. In the following discussions, the coefficient $(2\pi Z^2/\hbar)$ in Eq. (14) will be assumed to be equal and constant in all the chelates investigated.*2 Therefore, the transition probability may be proportional to the overlap between the phosphorescence spectrum and the absorption spectrum. The results obtained for the europium chelates are plotted in Fig. 7, and those for the terbium chelates are shown in



Triplet state energy (×10^{-3} cm^{-1})

Fig. 7. Overlap for europium chelates.
○: $^7F \rightarrow {}^5D_1$ △: $^7F \rightarrow {}^5D_0$



Triplet state energy (×10^{-3} cm^{-1})

Fig. 8. Overlap for terbium chelates.
a : trifluoroacetylacetonate
b : acetylacetonate

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10) Y. Matsuda, S. Makishima and S. Shionoya, This Bulletin, **42**, 356 (1969).

11) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

*2 This term may probably depend upon the mutual distance between the central ion and an oxygen atom of the ligand[10] but this distance is assumed to be not greatly changed among each β-diketone chelate in this case.

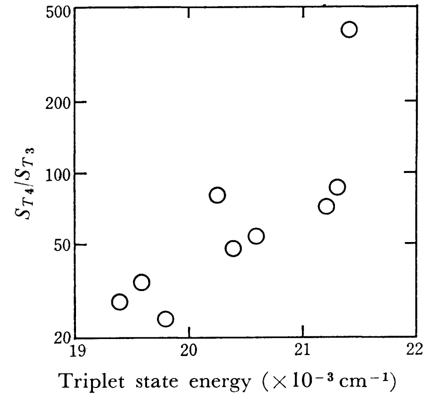

Fig. 9. The ratio of a transition probability for the $^5D_1$ level and the $^5D_0$ level of the europium ion.

Fig. 8, where the horizontal axis is the triplet state energy and where the circles show the values calculated for each β-diketone chelate. It can be seen in Fig. 7 that the overlap decreases as the triplet state energy increases. The ratio of the overlap for the $^5D_0$ and $^5D_1$ levels, that is, the ratio of the transition probability (S_{T4}/S_{T3}), is estimated from Fig. 7 and is shown in Fig. 9. As the triplet state energy increases, this ratio tends to increase exponentially, so that the excitation energy is transferred mainly from the triplet state to the $^5D_1$ level. The transition probability from the triplet state to the $^5D_0$ level is very small, but not zero. Therefore, the energy transfer to the $^5D_0$ level becomes important for the europium chelates which have the triplet state between the $^5D_1$ level and the $^5D_0$ level.

Since the energy of the $^5D_4$ level of the Tb^{3+} ion is about 20500 cm^{-1}, the value of the overlap is at its maximum for the β-diketone chelates with a triplet state energy of near 20500 cm^{-1}. This value of the overlap decreases rapidly or gradually according as the triplet state is lower or higher than the $^5D_4$ level.

The dependence of the energy transfer probabilities, S_{T4} and S_{T3}, on the energy difference must be taken into consideration, because these probabilities can reasonably be considered to depend upon the triplet state energy, as may be seen in Figs. 7 and 8. The energy transfer probability for the transition from the triplet state to the resonance level of the Eu^{3+} ion was obtained as 10^7—10^8 sec^{-1} from the quenching effects of anthracene on the fluorescence of europium chelates.[12] If the coefficient, $2\pi Z^2/\hbar$, in Eq. (14) is assumed to be 10^9, the energy transfer probability, S_{T4} (or S_{T3} from Fig. 8), can be obtained as 10^7—10^8 sec^{-1} using the values of the overlap shown in Fig. 7 or Fig. 8. This value of 10^7—10^8 sec^{-1} is coincident with the result obtained in Ref. 12 and seems reasonable. Therefore, the value of $2\pi Z^2/\hbar$ is taken as 10^9 and the energy transfer probability is obtained for each triplet state energy from the results shown in Figs. 7 and 8. Using these results, the fluorescence yield, η_{Eu}, for europium chelates is estimated from Eq. (11) and is plotted in Fig. 10, where $A_{S1}=A_{41}=A_{31}=0$, $A_{43}=10^6$ sec^{-1}, $A_{32}=10^3$ sec^{-1}, $A_{T1}=2\times10^7$ sec^{-1} (for 300°K), and 5×10^7 sec^{-1} (for 100°K, 200°K, and 300°K) are assumed. η_{Tb} is estimated from Eq. (13) and is plotted in Fig. 11, where $A_{S1}=A_{31}=0$, $A_{32}=10^3$ sec^{-1}, $A_{T1}=2\times10^7$ sec^{-1} (for 300°K), and 5×10^7 sec^{-1} (for 100°K, 200°K, and 300°K) are assumed. In both cases, the fluorescence yield decreases because of the thermal deactivation process where the energy difference is small. Where the energy difference is large, the fluorescence yield also decreases because of the decrease in the energy transfer probability due to the diminution in the overlap between the phosphorescence spectra of the ligands and the absorption spectra of the rare earth ions. Consequently, the fluorescence yield shows a maximum for the proper energy difference between the triplet state and the resonant level of the rare earth ion; the experimental results shown in Fig. 2 are, therefore, confirmed. The temperature depen-

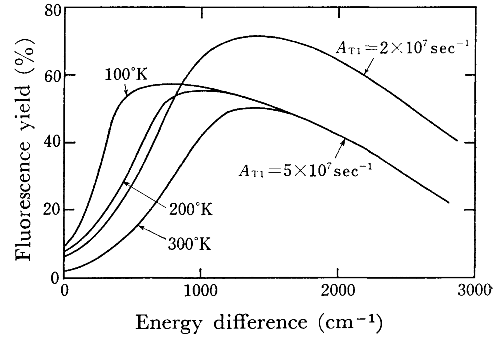

Fig. 10. Fluorescence yields *vs.* energy difference ($T-{}^5D_1$) for europium chelates.

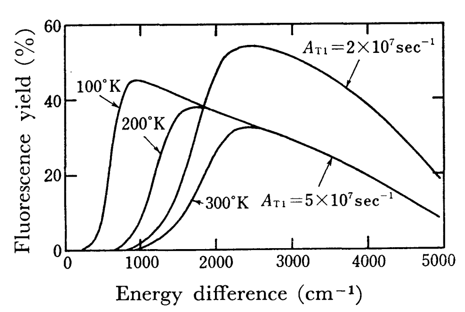

Fig. 11. Fluorescence yields *vs.* energy difference ($T-{}^5D_4$) for terbium chelates.

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[12] V. L. Ermolaev, E. A. Saenko, G. A. Domrachev, Yu. K. Khudenskii, and V. G. Aleshin, *Opt. Spectry.*, **22**. 466 (1967).

dences of fluorescence yields are also shown in Fig. 10 and Fig. 11, which show that the chelate compounds with small energy differences (*e.g.*, $Eu(CTFA)_4^-$, $Tb(BTFA)_4^-$, $Tb(TTA)_4^-$, and $Tb(PPBTFA)_4^-$) do not fluoresce at room temperature, but they begin to fluoresce if temperature is lowered. Since the thermal quenching for the fluorescent level decreases as the energy difference is large, the temperature dependence of fluorescence lifetimes in Fig. 3 is explained. Thus, several properties of the energy transfer mechanism for rare earth chelate compounds can be explained, but the explanation of the phenomena is qualitatively limited because so many undetermined factors in the system remain.

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